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Surface Water Quality in a Contrasted Land-Use River Catchment

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Abstract. To evaluate the current state quality of the surface water resources in a river catchment near the city of Leiria (Central Portugal), a water sampling programme was designed and has been carried out since September of 2017. The land uses of the basin area were also studied. The three sampling sites are located in the river Lis catchment, downstream from the river spring to the city of Leiria, and in the Ribeira do Sirol tributary. The sampling programme was performed according to ISO 5667 standards. At each sampling site and twice a year, the field parameters, the concentration of dissolved gases (O_2 and CO_2) and the alkalinity were measured in the water. As the Lis river discharge is widely variable, flow parameters were also measured. The composition of surface water was determined in dissolved and particulate material, being the samples filtered at site. The major and minor constituents, cations (Ca, Mg, Na, K, NH_4 and Fe) and anions (HCO_3, Cl, SO_4, PO_4, F, NO_3 and NO_2) were analysed. Data of the winter campaign show that the hydrochemical facies of Lis River water are mainly Ca-HCO_3. The chemical species are in dissolved forms and there is no evidence of nitrites, phosphates or fluoride in the surface waters. The concentration of Na, K and Cl, Mg and SO_4, increase downstream, after the Ribeira do Sirol tributary, whose basin is mainly of agricultural land use. The water of River Lis in the urban area of Leiria shows evidence of a mixture of the spring water and of the Ribeira do Sirol water, with little contributions of other water sources in the urban area, pointing to a greater concern with respect to sanitation and good environmental practices in the city of Leiria.

1. Introduction

Water, being essential for human life, is a relevant matter and off concern in today’s society. The UN Sustainable Development Goals (SDG6 and SDG11) [1] [2] points to *clean water and sanitation for all* in 2030, as a challenge for resilient and sustainable cities. Also, the evaluation of water quality in urban context has been underlined as a topic for well-being, public health and ecosystem services in water-wise cities [3].

Water quality is a driving force to understand human interactions with ecosystems, namely on urban areas, where the land use changes produce direct and indirect impacts [4]. In the Central Region of Portugal, Leiria is a district capital and center of the Leiria region NUTS III (Nomenclature of Territorial Units for Statistics, level III). According to the 2011 Census [5], Leiria has 126 897 residents with a notorious increase in the population from 1970 onwards and a continuous growth in the number of family households since 1950 [5]. More resident population and the related economic and social functions imply an increasing need for natural resources demand, however limited. Water is no exception. The dynamic of artificialization on small and medium sized cities, produce deep changes on land use and occupation [6], influencing the natural indicators and the water quality [7].

Leiria is located in the Lis River catchment area, a coastal basin in Portugal. Around the 90's of the 20th century, the agricultural areas represented 42% of the total area in terms of land use. Today, this number has declined to 31% and the land is occupied primarily by forest and semi-natural areas (58%) (Table 1) [4], [8], [9].

Table 1. Land Use in Lis river catchment [7]

Land Use	Area (%)
Forest and semi-natural areas	58%
Agricultural areas	31%
Artificial surfaces – Urban	8%
Artificial surfaces – Industrial, commercial and transport units	2%
Others	1%

The major part of the forested area is located in the western side of the county and is called *Pinhal d'El Rei*, which means King's Pinewood, but also mark the upstream areas of the Lis catchment

Leiria has been a study case for many authors and particularly the Lis and the Lena rivers have been analysed regarding the flood risk in urban areas; assessing surface water quality and water modelling; hydrological and management issues [10]-[13].

This study aims to: (1) characterize the actual quality state of the surface waters in river Lis catchment; (2) to investigate how does the quality of the surface waters changed with different land uses of the tributaries catchments, analysing mainly forested, agricultural and urban areas in the last few years Also, the study (3) tests if the municipal control of water quality is effective, and anticipates the climate changes future impacts.

2. Methods

2.1 Study area

Leiria is located in the Lis River catchment area, a coastal basin with approximately 900 km^2. The Lis river has about 40 km long, flowing from the south-eastern part of the basin to the Atlantic Ocean, in the northwest (Figure. 1). It is the most important source of surface water in the region. The Portuguese Environmental Agency (APA) has several surface water monitoring sites, as well as, stream-flow gauging stations in the Lis river catchment. Also, there are some meteorological and climatologic stations in the area (Figure. 1) [14].

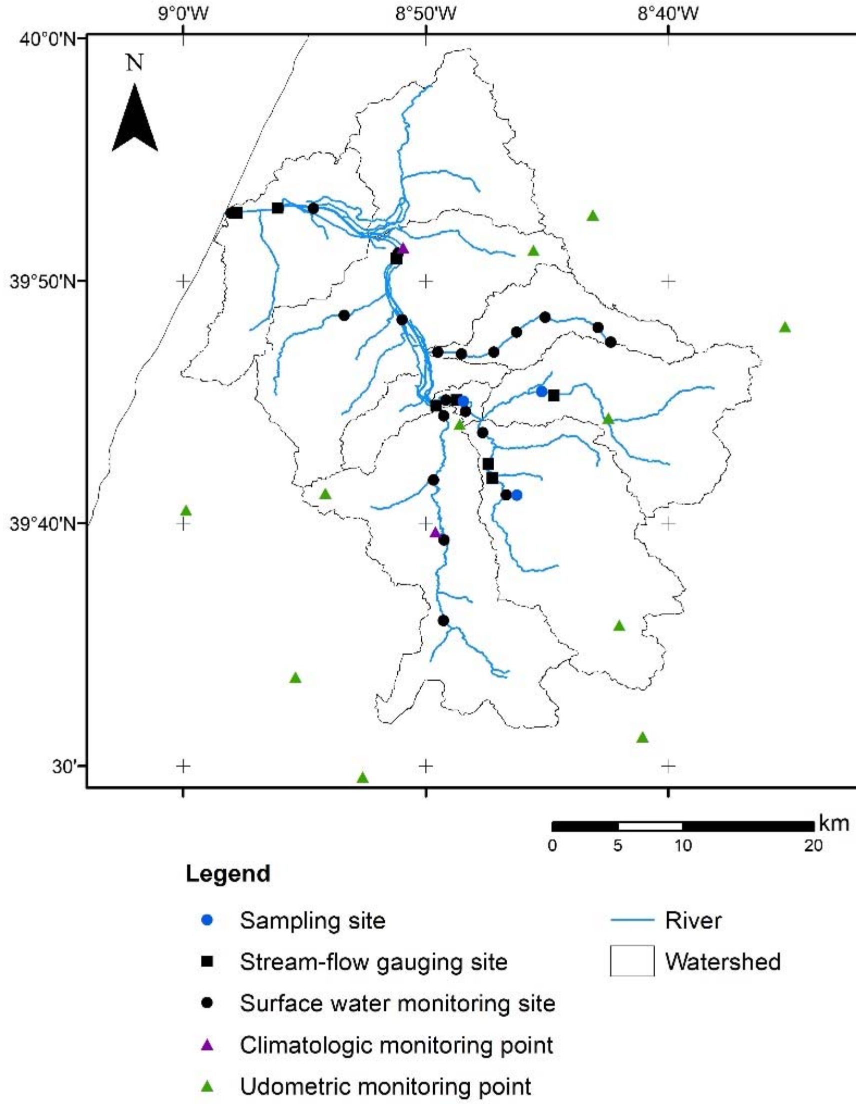

Figure 1. Lis river catchment area with the tributaries watersheds, sampling sites and the monitoring networks for climate, surface water quality and stream-flow.

The geologic outcrops are mainly of sedimentary materials, corresponding to holocenic dunes and eolian sands, alluvial and bottom valley deposits, fluvial terraces, Pliocene sandstones, clays and silts and the Jurassic carbonated rocks. The formations of magmatic origin correspond to domes and rocks are predominantly dolerites (Figure. 2) [15], [16].

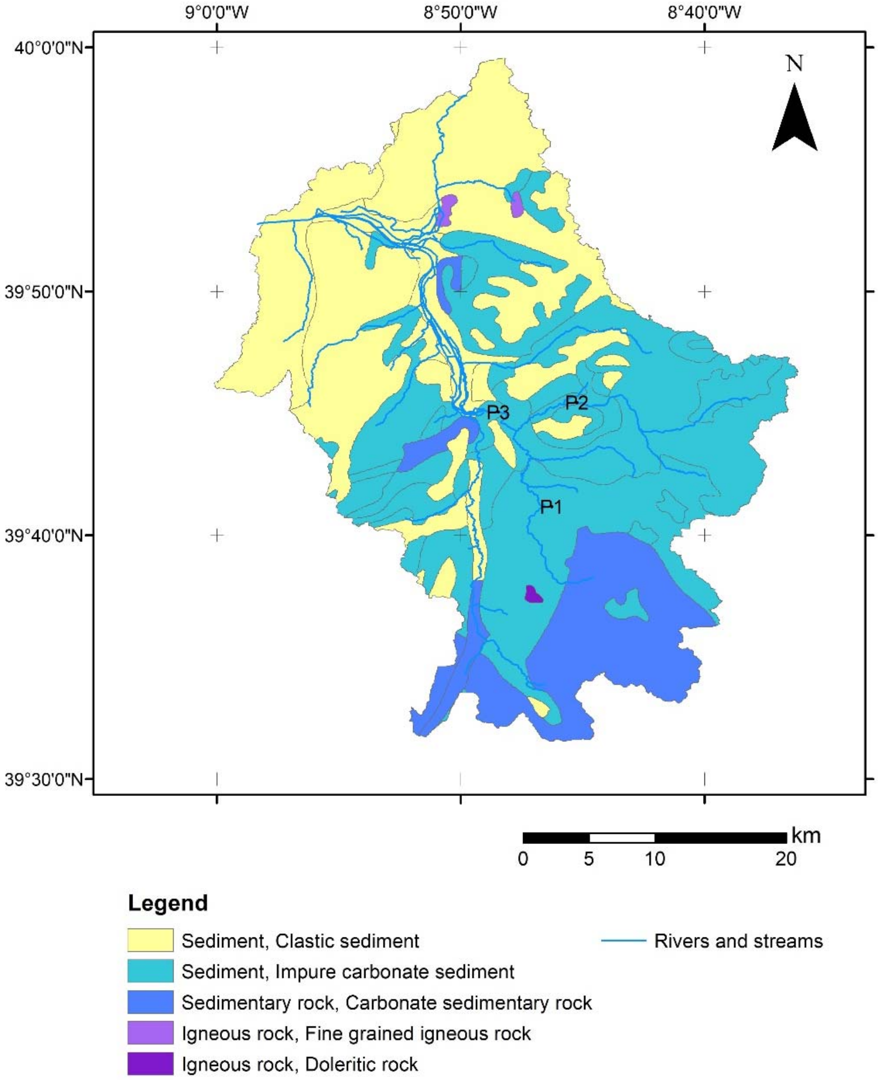

Figure 2. Geologic map of the Lis river catchment area and surroundings.

2.1.1 Sampling sites. The sample points were chosen based on the catchment land use, representing a forested areas (P1), agricultural areas (P2) and urban areas (P3) (Figure. 3). Also, river Lis flows from the sampling points P1 to P3, being P2 a point in the tributary *Ribeira do Sirol*. The P1 sampling point is located upstream, near the Lis river spring, in an area with carbonated rocks. P2 it's located in the Sirol tributary that drains into the main course before crossing the urban area (city of Leiria). Around this stream, it is possible to see areas of land with agricultural use, and river water is used to irrigate these fields. The third sampling point (P3) is located downstream, in the urban area of Leiria. The river course in this area is artificialized, preventing floods damages, no longer taking its original path.

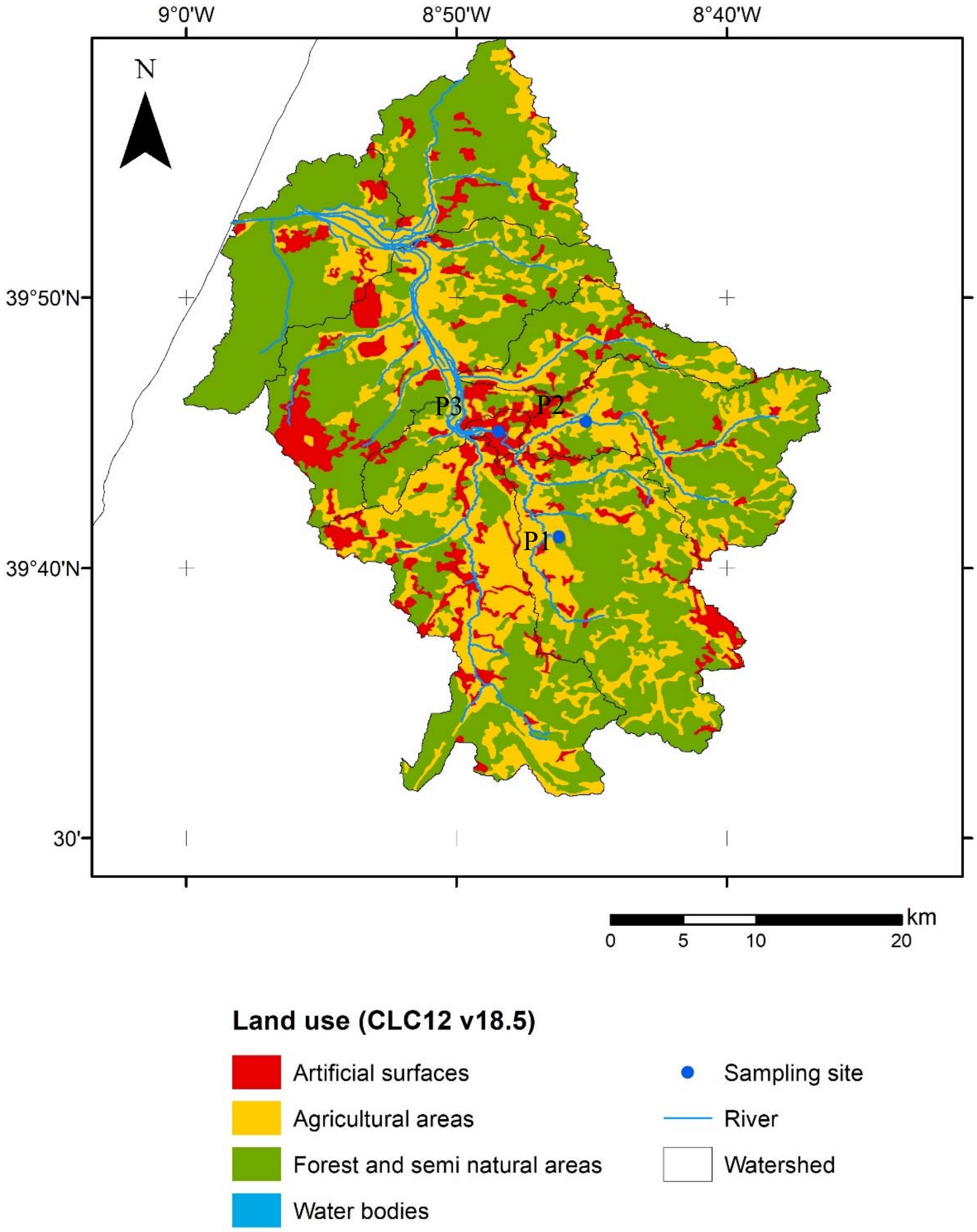

Figure 3. Land use and occupation (CLC12 v18.5) for the Lis catchment, with the sampling points and watersheds.

2.2. Sampling programme

The sampling programme was performed according to ISO 5667 standards [17]-[19]. At each sampling site and twice a year, the field parameters (pH, oxi-redox potential (ORP), dissolved oxygen (DO), electrical conductivity (EC), water temperature (T_w), air temperature (T_a) and turbidity) were tested. Also, the concentration of dissolved CO_2 and the alkalinity are being measured in the water. As the Lis river discharge is widely variable, flow parameters were also measured. The composition of surface water was determined in dissolved and particulate material, being the samples filtered at site.

The major and some minor constituents, cations (Ca, Mg, Na, K, NH_4 and Fe) and anions (HCO_3, Cl, SO_4, P_2O_5, F, NO_3 and NO_2) were determined. The water major anions (Cl, SO_4, Br, F, NO_3) were analysed by ion chromatography (IC) [20] and phosphorus was determined by the SMEWW 4500-P colorimetric method [21] in the Laboratory Department of Water And Sanitation of Leiria (SMAS Leiria) and the major cations (Ca, Mg, Na, K, NH_4) were determined by ion chromatography (IC) [22] in the ITeCons laboratory. Trace metal (Al, Cd, Sb, Pb, Cu, Fe and Mn) concentrations were determined by atomic absorption spectrophotometry (AAS-GC) in a graphite furnace [23].

3. Results and discussions

The winter sampling period was set to 13 March 2018, and the river flow had a great amount of suspended material, since it had rained in the previous week. Between 9 of March and 12 of March, the effective depth of precipitation was about 37 mm. The results are typical of natural surface waters evolving in a carbonated rocks environment (Tables 2 and 3).

Table 2. Field parameters collected on 13 March 2018.

Sample Point	Water Body	Land Use	T_a (ºC)	T_w (ºC)	pH	ORP (mV)	O_2 (mg/L)	CO_2 (mg/L)	EC (µS/cm)	Turbidity (NTU)
P1	Lis river	Forest	14.0	15.3	6.90	157.0	7.9	78	544	8.52
P2	Sirol Stream	Agricultural	15.6	14.1	7.90	131.0	9.3	55	495	9.86
P3	Lis river	Urban	17.9	15.6	7.96	121.4	9.4	66	554	10.6

Table 3. Chemical composition of the water samples (P1 to P3) in both dissolved (< 0.45 µm) and total forms ($P1_{total}$ to $P3_{total}$).

Sample Point *EQS values*	Total Alcalinity $CaCO_3$ (mg/L)	Ca (mg/L) -	Mg (mg/L) -	Na (mg/L) -	K (mg/L) -	NH_4 (mg/L) *0.2*	Cl (mg/L) -	NO_3 (mg/L) -	SO_4 (mg/L) -	Fe (mg/L) -	Mn (mg/L) *0.123*	Al (mg/L) -
$P1_{total}$	283	102	7	-	-	-	17	10	12	-	-	-
$P2_{total}$	231	76	10	-	-	-	25	10	22	-	-	-
$P3_{total}$	168	98	10	-	-	-	25	10	19	-	-	-
P1 (<0.45µm)	282	97	2,4	7,2	0,91	0,04	16	10	12	<0.02	0.007	<0.02
P2 (<0.45µm)	226	74	6,7	14	2,5	0,049	24	10	22	0.059	0.022	0.029
P3 (<0.45µm)	283	93	4,7	13	1,9	0,153	22	9	18	<0.02	0.009	<0.02

Notes: The constituents P_2O_5, F, NO_2, Cd, Sb, Pb and Cu, also analysed in all samples, had values below the detection limit. *EQS values* as recommended by the UK Technical Advisory Group on the Water Framework Directive [24]

Field parameters show that the pH increases downstream as well as the dissolved oxygen. Unlike those parameters, the ORP increases upstream. The turbidity values are high due to the heavy rainfall of the previous days.

The composition of surface water was determined in dissolved and particulate material. The major and minor constituents, cations (Ca, Mg, Na, K, NH_4) and anions (HCO_3, Cl, SO_4, P_2O_5, F, NO_3 and NO_2) were analysed as well as some trace constituents like Fe, Mn, Al, Cd, Sb, Pb and Cu (Table 3).

Water chemical data of the winter campaign show that the Lis river water samples have a distinct Ca-HCO_3 hydrochemical character (Figure 4). The chemical species are in dissolved forms and there is no evidence of nitrites, phosphates or fluoride in the surface waters. Also, the quantities of Cd, Sb, Pb and Cu are below the detection limits for the AAS technique (Table 2).

The Stiff diagrams for the three sampling points are illustrative of the main chemical processes interfering in the water composition (Figure 4).

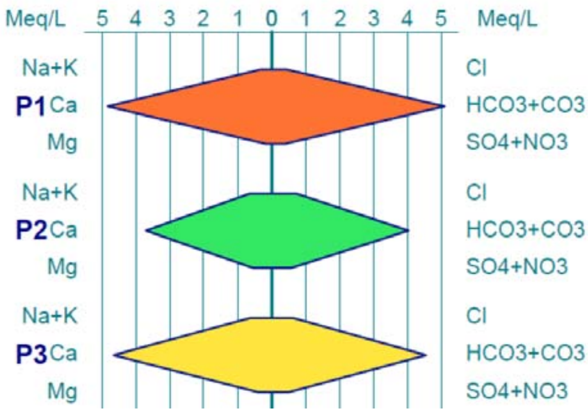

Figure 4. Stiff diagrams of the water collected in the sampling points P1 to P3.

Geological processes have a strong influence in the composition of groundwater and also on surface water. In the eastern uppermost part of the Lis river catchment the lithology is dominated by carbonated rocks and sediments, so the Ca-HCO_3 type of the Lis spring water is an evidence of the main geological conditions present in the recharge area. The surface water evolves then along the regional flow directions, depending on the chemical and biochemical interactions between the water, the geological materials and the environmental pollutants generated by human activity, providing a variety of dissolved constituents and suspended matter. The water of the Ribeira do Sirol has higher concentrations of Na, K, Mg, Cl and SO_4, and also Fe, Al and Mn than the other two water samples. This water has, however, lower amounts of alkalinity (HCO_3 in this case) and calcium. The first group of constituents increases downstream, after the Ribeira do Sirol tributary, whose basin is mainly of agricultural land use which may explain these results since they are present in most fertilizers, pesticides and sanitizers known to man [24]. The water collected in P3 shows evidence of a mixture between P1 and P2, with a lower contribution from the last (Table 2, 3 and Figure 4).

The concentration of ammonium in water increases downstream but more rapidly in the water collected in the city of Leiria (P3). In the water collected in P3, the value of ammonium is three times higher than in the P2 water. Nevertheless, this value is below 0.2 mg/L considered a natural level for groundwaters by the World Health Organization (WHO) and a low level for surface waters (that may contain up to 12 mg/L in natural conditions) [25]. The ammonium cation is involved in the biological processes of nitrogen fixation, mineralization, and nitrification [25]. This hypothesis could be verified by the results that show a decrease in nitrate in the same sample. Still, the presence of ammonia in the urban areas may be an indicator of faecal pollution [25], but in this case the value is under the environmental quality standards (EQS) limit for a high quality status [24]. There are no significant changes in the other analysed elements dissolved in water.

4. Conclusions

The European Water Framework Directive (WFD) (Directive 2000/60/EC) was created with the purpose of *"… establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater"* and thereby contributing to "*… the provision of the sufficient supply of good quality surface water and groundwater as needed for sustainable, balanced and equitable water use…"* [26]. According to the principles of this directive, standards for environmental quality and emission limit values for certain groups of pollutants were laid down as minimum requirements in the legislation. In 2008, the European Council wrote an amendment to this directive, the Directive 2008/105/EC (the Environmental Quality Standards Directive – EQSD) that set these quality standards as required by the WFD [27].

Surface water status is a classification process that assigns a status class to a particular water body. It is determined by the lower value of the ecological status and the chemical status of a water body. To achieve a good surface water status, the WFD requires that the surface waters have, at least, good ecological status and good chemical status [26]. The quality elements used to assess ecological status are: (i) biological quality elements; (ii) chemical and physicochemical quality elements, including general physicochemical quality elements and pollutants being discharged in significant quantities, which are referred to as *specific pollutants* in the annex VIII of the WFD; and (iii) hydromorphological quality elements. For assessing the chemical status of a river, the environmental quality standards (EQS) that needs to be known are the *priority substances and other pollutants*, defined in the annex I of the Directive 2008/103/CE [27]. The classification process will result in a status class for each surface water body. The class given will represent an estimate of the degree to which the aquatic ecosystem supported by surface water body has been altered by all the different pressures to which it is subjected. This means that the results of classification will reflect the impacts of a much wider range of pressures on the water environment. Land uses like artificial surfaces and agricultural areas could contribute to the increase of those pressures.

In this work we analysed the chemical and physicochemical quality elements in rivers, referred in terms of thermal, oxygenation, salinity, acidification and nutrient conditions measured by temperature, dissolved oxygen concentration, salinity, pH, and nutrients concentration (mainly dissolved phosphorus), respectively. The substances analysed that could be accounted for the chemical quality status [24] were Cd, Sb, Pb, Cu, Mn, Al, Fe, NH_4, NO_3 and NO_2. For the studied area during the sampling programme, all of the values were in the High quality status [24], [27]. The results show that the municipal concerns with surface water quality, sanitation and sustainable environmental practices could provide good indicators of ecological and chemical status.

Acknowledgments

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References

[1] United Nations Development Programme (UNDP), *UNDP. Support to the Implementation of Sustainable Development - Goal 6. Sustainable Management of Water and Sanitation.* (2016, Jan). [Online]. Available: http://www.undp.org/content/undp/en/home/librarypage/sustainable-development-goals/undp-support-to-the-implementation-of-the-2030-agenda/

[2] United Nations Development Programme (UNDP), *UNDP. Support to the Implementation of Sustainable Development - Goal 11. Sustainable Management of Water and Sanitation.* (2016, Jan). [Online]. Available: http://www.undp.org/content/undp/en/home/sustainable-development-goals/goal-11-sustainable-cities-and-communities.html

[3] The International Water Association (IWA), *The IWA Principles for Water-wise Cities.* (2016, Aug). [Online]. Available: http://www.iwa-network.org/wp-

content/uploads/2016/08/IWA_Principles_Water_Wise_Cities.pdf

[4] Z. Teixeira, H. Teixeira and J. C. Marques, "Systematic processes of land use/land cover change to identify relevant driving forces: Implications on water quality". *Science of the Total Environment,* 470–471, pp. 1320–1335. Fev, 2014. Available: https://doi.org/10.1016/j.scitotenv.2013.10.098

[5] INE, *Censos 2011 Final results - Portugal.* Portugal: Instituto Nacional de Estatística, 2011. (in Portuguese)

[6] M. Monteiro, and A.O Tavares, "What is the Influence of the Planning Framework on the Land Use Change Trajectories? Photointerpretation Analysis in the 1958–2011 Period for a Medium/Small Sized City. *Sustainability*, 7(9), 11727-11755, 2015. https://doi:10.3390/su70911727

[7] J.E. Clapcott, K.J. Collier, R.G. Death, E.O. Goodwin, J.S. Harding, D. Kelly, D., ...and R.G Young, "Quantifying relationships between land-use gradients and structural and functional indicators of stream ecological integrity". *Freshwater Biology*, 57(1), 74-90, 2012. https://doi.org/10.1111/j.1365-2427.2011.02696.x

[8] B. Meneses, E. Reis, M. J. Vale and R. Reis, "Modelling Land Use and Land Cover Changes in Portugal: A Multi-Scale and Multi-Temporal Approach", *Finisterra*, LIII, 107, pp. 3-26, 2018.

[9] European Environment Agency (EEA). CORINE land cover, CLC 2012 version v18.5.1 [database], 2016. Available: https://land.copernicus.eu/pan-european/corine-land-cover

[10] J.Vieira, A. Fonseca, V. J. P. Vilar, R. A. R. Boaventura and C. M. S. Botelho, "Water quality in Lis river, Portugal*", Environmental Monitoring and Assessment.*, vol. 184 (12), pp. 7125-7140, Dec 2012. Available: https://doi.org/10.1007/s10661-011-2485-9

[11] J.Vieira, A. Fonseca, V. J. P. Vilar, R. A. R. Boaventura and C. M. S. Botelho, "Water quality modelling of Lis River, Portugal*", Environ Sci Pollut Res*, vol. 20, pp. 508-524, Jan 2013. Available: https://doi.org/10.1007/s11356-012-1124-5

[12] P. Paíga, L. H.M.L.M. Santos, S. Ramos, S. Jorge, J G Silva and C Delerue-Matos. "Presence of pharmaceuticals in the Lis river (Portugal): Sources, fate and seasonal variation", *Science of the Total Environment* vol. 573, pp. 164–177, 2016. Available: http://dx.doi.org/10.1016/j.scitotenv.2016.08.089

[13] A. Fonseca, C. M. S. Botelho, R. A. R. Boaventura and Vilar, R. A. R., "Integrated hydrological and water quality model for river management: A case study on Lena River", Science of the Total Environment, vol. 485–486, pp. 474–489, 2014. Available: http://dx.doi.org/10.1016/j.scitotenv.2014.03.111

[14] Agência Portuguesa do Ambiente, "SNIAmb. SNIAmb –"National Environmental Information System", 2018. [Online]. Available: https://sniamb.apambiente.pt/ (in Portuguese)

[15] C. Teixeira, G. Zbyszewski, C.Torre de Assunção and G. Manuppella. "Geological Map of Portugal, scale 1:50.000, sheet 23-C, Leiria". LNEG - National Laboratory of Energy and Geology, Lisbon, 1968. (in Portuguese)

[16] A. Veiga and M. Quinta-Ferreira. "Diapir Mudstone Properties. Leiria, Portugal." *International Multidisciplinary Scientific GeoConference: SGEM: Surveying Geology & mining Ecology Management,* 2, p. 245, 2015.

[17] ISO 5667-1:2006(en), *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

[18] ISO 5667-3:2012(en), *Water quality — Sampling — Part 3: Preservation and handling of water samples*

[19] ISO 5667-6:2016(en), *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams.*

[20] ISO 10304-1:2007(en), *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate*

[21] SMEWW 4500-P B, E, Phosphorus, *SMEWW - Standard Methods for the Examination of Water*

and Wastewater, APHA, 2016.

[22] ISO 14911:1998(en), *Water quality — Determination of dissolved Li+, Na+, NH4+, K+, Mn2+, Ca2+, Mg2+, Sr2+ and Ba2+ using ion chromatography — Method for water and waste water*

[23] ISO 15586:2003(en), *Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace*

[24] UK Technical Advisory Group on the Water Framework Directive. *Updated Recommendations on Environmental Standards. River Basin Management (2015-21). Final Report,* November 2013 (revised January 2014). WFD, UK TAG, 2014. Available: http://www.wfduk.org/resources/phase-3-review-environmental-standards-201213

[25] World Health Organization (WHO). *Guidelines for drinking-water quality: fourth edition incorporating the first addendum.* Geneva: WHO Library Cataloguing-in-Publication Data, 2017.

[26] Directive 2000/60/EC of The European Parliament and of The Council of 23 October 2000 establishing a framework for Community action in the field of water policy.

[27] Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.