

Human Exposure to hydrogen sulphide Concentrations Near Wastewater Treatment Plants

Ana Flavia Locateli Godoi^a, Anderson Marlon Grasel^a, Gabriela Polezer^a, Andrew Brown^b, Sanja Potgieter-Vermaak^{b,c}, Débora Camargo Scremim^a, Carlos I. Yamamoto^d, Ricardo Henrique Moreton Godoi^{a*}

^a Environmental Engineering Department, Federal University of Parana, 210 Francisco H. dos Santos St., Curitiba, PR, 81531-980 Brazil.

^b Division of Chemistry and Environmental Science, Manchester Metropolitan University, Manchester, M1 5GD, UK.

^c Molecular Science Institute, University of the Witwatersrand, Johannesburg, South Africa.

^d Chemical Engineering Department, Federal University of Paraná/ UFPR, Curitiba, Paraná, Brazil.

* Corresponding author. Tel.: +55 41 3361 3482. E-mail address: rhmgodoi@ufpr.br

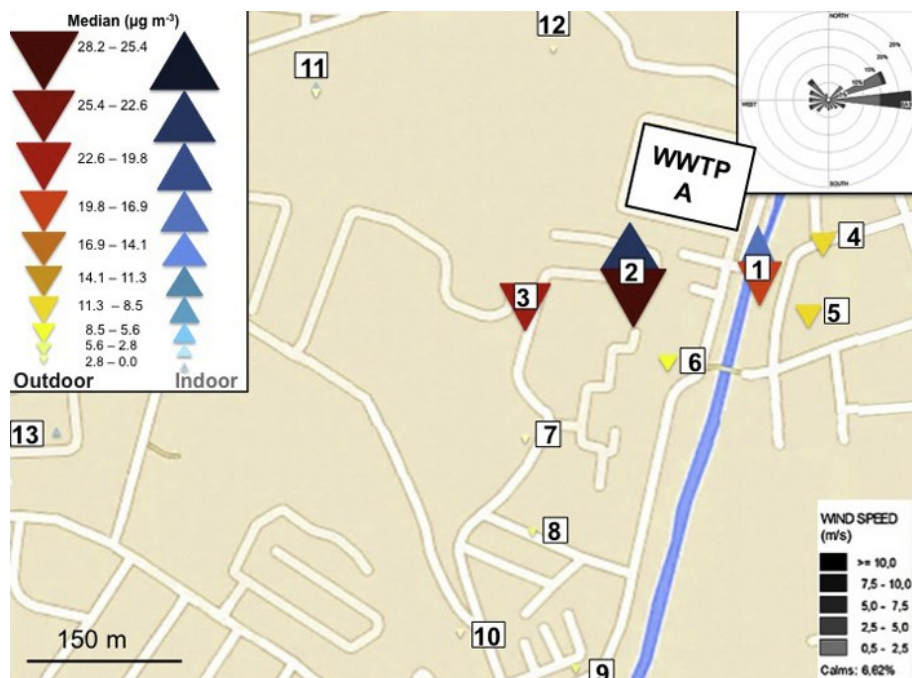
Abstract

The hydrogen sulphide (H₂S) levels from wastewater treatment plants (WWTPs) in Curitiba, Brazil have been quantified for the first time. H₂S generated by anaerobic decomposition of organic matter in WWTPs is a cause for concern because it is an air pollutant, which can cause eye and respiratory irritation, headaches, and nausea. Considering the requirement for WWTPs in all communities, it is necessary to assess the concentrations and effects of gases such as H₂S on populations living and/or working near WWTPs. The primary objective of this study was to evaluate the indoor and outdoor concentration of H₂S in the neighbourhood of two WWTPs located in Curitiba, as well as its human health impacts. Between August 2013 and March 2014 eight sampling campaigns were performed using passive samplers and the analyses carried out by spectrophotometry, presenting mean concentrations ranging from 0.14 to 32 µg m⁻³. Eleven points at WWTP-A reported H₂S average concentrations above

the WHO recommendation of $10 \mu\text{g m}^{-3}$, and 15 points above the US EPA guideline of $2 \mu\text{g m}^{-3}$. At WWTP-B the H_2S concentration was above US EPA guideline at all the sampling points. The I/O ratio on the different sampling sites showed accumulation of indoor H_2S in some instances and result in exacerbating the exposure of the residents. The highest H_2S concentrations were recorded during the summer in houses located closest to the sewage treatment stations, and towards the main wind direction, showing the importance of these factors when planning a WWTP. Lifetime risk assessments of hydrogen sulphide exposure showed a significant non-carcinogenic adverse health risk for local residents and workers, especially those close to anaerobic WWTPs. The data indicated that WWTPs operated under these conditions should be recognized as a significant air pollution source, putting local populations at risk.

Keywords: Hydrogen Sulphide, Air pollution, Odour, Anaerobic wastewater treatment, Health risk.

Graphical abstract:



1. Introduction

Human activities have contributed significantly to increased emissions of air pollutants at global, regional and local scales. It is important to know the source and concentration of pollutants for better pollution control and to assess the potential effects on human health.

H₂S is a colourless gas with a strong odour of rotten eggs produced under anaerobic conditions by organic matter decomposition from both natural (petroleum, volcanic) and anthropogenic sources (oil refining, wood pulp production, tanning industry) (WHO, 2000). Anaerobic wastewater treatment plants (WWTPs) and the degradation processes in landfills are significant sources of H₂S (Redondo et al., 2008; Capelli et al., 2009; Muñoz et al., 2010). Of the ten largest WWTPs existing in the world, eight are operational as anaerobic treatment facilities (Reynolds, 2012). Under anaerobic conditions, the biological reduction of sulphate to sulphide essentially occurs in the submerged part of sewers (Parande et al., 2006). Hydrogen sulphide emission is a physicochemical process involving both the water and air phases of sewer networks and is dependent on pH, temperature, hydraulic conditions of the water phase (Yongsiri et al., 2005). Only H₂S can be transferred to the air–water interface, resulting in an increase in the emission of H₂S from wastewater to the sewer atmosphere (Fu and Shen, 1990).

Unpleasant odours from WWTPs may cause acute social and economic conflicts due to poor quality of life and economic depreciation of the neighbouring real estate (Stellacci et al., 2010). Nuisance complaints about the odour emitted by WWTPs are registered in different parts of the world (Aristu, 2009; Billings, 2012; Wall, 2011). Besides the obvious unpleasant odour, the dominant cause for concern regarding H₂S pollution is its documented toxicity to humans. H₂S pollution effects are dose-related and can be detrimental to the nervous, cardiovascular and respiratory systems. Acute high-level concentration exposure can lead to eye damage, olfactory paralyzing perception, respiratory irritation, as well as pulmonary oedema, convulsions and even death (WHO, 2000). The long-

term exposure to low-level concentrations also affects human health negatively, e.g., causing nausea, headaches and respiratory problems (Lebrero et al., 2011).

As the nuisance H₂S odour threshold has been reported to be in the ranges 0.7 – 200 µg m⁻³, it is recommended to maintain levels at or below the lower limit to avoid community complaints (WHO, 1981). It has been established that daily inhalation exposure to H₂S has to be below 2.0 µg m⁻³ to ensure lifetime risk abatement (USEPA, 2003). Having said that, the World Health Organisation recognises the fact that information on the effects that long-term low dosage exposure to ambient H₂S is scanty (WHO, 2000). It therefore remains of interest to evaluate the air quality in terms of its H₂S content close to WWTP's.

This paper aims to provide data on the indoor and outdoor concentration of H₂S in the neighbourhoods of two WWTPs in Curitiba, Brazil. This provided baseline data that could serve as a reference point for future research. The data obtained were used in a risk-assessment protocol to estimate the likely effect on human health of the residents over a lifetime of exposure. This information can be used to aid local governmental policies, provide baseline data that could inform future changes in operation, as well as assist in future planning for new plants.

2. Experimental

As there have been complaints regarding unpleasant odours at and around the plant, the investigators decided to start the analysis of the air quality by monitoring H₂S levels, as it is also the main pollutant from degradation processes causing nuisance odours.

2.1 Sampling methodology

To protect the identity of the WWTPs, they will be referred as WWTP "A" and WWTP "B". These plants treat wastewater volumes of 560 L s⁻¹ and 1680 L s⁻¹ for A and B, respectively. Both wastewater treatment plants (WWTP) process mainly domestic Municipal wastewater through a conventional setup. The preliminary treatment aims to remove bulky and large solids, thus preconditioning

the effluent for the following treatment steps, including screening, flocculation, and flow equalization. In sequence, within the named primary treatment, sedimentation and/or flotation are employed to remove effluent's suspended and colloidal fractions. At the secondary treatment, the organic matter is removed through a biological process called Fluidized Bed Anaerobic Reactor (FBAR, or RALF in Portuguese), a Brazilian version of the Upflow Anaerobic Sludge Blanket - UASB. The hydraulic retention time at this step is only 8-10 hours, resulting in 65-75% organic matter removal efficiency. With the tertiary treatment, using iron chloride, some nutrients such as nitrogen and phosphorous, residual suspended solids, inorganics, and refractory organics that may have escaped from previous stages, are removed. Finally, the disinfection removes pathogens by chlorination. The sludge produced at the secondary step is also treated through thickening, dewatering, drying, and digestion in order to reduce its volume as well as to biologically stabilize the final product, which is usually then sent to landfills (although it also may be used as fertilizer).

H₂S was sampled using radial diffusion passive samplers (Radiello®, Fondazione Salvatore Maugeri, Padova, Italy). This sampler comprises a zinc acetate impregnated polyethylene adsorbing cartridge, surrounded by a cylindrical microporous diffusive body mounted on a supporting plate. When H₂S contacts the zinc acetate, it is converted to stable zinc sulphide, which is later extracted and assayed by sulphide ion (Pavilonis et al., 2013). Sampling took place for seven consecutive days. The temperature was recorded every 20 min during the weekly sampling campaigns.

Sampling was performed in houses and schools near the two WWTPs, which are located in two different residential areas in Curitiba.

Eight sampling campaigns were carried out, as listed in Table 1. Samplings locations were assigned as A1 to A13 for WWTP "A", and B1 to B5 for WWTP "B". Besides point A1 that was assessed during all campaigns, locations of WWTP "A" were evaluated in campaigns 1 to 4, and points of WWTP "B" in campaigns 5 to 8. Residential accommodation near the WWTPs has little or no insulation between the roof and walls, allowing easy diffusion of H₂S into the house.

Table 1 Collection period, season and sampling locations for each campaign.

Campaigns No.	Collection Period	Season	Sampling Locations ID	
			Indoor	Outdoor
1	06-20 August 2013	Winter	A1, A2, A11, A13	A1 to A12
2	20-27 August 2013	Winter	A1, A2, A11, A13	A1 to A12
3	13-18 December 2013	Summer	A1, A2, A11, A13	A1 to A12
4	06-13 February 2014	Summer	A1, A2, A11, A13	A1 to A12
5	17-24 February 2014	Summer	A1, B1, B2, B3, B5	A1, B1, B3, B4
6	28 Feb- 06 March 2014	Summer	A1, B1, B2, B3, B5	A1, B1, B3, B4
7	19-24 March 2014	Summer	A1, B1, B2, B3, B5	A1, B1, B3, B4
8	24-31 March 2014	Summer	A1, B1, B2, B3, B5	A1, B1, B3, B4

The sampling points were chosen based on three basic criteria: location with respect to the pollution source (WWTP) and the main wind direction, electrical support, and security against vandalism and theft. Table 2 presents the sampling points distances from the WWTP's.

Cartridges were installed at a height of 1.5 m inside residences, after permission was gained from residents. To enable a comparison between inside and outside air quality, samplers were positioned on the outside of the residences at an average height of 2.0 m. Radiello shelters (specifically designed for the diffusion tubes) were used to protect the samplers from precipitation. The Radiello samplers were exposed to air for a period of 15 days, after which the cartridge was removed from the diffusive body, sealed in its original tube and stored below 4 °C for analysis.

Table 2 Sampling points distances from WWTP's

Sampling Point	Distance from WWTP (m)
A1	101
A2	75
A3	179
A4	137
A5	172
A6	206
A7	345
A8	430
A9	565

A10	575
A11	481
A12	281
A13	790
B1	94
B2	70
B3	92
B4	99
B5	99

2.2 Analytical methodology

Cartridges were desorbed with 10 mL of ultrapure water followed by 0.5 mL of ferric chloride-amine solution. After stirring for 2 minutes, the samples were left to react at room temperature for 30 minutes.

The leachate solutions of H₂S samples were analysed using a spectrophotometer (Cary 50 Bio UV/Visible Spectrophotometer, Varian Inc., Australia) at a wavelength of 665 nm. The detailed extraction procedure is described in Fogo and Popowsky (1949). A calibration curve was prepared with eight points in triplicate using standard methylene blue solution (Sigma-Aldrich, St. Louis, MO). The calibration curve had linear correlation coefficient $R^2 > 0.995$, indicating that 99.5 % of the points can be described by the regression line. The analytical detection limit ($3 \mu\text{g L}^{-1}$) was determined as $3 \times \text{S.D.}/S$, where S.D. is the standard deviation of six blank samples (Procedural blanks were prepared as follows: unexposed cartridges from the same batch to those that were exposed were submitted to the same analysis protocol than the exposed cartridges) measurements and S is the method sensitivity given by the slope of calibration curve.

2.3 Health risk assessment for H₂S exposition

The data obtained was subjected to a health risk assessment using the Risk Assessment Information System (RAIS, 2013), which is based on a method created by the United States Environmental Protection Agency (USEPA, 1989; USEPA, 2013). The input parameters were similar to those quoted in Godoi et al. (2013). RAIS models both carcinogenic and non-carcinogenic (hazardous

quotient - HQ) adverse health risks. However, only HQ assessment was carried out for H₂S as it is not a carcinogen. The hazard quotient equations are listed below:

$$HQ = \frac{CDI_{HQ}}{RFC_i} \dots\dots\dots \text{Equation (1a)}$$

$$CDI_{HQ} \left(\frac{mg}{m^3} \right) = \frac{C \left(\frac{\mu g}{m^3} \right) \times ET \left(\frac{hours}{day} \right) \times EF \left(\frac{days}{year} \right) \times ED (years)}{ED (years)} \times \frac{1 \text{ days}}{24 \text{ hours}} \times \frac{1 \text{ years}}{365 \text{ days}} \times \frac{1000 \mu g}{1 \text{ mg}} \dots\dots \text{Equation (1b)}$$

The input values were H₂S concentrations in μg m⁻³ (C), exposure durations (ED - years), exposure frequency (EF - days/year), exposure time (ET - hours/day), and lifetime (LT - years). Besides that, the models use the Reference concentration of inhalation (RFC_i) value in mg m⁻³ for H₂S provided on the US EPA website (USEPA, 1989; USEPA, 2013).

Furthermore, different cohorts were identified; each with different input values (Table 3). Cohort 1 represents residents, who live and work in the area. Cohort 2 denotes a resident that lives in the area but studies or works away from WWTPs and Cohort 3 characterizes a person that works near WWTPs but resides quite a distance from the plant.

Table 3 Exposure considerations for assess each cohort health risk due to H₂S.

	Cohort 1	Cohort 2	Cohort 3
EF (days/year)	350	350	225
ET(hours/day)	24	15	8
ED (years)	1	1	1

The HQ assumes that there is a level of exposure, below which it is unlikely that an adverse non-carcinogenic health effect will be experienced. As the HQ is the ratio of the exposure level at a site to the reference dose, an HQ < 1 indicates that there is no significant risk of non-carcinogenic effects. On the other hand, an HQ > 1 means that there is a chance of non-carcinogenic effects occurring, with a probability that tends to increase as the value of HQ increases.

3. Results and Discussion

3.1 Indoor and outdoor H₂S concentrations

The indoor and outdoor concentrations (illustrated in Figures 1 and 2) showed that in general, both sampling areas showed similar results. As both plants operate under anaerobic conditions and have no effluent gas treatment system this result is not surprising. The waste water treatment process, as discussed in the introduction, can explain the relatively high concentrations observed.

H₂S indoor and outdoor concentration values for WWTP “A”, summarized in Fig. 1, ranged from 0.14 $\mu\text{g m}^{-3}$ to 32 $\mu\text{g m}^{-3}$. With just a few exceptions, mean concentrations of H₂S were mostly above levels recommended by USEPA (2.0 $\mu\text{g m}^{-3}$) suggesting potential adverse effects on human health. For sampling sites < 200 m from the plant, the concentration is substantially higher and ranged from 8 – 30 $\mu\text{g m}^{-3}$. Moreover, 89% of the samples collected in close proximity of the WWTP “A” had concentrations above 0.7 $\mu\text{g m}^{-3}$ and therefore could result in complaints from the community due to odour nuisance.

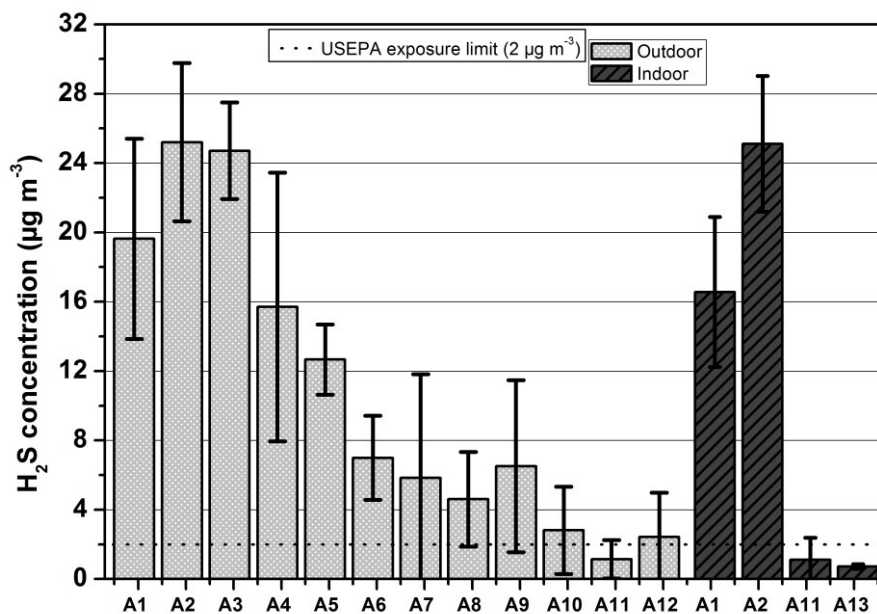


Fig. 1 Average and standard deviation of H₂S concentrations between the 4 campaigns (except for A1 that had 8 campaigns) for each sampling point at WWTP “A”.

H₂S concentration values ranged from 4.5 µg.m⁻³ to 18 µg.m⁻³ at the WWTP “B” sampling sites and are illustrated in Fig. 2. Average indoor and outdoor concentrations were above USEPA recommended levels (indicated in Fig. 2) for all the sampling sites. All the sampling sites for WWTP “B” were at similar distances from the plant and differed only in their geographical position to the plant. It is expected that the different concentrations are due to the predominant wind direction rather than distance as was the case with WWTP “A”. It is noticeable that high outdoor concentrations relates to high indoor concentrations and once again suggests possible adverse health effects in residents.

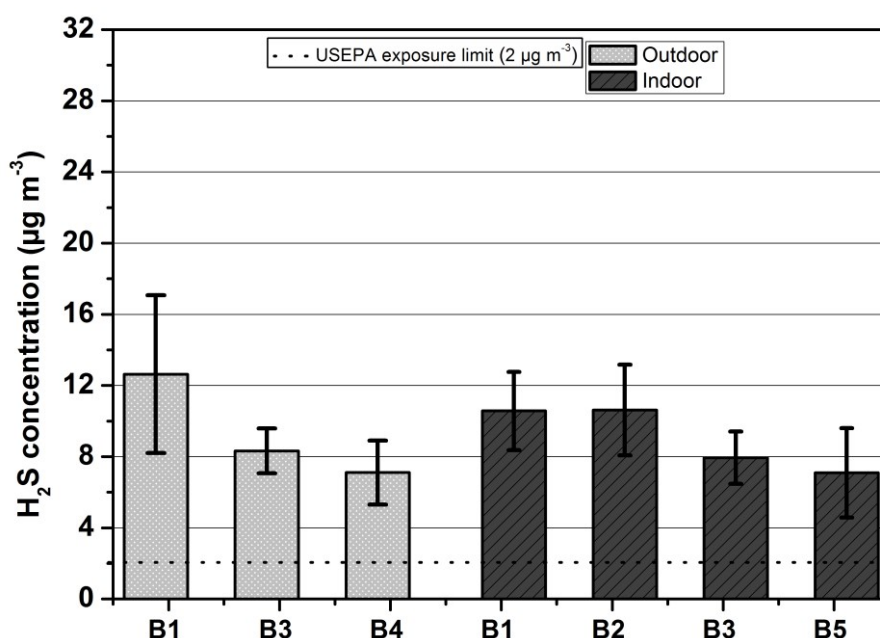


Fig. 2 Average and standard deviation of H₂S concentrations between the 4 campaigns for each sampling point at WWTP “B”.

The results obtained in our study are comparable with data reported by Stuetz et al. (1999) in the United Kingdom and Delgado et al. (1999) in Spain. All of whom found concentrations ranging from 5 to 15 µg m⁻³, near a WWTP. Zarra et al. (2008) in Italy, observed levels below those observed in this study but linked the presence of odorous compounds in ambient air with decreased tourism and economic activity. On the other hand, much higher concentrations were reported by Kim et al. (2013) in South Korea (around 80 µg m⁻³) and Dincer and Muezzinoglu (2007) in Turkey (ranging from 39 to 700 µg m⁻³).

A recent survey revealed that complaints about the odour emitted by WWTPs are reported all over the world (Heaney et al., 2011; Giuliani et al., 2013; Bruno et al., 2007) suggesting that the problem is not exclusive to tropical, undeveloped, or developing countries. Our results indicated concentrations several orders of magnitude above the background level, which is accepted as $0.3 \mu\text{g m}^{-3}$ for H_2S in air and above the threshold of perception of the odour, which is $0.7 \mu\text{g m}^{-3}$ (WHO, 1981).

To observe the influence and relationship of the geographical location of the sampling sites from the WWTP on the level of pollution, the sampling sites as well as the wind direction at each WWTP are displayed in Figures 3 and 4. The level of pollution is indicated by the size of the triangle so that hot spots can easily be observed. The more distant sites (A7-A13) at WWTP "A" were observed to have the lowest H_2S concentrations and ranged between 0 and $2.8 \mu\text{g m}^{-3}$. The intermediate distance sampling sites (A4 and A5) had concentrations between 8.5 and $11 \mu\text{g m}^{-3}$ and those nearest to the plant had the highest level of H_2S pollution, as expected and eluded to in the previous paragraph. However, despite being the closest point, site A1 does not exhibit the highest median H_2S concentration, suggesting the competing role of wind direction. As discussed previously, this was also evident for WWTP "B", where downwind sites showed the highest observed concentrations (Fig.4).

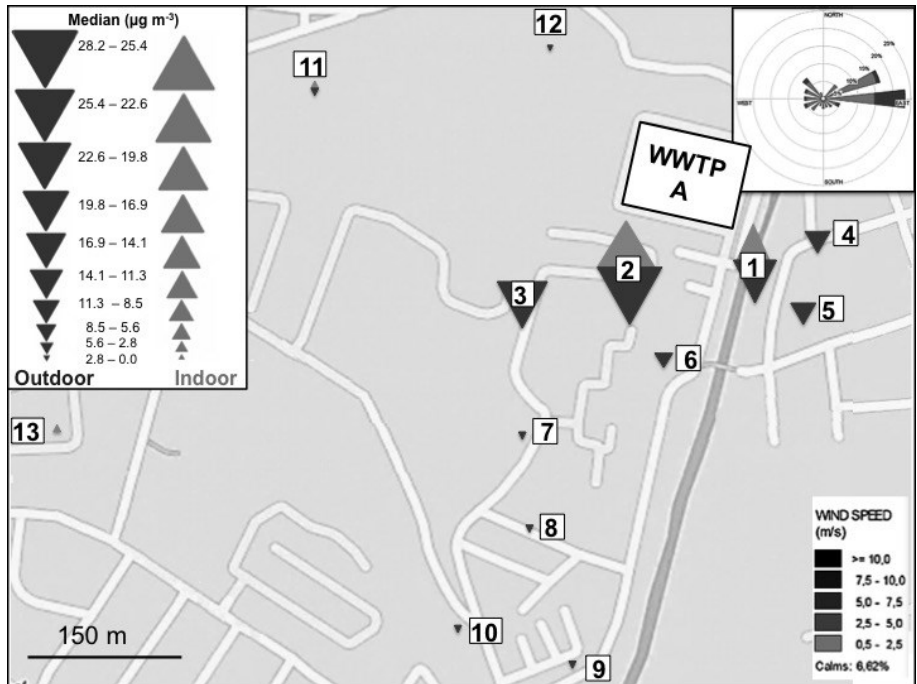


Fig. 3 Geographic distributions of indoor (up light grey triangles) and outdoor (down dark grey triangles) H_2S median concentrations for each sampling site in WWTP “A” area. The larger the size of the triangles the higher the concentrations.

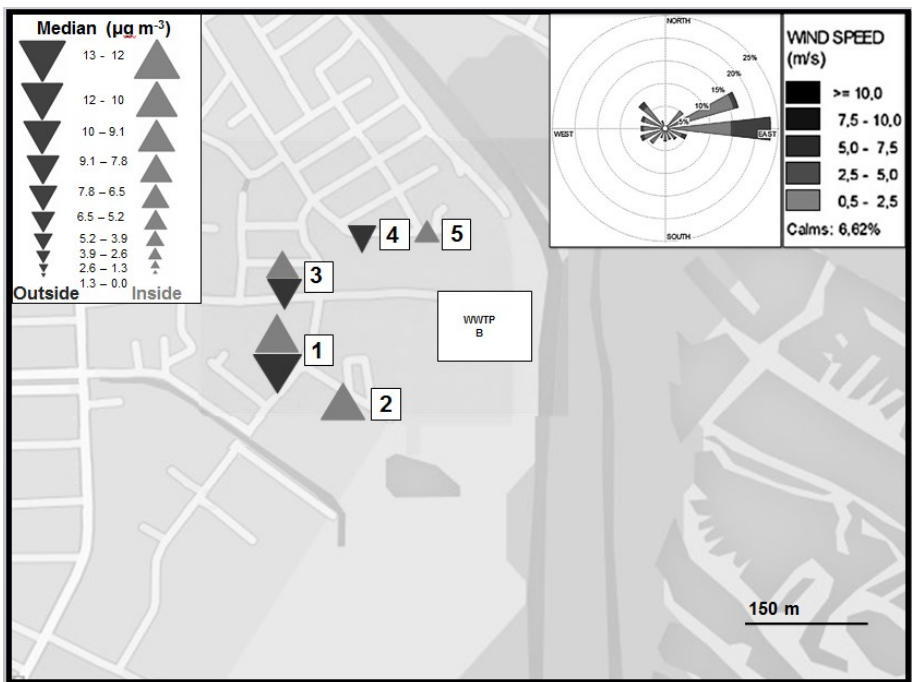


Fig. 4 Geographic distributions of indoor (up light grey triangles) and outdoor (down dark grey triangles) H_2S median concentrations for each sampling site in WWTP “B” area. The size of triangles represents concentrations.

To attempt a direct comparison between the two plants some of the measurement campaigns were run simultaneously. Table 4 presents the H₂S results obtained at sampling points A1 and B1 to B5, all at a distance ≤ 100 m, albeit in different geographical orientations.

Table 4 Indoor and Outdoor H₂S concentrations (µg.m⁻³) of 4 summer campaigns during which sampling took place simultaneously at the two plants investigated

	Campaign 5	Campaign 6	Campaign 7	Campaign 8
A1 – IN	16.1	18.8	11.8	17.1
A1 – OUT	15.3	23.9	11.1	19.6
B1 – IN	12.2	13.3	9.0	7.7
B1 - OUT	16.1	17.8	6.6	9.8
B2 – IN	13.9	12.5	10.5	5.6
B3 – IN	10.9	7.3	7.3	6.3
B3 - OUT	8.8	10.3	8.1	6.0
B4 - OUT	8.7	9.1	5.6	4.8
B5 - IN	8.2	11.0	4.5	4.7

Overall, the concentration levels across the 4 campaigns, where sampling was taking place simultaneously at the two plants, correlated reasonably well with each other with correlation coefficients (R²) ranging from 0.6 – 0.91. The poorest correlation was observed between campaigns 6 and 7, and the best between campaigns 6 and 8. If the data is separated into indoor and outdoor concentrations, the correlations changed. The indoor correlations improved and ranged between 0.69 (campaigns 7 and 8) and 0.99 (campaigns 5 and 7), as well as the outdoor correlations which varied between 0.4 (campaigns 5 and 7) and 0.96 (campaigns 6 and 8). Since the general tendency is good correlations for indoor concentrations but poorer correlations for outdoor concentrations, it is reasonable to postulate that indoor concentrations seemed to be buffered and less subject to fluctuations. This is of great concern for residents spending a lot of time indoors. If WWTP “A” is correlated with WWTP “B”, it is found that the indoor correlation coefficient was 0.17 and for outdoor 0.56, therefore reporting little correlation. On inspecting the concentration values this phenomenon is seen

due to concentrations at WWTP “B” dropping during campaigns 7 and 8. Taking into consideration that WWTP “B” has a higher volume throughput in comparison with WWTP “A”, it would be expected to produce higher concentrations. This is not observed from the data, but rather the contrary, whereby average concentrations at A and B are 16.7 and $9.2 \mu\text{g m}^{-3}$, respectively. This led us to deduce that concentration levels at each plant, and therefore the exposure levels, are determined by the microenvironment of the plant.

3.2 Evaluation of climate interference in H₂S concentrations

Figure 5 indicates the role of climatic conditions, by plotting outdoor concentrations of H₂S in WWTP “A” for sampling campaigns 1 and 2 (winter season), and 3 (summer season). The WWTP “B” had no campaign running during the winter season thus has no comparable climate data.

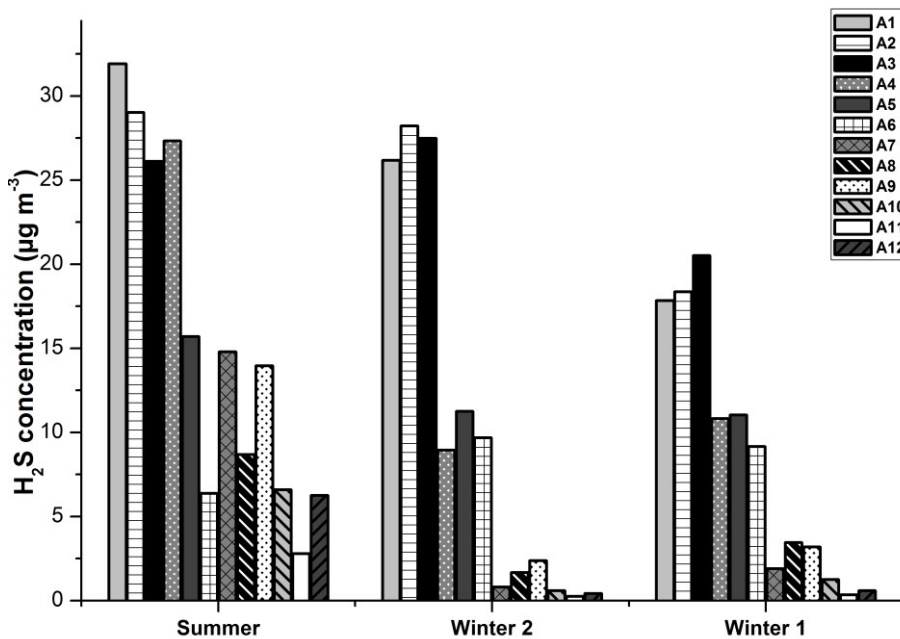


Fig. 5 The seasonal variance in H₂S concentration between the 12 outdoor sites at WWTP “A” during the summer (air temperature of 28°C), and winter campaigns 1 and 2 (air temperature of 13°C and 16°C , respectively).

Higher atmospheric temperatures increase the microbiological reaction rates during the treatment, resulting in increased H₂S production. Although hydrogen

sulphide production can be attributed to the presence of sulphide ions, organic matter, and dissolved oxygen, and / or variations in pH, retention time, stream velocity and surface area, as well wind direction and speed, rain, and problems with the treatment system, it is believed that temperature is the main contributor (Bentzen, 1995). The data displayed in Figure 5 certainly indicates increased H₂S generation during the summer campaign and concentrations that were on average 3.7 times higher (from 0.1 times at A3 – 11.4 times at A12) than during the two winter campaigns were reported. The only exception is at A6 where the winter concentration was 0.3 times higher during the winter campaign. The increase in H₂S generation, however, does not seem linear with an increase in air temperature in all cases and clearly, other factors must play a role. Even though the temperature difference between the two winter campaigns are only 3 degrees, the concentration differences are noticeable (sites A4, A7-A12 reported on average 37% higher values at 16 °C and sites A1-A3, A5-A6 reported on average 28% higher values at 13 °C). To verify these observations, Pearson correlations between the H₂S concentration and air temperature for each sampling point were calculated and are reported in Table 5. In general, strong positive correlations (> 0.9) are observed except for points A2 and A3 with correlations 0.7 and 0.51, respectively. A6 showed a strong negative correlation, which has been eluded to previously.

Table 5 Pearson correlation of outdoor air temperature and H₂S concentration for each sampling point from A1 to A12 OUT.

A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12
0.90	0.70	0.51	0.96	0.99	-0.95	0.97	0.91	0.97	0.96	0.98	0.98

3.3 Indoor-to-outdoor ratios of H₂S air levels

Although several indoor pollutants have endogenous sources, such as gas cookers emitting NO_x's, indoor H₂S is expected to be dominated by the infiltration of outdoor air. The type and the amount of pollutants carried into houses depend

on the occurrence of emission sources in the immediate neighbourhood (Zabiegala, 2006). I/O ratio data obtained from the different sampling sites were summarized to provide a general impression of the relationship between indoor and outdoor concentrations. I/O ratio is defined as:

$$\frac{I}{O} \text{ ratio} = \frac{C_{in}}{C_{out}} \quad \text{Equation (2)}$$

Where C_{in} and C_{out} are the indoor and outdoor H_2S concentrations respectively. When the I/O ratio $\gg 1$ one can conclude that endogenous emission sources are mainly responsible for the indoor air quality. If however, the I/O ratio ≈ 1 , both internal and external sources influence the indoor air quality to the same degree. For an I/O ratio $\ll 1$ the quality of outdoor air dominates the quality of indoor air. Figure 6 shows the I/O ratios for sampling sites A1, A2, A11, B1 and B3 over the campaign period.

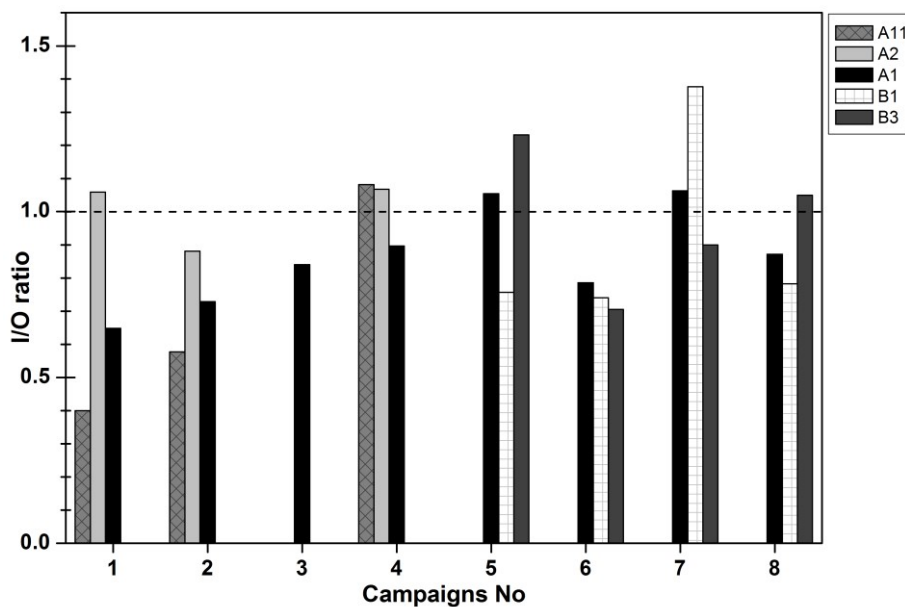


Fig. 6. Indoor/Outdoor (I/O) concentration ratios for each campaign at sampling sites A11, A2, A1, B1, and B3.

The data in Figure 6 display I/O ratios that are below 1 and therefore indicative of outdoor penetration dominating the indoor H_2S levels in 60% of the sites

investigated over all the campaigns. Forty percent of the ratios displayed values higher than 1, which could point to possible indoor sources. The lowest I/O ratios were recorded in campaigns 1 and 2 which took place during the winter, indicating that an indoor source is unlikely and infiltration from outside minimal. Point A2, however, showed a different profile in comparison to A1 and A11 with I/O ratios substantially higher and even above one. A2 has then also previously separated itself from the others as the site with the highest H₂S concentration over all sites and campaigns. Since data discussed earlier in this paper suggested that the main contributing factor for it, is its geographical location being directly downwind from the plant it is possible to conclude that low housing quality at this site can be one of the reasons for its higher ratio. The summer campaigns (3 – 8) had I/O ratios above or close to one, suggesting a bigger or dominant influence of outdoor H₂S in comparison with the winter campaigns. Since all the sites investigated for their indoor and outdoor H₂S levels displayed a ratio larger than one in at least one of the campaigns, it is important to remark that the residents in a 500 m radius of the two plants are just as much at risk in their homes than outside.

3.4 Health risk results

Simulations were performed with the RAIS calculator to identify the lowest concentration of H₂S that may cause adverse effects on human health, or when HQ is equal to one. For cohort 1 (residents living and working in the area) an H₂S concentration of 2.1 µg m⁻³ reported to an HQ equivalent to one, while for cohorts 2 (resident living in the area of monitoring but works outside the area) and 3 (resides away from the area, but work in the area), H₂S concentrations of 3.4 µg m⁻³ and 9.7 µg m⁻³, respectively would result in an HQ equal to one. Concentrations above these values could then statistically point to potential adverse effects to human health. Table 6 presents the percentage of samples at each WWTP that exceeded the threshold values calculated using the RAIS calculator.

Table 6 Percentage of samples at WWTP “A” and “B” exceeding the concentration limit of non-carcinogenic risk.

Concentrations above ($\mu\text{g m}^{-3}$)	WWTP “A” (%)	Risk for sampling points	WWTP “B” (%)	Risk for sampling points
2.1	62	A1 to A10, A12	100	B1 to B5
3.4	55	A1 to A9	100	B1 to B5
9.7	43	A1 to A5	39	B1 and B2

It is observed that at WWTP “A” the maximum percentage exceeding these threshold values is 62% for cohort 1, while it is 100% at B plant for both cohorts 1 and 2. It seems that the higher threshold value (cohort 3) is exceeded at sampling sites closest to the plants.

It is evident from the risk assessment that those who reside and work in the area of WWTP “A” (cohort 1) are at risk irrespective of the distance from the source. At points A9 and A10 (565 and 575 m away from the plant respectively) the hazardous quotient exceeds one but at A11 (481 m) and A13 (790 m) this is not the case. This is probably due to A9 and A10’s geographical location being down-wind from the plant. Those living in the area but working elsewhere (cohort 2), also are at risk, even at relatively distant locations such as point A9 at 565 m. The people living elsewhere but works at or close to the plant (cohort 3) will be at risk at distances close to the plant, such as 180 m.

The risk profile is different for the sites investigated at plant B, as these were all at a similar distance from the plant. For both cohorts 1 and 2, a risk is identified at all sampling points. For cohort 3, the risk is only significant at B1 and B2, both down-wind from the plant and therefore reporting much higher concentrations.

Health risk exposure (HQ values) of this study are comparable to those reported in a study conducted in Tianjin, China (Niu et al., 2014) and poses the question as to how the health of the workers and residents could be addressed.

4. Conclusions

The results indicated that the anaerobic process operated WWTPs are most likely the source of H₂S pollution in the two residential areas, as there is no other obvious source of H₂S nearby the sampling points. The odour complaints made

by the community were quantified for the first time. The concentrations ranged from $0.14 \mu\text{g m}^{-3}$ to $32 \mu\text{g m}^{-3}$ at plant A and $4.5 \mu\text{g.m}^{-3}$ to $18 \mu\text{g.m}^{-3}$ at plant B, which exceeded the nuisance odour level in 89% of the cases. In addition, the measured concentration levels exceeded the USEPA recommended value at 15 of the 18 points analysed. It appears that a better control of the microbiological processes within the UASB combined with the constant use of the gas scrubber should reduce H_2S emissions considerably.

These H_2S concentrations observed are indicative of the potential to cause chronic adverse health effects, such as eye irritation, headaches, and nausea (Kourtidis et al., 2008). These concentrations seemed to be influenced by geographical location, distance from the plant, weather conditions and indoor / outdoor environments. I/O ratios indicated that indoor pollution levels are mainly due to infiltration, but in some of the cases there may be an indoor source due to I/O ratios higher than 1. The health risk has been quantified using a risk calculator and indicated that up to 100% of the locations analysed reported hazardous quotients above 1 (this is the case for plant B and cohorts who reside and work in the area).

These findings are alarming from a social and public health point of view, as adverse health effects inevitably lead to increase hospital admissions, loss of working time, as well as government expenses. However, the authors recognise that wastewater treatment plants are essential and primarily to improve environmental and human health. What this investigation alerts to is that health issues can arise at WWTPs using anaerobic technology without stringent control, optimisation of the process and abatement of H_2S using gas scrubbers for example. The data displayed in this paper can assist in establishing a directive in developing countries, so that emissions of this particular pollutant can be limited. In addition, it could inform where mitigation of the pollutant is most important and may lead to the development of remedial processes at the existing plants.

Acknowledgements

The authors acknowledge CAPES for financial support.

References

Aristu I. 2009. Zaragoza and dozens of municipalities continue to suffer odour problems. Heraldo. Spanish report on internet newspaper.

http://www.heraldo.es/noticias/aragon/zaragoza_decenas_municipios_siguen_sufriendo_problemas_olores.html (accessed 10.07.2014).

Bentzen, G., Smit, A.T., Bennett, D., Webster, N.J., Reinholt, F., Sletholt, E., Hobsont, J., 1995. Controlled Dosing of Nitrate For Prevention of H₂S in a Sewer Network and The Effects On The Subsequent Treatment Processes. *Water Sci. Technol.* 31, 293-302.

Billings, R. 2012. Sewage odours prompt study of plant. *Portland Press Herald*. http://www.pressherald.com/2012/11/02/sewage-odours-prompt-study-of-plant_2012-11-03/ (accessed 28.05.2014).

Bruno, P., Caselli, M., Gennaro, G., Solito, M., Tutino, M., 2007. Monitoring of odour compounds produced by solid waste treatment plants with diffusive samplers. *Waste Manage.* 27,539–544.

Capelli, L., Sironi, S., Rosso, R.D., Céntola, P., 2009. Predicting odour emissions from wastewater treatment plants by means of odour emission factors. *Water Res.* 43,1977-1985.

Delgado, S., Alvarez, M., Rodriguez-Gomez, L.E., Aguiar, E., 1999. H₂S generation in a reclaimed urban wastewater pipe: case study: Tenerife (Spain). *Water Res.* 33,539-547.

Dincer, F., Muezzinoglu, A., 2007. Odour Determination at Wastewater Collection Systems: Olfactometry versus H₂S Analyses. *Clean: Soil, Air, Water*. 35,565-570.

Fogo, J.K., Popowsky, M., 1949. Spectrophotometric determination of hydrogen sulphide. *Anal. Chem.* 21,732-734.

Fu, X., Shen, W., 1990. *Physical-Chemistry*. China Higher Education Publisher, 4, 247–248.

Giuliani, S., Zarra, T., Naddeo, V., Belgiorno, V., 2013. Measurement of odour emission capacity in wastewater treatment plants by multisensor array system. *Environ. Eng. Manag. J.* 12,173-176.

Godoi, R.H.M., Godoi, A.F.L., de Quadros, L.Q., Polezer, G., Silva, T.O.B., Yamamoto, C.I., Van Grieken. R., Potgieter-Vermaak, S., 2013. Risk assessment and spatial chemical variability of PM collected at selected bus stations. *Air Qual. Atmos. Health*. 6,725-735.

Heaney, C.D., Wing, S., Campbell, R.L., Caldwell, D., Hopkins, B., Richardson, D., Yeatts, K., 2011. Relation between malodour, ambient hydrogen sulphide, and health in a community bordering a landfill. *Environ. Res.* 111847-111852.

Kim, K.H., Jo, S.H., Song, H.C., Pandey, S.K., Song, H.N., Oh, J.M., Sunwoo, Y., Choi, K.C., 2013. Diagnostic analysis of offensive odourants in a large municipal waste treatment plant in an urban area. *Int. J. Environ. Sci. Technol.* 10,261–274.

Kourtidis, K., Kelesis, A., Petrakakis, M., 2008. Hydrogen sulphide (H₂S) in urban ambient air. *Atmos. Environ.* 42,7476–7482.

Lebrero, R., Bouchy, L., Stuetz, R., Muñoz, R., 2011. Odour Assessment and Management in Wastewater Treatment Plants: A Review. *Environ. Sci Tech.* 41,915-950.

Muñoz, R., Sivret, E.C., Parcsi, G., Lebrero, R., Wang, X., Suffet, I.H., Stuetz, R.M. 2010. Monitoring techniques for odour abatement assessment. *Water Res.* 44,5129–5149.

Niu, Z.G., Xu, S.Y., Gong, Q.C. 2014. Health risk assessment of odours emitted from urban wastewater pump stations in Tianjin, China. *Environ. Sci. Pollut. Res.* 2,10349-10360.

Parande, A.K., Ramsamy, P.L., Ethirajan, S., Rao, C.R.K., Palanisamy, N., 2006. Deterioration of reinforced concrete in sewer environments. *Proc. Inst. Civ. Eng.-Municipal Eng.* 159, 11–20.

Pavilonis, B.T., O'Shaughnessy, P.T., Altmaier, R., Metwali, N., Thorne, P.S., 2013. Passive monitors to measure hydrogen sulphide near concentrated animal feeding operations. *Environ. Sci. Process Impacts.* 15,1271–1278.

RAIS. 2013. RAIS Risk Exposure Models for Chemicals User's Guide. <http://rais.ornl.gov/tools/rais_chemical_risk_guide.html>.

Redondo, R., Machado, V.C., Baeza, M., Lafuente, J., Gabriel, D., 2008. On-line monitoring of gas-phase bioreactors for biogas treatment: hydrogen sulphide and sulphide analysis by automated flow systems. *Anal. Bioanal. Chem.* 391,789 -98.

Reynolds J. 2012. The largest wastewater treatment plants around the globe. *Engineering News Record*. http://enr.construction.com/infrastructure/water_dams/2012/extras/0328/slideshow.asp?slide=1 (accessed 31.05.2014).

Stellacci, P., Liberti, L., Notarnicola, M., Haas, C.N., 2010. Hygienic sustainability of site location of wastewater treatment plants: A case study. I. Estimating odour emission impact. *Desalination.* 253, 51-56.

Stuetz, R.M., Fenner, R.A., Engin, G., 1999. Assessment of odours from sewage treatment works by an electronic nose, H₂S analysis and olfactometry. *Wat. Res.* 33,453-461.

USEPA, United States Environmental Protection Agency., 1989. Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A).

USEPA, United States Environmental Protection Agency., 2003. Toxicological review of hydrogen sulphide. EPA-635/R-03/005.

USEPA, United States Environmental Protection Agency., 2013. Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment).

Wall, P. 2011. In Case You Didn't Notice: Sewage Odours Are Drawing Fewer Complaints. *The New York Times*.
https://cityroom.blogs.nytimes.com/2011/10/13/in-case-you-didnt-notice-sewage-odors-are-drawing-fewer-complaints/?_r=0

WHO, World Health Organization. 1981. Hydrogen Sulphide. *Environmental Health Criteria* 19. <http://www.inchem.org/documents/ehc/ehc/ehc019.htm>

WHO, World Health Organization. 2000. Air quality guideline for Europe. Ed 2. Regional Publications, European Series, No. 91, Copenhagen.

Zarra, T., Naddeo, V., Belgiorno, V., 2008. Measurement, management and control of odours in wastewater treatment plants by portable GC-MS. *Chem. Engin. Trans.* 15,63-70.

Zabiegala, B. 2006. Organic Compounds in Indoor Environments. Pol. J. Environ. Stud.15, 383-393.

Yongsiri, C., Vollertsen, J., Hvitved-Jacobsen, T., 2005. Influence of wastewater constituents on hydrogen sulfide emission in sewer networks. J. Environ. Eng. 131, 1676–1683.