Monitoring and Performance Simulation, in terms of sulfides and hydrogen sulfide gas of an Industrial Wastewater Drainage System –Case Study of Alcanena, in Portugal

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Abstract: Wastewater undergoes physical, chemical and biological changes while flowing along sewer systems. In fact, when serving large areas, the travel time of the wastewater in the sewer systems may be of several hours, bringing significant changes, namely in the redox potential, dissolved oxygen and dissolved sulfides concentrations, chemical oxygen demand and pH. These changes are particularly important due to the potential increase of sulfide formation and release of hydrogen sulfide gas and the occurrence of corrosion, toxicity and offensive odors.

Septicity in drainage systems is aggravated by the discharge of effluents with high sulfides contaminating loads, like those that occur in tanneries. Regarding the tanning process, there are several physical-chemical and mechanical operations, however, it's the liming operation that generates effluents whit the highest contaminant load, especially in terms of sulfides. In Portugal, around 80% of tannery industries are located in Alcanena, being systematic the occurrences reported to AQUANENA and the City Council, about the offensive odors from the industrial drainage system and from the WWTP itself.

This paper intends to simulate the evolution of septic conditions along the industrial wastewater drainage system of Alcanena, using a model (AeroSept +) developed in the programming language *Visual Basic for Applications* (VBA), having as background, the results of the monitoring campaigns for sulfides and hydrogen sulfide gas, carried out in some reaches of the system.

Keywords: Septicity; Hydrogen Sulfide; Wastewater; Drainage systems; Tanneries; Alcanena.

1. Introduction

In the domain of sanitation infrastructures, in particular, those for the drainage of wastewater, the effects of urban expansion, mainly at the end of the last century, were reflected in the design and execution of increasingly extensive and complex systems. In drainage systems typical of large urban agglomerations, the travel times of wastewater are, usually, several hours, and the change refers to water quality is mainly reflected in the formation of sulfides.

The presence of dissolved oxygen in wastewater drainage networks helps to maintain high values of redox potential, thus inhibiting the activity of bacterial species, leading to the sulfate reduction to sulfide. One of the ways to control septicity from wastewater, especially in pressure collectors, is the injection of oxygen into the liquid mass.

For septicity conditions to occur in sewer systems (and subsequent hydrogen sulfide (H_2S) release onto the gas phase) certain conditions need to be met [1]. At the most upstream sections of wastewater drainage systems, dissolved oxygen (DO) concentrations are often close to saturation values, provided there are no total or partial flow obstructions. As wastewater progresses, and its travelling time increases, oxygen consumption is accentuated, and surface air-liquid oxygen transfer rates usually decrease. At a certain point, if the system is extensive enough and the oxygen consumption is not balanced out by superficial reaeration, the DO deficit reaches its maximum, i.e., DO content within the liquid becomes null, which may set the ideal conditions for sulfide formation (septicity conditions).

Moreover, redox potential tends to decrease simultaneously with DO concentration reduction. When this occurs, sulfide can be generated inside the wastewater, the biofilm or within sediments. In rising mains, or whenever pressurized flows occur, reactions are simpler since neither oxidation nor H_2S release onto the atmosphere take place.

When H_2S is released in confined environments, such as sewers or other wastewater system components, and is mixed with high moisture contents, it originates diluted sulfuric acid (H_2SO_4) known for its powerful corrosion properties on concrete surfaces [1]. In terms of impacts on human health, H_2S presents a very low olfactory detection threshold of about 0.00021 ppm , leading to potentially serious implications for the human organism with increasing concentrations. In that regard, confined spaces such as storage tanks, pumping stations and other accessible sites represent locations of increased risk, especially for utility workers.

One of the industries that contribute with effluents with high contaminating loads, especially in what concerns sulfides, is the Tannery Industry. The Tannery Industry is one of the oldest in the country, having developed predominantly in the Alcanena region due to the favorable conditions existing, namely the abundant existence of water, high temperatures, dry climate, and low productivity soil, in terms of agriculture.

The tanning process is an industrial process where each industrial unit use “their” processes, often adapted to their personal beliefs. Therefore, despite some basic similarities, there is no basic or universal concept for the tanning process. As a result, the wastewater from the tannery industry is heterogeneous in quality, depending on the operation or operations in progress. Considering all the operations usually involved in the tanning process, it is the liming that generates effluents with a higher contaminant load, especially in terms of sulfides [2].

Within the scope of this article, it was considered the industrial wastewater drainage system of Alcanena as a case study, surely the system in which the sulfide concentration reaches the highest values in the country and possibly in Europe, having been measured in the past, concentrations of total sulfides in the liquid mass above 500 mg S/L.

In this case, the occurrence of sulfides in the wastewater drainage system results directly from the discharge of effluents from the tannery industries. In order to regulate the wastewater discharges from the industries, and from other "clients", into the drainage system, the Municipality of Alcanena has a Wastewater System Regulation [3].

The main objective of this article is to apply an automatic calculation tool (AeroSept +) to assess the behavior of wastewater drainage systems from the point of view of the evolution of water quality, in terms of oxygen and sulfides concentrations in the liquid mass and hydrogen sulfide in the atmosphere of collectors.

To help in the evaluation of the results given by the model, there is some data available regarding sulfide and sulfur gas concentrations obtained through monitoring campaigns, carried out by AQUANENA, in close collaboration with HIDRA, Hidráulica e Ambiente Lda., which defined the sections to be monitored, the data to be obtained and the practical procedures.

2. Methodology

Case Study: Alcanena

The municipality of Alcanena, with a total area of 127 km², belongs to the Santarém District, in the Central region of Portugal. Currently, the wastewater drainage system of Alcanena is divided into two drainage systems, one for the transport of effluents of domestic origin and the other for the transport of effluents of industrial origin, with the collectors essentially constituted by PEAD pipes.

Briefly, the industrial wastewater system in the Alcanena region includes three main subsystems, with approximately 25 km of collectors in total and 660 manholes (the subsystem of Monsanto, Vila Moreira, and Gouxaria, with about 9, 5, and 11 km, respectively) with the system draining in a gravitational way to the Alcanena WWTP, which has tertiary treatment (activated sludge of medium load, with anoxic zones and nitrogen removal) (Figure 1). In addition to these main components, there are several complementary works or components, namely, the chromium recovery system, called SIRECRO, and the Alcanena landfill system.

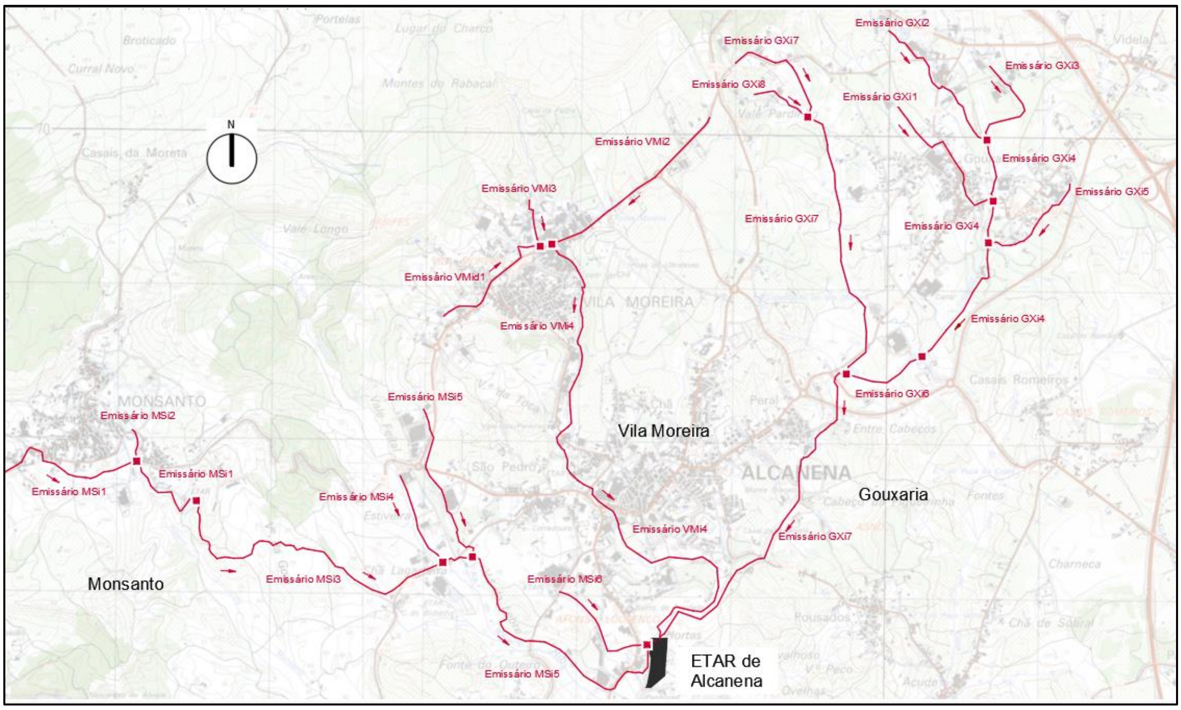

Figure 1 - Schematic representation of the Alcanena industrial system location.

At the Alcanena WWTP, the industrial effluent treatment process begins with its admission at the entry work, equipped with three Archimedes screws that are in operation, although the elevation of the wastewater is being carried out by electric pumps, with regulation by level buoys, once that two of the screws have limited lifting capacity. The components that compose the Alcanena drainage system can be consulted at HIDRA 2014 [4].

The industrial drainage system receives, essentially, the effluents discharged by the industrial units, where the tannery industries stand out. However, there is a part of the Vila Moreira industrial system that receives industrial and domestic wastewater (stretch VMid1) and there is also the punctual connection of two domestic subsystems to the industrial network.

There are systematic the reported occurrences to AQUANENA and the City Council relative to the offensive odors from the industrial drainage system and the WWTP itself. The reduced slopes at the final sections of the subsystems, together with the frequent entry into pressure, even in dry weather (as a result of the operation point of the electric pumps at the WWTP entrance work), prevent natural ventilation and self-cleaning of the collectors. contributing to the aggravation of silting and the release of offensive odors.

Sulphide and hydrogen sulfide gas monitoring campaign

The sulfide and Hydrogen sulfide gas monitoring campaigns were carried out in order to characterize the performance of the system from the point of view of the sulfide balance, and if possible to "calibrate" some parameters and variables of the forecast model, AeroSept +.

In parallel with the sulfide and Hydrogen sulfide gas monitoring campaigns, hydraulic variables (like the water height, water speed, water temperature and flow) and precipitation were also monitored. In the sulfide and sulfur gas monitoring campaigns, monitoring points were defined at the three industrial subsystems (Monsanto, Vila Moreira and Gouxaria), with their location indicated in Figure 2.

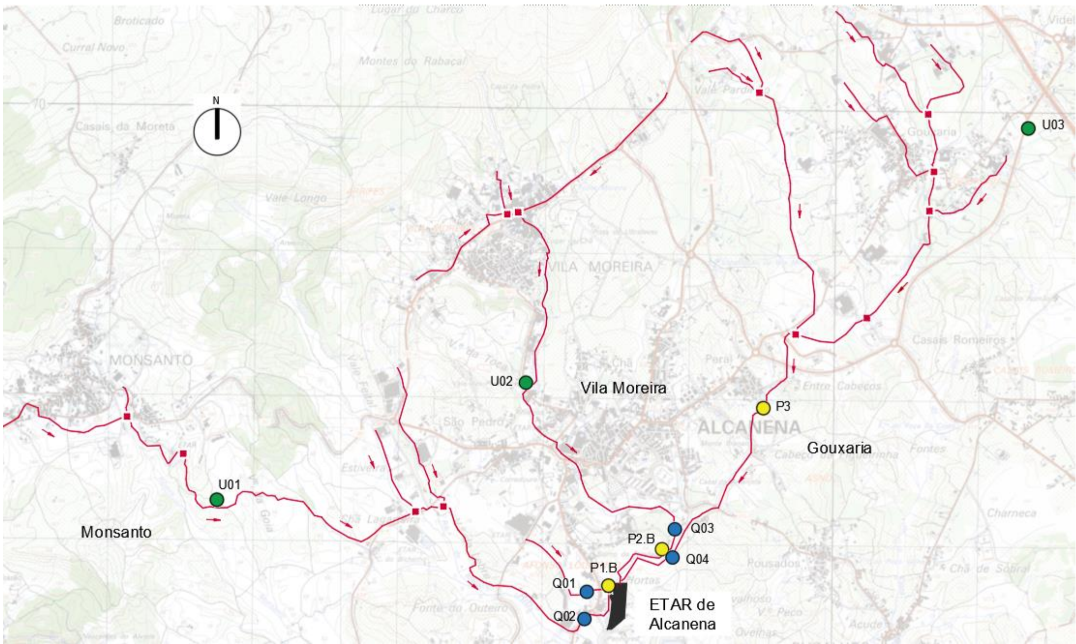

Figure 2 - Schematic representation of the chosen points for the monitoring campaigns.

In the monitoring campaign of the hydraulic variables, there were installed two measuring stations in the Monsanto subsystem, Q01 (MSi6.015) and Q02 (MSi5.063), one station in the Vila Moreira subsystem, Q03 (VMi4.076) and one station in the Gouxaria subsystem, Q04 (GXi7.102). The campaigns started on April 8, 2020, and ended on July 30, 2020, except in the case of post Q01, which started on April 7, 2020, and ended on July 23. . For the monitoring of precipitation, 3 udometers were installed (U01, U02 and U03), as shown in Figure 2. The precipitation records started on April 9 and ended on July 31, 2020, uninterrupted.

The sulfide and hydrogen sulfide gas monitoring campaign took place between July 6 and July 29, 2020. shows the maximum values observed in the scope of the monitoring campaigns, with regard to the concentrations of total (S_T) and dissolved (S_D) sulfides in the liquid mass and hydrogen sulfide gas (H_2S) in the atmosphere of the collectors.

Table 1 shows the maximum values observed in the scope of the monitoring campaigns, with regard to the concentrations of total (S_T) and dissolved (S_D) sulfides in the liquid mass and hydrogen sulfide gas (H_2S) in the atmosphere of the collectors.

Table 1 - Maximum concentrations observed in the context of the sulfides and hydrogen sulfide gas monitoring campaigns.

Section	[S_T] (mg/L)	[S_D] (mg/L)	[H_2S] (ppm)
P1.B (MSni6.019.A)	266.2	169.4	2188
P2.B (VMni4.080)	14.1	10.1	3838
P3 (GXni7.073)	486.8	259.9	3454

Regarding the dissolved oxygen concentrations, the results of the experimental campaigns indicate very low concentrations, in general, below 0.5 mg DO/ L.

Methodology and Procedures

To assess the concentrations of dissolved oxygen and total sulfides in the liquid mass, as well as hydrogen sulfide gas in the collector atmosphere, the AeroSept + model, developed in the Visual Basic for Applications (VBA) language was used. This model was based on another model already available, the AEROSEPT, developed in Matos (1992) [1], and has already been applied to several cases at the national level, such as the Ericeira or Costa do Estoril systems and at an international level, as for example Cape Verde and Mozambique.

As mentioned, the AeroSept mathematical model was adapted to simulate the sanitary behavior of the system based on theoretical and experimental studies by Pomeroy (1959) [5], Pomeroy and Parkhurst (1972) [6], Pomeroy and Parkhurst (1977) [7], Pomeroy and Parkhurst (1977) [8], Matos and Sousa (1989, 1990) [9, 10] and Matias (2015) [11]. For the aerobic phase, the expressions of reaeration and oxygen consumption in the liquid mass were used the ones from the American Society of Civil Engineers et al. (ASCE, 1989) [12], and the oxygen consumption in the biofilm presented in Matos (1992) [1].

Considering influent flow, in addition to the information provided by the monitoring campaigns of hydraulic variables, it was also taken into consideration the flows from industrial users included in the inspection activity carried out by AQUANENA. For modeling purposes and knowing that the inspected industries contribute only 40% of the average flow observed in the monitoring campaigns, the remaining 60% were distributed by the nodes where exists connections with other industrial units, not included in inspection activity. Regarding the nature of the flow, it was considered that only the inflows from the inspected industries contributed with sulfides.

Within the scope of the evaluation of the system performance, it was decided to simulate the 8 scenarios represented in Figure 3, being S the concentration of total sulfides discharged by the industrial units, with the pH of the liquid mass equal to 6 or 8.

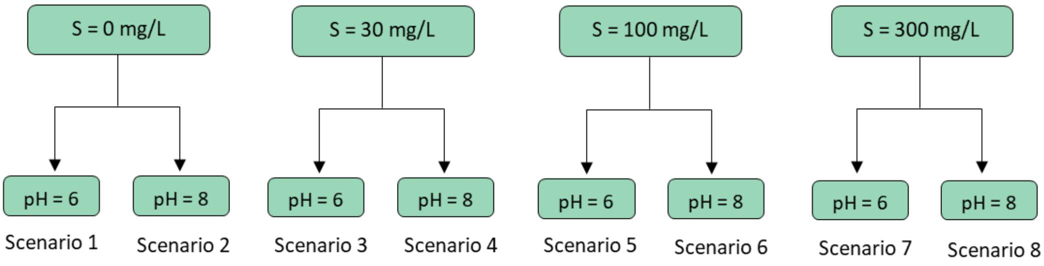

Figure 3 - Simulated scenarios by the AeroSept + model.

To choose the scenarios, were taken into account the maximum admissible values (MAV) and the maximum admissible punctual values (MAPV) of the wastewater to be discarded in the system, as established in the Regulation of the Wastewater System of the Municipality of Alcanena [3], equal to 30 and 100 mg / L, respectively, being this values corresponding to Class 1 industrial units (most disadvantageous situation).

However, and considering the results of the monitoring campaigns, other extreme scenarios were also considered(scenarios 7 and 8 with S = 300 mg S/L). It was also intended to understand the system's response in the absence of sulfides in influent discharged into the system (S = 0 mg S/L).

At the simulations performed, it was considered that the wastewater influent to the system, had oxygen concentrations equal to 10% of the saturation concentration. Since the collectors are made of PEAD, corrosion has not been considered.

3. Results and discussion

The results provided by the AeroSept + model indicate that, in general, septic conditions are verified in the system, therefore the concentration of dissolved oxygen is not relevant. The results regarding the concentration of total sulfides (S) and hydrogen sulfide gas (H2S), in the monitoring sections P1.B (Monsanto), P2.B (Vila Moreira) and P3 (Gouxaria), are presented in Figure 4 and Figure 5, respectively, according to the simulated scenarios.

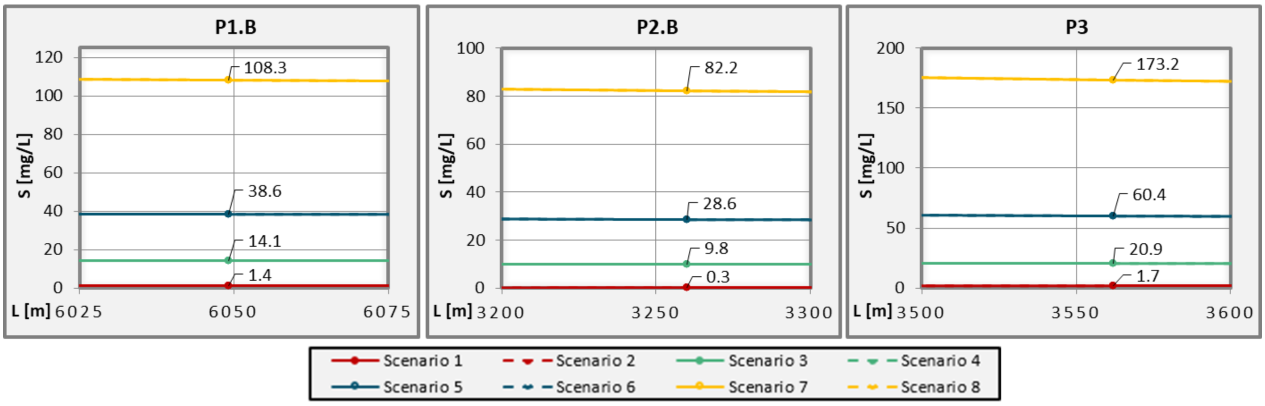

Figure 4 - Results for the total sulfides concentration in water mass, obtained by the AeroSept + Model, for the monitoring sections.

Regarding the results obtained by the AeroSept + model, in terms of the concentration of total sulfides (Figure 4), it can be resumed the following:

- Even in cases where is an absence of sulfides in the effluent discharged into the system (scenarios 1 and 2, S = 0 mg S/L), septic conditions are observed in the monitoring sections (P1.B - 1.4 mg S/L, P2.B - 0.3 mg S/L, P3 - 1.7 mg S/L);
- The reason for the concentration of sulfides be lower in the Vila Moreira subsystem (P2.B), compared to the Gouxaria subsystem (P3), is due, not only to the fact that there are more contributions of wastewater with domestic origin (S = 0 mg S/ L) but also by the fact that industrial discharges occur further away from the monitoring sections, with a reduction in the concentration of sulfides resulting from the reaction with oxygen from the reaeration along the stretch.

Comparing the results obtained by simulation with the maximum recorded in the monitoring campaigns (Table 1), it appears that in the Monsanto system (P1.B), the total sulfide concentration measured (266.2 mg S/L), exceeded the values simulated (maximum 108.3 mg S/L). In other words, this means that the discharge of sulfides by the industrial units exceeds, by far, the regulated limits, being the weighted value of the discharges will surely be higher than 300 mg S/L.

It the Vila Moreira subsystem (P2.B), scenarios 3 and 4 (S = 30 mg S/L), were the ones that came closest to the recorded values (14.1 mg S/L), with the simulated value equal to 9.8 mg S/L.

Finally, in the Gouxaria subsystem (P3), the simulated results are somewhat distant from the maximum recorded value (486.8 mg S/L), being the concentration obtained with scenarios 7 and 8 equal to 173.2 mg S/L. Once again, sulfide discharges occurred with concentrations much higher than those allowed, and compared to what was seen in the Monsanto subsystem, the weighted value of the discharges from the industrial units would also have been greater than 300 mg S/L.

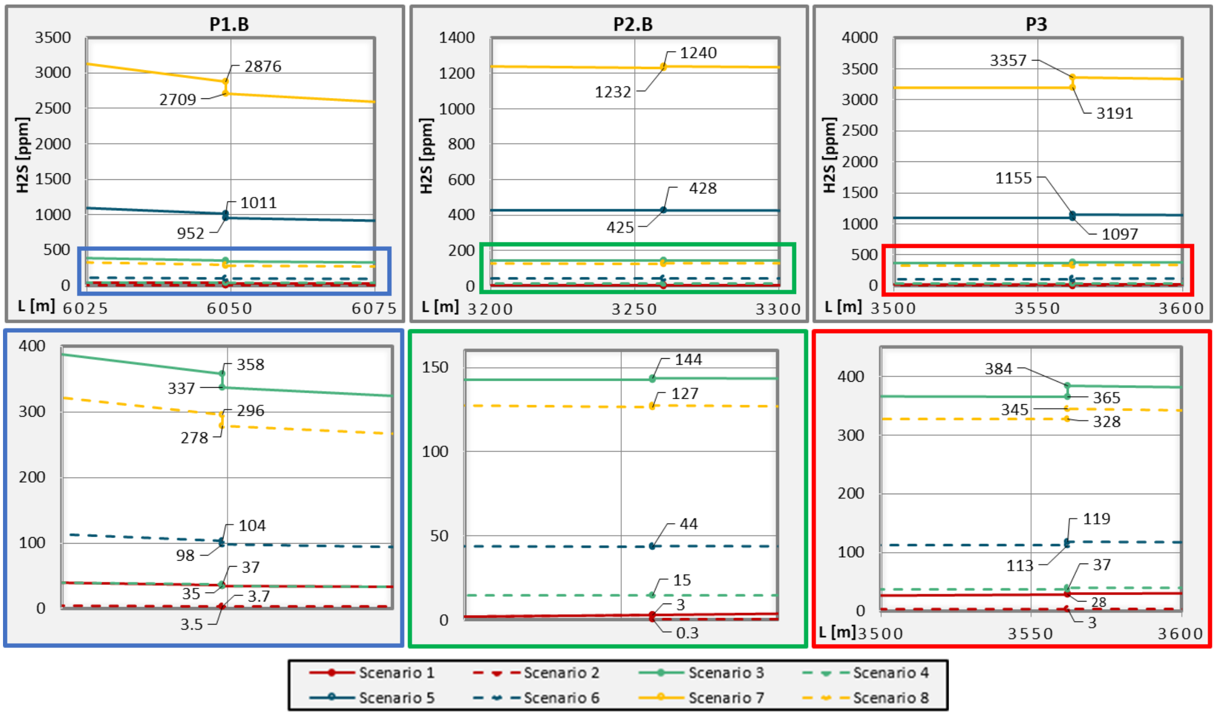

Figure 5 - Results for the hydrogen sulfide gas concentration in the collector atmosphere, obtained by the AeroSept + Model, for the monitoring sections.

Regarding the results obtained by the AeroSept + model, in terms of the concentration of hydrogen sulfide gas (Figure 5), it can be resumed the following:

- Even in scenarios 1 and 2 (S = 0 mg S/L), there are concentrations of hydrogen sulfide capable of causing strong and offensive odors, in the case of the Monsanto and Gouxaria subsystems (between 0.5 and 30 ppm), being, however, recognizable in the three subsystems (greater than 0.00047 ppm) [1];
- In scenarios 3 (S = 30 mg S/L, pH = 6), 5 (S = 100 mg S/L, pH = 6) and 7 (S = 300 mg S/L, pH = 6), the consequences are much more serious, being, in the case of scenario 5, in the Monsanto and Gouxaria subsystems, the presence in atmospheres with the concentration obtained may cause instant death [1]. This situation occurs in all subsystems, in case of scenario 7;
- However, for higher values of pH (scenarios 4 (S = 30 mg S/L, pH = 8), 6 (S = 100 mg S/L, pH = 8) and 8 (S = 300 mg S/L, pH = 8)), much lower concentrations of hydrogen sulfide are obtained, but still, capable of causing serious health problems (Loss of smell, respiratory problems, pulmonary edema, etc.) [1].

In the Monsanto subsystem, it was observed a maximum concentration of hydrogen sulfide of 2188 ppm, and the results of the simulation indicate that scenario 7 (ST = 300 mg S/L; pH = 6) was the closest to the measurement results, with a concentration of 2876 ppm.

In the Vila Moreira subsystem, it was observed a maximum concentration of hydrogen sulfide of 3838 ppm, and the results of the simulation indicate that scenario 7 (ST = 300 mg S/L; pH = 6) was the closest to the measurement results, with a concentration of 1240 ppm. However, there is a big difference between these two values, which can be explained by the fact that the discharged effluent had a pH below 6 and/or a concentration of total sulphide higher than legally admissible.

Finally, in the Gouxaria subsystem, it was observed a maximum concentration of hydrogen sulfide equal to 3454 ppm, with the results of the simulation, with scenario 7 (S = 300 mg / L; pH = 6), being the closest, with a concentration of 3357 ppm.

4. Conclusions and recommendations

Regarding the simulation of sulfides and hydrogen sulfide, scenario 7 (discharge of 300 mg S/L, pH = 6) is the one that best suits the maximum values observed in the monitoring campaigns, namely with regard to Monsanto and Gouxaria subsystems. This situation seems to confirm that at least a large part of the industrial units punctually discharges effluents with total sulfide concentrations much higher than 100 mg S/L, the limit value established by the discharge regulation, or even higher than 300 mg S/L.

In order to reduce the concentration of sulfides in the liquid mass, it is proposed to add Iron chloride in pre-treatment and monitoring stations, to be installed in each subsystem (Monsanto, Vila Moreira, Gouxaria). It can be also useful to adopt some source control strategies, in order to best control and reduce sulfide discharge from industrial units, such as the installation of dissolved sulfide concentration and temperature and pH probes for continuous measurements of these parameters in the bulk wastewater, at least in the main industrial units, with liming operations.

The fact that the system entry into pressure near the WWTP, at least in the peak hours, because of downstream conditions of the pumping system at the headworks of the WWTP causes the ventilation to stop, leading to an increase in the hydrogen sulfide concentration upstream of the place where the interruption occurs. In order to prevent the industrial system reaches from entering into pressure in the surroundings of the WWTP, it is recommended, as a possible intervention, the rehabilitation of the Archimedes screws chamber in the WWTP, lowering is starting operation level, which will allow all the air transported inside the sewer system to flow to the headworks at the WWTP, and then be properly treated at the WWTP scrubbers.

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