Numerical simulation of groundwater contamination around of Estarreja Chemical Complex (ECC)

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Contamination studies of the soils and water resources surrounding the Estarreja Chemical Complex (ECC) show very high values of electrical conductivity, pH values indicating both very acidic or alkaline conditions (depending on the areas), high concentrations of potentially contaminating chemicals (chloride, sulfate, nitrate, arsenic, mercury and some metals) and the trace presence of some organic compounds with high risk for Human health (aniline, benzene, nitrobenzene and vinyl chloride). Groundwater pollution is highly diffuse, associated with several sources of contamination and responsible for affecting the Aveiro Quaternary Aquifer System that is still used today for agriculture, domestic and industrial supply. The present work investigated the possible origins of the current groundwater contamination derived from pollutant emissions assuming to have a conservative behavior in their interaction with the aquifer material. The methodology used includes the development of a numerical model of groundwater flow and transport of solutes in steady state conditions and over a period of 30 years. The results confirm the interaction between groundwater and several ditches (Breja, Canedo and São Filipe) that drain the study area and the Veiros lagoon. The work concluded that both i) the locations of the old pyrite sludge parks and the current calcium hydroxide sludge park and ii) the waterways with contaminated sediments represent important sources of groundwater contamination, contributing also for the current contamination plume.

Keywords: Groundwater, Estarreja Chemical Complex, contamination, numerical simulation, Aveiro Quaternary Aquifer System

1. Introduction

The water is stored in several sites in globe, such as oceans or underground reservoirs when water infiltration achieve saturate zones of rocks. The recharge of aquifers occurs when the water goes to depth. The agriculture and industry contaminants follow the water resulting one of the most causes of pollution in groundwater, as it happens in Aquifer Quaternary System of Aveiro. This system is constituted by superficial aquifer, aquitard and a water body deeper, the aquifer of Quaternary base.

Globally, the system has an area of about 931 km2, being located in west of coastline of Portugal (Almeida, C. et al., 2000).

The study area is located in Norwest of Portugal nearly of Estarreja, in Aveiro region. The zone around of study area there is Ria de Aveiro that is known for prominent wildlife and it is a resources for activities such as agriculture and fishing. In this region was developed another activity, the industry that contribute for economic growth. The Estarreja Chemical Complex (ECC) is an industrial zone (Figure 1.1) with 2 km^2, it is located 1 km from Estarreja and it began its activity in the 30's. Although this activity is an advantage for local and country economics, it is harmful for public health. The discharges of industrial and domestic effluents without any treatment and careless confinement of waste in the soil also without due treatment were the main reason for this problem because the contaminants from these sites circulated in water lines and they arrived into superficial and underground water bodies. Beyond of CQE, the study area includes also water lines, such as Breja, São Filipe and Canedo ditches.

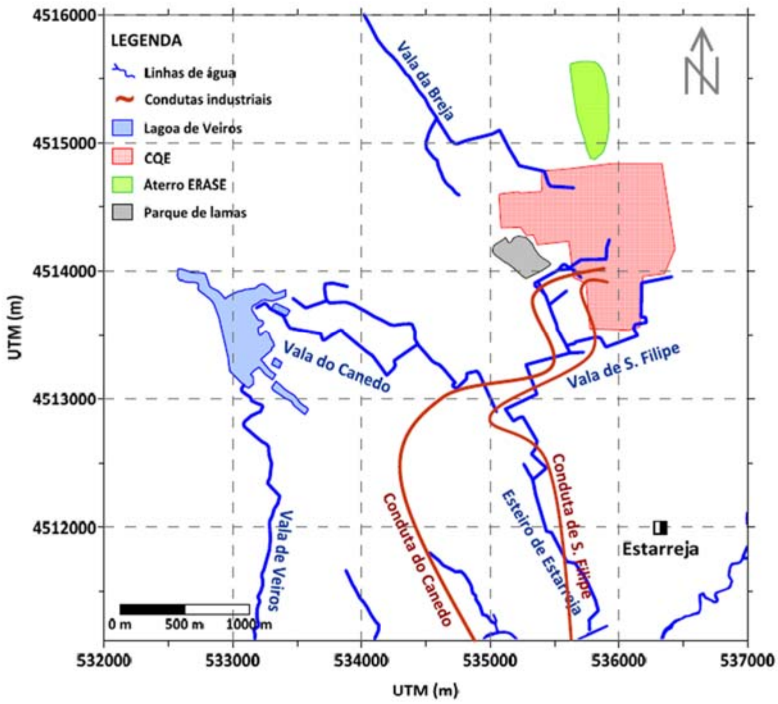

Figure 1.1 - Study area around of Estarreja Chemical Complex

The water, as vehicle of transport, contributes for conservative contaminants flux, being the worst scenario in terms of contaminants transport because the chemical structure of this type of compounds remains during the path. The exploitation of groundwater contaminated through the holes and wells is the main source of population supply in worldwide and this practice compromises the public health. Thus, for studying the behavior of contaminants in stored water in aquifers, the modulation can be a tool that it helps to studying the contamination plumes.

The construction of this model pass through to understand the real flux of the system and how it is influenced by water lines and superficial water bodies. Another objective of this study is recognize the hydrological characteristics of the system that affect the groundwater circulation. The past events about contaminations that promoted the state of study area in present, increase the interest of this study. The contamination plume generated by continuous emissions of pollutants is analyzed through numerical simulation of groundwater flux and the transport of mass during 30 years with interaction of water lines as drainage ditches and superficial water bodies for worst scenario. The design of plume contamination consider the presence of conservative elements and thus without retardation phenomena.

These pollutants can achieve long distances, because they aren't affected chemically and therefore, these cases are more problematic to solve, considering the difficulty to understand their path underground, since, it can get to quite a few meters of depth and circulate in several directions. This study analyze also the possibility to naturally attenuate the contamination plume, considering the influence of human activities as industry as Estarreja Chemical Complex.

2. Methodology

This study begins with a field visit to the study area and bibliographic review of the main studies about this thematic.

In a second phase, the hydrogeological information available was organized and processed for design conceptual model and for construction flow model. The basis of the model are three hydrogeological units, the surface aquifer, the aquitard and the aquifer of the Quaternary base. In order to construct these units, 37 surveys were obtained with the information of the lithography from the area until the rocky substrate and it is treated in a geographic information system.

The simulation of the underground flow begins using the MODFLOW program (Harbaugh, 2005), adjusting the conditions of recharge and defining boundaries and hydraulic properties for hydrogeological units. Based on the piezometry of the region, it is considered the simulation of the aquifer system in a steady state with calibration of the model and measured data of 79 water points.

After the simulation and calibration of the underground flow, it is established potential contamination sources and it is assumed that they are conservative contaminants, reason why the interaction with the environment and the degradation attenuation processes are minimal. The MT3DMS program (Zheng, 2010) was used to simulate the transport model, and results were compared with available hydrochemical data (Ordens, 2007; Neves, 2015) e and results of the cartography of contamination plumes by geophysical methods (Ordens, 2007).

In conclusions, it was analyzed the results and limitations of the methodology used to evaluate the origin and behavior of the contamination plume over the years and to evaluate its natural attenuation potential. Future studies and recommendations for the minimization of current contamination were also proposed.

3. Study area characterization

In terms of geology, the superficial aquifer is formed by dune and alluvial sand and silt-clayey soil covered by organic soil and the deep aquifer (Quaternary Base) is composed by loose conglomerates.

These two hydrogeological units are separated by a heterogeneous structure, the aquitard, with an irregular geometry due to sudden geological variations, both vertical and horizontal with predominance of sludge. The study area presents an average slope of 1%, where the courses water are drained to the Ria de Aveiro.

The measured piezometry of superficial aquifer and Quaternary base aquifer in study area allowed to determine the main directions of groundwater flow, which follow the topography of the region in direction of the main water lines, Aveiro estuary, Estarreja and Veiros lagoon. The underground flow is from Northeast to Southwest, being almost perpendicular to the western boundary of the study area in direction of Aveiro estuary and parallel to the southern border (Esteiro de Estarreja). It is also verified that water lines (drainage ditches) and Veiros lagoon influence piezometry of the study area.

The recharge of water bodies belonging to Aveiro aquifer has a high contribution of the infiltration from precipitation and interaction with surface water bodies present in the drainage ditches and in Veiros lagoon. In opposition, when there is excess water in superficial aquifer, the water table reaches the surface and appears natural discharge through drainage ditches and Veiros lagoon.

4. Results

4.1 Numerical model of flux underground

The model of groundwater flow is the support for contaminant transport model, aiming to understand the circulation of several contaminants. The hydraulic behavior through the lithological characteristics of each aquifer unit and also their interaction with water lines as drainage ditches and surface water bodies as Veiros lagoon are important elements for model elaboration.

In this model are considered stationary conditions, because it is intended to know the position of contamination plume through equilibrium conditions. In same sense, it should be noted that depressions are not significant over a long time period, with water pumping and natural discharges being compensated by recharge. Thus, it was considered that underground flow of the water bodies of the aquifer in the study zone is a dynamic system in equilibrium.

The boundary conditions established by hydrogeological knowledge of modeled area allows to determine the natural flow of the aquifer system. A factor that determines this flow is the eastern boundary in contact with the rocky substrate, occurring the highest piezometric levels in that zone. This fact led to consider this limit cells with constant potential for the model to assume the recognized water intake. Likewise, at the southern boundary, it was chosen to define cells with constant potential to reproduce the discharge of aquifer to Estarreja estuary in south of the model.

The model was calibrate to obtain the better solution as demonstrate in next table:

Table 4.1 – Calibrate values for selected parameters

Unidade hidroestratigráfica	K_h	K_v	Recharge	Condutance
	(m/d)	(m/d)	(mm/year)	(m^2/d)
Superficial Aquifer	12.0	2.0	200	-
Aquitard	0.01	0.001	-	-
Aquifer of Quaternary base	25.0	2.5	-	-
Drainage Ditches	-	-	-	0.1

These values resulted from values tabulated in bibliography according to the lithological materials present (Peixinho de Cristo, 1985; Custodio, et al., 1983).

In this simulation it is verified that piezometry of the model is very close to reality, where the main direction of groundwater flow is from east to west with some exceptions from northeast to southwest (Figure 4.1).

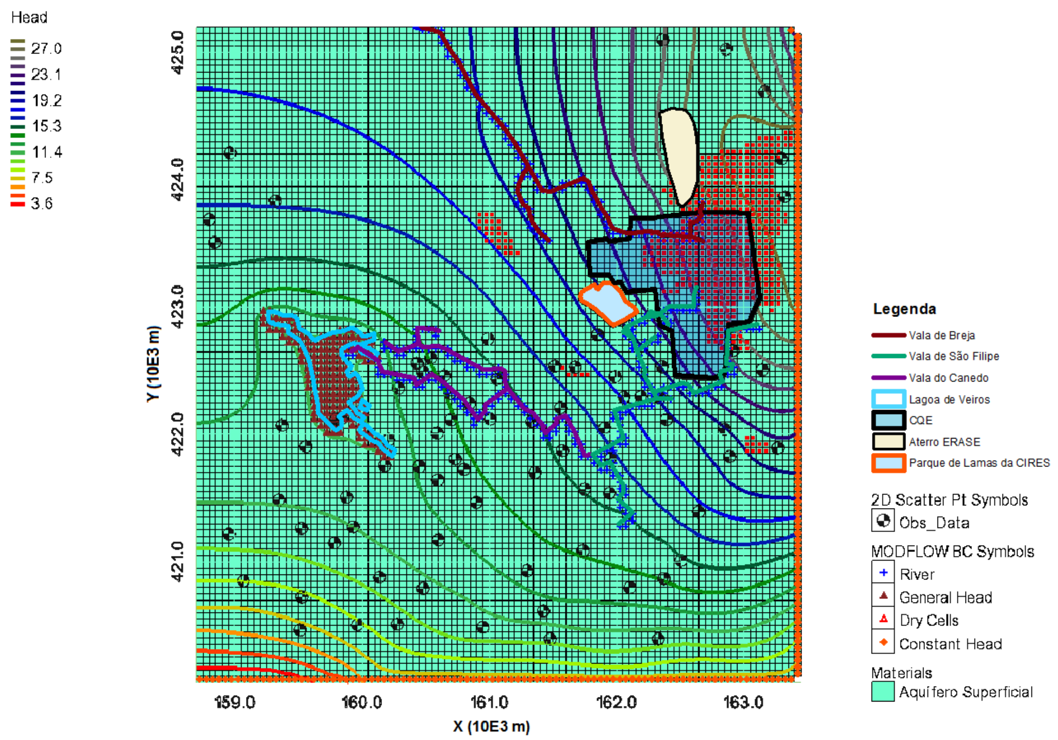

Figure 4.1 – Flux model with Flow model with respective influences and observation points

In this simulation, the observed points that compare with the calculated points are also represented, using the calibration line as shown in (Figure 4.2).

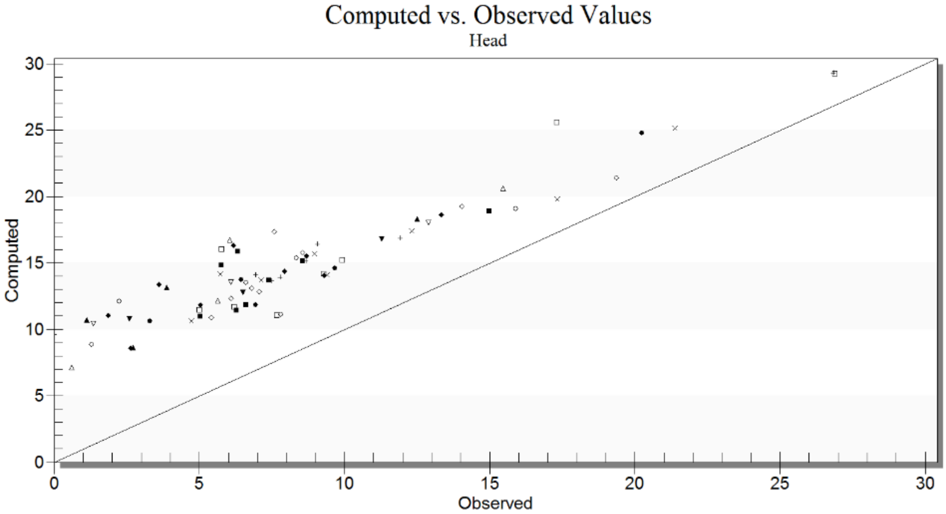

Figure 4.2 - Diagram with calibration line to compare levels observed in real scenario with calculated levels in the model

Analyzing the graph (Figure 4.2) and the correlation coefficient, for this last simulation of 0.93, a strong positive correlation is verified, despite a clear overestimation of the values. It was decided to maintain this overestimation, because the observed values refer to measurements at the end of a severe drought season between the years 2004 to 2006 and the calculated values refer to mean values.

Table 4.2 – Water balance of underground flow in study area

Cumulative Volumes	**Input**		**Output**	
	m^3	**%**	**m^3**	**%**
Constants Heads	610.67	4.43	7255.69	52.63
Drainage Ditches	132.6	0.96	1977.23	14.34
Veiros lagoon	0	0.00	4554.31	33.03
Recharge	13046.4	94.61	0	0.00
Total	13789.67	100	13787.22	100
Balance	2.45			

The constant potential cells are the element that most contribute in the output of groundwater, totaling about 53% of the outputs. The recharge is the component that has more expression in the model, with a contribution of more than 94% of input volume. The presence of drainage ditches is related to the piezometric level, they have a reduced contribution to water intake of the superficial aquifer but jointly with Veiros lagoon are a site of discharge of the groundwater bodies. In total, the balance is positive, so there is accumulation of water and there isn't reduction of the piezometric level, which in reality can be different because the exploitation of water by human action.

4.2 Transport model

The contaminants transport is based on flow model defined and it is simulated for the worst possible scenario, assuming zero retardation (conservative contaminants) and identifying possible contamination sources with more relevance, how hypothetically the plume of contamination can reach and which areas are most affected.

The contamination plumes reach the drainage ditches in some areas, especially the Canedo ditch where the influence of this ditch on the plume is evidenced, because in this place the plume is drawn towards the ditch section. This water line, as the others, is a vehicle of discharging superficial aquifer and therefore the plume is drawn because the water transporting contaminants passes to the ditches and these contaminants are eventually accumulate in its base, allowing permanence and increasing of pollutants in this local.

The simulation for contamination plume where the concentration is 5,000 mg/L (Figure 4.3) is considered for the CIRES Lamas Park and the park with sludges from Uniteca represented inside the CQE show more similarities with the plume mapped in 2006, whose theoretical depth is more superficial (11.8 m) and where the source of contamination of the CIRES Lamas Park is demonstrated. This comparison possibly mean that the contamination source originating from this park doesn't affect the superficial aquifer at higher depths in areas close to that source. Although, this fact doesn't cancel that it cannot contribute to a contamination in away zones of its origin by vertical dispersion processes that the constitution of superficial aquifer allows.

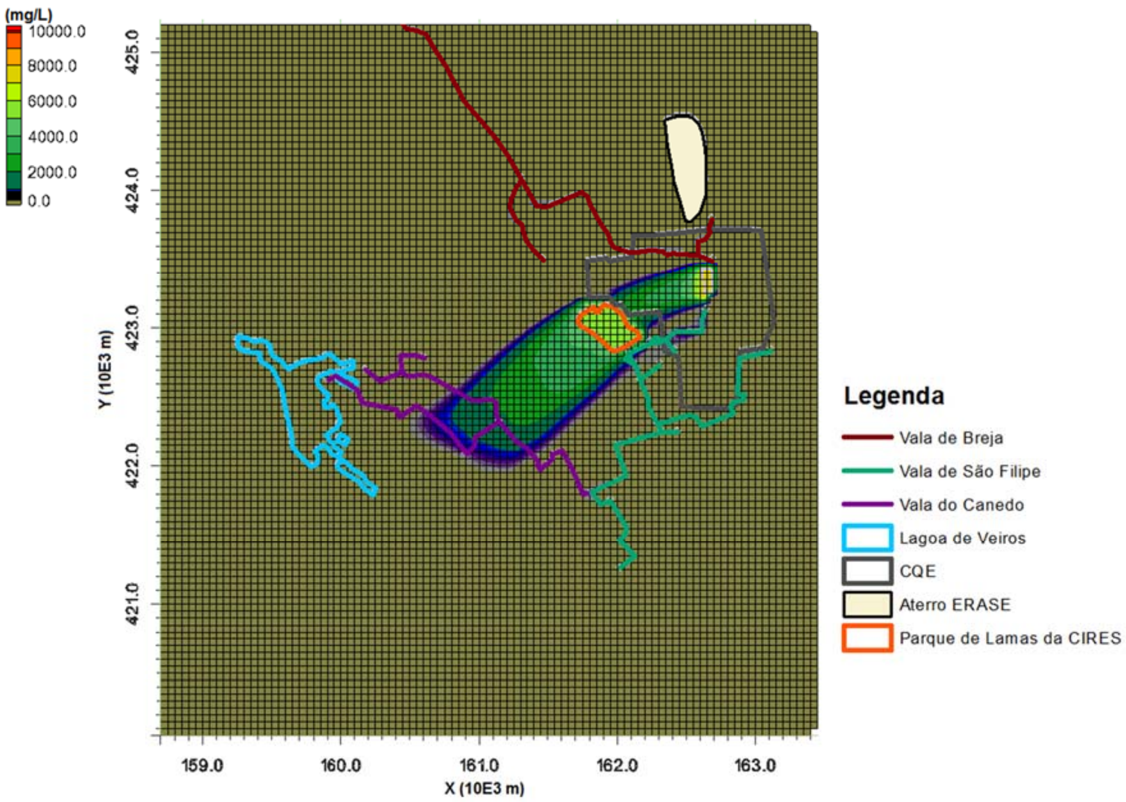

Figure 4.3 - Plume of contamination at 30 years of simulation with emission of contamination in the sludge parks of 5,000 mg / L

In the simulation where the concentration of emitting sources is 10,000 mg/L (Figure 4.4), the plume length is maintained comparing with previous simulation due to same simulation time in both cases but the range of concentration values inside of the plume in this simulation is much larger, as expected. The extension of the contamination plume that develops at the beginning of São Filipe ditch is also larger than the plume represented in previous simulation and it has the same direction of the underground flow as the larger plume. This smaller plume proves to have originated in the Uniteca sludge park, whose contamination ends up extending to the São Filipe ditch and here the influence of ditches on the contamination is verified again. There are some similarities between the mapped plume with a theoretical depth of 25.3 meters and this simulation in relation to the places where the contamination is highest, occurring mainly along the section of the São Filipe ditch near the western boundary of the CQE. Which means that this contamination is deeper than the contamination originating in the CIRES Sludge Park. This depth can be explained by the presence of the Canedo and São Filipe conduits, whose origin it is close to the initial section of São Filipe ditch.

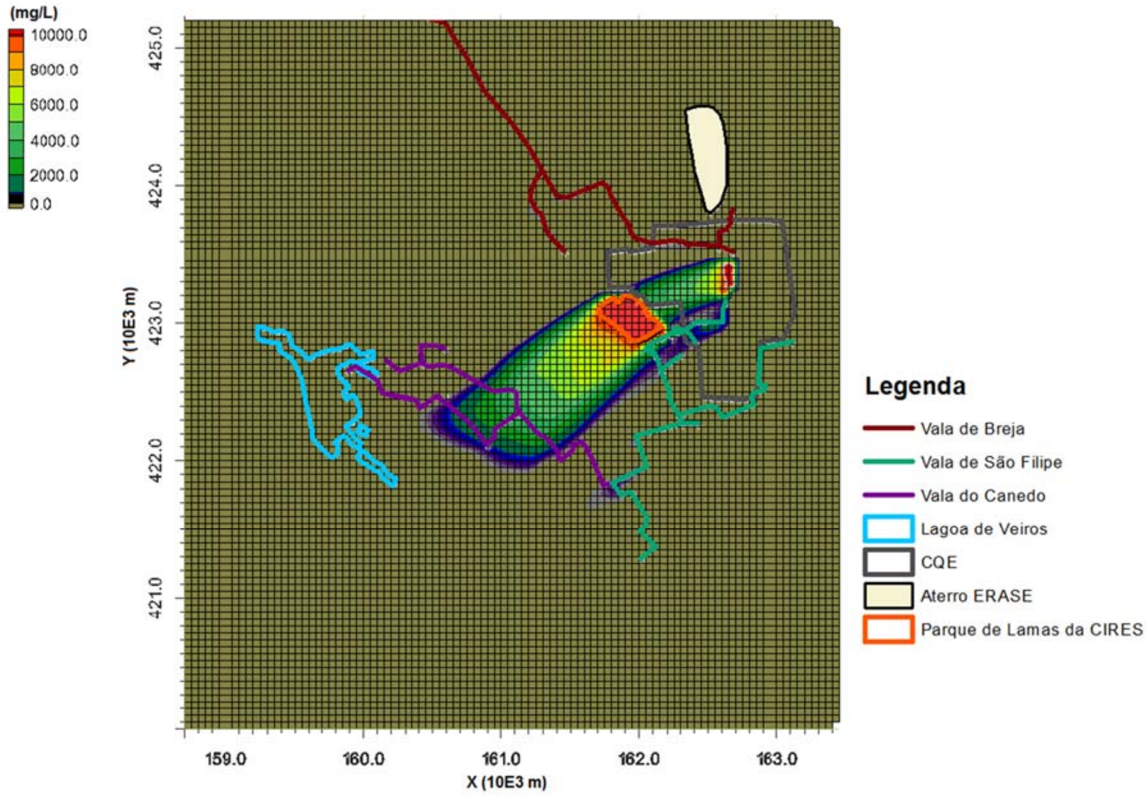

Figure 4.4 - Plume of contamination at 30 years of simulation with emission of contamination in the sludge parks of 10,000 mg / L

A similar scenario to the previous one was simulated, adding contamination points near the Canedo ditch (Figure 4.5) in order to understand the origin of contamination points that they aren't modeled previously and that they are represented in the contamination plume for the theoretical depth of 25.3 meters. In the past, there might have been a buried pipeline from CQE that would discharge effluents into the Canedo ditch in unidentified locations (Barradas, et al., 1991). This can be the explanation for the appearance of contaminations at higher depth than if the plumes of contaminations are influenced by drainage ditches or by contamination sources originating from the top of the superficial aquifer.

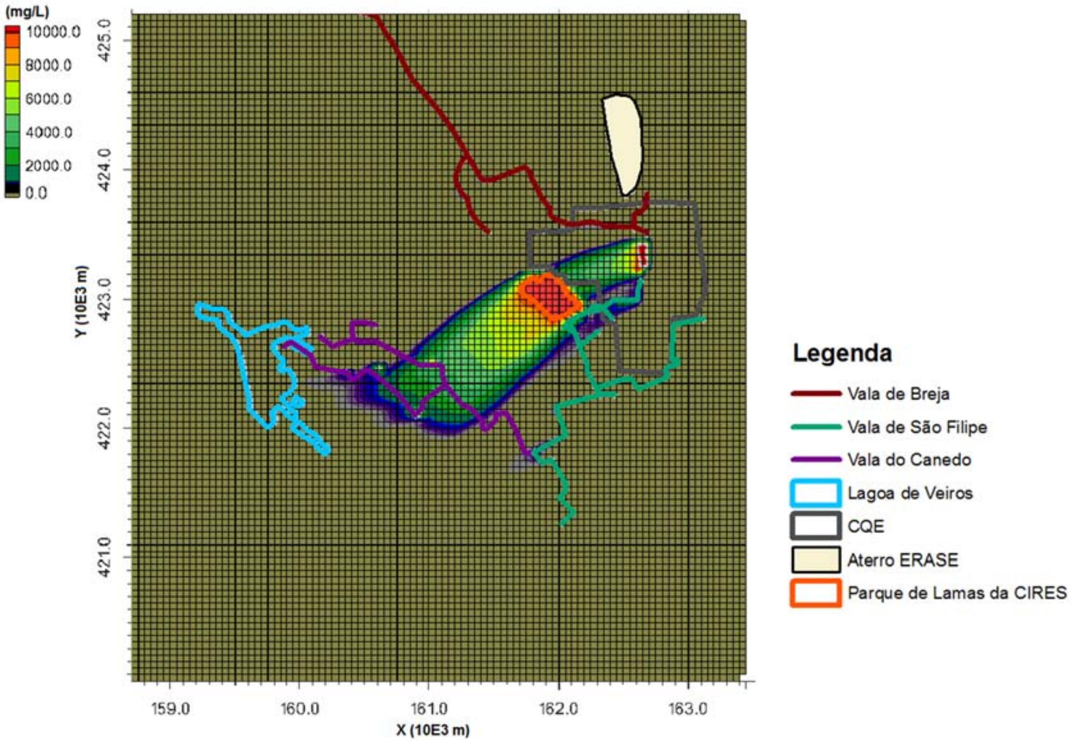

Figure 4.5 – Contamination plume at 30 years of simulation with emission of contamination in the parks of sludge of 10 000 mg / L with contamination points next to the Canedo ditch

5. Conclusions

The activity of Estarreja Chemical Complex began in the 1930s and since then relatively high amounts of contaminants have been emitted as evidenced mainly in mapped plumes. The simulations allow to conclude that contaminants reach long distances influenced not only by the drainage ditches but for other reasons not confirmed by real and concrete studies but where the conduits can be a strong possibility. The contamination plumes originate in the CQE and circulate under the influence of groundwater flow, reaching the lagoon of Veiros that ends up having an attenuating role. The interaction between surface and ground water bodies contributes not only to the entrance of contaminants into the superficial aquifer, promoting the design of the contamination plume but also for the exit of contaminants to the drainage ditches in areas covered by the plumes causing their entrainment along of these ditches. Besides to development of contamination along the study zone, there is also natural attenuation when the interaction is reversed, in other words, when there is discharge of the Veiros lagoon and drainage ditches. This attenuation that should happen easily due to characteristics of superficial aquifer is vulnerable by high concentration of pollutants and their nature because these pollutants don't suffer degradation processes over time and space.

The past events analyzed show that the risk is greater when these contaminations, mainly from industrial area of the study area, reach the population, cultivation and grazing areas and community access to this water through holes and even ditches drainage. The previously points of view explain the durability of the contamination area in superficial aquifer which are a justification for a more accentuated exploitation of Quaternary base aquifer that it is more protected from contaminations.

The modeling of transport of contaminants can have as final purpose the management and evaluation of the risk of contaminated sites and also to predict and test possible remediation measures to apply in places with a history marked by problems of contamination as it happens in the zone surrounding to the Estarreja Chemical Complex, being an environmental and also economic-financial advantage.

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