Evaluation of sulfides formation and quality parameters in the sludge pumping system of Guia WWTP

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Abstract: The existence of long wastewater pumping sewers is relatively common and problems associated with the formation of sulfides may occur. Nevertheless, there is a limited number of pumping sludge systems with a significant length, thus the knowledge about the processes that might occur in these circumstances is scarce. The objective of this investigation was to evaluate the quality parameters (namely the formation of sulfides and hydrogen sulfide) on a long sludge, based on the results obtained in several experimental campaigns. The sludge pumping system of Guia's WWTP, which is 4 km long, was used as a case study. The results of the campaigns results confirmed that the formation of sulfides is independent of the COD values and that its formation rate is practically constant. Furthermore, there is a direct relation between the sludge discharge and the concentration of hydrogen sulfide in the reception tank of sludge. These results can be used as a basis to control the consequences of sulfides, namely offensive odors, toxicity and corrosion.

Keywords: sludge, pumping systems, sulfides, quality parameters, experimental campaigns

1.   Introduction

The effects of urban growth has been reflected in the design and implementation of larger and more complex drainage systems, namely in the construction of pumping systems and treatment plants for wastewater and sludge. 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 about significant changes, namely in the redox potential, dissolved oxygen (DO) and dissolved sulfides concentrations, chemical oxygen demand (COD) and pH (Matos, 1992). In long pumping systems, with associated long wastewater travelling times, a major problem is the increased problems of septicity and hydrogen sulfide gas impacts.

One of the main mechanisms of sulfide production in the liquid phase is the reduction of sulfate to sulfide under anaerobic conditions (EPA, 1985). They can also have other origins, like direct discharges of industrial and domestic wastewater with sulfides, and the infiltration of water from aquifers with high concentrations of sulfides (Matos, 1992). In anaerobic conditions, wastewater contains both soluble and non-soluble sulfides. The soluble sulfides are a mix of sulfide ion (S^{2-}), hydrogensulfide ion (HS^-) and hydrogen sulfide (H_2S) and the proportions depend mostly on the pH. Non-soluble sulfides depend on the availability of metals that can react with ion sulfide and originate insoluble salts, such as iron sulfide and zinc sulfide.

Being one of the species of dissolved sulfides that, when in its gaseous form, may have important effects on urban infrastructures, hydrogen sulfide's (H_2S) concentration in the bulk water is acknowledged as one of the most relevant factors to understand interactions between anaerobic wastewater, in sewer atmosphere, odors, and corrosion of exposed materials. The main effects of H_2S on sewer infrastructures can be summarized as follows: building up of unpleasant odors; creation of toxic and

potentially deadly atmospheres in confined spaces and corrosion of gravity sewers, manholes and pumping stations (Matos, 1992).

The hydrogen sulfide gas, even in concentrations below 1 ppm, is corrosive to metals and, if oxidized on moist surfaces, may produce sulfuric acid and attack concrete, in some cases leading to the complete collapse of the structures (recently, an example with extreme concentrations and collapsed infrastructures was presented by Matias *et al.* (2013)). It has a characteristic odor of "rotten eggs" and is flammable in the range between 4.3 and 45.5% (EPA, 1985). The inhalation of this gas may cause headaches, nausea, eye and respiratory injuries and fatalities have occurred for values greater than or equal to 700 ppm (ASCE, 1989). This deadly gas is considered the primary cause of work related deaths of sewer system workers.

Several authors have proposed empirical formulas for predicting the rates of release of hydrogen sulfide gas and to estimate the formation of sulfide on filled or partially filled pipes (Hvitved-Jacobsen *et al.*, 2013). These formulas also allow to estimate the concentration of sulfides and can be used as a basis to control odor, toxicity and corrosion through the satisfaction of rules of maintenance and operation of the systems (e.g., periodic cleaning) and chemical treatment, for example, with the addition of air, pure oxygen or with addition of metal reagents (e.g., compounds of iron).

For the past decades, awareness of the effects of the formation and risks associated with sulfides on the performance of sewer systems has been increasing. However, little is known about the processes occurring in sludge pumping systems, probably because the existence of such systems with long pipes is not common. In Portugal, exists the example of the sludge pumping system of Guia's WWTP with a significant length and problems caused by the presence of sulfides.

The present work aims to contribute to the knowledge on the formation of sulfides in a pumping system of sludge with measurements "in situ" and laboratory analyses. Moreover, this study can be useful to the management entities as it can help them to better control and mitigate the problems caused by sulfides.

2. Methods

2.1 Sewage system of Estoril Coast

Since 1995, SANEST – Saneamento da Costa do Estoril, S.A is responsible for the management of the sewage system of Estoril's coast and responsible for the collection, transportation, treatment and disposal of the wastewater of 800 000 inhabitants of the municipalities of Amadora, Cascais, Oeiras and Sintra. This system includes the transport of wastewater over 155 km of sewage pipes, one main interceptor, thirteen gravity pipelines, nine pumping stations, one wastewater treatment plant (WWTP) and a submarine pipeline. The main interceptor has a length of 25 km and the submarine pipeline has a length of 3 km discharging at a depth of 45 m. The Guia WWTP (Figure 1) receives every day, an average of 155 000 m^3 of wastewater and is divided into two operating locations: the liquid phase treatment plant (LPTP) and the solid phase treatment plant (SPTP), located 4 km north. At SPTP the

odor treatment includes two types of deodorizing systems, namely chemical washing towers and activated carbon towers, to avoid significant emissions of odors and discomfort to neighbor populations.

Figure 1 – Liquid phase (left) and solid phase (right) of Guia WWTP (www.sanest.pt).

The treatment in LPTP includes sieving to remove gross solids, desanding solids to remove sand, degreasing and primary sedimentation to gravitational separation of flakes, with addition of reagents. The solid matter (sludge) is conducted to the sludge well before being pumped to SPTP. In this well, ferric chloride is added in order to control the formation of sulfides. Additionally, during the bathing season, the treatment is supplemented by adding reagents in the coagulation-flocculation step, filtration (with gravity sand filters to remove fine particles in suspension) and disinfection by ultraviolet radiation.

The treatment in SPTP includes tanks (that receive and homogenize sludge), centrifugation (to mechanical thickening), anaerobic digestion (in which the biological stabilization of sludge occurs), sludge dewatering (by centrifugation to remove part of the water) and thermal drying. The sludge pumping system of Guia WWTP includes two parallel pumping pipelines (A and B), with a 300 mm diameter and a length of 4213 m. Figure 2 presents photographs of the sampling collection in three sections: P1 section represents the beginning of the pumping pipeline in LPTP (near the pumps), P2 section, which is located approximately halfway through the pumping pipeline (bottom discharge) and P3 section, which corresponds to the final part of the pumping pipeline in SPTP (near the reception tank of sludge).

Figure 2 – Collection in P1 section (left), P2 section (middle) and P3 section (right).

2.2   Experimental campaigns

The experimental campaigns during non-bathing season were held on the 6th and 25th of February 2014, and during bathing season on the 7th, 8th and 9th of July 2014. These campaigns included "in situ" measurements and the collection of samples for laboratory analysis in one of the pumping pipelines (it was assumed that the conditions on both pipes were similar). During the non-bathing season, each day, four samples were collected in each section, and during bathing season in each section, were collected six samples on the 7th, four samples on the 8th and three samples on the 9th of July. To evaluate the potential of the sulfide formation without factors inhibiting the processes in sludge pumping system, the dosage of ferric chloride in the sludge well (LPTP) was interrupted at least 24 hours prior to the campaigns and the well and pumping pipelines were emptied.

The parameters measured "in situ" in the liquid phase were: temperature, pH, redox potential (ORP), dissolved oxygen (DO) and conductivity. The parameters measured in laboratory were: total sulfides (S_T), sulfates (SO_4^{2-}), total chemical oxygen demand (COD_T), total solids (TS) and total volatile solids (TVS) in P1 and P3 sections. In P2 section, only total sulfides were measured. Additionally, in P3 section the levels of oxygen, methane and hydrogen sulfide were measured in the gas phase. Because of some difficulties in collecting and measuring in section P2, in the summer season only P1 and P3 sections were used. The parameters measured "in situ" were the same as in non-bathing season and the parameters measured in the laboratory were S_T and COD_T.

An YSI 556 Multi-Probe System sensor was used to measure, in the liquid phase, the following parameters: pH (range: 0 to 14, accuracy: $\pm$ 0.2); ORP (range: -999 to 999 mV, accuracy: $\pm$ 20 mV); DO (range: 0 to 50 mg/L accuracy: $\pm$ 0.20 mg/L); electrical conductivity (range: 0 to 200 mS/cm, accuracy: $\pm$ 0.001 mS/cm) and temperature (range: -5 to 45 ºC, accuracy: $\pm$ 0.15 ºC). For measurements in the gas phase a portable multi-gas analyzer was used, which measured H_2S_g in the range from 0 to 200 ppm (accuracy: 1 ppm), methane (CH_4, 0 to 100% LEL) and oxygen (O_2, 0 to 25 %). The laboratory of IST analyzed S_T and SO_4^{2-} and the laboratory of SANEST analyzed COD_T, TS and TVS. The parameters were analyzed according to the Standard Methods for the Examination of Water and Wastewater (SMEWW), which are presented in Table 1.

Table 1 – Standard methods to laboratory analysis.

Parameters	Standard methods
Total sulfides (S_T)	SMEWW 4500 S2- A, B, C, F
Sulfates (SO_4^{2-})	SMEWW 4110 B
Total chemical oxygen demand (COD_T)	SMEWW 5220 C
Total solids and total volatile solids (TS and TVS)	SMEWW 2540 G

3. Presentation and discussion of results

3.1 Results during non-bathing season

The parameters measured "in situ" in the liquid phase were done with the sensor inside a bucket containing the collected sludge. As an example, Table 2 presents, only for the 1st day of campaigns, the results of "in situ" measurements of the sludge transported by the pumping system and in Figure 3 to Figure 5 the results obtained in the laboratory. In non-bathing season, the temperature remained regular, varying between 16 and 17 °C and the pH was slightly acid, ranging from 6.0 and 6.9, with a little tendency to decrease downstream. Regarding the redox potential, it ranged between -100 and -240 mV and the conductivity from 0.80 to 0.95 mS/cm. The dissolved oxygen concentration was close to zero. Concerning the laboratory results, in the upstream section, the concentrations of SO_4^{2-} was around 50 mg/L and the downstream section was around 20 and 30 mg/L. For the S_T, COD_T, TS and TVS parameters there was an increase over the pumping pipeline.

Table 2 – Results obtained "in situ" for the 1st day, non-bathing season.

| ID		1st DAY (6-2-2014)				
		Temp. (°C)	pH (-)	ORP (mV)	Cond. (mS/cm)	DO (mg/L)
Sample 1	LPTP 1	16.86	6.81	-109.58	0.82	0.88
	Discharge 1	16.76	6.68	-145.33	0.84	0.94
	SPTP 1	16.38	6.56	-194.40	0.84	1.23
Sample 2	LPTP 2	16.83	6.84	-92.10	0.83	0.60
	Discharge 2	16.68	6.69	-141.00	0.84	0.89
	SPTP 2	16.32	6.63	-191.28	0.84	1.08
Sample 3	LPTP 3	16.86	6.88	-107.20	0.83	0.52
	Discharge 3	16.67	6.70	-164.43	0.82	0.51
	SPTP 3	16.37	6.67	-175.08	0.84	0.91
Sample 4	LPTP 4	16.87	6.92	-90.65	0.82	0.44
	Discharge 4	16.63	6.73	-164.30	0.83	0.64
	SPTP 4	16.29	6.71	-171.10	0.83	0.97
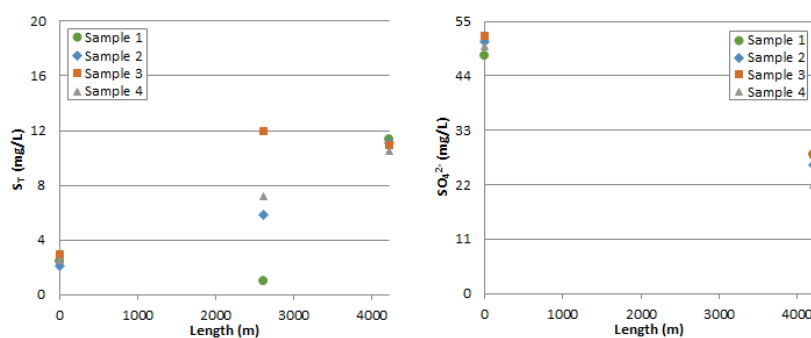
Figure 3 – Results obtained in the laboratory to S_T (left) e SO_4^{2-} (right) (6-2-2014).
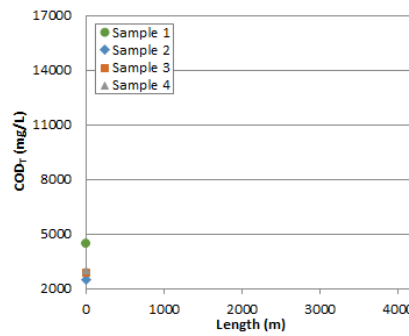
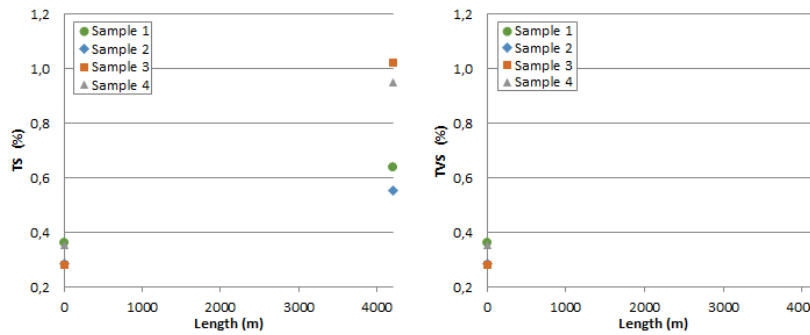Figure 4 – Results obtained in the laboratory to COD_T (6-2-2014).

Figure 5 – Results obtained in the laboratory to TS (left) e TVS (right) (6-2-2014).

In both days (6th and 25th of February), a ratio was found between the decrease of sulfates (ΔSO_4^{2-}) and the increase of sulfides (ΔS) as indicated in Table 3. In other words, the ratio $\Delta SO_4^{2-}/\Delta S$ takes systematically the value of 3, which shows that the biochemical reduction of sulfate ion has caused the sulfides formation in this sludge pumping system.

Table 3 – Auxiliary results for the rate between sulfates and sulfides, non-bathing season.

ID	1st DAY (6-2-2014)			2nd DAY (25-2-2014)		
	$\|\Delta SO_4^{2-}\|$ (mg/L)	ΔS (mg/L)	Relation $\|\Delta SO_4^{2-}\|/\Delta S$	$\|\Delta SO_4^{2-}\|$ (mg/L)	ΔS (mg/L)	Relation $\|\Delta SO_4^{2-}\|/\Delta S$
Sample 1	20	9	2	28	8	4
Sample 2	25	9	3	22	8	3
Sample 3	24	8	3	37	11	3
Sample 4	28	8	3	30	12	3
Average	24	9	3	29	10	3

Table 4 shows the results of the sulfides rate of formation (∆S/tr). The average rate of formation, referenced at 20 °C, is 1.7 mg/L.h and the real rate is 1.4 mg/L.h, corresponding the temperature of 16.6 °C, for a retention time of about 7 h.

Table 4 – Sulfides formation rate in the sludge pumping system, non-bathing season.

ID	1st DAY (6-2-2014)			2nd DAY (25-2-2014)		
	tr (h)	∆S/tr (mg/L.h)	∆S/tr a 20 °C (mg/L.h)	tr (h)	∆S/tr (mg/L.h)	∆S/tr a 20 °C (mg/L.h)
Sample 1	6.6	1.4	1.7	7.1	1.1	1.4
Sample 2	6.6	1.4	1.7	7.1	1.1	1.4
Sample 3	6.5	1.2	1.5	7.1	1.6	2.0
Sample 4	6.5	1.2	1.6	7.0	1.7	2.1
Average	6.5	1.3	1.6	7.1	1.4	1.7

The minimum, maximum and average results obtained from the measurements in the gas phase are shown in Table 5 in terms of hydrogen sulfide, methane and oxygen concentrations. Figure 6 shows the evolution of these parameters during the time for the four sampling done on the two days of campaigns. Overall, there was an increase in the concentration of hydrogen sulfide gas during pumping, for about 10 minutes (which are represented in gray in Figure 6), and a slow decrease during rest periods (lasting about 20 minutes). During pumping, the concentration of H_2S increased 1 ppm/min and 4 ppm/min, and during rest periods decreased 0.5 ppm/min and 2 ppm/min, respectively on the 1st and 2nd days. The reason for the difference to the average between these two days can be explained by the longer time without the addition of ferric chloride in the sludge well (in 2nd day the addition was interrupted at least 48 hours prior to the collections). In addition, the concentration of methane was constantly zero and the concentration of oxygen kept a constant value (21% of oxygen in air).

Table 5 – Results obtained in terms of H_2S, CH_4 and O_2 concentration in the gas phase, non-bathing season.

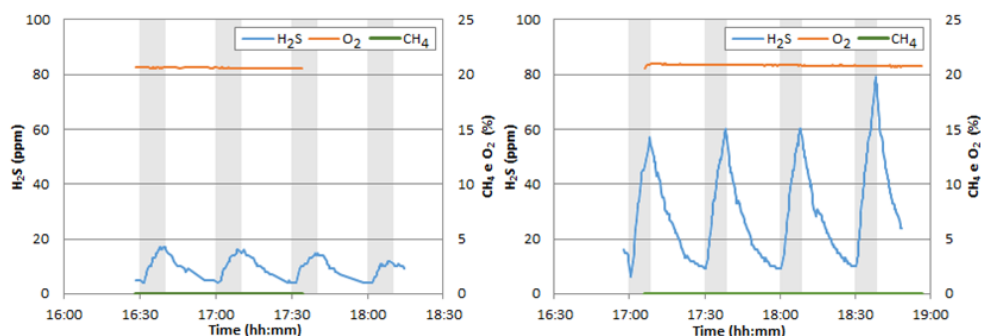|	1st DAY (6-2-2014)			2nd DAY (25-2-2014)		
	H_2S (ppm)	CH_4 (%)	O_2 (%)	H_2S (ppm)	CH_4 (%)	O_2 (%)
Minimum	4	0	20.6	10	0	19.3
Maximum	17	0	20.7	79	0	21.0
Average	10	0	20.6	40	0	20.9

Figure 6 – Concentration of H_2S, CH_4 and O_2 (1st day – left and 2nd day - right).

3.2   Results during bathing season

In the three days of campaigns, it was found that the temperature ranged between 22 and 24 °C, the pH continued slightly acid, between 6.5 and 6.8, the redox potential varied between -110 and -200 mV, the conductivity ranged between 1.35 and 1.50 mS/cm and the dissolved oxygen content was lower than 1 mg/L. The concentration of COD_T obtained ranged between 8 000 mg/L and 19 000 mg/L, and the formation of sulfides was always observed in the sludge pumping system. As an example, Table 6 shows the results of the "in situ" measurements only for the 2nd day (8-7-2014) and, in Figure 7, the ones obtained in the laboratory. The average sulfides' rate of formation, referenced at 20 °C, was also 1.7 mg/L.h, being the real rate of 1.9 mg/L.h, corresponding to the temperature of 22.8 °C and for a retention time of about 3 h.

Table 6 – Results obtained to 2nd day in summer season.

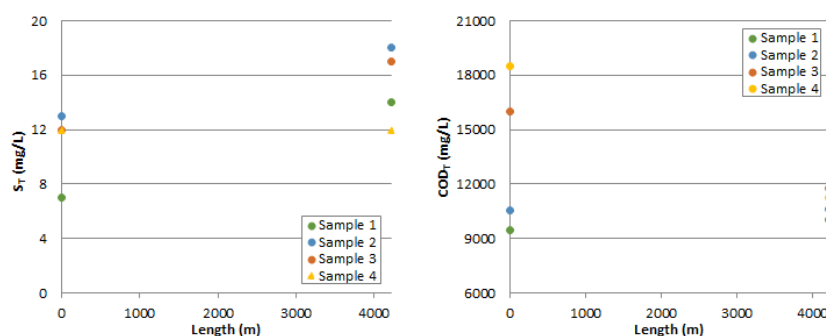| ID		2nd DAY (8-7-2014)				
		Temp. (°C)	pH (-)	ORP (mV)	Cond. (mS/cm)	DO (mg/L)
Sample 1	LPTP 1	22.50	6.68	-111.19	1.40	0.93
	SPTP 1	23.61	6.54	-111.16	1.42	0.92
Sample 2	LPTP 2	22.41	6.67	-125.13	1.42	0.48
	SPTP 2	23.00	6.56	-126.04	1.44	0.45
Sample 3	LPTP 3	22.35	6.68	-135.47	1.46	0.36
	SPTP 3	23.00	6.63	-137.29	1.50	0.35
Sample 4	LPTP 4	22.32	6.74	-139.48	1.49	0.32
	SPTP 4	23.21	6.62	-142.04	1.53	0.29

Figure 7 – Results obtained in the laboratory to S_T (left) e COD_T (right) (8-7-2014).

Table 7 shows the minimum, maximum and average concentration of hydrogen sulfide, with values between 1 and 7 ppm. As an example, Figure 8 presents the variation of hydrogen sulfide gas in the P3 section during the campaign on the 2nd day. The addition of ferric chloride in sludge well was stopped 24 hours before the beginning of the three days of campaign. However, the concentration of H_2S in the reception tank of sludge did not increase significantly during the pumping periods. This is probably by the pumping periods are higher, the rest periods are short and mainly because of the added reagents in the treatment of coagulation-flocculation step, in the summer season.

Table 7 – Results obtained of the concentration of H_2S in summer season.

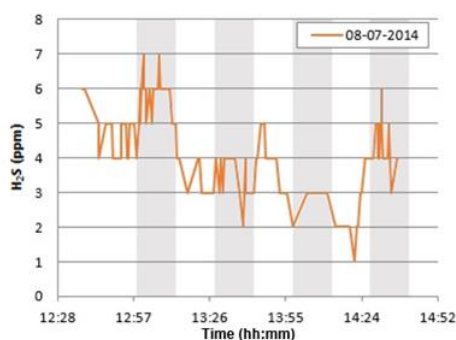|	H$_2$S (ppm)		
	1st DAY	2nd DAY	3rd DAY
Minimum	1	1	2
Maximum	5	7	6
Average	3	4	3

Figure 8 – H$_2$S Concentration evolution on the gas phase (2nd day).

4. Conclusion

The abundance of organic matter in the sludge pumping system resulted in the formation of sulfides independently of the values of COD in both periods, and the ratio between the variations SO_4^{2-} and S_T shows that sulfides formation is resulted by the biochemical reduction of sulfate ion.

Although the addition of ferric chloride in the sludge's well had been stopped over a dozen hours before each experimental campaigns, the background effects certainly conditioned the formation of sulfides and downstream consequences (offensive odors, corrosion). Additionally, the addition of reagents in the sedimentation and coagulation-flocculation processes, during the summer, also conditioned the release of hydrogen sulfide gas downstream the sludge pumping pipeline.

In both seasons, there a direct relationship between the discharge of sludge and the concentration of hydrogen sulfide gas was found in the reception tank of sludge. During periods of pumping, the concentration of hydrogen sulfide gas increased systematically and during rest periods, the concentration decreased, usually at a lower rate. The maximum and minimum concentration of hydrogen sulfide gas are believed to be conditioned by the starting and stopping of pumps, the air intake to treatment in deodorization and the condensation of hydrogen sulfide gas on the walls of the tank (corrosion).

In terms of total sulfides concentration, higher values were obtained in the bathing season (when compared to the non-bathing season), as a result of higher temperatures and flows, shorter retention time and the addition of reagents in wastewater treatment. However, the concentrations of hydrogen sulfide gas in the summer season were much lower than the ones obtained in non-bathing season. This is due to the precipitation of sulfides by the addition of reagents, which increased the total concentration but minimized the consequences downstream the pumping system, even with the addition of ferric

chloride being stopped in the sludge well for more than 48 hours before the campaigns. With these results, in the summer season, the effects of the presence of sulfides are mitigated by the characteristics of the system, thus can dispense the addition of ferric chloride in the well sludge.

The possible practical forms to control the risks associated with the release of hydrogen sulfide gas and/or minimize the addiction of reagents can be by reducing the periods of pumping with higher frequency of pumping per hour, increasing ventilation of air and varying the addition of ferric chloride in the well sludge, depending on the measurement of H_2S gas on the reception tank of sludge.

In future works, campaigns should include the addition of reagents to optimize the dosage of ferric chloride to be added to the sludge well, mostly for not-bathing season, and the continuous monitoring of H_2S gas concentration in the reception tank of sludge, as well as the measurement of ventilation flows. With these results it would be possible to devise a strategy that minimizes economic, social and environmental impacts.

References

American Society of Civil Engineers (1989). *Sulfide in Wastewater Collection and Treatment Systems.* ASCE Manuals and Reports on Engineering Practice No. 69, United States.

Environmental Protection Agency (1985). *Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants.* Design Manual, Washington.

Hvitved-Jacobsen, T., Vollertsen, J., Nielsen, A. H. (2013). *Sewer Processes - Microbial and Chemical Process Engineering of Sewer Networks.* CRC Press, United States.

Matias, N., Ferreira, F., Matos, J. S. (2013). *Odores, toxicidade e corrosão em sistemas de águas residuais – Potencialidades de aplicação de modelos de simulação.* 11º Simpósio de Hidráulica e Recursos Hídricos dos Países de Língua Portuguesa (11º SILUSBA), Maputo, Moçambique, 27-30 Maio.

Matos, J. S. (1992). *Aerobiose e septicidade em sistemas de drenagem de águas residuais.* Dissertação de Doutoramento em Engenharia Civil, Instituto Superior Técnico, Lisboa.