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Study of Dispersing Hydrogen Sulfide (H_2S) Generated from a Chemical Industry

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Nuisances caused by odors in industrial emissions are a problem with high frequency of community's complaints. Some industrial activities frequently emit small concentrations of odoriferous substances and these are often sufficient to affect the human olfactory system, which is highly sensitive. Odor emissions are less and less tolerated by society due to their effects on health and quality of life. Odorants emissions are becoming less tolerated by society due to their effects on health and quality of life. The present study aimed to evaluate the impact of odorous substances generated by gas emissions from a chemical industry, identifying odorous compounds by measuring the gases concentration levels and simulate their dispersion. At some points, fugitive H2S emissions were detected and it was noted that in the mapping plume concentration, depending on weather conditions, the plume could exceed the limits of the industry, generating uncomfortable in the population, even that the limits of perception of H2S were very low. The actions taken by the industry have been downplaying the problem, proven even by the environmental inspection local agency.

1. Introduction

The odor emitted by the chemical industry include a wide range of different chemicals. Regardless of structure or chemical function, the families of odoriferous substances confer a greater or lesser degree of perceived odor and a more or less nice feature to this perception (Carvalho, 2001).
According Antunes (2006), in general, the cause of the odor is associated with the presence of odorous compounds in the air, as a result of gaseous emissions of chemicals.
The transport and dilution of these pollutants in the micro and mesoscale depend on local weather phenomena and the influence of topography. In the process of atmospheric dispersion, major weather phenomena include wind, turbulence and atmospheric stability.
The present study aimed to evaluate the impact of odorous substances generated by gas emissions from a chemical industry, identifying odorous compounds by measuring the gases concentration levels and simulate their dispersion.

2. Materials and Methods

2.1 Characterization of the study area

The industry focus is characterized as a chemical company that converts part of oxhide, which is not used by tanneries in gelatine and hydrolyzed collagen. It has a total area of 69,270 m^2 with 12,000 m^2 of built area. The municipality to which the industry is inserted has a population of 66,290 inhabitants, with a population density of 77.70 inhabitants/km^2 (IBGE, 2010), little rugged, with hills and massive tabular and gently sloping hillsides. Its climate is temperate rain with dry winters (Aw in Köppen classification), with an average annual temperature of 23.1°C. Its location is north of the city, bordering the São Domingos Garden, located southwest of the company (Figure 1).

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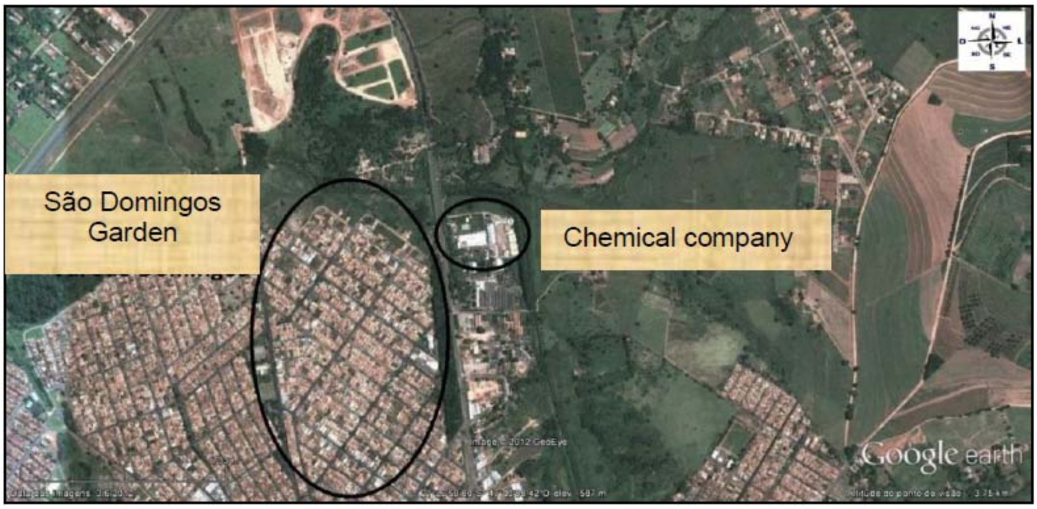

Figure 1: Location map chemical industry. Source: Google Earth (2013)

2.2 Odorous compounds, concentration and atmospheric dispersion

For the identification of odorant compounds was carried out an observational analysis, on-site, to identify possible broadcasting locations of odorant compounds present in the process (specific emissions, fugitive and evaporative), analyzing, from receipt of raw materials to the treatment of effluents.

The perception of greater odor intensities occurred in the region of the Effluent Treatment Plant, where is the Aerobics Lagoon and Biodigestor Anaerobic Upflow (UASB). In this region, it could be noticed a strong smell of rotten egg, related to the existence of hydrogen sulfide (H2S). The same perception was found, as applied questionnaire, which investigates odor perception by the population surrounding the odorant source (Silva Neto and Freitas, 2015). It is noticed also small amounts of gases like NH3, mercaptans, CH4 and some VOCs however, the industry's largest odor problem was the generation of H2S gas that it has become the focus of this study.

Preliminary measurements throughout the process were carried out and thus certain ten points as possible emitting hydrogen sulfide. A study of each point was carried out, determining the main characteristics related to the form of emission. To carry out the measurements of concentration, it was used a multi-gas portable detector QRAE II.

For each of the ten measured specific points, six measurements were conducted for five minutes each, for the concentration of H2S, with the detector always 1.5 m away from the emission source, so that the five measurements were obtained concentration peak, for each dot of each phase.

Based on the concentrations of the measured pollutant within the industry, were generated two hypothetical plumes to the emitted odors, using the SURFER 8.0 software. The first hypothetical plume was generated based on normal operating conditions of the industry and the second plume considering the drain operations and collection of samples for analysis, situations of great issue of H2S.

Aiming to simulate the dispersion of H2S, estimating their likely concentration in the industry environment, It was used the module software odors AID (Kawano, 2003). With this, it was possible to estimate the concentrations of pollutants through Gaussian models based on continuous and instantaneous emissions (type puff).

2.3 Activities in the industry to prevent odorous emissions

The actions undertaken by the industry were investigated and discussed, especially with regard to the emission of odors. It was surveyed to the changes in the production processes, through a systematic observation, document analysis and interviews with its employees.

Another issue investigated in this study were the nuisance complaints of H_2S odor, emitted by the company, registered in the Environmental Control Agency of the State of São Paulo (CETESB), by neighboring residents of the company.

3. Results and discussion

3.1 Study of the winds

The historical data obtained from the Agronomic Institute of Campinas (IAC), monitored from 1960 to 1991, shows the dominance of the North/Northeast winds, corresponding to geographical position of the industry in relation to São Domingos Garden. The historical monthly average speeds recorded from 1961 to 1990 are consistent with the year 2013. The average wind speed calculated from 1 January to 23 August 2013 was 2.0 m/s.

3.2 Continuous emissions

Figure 2 shows the average concentrations of H_2S for the six samples of peak concentration at each point of emission continues collected in the industry. These points correspond to sites where there is the presence of hydrogen sulfide gas under normal conditions of equipment operation.

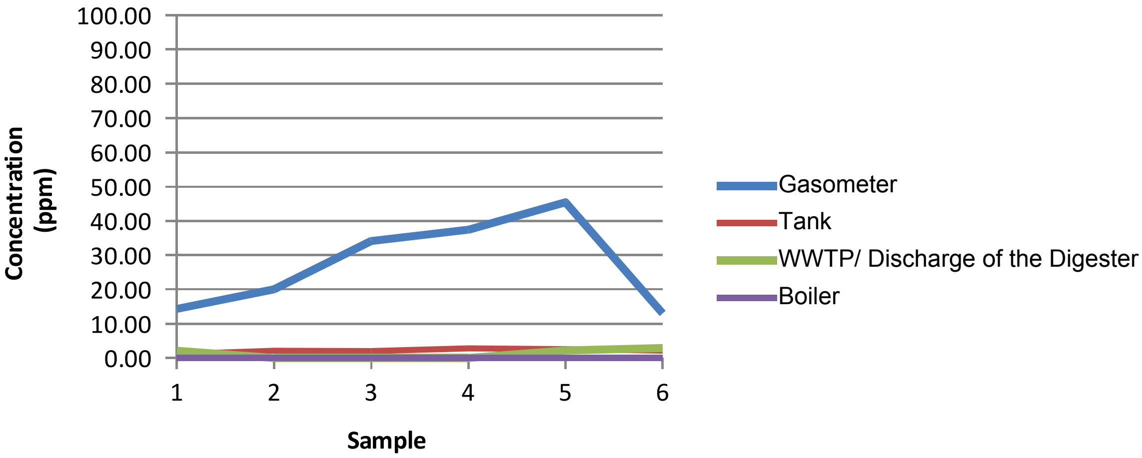

Figure 2: H_2S concentrations in normal operation

From Figure 2 can be seen the concentration of fugitive emissions, with H_2S values at Gasometer reaching 45.4 ppm. The average for the measurements was 27.4 ppm, an average high concentration for an emission that occurs continuously. This may be due, probably, to possible leaks in the flanges and gaskets biogas transport pipes. For the other sample points the concentrations found were significantly lower when compared to measures gasometer.

3.3 Intermittent emissions

Figure 3 depicts the concentrations measured in the drainage points or collection of material for analysis. These points release H_2S intermittently. It just occurs, in times that operations are being performed. The drainage points of the biogas line (1, 2 and 3) are points installed along the pipe between the living room of the Gasometer and Boiler, with an approximate length of 100 meters. The drains consisting of a ball valve, are designed to remove water droplets accumulated in the tubing. The variation in the concentration of H_2S measured as shown in Figure 3, it can be justified by air currents and positioning of the measuring apparatus. The values found for the three points are very high, sometimes extrapolating the measurement capability of the gas detector, corresponding to 100 ppm. The three points are purged three times daily, for approximately two minutes.

It was found that there is a big release of H_2S into the atmosphere in such procedures, since the purging is performed by opening the ball valve, releasing gas directly into the environment without any contention method.

Other sampling sites: Drain Flare, Drain UASB Biodigester and Drains Mixtures of Tanks, also had issues with high concentrations of H_2S.

It was possible to realize high concentrations in some samples in the Drain Flare, with a maximum of 66.8 ppm and average for six samples of 29.5 ppm. This wide variation in concentration may be due to saturation of the sodium hydroxide solution used to remove H_2S before firing because of the inefficiency of the oxidation process, resulting in the emission of H_2S in the purge operation. Greater control should be done so that such a situation would be avoided.

The high variations in H_2S concentrations in points Drain UASB Biodigestor (maximum of 39.2 ppm and 21.1 ppm average) and drain the tanks Mixtures (maximum of 52.9 ppm and 18.1 ppm average) may be due to changes in the formation of biogas inherent in the process occurring in the reactor.

It was found that the Biodigester used in WWTP was still not operating at full capacity. Therefore, a mixture of effluent with water was carried out by feeding the Biodigester. The equipment responsible for this operation are the mixing tanks which are responsible for maintaining the recirculation of the digester solution and perform the necessary correction of the pH by the sulfuric acid dosing. These variations may be due to the effluent mixing ratios with water in recirculating Biodigester not be well controlled.

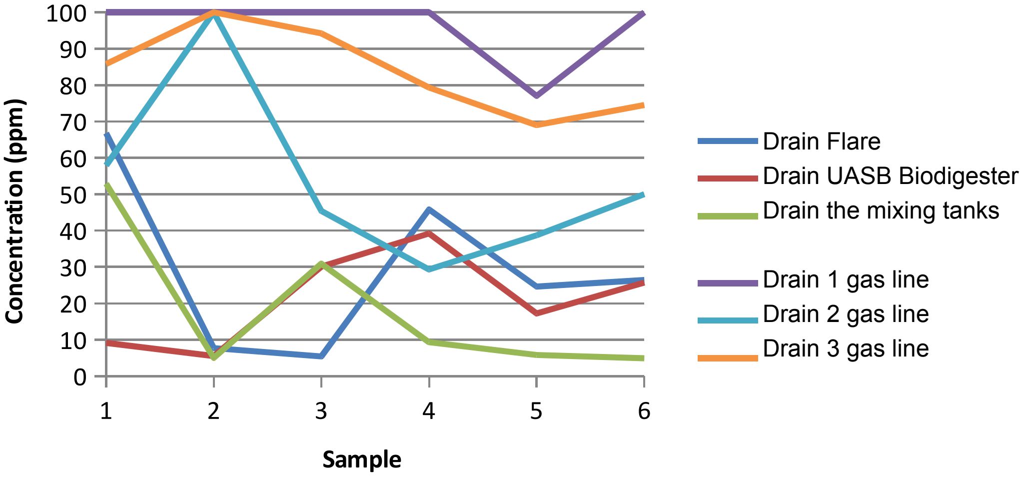

Figure 3: H_2S concentrations in drainage conditions and sampling

3.4 Plumes of H_2S concentration in industry

Through the Figures 4 and 5, it was observed the concentration of H_2S on the industry in two conditions. The first (Figure 4) represents the estimate of the generated plume in normal industrial operation, taking into account only the emissions of the Gasometer, Tank , Biodigester Discharge in WWTP and Boiler. Without taking into account the climatic conditions, it is observed that the plume has a higher concentration close to where is the Gasometer, with concentrations around 28 ppm. Next to the company's limits, the concentration is close to zero.

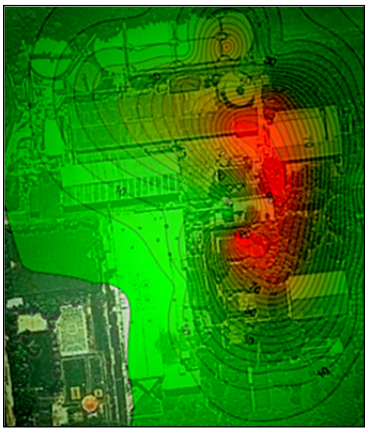

Figure 4: Chemical Industry and the H_2S concentration plume (ppm) under normal operating conditions

Figure 5: Chemical Industry and the H_2S concentration plume (ppm) in extreme conditions - drain and sampling

3.5 H_2S dispersion of the estimate in the atmosphere of the neighborhood

The dispersion of H_2S in the atmosphere was estimated by Mathematical Modeling.

Adding the maximum concentration of H_2S in the 10 sampling points, it has been estimated at a total concentration of 489 ppm. An average rate of emission of H_2S to fugitive emissions for fencing of 2,200 g/h was also estimated (EPA, 1995).

Some hypothetical conditions were established to simulate the concentration of pollutants:

- A point source was defined like a chimney 0.5 m in diameter and 1.5 m in length;
- The velocity of the flue gases was estimated as the historical average wind speed in the region;
- Briggs equations were used to calculate the elevation of the plume above the chimney, according to EPA (1995).

Table 1 sets out the parameters used to estimate the plume in the area studied.

Table 1: Parameters used to estimate the concentrations of the AID

Pollutant name issued	odours	------
Emission rate	0.00061	g/s
Temperature of the gases in the chimney (tc)	25	°C
Flue gas velocity (vc)	2	m/s
Chimney diameter (d)	0.5	m
Physical chimney height (h)	1.5	m
Region	Urbana	------
Extension of the square area under study	800	m
Type Gaussian model for calculating the dispersion	Model for instant emissions	------
Calculation elevation of the plume above the chimney in accordance with the equation:	Briggs	------
Receiver position to source	SW-South-west	------
Distance from the source to the receiver (x)	120	m
Receptor height (z)	10	m
Class of atmospheric stability	F-Moderately Stable	------
Wind speed (v)	2	m/s
Wind direction	NE-Northeast	------
Atmospheric pressure (Patm)	689,7	mmHg
Air temperature (tar)	25	°C
Wind speed corrected the stack height (vf)	1.915531039	m/s
Height where the wind was measured	2	m

The highest concentration after 2 min of emission puff was 0.1884 g/m^3, according to the AID software, equivalent to 0.00014 ppm. Figure 6 graphically illustrates this simulation.
It was observed that the greatest concentration is found in the neighborhood close to the perception limit of individuals to H_2S, which is 0.00042 ppm. The results presented in the questionnaire (Silva Neto and Freitas, 2015) indicated that 49.3% of individuals perceive the odour. This discrepancy can be explained by the following factors:
- H_2S leak points underestimated: concentrations were measured in 10 specific points, not taking into account the leakage in pipes and joints of the wastewater treatment system;
- Maximum capacity of reading of 100 ppm gas detector: at some points the concentration reached the maximum detector, masking the actual result;
- Odour memory effect: the persistence of the odour in the individual's memory, even if it ceases to exist.
Thus, using a device with greater measurement capability and expanding the measuring points of fugitive emissions are likely to reach an estimate of concentrations perceived by the surrounding population, confirming the results reported by questionnaire (Silva Neto and Freitas, 2015).

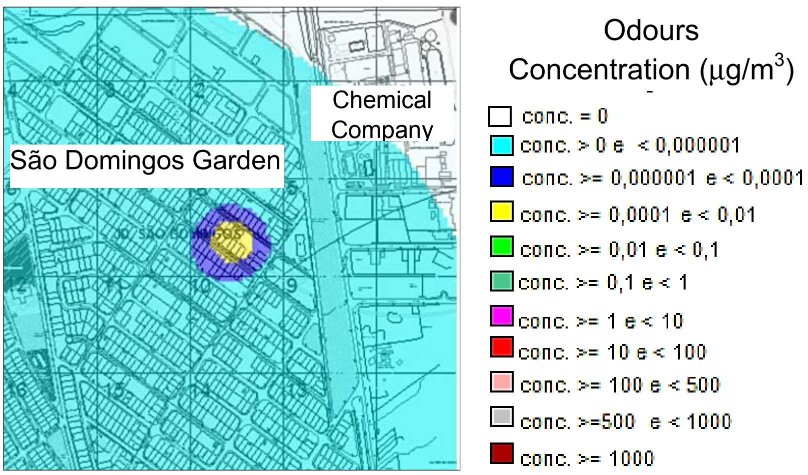

Figure 6: Odours concentration Plume disposed on the São Domingos Garden

3.6 Industry and prevention of odorous emissions

Industry is certified ISO 22000, Standard for Food Safety Management System Certification, and follows the prerequisites of ISO 14000 Standards (environment), OHSAS 18000 (Health and Safety).

Due to the need to comply with existing standards, Social Responsibility, concern for sustainability and also with the quality of life of the individual as a whole, a fact confirmed by the very company slogan - "Improving Quality of Life" - "Improving Quality of Life "- a number of actions were taken in pursuit of improvement, as shown by Table 2.

Table 2: Macro Schedule of actions taken by the industry

Year	Implemented action
2002	Creation, maintenance and Green Areas Preservation around Industry
2007	Expansion of Fertigation System
2008	Biofilter installation - Reception of Raw
2009	Installation Anaerobic Reactor with Burning System (Biodigester UASB)
2009	Installation Anaerobic Reactor with Burning System (Biodigestor UASB) - WWTP
2009	Biofilter installation - WWTP
2011	Startup Biogas burning system for steam generation
2011	Installation truck parking Raw Materials in Industrial District II (out of town)

4. Conclusions

At some points, fugitive H2S emissions were detected and it was noted that by mapping a plume concentration, depending on weather conditions, the plume could exceed the limits of the industry, generating uncomfortable in the population, since the limits of perception of H2S are very low. The actions taken by the industry is having effect and minimizing the problem seems a concrete fact, attested even by the local environmental inspection agency.

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