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Water quality in Minho/Miño River (Portugal/Spain)

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Abstract Minho River, also called Miño (in Spain), extends to about 300 km from Spain to Portugal. The source of the river lies in Spain and in the last 75 km, the river defines the border between Portugal and Spain. Under the scope of a cooperation project between North Portugal and Galicia region of Spain, titled: "Valorization of the natural resources of the Minho/ Miño drainage basin", seven water-sampling campaigns were carried out during the last 2 years in Minho River basin. Seven sampling sites were selected along the international stretch, and five were chosen in the main Portuguese and Spanish tributaries of Minho River. Water quality based on the physicochemical and microbial parameters was assessed. According to the Portuguese legislation for surface waters, the international section of Minho River presents a reasonably good water quality (BOD_5 <5 mg/L, TNK <2 mg/L, and total phosphorous <1 mg P/L). Valença and Louro were found to be the most polluted sampling sites and Louro the most polluted tributary (maximum values observed: TSS=26 mg/L, BOD_5=6.6 mg O_2/L, COD=20.8 mg O_2/L, total nitrogen=9.9 mg N/L; minimum value observed: OD=1.3 mg O_2/L). A one-dimensional stream water quality model QUAL2Kw was calibrated using data measured in field surveys along the international stretch of Minho River. QUAL2Kw was also used to predict the impact of flow conditions, discharges, and tributaries on the water quality of international stretch of Minho River, essential to establish proposals for management and planning of Minho River Basin.

Keywords Water quality · Minho River · Modeling · QUAL2Kw

Abbreviations

AAS	Atomic absorption spectroscopy
Alk	Alkalinity
AS	Anionic surfactants
BOD_5	Biochemical oxygen demand
Cl-a	Chlorophyll-a
COD	Chemical oxygen demand
CV	Cold vapor
DL	Detection limit
DOC	Dissolved organic carbon
F	Flame
FC	Fecal coliform
FS	Fecal streptococcus
GF	Graphite furnace

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Har	Hardness
HG	Hydride generation
N_{am}	Ammonium nitrogen
P_{hyd}	Hydrolysable phosphorus
TC	Total coliform
TNK	Total Kjeldahl nitrogen
TSS	Total suspended solids
Tur	Turbidity
VSS	Volatile suspended solids

Introduction

Water is one of the prime elements responsible for life on earth and fresh non-contaminated water can be a finite resource. Rivers have been used by mankind as a source of water, food, transport, and others from ancient times.

Minho (in Portuguese), or Miño (in Spanish and Galician), is an international river with an extension of about 300 km. Minho source lies in Pedregal of Irimia, 50 km north of Lugo in Galicia, Spain (Serra de Meira, Lugo, at 750 m of elevation) and in the last 75 km the river defines Portugal and Spain border. Minho River reaches the Atlantic Ocean near Caminha (Portugal) or La Guardia (Spain). Drainage basin covers a total area of 17,080 km^2, of which only 5 % is situated in the Portuguese territory (PBH 2001).

The identification of Minho River as a site of European Union importance, by Natura 2000 network (Portaria nº829/2007), proved the ecological importance of this natural resource. However, Minho drainage basin is under some threats, such as flow variation in the international section caused by Frieira dam discharges (near the beginning of international stretch), possible construction of more dams and, industrial, domestic, and agricultural pollution sources. In Portugal, Minho basin is located in a region with considerably lower industrial implementation, although some kind of industrial pollution risk exists due, principally, to beverage, food, chemical, and metallurgical industrial activity (PBH 2001). In Spain, industrial pollution is relatively high, mainly due to the industries in Porriño (Tui city), that have been associated with the main cause of Louro River contamination. Other pollution risk in Minho drainage basin is the diffuse pollution related to agriculture and the use of fertilizers (PBH 2001). To reinforce the development of cross-border economic relationships, the cooperation project POCTEP_NATURA_MIÑO_MINHO 2009–2010, between North Portugal and Galicia region of Spain, titled “Valorization of the natural resources of the Minho/Miño drainage basin”, was initiated in 2009. The main goal of the project was to evaluate the natural resources of the Minho River basin; identify natural risks caused by climate change; and propose management, planning, and improvement measures for the basin. The project partners consist of a multidisciplinary team, which includes the Faculty of Engineering University of Porto (FEUP), whose main task include the evaluation of water quality in the international stretch of Minho River. Specific objectives of the river monitoring program included: (1) determination of water quality parameters, (2) collection of current information about water quality, (3) evaluation of the impact of tributaries and industrial/domestic discharges on the water quality of international section, and (4) prediction of water quality under different scenarios using the QUAL2kw model.

Mathematical models have become important tools to evaluate the complex relationship between point and diffuse pollution sources and the consequences for the receiving water bodies (Deksissa et al. 2004). QUAL2E model (Brown and Barnwell 1987) has been widely used to describe water quality in several water streams, e.g., Whippany River, New Jersey, USA (Orden and Uchrin 1993), Sava River, Slovenia (Drolc and Konkan 1996, 1999), and Yamuna River, India (Paliwal et al. 2007). QUAL2Kw (Pelletier et al. 2006) is an update version of QUAL2K model (Chapra and Pelletier 2003) and QUAL2E. QUAL2Kw was used for water quality modeling of the following rivers: Bagmati River, Nepal (Kannel et al. 2007), Lis River, Portugal (Vieira 2007), and Itapanhaú River, Brazil (Mendes 2010). QUAL2Kw is programmed in VBA (Visual Basic for Applications) and uses *Microsoft Excel* as graphical user interface. The model simulates the transport of conventional pollutants along the course of a river and can be used to simulate several variables as temperature, pH, carbonaceous biochemical oxygen demand (BOD_5), sediment oxygen demand, ammonium, organic and nitrate nitrogen, and organic and inorganic phosphorous. It considers the river as a segmented water course (river divided in reaches). Data for point sources (tributaries, pollutant loadings from industrial discharges), diffuse sources (such as diffuse pollution from agricultural areas), and abstractions of water can be inputs to any reach. For each element, the model performs hydrologic, thermal, and mass balances, supposing one-dimensional steady-flow and a complete degree of mixture in each reach. Detailed information about QUAL2Kw model could be found in the user manual and in the theory manual (Pelletier and Chapra 2008). Meteorological data (temperature, wind speed, and solar radiation), hydraulic characteristics of the river, quantitative and qualitative characterization of discharges entering the stream, data about abstractions of water, and its quality, are also necessary to be collected and can be used as input for QUAL2Kw model. QUAL2Kw also allows an automatic calibration of the water quality model if experimental data, at different river locations, is available. The model uses a genetic algorithm to find kinetic constants and other model parameters that minimize differences between observed and predicted values. After model calibration, QUAL2Kw can be used to simulate different scenarios and then predict the influence of different factors on water quality.

The aim of the present study is to evaluate the water quality in the international stretch of Minho River through several water sampling campaigns; to evaluate the impact of tributaries and industrial/domestic discharges on the water quality of international section; and predict the water quality under different scenarios using the QUAL2Kw model.

Material and methods

Sampling sites

Figure 1 presents a scheme of the international stretch of the Minho River and its main tributaries. Seven sampling sites were selected to be monitored, namely: Frieira (F), Alevadas (Ale), Cabo (Cab), Salvaterra do Minho (SM), Valença (Val), Vila Nova de Cerveira (VNC), and Caminha (Cam). Frieira is the upstream point of the international stretch. Sampling was performed 2 km from the Frieira dam. Five sampling sites were selected in Mouro River (Mou), Manco River, Tea River (Tea), Louro River (Lou), and Coura River (Cou) tributaries.

Sampling

Seven water sampling campaigns were carried out in different seasons corresponding to different hydraulic conditions: May 2009, July 2009, October 2009, January 2010, March 2010, July 2010, and October 2010. In the tributaries, sampling was done close to the middle of the river. In Minho River, samples were collected near the banks however, in relatively turbulent waters, in order to obtain representative samples.

Analytical methods

Surface water samples, from each one of the sampling sites, were analyzed to determine several physicochemical and microbiological parameters. Temperature (*T*), oxidation–reduction potential, pH, and dissolved oxygen were measured in situ using a portable multiparameter (Hanna Instruments 9828). Other parameters were determined in laboratory according to the methods listed in Table 1 (Clesceri et al. 2005).

Results and discussion

Monitoring

Surface water quality was analyzed in seven sampling campaigns and results were compared with the Portuguese standards (DL 236/98—Table 2). INAG (2006) (Portuguese Institute of Water) standards were

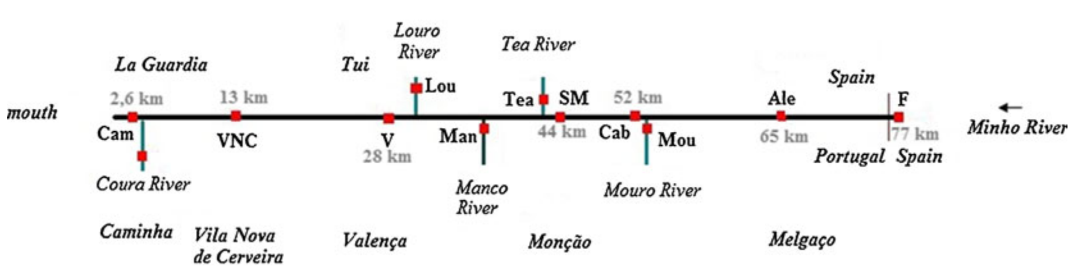

Fig. 1 International stretch of Minho River and sampling sites

Table 1 Parameters analyzed in surface water samples and analytical methods used

Parameter	Method	DL	Reference (method)
DOC	Catalytic oxidation at 700 °C (Shimadzu TOC 5000 A analyzer)	0.5 mg C/L	APHA, 1998 (5310) (Clesceri et al. 2005)
BOD_5	Oxygen consumed in 5 days at 20 °C, with nitrification inhibition	2.0 mg O_2/L	APHA, 1998 (5210) (Clesceri et al. 2005)
COD	Oxidation with potassium dichromate, closed reflux method	10.0 mg O_2/L	APHA, 1998 (5220) (Clesceri et al. 2005)
TSS	Gravimetric method; drying of solid residue at 105 °C	2.0 mg/L	APHA, 1998 (2540) (Clesceri et al. 2005)
VSS	Gravimetric method; oxidation of suspended solids at 550 °C	2.0 mg/L	APHA, 1998 (2540) (Clesceri et al. 2005)
N_{am}	Ammonia selective electrode method	0.08 mg N/L	APHA, 1998 (4500-NH_3) (Clesceri et al. 2005)
N_{total}	Digestion at 110 °C with potassium persulfate and colorimetric method of brucine	0.2 mg N/L	APHA, 1998 (4500-N) (Clesceri et al. 2005); ASTM 1973 (ASTM 1973)
NO_3^-	Ion chromatography (Dionex DX-120 Ion Cromatograph)	0.2 mg NO_3^-/L	APHA, 1998 (4110-B) (Clesceri et al. 2005)
NO_2^-	Ion chromatography (Dionex DX-120 Ion Cromatograph)	0.01 mg NO_2^-/L	APHA, 1998 (4110-B) (Clesceri et al. 2005)
TNK	Difference between total N and (N–NO_3 + N–NO_2)		
P_{total}	Ammonium persulfate digestion; ascorbic acid method	0.1 mg P/L	APHA, 1998 (4500-P) (Clesceri et al. 2005)
P_{hyd}	H_2SO_4 hydrolysis; ascorbic acid method	0.1 mg P/L	APHA, 1998 (4500-P) (Clesceri et al. 2005)
Alk	Potentiometric titration	0.5 mg $CaCO_3$/L	APHA, 1998 (2320-B) (Clesceri et al. 2005)
Har	EDTA titrationn	2.0 mg $CaCO_3$/L	APHA, 1998 (2340-C) (Clesceri et al. 2005)
Cl^-	Ion chromatography (Dionex DX-120 Ion Cromatograph)	0.8 mg Cl^-/L	APHA, 1998 (4110-B) (Clesceri et al. 2005)
SO_4^{2-}	Ion chromatography (Dionex DX-120 Ion Cromatograph)	1.8 mg SO_4^{2-}/L	APHA, 1998 (4110-B) (Clesceri et al. 2005)
AS	Methylene blue extraction	4 μg LAS/L	APHA, 1998 (5540-C) (Clesceri et al. 2005)
Tur	Turbidimetry (Turbiquant, Merck)		APHA, 1998 (2130-B) (Clesceri et al. 2005)
As_{total}	HNO_3 digestion; AAS—HG	1 μg/L	APHA, 1998 (3030-E; 3114-B) (Clesceri et al. 2005)
Cd_{total}	HNO_3 digestion; AAS—GF	0.5 μg/L	APHA, 1998 (3030-E; 3113-B) (Clesceri et al. 2005)
Pb_{total}	HNO_3 digestion; AAS—GF	10 μg/L	APHA, 1998 (3030-E; 3113-B) (Clesceri et al. 2005)
Cr_{total}	HNO_3 digestion; AAS—F	0.05 mg/L	APHA, 1998 (3030-E; 3111-D) (Clesceri et al. 2005)
Cu_{total}	HNO_3 digestion; AAS—F	0.1 mg/L	APHA, 1998 (3030-E;3111-B) (Clesceri et al. 2005)
$Hg_{pseudo\text{-}total}$	Acid digestion HNO_3/HCl 70 °C CV-AAS (GBC-Hydride Generator HG3000)	1 μg/L	EPA 2001 (Method 200.7) (EPA 2001)
Ni_{total}	HNO_3 digestion; AAS—GF	20 μg/L	APHA, 1998 (3030-E; 3113-B) (Clesceri et al. 2005)
Zn_{total}	HNO_3 digestion; AAS—F	0.1 mg/L	APHA, 1998 (3030-E; 3111-B) (Clesceri et al. 2005)
FC	Membrane filtration		APHA, 1998 (9222-D) (Clesceri et al. 2005)
TC	Membrane filtration		APHA, 1998 (9222-B) (Clesceri et al. 2005)
FS	Membrane filtration		APHA, 1998 (9230-C) (Clesceri et al. 2005)
Cl-a	Acetone extraction, spectrometric determination	0.1 μg/L	NP 4327 1996

used for microbiological indicators and chemical oxygen demand (Table 3). INAG standards classify water quality in five levels according to its characteristics for multiple uses.

Table 2 Minimum surface water quality (adapted from Decreto-Lei 236/98)

Parameter	MAV[a]	Parameter	MAV[a]
pH	9.0	Sulfate	250 mg SO_4^{2-}/L
Temperature	30 °C	Anionic surfactants	0.5 mg/L
Dissolved oxygen	50 % of saturation[b]	Total arsenic	0.1 mg As/L
Ammonium nitrogen	1 mg N/L	Total cadmium	0.01 mg Cd/L
BOD_5	5 mg O_2/L	Total lead	0.05 mg Pb/L
TNK (Kjeldahl nitrogen)	2 mg N/L	Total chromium	0.05 mg Cr/L
Total phosphorous	1 mg P/L	Total mercury	0.001 mg Hg/L
Chloride	250 mg Cl^-/L	Total nickel	0.05 mg Ni/L
		Total zinc	0.5 mg Zn/L

[a]MAV, maximum admissible values

[b]Minimum admissible value

According to Table 4, international stretch of Minho River showed generally good physicochemical water quality. Dissolved oxygen values, always above 72 % of saturation, also indicated a well-oxygenated water course. However, in certain dates, Vila Nova de Cerveira, Valença, and Caminha showed values of total Kjeldahl nitrogen (4 mg N/L), chromium (0.18 mg Cr/L), and mercury (0.003 mg Hg/L) above the standard limits. Since agriculture practice is very common in the soils surrounding Minho River, it would be expected to have problems with nitrogen and phosphorous compounds due to diffuse pollution in this region. But, in fact, only the Kjeldahl nitrogen was found to be of concern. With exception for Vila Nova de Cerveira, Valença, and Caminha in one sampling campaign, nitrate and total phosphorous concentrations were below 5 and 0.2 mg/L, respectively, which is typical of an excellent water quality. The data obtained for microbiological parameters clearly identified Valença (maximum values observed: total coliforms=2.7×10^5 cfu/100 mL; fecal coliforms=1.2×10^6 cfu/100 mL; fecal *Streptococcus*=1.8×10^5 cfu/100 mL) as the most polluted site according to INAG classification, indicating a poor water quality. However, Valença sample point was near a small community without any basic sanitation, and probably use the river to discharge all kinds of wastes, which can influence significantly the water quality at this location.

The high concentration of chloride ions in Caminha sampling point is due to the sea effect, although sample collection was always performed during low tide.

Among the five tributaries studied, Louro was identified as the most polluted. Dissolved oxygen (minimum value observed, 1.3 mg O_2/L), biochemical oxygen demand (maximum value observed: BOD_5=6.6 mg O_2/L) and total Kjeldahl nitrogen (9 mg N/L) parameters exceeded Portuguese standards in six of the seven campaigns performed. Microbiological concentrations also presented high values (maximum values observed: total coliforms=1.6×10^6 cfu/100 mL; fecal coliforms=2.0×10^4 cfu/100 mL; fecal *Streptococcus*=3.8×10^5 cfu/100 mL) indicating poor water quality. Spanish authorities have taken strict measures to improve the quality of Louro, but illegal wastewater discharges from meat industry have been reported (Filgueiras et al. 2004). Tea and Coura rivers show a good water quality, and only few parameter values were above the permissible limits. With the exception of Louro, Minho tributaries presented a

Table 3 Surface water courses classification for microbiological parameters, according to multiple uses (adapted from INAG)

	A Excellent	B Good	C Reasonable	D Bad	E Very bad
Total coliform (cfu/100 mL)	≤50	51–5,000	5,001–50,000	>50,000	–
Fecal coliform (cfu/100 mL)	≤20	21–2,000	2,001–20,000	>20,000	–
Fecal streptococcus (cfu/100 mL)	≤20	21–2,000	2,001–20,000	>20,000	–
COD (mg O_2/L)	≤10.0	10.1–20.0	20.1–40.0	40.1–80.0	>80.0

Table 4 Water quality in Minho River international stretch and tributaries: comparison between observed values and Portuguese standards

		C	*VNC*	*V*	*SM*	*Cab*	*Ale*	*Fr*	*Cou*	*Lou*	*Tea*	*Mou*	*Man*
Portuguese Legislation (DL 236/98)	T	●●●●●●●	●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	DO	●●●●●●●	●●●●●●●	●●●●●●●	●●●●-●●	●●●●-●●	●●●●-●●	●●●●●●●	●●●●●●●	××●●●×●	●●●●-●●	●●●●-●●	-●●●●●●
	pH	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	BOD_5	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	×××●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	TNK	--●●×-●	●×●●●××	×●●●×●●	●●●●●●●	●●●●●●●	●×●●●●●	●●●●●●●	●●●●××●	××●●×××	×●●●●×●	●●●●●×●	-●●●●××
	N_{am}	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●×●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	P_{total}	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	Cl^-	+++●●++	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	SO_4^{2-}	●×●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	AS	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	total As	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	total Cd	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	total Pb	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	total Cr	●●●●●●●	×●●●●×●	×●●●●×●	●●●●●●●	●●●●●●●	●●●●●×●	●●●●●×●	●●●●●×●	●●●●●×●	●●●●●×●	●●●●●×●	-●●●●×●
	total Cu	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	total Hg	●●●●×●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●×●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	total Ni	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●×	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
	total Zn	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	●●●●●●●	-●●●●●●
INAG	COD	AABAABA	ABAAAAA	AAAABBA	AAAAABA	AAAAAAA	AAAAAAA	AAAAAAA	AAAAAAA	BCBABBA	AAAAABA	AAAAAAA	AAAAAAA
	TC	ACCBBCB	ACBCBCB	CCADDCB	ABACBCB	ACACBAB	A-BBBAB	ABABBBB	ACCBBBA	DDDDDDA	BCBBCCC	ACBBBAA	-BBBBCB
	FC	AABBBBB	AABCBBB	DCADDCC	AAACBAB	ACACAAB	ABBCCAA	ABACBBB	AABBAAA	DCAACCA	CBBACAC	ABBAAAA	-ABBBBB
	FS	ABBBBBB	AABBBBA	CABBCBB	ABBBBBB	ABBBBBB	ABABBAA	ABBBBBB	AABBABB	DCCCCCC	ABBBBBB	ABBBBBB	-BAABBB

DL 236/98: × not in agreement; ● in agreement; + not in agreement due to the sea effect. INAG: ■ A—excellent; ■ B—good; ■ C—reasonable; ■ D—bad; -values not measured (each one of the symbols represents water quality evaluation in each one of the seven water sampling campaigns)

reasonably excellent microbiological water quality (Table 4).

QUAL2Kw modeling

QUAL2Kw model was used in the present study to simulate the water quality in international section of Minho River, from Frieira (immediately upstream of the start of the international stretch) to Minho River base level in the Atlantic sea, which is equivalent to a stretch with 77 km. River width in the studied stretch varies nearly from a few meters to almost 2 km in the estuary. International stretch was divided in 52 reaches, with variable lengths (between 430 m and 2.9 km; Fig. 2). Manning roughness coefficient was assumed as 0.04, since Minho River is a natural stream channel, clean and straight (Chow et al. 1988). Model calibration was based on data obtained from the fifth water sampling campaign in March, 2010. The point pollution sources considered were: (1) Mouro, Tea, Manco, Louro, and Coura rivers and (2) inventoried industrial and wastewater treatment discharges. Three surface water extractions were also considered in the studied stretch. Diffuse pollution was not taken into account in Minho River modeling because the risk of diffuse pollution from the banks is very low: in respect to phosphorus and nitrogen, values of 0–20 kg P/km^2/year and 0–200 kg N/km^2/year have been reported (PBH 2001).

Auto-calibration

Automatic calibration was used to determine the kinetic rate constants values and other model parameters (Table 5) that maximize the goodness of fit of the model predictions compared to the measured data (Pelletier and Chapra 2008) collected in March, 2010. Euler solution method and Newton–Raphson for pH were selected to be used in the integration process. Hyporheic exchange and pore water quality simulation were done at the first level, considering the following assumptions: (1) 10 cm as the sediment thickness, (2) sediment thermal diffusivities in the range of 0.0051–0.0079 cm^2/s and conductivities, 1.57–2.5 W/m/°C, according to thermal properties of different kind of materials reviewed by Pelletier and Chapra (2008).

The genetic algorithm provided by QUAL2Kw was used for auto-calibration. Population size and number of generations (user-selected parameters) were defined as 50 and 25, respectively, resulting in a total of 1,300 runs.

Input data included (1) flow (739 m^3/s) and water quality constituents concentrations in Frieira (the headwater from which the simulation was done), (2) point sources information (water quality constituents concentrations and flows), and (3) water quality data obtained from sampling sites in the international stretch (for the calibration process). Flow rate values of Spanish

Table 5 QUAL2Kw model parameters obtained in the calibration

Parameter	Value	Auto-cal	Min value	Max value
Carbon (gC)	40	No		
Nitrogen (gN)	7.2	No		
Phosphorus (gP)	1	No		
Dry weight (gD)	100	No		
Chlorophyll (gA)	1	No		
ISS settling velocity (m day^{-1})	1.58	Yes	0	2
Slow CBOD hydrolysis rate (day^{-1})	4.32	Yes	0	5
Slow CBOD oxidation rate (day^{-1})	0.48	Yes	0	0.5
Fast CBOD oxidation rate (day^{-1})	1.59	Yes	0	5
Organic N hydrolysis (day^{-1})	0.47	Yes	0	5
Organic N settling velocity (m day^{-1})	0.02	Yes	0	2
Ammonium nitrification (day^{-1})	4.18	Yes	0	10
Nitrate denitrification (day^{-1})	1.67	Yes	0	2
Sed. denitrification transfer coeff. (m day^{-1})	0.80	Yes	0	1
Organic P hydrolysis (day^{-1})	0.78	Yes	0	5
Organic P settling velocity (m day^{-1})	1.33	Yes	0	2
Inorganic P settling velocity (m day^{-1})	0.14	Yes	0	2
Sed. P oxygen attenuation half sat. constant (mgO_2L^{-1})	1.40	Yes	0	2
Phytoplankton max growth rate (day^{-1})	2.28	Yes	1.5	3
Respiration rate (day^{-1})	0.069	Yes	0	1
Death rate (day^{-1})	0.035	Yes	0	1
Nitrogen half sat. constant (μg NL^{-1})	130	Yes	0	150
Phosphorus half sat. constant (μg PL^{-1})	45.6	Yes	0	50
Inorganic carbon half sat. constant (mol L^{-1})	1.04×10^{-4}	Yes	1.30×10^{-6}	1.30×10^{-4}
Phytoplankton use HCO_3^- as substrate	Yes			
Light model	Half saturation			
Light constant (Langleys day^{-1})	67.2	Yes	28.8	115.2
Ammonia preference (μg NL^{-1})	8.67	Yes	0	25
Phytoplankton settling velocity (m day^{-1})	1.06	Yes	0	5
Bottom plants:				
Growth model	zero-order			
Max growth rate (gD m^{-2} day^{-1})	37.5	Yes	0	100
First-order model carrying capacity (gD m^{-2})	100	No		
Basal respiration rate (day^{-1})	0.38	Yes	0	0.5
Excretion rate (day^{-1})	0.15	Yes	0	0.5
Death rate (day^{-1})	0.36	Yes	0	0.5
External nitrogen half sat. constant (μg NL^{-1})	9.84	Yes	0	300
External phosphorus half sat. constant (μg PL^{-1})	23.5	Yes	0	100
Inorganic carbon half sat. constant (mol L^{-1})	1.18×10^{-4}	Yes	1.30×10^{-6}	1.30×10^{-4}
Bottom algae use HCO_3^- as substrate	Yes			
Light model	Half saturation			
Light constant (Langleys day^{-1})	82.0	Yes	1	100
Ammonia preference (μg NL^{-1})	8.30	Yes	1	100
Subsistence quota for nitrogen (mg NgD^{-1})	62.8	Yes	0.072	72

Table 5 (continued)

Parameter	Value	Auto-cal	Min value	Max value
Subsistence quota for phosphorus (mg PgD^{-1})	0.35	Yes	0.01	10
Maximum uptake rate for nitrogen (mg NgD^{-1} day^{-1})	1,174	Yes	350	1,500
Maximum uptake rate for phosphorus (mg PgD^{-1} day^{-1})	146	Yes	50	200
Internal nitrogen half sat ratio	1.34	Yes	1.05	5
Internal phosphorus half sat ratio	2.88	Yes	1.05	5
Detritus dissolution rate (day^{-1})	3.30	Yes	0	5
Detritus settling velocity (day^{-1})	1.06	Yes	0	5
Fecal coliform decay rate (day^{-1})	2.74	Yes	0	5
Fecal coliform settling velocity (m day^{-1})	1	No		
COD decay rate (day^{-1})	0.11	Yes	0	1
COD settling velocity (m day^{-1})	0.33	Yes	0	1.2

tributaries were provided by *Confederación Hidrográfica del Miño-Sil*. Flow rates in Portuguese tributaries, Coura, Manco, and Mouro, were not monitored. It was considered that Coura and Mouro presented the same flow rate as Louro (12.6 m^3/s) and Tea (30.9 m^3/s), respectively, and Manco, a fifth part of Louro (2.52 m^3/s).

The data used for the calibration and the fitting process included water temperature, conductivity, alkalinity, pH, fast-reacting CBOD, inorganic suspended solids, organic and inorganic phosphorous, organic, ammonium and nitrate and nitrite nitrogen, chlorophyll-a, and fecal coliform. The following parameters were not used for the fitting to avoid over-fitted calibration: (1) conductivity measured in Caminha, due to the high influence of sea, (2) nitrogen compounds in Caminha due to the influence of chlorides in the analytical method, and (3) Valença water quality data, because previous calibrations showed that those values clearly decrease the quality of the fitting (probably due to the influence of a small community without any basic sanitation that lives near this sample point).

QUAL2Kw model uses fast-reacting and slow-reacting biochemical oxygen demands ($CBOD_f$ and $CBOD_s$). BOD_5 (with nitrification inhibition) measured in the samples was converted to ultimate carbonaceous biochemical oxygen demand ($CBOD_u$) by Eq. 1 and equalized to $CBOD_f$. In tributaries and point sources, $CBOD_s$ was considered null, as suggested by Pelletier and Chapra (2008).

$$CBOD_u = \frac{BOD_5}{1 - e^{-5\times 0.18}} \tag{1}$$

Flow and water quality data from industrial wastewaters and wastewater treatment plant discharges, entering the international stretch of Minho River from the Spanish side, were obtained from *Confederácion Hidrográfica del Minho-Sil*. From Portuguese side, municipal authorities provided quantitative and qualitative data. Unknown parameter values were estimated by the maximum admissible level accepted by Portuguese legislation for discharges in water courses. The evolution of the goodness of the fitting, during the 1,300 runs of the automatic calibration, is depicted in Fig. 3.

Conductivity and temperature model profiles described quite well the observed data (Fig. 4). Along the international stretch, conductivity was almost constant and equal to 83 μS/cm. Dissolved oxygen predicted profile (data not shown) shows a slight decrease along the international stretch (from 12 mg/L in Frieira to 9 mg/L near the mouth), indicating a well-oxygenated water course.

Fast-reacting carbonaceous biochemical oxygen demand was also well described by the model and the obtained profile confirms a decrease of the biodegradable matter concentration along the river. In the international stretch, model predictions showed a maximum value of fast-reacting CBOD of 1.9 mg O_2/L near Valença. Chemical oxygen demand (COD) and dissolved organic carbon (DOC) profiles (not shown) also showed no significant variations along the river and very low concentrations (below 2.2 mg C/L and 5 mg O_2/L, respectively). For nitrogen compounds, a considerable good fitness between predicted and

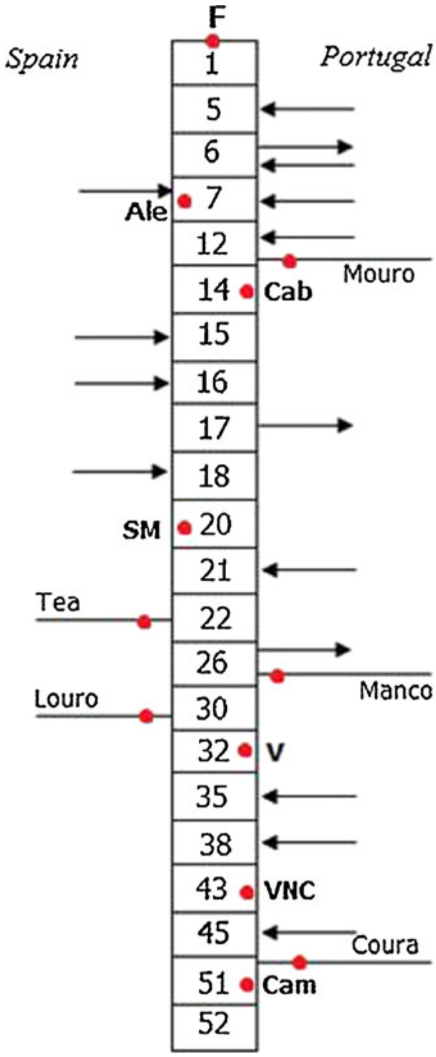

Fig. 2 Simplified scheme of modeled system using QUAL2Kw (*arrows* represent abstractions of water from Minho River or discharges inflow in Minho River)

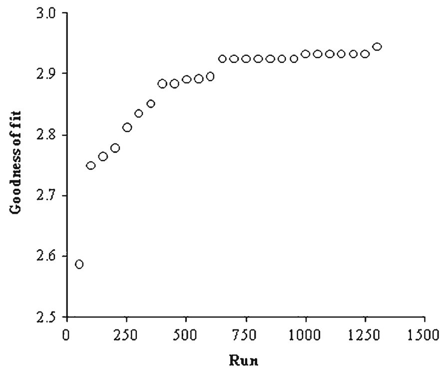

Fig. 3 Goodness of fit evolution during automatic calibration using the genetic algorithm

observed values for nitrate, nitrite, and ammonium was obtained. For organic nitrogen, experimental values were not very well described by the model. Simulated curve for organic N indicated almost constant concentration along the international stretch (0.7 mg N/L), while measured values in Cabo and Vila Nova de Cerveira (1.0 and 0.9 mg/L, respectively) were slightly higher. Ammonium–nitrogen concentration profile showed a decrease along the river, as a result of nitrification, and predicted a final concentration of 0.01 mg N_{am}/L near Caminha. Phosphorous calibration was obtained with success (organic, inorganic, and total forms), showing very low values (below 0.1 mg P/L). Alkalinity profile (not shown) indicated almost constant value along the river, 16 mg $CaCO_3$/L, and the pH profile showed a slight decrease from 7.2 (at Frieira) to 6.8 at the base level. The values obtained for the physicochemical parameters for the river water in the international stretch revealed a reasonably good quality.

The data for *fecal coliform* concentration (Fig. 4) was well described by the model with the exception for Alevadas sampling site. The profile obtained for this parameter was of great importance, as it predicted high *fecal coliform* concentrations in points which were not monitored. A value of 4.6×10^3 cfu/100 mL was predicted near Valença city, at a distance of 25 km to the mouth, which can be associated to Louro River tributary contribution and illegal discharges at this location. At a distance of 44 km to the mouth a marked increase in fecal coliforms was also predicted. Model predictions between Salvaterra do Minho (or Monção) and Vila Nova de Cerveira (or Centinela) indicated poor water quality in this section. Observed fecal coliform at Valença sampling site (8.0×10^4 cfu/100 mL, not used in the calibration), was much higher than the predicted value, which confirms a high pollution level in terms of fecal coliform on this site.

Water quality modeling in different scenarios

Once calibrated, QUAL2Kw allows the prediction of water quality under different scenarios. In this work, the model was used to evaluate the impact of extreme conditions of flow rate, which is an important factor to be studied in Minho River. Flow rate along the international stretch is mainly defined by Frieira dam, causing a flow rate variability during the year. Other scenarios were also simulated in the present work, in

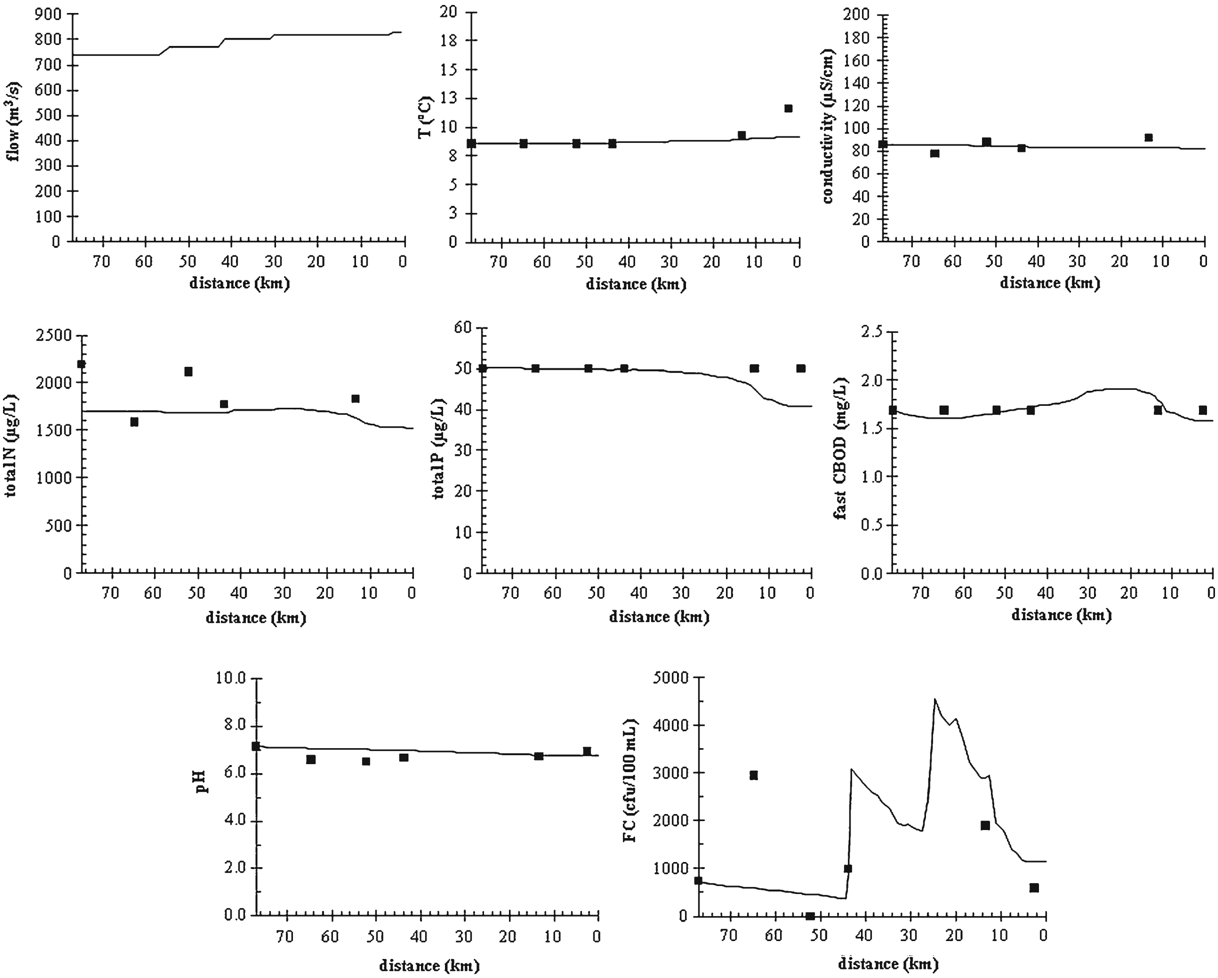

Fig. 4 Predicted and observed data along the international stretch of Minho River

order to evaluate the impact of discharges and tributaries on Minho River water quality.

Flow rate QUAL2K model was calibrated for a headwater flow rate (Freira sampling point) of 739 m^3/s. Figure 5 presents the simulated curves for a scenario of extreme conditions of minimum flow rate (339 m^3/s), according to the data available. Considering this extreme flow rate condition, predicted flow at the mouth of Minho River decreased from 829 to 429 m^3/s, and travel time increased from 1.34 to 1.75 days. The pH, temperature, conductivity, suspended inorganic solids, and alkalinity (profiles not shown) showed no significant effect. Total phosphorus (profile not shown) showed no change from Frieira to a distance of about 35 km to the base level of the river. Downstream 35 km, a reduction of phosphorous concentration (up to 25 %) was predicted, thus, very low levels of the former are expected to still be observed in the international stretch. Fast-reacting CBOD values decreased downstream of Valença with the flow reduction (Fig. 5), which is related to the increase of the travel time, increasing the water course self-depuration capacity. The organic nitrogen concentration profile predicted by the model shows an increase of 16 % from 40 km distance towards the mouth, but the values were always below Portuguese standards for Kjeldahl nitrogen. The values of physicochemical parameters suggested that a reduction of flow rate is expected to keep the river with a reasonably good water quality. The predicted results related to the microbial contamination of the river shows an aggravation (Fig. 5) of the water quality in river section from 45–10 km (distances to the mouth).

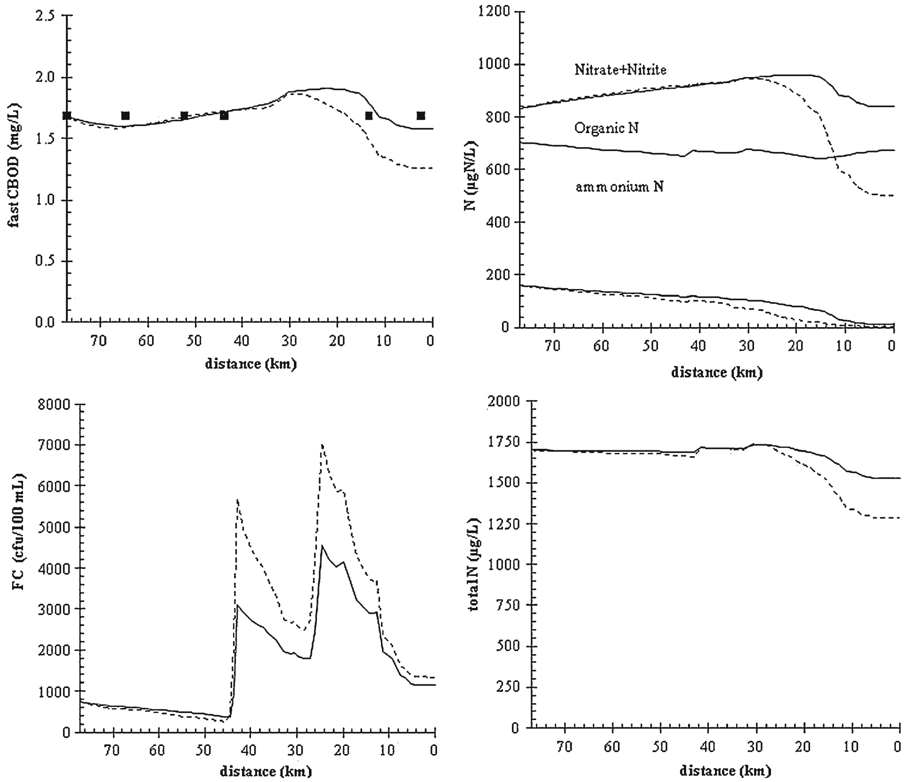

Fig. 5 Predicted profiles along Minho River international stretch for two flow conditions in Frieira: 739 m^3/s (*solid line*) and 339 m^3/s (*dashed line*)

According to these results, low flow rate situations increase greatly the microbiological contamination.

Tributaries and discharges impact on water quality of Minho River international stretch In order to compare the impact of direct effluent discharges into Minho River and the impact of tributaries, the following scenarios were simulated using the QUAL2kw model: (1) discharges in Minho River were eliminated from the model; (2) tributaries were eliminated from the model; and (3) discharges and tributaries were both eliminated. Situation (0) was considered the real situation used for calibration.

Water quality in Minho River depends mainly on the tributaries, with the exception of fecal coliform (Fig. 6). The similarity between predicted curves for scenarios (0) and (1) revealed no significant impact of discharges. Inflow volumes were, in fact, less than 0.5 % of the total flow in Minho River international stretch. Predicted profiles showed that, in the studied conditions, tributaries are responsible for: (1) a slight increase (7 %) of fast-reacting CBOD from 31 km towards Caminha (which has no significance since these parameters showed values less than 2 mg O_2/L) and (2) increase (up to 14 %) of organic nitrogen from 43 km towards river mouth (Fig. 6) and 20 % increase in the ammonium nitrogen (Fig. 6). The impact of tributaries was only observed after the confluence of Tea and Louro, showing that the influence of these two rivers is the most significant. Simulations also revealed that conductivity, pH, total phosphorous, and COD (data not shown) depends mainly on the water quality upstream (in Frieira), since neither affluent nor discharges showed significant influence on their profiles along the river. Pathogenic discharges were found to be the main cause of the contamination from Monção towards river mouth (Fig. 3). Near Valença (28 km to the river mouth), a significant contribution of tributaries was also observed, as a result of Louro River.

Conclusions

Surface water in the international stretch of Minho River presented a good physicochemical quality, according to the seven water-sampling campaigns performed. Total Kjeldahl nitrogen (4 mg N/L),

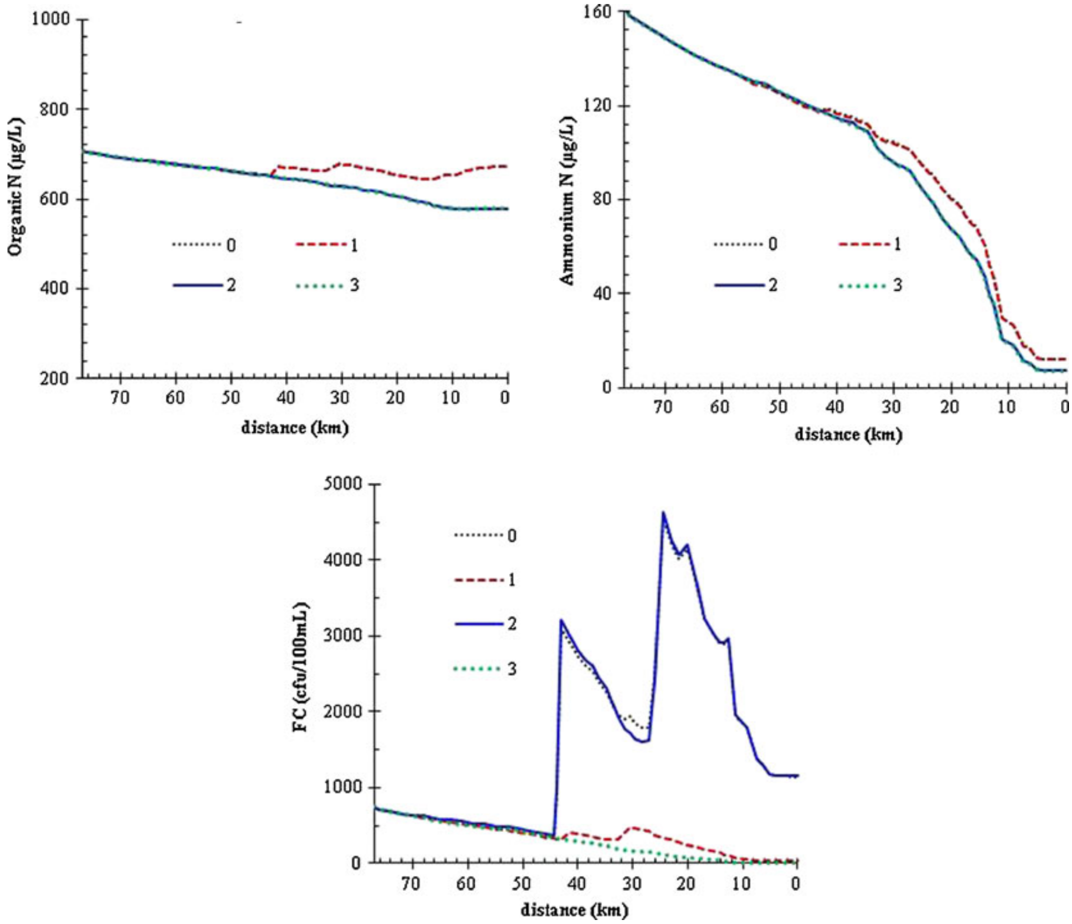

Fig. 6 Simulated profiles along Minho River international stretch considering four different scenarios: (*0*) real situation, (*1*) eliminating discharges from the model, (*2*) eliminating tributaries from the model, and (*3*) eliminating discharges and tributaries

chromium (0.18 mg Cr/L), and mercury (0.003 mg Hg/L) were the few parameters that exceeded the minimum Portuguese limits for surface waters quality in few sampling campaigns. Minho River section between Monção and Vila Nova de Cerveira cities was identified as a problematic stretch taking into account the high values generally observed for fecal coliform contamination (maximum values observed at Valença sampling point: total coliforms=2.7×10^5 cfu/100 mL, fecal coliforms=1.2×10^6 cfu/100 mL, fecal *Streptococcus*=1.8×10^5 cfu/100 mL). According to the QUAL2kw predictions, pathogenic concentration in Minho River section between Monção and Vila Nova de Cerveira was greatly affected by the river flow rate, which resulted in the deterioration of the water quality level for low flow rate conditions. From the studied tributaries, Louro River presented the most polluted samples (dissolved oxygen-minimum value observed=1.3 mg O_2/L; biochemical oxygen demand and total Kjeldahl nitrogen-maximum values observed, 6.6 mg O_2/L and 9 mg N/L, respectively). Generally, tributaries, especially the Spanish ones, have a low, but significant effect in physicochemical water quality in Minho River. The discharges into Minho River are responsible for the pathogenic contamination.

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