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Water Quality Modeling in Headwater Catchments: Comprehensive Data Assessment, Model Development and Simulation of Scenarios

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Abstract: Water quality is a major concern globally and in headwater catchments of developing countries it is often poorly managed. In these catchments, having scarce and heterogeneous information hinders the development of water quality assessments and predictive models to support management. To address this issue, the authors propose a framework of three stages that allows for: (i) conducting a comprehensive assessment of water quality; (ii) the development of a mountain stream water quality model based on said assessment; and (iii) the simulation of scenarios with the model to resolve conflicts between uses and quality of water. The framework involves multivariate analyses of principal components and clusters and follows a novel modeling protocol mainly designed for mountainous streams in developing countries. Applied to an Andean catchment in Colombia, the first stage of the framework revealed the catchment's most significant water quality constituents and the most polluted season. The problematic constituents in this catchment include pathogens, nutrients, organic matter, and metals such as the highly toxic Cr and Pb, while water pollution is the highest during the driest months of the year (i.e., January to March). In the second stage, the model was calibrated reproducing the concentrations of pathogens, organic matter, and most nutrients, and showed a predictive capacity. This capacity was measured with an objective function to be minimized based on a normalized root mean square error. It increased only 14% when verified with a different dataset. In addition, during the third stage of the proposed framework, the simulation of alternative scenarios showed that centralized treatment is not sufficient to make water safe for potabilization and agriculture in the catchment. For this reason, improving water quality in the sub-basins at the highest altitudes is required. The proposed framework can be applied in other headwater catchments where information is limited, and where an improved management of water quality is needed.

Keywords: water quality; modeling; multivariate statistics; mountain rivers; headwater catchments; pollution; decision support; QUAL2k; WASP

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1. Introduction

Water quality is globally endangered, and it is expected to worsen. Today, more than one third of the world's population does not have access to safe drinking water, while waterbodies receive an increasing amount and diversity of pollutants [1]. In the coming decades, mega-urbanization and climate change will lead to more serious eutrophication and algal blooms, less dissolved oxygen in water, and traditional wastewater treatment systems rendered insufficient [2,3]. To address these issues, possible strategies include engaging stakeholders to keep contaminants in closed loops and designing automated water quality control operations [1,2]. Accordingly, solving global water quality problems is simultaneously critical and complex.

Complexity is higher in mountainous regions of developing countries. Most of the people living in mountains worldwide are located in these types of countries (more than

600 million) [4]. As a consequence, mountains in these countries have significant population density. This density results in significant amounts of pressure on headwaters, normally causing degradation of their ecosystems, and restricting their significant potential to retain pollutants [5–10]. In addition, developing countries often have limited resources, information, and research capability [5]. In these challenging circumstances, it is very difficult to manage water quality.

Water quality assessments and models are broadly used for water management. For example, assessing diverse pollutants in water allows for decision support, designing restauration programs, and detecting hazards along river basins [11–14]. In these assessments, multivariate statistics are often utilized for analyzing complex datasets, and identifying relevant contaminants and sites with similar pollution levels. In these statistics, analyses of principal components (PCA), clusters (CA), and factors (FA) are perhaps the most common [15–21]. Models are also applied widely. They have been useful in identifying global trends such as the interactions between riverine respiration and organic matter [22], and for designing water management programs. These programs include the European Water Framework, the Australian Bioregional Assessments, and several programs based on the total maximum daily load concept [23–28]. Models have also been employed to propose pollution control strategies in multiple catchments [29–38]. Hence, water quality assessments and models have great potential to improve water quality management [39].

Despite these capabilities, several obstacles limit the application of such water quality assessments and models in headwater catchments of developing countries. Among these obstacles, the combination of scarcity and heterogeneity of water quality data is perhaps one of the most significant. In emerging economies, several documents report a lack of hydrological data [40,41]. Concurrently, water quality information has been reported as being insufficient even in more developed countries [42]. About heterogeneity, water quality records usually have this characteristic due to the high number of variables that they are comprised of [20]. Explicitly in headwaters, these records are also heterogeneous because of hydrological variability, dynamic uses of water and land use changes [43,44]. In Andean catchments, said features are foreseen to increase with climate change and population growth [45]. For example, it has been shown that the upper Bogota River Andean basin will assimilate nutrients and organic matter more quickly, while its water pH and concentration of dissolved oxygen will decrease [46]. That being the case, having scarce and heterogeneous water quality data significantly restrains the development of water quality assessments and models in the regions of interest.

The authors address the issue of having data of the mentioned characteristics (i.e., limited yet heterogeneous) by proposing a framework of three stages and several activities. In headstream catchments of developing countries, the framework allows for: (i) a comprehensive assessment of water quality; (ii) the development of a mountain stream water quality model supported by said assessment; and (iii) the simulation of scenarios with the model to resolve conflicting situations between uses and quality of water. In the first stage, multivariate statistic techniques are employed to identify pollution regimes, to find the most relevant regional contaminants, and to prepare data for modeling. In the second stage, a mountain stream water quality model is implemented, calibrated, and verified. In the third stage, conflicts between uses and quality of water are identified, and then several scenarios to address and analyze these conflicts are simulated.

In this study, the framework is applied to a headwater catchment in the Colombian Andes, where a dataset comprised of both primary and secondary records is available. To the best of our knowledge, this research is unique since no previous work has considered in detail these three stages in the headwaters of developing countries. In addition, it contemplates important aspects when modeling mountainous rivers in these areas. These aspects include a substantial influence of dead zones affecting solute transport [47–50], as well as several processes taking place at higher rates compared to other streams, namely, organic pollutants assimilation [51–56], bacterial loss [57,58], nitrification and uptake of nutrients by periphyton [59], and exceptionally high dissolved oxygen reareation rates [60,61].

These special characteristics result from the varied geomorphology of mountainous streams where pools, riffles, steps, plane beds and cascades are usually found [62]. In the pools, settling and oxidation of organic matter are promoted because water velocity decreases. Meanwhile, in the riffles and cascades, reareation, pathogen death and nutrient uptake are promoted because light penetrates down to the streambed, reaching the periphyton, and water speeds up increasing turbulence. Considering the aforementioned, this paper intends to improve the understanding of water quality in these catchments and serve as a guide for researchers, practitioners, and decision-makers.

2. Materials and Methods

The proposed framework is presented in this section. Specifically, an outline of the three stages and proposed activities is displayed in Table 1. Then, the case study where the framework is applied is introduced, followed by a description of all stages and activities in the subsequent sub-sections.

Table 1. Framework of stages and activities.

Stages	Activities
Stage 1: Information Analysis	Collection of information Definition of sites with similar water quality Definition of relevant water quality constituents Spatiotemporal distribution of water quality Analyses of data quality, consistency, and validity
Stage 2: Development of a water quality model	Model selection Characterization of river hydraulics and solute transport Water quality model implementation, calibration, and verification
Stage 3: Simulation of scenarios	Identification of potential conflicts Simulation of critical scenario Simulation of alternative water quality scenarios (e.g., sanitation, treatment infrastructure and climate change)

2.1. Description of the Case Study

The Lenguazaque River Basin (Figure 1) is a headwater catchment in the Eastern Colombian Andes, mainly formed by tertiary and cretaceous rock as well as lacustrine and alluvial deposits [63,64]. Its climate is characterized by bimodal rainfall and streamflow regimes, with an input precipitation estimated in 800 mm per year, and with a mean relative humidity close to 80% [64,65]. In addition, the catchment has a stable yearly average temperature of about 13 °C with significant daily variations (1 to 20 °C) typical of tropical rivers [65]. Given its climate and high elevation, typical vegetation in the study area comprises endemic species of high Andean forests, paramos and sub-paramos [65–67]. Nevertheless, said vegetation is significantly altered by activities such as agriculture and coal mining [68–76]. It is important to mention that these streams receive domestic wastewater discharges from about 10,000 inhabitants without appropriate wastewater treatment [27,37], as well as numerous additional sources of contamination [71–74]. Given this background, the case study is well suited to fulfill the objectives of present research.

Concerning the catchment's streams and sub-basins (Figure 2), the Tibita River and Ovejeras Creek, in the upper sub-basins 4 and 5 (S4 & S5), come together in sub-basin 3 (S3) to form the main course of the Lenguazaque River. Downstream, the river flows through the Lenguazaque urban area, merges with Mojica Creek (S2), and continues to the outlet in sub-basin 1 (S1). The map in Figure 2 also shows all monitoring sites where water quality data are available, which are scattered and cover most of the basin's streams. In these sites, the datasets include 55 samples of surface water, wastewater, and sediments from both primary and secondary sources (Table 2). In the following sections of the paper, additional remarks on these datasets are provided.

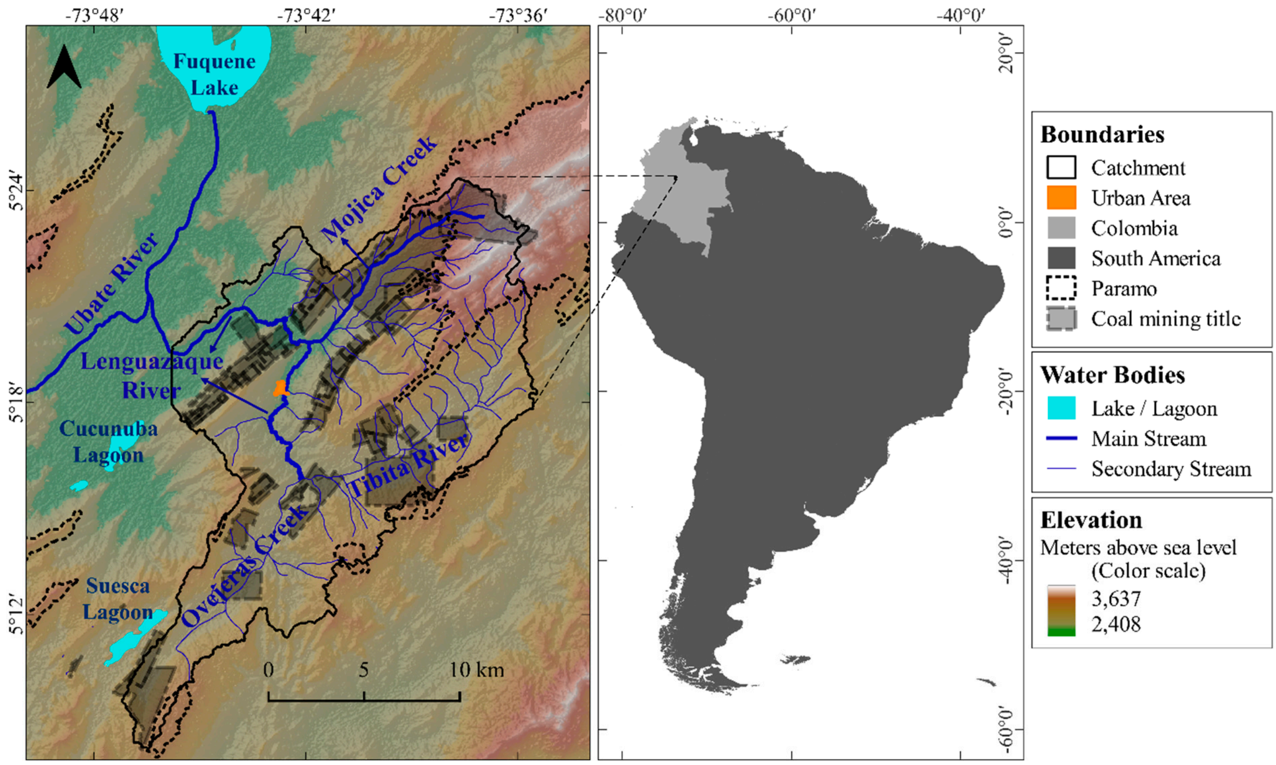


Figure 1. Location of the case study.

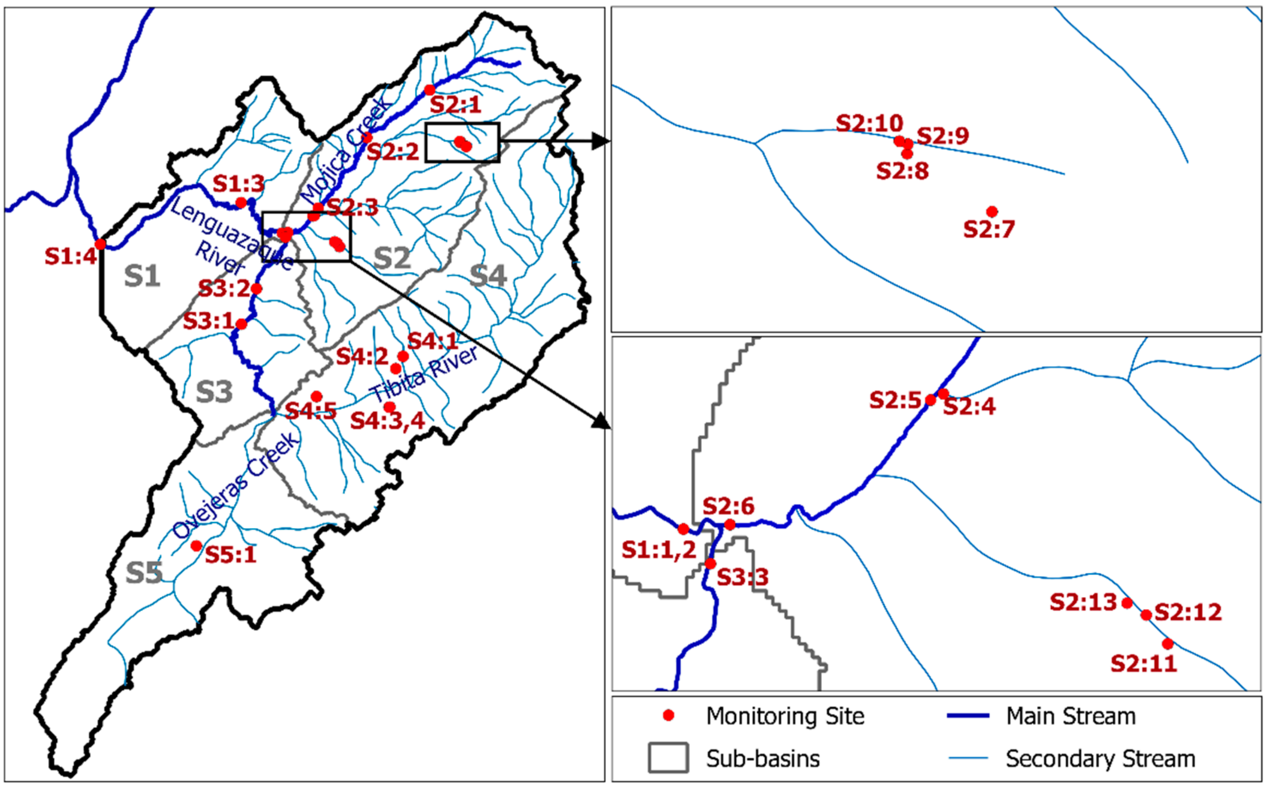


Figure 2. Location of sub-basins and monitoring sites.

Table 2. Summary of available information.

Feature	Primary Data	Secondary Data	All Data
Surface water samples	Yes	Yes	Yes
Sediment samples	Yes	No	Yes
Domestic wastewater samples	No	Yes	Yes
Mining wastewater samples	No	Yes	Yes
Date of first sample	16 September 2017	11 September 2013	11 September 2013
Date of last sample	7 March 2020	6 November 2019	7 March 2020
Number of years sampled	3	6	7
Number of sampled quarters of the year	3	4	4
Number of campaigns	3	22	25
Number of samples	13	42	55
Number of constituents per sample	5–68	19–58	5–68
Number of sampled locations	10	16	26
Number of records	749	1584	2.333
Records below detection	201	650	851

2.2. Stage 1: Information Analysis

2.2.1. Collection of Information

In this stage, digital elevation models (DEM) and geographical information on local streams were collected first. Here, DEM were obtained from the ASTER Global Digital Elevation Map [77] while stream information was collected from the local geographical institute IGAC [78]. The DEM and cartography were then employed to delineate the catchment of interest and to display it on a map. The automatic catchment delineation tool included in the SWAT+ QGIS interface [79] was used for this purpose. Afterwards, historical water quality records available in the study area were requested from local stakeholders and environmental agencies. In this project, information was requested from the local environmental agency CAR since it oversees the study area and monitors its water quality. Next, primary water quality information was collected following appropriate sampling protocols for water quality modeling [42,80]. Collecting primary data in this manner is important since secondary records are not generally collected for modeling purposes. During monitoring, samples of sediments were also included since they interact with the water column and potentially adsorb pollutants [14], making them important for assessing and modeling water quality later on. Further details on the collection of primary water quality data are discussed in the next section of the paper. Once all samples were collected, laboratory analyses were conducted following standard methods [81], and all results were carefully stored and analyzed. A database structure designed for water resources [82] was employed to simplify the storage, management, and analysis of both primary and secondary data.

2.2.2. Definition of Sites with Similar Water Quality

After gathering all data, univariate statistics were computed for every water quality constituent, at each location with available records. These statistics include mean, range, standard deviation, and number of non-detected values, since they provide meaningful insights on regional pollution levels [15,16]. Then, multivariate statistics were employed to establish clusters of sites with similar water quality. For this purpose, records are normalized with the z-scores method, and a hierarchical agglomerative cluster analysis (CA) is performed [17–19]. In this study, normalization and CA were implemented in Matlab, using Euclidean distance and Ward's method to determine the similarity and number of clusters, respectively. Finally, sites where water quality was similar were classified using the resulting CA dendrogram, often aided by professional judgement and field observations. These multivariate statistics simplify subsequent analyses, since data collected at multiple sites is summarized in several groups with similar characteristics.

2.2.3. Definition of Relevant Water Quality Constituents

Multivariate statistics were also employed to determine relevant water quality constituents in the headwater streams of interest. Potentially relevant constituents include all those for which information is available. In this study, said constituents include acidity, alkalinity, carbonaceous biochemical oxygen demand (CBOD), chemical oxygen demand (COD), chlorophyll A, color, dissolved oxygen (DO), E. Coli, total and fecal coliforms, electrical conductivity (EC), hardness, oils and fats, pH, phenols, solids, surfactants, total organic carbon (TOC), turbidity, organic and inorganic species of nitrogen and phosphorous, and diverse ionic constituents (i.e., Cl^-, CN^-, $S_2{}^-$, $SO_4{}^{2-}$) and metals (i.e., Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Va, Zn). These constituents are first separated into conventional determinands and toxicants. Here, conventional refers to determinands that can be removed with conventional wastewater treatment, while toxicants include all the remaining constituents. Next, for each group, records are normalized and a PCA is performed. As in the previous case, normalization and PCA were implemented in Matlab. From this analysis, the resulting principal components (PC) and coefficients show how much of the dataset variance is explained by each water quality determinand. Duly, constituents in the first components and with greater coefficients are considered more relevant, as they contribute more to the total variance.

2.2.4. Spatiotemporal Distribution of Water Quality

The distribution of water quality in space and time is described using boxplots and maps of the catchment of interest. Regarding spatial distribution, previously identified clusters are displayed on these maps, while concentrations of all relevant constituents are summarized in boxplots. Using clusters to group observed concentrations is convenient, since information from many sites is downsized to a few groups with similar characteristics. In terms of temporal distribution, yearly pollution regimes are displayed in boxplots as well. In these plots, the different hydrological seasons in the study area (e.g., typical rainy and dry seasons) are employed to group water quality data. Grouping data in this manner allows for the interpretation of yearly pollution regimes keeping consistency with local hydrology. Once the maps and plots are built, they are used to assess the most polluted locations, analyze yearly contamination patterns, as well as possible contamination sources. In this project, boxplots and maps were built in Matlab and QGIS, respectively.

2.2.5. Analysis of Data Quality, Consistency, and Validity

Previous analyses provide significant insights on the strengths and limitations of datasets and, therefore, on their quality, consistency, and validity. Having several years of records of wet and dry seasons is ideal, since finding larger datasets is not common where information is scarce. In the present research, data from 55 samples (~2300 records) were available, collected for seven years during different hydrologic seasons in the catchment (see Table 2). From these records, missing values were replaced when needed to complete the magnitudes needed to develop the water quality models in the next stage. Here, 30 missing records were replaced for subsequent model development. Specifically, substitute values are computed based on correlations or chemical equations relating the missing value to other water quality determinands and discharge records from the same sample [20]. It is worth mentioning that it is possible to use statistical load analysis to compute these values [83]. Yet, this alternative could be limited if datasets are not large enough to complete such an analysis.

2.3. Stage 2: Development of a Water Quality Model

Developing a mountain river water quality model requires an appropriate modeling protocol [84,85]. In the present research, a protocol designed mainly for mountainous rivers in developing countries is followed [80]. During Stage 1, the initial field inspection and preliminary research activities suggested in this protocol are covered. For this reason, the following subsections describe the subsequent activities of the protocol, focusing on headwater catchments (i.e., model selection, characterization of river hydraulics and solute transport, and water quality model implementation, calibration, and verification).

2.3.1. Model Selection

Having generally small creeks and streams, headwater river networks can usually be modeled as one-dimensional. For this purpose, using an existing model is a practical choice instead of programming a suited solution because verifying the code of a new program requires significant time and resources. Accordingly, two existing models are considered in this project: QUAL2Kw [86] and WASP [87]. These models are offered free of charge [88,89], have been widely applied [33–36,90], and can simulate depletion of dissolved oxygen in polluted systems. On top of that, the models calculate sediment water interactions endogenously, as well as all processes involving aquatic plants and other conventional determinands. This is especially important in developing countries where streams can reach anoxic conditions [38], and in mountainous streams where aquatic plants play a major role in nutrient uptake and photosynthetizing oxygen [59]. In particular, the more user friendly QUAL2Kw model is useful for simulating conventional water quality determinands, mainly under steady state conditions, whereas WASP can be used to model these determinands and toxicants under steady state and dynamic conditions.

2.3.2. Characterization of River Hydraulics and Solute Transport

The river reaches being modeled here are first selected from previous analyses, specifically from the streams located in the catchment where data is available. Afterwards, the reaches are divided into segments using hydrological and topographical nodes [91]. Each segment is geomorphologically classified using a decision tree that requires values of slope and areas in the catchment as sole inputs [62]. These values are easily extracted from the information collected in Stage 1. Based on the segmentation, hydraulic characteristics are computed for each segment, which is often challenging in mountainous rivers because of their varied geomorphology and the different sizes of riverbed materials [92].

In QUAL2kw and WASP, the hydraulics of each segment needs to be defined using either Manning's equation or power functions of discharge, depth, and velocity as [93,94],

$$Q = VA = \frac{1}{n} A R^{2/3} S^{1/2}, \tag{1}$$

$$H = aQ^{b}\ ;\ V = \alpha Q^{\beta}, \tag{2}$$

where Q is discharge, H is depth, V is the average cross-section velocity of water, A is the area of said section, n is Manning's roughness coefficient, R is the hydraulic radius, S is the friction slope, and a, α, b and β are the coefficients and exponents of the power functions.

Accordingly, values of the parameters of Equations (1) and (2) are computed for each segment and loaded into the model, depending on the information available at each site. If estimates of A, n, R, and S are available at a reach scale, Equation (1) is used. On the contrary, Equation (2) is employed by estimating values for a, α, b and β using streamflow rating curves or data from tracer experiments conducted under various flow conditions [48,95].

After defining hydraulic characteristics of all segments, solute transport is described in terms of dispersion coefficients (D) as required in QUAL2kw and WASP. Preferably, D is calibrated from data collected during tracer experiments as a parameter of the advection dispersion equation (ADE) [96]. Simultaneously, the river's cross-sectional area (A) is calibrated as a second effective parameter of said equation. This is required because the always non-uniform cross-sections found in mountain streams make it impossible to accurately estimate A at a reach scale. The Generalized Likelihood Uncertainty Estimation (GLUE) method [97] included in the Solute Transport Software [98] allows for the calibration of both D and A based on data from tracer experiments [48].

In the absence of tracer information, D is estimated from synthetic tracer experiments based on the equivalences between ADE and the Aggregated Dead Zone (ADZ) model [47,48,99,100]. The ADZ model is employed because it has been shown to describe solute transport in mountain rivers adequately [48]. Meanwhile, the parameters of the ADZ model are related to water velocities as [47,100],

$$DF = \frac{T_r}{\bar{t}} = 1 - \frac{\tau}{\bar{t}} = 1 - \frac{V}{V_{max}}, \quad (3)$$

where $\bar{t}$, and τ represent said parameters, V and V_{max}, individually refer to average and maximum water velocities, and DF and Tr are measures of solute transport that can be derived when $\bar{t}$, and τ are known. Conceptually, DF is defined as the solute's dispersive fraction, T_r is the ADZ residence time, $\bar{t}$ is the solute's mean travel time, and τ is the solute's advective time delay. In turn, velocities V and V_{max} are measured with a flow meter following a cross-section flow gauging procedure [95]. Hence, DF is estimated with Equation (3), based solely on values of V and V_{max}. Then, the synthetic tracer experiments are conducted by introducing the DF estimates in the ADZ model to simulate the transport of instantaneous tracer injections in the streams being modeled. The simulation leads to obtaining synthetic pollutographs downstream, which are then used to calibrate D and A. The GLUE method and Solute Transport software allow for such calibration as mentioned before, this time with synthetic tracer data.

Once D and hydraulic characteristics are known for all streams, the Peclet and Courant numbers are computed to determine appropriate segment lengths and time steps for numerical simulations. Details on the calculation of these numbers to determine such lengths and time steps are reported in the literature [101]. It is important to highlight that knowing the hydraulics and solute transport of the streams of interest is key for planning the collection of primary water quality information. Explicitly, it allows for scheduling the collection of samples following the mass of water downstream under the Lagrangian sampling approach, as required by some water quality modeling protocols [42,80].

2.3.3. Model Implementation, Calibration, and Verification

To implement a model in the catchment of interest, all river reaches are loaded into the model's user interface, as well as their hydraulic and solute transport characteristics. Afterwards, the relevant state variables and parameters of the model to be calibrated are specified. A summary of these variables and parameters for conventional constituents in QUAL2kw is presented in Table 3. Next, typical value ranges for all parameters are obtained from relevant literature. Observe that organic pollutant assimilation, pathogen death or bacterial loss, nitrification, uptake of nutrients and reareation rates can have specific values in mountainous rivers, as mentioned in the introduction. For this reason, Table 3 presents a summary of these values for rivers in general [102], and an outline of typical magnitudes found in mountainous streams [51–61,103,104].

Subsequently, calibration and verification datasets are separated using the primary data previously collected during different monitoring campaigns. Here, one monitoring campaign was used for calibration and one more for verification. In addition, an objective function (OF) to measure model performance based on the root mean square error ($RMSE$) was specified as,

$$OF = \frac{1}{n}\sum_{i=1}^{n} \frac{1}{N_i} RMSE_i, \quad (4)$$

where n is the number of state variables in the model, i is an integer identifier for each of these variables, and N_i is a normalization factor for state variable i. For each of these variables, $RMSE_i$ is the root mean square error defined as [105],

$$RMSE_i = \sqrt{\sum_{j=1}^{m} \left(Y_j^{obs} - Y_j^{sim}\right)^2}, \quad (5)$$

where m is the number of observations available for variable i, j is an integer identifier for each observation, and Y_j^{obs} and Y_j^{sim} are its corresponding observed and simulated values. Meanwhile, the normalization factor N_i in Equation (4) is defined as,

$$N_i = \frac{1}{2}\left(\frac{1}{m}\sum_{j=1}^{m} Y_j^{obs} + \frac{1}{m}\sum_{j=1}^{m} Y_j^{sim}\right), \tag{6}$$

where all terms are as defined previously. The purpose of normalization is giving all state variables comparable weights in the objective function *OF*. It is important to highlight that other performance metrics can be used to define said function, such as Nash Sutcliffe Efficiency (*NSE*). The *RMSE* is employed here because it avoids a possible underestimation of model fitness when having a limited number of observations.

Table 3. State variables and parameters for QUAL2Kw.

Constituent Group	State Variables *	Parameters	General Ref. Values [91] Median (Min, Max)	Mountain Rivers Ref. Values Median (Min, Max) [Ref]		Units
Solids	Inorganic suspended solids (ISS)	Settling rate (vss)	0.61 (0, 1.9)	0.38 (0.01,3.00)	[59,103]	m day^{-1}
	Organic solids: Detritus (Det)	Dissolution rate (kdt)	0.63 (0.001, 5)	0.22 (0.01, 1.97)	[59,103]	day^{-1}
		Settling rate (vdt)	0.5 (0, 4.8)	0.62 (0.10, 0.95)	[59]	m day^{-1}
Organic matter & Pathogen bioindicators	Slow CBOD ($CBOD_S$)	Hydrolysis rate (khc)	0.82 (0, 4)	0.52 (0.01, 3.00)	[59]	day^{-1}
		Oxidation rate (kdcs)	0.2 (0, 5)	-		day^{-1}
	Fast CBOD ($CBOD_F$)	Oxidation rate (kdc)	2.5 (0.02, 4.3)	0.39 (0.10, 39.05)	[51,59,103]	day^{-1}
	Total Coliforms (TC)	Decay rate (kpath)	-	0.55 (0.48, 0.66)	[57,58]	day^{-1}
		Settling rate (vpath)	-	1.50 (0.32, 3.89)	[57,58]	m day^{-1}
Nutrients	Organic Nitrogen (N_{org})	Hydrolysis rate (khn)	0.2 (0.001, 4.3)	0.47 (0.01, 3.36)	[53,59,103]	day^{-1}
		Settling rate (von)	0.11 (0, 1.8)	1.05 (0.27, 2.16)	[55]	m day^{-1}
	Ammonium (NH_4^+)	Nitrification rate (kn)	2.5 (0.01, 10)	0.74 (0.15, 9.00)	[53,59,103]	day^{-1}
	Nitrates (NO_3^-)	Denitrification rate (kdn)	1 (0, 1.9)	0.21 (0.00, 0.68)	[53,103]	day^{-1}
	Organic Phosphorous (P_{org})	Hydrolysis rate (khp)	0.43 (0.001, 4.2)	0.73 (0.01, 4.00)	[59,103]	day^{-1}
		Settling rate (vop)	0.1 (0.003, 1.8)	1.09 (0.18, 4.95)	[55]	m day^{-1}
	Inorganic Phosphorous (P_{inorg})	Settling rate (vip)	0.9 (0, 2)	0.99 (0.31, 4.57)	[55]	m day^{-1}
Plants & algae	Phytoplankton (Phyto)	Max. Growth rate (kga)	2.5 (0.2, 4.1)	-		day^{-1}
		Respiration rate (krea)	0.1 (0.015, 0.7)	-		day^{-1}
		Death rate (kdea)	0.05 (0, 0.59)	-		day^{-1}
		Settling rate (va)	0.15 (0, 2)	-		m day^{-1}
	Bottom plants (BotP)	Max. Growth rate (kgaF)	15 (1.3, 100)	-		gDm^{-2}day^{-1}
		Basal Resp. rate (krea1F)	0.2 (0.007, 1.2)	-		day^{-1}
		Photo Resp. rate (krea2F)	0.6 (0.3, 0.6)	-		-
		Excretion rate (kexaF)	0.05 (0, 0.1)	-		day^{-1}
		Death rate (kdeaF)	0.05 (0, 0.59)	-		day^{-1}
		Subsistence N (Nbmin)	7.4 (7.2, 72)	-		mg/gD
		Subsistence P (Pbmin)	2.9 (1, 10)	-		mg/gD
		Max. uptake N (Nupmax)	364 (100, 720)	-		mg/gD/day
		Max. uptake P (Pupmax)	100 (50, 200)	-		mg/gD/day
		Half sat N (kNratio)	2.2 (0.9, 9)	-		-
		Half sat P (kPratio)	1.4 (0.09, 4.6)	-		-

* In mountain rivers, the Tsivoglou-Neal equation is recommended to account for reareation of dissolved oxygen in the model [60,61].

After preparing the objective function, the QUAL2Kw model is run with boundary conditions taken from the calibration dataset. For calibration, parameters are initially adjusted manually to improve model performance as much as possible. Specifically, parameters are varied in the ranges previously obtained from the literature. The PIKAIA genetic algorithm included in QUAL2Kw [106] is then employed to finish calibration automatically [86]. Once calibrated, the model is run with data collected from a different campaign, namely the verification dataset. The strengths, limitations, and predictive capacity of the model are finally evaluated based on its performance with this different dataset, measured with the same objective function *OF*. It is important to mention that when data from additional monitoring campaigns are available, it is recommended to use campaigns representative of the lowest and highest flow conditions for calibration, and those related with intermediate flows for verification [38].

2.4. Stage 3: Simulation of Scenarios

2.4.1. Identification of Potential Conflicts

The simulation of alternative scenarios with the model requires first identifying potential conflicts between water quality and uses of water in the catchment [80]. To this end, information about these uses and their corresponding water quality standards are obtained from local regulations. Next, water quality data available at all clusters of monitoring sites are compared to these standards. When such standards are not met in a particular cluster, a potential conflict exists in the sites that it comprises. It is worth mentioning that placing water uses and clusters of monitoring sites on a map of the catchment facilitates such comparison. In the clusters where conflicts are found, the values that are farthest from complying with each water quality standard are reported. The magnitude of these values provides a comparative estimate of the relevance of each conflict. For simplicity, these magnitudes are referred to here as critical values. Finally, conflicts are analyzed in view of these values, as well as the location of water uses and clusters.

2.4.2. Simulation of the Critical Scenario

Once conflicts are analyzed, a scenario describing the most polluted condition in the catchment is defined. This definition is based on the yearly pollution regimes previously outlined in Stage 1. These regimes allow for the establishment of the season when this condition occurs. When this season is identified, values of streamflow and concentration representing it are computed. In the case of streamflow, representative values follow design conditions for steady flows defined as [107],

$$S = XQT, \tag{7}$$

where, S is the value of streamflow, X is an averaging period in days, Q is flow, and T is the return interval in years. Accordingly, in the critical scenario, S is equivalent to the X-day average flow expected to occur every T years (e.g., *7Q10* and *4Q3*). In the case of concentration, characteristic values are obtained from maximum and minimum historical water quality observations. Maximum values describe the most polluted condition for most water constituents, while minimum amounts are employed for dissolved oxygen, alkalinity, and pH, for example. When values of flow and concentration are established for all boundaries and discharges in the model, it is employed to simulate the response of the catchment to these critical conditions, and results are analyzed in view of the previously identified conflicts.

2.4.3. Simulation of Alternative Scenarios

Here, two alternative scenarios are simulated and evaluated. These alternatives consider the critical scenario as a baseline and aim to solve existing conflicts between uses and quality of water. These scenarios center either on conventional water quality determinands or toxicants, consistent with the implemented model. The first alternative comprises of the addition of wastewater treatment to the main sources of conventional pollutants in the critical scenario. To simulate such an addition, typical efficiencies of wastewater treatment are obtained from related literature [108]. Then, these efficiencies are employed to compute the reduction of polluting loads entering the streams of the catchment. Based on these reductions, concentrations of the critical scenario are modified, and the model is run to complete the simulation. If the resulting concentrations do not solve all found conflicts, the second alternative takes place. Such an alternative centers on finding the additional measures needed to solve these conflicts. Particularly, these measures are described in terms of the reduction of polluting loads needed to comply with water quality standards. To achieve said description, these loads are gradually reduced until reaching the standards, and the impact of the reduction is evaluated with the model. It is important to highlight that the model can also be employed to simulate other alternative scenarios such as changes in climate and land use [46,109].

3. Results and Discussion

3.1. Stage 1: Information Analysis

3.1.1. Collection of Information

Besides the location of water quality monitoring sites and the summary of available information shown previously in Figure 2 and Table 2, a detailed description of these sites is provided in Appendix A (Table A1). Overall, the mentioned figure and tables show that the datasets comprise most streams and sub-basins, and that secondary datasets are larger than primary records. Particularly, secondary data were collected in 22 monitoring campaigns while primary records were gathered in only three. Combined, all records comprise numerous constituents of water quality in samples of surface water, wastewater, and sediments. These records were collected for seven years (2013–2020) and in different periods of the year, yet a significant amount (~36%) lies below laboratory detection limits (see Table 2). It is noteworthy to mention that the local Environmental Agency (CAR) provided all secondary data, and that a portion of records collected before 2019 was used in previous projects [14,37].

3.1.2. Definition of Sites with Similar Water Quality

The resulting CA dendrogram and clusters of sites with similar water quality are presented in Figure 3 and Table 4, respectively. Detailed univariate statistics are provided as Supplementary Materials (Section S1 for conventional constituents and Section S2 for toxicants). As shown, the CA algorithm grouped 55 water quality samples into six sets with similar characteristics, all collected at specific sub-basins and sites. The number of times that a sample appeared in each group was important for defining the definitive clusters in Table 4. This is because some samples belonged to more than one set in the dendrogram, even when collected at the same site (e.g., S1:3 and S1:4). Thus, field observations and professional judgement contributed to the definitive classification. According to these results, subsequent analyses can be simplified by downsizing data from 26 monitoring sites to six groups with similar features.

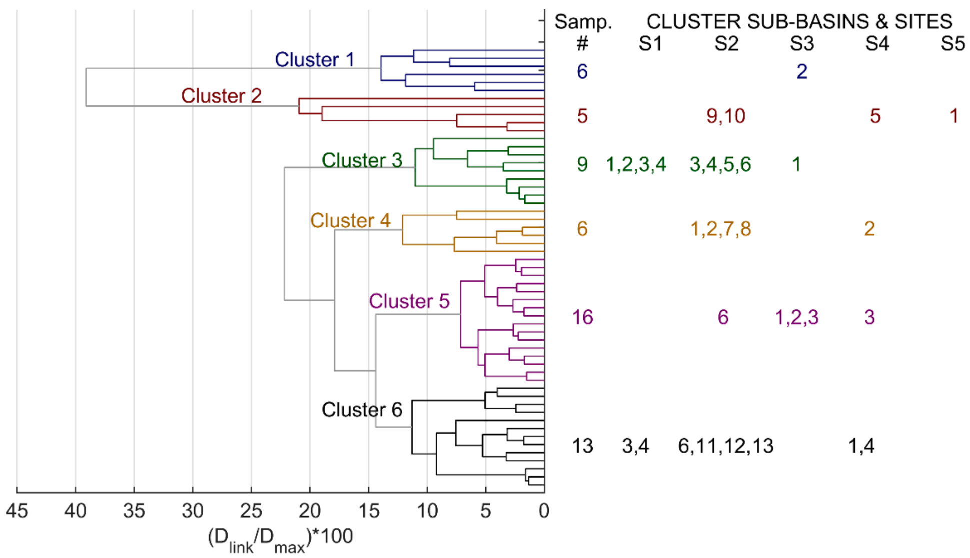


Figure 3. Cluster analysis dendrogram.

Table 4. Clusters of sites with similar water quality.

Cluster	Description	Sub-Basins and Sites
C1	Domestic Wastewater Discharge	S3:2
C2	Most Polluted Creeks and Mine Drainages	S1:2; S2:9,10; S4:4,5; S5:1
C3	Mojica Creek below 2600 m of elevation	S2:3,4,5,6
C4	Other Mine Drainages and Creeks	S2:1,2,7,8; S4:2,3
C5	Baloncitos Creek Area and Mine Drainage at S4	S2:11,12,13; S4:1
C6	Lenguazaque River	S1:1,3,4; S3:1,3

3.1.3. Definition of Relevant Water Quality Constituents

Resulting PCA coefficients for relevant constituents are presented in Table 5. More precisely, these results include values for the first three principal components of conventional and toxic determinands, as well as their contribution to the total variance. Absolute coefficients above 0.2 were considered significant, and the first three principal components explain more than 59% of the total variance. Subsequent components explained less than 10% of the variance without appending further contaminants. As a result, these components were not considered relevant. As shown, relevant conventional constituents include pathogens, nutrients, solids, pH, hardness, DO, CBOD and COD, whereas toxicants include Cl^-, phenols, sulfur compounds, and several metals such as aluminum, iron, zinc, and nickel, and even the highly toxic Cr and Pb. According to these results, modeling efforts should focus on these constituents and toxicants.

Table 5. PCA coefficients for relevant conventional and toxic constituents.

Conventional Constituents	Principal Components			Toxicants	Principal Components		
	PC1	PC2	PC3		PC1	PC2	PC3
EC	-	0.392	-	Al	0.3	-	-
Alk	0.25	-	-	As	0.202	-	-
Acidity	-	0.404	-	Ba	-	0.323	−0.341
pH	-	−0.355	-	Ca	-	0.435	-
Hardness	-	0.420	-	Cl^-	-	0.42	-
E. Coli *	0.23	-	0.500	Co	0.251	-	-
TC *	0.22	-	0.561	Cr	0.244	-	−0.252
Total Solids	0.26	-	-	Cu	0.277	-	−0.219
Suspended Solids	0.20	-	-	Fe	0.334	-	-
Volatile Solids	-	-	0.234	K	-	0.29	-
DO	−0.21	-	-	Li	-	-	0.429
Slow CBOD	-	-	0.388	Mg	-	0.386	-
Fast CBOD	0.26	-	-	Mn	0.264	-	0.313
Total COD	0.24	-	-	Na	-	0.425	-
Soluble COD	0.21	-	-	Ni	0.304	-	-
NH_4^+	0.26	-	-	Pb	0.222	-	-
Total Kjeldahl N	0.25	-	-	Phenol	-	−0.209	-
Total N	0.24	-	-	S_2^-	0.299	-	-
Soluble Reactive P	0.21	-	-	SO_4^{2-}	-	-	0.458
Total P	0.25	-	-	V	0.238	-	-
Phyto	-	-	0.32	Zn	0.326	-	-
Variance %	37%	17%	14%	Variance %	36%	13%	10%

* *E. Coli* and TC were measured in MPN/100 mL and CFU/100 mL in PC1 and PC3, respectively, using the standard method guidelines [81]. For MPN, the 9221 Multiple-Tube Fermentation technique was employed with EC broth. For CFU, the 9222 Membrane Filter technique was employed with m-ColiBlue media.

3.1.4. Spatiotemporal Distribution of Water Quality

The spatial distribution of conventional and toxic constituents in water is summarized in Figures 4 and 5, respectively. In the first case (Figure 4), conductivity and solids suggest that sites in clusters C1 and C2 are the most polluted, although their water quality is different. This is because domestic wastewater (C1) has the highest concentration of nutrients, pathogens, oxygen demanding substances, and the least oxygen, while contaminated creeks and mine drainages (C2) are the most acidic, yet they have the least number of pathogens. In contrast, sites in C3, C4 and C5 have a more neutral pH and less nutrients than C2, whereas the Lenguazaque River (C6) is slightly acidic and has a wide range of dissolved oxygen. In the second case (Figure 5), sites in C2 have the greatest concentrations of metals and sulfur compounds in water, although significant proportions are found in other clusters as well. Complementarily, the concentration of metals in sediments is shown in the Supplementary Materials (Figure S3.1). Here, considerable concentrations are observed in clusters C3, C4 and C6, where data were collected, even of the highly toxic Hg and Cd. These toxicants could therefore be accumulating in riverbeds since they were not detected in water.

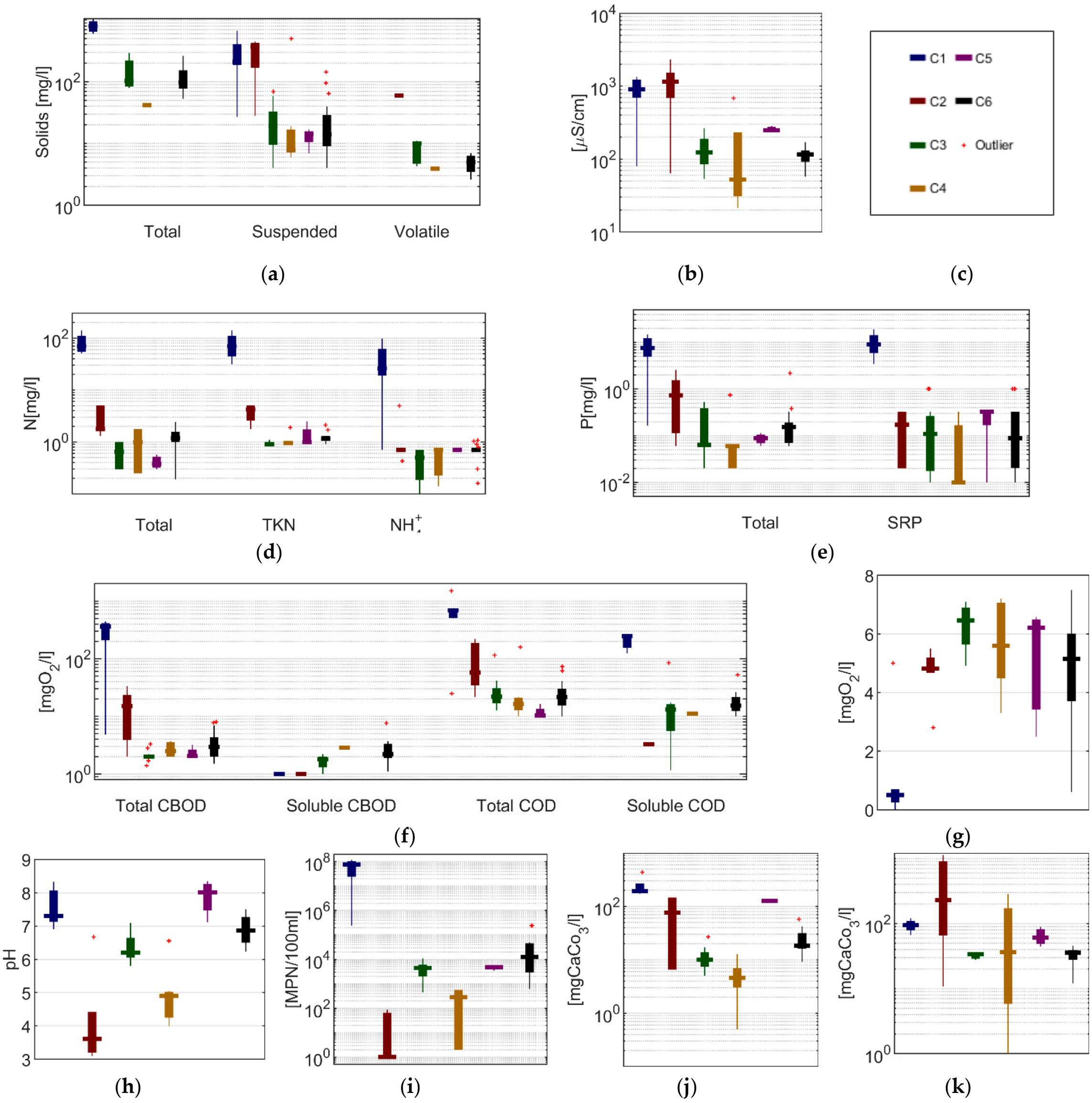


Figure 4. Spatial distribution of conventional water quality determinands: (**a**) solids; (**b**) EC; (**c**) legend; (**d**) nitrogen; (**e**) phosphorous; (**f**) oxygen-demanding constituents; (**g**) DO; (**h**) pH; (**i**) total coliforms; (**j**) total alkalinity; (**k**) total hardness.

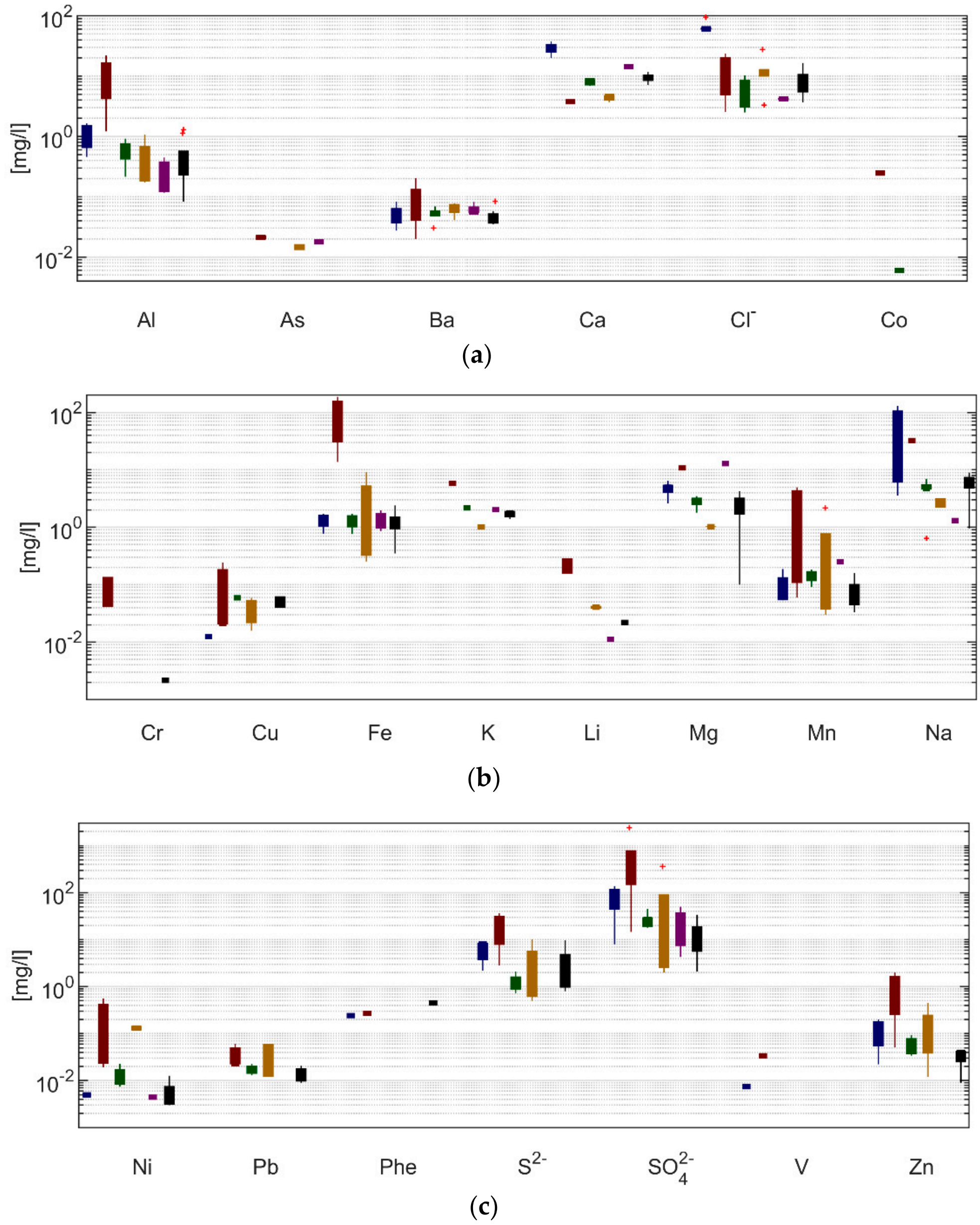


Figure 5. Spatial distribution of toxicants in water: (**a**) Al, As, Ba, Cl^- and Co; (**b**) Cr, Cu, Fe, K, Li, Mg, Mn and Na; (**c**) Ni, Pb, Phenol, S^{2-}, ${SO_4}^{2-}$, V and Zn.

Turning to temporal distribution, yearly pollution regimes in the Lenguazaque River (C6) are presented in Figure 6 for conventional constituents. This group suggests that the first three months of the year are the most polluted. This is because the highest values of EC, CBOD, COD and P occur then, as well as the lowest magnitudes of pH and OD. These months are also part of the driest season of the year [64]; thus, such pollution levels could be related to the limited capacity to dilute contaminants during that time. Not to mention, mean concentrations of solids are higher during the rainy seasons of the second and fourth quarters [64]. This is consistent with the higher amount of sediment transport expected during these seasons. Moreover, peak concentrations of pathogens occur during the drier first and third quarters, although such concentrations are significantly high throughout the year. Complementarily, toxicant regimes are provided as Supplementary Materials (Figure S3.2). Note that pollution trends are not as easily identified for this group. Yet, reported magnitudes are indicative of typical concentrations of toxicants and their yearly variation. In any case, increasing the size of the dataset through more frequent monitoring could reveal further water quality trends and regimes.

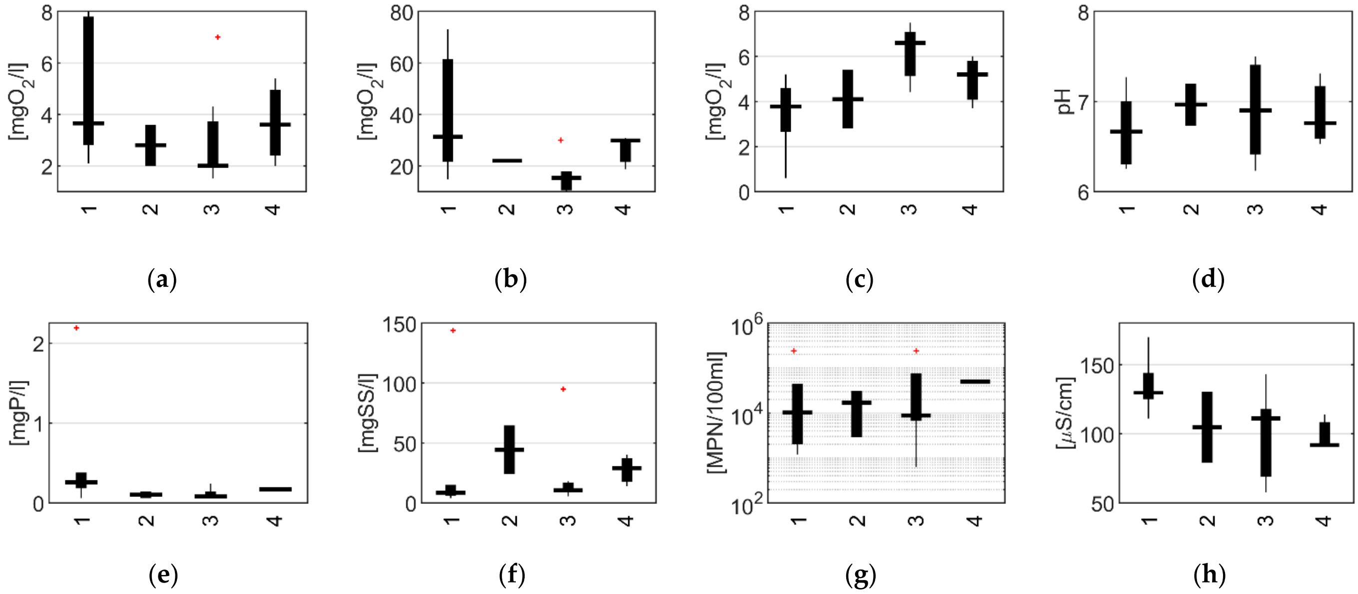


Figure 6. Temporal distribution of conventional constituents in C6: (**a**) CBOD; (**b**) COD; (**c**) DO; (**d**) pH; (**e**) total P; (**f**) total suspended solids; (**g**) TC; (**h**) EC.

3.1.5. Analysis of Data Quality, Consistency, and Validity

Previous analyses suggest strengths and limitations of the datasets. Specifically, having records of numerous water constituents of wet and dry seasons from several years, and including sediments, are perhaps the most significant strengths. The reason for this is that such features allowed for the clustering of monitoring sites into meaningful categories, the identification of relevant constituents, and for the description of spatiotemporal pollution trends. Conversely, having many values below detection and few sediment samples are notable limitations. Such restrictions limit a clearer definition of spatiotemporal trends and understanding of the potential accumulation of toxicants in riverbeds. Accordingly, it is important to consider these strengths and limitations when developing the model and interpreting its results.

3.2. Stage 2: Development of a Water Quality Model

3.2.1. Model Selection

Given the numerous water quality constituents found in the study area, it is possible to model both conventional constituents and toxicants using the two models mentioned in the methodology section. Here, modeling efforts focus on conventional water quality determinands under steady state conditions using the QUAL2Kw model.

3.2.2. Characterization of River Hydraulics and Solute Transport

The streams included in the model are displayed in Figure 7, together with the monitoring sites located within their boundaries. As presented, Mojica Creek is identified as Stream A, while the Lenguazaque River is represented by streams B and C. It is important to highlight that monitoring sites do not cover all tributaries, and most likely not all pollution sources, conferring uncertainty on the model. A detailed description of the longitudinal profile of the three streams and their geomorphological classification is provided as Supplementary Materials (Figure S4.1 and Table S4.1). Here, four geomorphological classes were found for Stream A (i.e., step-pool, cascade, pool-riffle and plane bed), while only one was identified for all segments of Streams B and C (i.e., pool-riffle). Considering these streams and their classification, a detailed summary of hydraulic and solute transport features of all modeled segments is presented in Table S4.2. This table shows that it was possible to represent the hydraulics of most segments using Manning's equation (Equation (1)), while only the last seven segments of Stream C required using power functions of flow (Equation (2)). Dispersion coefficients *D* and cross-sectional areas were estimated using Equation (3) and corroborated with synthetic tracer experiments since no field data from tracer experiments were available.

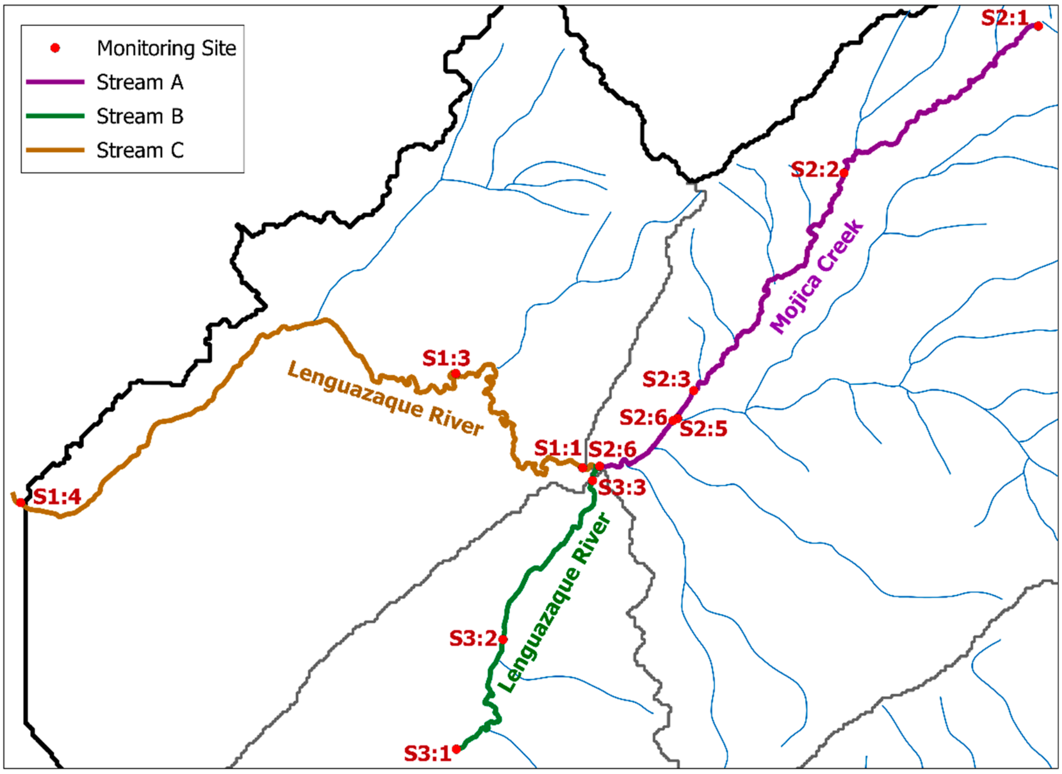


Figure 7. Modeled streams and monitoring sites.

3.2.3. Model Implementation, Calibration, and Verification

Results of the QUAL2Kw model performance obtained with calibration and verification datasets are summarized in Table 6. As shown, the best values of the objective function (Equation (4)) during calibration were obtained for Stream C, followed by Streams A and B. Turning to verification, optimal parameters led to an error 14% higher compared to calibration, while the confidence interval maintained similar magnitudes. This suggests that the model has a certain predictive capacity despite the mentioned uncertainty and limitations.

Table 6. Model performance with calibration and verification datasets.

Dataset	Stream	OF Results (Equation (4))			
		Sites Included (Equations (3) and (4))	Optimal Parameters	Quantile 2.5	Quantile 97.5
Calibration	A	S2:1,2	0.170	0.182	0.215
		S2:3,5,6	0.147	0.158	0.159
	B	S3:3	0.416	0.544	0.629
	C	S1:1,3	0.010	0.019	0.021
	All	S1:1,3; S2:1,2,3,5,6; S3:3	0.243	0.250	0.294
Verification	All	S1:4; S2:1,6; S3:3	0.278	0.280	0.285

Such capacity is visible for the results of the model. Examples of these results are shown in Figure 8, while plots for all state variables and streams are provided as

Supplementary Materials (See Figures S5.1–S5.10 for calibration and Figures S6.1–S6.11 for verification). During calibration, the model reproduced observations reasonably well except in certain cases. These cases include the underestimation of pathogens in S2:2, and the overestimation of ISS and P_{org} in S2:5, also happening for DO, P_{inorg} and pH in S3:3. Turning to verification, most observations were also captured, except for some discrepancies at sites S1:4 and S2:6. In the first site, said discrepancies include DO and pH which were under and overestimated, respectively. In the second site, several constituents were underestimated such as CBOD, organic N, and inorganic P. The plots also show the ranges of historical concentrations in S3:1, as well as the response of the model to minimum and maximum concentrations observed for domestic wastewater (S3:2).

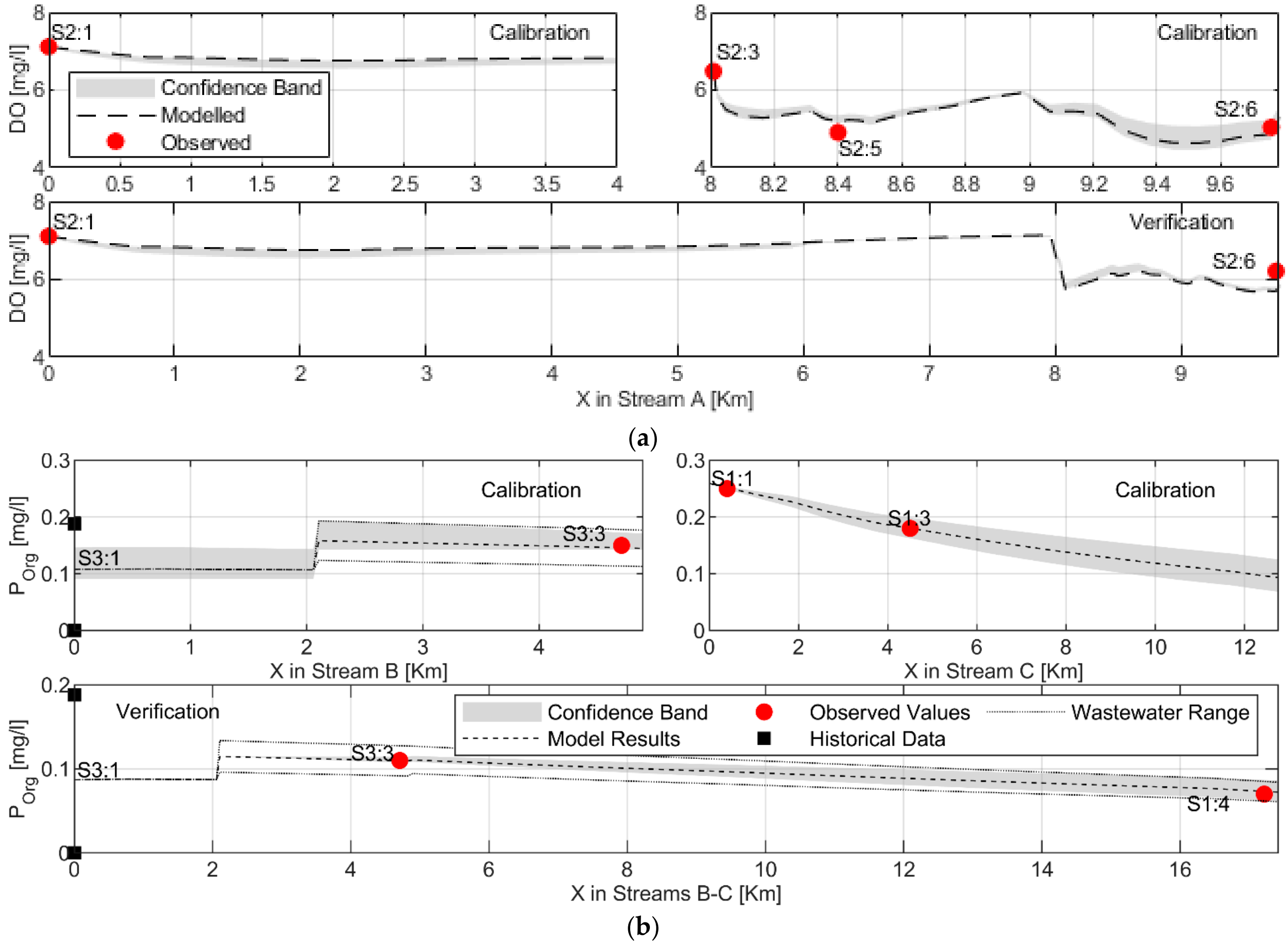


Figure 8. Model results and observations during calibration and verification: (**a**) dissolved oxygen in Stream A; (**b**) organic phosphorus in Streams B and C.

An analysis of model uncertainty and parametric sensitivity are provided as Supplementary Materials (Figures S7.1–S7.12). In this analysis, scatter plots show the influence of all parameters considered in the model on the objective function OF. In addition, these plots display the ranges used for calibrating the parameters. Based on these results, a summary of the parameter values and those found to be sensitive is presented in Table S6.1. As shown, only 19 out of 31 parameters were sensitive to the modeled inputs. Most of these parameters were part of the model comprising of the first segment of Stream A, and Stream C. In contrast, only a few parameters were sensitive in the model comprising of the second segment of Stream A and Stream B. Hence, in these streams, the model is more uncertain and presents more issues with parametric equifinality.

3.3. Stage 3: Simulation of Scenarios

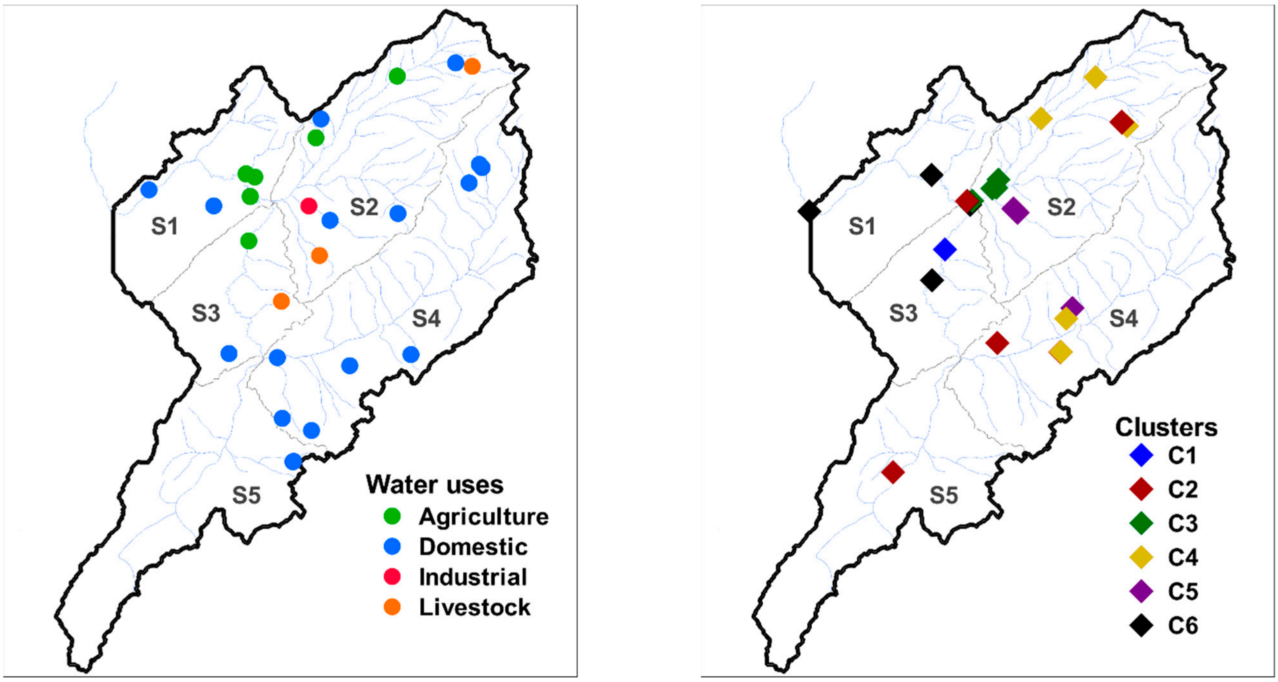
3.3.1. Identification of Potential Conflicts

Uses of water [110] and clusters of monitoring sites in the study area are presented in Figure 9. For each use, water quality standards are found in local regulations [110]. Based on these standards, uses and clusters, the resulting critical values are presented in Table 7. Such values indicate the potential conflicts found in the different groups of monitoring sites. In C1, values of pathogens, nutrients, phenols, and dissolved oxygen lead to potential conflicts when using water for potabilization, recreation and conservation purposes. Bear in mind that C1 comprises of only one site where domestic wastewater is monitored (See Tables 2 and A1). Since such water is likely not used for any purpose, no actual conflict is expected in this case. In the remaining clusters (C2–C6), critical values lead to potential conflicts for all regulated uses of water. These conflicts can be particularly serious in C2 because most standards were violated at these locations. Nevertheless, conflicts can be significantly different depending on individual uses of water in the catchment.

Table 7. Critical values for regulated constituents and uses of water.

Water Use	Constituent	Standard	Units	Critical Values					
				C1	C2	C3	C4	C5	C6
Potabilization by conventional means	pH	5–9	pH	-*	3.1	-	4.0	-	-
	TC	<20,000	MPN/100 mL	120×10^6	-	-	-	-	240,000
	NH_4^+	<1	mg/L	97.8	5.0	-	-	-	1.06
	Cr^{+6}	<0.05	mg/L	-	0.14 **	-	-	-	-
	Pb	<0.05	mg/L	-	0.06	-	0.06	-	-
	Phenol	<0.002	mg/L	0.24	0.27	-	-	-	0.45
	SO_4^{2-}	<400	mg/L	-	2430	-	-	-	-
Potabilization by disinfection only	pH	6.5–8.5	pH	-	3.1	5.8	4.0	-	6.23
	TC	<1000	MPN/100mL	-	-	11,000	-	5500	240,000
	NH_4^+	<1	mg/L	97.8	5.0	-	-	-	1.06
	Cr^{+6}	<0.05	mg/L	-	0.14 **	-	-	-	-
	Pb	<0.05	mg/L	-	0.06	-	0.06	-	-
	Phenol	<0.002	mg/L	0.24	0.27	-	-	-	0.448
	SO_4^{2-}	<400	mg/L	-	2430	-	-	-	-
Agriculture	pH	4.5–9	pH	-	3.1	-	4.0	-	-
	TC	<5000	MPN/100mL	-	-	11,000	-	5500	240,000
	Al	<5	mg/L	-	21.99	-	-	-	-
	Cu	<0.2	mg/L	-	0.24	-	-	-	-
	Cr^{+6}	<0.1	mg/L	-	0.14 **	-	-	-	-
	Fe	<5	mg/L	-	187	-	9.1	-	-
	Mn	<0.2	mg/L	-	4.96	-	2.15	0.25	-
	Ni	<0.2	mg/L	-	0.56	-	-	-	-
Livestock	pH	4.5–9	pH	-	3.1	-	4.0	-	-
	TC	<5000	MPN/100mL	-	-	11,000	-	5500	240,000
	Al	<5	mg/L	-	21.99	-	-	-	-
Recreation	pH	5–9	pH	-	3.1	-	4.0	-	-
	TC	<1000	MPN/100mL	-	-	11,000	-	5500	240,000
	DO	>0.7 sat	mg/L	0	2.8	4.91	3.3	2.49	0.6
	Phenol	<0.002	mg/L	0.24	0.27	-	-	-	0.448
Conservation	pH	6.5–9	pH	-	3.1	5.8	4.0	-	6.23
	DO	5	mg/L	0	2.8	4.91	3.3	2.49	0.6
	Toxicants	<0.1	96-h LC_{50} ***	uncertain	uncertain	uncertain	uncertain	uncertain	uncertain

* refers to no conflict found; ** value for Total Cr since Cr^{+6} was not measured; *** 96-h LC_{50} refers to the concentration of a toxicant leading to the death of 50% of certain organisms in 96 h. Since conservation is not a documented use of water in the catchment, there are not records of local organisms of interest. Therefore, the compliance of this standard and the existence of conflicts are uncertain in this case, as stated on the last row of the table.



(**a**) (**b**)

Figure 9. Location of: (**a**) water uses; (**b**) sites in each cluster.

In the case of agriculture, water is collected for irrigation from the main streams in sub-basins S1, S2 and S3 (Figure 9a). Since these streams are close to sites in clusters C1, C4 and C6 (Figure 9b), crops in these sub-basins are likely irrigated with water of low quality. Crops are no doubt exposed to significant concentrations of pathogens in S1 and S3, while in S2 they are irrigated with an acid pH and high amounts of Fe, and Mn. Concerning domestic use, water is collected in many locations in all sub-basins (Figure 9a). Among these locations, potabilization could be compromised in sub-basins S2, S3 and S4, nearby sites in clusters C2 and C4 (Figure 9b). This could happen because high concentrations of NH_4^+, Pb, SO_4^{2-} and phenols have been reported in these clusters, as well as an acid pH. About livestock and industrial uses, no relevant conflicts are expected since water is not collected near polluted locations in the first case, while no standards are violated in the second. It is important to highlight that no clear locations are delimited for recreational and conservation uses of water in the catchment. Stakeholders have yet identified certain areas as having potential for conservation, especially those near strategic ecosystems such as paramos [65]. Nevertheless, the numerous toxicants and critical values found for coliforms, dissolved oxygen and pH, even very close to these ecosystems, make water likely unhealthy for regional biota. Given these results, it is generally unsafe to use water from sites included in this study for any purpose, at least without previous inspection and possibly treatment.

3.3.2. Simulation of Critical Scenario

For site S1:1 (see Figure 7), the results of design conditions for steady flows are shown in Table 8. These results are based on daily streamflow records available for this location [64]. It is important to highlight that such flows are consistent with typical observations during the driest season [64], also identified previously as the most polluted (see Figure 6). Thus, they are representative of the critical scenario of the catchment. In addition, model outcomes for total coliforms are shown in Figure 10, and plots for other regulated constituents are provided as Supplementary Materials (Figures S8.1–S8.4). Here, total coliforms and dissolved oxygen do not generally meet any standard, while pH and NH_4^+ do so partially. Coliforms are particularly serious as they threaten current agricultural and domestic uses, whereas NH_4^+ and pH disable potabilization in certain sections of the river. Combined with the low contents of dissolved oxygen, these constituents also restrict recreation and conservation uses of water. According to verification results, these predictions could have several limitations such as possible under and overestimation of dissolved oxygen and pH near the outlet of the basin, respectively.

Table 8. Design conditions for steady flow at site S1:1.

XQT (Equation (7))	Value	Units
1Q2	0.273	m^3s^{-1}
1Q3	0.223	m^3s^{-1}
4Q3	0.170	m^3s^{-1}
7Q10	0.236 *	m^3s^{-1}

* Used for simulation.

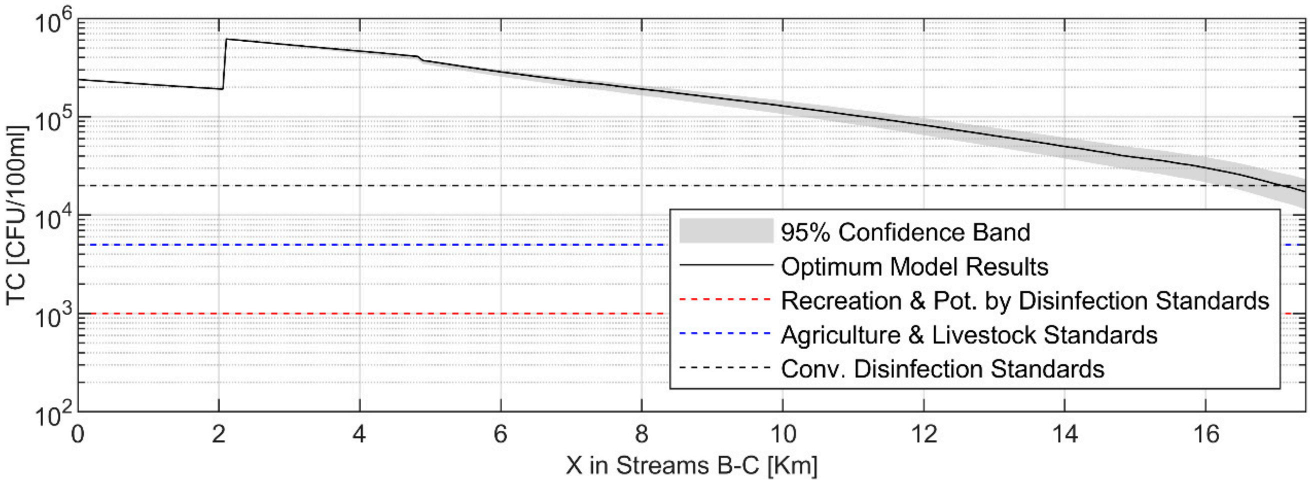


Figure 10. Critical scenario results for total coliforms in Streams B and C.

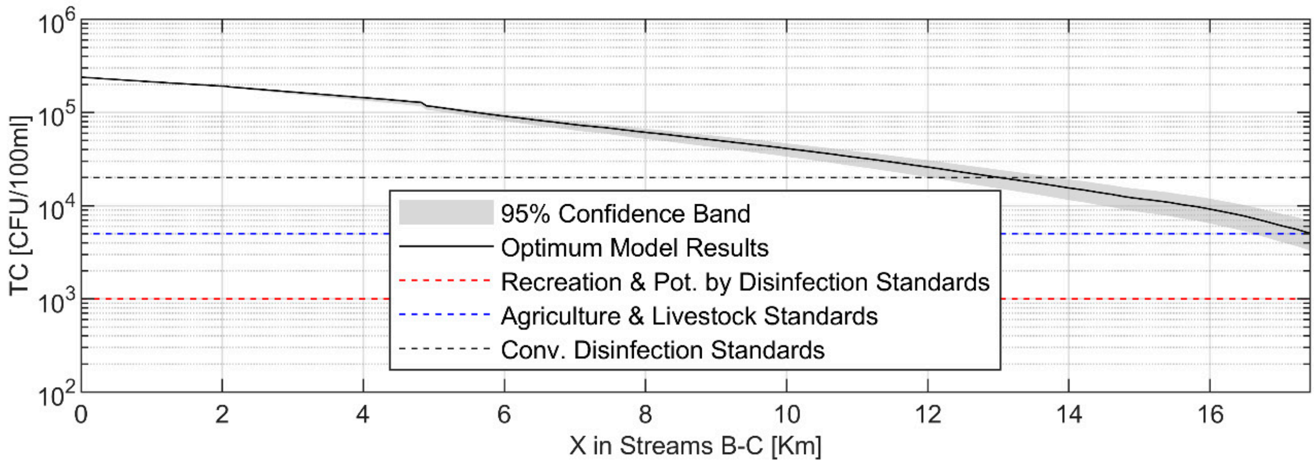
3.3.3. Simulation of Alternative Scenarios

The definition of the two alternative scenarios is summarized in Table 9, and the resulting concentration of total coliforms in these scenarios is shown in Figure 11. Model results for additional regulated constituents are included as Supplementary Materials (Alternative 1: Figures S9.1–S9.4; Alternative 2: Figures S10.1–S10.4). About the first alternative, results show that adding treatment to the main discharge of domestic wastewater (site S3:2) does not solve the conflicts described previously. Particularly, removing virtually all pathogens from such discharge does not make water suitable for agriculture (Figure 11a). Moreover, such treatment has a very limited influence on the concentrations of NH_4^+, DO and pH. Thus, solving the conflicts requires additional improvements of water quality upstream, as simulated in the second alternative (Figure 11b). In this alternative, polluting loads from Sites S3:1 and S2:6 were significantly reduced to comply with agricultural standards, and the concentration of DO and pH were also increased. Accordingly, having water of appropriate quality, even during the most polluted season, requires significant efforts in the study area. These efforts include reducing polluting loads coming from all significant sources including the main discharge of domestic wastewater, as well as those leading to poor water quality upstream in sub-basins S2, S4 and S5.

Table 9. Description of alternative scenarios in the case study.

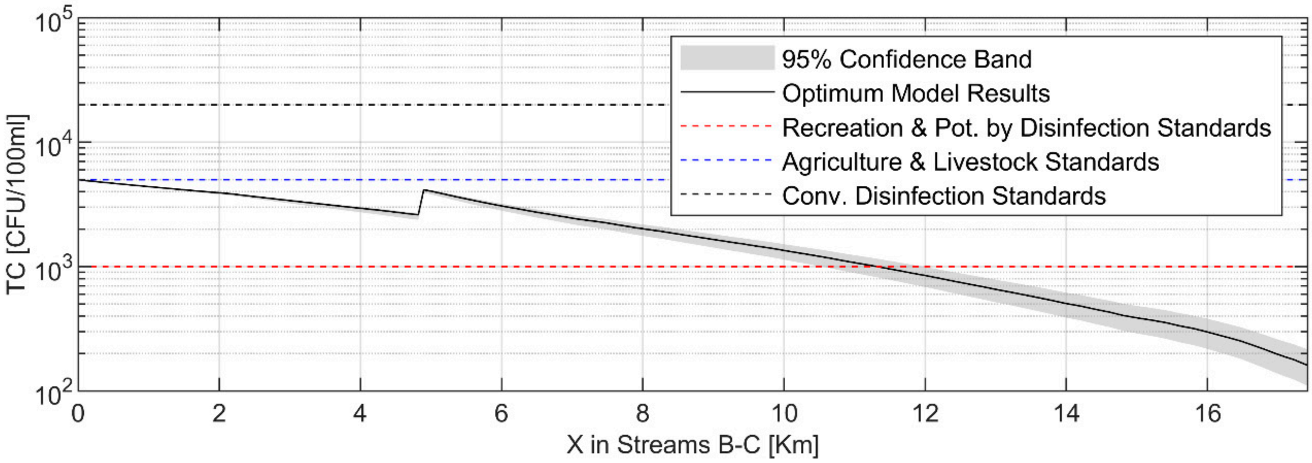
Site	Constituent	Load in Critical Scenario	Load Reduction Compared to Critical Scenario			
			Alternative 1		Alternative 2	
		[kg day^{-1}] *	[%]	[kg day^{-1}] *	[%]	[kg day^{-1}] *
S3:1—Headwater of Stream B	TC	4.35×10^{13}	-	-	97.92%	4.26×10^{13}
	ISS	2124.25	-	-	-	-
	Det	485.39	-	-	75.00%	364.05
	$CBOD_F$	141.36	-	-	85.00%	120.15
	$CBOD_S$	154.01	-	-	85.00%	130.91
	COD	1112.72	-	-	85.00%	945.82
	N_{org}	4.19	-	-	67.18%	2.81
	NH_4^+	19.37	-	-	30.00%	5.81
	P_{org}	1.81	-	-	-	-
	P_{inorg}	1.59	-	-	-	-
S3:2—Discharge of Domestic Wastewater	TC	7.915×10^{13}	99.99%	7.914×10^{13}	99.99%	7.914×10^{13}
	ISS	0.37	85.00%	0.32	85.00%	0.32
	Det	36.98	85.00%	31.43	85.00%	31.43
	$CBOD_F$	37.96	85.00%	32.26	85.00%	32.26
	$CBOD_S$	41.35	85.00%	35.15	85.00%	35.15
	COD	26.06	75.00%	19.54	75.00%	19.54
	N_{org}	3.69	30.00%	1.11	43.01%	1.59
	NH_4^+	6.03	10.00%	0.60	10.00%	0.60
	P_{org}	0.12	30.00%	0.04	125.73%	0.15
	P_{inorg}	0.90	30.00%	0.27	30.00%	0.27
S2:6—Mojica Creek	TC	3.63×10^{11}	-	-	-	-
	ISS	75.72	-	-	-	-
	Det	17.30	-	-	50.00%	8.65
	$CBOD_F$	5.20	-	-	75.00%	3.90
	$CBOD_S$	5.67	-	-	75.00%	4.25
	COD	134.41	-	-	85.00%	114.25
	N_{org}	1.26	-	-	50.00%	0.63
	NH_4^+	0.47	-	-	50.00%	0.24
	P_{org}	0.44	-	-	-	-
	P_{inorg}	0.32	-	-	-	-

* Total coliforms (TC) are expressed in MPN day^{-1}.



(a)

Figure 11. *Cont.*



(**b**)

Figure 11. Model results for total coliforms in: (**a**) alternative scenario 1; (**b**) alternative scenario 2.

4. Conclusions

4.1. Information Analysis

Previous results in the case study show that the different analyses employed were suitable to collect, organize, and assess limited yet heterogeneous water quality records. These analyses were particularly useful in identifying the most relevant contaminants and clusters of sites with similar pollution levels. Additionally, summarizing water quality information with these clusters allowed for the identification of the most polluted sites, the description of yearly contamination patterns, and the recognition of conflicts between uses and quality of water. In addition, it was possible to evaluate the quality, consistency, and validity of data. Given these outcomes in the case study, it is possible to anticipate that employing these analyses in other headwater catchments, facing similar challenges, could be valuable as well. Gaining similar insights on contamination levels, patterns, and conflicts could be important for researchers, policy makers and stakeholders. Furthermore, results of these analyses could lay the groundwork for the subsequent development of water quality models.

4.2. Development of a Water Quality Model

Starting from previous analyses, the proposed activities were suitable for implementing, calibrating and verifying a water quality model in the catchment of interest. Focusing on conventional water constituents under steady state conditions, it was possible to obtain a QUAL2kw model with a certain predictive capacity supported by the values of the objective function during calibration and verification. The careful analysis of the parameters and their uncertainty allowed us to recognize model limitations, as well as the role of all constituents to achieve a good performance.

About the limitations, having a difficult terrain was a significant source of uncertainty since it impeded reaching every pollution source and including it in the model. In addition, not having data collected on-site from tracer experiments also adds uncertainty to the velocity of pollutants traveling in the catchment. Note that Equation (3) and synthetic experiments allowed for an estimation of dispersion coefficients (D) that is in line with typical values in mountain rivers. Yet, having field data is always preferable since it allows for precise estimates of pollutant's velocities, which is key to reduce uncertainty. Since these issues can be found in other headwaters of developing countries, present research could serve as a reference for designing improved monitoring protocols in similar catchments. In any case, acknowledging the limitations is especially important when simulating alternative scenarios and making future improvements to the model.

Turning to the role of all constituents, involving plants and algae was key to reproduce the concentrations of nutrients and dissolved oxygen in the modeled streams. This confirms the importance of such aquatic organisms in the balance of nutrients and oxygen in mountainous streams. Finally, given the numerous toxicants found, subsequent work should focus on implementing WASP for those found relevant after the analysis of principal components.

4.3. Simulation of Scenarios

Based on previous analyses and model development, the activities proposed allowed for the identification of potential conflicts between uses and quality of water. This is a key step before simulating scenarios because it allows for the detection of conflicting situations that need to be addressed. Grouping monitoring sites in clusters played a significant role, since identifying conflicts in a few groups is simpler than assessing monitoring sites individually. If details on these sites are needed, it is always possible to disaggregate data and evaluate the components of each cluster separately. The critical scenario is valuable as well, considering that it represents the most polluted season in the catchment. Hence, local stakeholders need to change that scenario if they intend to use water of appropriate quality throughout the year.

Simulating alternative scenarios provided two main findings to pursue change. First, adding treatment to the main discharge of domestic wastewater is not sufficient for resolving the identified conflicts. This means that centralized treatment is already insufficient to manage pollution in the case study, despite centralized treatment's capacity to remove significant polluting loads. Second, preventing conflicts requires improving water quality in the sub-basins at the highest altitudes. Given the numerous and diverse sources of pollution, improvement requires the commitment of different local stakeholders. Furthermore, the amount and diversity are not unique to this area, making the proposed framework potentially useful to simulate scenarios in other regions. In particular, this framework should support the definition of conflicting situations, as well as the dimensioning of possible solutions. Take into consideration that it is possible to design and simulate many additional scenarios, yet the two proposed here can be practical points of reference.

4.4. Suggestions for Further Work

Future work could take several pathways. One of them is related to improving the analysis of water quality information. We believe this path is important since several subjective assumptions were required when performing the analysis. When classifying monitoring sites in clusters, these assumptions include the interpretation of the dendrogram aided by professional judgement and the arbitrary selection of methods to build this diagram with CA. When defining the most relevant constituents, splitting data into conventional and toxic constituents may also be considered arbitrary, as well as the coefficient thresholds used in PCA. Accordingly, further research on this subject could lead to the establishment of better criteria to avoid subjective assumptions. These criteria could lead to making the analysis more efficient and even automatic.

A second pathway is related to reducing model uncertainty and increasing its predictive capacity. As previously stated, a difficult terrain makes it hard to reach and sample every pollution source, and therefore contributes to model uncertainty. As a consequence, designing improved monitoring protocols and sampling equipment are key aspects to reduce such uncertainty. The improvements should be directed to reducing monitoring costs as well as to facilitate sampling in difficult terrains. In addition, the high number of undetected values and the few records in sediments were highlighted as significant limitations. Facing the limitations is possible by using more sensitive detection equipment, as well as monitoring sediments more frequently. Reducing such uncertainty could lead to better models, better predictions, and lay the foundations for the development of accurate models for toxicants.

A third pathway centers on improving water quality in headwater catchments of developing countries. To this end, the case study provided evidence on how the proposed framework can be useful for several purposes. These purposes include describing yearly pollution regimes, identifying the most polluted locations, and estimating the load reduction required to resolve water quality conflicts. Correspondingly, replicating this framework in other comparable catchments should be useful for similar aims. The case study also exemplified how traditional centralized treatment is already insufficient for facing current pollution issues, even at high altitudes. Therefore, significant efforts are needed to design innovations that allow for the management of these issues, in an environment of difficult terrains and limited resources. Every effort in these regions is meaningful, as they are home to more than 600 million inhabitants.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15050868/s1, These materials comprise a PDF document including all tables and figures mentioned in the results section. Here, Section S1 contains four Tables describing univariate statistics for conventional water quality determinands. Section S2 also contains four Tables describing the same statistics for toxicants. Section S3 contains two Figures, the first dedicated to the spatial distribution of toxicants in sediments, and the second to temporal distribution of toxicants in the catchment. Section S4 focuses on the detailed characterization of river hydraulics and solute transport, presented in two Tables and one Figure. Section S5 presents 10 Figures containing all plots resulting from model calibration. Section S6 presents 10 similar Figures, this time for model verification. Section S7 shows detailed results on parametric uncertainty in one Table and 12 Figures. Section S8 presents four Figures describing results of the critical scenario, while Sections S9 and S10 show eight Figures describing the results of the two alternative scenarios. Data and Code are also available as described in the Data Availability Statement below.

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Data Availability Statement: In addition to the Supplementary Materials, the datasets, QUAL2Kw models and code developed for the present project are available for download in the following online repository: Fernandez, N. (2022). Repository of Water Quality Datasets & Models for the Lenguazaque River Basin (Cundinamarca, Colombia)", Mendeley Data, V1, https://doi.org/doi:10.17632/4xkc5jtjj5.1.

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Appendix A

Table A1. Description of monitoring sites.

Sub-Basin	Long, Lat [Dec. Degrees]	Elevation [MAMSL]	Stream	Description	Source
S1	−73.70, 5.33	2559.2	Lenguazaque River	Downstream S2 Confluence	Primary
	−73.70, 5.33	2559.2	Mine Drainage	Pipe downstream S1-1	Primary
	−73.71, 5.34	2551.4	Lenguazaque River	Downstream Coking Plant	Primary
	−73.76, 5.32	2544.9	Lenguazaque River	Basin Outlet	Primary and Secondary
S2	−73.65, 5.38	3036.8	Mojica Creek	Near Paramo	Primary
	−73.67, 5.36	2801.0	Mojica Creek	Between S2-1 and S2-3	Primary
	−73.69, 5.34	2569.5	Mojica Creek	Upstream S2-4 Confluence	Primary
	−73.69, 5.33	2566.9	Hondura Creek	Upstream S2-3 Confluence	Primary
	−73.69, 5.33	2566.7	Mojica Creek	S2-3 and S2-4 Confluence	Primary
	−73.70, 5.33	2559.7	Mojica Creek	Upstream S3 Confluence	Primary and Secondary
	−73.63, 5.36	3277.0	Mine Drainage	Pablo Gonzalez Mine	Secondary
	−73.64, 5.36	3218.0	Unnamed Creek	Upstream Corales Mine	Secondary
	−73.64, 5.36	3225.0	Mine Drainage	Corales Mine	Secondary
	−73.64, 5.36	3214.0	Unnamed Creek	Downstream Corales Mine	Secondary
	−73.68, 5.32	2715.0	Baloncitos Creek	Upstream Chorrera	Secondary
	−73.68, 5.32	2700.0	Chorrera Creek	Receives Mine Drainage	Secondary
	−73.68, 5.32	2696.0	Baloncitos Creek	Downstream Chorrera	Secondary
S3	−73.71, 5.30	2570.0	Lenguazaque River	Tapias Monitoring Station	Secondary
	−73.71, 5.31	2564.7	Domestic Wastewater	Lenguazaque Discharge	Secondary
	−73.70, 5.33	2559.3	Lenguazaque River	Upstream S2 Confluence	Primary
S4	−73.66, 5.28	2847.0	Mine Drainage	San Sebastian Mine	Secondary
	−73.66, 5.28	2818.0	Mine Drainage	San Jose Mine	Secondary
	−73.66, 5.27	2820.0	Palizada Creek	Upstream Mine Drainage	Secondary
	−73.66, 5.27	2819.0	Palizada Creek	Downstream Mine Drainage	Secondary
	−73.69, 5.27	2774.0	Mine Drainage	Chuscal Mine	Secondary
S5	−73.73, 5.22	2784.0	Mine Drainage	Unknown Mine	Primary

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