Modeling copper pollution from road Runoff in a peri-urban catchment in Portugal by using MIKE SHE, and MIKE 11 coupled with ECO Lab

RICARDO VALENCIA
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Summary

Economic development in an area attracts more people to live in it. This increment drives the necessity to improve available infrastructures, such as roads, to satisfy a higher demand. Increasing number of vehicles and larger roads have raised the concern about possible water pollution, particularly by heavy metals. In this thesis, copper from road runoff sources in a peri-urban catchment in Portugal was investigated. The catchment is located in the Coimbra region, center of Portugal, and occupies an extension of 6.2 km². The study is based on modelling, using a hydrological model able to simulate rainfall-runoff processes, and coupled with a water quality model capable to simulate the chemical reactions that affect copper pollution, assuming the road runoff as the only source within the catchment. According to the literature review, there have been several attempts of water quality modelling, mainly eutrophication process related with nitrogen, but not so many regarding metal pollution. In a previous study a physical based hydrological model MIKE SHE was coupled with the hydraulic model MIKE 11, this was considered as the original model. This model was updated and coupled with ECO Lab to simulate water quality processes. The hydrological results show an improvement compared with the original model, as evidenced by an increase of the Nash-Sutcliffe efficiency coefficient from 0.59 to 0.77 and on the coefficient of determination from 0.64 to 0.79. For the copper modelling, different scenarios were used to define which parameters have the greatest influence; also to analyze model behavior two approaches were used, assuming that road runoff gets into the river in four punctual locations and also that the runoff income is distributed along the river branches. For punctual sources, the highest concentrations were present in points where the incoming sources of copper were located in the tributaries. When reaching the main stream, copper concentrations are rapidly reduced due to dilution effect. On the other hand, distributed sources approach gives higher concentrations near the catchment outlet than in the upstream tributaries. Modeling results regarding copper concentration along the river were compared with fresh water quality criteria, from USEPA and from Portuguese Legislation for surface water quality. The punctual sources approach modelling gives higher river length with dissolved copper concentrations above those limits, compared with distributed sources. At the outlet of the catchment boundary values have the biggest influence on the model results. For the rest of the river, resuspension rates have bigger influence than the organic carbon partitioning coefficient. Modeled copper values do not agree well with the measured values particularly for periods with higher discharge as the model simulates lower concentration with higher discharge and vice versa. Copper boundary values for the model represents a big challenge considering the limited data available. Another important aspect is the difference in time-steps for the water quality modelling and for the hydrological modelling due to the limitation in data availability.
Modellering av kopparförorening från vägavrinning i ett peri-urbant avrinningsområde i Portugal genom att använda MIKE SHE och MIKE 11 tillsammans med ECO Lab.

Resumen

El desarrollo económico en una zona atrae más gente a vivir en ella. Este incremento impulsa la necesidad de mejorar la infraestructura vial disponible, como carreteras, para satisfacer una mayor demanda. El aumento del número de vehículos y carreteras ha generado una preocupación por la posible contaminación de agua, particularmente por metales pesados provenientes de los automotores. Por tanto, esta investigación se enfocó en el comportamiento del escorrentía de carreteras en una cuenca periurbana de Portugal. La cuenca está situada en la región de Coimbra, centro de Portugal, y ocupa una extensión de 6.2 km². El estudio se basa en un modelamiento utilizando un modelo hidrológico capaz de simular procesos de lluvia-escorrentía, y un modelo de calidad del agua capaz de simular las reacciones químicas que influyen en la contaminación por cobre, asumiendo que la escorrentía es la única fuente dentro de la cuenca. De acuerdo a la revisión bibliográfica se han realizado varios intentos de modelación de calidad del agua, principalmente procesos de eutrofización relacionados con nitrógeno, pero no se encontró mucha información en relación con la contaminación por metales. En un anterior estudio, un modelo hidrológico en MIKE SHE fue acoplado con el modelo hidráulico en MIKE 11. Este modelo fue mejorado y acoplado con ECO Lab para simular procesos de contaminación y calidad del agua. Los resultados hidrológicos muestran una mejora en comparación con el modelo original, traducido por un aumento en el coeficiente de eficiencia Nash-Sutcliffe de 0,59 a 0,77 y en el coeficiente de determinación $R^2$ de 0,64 a 0,79. Para el modelamiento de cobre se utilizaron dos escenarios, el primero suponiendo que la escorrentía ingresa al río en cuatro ubicaciones puntuales; y el segundo, que el ingreso es distribuido a lo largo de la vertiente del río. Para las fuentes puntuales, las concentraciones más altas se presentaron en los puntos donde la escorrentía ingresaba al río. Sin embargo, dichas concentraciones eran reducidas rápidamente debido a un proceso de dilución principalmente. Por otra parte, con fuentes distribuidas, las mayores concentraciones fueron cerca de la salida de la cuenca. Los resultados del modelamiento de cobre a lo largo del río fueron comparados con los criterios de calidad de agua dulce, tanto de la USEPA como de la Legislación Portuguesa. Con fuentes puntuales, una mayor longitud del río presenta concentraciones de cobre disuelto por encima de dichos límites, en comparación con fuentes distribuidas. Las concentraciones límite establecidas en el modelo influyen mayormente en las concentraciones simuladas en los puntos cercanos a la salida de la cuenca. Para el resto del río, las tasas de resuspensión tienen mayor influencia en comparación con las concentraciones límite y con el coeficiente partición carbono-orgánico (Koc). Los valores de cobre modelados no concuerdan con los valores medidos, especialmente para períodos con mayores descargas, ya que el modelo simula una menor concentración con una descarga mayor y viceversa. Definir los valores límite de cobre para el modelo representa un gran desafío considerando los limitados datos disponibles. Otro aspecto importante fue la diferencia en la frecuencia entre los datos generados por el proceso hidrológico debido a la limitación de los mismos, y los datos usados para comparar las concentraciones de cobre simuladas con las mediciones. Finalmente algunas ideas para mejorar el modelo actual son presentadas y analizadas.
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Abstract

Economic development in an area attracts more people to live in it. This increment drives the necessity to improve available infrastructure, like roads for instance, to satisfy a higher demand. Bigger roads and higher number of vehicles have raised the concern about possible pollution coming from these sources. In this thesis, copper coming from road runoff in a peri-urban catchment in Portugal was analyzed. The catchment is located in the Coimbra region, center of Portugal. In order to model copper pollution in road runoff, it is necessary to couple a hydrological model and a water quality model. Based on a previous study (Kalantari, Ferreira, Walsh, Ferreira, & Destouni, 2017) a physical based hydrological model MIKE SHE coupled with the hydraulic model MIKE 11 was updated and further coupled with ECO Lab to simulate water quality and ecological processes. The results show an improvement of the hydrological model compared with the original one, nash-sutcliffe efficiency was raised from 0.59 to 0.77 and the coefficient of determination varied from 0.64 to 0.79. For copper the model behavior for punctual and distributed sources was analyzed. For punctual sources, highest concentrations were present in the grid points where the incoming sources were located in the tributaries, and these concentrations are rapidly reduced downstream. On the other hand, distributed sources approach gives higher concentrations near the end of the river than in the tributaries upstream. Comparing time-averaged model results along the river, with fresh water quality criteria according to U.S. EPA (2004), for punctual sources an extension of 978 meters (7.6% of the river) presents a concentration above CCC or CMC, on the contrary, for distributed sources the extension is lower with 494 meters (3.8%). The organic carbon partitioning coefficient have bigger influence on the results than other factors, nevertheless this influence is not marked. Modeled copper values do not agree well with the measured values specially for periods with higher discharge as the model simulates lower concentration with higher discharge and viceversa. Copper boundary values for the model represent a big challenge considering limited data available. This thesis gives good overview about the coupling process between MIKE 11 and ECO Lab, as well as analyzes the importance of some factors as well as model limitations and uncertainties.

Key words: Copper modelling, hydrology, water quality, MIKE 11 - ECO Lab
1. Introduction

Human activities can lead to environmental pollution. These pollution sources are usually classified in point and non-point sources. While point sources regard to discharges at specific locations, non-point sources are characterized by multiple discharge points spread over an area (Kamarudzaman, et al., 2011; Kubota & Tsuchiya, 2009). During the 90’s in USA for example, it was determined that near 30% of the water quality problems were related to storm water discharged or non-point sources pollution, this included agricultural runoff, urban runoff and mine drainage (USEPA, 1998). Rainfall that falls in an area can infiltrate or flow on the surface or subsurface layers (Gunawardena, et al., 2013). This flow can carry all kind of materials located on the surface or subsurface layers and deposit it in water bodies, becoming non-point source pollution principally in urban and agriculture areas. In urban areas, due to the absence of filtering associated to infiltration processes, runoff can be a source of several pollutants such as: sediments, nutrients, pathogens, petroleum hydrocarbons, heavy metals, among others (California Coastal Commission, 2002).

The Urbanization and its implication in hydrological processes is a well-documented area of study around the world (The Unesco Press, 1974; O'Driscoll, et al., 2010; Wong, et al., 2012; Song, et al., 2014). In Portugal, and particularly in the catchment under study, Ribeira dos Covões, several reports about the impacts of urbanization and hydrology and water quality have been published (Ferreira, et al., 2011, 2015, 2016b; Kalantari, et al., 2014a, 2017;).

Roads are a key infrastructure with urbanization; furthermore roads have been important for the development of countries development (Chohan, 2011). A higher economic growth implies more people to serve, and this situation carries the necessity of building bigger roads to couple increasing vehicular traffic. Nevertheless, this increase in the amount of cars and in road size has raised the concern about water pollution coming from them. During 80’s and 90’s road runoff pollution was included as urban runoff (Wu, et al., 1998). Nevertheless, nowadays roads are considered a non-point source of environmental pollution, that can be analyzed separately from urban runoff and can contribute with some pollutants affecting both surface and groundwater (Yannopoulos, 2012).

There are different substances linked with roads such as: deicing salt, oil or other spills, and metals coming from vehicular traffic (Kim, et al., 2015; The World Bank, 1997). Interactions and transport of metals as well as other antrophogenic constituents is controlled by distinct processes, such as dry deposition (Wu, et al., 1998), physicochemical interactions between water and solid phases, suspension of constituents, and aquatic chemistry (Dean, et al., 2005). Metals that are deposited and accumulated on roads can be washed off during storm events, reaching the water bodies inside the catchment. Urban runoff is considered a significant source of copper and other metals in natural waters (Nason, et al., 2012; Kayhanian, et al., 2007; German & Svensson, 2002).

There have been some studies regarding the characterization of roads and highway runoff. Wu, et al., (1998) characterized and estimated pollutant loading from three different highway segments in North Carolina, USA, they found that 20% of TSS, and near 80% of Nitrogen were due to atmospheric deposition. Kayhanian, et al. (2007) analyzed the characteristics of several rain events during 2000 – 2003 in California, USA, to find correlations between rainfall characteristics and some water constituents like nutrients (N), suspended sediments
(TSS), metals and dissolved minerals, driven by surrounding highways. This study showed that total metal concentration are highly correlated with total iron concentration, and that stronger relationships were present between organic carbon and TSS. Furthermore, there are some studies (Dean, et al., 2005; Guo, et al., 2006) regarding copper speciation in highway runoff, finding that copper is mostly bounded to carbonates or organic material.

In order to analyze the behavior of a metal in the environment it is possible to find bibliographical information about general behavior patterns, but if another approach is needed, modelling becomes an available and important option. Modelling metal pollution or water quality in rivers needs to couple a hydrological model with a water quality/pollution model. There are various softwares that have been used to accomplish this objective as AQUASIM, CE-QUAL, or MIKE 11 (Arheime & Olsson, 2003). While there is extensive literature focusing on water quality modelling considering the effect of nitrogen and eutrophication processes, and not so many regarding copper pollution modelling.

In a previous study developed by Hävermark (2016) Kalantari et al. (2017) a hydrological model by coupling MIKE SHE and MIKE 11 for the Ribeira dos Covões catchment was developed. Moreover, MIKE 11 can be coupled with a water quality/pollution model called ECO Lab that has an specific template to model metal pollution in rivers. Considering the previous aspects, modelling of metal pollution coming from roads and using MIKE SHE, and MIKE11 coupled with ECO Lab will be developed.

In order to address this research gap the present study aims to simulate the influence of the spatial distribution of urban areas on surface water quality with focus on copper concentration from roads to the streams in a small peri-urban catchment in central Portugal. Copper pollution was taken considering data available and the use of copper in brake pads or other devices for vehicular traffic (Solomon, 2009). The specific objectives were to:

- Improve the hydrological model developed by Hävermark (2016), increasing its stability.
- Define the most significant parameters that affect the performance of copper modeling in the studied catchment.
- Analyze and compare model results with field data obtained from previous studies.

2. Background

2.1. Copper

Copper is classified as a noble metal element with an atomic mass of 63.546 g/mol, and its two main oxidation states +1 and +2.

Copper (I)

This form is the cuprous ion, and it is oxidized rapidly in aqueous solution to form copper (II) and copper (0). Normally, cuprous compounds are colorless.

Copper (II)

This form includes the cupric ion, Cu2+, and is the most important oxidation state of copper. This state is normally found in fresh water.
Most cupric compounds are green or blue, and soluble in water. The aqueous ion Cu2+ is mildly hydrolyzed in neutral solutions forming dimer copper hydroxide Cu2(OH)22+. Complexes formed by copper (II) commonly have blue or green color, and are stronger than for other (+2) metals (Georgopoulos, et al., 2001).

This metal can be found naturally in an elemental form and also in minerals as chalcopyrite (CuFeS2) chalcocite (Cu2S), covellite (CuS), and bornite (Cu5FeS4). It is stable in pure dry air at room temperature, but in humid air it forms a green patina of basic salt (Georgopoulos, et al., 2001). Nowadays, copper is widely used in several products like alloys, coins, jewelry, automobile parts, as well as in agriculture as an additive or a pesticide (Salminen, et al., 2005; Solomon, 2009). Related to vehicular traffic, copper can be present in the vehicle breaking pads and deposited on the impervious surfaces like roads, being one of the most important copper sources (Moran, 2004).

Environmental fate of copper

The fate of copper in the environment is complex and influenced by pH, dissolved oxygen, and the presence of oxidizing elements, chelating compounds or ions (Syila, 1975). Surface oxidation of copper produces copper (I) oxide or hydroxide (World Health Organization, 2004). Often, copper(I) is oxidized to copper (II) that is mobile in the environment and can become toxic (Cornelis, et al., 2005). However if copper (I) forms complexes with abundant ammonium or chloride ions, it may to some extent remain stable in aqueous solution. Copper is less bioavailable at pH above 7, due to the formation of carbonates and oxides (Cornelis, et al., 2005). Dean, et al., (2005) found that in highway runoff the two main species of dissolved copper were Cu-DOM (dissolved organic matter) and copper carbonate (CuHCO3+ and CuCO3(aq)).

Copper is moderately soluble in water, and binds easily to clay and organic matter. Copper is strongly adsorbed specially at high pH (Pare, et al., 2012). Therefore, it is expected to have higher concentrations in the sediments and in particulates rather than in the dissolved fraction. In fact, according to the geochemical baseline database (FOREGS) of the Geochemical Atlas of Europe, the median concentration of dissolved copper in surface water in throughout Europe, the fraction that passes through a filter of 0.45 µm size, is almost 20 times lower than the concentration of copper found in sediments with a size fraction minor than 0.15 mm. Moreover, in sediments, copper presents a good correlation (r>0.4) with Fe, V, Co, Ni, Zn and a weak correlation with As, Sb, Pb and Cr (Salminen, et al., 2005). The most toxic form of copper is the cupric ion (Cu+2) when it is soluble (Solomon, 2009). The speciation of copper (II) in aquatic systems must consider inorganic and organic complexation, and adsorption and precipitation processes. Copper will form complex with anions like sulfates, phosphates, hydroxides, nitrates and carbonates and it can also precipitate with these if the solubility is exceeded (Cuppert, et al., 2006). Copper(II) will form soluble Cu hydroxides that dominate at pH > 7. If carbonates are present in the water, copper carbonates, especially CuCO3, will predominate at pH > 8 (Cornelis, et al., 2005). In the inorganic system, the amount of free copper(II) is reduced with an acidification of the water. For water with higher than natural pH, hydrolysis and precipitation reactions dominate the chemistry of copper(II). On the other hand, the presence of these organic compounds will strongly influence the speciation of copper, indeed organic ligands typically dominate copper speciation (Nason, et al., 2012; Bruland, et al., 2000). In most aquatic systems, free copper(II) concentrations will be reduced to very low values, due to the processes of hydrolysis, precipi-
tation, complexation and adsorption (Sylva, 1975). The total concentration of dissolved copper in water is composed by free copper(II) plus, inorganic and organic copper complexes (Nason, et al., 2012), and due to the high solubility of some copper minerals, waters exposed to those can have increased concentration of copper in solution (Cornelis, et al., 2005).

Regarding the ecological behavior, copper is bio concentrated in animals or plants; for this reason, copper concentrations are expected to be higher in alive beings that in the sediments. However, it is not biomagnified in food webs; this means that the concentrations found in predators are not higher than the one found in their preys (Solomon, 2009).

Biological functions and sensitivity to copper

Copper is an essential trace nutrient for humans, other mammals, fish and shellfish, and in general for all living organism (Durukan, et al., 2011). It is needed for some biological process as the formation of hemoglobin, pigment that transport oxygen in the blood, or in many electron transfer enzyme. For instance, an adult human needs around 1.2 mg/day. However, it has more toxic effects on aquatic species, with copper being used as a component of several algacides and herbicides (Palmer, 2014). It can have negative effects on survival, growth and reproduction rates as well as alterations in brain function, enzyme production and metabolism (US EPA, 2017).

Sensitivity to copper depends on each organism, for instance fish and crustaceans are 10 to 100 time more sensitive than mammals, whereas blue-green algae species can be even 1,000 time more sensitive than mammals. For this reason, copper is an exception to the rule that says that animals are more sensitive to metals than aquatic plants (U.S. Department of Health and HUman Services, 2004).

2.2. Modelling tool for water quality

When the behavior of a substance in the environment needs to be assessed, two main parts must be considered: first, the intrinsic characteristics of the substance, and second the characteristics of the medium where the substance will be present. Thus, a coupling between a hydrological model and a water quality model is needed (Arheim & Ölsson, 2003). The model developed in MIKE SHE is a deterministic, dynamic, physically based and distributed hydrological model that has been described and used in many previous hydrological studies (Kalantari, et al., 2014a; 2014b; 2015), namely in Portugal (Hävermark, 2016) and Kalantari, et al. (2017). For the water quality modeling there are several tools like SWAT, WASP, QUALs, and inside MIKE software pack there is a template called ECO Lab that can be coupled with MIKE 11 or MIKE SHE to tackle water quality process (Li & Gao, 2014).

2.2.1. MIKE 11

MIKE 11 is fully dynamic, one-dimensional (1D) modelling tool for rivers and channel systems that was updated and its name was changed to MIKE HYDRO River. The main applications of this software are flood analysis, dam break analysis, ecology and water quality assessments, sediment transports and optimization of reservoirs, and river structure operations, among others (DHI, 2016 b).
The core of this modeling tool is the Hydrodynamic module (HD) used as the base for flood forecasting, advection – dispersion, water quality and non-cohesive sediment transport modules. MIKE 11 is formed by several editors like network, cross section, boundary, parameter, ECO Lab, advection-dispersion, rainfall-runoff among others. The integration between all these modules is done by using the simulation editor. The basic Hydrodynamic module is shown in Figure 1 (DHI, 2016 c).

![MIKE 11 Simulation editor](image)

Figure 1 MIKE 11 Simulation editor.

MIKE 11 is based on three main assumptions: first, water is incompressible and homogenous; second, bottom slope is small; and third, the flow everywhere is parallel to the bottom (i.e. wave lengths are large compared with water depths) (Popescu, 2002).

The hydraulic variables considered in MIKE 11 are presented in Figure 4.

![Hydraulic Variables considered in MIKE 11](image)

Figure 2 Hydraulic Variables considered in MIKE 11 (Popescu, 2002).

Flow in an open channel is ruled by the Saint-Venant equations in one dimension, also called shallow water equations. There are two equations (1) the mass conservation and (2) the momentum conservation, whose parameters are shown in Figure 2 (Popescu, 2002).
\[ \frac{\partial Q}{\partial x} + \frac{\partial A}{\partial t} = q \]  
Equation 1

\[ \frac{\partial Q}{\partial t} + \frac{\partial (\alpha Q^2/A)}{\partial x} + gA \frac{\partial h}{\partial x} + \frac{gQ|Q|}{(C^2 AR)} = 0 \]  
Equation 2

Where the independent variables are space \((x)\) and time \((t)\), and the dependent variables are discharge \((Q)\) and water level \((h)\).

The Mike 11 model needs to be stable enough to perform the calculations during the whole simulation period, several stability criteria are used to express the stability of the model and are presented in the next section.

MIKE 11 stability criteria

Time step is a crucial aspect to be defined before the modelling process. MIKE 11 provides 7 criteria:

- |resid (BC)/BC| This is a measure for the largest error introduced at the boundaries. MIKE 11 interpolates the boundary values between \(t\) and \(t+\Delta t\), using linear interpolation. This coefficient is greater when the value estimated with the interpolation differs with the actual boundary value.

- |delQ| is a measure of the largest acceptable discharge change in any point of the grid, within a time step. This measurement helps to reduce the time step when big changes appear.

- |delQ/Q| is a measure of the largest acceptable relative discharge change in the grid, within a time step. This measurement helps to reduce the time step when big changes appear.

- |delh| is a measure of the largest acceptable water level change in the grid, within a time step. This measurement helps to reduce the time step when big changes appear.

- |delh/h| is a measure of the largest acceptable relative water level change in the grid, within a time step. This measurement helps to reduce the time step when big changes appear.

- |Courant (HD)| it specifies the maximal length, expressed in terms of grid cells, that information travels within a time step (Equation 3). HD courant number refers to the momentum equation and \(\Delta x\) is referred to the distance between two \(h\)-points. This number can be as high as 10 – 20.

\[ C_{HD} = \frac{(\nu + \sqrt{\phi} \Delta t)}{\Delta x} \]  
Equation 3

- |Courant (AD)| It specifies the maximal length expressed in terms of grid cells that the species are convected within a time step (Equation 4). AD courant number solver includes both \(h\) and \(Q\) points, for this reason \(\Delta x\) is referred to half of the distance between two \(h\)-points. This number must be normally less than 1 but the model can be stable even until courant numbers of 2.

\[ C_{AD} = \frac{\nu \Delta t}{\Delta x} < 2 \]  
Equation 4

This criterion allows the model to reduce the time step, when flow velocity increases and vice versa.
MIKE 11 Hydrodynamic (HD) module

The MIKE 11 HD module solves the equations for the conservation of continuity and momentum, i.e. the Saint Venant equations (DHI, 2016c). This solution is based on an implicit finite difference scheme that can solve the kinematic, diffusive, or dynamic equation. The water level and flow are calculated at each time step, where the mass equation is centered on the water level points (h-level) and the momentum equations are centered on the discharge points (Q-points). By default the equations are solved with 2 iterations, the first one starts from the results of the previous time-step, and the second uses the centered values from the first iteration (Fleeno & Jensen, 2003).

2.2.2. ECO Lab

ECO Lab is a numerical software, developed by DHI that allows modeling aquatic systems and processes like eutrophication, water quality, and heavy metal transport. It functions as a module in MIKE package and can be used in MIKE 11, MIKE SHE, MIKE 21, and MIKE 3. This ECO Lab module, which is coupled with the advection-dispersion modules, describes physical and chemical processes and its interactions with the ecosystem. In order to do this, ECO Lab uses processes, which based on constants and forcings, describe the change over time of the state variables. All these components must be included in the ECO Lab template, that is the file that contains the mathematical definitions of the ECO Lab model (DHI, 2016e). It is possible to create a new template, but also DHI provides several already defined templates as: heavy metals, different levels of water quality, oil spills, among others.

ECO Lab consists of coupled differential equations, one for each state variable. These equations summarize the processes involved in the specific variable. When a process is related with more than one state variable, the differential equations are said to be coupled (DHI, 2016f).

There are two types of processes in ECO Lab, transformation and settling. The main difference between both processes is that transformation does not depend on neighboring points and settling does. Settling is a process where a state variable is transported, thus it depends on information from neighboring points (DHI, 2016f).

During a simulation, the model system integrates one time step by simulating the transport of advective state variables based on hydrodynamics. Initial concentrations or updated AD concentrations, coefficients, constants and forcings are loaded in the ECO Lab object. Then, ECO Lab evaluates and integrates one time step, and returns updated concentration values, to the general flow model system that advances one time step (Figure 3) (DHI, 2016f).
ECO Lab heavy metal (HM) template

This template can be used to investigate heavy metal impacts on aquatic ecosystems and accumulation in sediments. It considers two phases, water phase and sediment one (10 upper cm), and also the different relations between them. In the water phase it takes into account the adsorption/desorption of metals from the suspended matter. In the sediment phase it includes the adsorption/desorption of metals from sediments to the pore water. Finally, the links between both phases include: sedimentation of the suspended matter, resuspension of settled materials, and diffusion exchanges between pore water and the water phase and vice versa. This template assumes that sediment characteristics as porosity, density of particles and pore water are constant over time (DHI, 2016 e). All the phases and processes included in this template are shown in Figure 4.

Sedimentation/resuspension of copper is part of the sedimentation/resuspension of suspended material, because the suspended matter that changes the phase brings attached the metal. However, dimensionally, both have different units, for copper is [g Cu] of copper and for suspended matter is [g SS], for this reason in Figure 4 they were placed in different boxes.
3. Study area

3.1. Location

The study was performed in Ribeira dos Covões catchment in the municipality of Coimbra, center part of Portugal (Figure 5), and has an area of 6.2 km².

3.2. Climate

The catchment presents a Mediterranean climate. The annual average temperature is 15° C and the rainfall is about 892 mm, taking as a source the precipitation series between 1941 and 2000. Regarding precipitation, two contrasting seasons can be defined, a hot and dry summer between June and August, and a winter with high pluviosity rate between November and March (Hävermark, 2016).
3.3. Land use

From the 70’s, an urbanization process has been present in the catchment. The increment in urban areas has been in decrement of agricultural land principally that has changed from almost 25% of the area in early 70’s to less than 5% in 2012 (Hävermark, 2016). The land use changes between 1958 and 2012 are present in Figure 6.

![Figure 6 Land use changes from 1952 until 2012 in the Ribeira dos Covões catchment (Hävermark, 2016).](image)

3.3.1. Roads and Highways in the catchment

The area consisting by all roads in the catchment is 0.38 km², where medium traffic is the biggest one with 42%, followed by low traffic with 23%, high traffic 14% and IC2 highway 18% respectively. Figure 7 presents the roads inside the catchment, and its classification.

![Figure 7 Roads in Ribeira dos Covões Catchment.](image)
Road runoff can be a source of one or some of the contaminants like deicing salt, oil or other spills, and metals dispersed in soil and sediment. It depends on the characteristics of urban/suburban areas nearby, the amount of cars, and road characteristics itself. The pollution source is created when chemicals, automotive oils, debris from breaks or other parts of the car are washed off during a rain event and carried as runoff to rivers, streams, lakes or bays (Wilson, 1999; Prestes, et al., 2006).

There are several factors that can affect the fate and amount of pollutants coming from road. Some of the “road” factors are traffic volume, road design, surrounding land use, and spills (Wilson, 1999; Irish, et al., 1998). Higher pollutant amount is expected for roads with higher traffic volume, however wind or turbulence caused by cars can act as attenuating factors (U. S. Department of Transportation, Federal Highway Administration in cooperation with Office of Environment and Planning, 1998). In general, pollutant load in road runoff is related to causal variables during the rainstorm event, the antecedent dry days, and the characteristics of previous rainstorm event (Irish, et al., 1998). At the beginning of the storm event, pollutant concentration is higher, this phenomena is called “first flush”, concentration that tends to be reduced with time (Prestes, et al., 2006). Moreover, the process responsible for the generation, accumulation, and washoff depends on each rainfall constituent (Irish, et al., 1998). Wu, et al. (1998) found that for some pollutants, loads were associated with automobile traffic, and just total suspended solids load had strong positive correlation with traffic volume during the storm. Kayhanian, et al., (2007) found that maximum rain intensity and the impervious fraction in the surrounding areas of the road do not have big influence on the concentration of parameters as metals, dissolved minerals or organic carbon (TOC); and that particulate matter is stronger related with dissolved minerals or TOC, rather than with metals.

3.4. Information sources for modelling

HYDROLOGICAL MODEL – The hydrological model developed by Hävermark (2016) and Kalantari et al. (2017) was the starting point. This model contains information about land use, topography of the area, climatic variables like precipitation, air temperature and evapotranspiration, soil profiles, geological layers, roughness characteristics of the catchment, and a river network for MIKE 11.

Copper

Two data sources were available. First, information about the characteristics of road runoff, with data about pH, solids in the water, and metals concentrations (Ferreira, et al., 2016 a). Second, water quality data in the river regarding chemical oxygen demand (COD), nitrate, ammonium, phosphorus, copper and zinc concentrations, and sediments characteristics taken from a previous study performed in this catchment (Ferreira, et al., 2016b).

Both runoff and surface water quality data were collected at different time periods. Water quality data was collected between October 2011 and March 2013, during 10 storm events. On the other hand, road runoff characterization data was collected between May and December 2013, over 7 storms. In Figure 8, data points locations for both studies are presented.

Road runoff data will be used as the “source” of copper, and water quality data will be used to compare with the results obtained in the model to calibrate and validate them. Considering the kind of data available, road runoff will be considered as the only copper sources
by two factors: lack of information to quantify different sources and it will provide information about how big is the importance of copper coming from this sources compared to total copper present in the catchment.

Figure 8 Location of water quality and surface runoff measurements.

Copper is moderately soluble in water, and binds easily to sediments and organic matter. Copper is strongly adsorbed to clay materials depending on the pH. Therefore, it is expected to have higher concentrations of copper in the sediments rather than in the dissolved fraction. In fact, according to the geochemical baseline database (FOREGS) of the Geochemical Atlas of Europe, the median concentration of dissolved copper in Europe, fraction that passes through a filter of 0.45 µm size, is almost 20 times lower than the concentration of copper found in sediments with a size fraction minor than 0.15 mm. Moreover, in sediments, copper presents a good correlation (>0.4) with Fe, V, Co, Ni, Zn and a weak correlation with As, Sb, Pb and Cr (Association of the Geological Surveys of The European Union/the Geological Survey of Finland., 2006). The most toxic form of copper is the cupric ion (Cu^{+2}) when it is soluble (Solomon, 2009). The speciation of copper (II) in aquatic systems must consider inorganic and organic complexation, and adsorption and precipitation processes. Copper will form complex with anions like sulfates, phosphates, hydroxides, nitrates and carbonates that can precipitate if the solubility is exceeded (Cuppett, Duncan, & Dietrich, 2006). Copper II will form soluble Cu hydroxides that dominate a pH > 7. If carbonates are present in the water, copper carbonates, especially CuCO3, will predominate at pH > 8 (Cornelis, Caruso, Crews, & Heumann, 2005). In the inorganic system, the amount of free copper (II) is reduced with an acidification of the water. For water with a natural pH expected, hydrolysis and precipitation reactions dominate the chemistry of copper (II). On the other hand, the presence of these organic compounds will vary the speciation of copper, indeed organic ligands typically dominate copper speciation (Nason, Sprick, & Bloomquist, 2012; Bruland, Rue, Donat, Skrabal, & Moffett, 2000). In most aquatic systems, free copper (II) concentrations will be reduced to very low values, due to the processes of hydrolysis, precipitation, complexation and adsorption (Sylva, 1975). Total concentration of dissolved copper in water is composed by free Copper II, and inorganic and organic copper complexes (Nason,
Sprick, & Bloomquist, 2012), and due to the high solubility of some copper minerals, waters exposed to those can have increased concentration of copper in solution (Cornelis, Caruso, Crews, & Heumann, 2005).

Regarding the ecological behavior, copper is bio concentrated in animals or plants; for this reason, copper concentrations are expected to be higher in alive beings that in the sediments. However, it is not bio-magnified in food webs; this means that the concentrations found in predators are not higher than the one found in their preys (Solomon, 2009).

Biological functions and copper sensitivity

Copper is an essential trace nutrient for humans, other mammals, fish and shellfish, and in general for all living organism (Durukan, Şahin, Şatroğlu, & Bektaş, 2011). It is needed for some biological process as the formation of hemoglobin, pigment that transport oxygen in the blood, or in many electron transfer enzyme. For instance, an adult human needs around 1.2 mg/day. However, it has more toxic effects on aquatic species, with copper being used as a component of several algaeicides and herbicides (Palmer, 2014). It can have negative effects on survival, growth and reproduction rates as well as alterations in brain function, enzyme production and metabolism (US EPA, 2017).

Sensitivity to copper depends on each organism, for instance fish and crustaceans are 10 to 100 time more sensitive than mammals, whereas blue-green algae species can be even 1.000 time more sensitive than mammals. For this reason, copper is an exception to the rule that says that animals are more sensitive to metals than aquatic plants (U.S. Department of Health and HUman Services, 2004).

4. Methodology

4.1. Hydrological Modelling

The stability of the hydrological model developed by Hävermark (2016) was needed to be improved, for this reason all the changes done were connected to the hydraulic part of the modelling (MIKE 11). None of the MIKE SHE coefficients and characteristics such as land use, detention storage, geological layers among etc, were modified.

In MIKE 11, considering that the courant number stability criterion \( Cr_{AD} = \frac{v \cdot \Delta t}{\Delta x} < 2 \) needs to be fulfilled and that for ecological simulation time step needed is very short, less than 1 minute (\( \Delta t \)). In order to reduce \( Cr_{AD} \) it is possible to increase \( \Delta x \) or reduce the velocity \( v \) of the flow. To increase \( \Delta x \) some cross sections were eliminated; and to reduce \( v \), river slope was modified in some parts. Furthermore, some river branches were extended and one more was included.

Another component that needed to be changed was the boundary file (.bnd11). Boundaries for the hydrodynamic modelling (HD) kept the same, and boundaries for the (AD) modelling were defined. Moreover, copper sources had also to be included. Four points were used as point pollution sources. In each point, all the ECO Lab template variables must be specified.

Because the road runoff characterization measurements (sources) and water quality measurements were taken at different time slots (Fig. 8), it was assumed that sources “behavior” was constant over time. In this way, it was possible to shift sources data to the modelling time period, to have “sources” and water quality measurements in the same time
period, as it is shown in figure 9. The modelling period was between September 15, 2011 and March 29, 2013

![Figure 9 Time periods for data used during the modelling.](image)

Four efficiency criteria coefficients were obtained, RMSE, relative error, Nash-Sutcliffe efficiency and coefficient of determination $r^2$ (Kraus, et al., 2005) to see the quality of the hydrological modelling process.

### 4.1.1. Water quality measurements

Water quality variation was analyzed in four different places across the streams inside the Ribeira dos Covões catchment between October 2011 and March 2013 (see water quality points in Fig. 7). Three to 15 samples were collected manually at each site during 10 storm events, covering the rising limb, peak and falling limb of the storm events. These storm events were at the end of the dry period in summer, and during the rainy period within each season, to cover seasonal variation. Some of these storm events lasted more than one day, and the samples were taken without a regular time interval between each other. Variables measured and analysed in the streams were pH, chemical oxygen demand, kjedahl nitrogen, ammonium, nitrate, total dissolved phosphorus and heavy metals Cu and Zn (Ferreira C., Walsh, Costa, Coelho, & Ferreira, 2016b).

Considering the location of the sources and the water quality measuring points, uniquely two water quality points could be used ESAC and PB, due to the fact the other two point were upstream the sources.

### 4.1.2. Sources of copper - Road runoff

The sampling was performed with an irregular time interval, during the four seasons, including 7 storm events. In each site, three samples were collected with a sampling device that allowed to have, (1) a 5 liters first sample at the beginning of the rain event, when this was full a second sample of (2) 35 l was taken, and later finally a (3) 70 l sample. Therefore three concentrations for each parameter and for each rain event were available. Sampling points were chosen to analyze different traffic loads: IC2 is located in a highway with high traffic load (~26,000 cars/day), located NE of the catchment; P5 and P6 are roads with medium vehicular traffic (5,700 and 850 cars/day) located in the middle of the catchment; and P4 is a road with low traffic (45 cars/day) located in the upper part of the catchment. Variables measured and analysed were pH, conductivity, turbidity, solids: total, volatile, suspended, and volatile suspended, and heavy metals: cadmium, copper, lead and zinc (Ferreira, et al., 2016a).

Model requires that all data have the same time step, as the variables used for the hydrological model had daily values, then daily values of copper concentrations for the sources were also needed.

The heavy metal template used includes 6 state variables, 3 in the water phase that are transported with the current - dissolved copper (SCu), adsorbed copper (XCu) and mass of suspended matter (XSS); and 3 in the sediment phase that are not transported - adsorbed cop-
Transported variables

Daily values series for each variable for the whole simulation period was needed. For this, it was assumed as these variables are transported with the storm flow they will have a constant value for days without rain and an increment for rainy days. The concentration increments were determined based on two factors: i) rainfall amount and ii) number of antecedent dry days. These two main factors were considered based on literature review (Irish, et al., 1998; Kayhanian, et al., 2007; Wilson, 1999), and previously shown in the antecedent section about road runoff pollution.

In the road runoff, graphical linear relationships between flow-weighted measured concentrations and rainfall were obtained (C vs Rainfall) for the three variables in each point. Flow weighted measured concentrations were obtained according to equation 5, and results of the linear relationships coefficients (R²) between rainfall and the variables are presented in Table 1 and Figure 10.

$$C_{Pn} = \frac{(C_{Pn-5L} \times 5L) + (C_{Pn-35L} \times 35L) + (C_{Pn-70L} \times 70L)}{110L}$$

Equation 3

![Figure 10 Linear relationships between dissolved copper concentration and rainfall.](image)

**Table 1** linear relationship coefficients (R²) between rainfall and transported variables.

<table>
<thead>
<tr>
<th>Variable</th>
<th>R²</th>
<th>Dissolved copper</th>
<th>Suspended matter</th>
<th>Total copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC2</td>
<td>0.265</td>
<td>0.563</td>
<td>0.544</td>
<td></td>
</tr>
<tr>
<td>POINT 4</td>
<td>0.034</td>
<td>0.785</td>
<td>0.852</td>
<td></td>
</tr>
<tr>
<td>POINT 5</td>
<td>0.036</td>
<td>0.436</td>
<td>0.384</td>
<td></td>
</tr>
<tr>
<td>POINT 6</td>
<td>0.791</td>
<td>0.632</td>
<td>0.056</td>
<td></td>
</tr>
</tbody>
</table>

When the R² coefficient was higher or equal to 0.6 the linear relation between rainfall and the variable (equation 6) was used to define the insource copper concentration [C].

Variable [C] = [C] from rainfall + [C] from dry days

Equation 6
The concentration of the variable under analysis is equal to a concentration derived from rainfall intensity and the concentration derived from the number of previous dry days.

On the other hand, when the R2 coefficient was lower than 0.6 the mean value of the variable and two factors were used (equation 7). This equation gives proportionality between the amount of rainfall and the number of dry days with the concentration \([C]\).

\[
\text{Variable } [C] = (\text{Average Cu } [C]) \times (1+\#\text{Dry days factor} + \text{Rainfall Factor})
\]

Equation 7

The concentration of the variable under analysis is equal to the average copper concentration in each point, times 1 plus two factors one from rainfall and one from number of previous dry days. The factors were obtained empirically, to fulfill the condition that the average value for the whole serie is the same than the average value obtained in the samples, for each point.

Concentration derived from antecedent dry days was included in both equation based on the number of days and a weighting factor.

Considering this approach, the concentration of dissolved copper in the insource point 1 (IC2) is shown in Figure 11. The same criteria were used to define concentrations for the rest of transported variables in the four insource points.

![Figure 11 Source concentration of dissolved copper in P1(IC2).](image)

### Not transported variables

For the variables, adsorbed copper in sediments (XCuS), dissolved copper in pore water (SCuS) and mass of sediments (Xsed), a constant value over time was used. Values were obtained differently for each variable:

- **Adsorbed copper on sediments XCuS:** Copper values from Ferreira, et al., (2016b) were used as references for the concentration of adsorbed copper in sediments. Two main assumptions were done; first, sediments had a proportion fraction of 70% of 2 mm material, 25% of 125 um, and 5% of 63 um; second, the thickness of sediments was 10 cm.

- **Dissolved copper in pore water SCuS:** A value of 0.0368 was used for the dissolved copper concentration based on the av-
verage of dissolved copper found in the river according to Fer-

- Mass of sediments: the same two assumptions of the adsorbed
copper were used for the mass of sediments. Furthermore, it
was assumed that dry densities for different fractions were:
1300 kg/m³ for 63 um, 1400 kg/m³ for 125 um, and 1900
kg/m³ for 2 mm (Verstraeten & Poesen, 2001).

A resume table with the pollution sources for the variables is present-
ed in Table 2.

**Table 2 Pollution sources for the non transported variables used during the mod-
elling.**

<table>
<thead>
<tr>
<th>POINTS</th>
<th>( S_{CuS} ) [g/m²]</th>
<th>( X_{CuS} ) [g/m²]</th>
<th>( X_{Sed} ) [g/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC2</td>
<td>0.047</td>
<td>1.08</td>
<td>153</td>
</tr>
<tr>
<td>P4</td>
<td>1.150</td>
<td>2.25</td>
<td>153</td>
</tr>
<tr>
<td>P5</td>
<td>0.096</td>
<td>2.57</td>
<td>150</td>
</tr>
<tr>
<td>P6</td>
<td>0.096</td>
<td>4.77</td>
<td>150</td>
</tr>
</tbody>
</table>

Once the sources concentrations were obtained, two different analyses
were performed, one with punctual sources and another with distrib-
uted sources along some parts of the river.

In the punctual sources analysis, the four sites stablished for metal
pollution (Figure 8) were used. On the other hand, for the distributed
sources the catchment was subdivided in subcatchments according to
the tributaries, and inside each subcatchment the area occupied by
different roads was considered. The total concentration of copper was
obtained as a weighted average of the concentrations used for punctu-
al sources, according to the proportion of each road inside each sub-
catchment. Then, this concentration was distributed along the last
quarter of each tributary. It was distributed just in the last quarter of
each tributary considering that not all the runoff that carries copper
goes directly to the river, instead it can be retained or travel in the
subsurface runoff, and reach the tributary downstream.

**4.1.3. Time Steps used**

MIKE SHE model used an initial time step of 1 hour, with maximum
alloweds time steps of 3 hours for the three compartments, overland
flow, unsaturated and saturated zone. On the other hand, for MIKE11
a 30 seconds time step was used during the modelling, this value was
the higher possible without having instability errors regarding advec-
tion dispersion (AD) courant number; and the results were saved each
24 hours, to have daily concentrations of copper over time.

**4.1.4. Boundary Conditions**

Two different kind of boundary conditions had to be included in the
model, boundaries for the hydrodynamic modelling (HD) and
boundaries for the Adversion-Dispersion (AD) ECO Lab modelling.
HD and AD boundaries were 8 in total, 7 “open-inflow” boundaries at the beginning of the river branches with zero values for the discharge and for the ECO Lab variables, and one “open-water level” boundary at the end of the river with a constant water level value of 33 m, that is the elevation of the bottom of the river, for the HD. And non-zero values for the ECO Lab variables for the AD. These ECO Lab AD boundaries were obtained from the water quality data, and the values used were: 0.05 mg/l dissolved copper, 0.1 mg/l adsorbed copper, 0.1 g/m² dissolved copper in pore water, 6 g/m² adsorbed copper in sediments, 150 mg/l suspended solids, and 153 g/m² mass of sediments.

Moreover, metal sources have to be defined also in the boundary file. Four “point source” boundaries were located in the sites showed in Figure 8. For each source, values for the variables must be defined. Here, the insource time series previously obtained, and showed in the section 4.1.2, were used. In the ECO Lab template, initial concentrations of the six variables specified for the model were assumed to be 0, therefore the non presence of previous copper pollution in the river was stated for the model.

An image of the boundary file used for the model is presented in Figure 12.

```
Boundary Description | Boundary Type | Branch Name | Chaining | Chaining | Gate ID | Boundary ID
---------------------|---------------|-------------|----------|----------|---------|-------------
1 Open Inflow | Ephemeral2 | 0 | 0 | 0 | 0 |
2 Open Inflow | Ephemeral2 | 0 | 0 | 0 | 0 |
3 Open Inflow | Ephemeral2 | 0 | 0 | 0 | 0 |
4 Open Inflow | Perennial | 0 | 0 | 0 | 0 |
5 Open Inflow | Ephemeral3 | 0 | 0 | 0 | 0 |
6 Open Inflow | Ephemeral3 | 0 | 0 | 0 | 0 |
7 Open Inflow | Ephemeral3 | 0 | 0 | 0 | 0 |
8 Open Water Level | Perennial | 1084.243989547 | 0 | 0 | 0 |
9 Point Source Inflow | Ephemeral | 1017.224910218 | 1029 | HNL | HNL |
10 Point Source Inflow | Ephemeral | 96.8955299464 | 109 | HNL | HNL |
11 Point Source Inflow | Ephemeral | 1645.325884873 | 1379 | HNL | HNL |
12 Point Source Inflow | Ephemeral | 1645.325884873 | 1459 | HNL | HNL |
```

Figure 12 Boundary file (.bnd11) used for the modeling.

### 4.1.5. ECO Lab coefficients and constants

Heavy metal template includes 16 constants that are presented in Figure 13.

The 5 first constants, organic-carbon partitioning coefficient (Koc), desorption rates (kw and ks), and organic carbon fractions (foc) are related each other according to:
Organic carbon partitioning coefficient (KOC) is the key concept in the Heavy metal modelling, and it depends on the metal, temperature, pH, and salinity. In order to estimate KOC, it was needed to have the partitioning coefficient (kd) and the fraction of organic carbon (foc).

According to a research made by the US Environmental Protection Agency (2005), it was found that the logarithm of the partitioning coefficient between suspended matter and water (log $k_d$) had a variation between 3.1 and 6.1, based on 70 sources; and the partitioning coefficient between sediment and pore water (log $k_{ds}$) had a bigger range between 0.7 and 6.2, based on 12 sources. Median values were used for both cases. However, it must be said that $k_d$ and $k_{ds}$ can vary greatly, therefore this was just a rough estimation that needed to be done.

$$K_d = f_{OC} \times K_{OC}$$

$K_d$: partitioning coefficient between particulate matter and water; $f_{OC}$: fraction of organic carbon; $K_{OC}$: organic carbon partitioning coefficient

$$K_d = \frac{k_a}{k_w}$$

$K_d$: partitioning coefficient between particulate matter and water; $k_a$: adsorption rate; $k_w$: desorption rate in water

$$K_{ds} = \frac{k_a}{k_s}$$

$K_{ds}$: partitioning coefficient between sediments and pore water; $k_a$: adsorption rate; $k_s$: desorption rate in sediment

Suspended matter-water

Log $K_d = 4.7$ (median value)

Sediments-pore water

Log $K_{ds} = 4.2$ (median value)

Then $K_d = 50118$ and $K_{ds} = 15848$

Fraction of organic carbon in suspended matter was got from the road runoff characterization data according to equation 8 presented below, the average values for the suspended solids and total volatile suspended solids were used.

$$f_{OC} = \frac{\text{Avrg (total suspended solids)}}{\text{Avrg (total volatile suspended solids)}}$$

Equation 4

$$f_{OC} = \frac{120 \frac{mg}{l}}{201.2 \frac{mg}{l}} = 0.6$$
With \( K_d \) and \( \text{foc} \), \( K_{oc} \) was estimated.

\[
K_{oc} = \frac{K_d}{\text{foc}} = \frac{50118}{0.6} = 83531
\]

Also, with \( k_d \) and \( k_{ds} \) known it was possible to obtain desorption rates in water (\( k_w \)) and sediments (\( k_s \)). Assuming that adsorption was higher in the suspended matter than in the sediments. Therefore, desorption rate in water was assumed to be slightly lower than in sediments.

Then \( K_w = 0.1 \quad \text{and} \quad K_s = 0.12 \)

Thickness of water film, ratio between thickness of diffusion layer in sediment and sediment thickness, and factor due to bioturbation kept the original values specified in the template, because there was not information related to these values that could be used.

Density of dry sediments; considering that the sediment information available shown that there were three fractions (63 um, 125 um and 2 mm) with different proportions, the weighted average density was obtained according to equation 9. Density values were taken from Verstraeten & Poesen (2001).

\[
Density = 0.05 \times \frac{K_g}{m^2} + 0.25 \times 1400 \frac{K_g}{m^2} + 0.7 \times 1900 \frac{K_g}{m^2} \quad \text{Equation 5}
\]

\[
Density = 1750
\]

Table 3 A resume with all the constants and coefficients used for the model.

<table>
<thead>
<tr>
<th>CONSTANTS</th>
<th>AD RIVER END BOUNDARY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic-carbon partitioning coefficient (( K_{oc} ))</td>
<td>83531 l/kg</td>
</tr>
<tr>
<td>Desorption rate in water</td>
<td>0.1 day(^{-1})</td>
</tr>
<tr>
<td>Desorption rate in sediment</td>
<td>0.12 day(^{-1})</td>
</tr>
<tr>
<td>Fraction of organic carbon in suspended solids SS (( \text{foc} ))</td>
<td>0.6</td>
</tr>
<tr>
<td>Fraction of organic carbon in sediment (( \text{foc} ))</td>
<td>0.7</td>
</tr>
<tr>
<td>Thickness of water film</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>Ratio between thickness of diffusion layer in sediment and sediment thickness</td>
<td>0.2</td>
</tr>
<tr>
<td>Factor for diffusion due to bioturbation etc.</td>
<td>1</td>
</tr>
<tr>
<td>Mole weight of Heavy metal</td>
<td>64 g/mol</td>
</tr>
<tr>
<td>ECO Lab time step (FIXED)</td>
<td>30 s</td>
</tr>
<tr>
<td>Density of dry sediment</td>
<td>750 kg/m(^3)</td>
</tr>
<tr>
<td>Porosity of sediment</td>
<td>0.3</td>
</tr>
<tr>
<td>Settling velocity of SS</td>
<td>0.1 m/day</td>
</tr>
<tr>
<td>Resuspension rate</td>
<td>1 g/m(^2)/day</td>
</tr>
<tr>
<td>Particle production rate</td>
<td>1 g/m(^2)/day</td>
</tr>
<tr>
<td>Critical current velocity for sediment resuspension</td>
<td>1</td>
</tr>
</tbody>
</table>
Porosity of the sediment, a value of 0.3 was used taken from Yu, Kangboj, Wang, & Cheng (2015).

Settling velocity of the suspended solids was defined as 0.1 m/day. This assumption was made considering that this is an small river with an small sediment layer.

Resuspension and particle production rate kept the original values found in the Heavy metal template, “one” for both cases.

5. Results and discussion

5.1. Hydrological results

The hydrological results obtained with the model were analyzed by comparing discharge values calculated with the ones measured. The results for the efficiency criteria used are shown in table 4; moreover, in Figure 14 the graph of discharge modelled and measured, and rainfall is presented. As it was previously stated, the hydrological model was develop by Hävermark (2016) and in this study the model was uniquely improved regarding discharge simulation efficiency and stability.

|                  | $\sum(|obs-mod|)$ | RMSE  | Relative error (%) | Nash-Sutcliffe E | Coefficient $r^2$ |
|------------------|-------------------|-------|--------------------|------------------|-------------------|
| Hävermark Results| -                 | -     | -                  | 0.59 Calib.      | 0.64 Calib.       |
|                  |                   |       |                    | 0.58 Valid.      | 0.62 Valid.       |
| Actual Model     | 9.58              | 0.027 | 49.95              | 0.77             | 0.796             |
| Results          |                   |       | Eq: $y = 0.7405x +$0.0015 |                   |                   |

Figure 14 Discharge modelled and measured, and rainfall.
5.2. Copper model results

The model generates copper concentrations along the river. In each grid point, concentrations of all the variables were generated.

5.2.1. Considering punctual sources

Concentrations are highest in the grid points where the incoming sources are located. Downstream, after this concentration peak, copper concentrations tend to be reduced due to dilution and adsorption processes. Concentrations in Ephemeral 4 for instance (Figure 15), where two punctual sources were located, copper concentration is raised after the first punctual sources (HMS6) and it shows highest peak values in the location of the second punctual source (HMS5). Downstream, this peaks tend to be reduced but following the same pattern. Concentrations along Ephemeral 4 that show what was previously stated are presented in Figure 15, as well as the location of the copper insources. Moreover, comparing copper behavior with rainfall, the general pattern that can be stated for this section of the river is that copper concentrations raise with higher rainfall and vice versa. Considering that distances travelled by copper are not long, between insource point and points where results are presented, copper concentration in the river is mostly driven by the road wash off process.

On the other hand, near catchment outlet, model generates highest concentrations when the river discharge is zero, and lowest concentration with high discharges; probably because it considers dilution and processes like resuspension, adsorption, sedimentation, etc. Near the catchment outlet, concentration values generated by the model for zero-discharge periods corresponds to a value little lower than the AD boundary level defined at the end of the river (Perennial). In Figure 16, copper concentrations modelled in two different points in the river for the whole time period assuming punctual sources are...
Presented. Points chosen were, near the catchment outlet from now called Perennial-1, and in a copper insource location.

As it can be seen, just after the incoming source points, as it is shown in P1 in Figure 16, concentration reach values higher than 0.20 mg/l, values that are rapidly reduced downstream.

![Figure 16 Dissolved copper concentrations generated at the end of the river and in an incoming source point, considering point sources.](image)

5.2.2. **Considering distributed sources**

Distributed sources approach gives higher concentrations at the catchment outlet than in the upstream tributaries. Highest concentrations are generated when the discharge of the river is zero. Highest concentration values obtained with this approach is 0.043 mg/l, lower value compared with what happened with punctual sources, where concentrations reached more than 0.20 mg/l just after the incoming source. Figure 17 shows the concentration obtained with the model, in three points of the river Network.

![Figure 17 Dissolved copper concentrations generated at the end of the river and in two different points of the river network, considering distributed sources.](image)
5.2.3. Comparison between punctual and distributed sources modelling

With distributed sources, time-averaged values during the whole period of time is higher specially at the end of Ephemeral 7 and in Perennial-1. On the contrary, when punctual sources are analyzed, higher concentrations are presented in the end of Ephemeral 4 and Ephemeral 7, and in the end of the river, locations and copper concentrations are presented in Figure 18.

Comparing time-averaged model results with fresh water quality criteria according to U.S. EPA (2004), that defines a criterion maximum concentration (CMC) of 0.013 mg/l, and a criterion continuous concentration (CCC) of 0.009 mg/l, or with the Portuguese Legislation for minimum water quality criteria that defines 0.10 mg/l, it can be seen that when punctual sources are used for the analysis, a longer extension of river presents a time-averaged concentration higher than CCC, more than double length compared with distributed sources analysis, specially due to high copper concentration presented in the Ephemeral 4 branch (Figure 19). Nevertheless, according to the model, percentage of river extension that presents concentrations above CCC is 3.8% for distributed sources and 7.6% for punctual sources, which are relative low values. On the other hand, modelling results compared with the Portuguese Legislation for minimum surface water quality that establishes a maximum of 0.1 mg Cu/l (Ministerio Do Ambiente Portugal, 1998), shows that length of river above that limit is lower than 5% of the total river extension.
5.2.4. Comparing model results with measured data

Near the catchment outlet and in an upstream point in Ephemeral 5, some water quality measurements were performed by Ferreira, et al. (2016 b). Then, dissolved copper results obtained from the model were compared with the measured concentrations adapted to daily values. Figure 20 shows both concentrations in Perennial-1 of the river, as well as the fresh water quality criteria for copper according to the U.S. EPA (2004). As it can be seen, almost all the measurements done, as well as the results in Perennial-1 are above CCC and CMC for the majority of the time. As a specification about Figure 20, concentration values when there was not discharge were removed, considering that it is not possible to have dissolved copper in the water phase when this phase is not present at all. The model shows bad results compared with measured values, with negatives Nash-Sutcliffe values and $R^2$ coefficients lower than 0.01. In general, copper values modelled were smaller than the ones measured, specially for days with high discharge ($q > 0.25 \text{ m}^3/\text{s}$), which shows that other copper sources not considered such as sewage leaks, atmospheric deposition, or other phenomena like mobilization during rain event due to an increment in the ground water level, can have more influence than roads in the amount of copper present in the river.

Regarding the upstream point in Ephemeral 5, the representation of those results is difficult considering the big difference between measured and modelled values that are near 10 times lower. Measured values were punctual copper concentration at different times of the storm events. From this data, daily copper concentrations were obtained by using the flow weighted average of all the measurements done the same day.
AD boundary values defined at the outlet of the catchment have bigger influence on the concentrations simulated in the near point (Perennial 3167.05), compared with Koc, and resuspension rate. In the rest of the river, resuspension rates have bigger influence than Koc. Analysis for two different points in the river is presented in table 5, where the percentage of variation of the time-averaged copper concentration compared with original model results is shown.

Table 5 Variation in the time-averaged concentration in Perennial 3167.05 and in Ephemeral 4-1832.

<table>
<thead>
<tr>
<th>Copper Concentration</th>
<th>Original value</th>
<th>Higher Koc</th>
<th>Higher resuspension rate</th>
<th>Higher AD Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perennial 1</td>
<td>[mg/l] 0.02791</td>
<td>0.0277</td>
<td>0.0269</td>
<td>0.035</td>
</tr>
<tr>
<td>[% variation]</td>
<td>-</td>
<td>0.75</td>
<td>3.62</td>
<td>25.40</td>
</tr>
<tr>
<td>E-4-1832</td>
<td>[mg/l] 0.000235</td>
<td>0.00234</td>
<td>0.00236</td>
<td>0.00235</td>
</tr>
<tr>
<td>[% variation]</td>
<td>-</td>
<td>1.173</td>
<td>0.742</td>
<td>0</td>
</tr>
</tbody>
</table>

5.3. Discussion

5.3.1. Model Performance

Regarding hydrological results, the model has some problems to represent very low discharges, in this case, simulated discharge is “zero” when the measured ones are lower than 1.5 l/s at the end of the catchment, therefore the model is not so sensitive to simulate this. The coefficient of determination r² can be between 0 and 1, with 0.78 for this case; with this coefficient only the dispersion is quantified, thus if the model over/underpredicts sistematically values, it can give also good r² values; for this reason, the coefficients α and β from the linear
regression equation (Table 4) must be analyzed also (Kraus, et al., 2005). The intercept $\alpha$ should be close to zero, 0.0015 in this case; and gradient $b$ should be close to 1, 0.74 in this case, which shows that even though the model can still be improved, it gives good results. Regarding Nash-Sutcliffe efficiency, when closer to one the model gives better fit, in this case the value was 0.77. However, due to the fact that this coefficient uses squared values, it gives over estimation of the model performance with peak flows and under estimation during low flow conditions. Compared with the previous study (Hävermark, 2016) the model gives better results as it could be observed in the coefficients presented in Table 4. The improvement of the model was obtained by including some extra river branches (a more complete stream network), relocating some cross sections, and increasing river slope precision to gain more stability considering that the time step needed to be used for copper modelling (30 seconds) was much smaller than for previous work (5 minutes).

Copper sources inside the catchment are an important factor to consider when analyse the results. In the model road runoff was considered as the only source of copper within the catchment. Nevertheless, there are other possible sources as architectural copper (Moran, 2004), corrosion and leaching from house products (ICON, 2001), or atmospheric deposition. In fact, regarding atmospheric deposition, copper deposition is associated with small particle sizes, less than 10 µm and is directly and positive correlated with traffic congestions and inverse correlated with the average daily traffic (Gunawardena, et al., 2013). Moreover, Wu et al., (1998) found that atmospheric deposition can represent almost 20% of TSS in a catchment in North Carolina, and for metals this percentage can vary between 10 and 50%, that shows that these source is not insignificant.

Another problem was the complexity of the processes that define copper concentration in road runoff, because the analysis to understand it and to define the “sources” was only done considering two main factors number of previous dry days and rainfall intensity, however as it was previously shown in Table 1 correlations are very low. Therefore, some process and circumstances were not correctly analysed or were not taken into account due to a lack of data for this specific catchment. Having a better knowledge, and understanding in a better way how copper is carried by road runoff could help to improve copper sources coming in road runoff. Indeed according to Irish, et al.. (1998), oil load coming with rainfall or suspended solid load, depends on process that are specific for each constituent.

The organic carbon partitioning (Koc) has lower influence in the model results than changes in resuspension rate coefficient. Nevertheless, changes performed are not drastic neither for Koc nor for resuspension rates, as can be seen in Table 5. Considering the assumptions needed to obtain Koc, it is expected that the range of applicable Koc values will be big; because it is based on logarithmic values of the partitioning coefficients (kd), where small changes in the logarithmic can result in big Koc variations.
Regarding copper concentrations at the catchment outlet, boundary conditions influence drastically this copper concentrations due to its spatial proximity. The use of a constant boundary value for the whole period of time reduces the accuracy of the modelling process. This is because the model has a specified concentration defined by the AD boundary that need to be reached at the outlet of the catchment, thus a change in these values will modify also the concentrations simulated in the near upstream part of the catchment outlet (Table 5).

Comparing copper concentrations measured and model results, MIKE SHE, coupled with MIKE 11 and ECO Lab provide bad results specially on days with big discharge (q > 0.25 m³/s). This may be linked with different time-steps between copper data available and hydrological parameters that influence hydrological results. Whereas the model generates copper values analyzing the ecological behavior of the metal in the ecosystem and gives daily values based on precipitation and evapotranspiration data used in the hydrological part, copper measurements regard to individual samples, collected in different stages of several storm events, representing a more instantaneous behavior. In order to compare with model results, it was necessary to estimate daily copper concentration, based on weighted average of all the measurements. This generalization, despite that being necessary in order to compare the results, can face a big problem because uniquely with some measurements along the hydrograph, a daily value had to be obtained. Furthermore, the daily model results may include non rainy periods/storms.

At the end of the river and in ephemeral 5, model results do not fit with the concentration measurements. Specially during the days with high rainfall when the model gives low copper concentration. Nevertheless, in Perennial-1 model results and are inside a certain limit similar to the limits for the measured values (Figure 20). On the contrary, in ephemeral 5, model gives very low values compared with what was measured, specially in days with high rainfall. For this reason, it is possible that other copper source(s) is present, or it also can be possible that road runoff gets into the river in a downstream point that what was actually considered. Furthermore, considering the tendency of copper to be bounded to the organic matter, in catchments with shallow groundwater level, rainfall events play a key role in the mobilizing process of copper or other metals bounded to the organic matter (Tejshree, 2015).

On the other hand, considering that the guideline value for copper in drinking water is 2 mg/l (World Health Organization, 2008), this concentration is not exceeded in any modelling attempt not even in the insources point considering punctual sources, nor in the measurements done in the river. Finally regarding copper toxicity, this is not particularly toxic for humans, but for fish, the recommended limit values are between 0.04 and 0.112 mg/l depending on the hardness of water and the presence of dissolved organic carbon (Environmental Protection Agency of Ireland, 2001).

Another consideration that should be taken into account is that as it was previously stated, copper is mostly bounded to suspended matter.
or sediments expecting higher concentrations here rather than in the dissolved phase in water, for this reason and considering that some parts of the river are dried out in some parts of the year, sediments are more exposed to the wind erosion or other climatological factors, that can spread around the catchment sediments with copper bounded.

5.3.2. Model limitations and uncertainties

Some factors that can affect the quality of the model are: (1) the time difference between data available and date needed for the model, while one are very punctual and instantaneous; the other needs more constant values that can represent the general behavior; (2) generalizing constants for the whole catchment might carry some accuracy problems and raise the uncertainty of the model. The complexity of the model requires more data and information regarding sources and coefficients used for the modelling. This complexity, despite that can give better and more precise results than a simpler model, requires also better and more specific data and information. Specially, regarding the concentrations of non-transported variables like mass of sediments, and concentrations in sediment and pore water, those values were assumed constants for the whole river, but in reality it can vary spatially and temporally. This assumption, reduces the accuracy of the model and some of the parameters were only obtained from bibliographical sources due to the lack of direct information from the catchment.

Another model uncertainty is related to copper sources and copper present in the river before the modelling time. In this case it was assumed that no copper was present in the river when the simulation starts, and that copper sources are just related to road runoff. Some other sources of copper can be present in the catchment, but the uncertainty about its presence or not avoided to use it during the modelling.

In general, better model results can be expected with non ephemeral rivers, based on the fact that during no-discharge periods the model can not handle it correctly regarding dissolved copper, adsorbed copper and suspended sediments. In this case for instance, model generates highest dissolved copper concentrations when discharge is lowest or even zero. Considering that the basis of the model is that there are two phases under analysis, water and sediments, when the river is dried out, water phase is not present and this goes against the initial basis of the model. In deed Marrero (2013), simulated mercury pollution in a non ephemeral river obtaining relationships between discharges and mercury mass rates curves at several sites in a catchment in Florida.

5.3.3. Possible model improvements

For future work, some aspects should be considered to improve the model, namely related with the copper sources as well as with data for calibrating and validating the model. Regarding the sources, in this study some big generalizations were done about the presence of copper in road runoff. It would be necessary to include other possible copper sources, as runoffs from different surfaces like ceilings and not only roads.
Another option can be to assume different sources of copper for different urban developments, and roads can be included as one type of surface. In this way, sources could represent in a better way the real patterns. On the other hand, it would be necessary to improve substantially the measurements that the model will be compared with. It must be taken into account that model produces general ecological behavior of the metal in the environment, therefore the measurements must be done systematically along a period of time to have more general concentrations. As it was previously stated, the problem with actual measurements used to compare model results, was that samples were collected to catch an instantaneous phenomenon of runoff carrying copper previously deposited on roads, whereas other processes as sedimentation and resuspension could be relevant.

Regarding model specifications, an smaller grid can be used, however the time step must also be smaller, in order to maintain the courant number < 2 stability criterion. In this sense, it would be helpful to first develop a stable hydrological model with more precise precipitation data, lower time steps than daily values, for the whole modelling time. Then, based on this, develop a hotsart and reduce the period under analysis to focus on specific months or days along the year and run the model with 30 seconds time step but collecting the hydrological and water quality results per 5 or 10 minutes to have better and more comparable metal results.

Another aspect to consider is the use of more specific sediment characteristics for different sections of the river, considering anthropogenical influence in the area like sites under construction of areas more prone to be affected by erosion. This can enhance the accuracy and precision of the model. Another very important factor to be considered is the boundary values used at the end of the river, concerning copper concentrations. This boundary value influences greatly the values obtained in the upstream grid point, used to compare with the measured concentrations, therefore the use of non-constant values over time could help to improve the model. Regarding ECO Lab constants for the model, Koc and resuspension rate should be considered as the main constants for model calibration and validation.

6. Conclusions

- The hydrological model results show an improvement (R² = 0.79, NS = 0.77) compared with the previous version of the model (R² = 0.68, NS =0.58). It simulates fairly well the discharge in the river along the modelling period (September 2011 – March 2013), although major differences with measurement data are recorded at the end of the rainy season (April – May).

- Courant numbers AD and HD were the most important stability criteria for the MIKE 11 + ECO Lab model, especially considering the necessity to have a small time step (t = 30 seconds) which influences directly the mentioned criteria.

- AD boundary values are the most important factor that influences copper concentrations modelled in Perennial-1, mainly due to its closeness. On the other hand, for the rest of the river the organic car-
bon partition coefficient (Koc) has bigger influence than resuspension or desorption rates.

- The model generates higher copper concentrations when there is less discharge in the river and vice versa, as the general behavior. Nevertheless, when punctual sources are used, copper concentrations generated in the location point have the opposite behavior, with highest concentrations with higher rainfall, but this peak is rapidly diluted downstream.

- The modelled copper concentrations were in poor agreement with copper measurements in two different points. Nevertheless, in the point near the end of the river both concentrations are below the expected limit. However, in the upstream point in ephemeral 5 tributary, the modelled concentrations are in general approximately 10 times smaller than the ones measured.

- Time step differences between measured copper data used to calibrate and validate the results and model results were the biggest challenge to be tackled during the modelling process.

- The length of river that has a concentration above 0.09 mg/l (USEPA water quality criteria) or 0.10 mg/l (Portuguese Legislation for minimum water quality) is higher when punctual sources are considered compared with distributed sources approach. However it represents less than 10% of total river extension for both cases. Dissolved copper concentrations in the water phase include distinct chemical forms, without taking into account copper speciation.

- Further work is necessary to improve the model.
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