

Article



Modeling the Impact of Urban and Industrial Pollution on the Quality of Surface Water in Intermittent Rivers in a Semi-Arid Mediterranean Climate

Abdelillah Bouriqi^{1,2,*}, Naaila Ouazzani² and Jean-François Deliege^{1,*}

- ¹ PeGIRE Laboratory, RU FOCUS-Aquapôle, Liege University, 4000 Liege, Belgium
- ² EauBiodiCc Laboratory, Water, Biodiversity and Climate Changes, Faculty of Sciences Semlalia, Cadi Ayyad University, Marrakech 40000, Morocco; ouazzani@uca.ac.ma
- * Correspondence: abdelillah.bouriqi@doct.uliege.be (A.B.); jfdeliege@uliege.be (J.-F.D.)

Abstract: Ensuring the protection of the aquatic environment and addressing the water scarcity and degradation of water quality in the Mediterranean region pose significant challenges. This study specifically aims to assess the impact of urban and industrial pollution on the ZAT River water quality. The study exploits a combination of field measurements and mathematical simulations using the PEGASE model. The objective is to evaluate how water quality changes throughout the different seasons and to determine whether olive oil factories discharge industrial wastewater into the river. The study reveals that the river water quality remains relatively stable along its course, up to km 64 in winter and km 71.77 in summer, where poor water quality is recorded. This degradation can be attributed to multiple factors. One of these factors is the discharge of industrial wastewater, which accounts for 47% of the COD pollution load. This industrial wastewater is released into the river without treatment during the production period (January-February) and inactivity period (March-May). The combined impact of urban and industrial wastewater is also associated with the decrease in water flow resulting from water withdrawals due to irrigation canals and groundwater recharge, which both contribute to the observed changes in river water quality. Importantly, field measurements combined with results obtained from the calibrated model provide compelling evidence of unauthorized wastewater discharges from the olive oil factories into the river. These results emphasize the need for stricter regulation, such as developing water quality monitoring strategies based on the use of modeling methodologies. They also emphasize the importance of improving wastewater management practices, such as setting up treatment plants for different sources of pollution or developing a co-treatment plant to mitigate the adverse impact of industrial pollution on river water quality.

Keywords: water quality modeling; PEGASE model; industrial wastewater; urban wastewater

1. Introduction

Water pollution caused by increasing pollution loads due to industrialization and urbanization is a major challenge issue in many parts of the world [1]. Morocco, renowned for its frequent droughts for six consecutive years, faces mounting pressure on its water supplies [2]. Wastewater from urban and rural areas and industries degrades water resources. The combination of drought and increased pollution makes it challenging to dilute and disperse wastewater into rivers, increasing the cost of water treatment and adding pressure to provide acceptable water quality for agricultural, industrial, and drinking requirements [3]. In Morocco, wastewater is often discharged without prior treatment [4,5], considerably reducing the quality of water resources, especially surface water [6].

In the Mediterranean region, small rivers frequently experience a significant decrease in their water flow, particularly during dry periods. This reduction in water volume exacerbates the concentration of pollutants [7,8]. The rivers in this region, particularly



Citation: Bouriqi, A.; Ouazzani, N.; Deliege, J.-F. Modeling the Impact of Urban and Industrial Pollution on the Quality of Surface Water in Intermittent Rivers in a Semi-Arid Mediterranean Climate. *Hydrology* 2024, *11*, 150. https://doi.org/ 10.3390/hydrology11090150

Academic Editor: Tommaso Moramarco

Received: 7 August 2024 Revised: 2 September 2024 Accepted: 6 September 2024 Published: 11 September 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). in Morocco, are exposed to pollution due to wastewater from olive oil mills located near the rivers [5]. They also suffer from landfill leachate pollution from uncontrolled landfills located near the rivers [9]. Moreover, most villages and towns are situated on the riverbanks, which causes them to discharge untreated pollutants into them [10]. These urban and industrial contaminants often include high levels of nutrients such as carbon, nitrogen, and phosphate [11], as well as a range of pathogens such as bacteria, viruses, and parasites [12]. Some industrial pollutants, such as landfill leachate, can contain high levels of heavy metals, pesticides, and chemicals [13]. Olive mill wastewater also contains high levels of polyphenols and salts, with acid discharge [14]. These contaminants lead to reduced oxygen levels, increased pollutant concentrations, and fluctuations in temperature and acidity [15]. All these factors contribute to poor to very poor water quality parameters in rivers [16].

Assessing the dynamics of pollution and establishing the sources of pollutants and the waterbody most at risk at the watershed scale is a complex problem, as it involves significant uncertainty in the spatiotemporal variables [17]. Conventional methods of monitoring surface water quality do not offer a holistic perspective on pollution dynamics in time and space [18,19]. Therefore, the use of mathematical models to simulate river water quality and pollutant dynamics is crucial for a better understanding and integrated management of water resources [20]. Modeling also allows us to forecast the results associated with the scenarios proposed by decision-makers [21]. River quality models focus on using large amounts of data to create a model that closely reflects reality [22].

The classic equations for simulating DO (dissolved oxygen) and BOD (biochemical oxygen demand) in rivers were derived by Streeter and Phelps in 1925. These equations have served as the foundation for numerous water-quality models created worldwide since then [23]. In the past twenty years, the domain of water-quality modeling has undergone significant advancements due to various factors, including the utilization of data, advancements in processor computing power, better technological control, advancements in algorithms, and other related developments in hydrology [24]. These advancements have led to the creation of various models, including PEGASE [25]. In the last 20 years, there has been a significant improvement in creating water-quality models that are robust and can simulate river quality in one, two, or three dimensions [26]. The need to adapt models for understanding watershed behavior at different spatial resolutions arose as stakeholders increasingly relied on forecasting water management tools [27,28]. This is the case, for example, in Europe, where many river basin agencies rely on the PEGASE model to forecast river quality, such as the Rhine–Meuse water agency [29]. However, unlike Europe, where there is a wealth of available data that enhance the operational efficiency of models, applying the same models to water basins in Africa, in particular, is exceedingly challenging due to data scarcity and the associated difficulties in obtaining them [30].

The PEGASE model is one of the models used in North African basins, and it has demonstrated its ability to generate accurate results despite the scarcity of data and the associated challenges in acquiring them [31]. The model has been applied to significant watersheds throughout Western Europe, including the Scheldt, Adour, Loire, Moselle, Garonne, Meuse, and others [29,32]. The model was initially created for the Belgian Walloon Area and has since been applied in various research conducted in Africa, particularly in Algeria and Tunisia [31]. The model's ability to quantify the nonlinear impact of pressures on rivers and describe the relationships between watersheds and rivers is one of its most original features [25].

The characteristics of this model include a spatial discretization that enables accurate simulation of both large and small river basins [33]. The model is a physics-based water quality model with a complete representation of key biogeochemical processes, a complete and consistent description of all discharge loads necessary to establish pressure–impact relationships, and a user-friendly interface that allows appropriate authorities to operate the software independently [29]. This model is deterministic and provides a detailed depiction of the physical and chemical processes under surrounding conditions [34]. It

uses a series of kinetic equations that depict the system dynamics and changes in biological processes [25,31]. The majority of these model parameters, except for those related to soil functions, do not require adjustment or calibration because they have biological, chemical, or physical significance [25].

Previous studies on industrial wastewater discharge and its environmental effects in Rwanda, Ethiopia, and China [35–37], as well as predictive simulation studies on water quality improvement measures in river basins, have underscored the criticality of understanding and mitigating the impacts of pollution on water bodies [4,38]. These investigations have highlighted the complexities and consequences of industrial and urban pollution on river ecosystems. Furthermore, research on extreme events like freshwater anoxia in Belgium due to industrial accidents in France has emphasized the urgency of effective pollution control measures [33].

The objective of this study is to explore highly contaminated regions and identify pollution sources in the ZAT River basin. It specifically investigates whether olive oil factories are discharging industrial wastewater into the ZAT River. The study examines the pollution levels during active months such as January and February and compares them to non-production periods. Ultimately, the research aims to quantify the total industrial pollution discharged into the ZAT River relative to the annual production levels.

2. Materials and Methods

2.1. Study Area

The ZAT River basin is one of the sub-basins in the Tensift river watershed, which covers an area of 20,450 km² in central Morocco, extending from the Atlas Mountains to the Atlantic Ocean [39]. The ZAT River sub-basin (Figure 1) covers an area of 921 km² [40]. Altitude has a significant influence on the region's Mediterranean climate, with heights varying between the northern and southern halves of the basin at 430 m downstream and 3911 m upstream, respectively. The average slopes of the upper and lower slopes are 19% and 0.88%, respectively [41]. Downstream, the ZAT River sub-basin is distinguished by the prevalence of igneous rocks, with Triassic rocks dominating from the middle to the bottom and sedimentary rocks present downstream [42]. The main river, which is 89 km long, drains the ZAT River sub-basin [39]. About km 62, there is a solitary station for monitoring precipitation and outflow in the main river. This station reported an average flow of 3.33 m³/s and 255 mm of precipitation annually [43]. According to Bouimouass et al. (2020) [44], the downstream area of the ZAT River is characterized by high water depletion caused by irrigation canals and groundwater recharge, as well as average evaporation rates of 1600 mm per year [45]. The basin is characterized by a concentration of urban and industrial pollution downstream of the river, along with some agricultural activity [16].

2.2. Data Collection and Water Quality Monitoring

Application of the PEGASE model in the ZAT River basin (Figure 2), we established a comprehensive database that included geographical, hydrometeorological, pollution, and quality measurement data. We downloaded spatial data as a digital elevation model (DEM). The DEM was obtained from LANDSAT 8 with SRTM resolution of 30×30 m (Shuttle Radar Topography Mission). Using the DEM, we identified the ZAT River basin and assessed its drainage patterns, elevation, and slope data. We processed the DEM data using the Geographic Information System (GIS) interface of the ArcGIS[®] program [43]. We collected and analyzed daily hydrometeorological data (solar radiation, daily flow, and water temperature recorded in the ZAT River basin), as well as data on human activities and discharges (livestock, domestic effluents, etc.). We characterized all sources of pollution (urban, industrial, agricultural), including their GPS location, quantity of discharges (m³/d), pollution loads (Kg COD/d), population equivalent (L/inhab/d), and pollution concentration (mg/L) [16]. This information was provided by the local Watershed Agency and through our field survey, sampling, and laboratory analysis (Table 1).



Figure 1. Geographic location of the studied stations (S1 to S9) in ZAT River, Morocco.



Figure 2. A workflow scheme of the methodology used in this study.

Table 1. Summary of data used in this study.	Table 1.	Summary	of data	used in	this	study.
--	----------	---------	---------	---------	------	--------

Data	Format	Period/Frequency	Data Source
Hydro-geographical data	Shapefile	2021	Tensift Hydraulic Basin Agency
Digital terrain model 30 m	Rasters	2021	Tensift Hydraulic Basin Agency
Land use map	Shapefile	2021	Tensift Hydraulic Basin Agency
Flow measurement	Excel file	Daily from 1990 to 2021	Tensift Hydraulic Basin Agency
Rainfall	Excel file	Daily from 1990 to 2021	Tensift Hydraulic Basin Agency
River temperature	Excel file	Daily from 2021	Tensift Hydraulic Basin Agency
Insolations	Excel file	Every 30 min from 2021	Tensift Hydraulic Basin Agency
Withdrawals	Excel file	2021	Tensift Hydraulic Basin Agency
Discharge data	Excel file	2021	Tensift Hydraulic Basin Agency
Quality data	Excel file	Every 15 days for 6 months until 2021	Sampling campaign and laboratory analysis

Monitoring campaigns were carried out during the winter (5 and 19 January, 2 and 6 February), spring (2 and 16 March, 6 and 20 April, 4 and 18 May), and summer (1 and 15 June) of 2021. In the field, we measured dissolved oxygen (DO), water temperature (T°), electrical conductivity (EC), and pH using a multiparameter instrument (HANNA HI 9829, Romania). We collected samples in the field, and subsequently, we analyzed other parameters such as chemical oxygen demand (COD), ammonium ion (NH₄⁺), and orthophosphate (PO₄³⁻) in the laboratory according to AFNOR standards [46].

2.3. Pollution Sources

Different sources of onsite pollution exist in downstream ZAT River area: wastewater from olive oil extraction units (OMW), wastewater from the slaughterhouse existing near the part of ZAT River called Ait Ourir River (SW), leachate from the local public landfill (LL), and domestic wastewater discharged from Ait Ourir town (EU). To have a global idea about these different kinds of pollution, three sampling campaigns were conducted on 11 May 2021, 18 April 2021, and 25 May 2021 to collect samples from multiple sources, sampling points located 10 m from the discharge point at the slaughterhouse, landfill, and town of AIT Ourire. For olive oil mills, sampling points at the mills. (Figure 1). The mean characteristics of such sources of pollution are described in Table 2.

For the quantity of discharges (m^3/d) for each pollution source, information was provided by the local Watershed Agency.

Table 2. The mean (n = 3) physicochemical properties of the discharged wastewater into the river surrounding. EU: urban wastewater, SW: slaughter wastewater, OMW: olive mill wastewater, Ll: landfill leachate.

Parameters	Units	Discharge Limit Values in River	EU	SW	OMW	LL
Discharge volume	m ³ /d		3072	110	52	50
рН		5.5–9.5	8.01 ± 0.22	7.74 ± 0.12	5.76 ± 0.31	7.52 ± 0.15
CE	µs/cm	2700	1474 ± 144.31	2580 ± 175.11	$18,\!590\pm250.12$	8490 ± 310.04
COD	mgO_2/L	250	1342 ± 30.91	2509 ± 44.2	$193{,}565\pm500.32$	2576 ± 120.41
NH4 ⁺	mg/L		90 ± 0.87	46.13 ± 1.47	74.01 ± 1.61	73.40 ± 2.01
NO ₃ -	mg/L	NTK = 40	3.02 ± 0.16	9.48 ± 0.62	20.01 ± 0.41	12.19 ± 0.86
NO ₂ -	mg/L	-	6.11 ± 1.01	11.35 ± 0.96	62.20 ± 2.05	12.46 ± 0.51
PO4 ³⁻	mg/L	Pt = 15	4.04 ± 0.26	21.22 ± 2.41	34.58 ± 0.11	3.01 ± 0.09
COD Pollutant load	KgO ₂ /d		4123	276	10.151	129

2.4. Modeling Approach

PEGASE is an integrated river basin model that enables the deterministic simulation of river quality based on the structure of the river network, hydro-meteorological conditions, and natural and anthropogenic impacts such as point and diffuse discharges. The Aquapôle R&D team at the University of Liège developed this physics-based model [32]. The model is a tool for studying the behavior of the hydro system, quantifying relationships between pressure and impact, and determining the management strategies required to achieve specific goals. The model explains the flow of water and pollutants through the river system to the outlet [25]. It can manage several rivers at once and large watersheds with a precise spatial resolution of 200 m, offering a simple way to understand the data produced by generating maps and 2D graphics [29].

In reality, the model is a one-dimensional river model that uses physical calculations to dynamically represent the river behavior. A selection of rivers is used to depict the hydrographic network, which is discretized into nodes that allow for the transmission of data and the extraction of findings. The segments of the rivers have varying lengths. The model uses the idea of diffuse soil functions and uses a semi-statistical method to only determine the diffuse contribution of soils. Processes are described in a mechanistic manner using a set of kinetic equations. The model explicitly takes into consideration the ongoing outflows of wastewater from factories, cities, sewers, and treatment facilities as point sources of nutrients [25,33].

2.5. Model Implementation

Preprocessing and Parameterization of the PEGASE Model

The implementation of the model in the ZAT River basin began with the construction of the hydrogeographic database. This required a number of spatial data, such as the hydrographic network, hydrographic zones, digital terrain model, and land use [32]. PEGASE preprocessing algorithms, useful for modeling, were applied to construct and verify the topology of the hydrographic network, the altimetric profiles of rivers, and the connectivity (Figure 3). These preprocessing steps resulted in the following:

- Sequencing and orienting river segments to construct a topologically correct hydrographic network.
- Selection of nodes and generation of altimetric profiles for rivers, imposing a smooth downstream altitude decrease.
- Generation of basin/river connectivity by calculating the steepest path between cells and computing flow parameters on the basin (distances to rivers, altitude differences, etc.).
- Addition of information regarding land use and livestock.

Once the physical characteristics of the hydrographic basin and rivers were introduced, preprocessing of discharge and measurement station data (river flow measurements, solar radiation, temperature, water quality, discharges, etc.) could be performed to format them correctly and position them on the modeled hydrographic network with specific information (discharge load, river width, etc.) [29]. Before running PEGASE simulations, we specify the following information (simulation period, non-stationary parameters, output points for results, characterization of discharges, reductions, etc.), taking into account the specificities of the Moroccan context (estimation of population equivalent, imposition of a characteristic low-flow rate for intermittent watercourses, etc.) [25]. Field measurements are used to calibrate soil functions, and field measurements are necessary for the validation phase of the model simulation results, where calculated values are compared with measured values for a given day and location [31]. Accurate input data are essential for modeling river ecosystems, as it directly influences the reliability of predictions regarding pollutant loads and flow rates. High-quality data enhances model performance, allowing for effective assessments of water quality changes and pollution impacts [47–49]. The integration of diverse datasets, including real-time and historical data, is crucial for capturing spatial and seasonal variations, which supports informed decision-making in water resource management [50,51]. However, low-quality data can significantly hinder model accuracy. It has been highlighted during the studies regarding the challenges posed by data errors during calibration [49,52–54].



Figure 3. Preprocessing of geographical data with PEGASE.

2.6. Model Calibration

A calibration is necessary for PEGASE soil functions. Some soil functions have been adjusted for certain basins in prior studies, and only a few calibrations are needed when using the model for new basins, including those related to soil functions. The main part of the parameters is determined experimentally or based on a literature review; a few ones were fitted on specific basins by calibration undertaken in previous studies [25]. For the present application on the ZAT River Basin, the following parameters were adjusted:

- Norm of daily consumption of an inhabitant equivalent.
- Daily distribution of the elements (carbon, nitrogen, and phosphorus) of raw wastewater of an inhabitant equivalent.
- The soil leaching functions for the different land uses of the basin (urban, agricultural, forests, meadows, plantations, and miscellaneous). The concentration levels (i.e., soil leaching functions) for each soil occupancy are mainly projected using data obtained from measurements conducted in the upper part of the watershed.
- The flow of the river downstream km 62 is characterized by water abstraction toward irrigation canals and a consequent decrease in flow caused by soil infiltration (un-

For the calibration and adjustment, we selected 15 June 2021, which corresponds to a summer period with a calculated flow rate of 1.18 m³/s at km 64. This period is characterized by the absence of industrial activity from olive oil factories.

We calibrated diffuse inputs from the soil based on points 1, 2, and 3 upstream of the rivers and adjusted the concentrations of the diffuse inputs from the soil until we obtained results similar to the measured results at three points upstream. Concerning this parameter, the input values are as follows in Table 3.

Parameter (g/m ³)	Miscellaneous	Urban	Agricultural	Meadow	Plantation	Forest
Dissolved Organic Carbon Rapidly Degradable	0.03	0.06	0.06	0.06	0.06	0.06
Dissolved Organic Carbon Slowly Degradable	0.06	0.12	0.12	0.12	0.12	0.12
Dissolved Organic Carbon Non-Degradable	0.14	0.28	0.28	0.28	0.28	0.48
Particulate Organic Carbone Rapidly Degradable	0.04	0.08	0.08	0.08	0.08	0.08
Particulate Organic Carbone Slowly Degradable	0.02	0.04	0.04	0.04	0.04	0.04
Particulate Organic Carbon Non-Degradable	0.09	0.18	0.18	0.18	0.18	0.38
Nitrate	0.00008	0.0004	0.0006	0.0006	0.0015	0.00016
Nitrite	0.0002	0.0004	0.0004	0.0004	0.0004	0.0004
Ammonium	0.003	0.006	0.01	0.01	0.01	0.004
Dissolved Organic Nitrogen Degradable	0.005	0.01	0.01	0.01	0.01	0.006
Dissolved Organic Nitrogen Non-Degradable	0.04	0.08	0.08	0.08	0.08	0.12
Particulate Organic Nitrogen	0.01	0.02	0.024	0.024	0.02	0.016
Dissolved Orthophosphate	0.002	0.006	0.008	0.008	0.01	0.0012
Linked Orthophosphate	0	0	0	0	0	0
Dissolved Organic Phosphorus	0.0005	0.001	0.002	0.002	0.002	0.001
Particulate Organic Phosphorus	0.0015	0.003	0.004	0.004	0.006	0.004

Table 3. The values of the soil leaching function for the different land uses.

For the flow rate, which decreases downstream of the river, we modeled irrigation channels that diverted a flow rate of $5 \text{ m}^3/\text{s}$ for irrigation with a maximum diversion limit of 95% of the river capacity and a flow rate of $1 \text{ m}^3/\text{s}$ for groundwater recharge with a maximum diversion limit of 5% of the river capacity.

For urban discharges, the best adjustment obtained gives a water consumption of 60 L/inhabitant/d and 9 gC/inhabitant/d, 0.3 gN/inhabitant/d, and 0.03 gP/inhabitant/d for the villages. For the city of AIT OURIR, the best adjustment obtained gives a water consumption of 120 L/inhabitant/d and 18 gC/inhabitant/d, 0.6 gN/inhabitant/d, and 0.06 gP/inhabitant/d.

Values of these four input parameters in the PEGASE model are adjusted until all the simulated values of the five water quality parameters (dissolved oxygen (DO), water temperature (T°), chemical oxygen demand (COD), ammonium ion (NH_4^+), and orthophosphate (PO_4^{3-})) considered here reach satisfactory fitting of the measured values.

We verified our calibration by comparing the calculated results with the measured results for the date of 15 June 2021. We visualized the results on longitudinal graphs and used three statistical parameters to evaluate the performance of the calibration: R^2 (coefficient of determination), RMSE (root mean square error), and PBIAS (percentage bias). According to Boukari et al. (2018), an R^2 value greater than 0.4 is considered satisfactory, and a PBIAS value less than ± 30 is also deemed satisfactory [55–57].

2.7. Model Validation

For validation, we selected three dates: 19 January 2021, in winter; 16 March 2021, in spring; and 1 June 2021, in summer. We also chose point 9 located downstream of the river (71.77 km) for temporal calibration. We will use three statistical parameters to evaluate the model performance: R² (coefficient of determination), RMSE (root mean square error), and PBIAS (percentage bias). An R^2 value greater than 0.4 is deemed satisfactory [31], while values between 0.75 and 0.85 are considered good, and those above 0.85 are classified as very good [55–57]. Additionally, the Percent Bias (PBIAS) metric is essential for evaluating model accuracy, with values between $\pm 30\%$ to $\pm 20\%$ regarded as satisfactory, $\pm 20\%$ to $\pm 15\%$ as good, and below $\pm 15\%$ as very good [55–57]. These metrics are widely recognized for evaluating environmental model performance [58,59]. The coefficient of determination or The Pearson linear coefficient of determination, denoted as R², is a measure of the effectiveness of predicting a linear regression model. It assesses the similarity of linear trends between estimated and observed values [60]. To complement this evaluation, one can also use RMSE, which represents the standard deviation of the differences between predicted and observed values in terms of the unit of the studied variable [61]. Additionally, the addition of PBIAS can help quantify the differences between predicted and observed values in terms of percentage of the standard deviation [62]. A high R^2 alone does not provide a comprehensive view of the unmatching between calculated and measured values. That justifies the use of other statistical parameters such as RMSE and PBIAS, along with graphical observation, to provide an overall view of assimilation quality [58,59].

2.8. Scenario Analyses

After conducting reference simulations for the year 2021, we compared them to new scenarios under the same hydraulic conditions, and we have developed four scenarios (Table 4).

Scenario	Description	COD Pollutant Load (KgO ₂ /d)	Months
1	Olive oil factories release 100% of COD load daily production into the river over a two-month period.	10,151	January, February
2	Olive oil factories release 10% of COD load daily production into the river over a two-month period.	1015.1	January, February
3	Olive oil factories release 20% of their daily production into the river over a six-month period.	2030.2	January to June
4	Olive oil factories release 50% of their wastewater production into the river over a six-month period.	5075.5	January to June

Table 4. Table of pollutant release scenarios for olive oil mills.

3. Results

3.1. Model Calibration 15 June 2021

We examined the daily concentrations of the parameters calculated by the model and compared them to measured values obtained for the following variables—water temperature, dissolved oxygen, ammonium, orthophosphates, and chemical oxygen demand during the monitoring campaign conducted on 15 June 2021 (Figure 4), to assess the effectiveness of the model in modeling river water quality.



Figure 4. Longitudinal evolution of physicochemical parameters before calibration (blue line) and after calibration (green line) compared with the measured value (black dots) along the ZAT River on 15 June 2021.

We chose to conduct the comparisons along the ZAT River at nine points (Figure 1). These comparisons allowed us to evaluate the quality of the simulation results and the model ability to account for the sizing procedures of the study river. They also allowed us to observe how the studied parameters evolved spatially.

The graphs in Figure 4, representing measured and simulated concentrations along the ZAT River, were used to conduct the analysis. The coefficient of determination (R^2), root-mean-square error (RMSE), and Percent Bias, which are three common statistical measures, were used to evaluate the fit.

The simulation results were accurate and reliable, with the simulated values being of the same order of magnitude as the data for the majority of the variables studied. The simulations were satisfactory for all parameters, with R² values above 0.4 and PBIAS values also below $\pm 30\%$ for all parameters. For the calibration results of the parameters COD, T°, DO, NH₄⁺, and PO₄³⁻, the model showed satisfactory to very good performance on all indicators, including RMSE, R², and Percent Bias. The R² values were above 0.66, and the

PBIAS was below 16%. In terms of graphical comparison, the results appear consistent, with the exception of temperature, which showed a variation at the downstream end of the river between measured and calculated values with an RMSE of 4.43 °C. Overall, when considering the product and field measurements, we observe that pollutant concentrations remain low along the river up to km 71. Afterward, there is a significant increase in pollutant concentration due to the discharge of pollutants from the city of Ait Ourir.

3.2. Model Validation

To validate the effectiveness of the model in modeling river water quality, we examined the daily concentrations of the parameters calculated by the model and compared them to measured values. The validations were conducted using monitoring data from campaigns in winter (19 January 2021), spring (16 March 2021), and summer (1 June 2021). We use the following parameters: water temperature, dissolved oxygen, ammonium, orthophosphates, and chemical oxygen demand. To validate the simulation results, we conducted comparisons along the ZAT River at nine points and performed a temporal comparison downstream of the river at km 71.77 in station 9 (Figure 1). These comparisons allowed us to observe the spatial and temporal evolution of the studied parameters. The graphs in Figures 5–8, representing the measured and simulated concentrations along the ZAT River, were used for the analysis. We conducted a validation using three common statistical coefficients: the coefficient of determination (R²), root-mean-square error (RMSE), and Percent Bias (Figures 5–8). The results were satisfactory both in terms of statistical analysis and graphical comparison.

3.2.1. Validation in Winter 19 January 2021

Figure 5 presents the graphical results of the model simulation for the physicochemical quality of the ZAT River during winter (19 January 2021) for each parameter. The temperature gradually increased from the source to the estuary but did not exceed 10 °C. Dissolved oxygen concentrations above 10 mgO₂/L were observed along the river in all seasons, extending from the source to km 64 during winter. Subsequently, dissolved oxygen concentrations decreased to less than 6.37 mgO₂/L based on the measured value and 0.31 mg/L according to the calculated value at station 9. Regarding chemical oxygen demand (COD), low concentrations were observed from the source to 64 km, followed by an increase of 64.54 mgO₂/L based on the measured value and 199.95 mgO₂/L according to the calculated value and 199.95 mgO₂/L based on the measured value at all upstream stations, with a slight increase between km 64 and km 71.77. However, their concentrations increased thereafter by 0.82 mgN/L NH₄⁺ and 0.22 mgP/L PO₄³⁻ based on the calculated value, and by 0.86 mgN/L NH₄⁺ and 0.28 mgP/L PO₄³⁻ based on the calculated value at station 9.

It is important to note that the concentrations remain low until km 64 and then gradually start to increase. However, there is a sharp increase after km 71 due to industrial activities and pollution from the city of Ait Ourir during this period. The graphic comparison indicates a correlation between the calculated results and the measurements, except for the chemical oxygen demand (COD) and dissolved oxygen (DO) parameters downstream the river, which exceeded the difference between the measured values and the calculated values. The R² values were greater than 0.78 and the PBIAS was less than 27.30%, except for the chemical oxygen demand (COD) parameter, which exceeded the expected values with a percentage bias (PBIAS) of 205.8%. This difference between the measured values and the calculated values for chemical oxygen demand (COD) and dissolved oxygen (DO) parameters downstream the river is attributed to our assumption in the model that factories discharge 100% of their pollutants, whereas in reality, they discharge a lower amount.



Figure 5. Longitudinal evolution of physicochemical parameters along the ZAT River on 19 January 2021, with simulated value in blue line and measured value in black dots.

3.2.2. Validation in Spring 16 March 2021

Figure 6 presents the graphical results of the model simulation for the physicochemical quality of the ZAT River during spring (2 March 2021) for each parameter. The temperature gradually increased from the source to the estuary but did not exceed 13 °C. Dissolved oxygen concentrations above 10 mgO₂/L were observed along the river in all seasons, extending from the source to 71 km during spring. Subsequently, dissolved oxygen concentrations decreased to less than 7.70 mgO₂/L based on the measured value and 9.97 mgO₂/L based on the calculated value at station 9.

Regarding chemical oxygen demand (COD), low concentrations were observed from the source to 71 km, followed by an increase of 16.08 mgO₂/L based on the measured value and 7.97 mgO₂/L based on the calculated value at station 9. NH_4^+ and PO_4^{3-} concentrations were generally low at all upstream stations. However, their concentrations increased thereafter by 0.41 mgN/L NH_4^+ and 0.041 mgP/L PO_4^{3-} based on the measured value, and by 0.056 mgN/L NH_4^+ and 0.029 mgP/L PO_4^{3-} based on the calculated value at station 9.

Regarding the spring season, which experiences a flow rate higher than $10 \text{ m}^3/\text{s}$ at 62 km, the R² results were generally acceptable, exceeding 0.46, and the PBIAS results were less than 23%. Most parameters yielded satisfactory results, except for NH4, which showed a significant deviation with a PBIAS percentage higher than 85%. In the graphic comparison, it is obvious that downstream of the river, the model provides significantly different results between the measured values and the calculated values for COD, DO, NH₄⁺, and PO₄³⁻. This is probably due to the fact that in our model, we considered that olive oil factories only discharge pollutants during the production period, i.e., January and February. However, it appears that the olive oil factories continue to release pollutants during other months despite the production break.



Figure 6. Longitudinal evolution of physicochemical parameters along the ZAT River on 16 March 2021, simulated value (blue line), measured value (black dots).

3.2.3. Validation in Summer 1 June 2021

Figure 7 presents the graphical results of the model simulation for the physicochemical quality of the ZAT River during summer (1 June 2021) for each parameter. The temperature gradually increased from the source to the estuary but did not exceed 21 °C on the measured value and 16 °C based on the calculated value at station 9. Dissolved oxygen concentrations above 6 mgO₂/L were observed along the river, extending from the source to 71.11 km

during the summer. Subsequently, dissolved oxygen concentrations decreased to less than $3.72 \text{ mgO}_2/\text{L}$ based on the measured value and $3.36 \text{ mgO}_2/\text{L}$ based on the calculated value at station 9.

Regarding chemical oxygen demand (COD), low concentrations were observed from the source to 71.77 km, followed by an increase of $58.37 \text{ mgO}_2/\text{L}$ based on the measured value and $56.40 \text{ mgO}_2/\text{L}$ based on the calculated value at station 9. NH₄⁺ and PO₄³⁻ concentrations were generally low at all upstream stations. However, their concentrations increased thereafter by 0.82 mgN/L NH₄⁺ and 0.19 mgP/L PO₄³⁻ based on the measured value, and by 0.80 mgN/L NH₄⁺ and 0.21 mgP/L PO₄³⁻ based on the calculated value at station 9.

Regarding the summer season, characterized by the absence of industrial activity and a flow rate below 1.9 m³/s at km 62, satisfactory results were obtained. The R² coefficient exceeded 71%, and the PBIAS was below 18%. Even in the graphic comparison, the results generated by the model are close to the field measurements, except for temperature, which showed a variation at the downstream end of the river between measured and calculated values, with an RMSE of 3.43 °C. Calibration and validation were more consistent during the summer compared with winter and spring, except for the temperature downstream the river.



Figure 7. Longitudinal evolution of physicochemical parameters along the ZAT River on 1 June 2021, simulated value (blue line), measured value (black dots).

3.2.4. Validation at Point 9 at 71.77 km

Figure 8 presents the graphical representation of the model simulation results, illustrating the temporal changes in the physicochemical water quality of station 9 in the ZAT River from 1 January 2021 to 30 June 2021. The temperature showed a gradual increase from winter to summer, with maximum values of 21 °C in summer and 15 °C in winter and spring.



Figure 8. Temporal evolution of physicochemical parameters along the ZAT River in point 9, at 71.77 km, simulated value (blue line), measured value (black dots).

During the spring season, dissolved oxygen concentrations were observed to be above 7 mgO₂/L. In summer, measured dissolved oxygen values ranged from 3.72 to $3.57 \text{ mgO}_2/\text{L}$, while calculated values ranged from $3.57 \text{ to } 0.5 \text{ mgO}_2/\text{L}$. However, in winter, there was a notable disparity between field measurements and model-based calculations. Measured values ranged from $6.5 \text{ to } 5 \text{ mgO}_2/\text{L}$, while calculated values ranged from $0.05 \text{ to } 0.01 \text{ mgO}_2/\text{L}$, except for the ninth and tenth days of January, where higher measured

values exceeding $10 \text{ mgO}_2/\text{L}$ were recorded due to elevated flow rates ranging from 5.8 to 2.3 m³/s. Regarding the chemical oxygen demand (COD), measurements during the summer season ranged from 58.37 to 66.96 mgO₂/L, while in spring, they ranged from 16.16 to 58.95 mgO₂/L for measured values and 7.97 to 56.98 mgO₂/L for calculated values. In winter, significant differences were observed between the measured and calculated results, with measured values ranging from 64.54 to 79.05 mgO₂/L and the calculated results exceeding 200 mgO₂/L. For nitrogen (NH₄), measurements in the summer season varied between 0.82 and 0.88 mgN/L, while in spring, they ranged from 0.36 to 0.85 mgN/L. In winter, nitrogen measurements ranged from 0.82 to 1.23 mgN/L. As for phosphorus (PO₄), measurements during the summer season ranged from 0.19 to 0.21 mgP/L, while in spring, they ranged from 0.22 to 0.45 mgP/L.

When comparing the quality parameter variations at station 9, located at km 71.77, most parameters showed satisfactory measurements. The R² values were greater than 0.51 and the PBIAS was less than -32.70%, except for COD, which exhibited an 84.60\% positive bias PBIAS. This discrepancy can be attributed to the winter months, where the model significantly overestimated the values. However, the model performed well with minor deviations during other months, primarily due to reduced flow and increased pollutants in winter. Overall, the simulations provided reasonable estimates for all parameters and accurately represented the behavior of the watershed. This highlights the robustness of the PEGASE model in simulating these elements and its potential ability for studying the water quality status in the ZAT River basin. This includes temperature, ammonium, and orthophosphate in all seasons, and dissolved oxygen and chemical oxygen demand in the months least exposed to the influence of olive oil mills (Figure 8).

3.3. Scenario Analyses

Figure 9 illustrates the simulation results of the model for the physical and chemical quality of the ZAT River under four scenarios:

In the first scenario, we assumed that olive oil factories, which produce a COD pollutant load of 10,151 KgO₂/d during the months of January and February, release the same amount of COD pollutant load every day during this period. Additionally, we considered that the ZAT River does not experience any pollution from olive oil factories from March to June. In this scenario, the results indicated that the dates 18 May, 1 June, and 15 June are not affected by the factories. However, during the period from March to May, the model provided lower results compared with the field measurements, suggesting that olive oil factories release a certain percentage of wastewater during this period despite the production break. Furthermore, for the months of January and February, the model produced calculated values significantly higher than field measurements, indicating that the factories do not release 100% of their daily production.

In the second scenario, where we assumed that olive oil factories release 10% of their daily production in January and February and nothing during the other months, the results matched the field measurements for January and February. Therefore, it can be concluded that 10% of the daily production reaches the river during this period.

In the third scenario, where we assumed that olive oil factories operating and producing wastewater in January and February release 20% of their daily production over a six-month period, we found a match during the period 6 April 2021, 20 April 2021, and 4 May 2021. Consequently, 20% of the daily production reaches the river during this period.

Regarding the fourth scenario, where we assumed that olive oil factories release 50% of their wastewater production over a six-month period, the model results showed a close approximation during the high-flow period in March. Thus, it can be considered that olive oil factories release 50% of their daily production in March.

In conclusion, from the first, second, third, and fourth scenarios, we can deduce that the olive oil factories release their waste as follows: they discharge around 10% of the daily production of their daily waste during the production months of January and February, 50% of the daily production in March, and approximately 20% of the daily production in the month of February and the beginning of May. Furthermore, we observe that there is no significant impact from olive oil factories in late May and during the summer season.



Figure 9. Temporal evolution of chemical oxygen demand parameters along the ZAT River at point 9, at 71.77 km, simulated value (blue line), measured value (black dots).

3.4. Dissolved Organic Carbon Balance under Two Scenarios

Carbon organic dissolved inputs and outputs were assessed between station 6 (60.35 km) and station 9 (71.77 km) under two scenarios. In the first scenario, oil mills discharged 100% of their daily wastewater into the river over two months in January and February. In contrast, in the final scenario, oil mills discharged 10% of their daily wastewater in January and February, 50% in March, and 20% between 1 April and 15 May. During 16 April and 31 June, there was no discharge of wastewater from the oil mills.

In the first scenario (Figure 10), the total pollution load reaches 594 kg C/d, with a major contribution from industrial pollution, which accounts for 377 kg C/d. Urban pollution comes in second with 147 kg C/d. In addition, upstream flux contains 325 kg C/d with a flow rate of 4.27 m^3 /s. The downstream flux shows a presence of 576 kg C/d with a flow rate of 1.88 m^3 /s. The river's self-purification gets rid of 346 kg C/d through withdrawals, contributing 277 kg C/d, and undergoes a total biodegradation of 69 kg C/d.



Figure 10. First scenario (the oil mills discharged 100% of their daily wastewater into the river over two months in January and February).

In the final scenario (Figure 11), industrial pollution decreases to 178 kg C/d, representing 47% of total industrial pollutants, a 53% reduction on the initial input to the river in the first scenario. The downstream flux then reaches 435 kg C/d, resulting in a reduction of 24.5%. In the second scenario, the river's self-purification eliminates 255 kg through withdrawals and 18 kg C/d through biodegradation, including 12 kg C/d through planktonic biodegradation and 7 kg C/d through biofilm biodegradation. The second scenario demonstrates that 93% of pollutants disappearing in the hydrographic network are eliminated through water withdrawals performed by irrigation channels and groundwater recharge.



Figure 11. Final scenario (The oil mills discharged 10% of their daily wastewater in January and February, 50% in March, and 20% between 1 April and 15 May, with 0% discharge of wastewater from the oil mills between 16 April and 31 June).

4. Discussion

4.1. Performance of the Model

A validation methodology was adopted to assess the effectiveness of the PEGASE model in water quality modeling. This included comparing daily concentrations of parameters calculated by the model with measured values. The studied parameters encompassed water temperature, dissolved oxygen, ammonium, orthophosphates, and chemical oxygen demand (COD), collected during the monitoring campaign on 15 June 2021. Model validation was performed using data from measurement campaigns conducted in winter

(19 January 2021), spring (16 March 2021), and summer (1 June 2021), as well as temporal validation downstream at station 9 located at km 71.77 along the river.

Comparisons were conducted at nine points along the ZAT River (Figure 1), allowing a detailed assessment of simulation results quality and the model's ability to represent river sizing procedures. Graphs from Figures 4–8, depicting measured and simulated concentrations, were analyzed using statistical measures such as the coefficient of determination (R²), root mean square error (RMSE), and percentage bias (PBIAS). These metrics are widely recognized for evaluating environmental model performance [58,59].

We can consider providing a close representation of reality if statistical parameters such as R², RMSE, and percentage bias indicate satisfactory performance after calibration and validation [42,43,63]. The ability to produce a model with a high degree of performance is a sign of model strength [22], especially when used in African basins where data availability and accessibility are an issue [30].

The results were satisfactory in terms of both statistical analysis and graphic comparison, with R² values above 0.4 and PBIAS values also below $\pm 30\%$ for all parameters. As a result, the PEGASE model demonstrated its robustness when approximating reality, even without complex calibration, as being a physical-based model. Research conducted in Africa in semi-arid Mediterranean regions has used this model to assess water quality [31]. This study yielded satisfactory results, affirming the model's efficiency even in semi-arid climates and data-scarce areas [31].

However, the model was unable to produce a temperature value close to the measured value in the field in the summer. The differences between modeled and field-measured water temperatures can be attributed to several interrelated factors, including data limitations, methodological approaches, and timing of measurements. Understanding these factors is crucial for improving model accuracy and reliability. The absence of daily water temperature data necessitated the use of daily air temperature, which was smoothed through a moving average. This approach introduces uncertainty in the temperature estimates, as air and water temperatures can diverge significantly, especially in summer [64]. The model's reliance on altitude to calculate temperature variations along the river fails to account for the complex thermal dynamics of water bodies. An altitudinal gradient can lead to significant temperature differences, particularly in varying climatic conditions [65]. The temporal lag in water temperature measurements, where upstream measurements are taken earlier than downstream, exacerbates the issue during summer. Rapid water temperature changes can occur throughout the day, leading to higher downstream temperatures that the model does not capture accurately, particularly in summer when temperatures can fluctuate dramatically throughout the day [66,67]. When these three factors are considered together, they explain why the temperature measured downstream is significantly higher than the temperature calculated by the model. This also explains why the validation results for winter and spring temperatures were better than the calibration results for summer. The model remains effective for monitoring river water quality. However, it is also marked by certain weaknesses, such as the absence of a full physical-based hydrodynamic model to estimate soil fluxes or inputs. It can be fixed by coupling PEGASE to another specific soil model, such as the SWAT model, according to Boukari's research [31].

4.2. Physicochemical Parameters

The ZAT River basin, which has a predominantly Mediterranean climate, is strongly influenced by the altitude [39], resulting in an increase in temperature downstream [68]. The stability of dissolved oxygen in the water is related to temperature and altitude [69]. When the temperature is low and the gradient is high, the dissolved oxygen saturation of the river increases [70]. This is the case along the ZAT River from the crest to km 64. The area between km 64 and 71.77 is characterized by the stability of the dissolved oxygen concentration in spring and summer because the olive oil factories were not in operation during this period. However, the same area experienced a decrease in dissolved oxygen and an increase in carbon in winter due to the operation of olive oil factories during that time.

Other studies have also confirmed this [71]. After km 71.77, the ZAT River experienced a sharp decrease in dissolved oxygen and an increase in carbon concentration in winter and summer, which is related to the production of olive oil factories, leachate from landfills and slaughterhouses located near the river, and urban discharges from the city of Ait Ourir, as well as the decrease in flow in these areas. During this period, the river loses its capacity to reduce the concentration of pollutants compared with the spring, which had the highest flow of 10 m³/s, contributing to an increase in the river capacity to reduce pollutant concentrations [72,73].

Concerning pollutants NH_4^+ and PO_4^{3-} , their concentrations significantly increase after Km 71.77 in both winter and summer, which is directly related to urban discharges, landfills, slaughterhouses, and olive oil plants. These sources discharge without prior treatment and without considering the limits imposed by the authorities. Additionally, this height is associated with a decrease in flow in winter and summer, unlike spring, which provides the river with high flow, favoring the process of dilution [74,75]. Several studies have shown the effects of olive oil factories on increasing the levels of pollutants in rivers, reducing the levels of dissolved oxygen, and leading to the phenomenon of eutrophication. These effects cause the loss of the river's self-purification capacity and ecological characteristics [76]. Other studies have also revealed the impact of waste leachate on groundwater and surface water pollution, reducing the quality of rivers and weakening their biodiversity [77].

The discharge of untreated urban waste is one of the main factors that negatively affect river quality, and the rivers of the Mediterranean region, which experience instability and decline at various times of the year, are the most impacted by these pollutants. These pollutants are discharged without prior treatment or meeting the required standards [78–80].

The application of the PEGASE model successfully replicated the seasonal patterns, revealing the spatial and seasonal behavior of the basin. An increase in pollutants was observed in winter after 64 km, followed by a larger increase after 71.77 km in both summer and winter, whereas the river quality remained stable in spring, which had a significant flow. With the use of this model, we determined the impact of each source of pollution and highlighted the concentration consequences of discharging pollution sources without treatment during low flow periods.

4.3. Scenario Analysis

The results of our simulation model for the physical and chemical quality of the ZAT River under different scenarios provide information on olive oil plant wastewater discharge practices and their impact on the river. These scenarios highlight the different levels of pollution in different months and help us understand the temporal patterns of wastewater discharge.

Interestingly, the results indicated that the factories did not fully discharge their daily production during January and February. These findings indicate that there might be partial wastewater release during the production break. Thanks to the different scenarios, we were able to analyze the impact of four different scenarios of pollution load (variation over time) linked to olive oil mills. They tend to discharge around 10% of their daily production during the production months of January and February, approximately 50% in March, and around 20% in February and the beginning of May. It is noteworthy that there is no significant impact observed from the olive oil factories in late May and during the summer season. The results of this previous proposal relate to field measurements, providing further evidence of unauthorized release of wastewater from the olive oil factories into the river.

This study highlights the impact of olive press wastewater on the quality of the ZAT river. As a result of the industrial wastewater discharge, the concentration of COD was 79 mgO₂/L in winter and 66.99 mgO₂/L in summer, which indicates poor water quality according to Moroccan standards since these concentrations exceed the threshold of 40 mgO₂/L, indicating poor water quality according to the same standards [81].

The results are consistent with other studies that have also emphasized the increase in pollutant levels in rivers and the reduction of their self-purification capacity due to industrial wastewater [82]. Olive mill wastewater is regarded as hazardous water that significantly impacts the surface water quality and disrupts the natural self-purification process of the river [15]. Additionally, these wastewaters adversely affect the chemical composition and aquatic life in rivers [76].

To address this issue, measures need to be taken, including the implementation of stricter regulations to control pollutant discharges from olive presses and urban wastewater. Furthermore, improving wastewater treatment practices and continuous monitoring of water quality are recommended. This study underscores the importance of a balanced approach between economic activity and environmental preservation to ensure the sustainability of freshwater resources. Considering that small and medium-sized mill owners often lack the financial, human, and technical resources required to invest in water treatment, it is crucial for stakeholders to devise applicable solutions [83]. These may include supporting individual wastewater treatment systems for each factory, establishing centralized treatment stations for collective water collection and treatment, or co-treatment industrial and municipal wastewater treatment systems. Several studies have highlighted the effectiveness of such approaches [82,83].

Modeling is a valuable tool for monitoring factories compliance with wastewater release regulations. It allows for the evaluation and prediction of the impact of wastewater discharges on water quality by simulating the behavior and dispersion of pollutants in rivers [18]. Models take into account various parameters such as wastewater characteristics, river flow rates, weather conditions, and hydrodynamic characteristics. Research has shown that modeling techniques are valuable in assessing the discharge of wastewater, predicting the spread of pollutants, and identifying areas with a high risk of pollution [27,28]. For instance, the PEGASE model has been utilized to simulate the fate of cocaine in surface waters, enabling the estimation of cocaine consumption and the identification of its sources in the Scheldt Basin and the Walloon region of Belgium in 2007 [32]. Similarly, modeling was used to investigate the incident of fish mortality in the Walloon River in Belgium in 2020, which was attributed to dissolved oxygen depletion caused by the release of wastewater from a sugar factory in France [33].

4.4. Dissolved Organic Carbon Balance under Two Scenarios

The study investigated the balance of dissolved organic carbon (DOC) under two different scenarios of wastewater discharge from oil mills into a river. The first scenario involved the oil mills discharging 100% of their daily wastewater into the river during January and February, while the second scenario had varying discharge rates over a longer period, with 10% in January and February, 50% in March, 20% between 1 April and 15 May, and 0% from 16 April and 31 June. The study aimed to assess the inputs and outputs of carbon organic dissolved in the river under these scenarios.

The findings of this study demonstrate the impact of different wastewater discharge scenarios on the dissolved organic carbon balance in the river. The first scenario, with higher wastewater discharge, led to increased industrial and urban pollution and higher downstream flux. Conversely, the second scenario, which witnessed a 53% reduction in wastewater discharge, led to a decrease of 24.5% in downstream pollution. The study highlighted that 93% of the pollutants disappearing in the hydrographic network were eliminated through water withdrawals performed by irrigation channels and groundwater recharge.

However, despite the reduction in pollutant levels through withdrawals and selfpurification, a significant amount of pollutants still persists in the discharge, totaling 435 kg C/d (with a flow rate of 1.88 m³/s). This results in a chemical oxygen demand (COD) concentration of 79 mgO₂/L in winter and 66.99 mgO₂/L in summer, which indicates poor water quality according to Moroccan standards since these concentrations exceed the threshold of 40 mgO₂/L. To achieve good water quality in the river, decision-makers should implement effective strategies to lower the DCO concentrations from levels above $40 \text{ mgO}_2/\text{L}$ to below 35 mg/L.

This information is invaluable for regulatory authorities and plant managers, enabling them to take preventive measures and improve wastewater treatment facilities. Modeling also provides the opportunity to test hypothetical scenarios, thus assisting decision-makers in making informed decisions and implementing appropriate management measures to minimize the impact of wastewater discharges on aquatic ecosystems. In summary, the use of modeling promotes effective factory monitoring and sustainable management of freshwater resources [21].

5. Conclusions

In conclusion, the combination of physicochemical simulations using the PEGASE model, field measurements, and hydrological modeling had provided a comprehensive understanding of the temporal and spatial variations in water quality within the ZAT River. This approach identified pollution hotspots and quantified the relative contributions of different pollution sources. The analysis focused on assessing the real impact of urban and industrial pollution on the river water quality.

To summarize the results of the different scenarios analyzed, we can deduce the wastewater release methods used by olive oil mills. During the production months of January and February, they tend to discharge approximately 10% of their daily production. In March, the discharge increases to around 50%, while in February and the beginning of May, it amounts to roughly 20%. Notably, there is no significant impact observed from the olive oil factories in late May and during the summer season.

The discharge of industrial wastewater has resulted in a daily level of industrial pollution of 178 kg C/d, accounting for a 47% contribution to the overall industrial pollutants. Additionally, urban pollution makes a significant contribution of 174 kg C/d. Upstream flux contains 325 kg C/d with a flow rate of 4.27 m³/s. Despite the reduction in pollutant levels through withdrawals and self-purification, a significant amount of pollutants still persists in the discharge, totaling 435 kg C/d with a flow rate of 1.88 m³/s. Consequently, this leads to a chemical oxygen demand (COD) concentration of 79 mgO₂/L in winter and 66.99 mgO₂/L in summer, indicating poor water quality according to Moroccan standards, as these concentrations exceed the threshold of 40 mgO₂/L. Addressing this issue necessitates the implementation of stricter regulations to control pollutant discharges and the improvement of wastewater treatment management.

Furthermore, modeling techniques have proven to be valuable tools for assessing compliance with wastewater release regulations and predicting the dispersion of pollutants. By simulating the behavior of pollutants in rivers, modeling highlights the impact of wastewater discharges and provides decisions regarding wastewater treatment and management.

The research highlights the theoretical implications of the complexities of urban and industrial pollution on river ecosystems and urges managers to implement comprehensive pollution control strategies to minimize the effects of pollutants on river water quality. Practical recommendations include implementing strict regulations on industrial discharges. Improving water quality monitoring through advanced modeling methodologies. In addition, one can address the improvement of wastewater management by establishing treatment plants for different pollution sources or developing a co-treatment plant to mitigate the negative impact of industrial pollution on river water quality. To maintain ecological flow and minimize the impact of pollutants in the ZAT River, the proportion of water withdrawn for agricultural uses should be minimized during periods of low flow.

Author Contributions: Investigation, Conceptualization, Formal Analysis, Software, Methodology, Writing—Original Draft Preparation, Writing—Reviewing and Editing: A.B.; Conceptualization, Resources, Supervision, Methodology, Visualization, Validation, Funding acquisition, Project Administration, Writing—Review and Editing: J.-F.D.; Conceptualization, Resources, Supervision, Methodology, Visualization, Project Administration, Writing—Review and Editing: J.-F.D.; Conceptualization, Resources, Supervision, Methodology, Visualization, Project Administration, Writing—Review and Editing: N.O. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Most of the data presented in this study are available in the article. Additional information is available on request.

Acknowledgments: We would like to thank the Tensift Hydraulic Basin Agency (THBA) for providing the data used in this work, and we also appreciate the Erasmus Project and Wallonie-Bruxelles International (WBI) for providing the funding necessary to complete this study.

Conflicts of Interest: The authors declare that they have no competing interests.

References

- 1. Zhou, K.; Wu, J.; Fan, J.; Liu, H. Drivers of Regional Environmental Pollution Load and Zoning Control: A Case Study of the Yangtze River Economic Belt, China. *Chin. Geogr. Sci.* 2022, *32*, 31–48. [CrossRef]
- Toreti, A.; Bavera, D.; Acosta Navarro, J.; Arias Muñoz, C.; Barbosa, P.; Jager, A.D.; Ferraris, L.; Fioravanti, G.; Grimaldi, S.; Hrast Essenfelder, A.; et al. *Drought in the Mediterranean Region: January 2024 GDO Analytical Report*; Publications Office of the European Union: Luxembourg, 2024. [CrossRef]
- 3. Sehlaoui, H.; Hassikou, R.; Moussadek, R.; Zouahri, A.; Douaik, A.; Iiach, H.; Ghanimi, A.; Dakak, H. Evaluation of Water Quality for Agricultural Suitability in the Benslimane Region, Morocco. *Environ. Monit. Assess.* **2020**, *192*, 587. [CrossRef]
- 4. Nizar, Y.; Igouzal, M.; Touazit, A. Water Quality Modelling of the Sebou River Estuary Before and After the Installation of the Kenitra City's Wastewater Treatment Plant. *Ecol. Eng. Environ. Technol.* **2022**, 23, 264–274. [CrossRef] [PubMed]
- Safaa, K.R.; Anouzla, A.; Abrouki, Y.; Loukili, H.; Kastali, M.; Souabi, S. Management of Olive Oil Mill Wastewater in Morocco. In Wastewater from Olive Oil Production: Environmental Impacts, Treatment and Valorisation; Souabi, S., Anouzla, A., Eds.; Springer Water; Springer International Publishing: Cham, Switzerland, 2023; pp. 183–212, ISBN 978-3-031-23449-1.
- 6. Kutralam-Muniasamy, G.; Pérez-Guevara, F.; Roy, P.D.; Elizalde-Martínez, I.; Chari, S.V. Surface Water Quality in the Upstream of the Highly Contaminated Santiago River during the COVID-19 Lockdown. *Environ. Earth Sci.* 2022, *81*, 316. [CrossRef] [PubMed]
- 7. Morsy, A.; Ebeid, M.; Soliman, A.; Halim, A.A.; Ali, A.E.; Fahmy, M. Evaluation of the Water Quality and the Eutrophication Risk in Mediterranean Sea Area: A Case Study of the Port Said Harbour, Egypt. *Environ. Chall.* **2022**, *7*, 100484. [CrossRef]
- Tornés, E.; Alández-Rodríguez, J.; Corrochano, A.; Nolla-Querol, P.; Trapote, M.C.; Sabater, S. Impacts of Climate Change on Stream Benthic Diatoms—A Nation-Wide Perspective of Reference Conditions. *Hydrobiologia* 2022, 849, 1821–1837. [CrossRef]
- 9. El Mouine, Y.; El Hamdi, A.; Morarech, M.; Valles, V.; Yachou, H.; Dakak, H. Groundwater Contamination Due to Landfill Leachate—A Case Study of Tadla Plain. *Environ. Sci. Proc.* **2022**, *16*, 53. [CrossRef]
- 10. Nahli, A.; Oubraim, S.; Chlaida, M. Application of the Biotic Indices for Water Quality and Resilience Assessment of a Disturbed Stream. *Biologia* 2022, 77, 2887–2904. [CrossRef]
- Oubane, M.; Khadra, A.; Ezzariai, A.; El Fels, L.; Kouisni, L.; Hafidi, M. Micronucleus Assay Based on Vicia Faba Roots as a Tool to Assess the Performances of Wastewater Treatment Systems. *Environ. Technol. Innov.* 2020, 19, 100903. [CrossRef]
- Aziz, A.; Basheer, F.; Sengar, A.; Irfanullah; Khan, S.U.; Farooqi, I.H. Biological Wastewater Treatment (Anaerobic-Aerobic) Technologies for Safe Discharge of Treated Slaughterhouse and Meat Processing Wastewater. *Sci. Total Environ.* 2019, 686, 681–708. [CrossRef]
- Saadoun, L.; Campitelli, A.; Kannengiesser, J.; Stanojkovski, D.; El Alaoui El Fels, A.; Mandi, L.; Ouazzani, N. Potential of Medium Chain Fatty Acids Production from Municipal Solid Waste Leachate: Effect of Age and External Electron Donors. *Waste Manag.* 2021, 120, 503–512. [CrossRef] [PubMed]
- 14. Zahi, M.R.; Zam, W.; El Hattab, M. State of Knowledge on Chemical, Biological and Nutritional Properties of Olive Mill Wastewater. *Food Chem.* 2022, *381*, 132238. [CrossRef] [PubMed]
- Smeti, E.; Kalogianni, E.; Karaouzas, I.; Laschou, S.; Tornés, E.; De Castro-Català, N.; Anastasopoulou, E.; Koutsodimou, M.; Andriopoulou, A.; Vardakas, L.; et al. Effects of Olive Mill Wastewater Discharge on Benthic Biota in Mediterranean Streams. *Environ. Pollut.* 2019, 254, 113057. [CrossRef] [PubMed]
- Bouriqi, A. Typology and Classification of Water Quality in an Intermittent River in a Semi-Arid Mediterranean Climate. *Environ.* Monit. Assess. 2024, 196, 381. [CrossRef] [PubMed]
- 17. Fu, B.; Merritt, W.S.; Croke, B.F.W.; Weber, T.R.; Jakeman, A.J. A Review of Catchment-Scale Water Quality and Erosion Models and a Synthesis of Future Prospects. *Environ. Model. Softw.* **2019**, *114*, 75–97. [CrossRef]
- Bai, J.; Zhao, J.; Zhang, Z.; Tian, Z. Assessment and a Review of Research on Surface Water Quality Modeling. *Ecol. Model.* 2022, 466, 109888. [CrossRef]
- 19. Uddin, M.G.; Nash, S.; Olbert, A.I. A Review of Water Quality Index Models and Their Use for Assessing Surface Water Quality. *Ecol. Indic.* 2021, 122, 107218. [CrossRef]
- 20. Ejigu, M.T. Overview of Water Quality Modeling. Cogent Eng. 2021, 8, 1891711. [CrossRef]
- 21. Wang, Q.; Li, S.; Jia, P.; Qi, C.; Ding, F. A Review of Surface Water Quality Models. Sci. World J. 2013, 2013, e231768. [CrossRef]
- 22. Herrera, P.A.; Marazuela, M.A.; Hofmann, T. Parameter Estimation and Uncertainty Analysis in Hydrological Modeling. *WIREs Water* 2022, 9, e1569. [CrossRef]

- 23. Cox, B.A. A Review of Currently Available In-Stream Water-Quality Models and Their Applicability for Simulating Dissolved Oxygen in Lowland Rivers. *Sci. Total Environ.* **2003**, *314–316*, 335–377. [CrossRef] [PubMed]
- Deliège, J.-F. Method to Integrate Models, Adapted to Multicompartimented Hydrological Systems. Ph.D. Thesis, Liege University, Liege, Belgium, 2013. Available online: https://hdl.handle.net/2268/145793 (accessed on 9 January 2024).
- 25. Everbecq, E.; Grard, A.; Magermans, P.; Deliège, J.-F. Water Framework Directive and Modelling Using PEGOPERA Simulation Software. *J. Model. Optim.* **2019**, *11*, 36–50. [CrossRef]
- 26. Sharma, D.; Kansal, A. Assessment of River Quality Models A Review. Rev. Environ. Sci. Biotechnol. 2013, 12, 285–311. [CrossRef]
- 27. Mateus, M.; Vieira, R.D.S.; Almeida, C.; Silva, M.; Reis, F. ScoRE—A Simple Approach to Select a Water Quality Model. *Water* 2018, *10*, 1811. [CrossRef]
- 28. Romano, O.; Akhmouch, A. Water Governance in Cities: Current Trends and Future Challenges. Water 2019, 11, 500. [CrossRef]
- 29. Grard, A.; Everbecq, E.; Magermans, P.; Bourouag, M.; Deliège, J.-F. Transnational Modelling of the Meuse District with PegOpera Simulation Software. *Int. J. River Basin Manag.* **2014**, *12*, 251–263. [CrossRef]
- Papa, F.; Crétaux, J.-F.; Grippa, M.; Robert, E.; Trigg, M.; Tshimanga, R.M.; Kitambo, B.; Paris, A.; Carr, A.; Fleischmann, A.S.; et al. Water Resources in Africa under Global Change: Monitoring Surface Waters from Space. *Surv. Geophys.* 2023, 44, 43–93. [CrossRef]
- Boukari, A.; Everbecq, E.; Ben Abdallah, S.; Magermans, P.; Grard, A.; Habaieb, H.; Deliège, J.-F. Modelling Catchment Scale Agricultural Pollution in North Tunisia Using the PEGASE Model. In *Recent Advances in Environmental Science from the Euro-Mediterranean and Surrounding Regions*; Kallel, A., Ksibi, M., Ben Dhia, H., Khélifi, N., Eds.; Springer International Publishing: Cham, Switzerland, 2018; pp. 835–837.
- 32. Deliege, J.-F.; Everbecq, E.; Magermans, P.; Grard, A.; Bourouag, T.; Blockx, C.; Smitz, J. Pegase, an Integrated River/Basin Model Dedicated to Surface Water Quality Assessment: Application to Cocaine. *Acta Clin. Belg.* **2010**, *65*, 42–48. [CrossRef]
- Grard, A.; Everbecq, E.; Magermans, P.; Deliège, J.-F. Modelling a Severe Transient Anoxia of Continental Freshwaters Due to a Scheldt Accidental Release. *Hydrology* 2021, 8, 175. [CrossRef]
- 34. Safiolea, E.; Baki, S.; Makropoulos, C.; Deliège, J.F.; Magermans, P.; Everbecq, E.; Gkesouli, A.; Stamou, A.; Mimikou, M. Integrated Modelling for River Basin Management Planning. *Proc. Inst. Civ. Eng. Water Manag.* **2015**, *164*, 405–419. [CrossRef]
- 35. Dufatanye, I.; Lee, Y.; Kim, H.; Lee, S. Industrial Wastewater Discharge and Compliance Investigation for Environmentally Resilient Rwanda. *Water* 2022, *14*, 3100. [CrossRef]
- 36. Lemessa, F.; Simane, B.; Seyoum, A.; Gebresenbet, G. Assessment of the Impact of Industrial Wastewater on the Water Quality of Rivers around the Bole Lemi Industrial Park (BLIP), Ethiopia. *Sustainability* **2023**, *15*, 4290. [CrossRef]
- 37. Liu, Y.; Wang, J.; Cao, S.; Han, B.; Liu, S.; Chen, D. Copula-Based Framework for Integrated Evaluation of Water Quality and Quantity: A Case Study of Yihe River, China. *Sci. Total Environ.* **2022**, *804*, 150075. [CrossRef] [PubMed]
- Ye, Y.; Zhang, J.; Liu, H.; Zhu, W. Predictive Simulation Study on the Effect of Small and Medium River Basin Outfall Treatment Measures on Water Quality Improvement. *Water* 2023, 15, 2359. [CrossRef]
- Benkirane, M.; Laftouhi, N.-E.; Khabba, S.; de la Hera-Portillo, Á. Hydro Statistical Assessment of TRMM and GPM Precipitation Products against Ground Precipitation over a Mediterranean Mountainous Watershed (in the Moroccan High Atlas). *Appl. Sci.* 2022, 12, 8309. [CrossRef]
- 40. Boudhar, A.; Duchemin, B.; Hanich, L.; Jarlan, L.; Chaponnière, A.; Maisongrande, P.; Boulet, G.; Chehbouni, A. Long-Term Analysis of Snow-Covered Area in the Moroccan High-Atlas through Remote Sensing. *Int. J. Appl. Earth Obs. Geoinf.* **2010**, *12*, S109–S115. [CrossRef]
- Chehbouni, A.; Escadafal, R.; Duchemin, B.; Boulet, G.; Simonneaux, V.; Dedieu, G.; Mougenot, B.; Khabba, S.; Kharrou, H.; Maisongrande, P.; et al. An Integrated Modelling and Remote Sensing Approach for Hydrological Study in Arid and Semi-arid Regions: The SUDMED Programme. *Int. J. Remote Sens.* 2008, 29, 5161–5181. [CrossRef]
- 42. Bouaida, J.; Witam, O.; Ibnoussina, M.; Delmaki, A.E.F.; Benkirane, M. Contribution of Remote Sensing and GIS to Analysis of the Risk of Flooding in the Zat Basin (High Atlas-Morocco). *Nat. Hazards* **2021**, *108*, 1835–1851. [CrossRef]
- Benkirane, M.; Laftouhi, N.-E.; Mansouri, B.E.; Salik, I.; Snineh, M.; Ghazali, F.E.E.; Kamal, S.; Zamrane, Z. An Approach for Flood Assessment by Numerical Modeling of Extreme Hydrological Events in the Zat Watershed (High Atlas, Morocco). *Urban Water J.* 2020, *17*, 381–389. [CrossRef]
- 44. Bouimouass, H.; Fakir, Y.; Tweed, S.; Leblanc, M. Groundwater Recharge Sources in Semiarid Irrigated Mountain Fronts. *Hydrol. Process.* **2020**, *34*, 1598–1615. [CrossRef]
- Er-Raki, S.; Chehbouni, A.; Khabba, S.; Simonneaux, V.; Jarlan, L.; Ouldbba, A.; Rodriguez, J.C.; Allen, R. Assessment of Reference Evapotranspiration Methods in Semi-Arid Regions: Can Weather Forecast Data Be Used as Alternate of Ground Meteorological Parameters? J. Arid. Environ. 2010, 74, 1587–1596. [CrossRef]
- El Ghadraoui, A.; Ouazzani, N.; Saf, C.; Ahmali, A.; Hejjaj, A.; Aziz, F.; Bubba, M.; Mandi, L. Behaviour of Physicochemical and Microbiological Characteristics of Vertical Flow Constructed Wetland Substrate after Treating a Mixture of Urban and Olive Mill Wastewaters. *Environ. Sci. Pollut. Res.* 2021, 28, 55433–55445. [CrossRef] [PubMed]
- Mahlathi, C.D.; Brink, I.; Wilms, J.M. Comparative Analysis of Hydrodynamic Flowrate Sources as Drivers of Water Quality Models for Nitrogenous Compounds in Complex Ungauged South African Rivers. *Water Pract. Technol.* 2024, 19, 1710–1725. [CrossRef]

- Wu, X.; Marshall, L.; Sharma, A.; Duan, Q. Identifying Input and Output Data Errors in the Calibration of a Water Quality Model Using Bayesian Error Analysis with Reordering (BEAR) Method. In Proceedings of the Copernicus Meetings, Vienna, Austria, 14–19 April 2024.
- Miller, O.; Ator, S.; Hess, M.; Jones, D.; Longley, P.; McDonnell, M.; Miller, M.; Putman, A.; Robertson, D.; Saad, D.; et al. Perspectives on Dynamic Water Quality Modeling across Continental and Watershed Scales. In Proceedings of the Copernicus Meetings, Vienna, Austria, 14–19 April 2024.
- 50. Najjar-Ghabel, S.; Piadeh, F.; Behzadian, K.; Ardakanian, A. Integrated Data-Driven Approach for Early Pollution Detection and Management in the Thames River Ecosystem. In Proceedings of the Copernicus Meetings, Vienna, Austria, 14–19 April 2024.
- 51. Rong, Y.; Qin, C.; Yen, H.; Sun, F.; Du, P.; Zeng, S. Taking Full Advantage of 'Low-Quality' Datasets in Watershed Modeling and Management: From a Perspective of Parameter Calibration. *J. Environ. Manag.* **2024**, *351*, 119955. [CrossRef]
- 52. van Leeuwen, C.C.E.; Mulder, V.L.; Batjes, N.H.; Heuvelink, G.B.M. Effect of Measurement Error in Wet Chemistry Soil Data on the Calibration and Model Performance of Pedotransfer Functions. *Geoderma* **2024**, 442, 116762. [CrossRef]
- Cameron, D.; Hartig, F.; Minnuno, F.; Oberpriller, J.; Reineking, B.; Van Oijen, M.; Dietze, M. Issues in Calibrating Models with Multiple Unbalanced Constraints: The Significance of Systematic Model and Data Errors. *Methods Ecol. Evol.* 2022, 13, 2757–2770. [CrossRef]
- 54. Adedeji, I.C.; Ahmadisharaf, E.; Sun, Y. Predicting In-Stream Water Quality Constituents at the Watershed Scale Using Machine Learning. *J. Contam. Hydrol.* 2022, 251, 104078. [CrossRef]
- 55. Djagba, J.F.; Johnson, J.-M.; Saito, K. Can Soil Fertility Properties in Rice Fields in Sub-Saharan Africa Be Predicted by Digital Soil Information? A Case Study of AfSoilGrids250m. *Geoderma Reg.* 2022, *30*, e00563. [CrossRef]
- 56. Das, B.; Jain, S.; Singh, S.; Thakur, P. Evaluation of Multisite Performance of SWAT Model in the Gomti River Basin, India. *Appl. Water Sci.* **2019**, *9*, 134. [CrossRef]
- 57. Pérez-Sánchez, J.; Senent-Aparicio, J.; Segura-Méndez, F.; Pulido-Velazquez, D.; Srinivasan, R. Evaluating Hydrological Models for Deriving Water Resources in Peninsular Spain. *Sustainability* **2019**, *11*, 2872. [CrossRef]
- 58. Ritter, A.; Muñoz-Carpena, R. Performance Evaluation of Hydrological Models: Statistical Significance for Reducing Subjectivity in Goodness-of-Fit Assessments. *J. Hydrol.* 2013, 480, 33–45. [CrossRef]
- 59. Di Bucchianico, A. Coefficient of Determination (2). In *Encyclopedia of Statistics in Quality and Reliability;* John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2008; ISBN 978-0-470-06157-2.
- 60. Hodson, T.O. Root Mean Square Error (RMSE) or Mean Absolute Error (MAE): When to Use Them or Not 2022. *Geosci. Model Dev.* **2022**, *15*, 5481–5487. [CrossRef]
- 61. Tikhanychev, O. The Phenomenon of "Bias of Assessment" as the Basis of a Behavioral Model and a Potential Source of Problems. In *Proceedings of the Networked Control Systems for Connected and Automated Vehicles*; Guda, A., Ed.; Springer International Publishing: Cham, Switzerland, 2023; pp. 841–848.
- 62. Lahcen, M.; Fetnassi, N.; Ghamizi, M. Floristic Study and Assessment of the Environmental Factors Governing the Distribution of Riparian Plants in the Zat Sub-Basin: Tensift Watershed, Morocco. J. Anim. Plant Sci. 2020, 45, 7900–7915. [CrossRef]
- 63. Caissie, D.; El-Jabi, N.; Satish, M.G. Modelling of Maximum Daily Water Temperatures in a Small Stream Using Air Temperatures. *J. Hydrol.* 2001, 251, 14–28. [CrossRef]
- 64. Sleziak, P.; Jančo, M.; Danko, M. Dynamics of Water Temperature in a Small Mountain Catchment. *Adv. Hydrol. Sci.* 2023, 24, 43–51. [CrossRef]
- 65. St-Hilaire, A.; Ouarda, T.B.M.J.; Bargaoui, Z.; Daigle, A.; Bilodeau, L. Daily River Water Temperature Forecast Model with a K-Nearest Neighbour Approach. *Hydrol. Process.* **2012**, *26*, 1302–1310. [CrossRef]
- Tavares, M.H.; Cunha, A.H.F.; Motta-Marques, D.; Ruhoff, A.L.; Fragoso, C.R.; Munar, A.M.; Bonnet, M.-P. Derivation of Consistent, Continuous Daily River Temperature Data Series by Combining Remote Sensing and Water Temperature Models. *Remote Sens. Environ.* 2020, 241, 111721. [CrossRef]
- 67. Rego, F.; Rocha, M.S. Climatic Patterns in the Mediterranean Region. Ecol. Mediterr. 2014, 40, 49–59. [CrossRef]
- 68. Rajwa-Kuligiewicz, A.; Bialik, R.; Rowiński, P. Dissolved Oxygen and Water Temperature Dynamics in Lowland Rivers over Various Timescales. J. Hydrol. Hydromech. 2015, 63, 353–363. [CrossRef]
- 69. Cox, B.A. A Review of Dissolved Oxygen Modelling Techniques for Lowland Rivers. *Sci. Total Environ.* **2003**, 314–316, 303–334. [CrossRef]
- 70. Benaddi, R.; Bouriqi, A.; Ouazzani, N. The Environmental Problem of Olive Mill Waste Water in Morocco: Data Analysis and Characterization. *Int. J. Curr. Sci. Res. Rev.* **2022**, *05*, i5–i51. [CrossRef]
- Bellos, D.; Sawidis, T. Chemical Pollution Monitoring of the River Pinios (Thessalia—Greece). J. Environ. Manag. 2005, 76, 282–292. [CrossRef] [PubMed]
- 72. Sidabutar, N.V.; Namara, I.; Hartono, D.M.; Soesilo, T.E.B. The Effect of Anthropogenic Activities to the Decrease of Water Quality. *IOP Conf. Ser. Earth Environ. Sci.* 2017, 67, 012034. [CrossRef]
- 73. Fouzi, T.A.; Youness, M.; Bouchra, L.; Ali, B. Spatio-Temporal Typology of the Physico-Chemical Parameters of a Large North African River: The Moulouya and Its Main Tributaries (Morocco). *Afr. J. Aquat. Sci.* **2020**, *45*, 1–11. [CrossRef]
- 74. Kumar, B.; Singh, U.K.; Ojha, S.N. Evaluation of Geochemical Data of Yamuna River Using WQI and Multivariate Statistical Analyses: A Case Study. *Int. J. River Basin Manag.* **2019**, *17*, 143–155. [CrossRef]

- 75. Pavlidou, A.; Anastasopoulou, E.; Dassenakis, M.; Hatzianestis, I.; Paraskevopoulou, V.; Simboura, N.; Rousselaki, E.; Drakopoulou, P. Effects of Olive Oil Wastes on River Basins and an Oligotrophic Coastal Marine Ecosystem: A Case Study in Greece. *Sci. Total Environ.* **2014**, *497–498*, 38–49. [CrossRef]
- 76. Benaddi, R.; Ferkan, Y.; Bouriqi, A.; Ouazzani, N. Impact of Landfill Leachate on Groundwater Quality–A Comparison Between Three Different Landfills in Morocco. *J. Ecol. Eng.* **2022**, *23*, 89–94. [CrossRef]
- 77. El Hmaidi, A.; Talhaoui, A.; Manssouri, I.; Jaddi, H.; Ousmana, H. Contribution of the Pollution Index and GIS in the Assessment of the Physico-Chemical Quality of the Surface Waters of Moulouya River (NE, Morocco). Water Ind. Biotechnol. 2020, 106, 45–54. [CrossRef]
- 78. Talhaoui, A.; El Hmaidi, A.; Jaddi, H.; Ousmana, H.; Manssouri, I. Calcul De L'indice De Qualité De L'eau (IQE) Pour L'évaluation De La Qualité Physico-Chimique Des Eaux Superficielles De L'Oued Moulouya (NE, Maroc). *Eur. Sci. J.* **2020**, *16*. [CrossRef]
- Vatanpour, N.; Malvandi, A.M.; Hedayati Talouki, H.; Gattinoni, P.; Scesi, L. Impact of Rapid Urbanization on the Surface Water's Quality: A Long-Term Environmental and Physicochemical Investigation of Tajan River, Iran (2007–2017). *Env. Sci. Pollut. Res.* 2020, 27, 8439–8450. [CrossRef]
- Qalmoun, A.; Bouzrarf, K.; Belqat, B. Assessment of the Ecological Status of the Oum Er-Rabie River Basin (Central Morocco) through Physicochemical, Bacteriological Parameters and Biotic Indices. *Biologia* 2022, 77, 1–15. [CrossRef]
- Khdair, A.; Abu-Rumman, G. Evaluation of Environmental Pollution from Olive Mill Wastewater. *Fresenius Environ. Bull.* 2017, 26, 2537–2540.
- 82. Khdair, A.; Abu-Rumman, G. Sustainable Environmental Management and Valorization Options for Olive Mill Byproducts in the Middle East and North Africa (MENA) Region. *Processes* **2020**, *8*, 671. [CrossRef]
- Mansour, T.; Mandi, L.; Ahmali, A.; El Ghadraoui, A.; Faissal, A.; Hejjaj, A.; Del Bubba, M.; Ouazzani, N. Effect of Poly-Phenols on Activated Sludge Biomass during the Treatment of Highly Diluted Olive Mill Wastewaters: Biomass Dynamics and Purifying Performances. *Water Sci. Technol. Water Supply* 2020, *82*, 1416–1429. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.