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Monitoring olfactory impacts associated with wastewater treatment plants by using diffusive samplers for the determination of hydrogen sulphide

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A monitoring programme based on an indirect method was conducted to assess the olfactory impact of a wastewater treatment plant. The method involves both H_2S passive sampling using Palmes-type diffusion tubes impregnated with silver nitrate and fluorometric analysis employing fluorescein mercuric acetate. The quantification limit of the procedure is 0.61 ppb for a 5-day sampling, which allows the H_2S immission (ground-concentration) level to be measured within its low odour threshold, from 0.5 to 300 ppb. Two different approaches were applied, one intensive and the other extensive, and concentrations within the H_2S low odour threshold were quantified at each sampling point. The results of the intensive sampling reveal the spatial structure of the impact field, which shows a strong dependence on the prevailing weather conditions, whereas the systematic measurements at fixed points near the facility over long periods of time reflect the seasonal variability of H_2S concentrations. From these results, it can be concluded that the procedure shows good potential for monitoring the olfactory impact around facilities where H_2S emissions are dominant.

1. Introduction

It is estimated that from 13-20% of the population in some European countries are annoyed by environmental odours (Hudon et al., 2000). In fact, the majority of public complaints presented to regulatory agencies in both Europe and North America are related to odour annoyance (Leonardos, 1995).

Hydrogen sulphide (H_2S) is a colourless gas that occurs naturally during wastewater treatment processes by means of bacterial action on organic matter under anaerobic conditions (Stuetz et al., 2001). In general, the importance of H_2S determination in air lies in its toxicity and in the unpleasant odour that it entails. H_2S has a noxious odour even at trace level concentration, with a low odour threshold which ranges from 0.5 to 300 ppb, although 18 ppb can be considered the standard concentration detectable by the human nose (Devos et al., 1990).

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Wastewater treatment plants (WWTP) have been identified as potential sources of offensive odours, and H_2S has not only been associated with the existence of olfactory impacts, but it has also been shown to exhibit a clearly dominant role over other odorants (Leonardos, 1995). The odour intensity of binary, ternary and quaternary mixtures prepared with odorants characteristic of a WWTP is very close to that of the dominant component in the mixture and, consequently, this compound can give an indication of the total olfactory impact (Stuetz et al., 2001). As H_2S is often present in higher concentrations than other odorants in the air around a WWTP, it can be used as a valid marker for the odours arising from such facilities.

Silver sulphide (Ag_2S) is formed from H_2S absorption onto silver nitrate ($AgNO_3$). It can be quantified by a fluorometric method employing fluorescein mercuric acetate (FMA) complexes that are quenched by the presence of sulphide. This method is highly sensitive, as it combines the low detection limits for fluorescent compounds offered by this analytical technique with the preconcentration of the analyte on the sampler. It has been applied successfully in outdoor and indoor environments (De Santis et al., 2006; Shooter et al., 1995).

Passive samplers have several advantages over active techniques: lower cost, permitting the simultaneous deployment of a large number of samplers at different sites; greater simplicity, because the flow does not have to be adjusted; and greater autonomy, since an electrical supply is not required and sampling periods can be extended. On the other hand, passive samplers generally perform poorly with respect to temporal variability because they provide averaged concentrations over the entire sampling period instead of instantaneous ones. Nevertheless, a strategy based on this sampling method could be useful for characterizing the olfactory impact around a WWTP, as it could maximize the cost/performance ratio.

This paper reports the results obtained with a procedure based on diffusive sampling using Palmes-type dosimeters equipped with $AgNO_3$ impregnated supports and analysis by the FMA fluorometric method for monitoring the olfactory impact around a WWTP.

2. Methods

2.1 Monitoring Strategy

In the context of this project, a two-year monitoring programme was carried out at four WWTPs located in the Valencian Community (Spain).

Eight intensive sampling campaigns were conducted inside and outside each plant for five days during several periods to cover different climatic scenarios. Passive samplers were placed at fifteen internal points which were located at the perimeter of the plant and at intermediate points in relation to the potential focus, all of them out of the direct influence of the emissions. The objective was triple: to monitor the concentrations around the production area, to document the presence of concentration gradients and to determine the average plant emission. In addition, nine external points, covering several kilometres around the plant, were distributed on the basis of the wind pattern and orography in the area under study to evaluate the atmospheric dispersion. Results could reveal the spatial structure of the impact field which is usually strongly dependent on the prevailing weather conditions.

Also, a two-year extensive campaign was conducted inside each facility to systematically monitor H_2S levels, after four internal points were considered representative of the immission (ground-level concentration) field. The passive samplers were deployed once a month for five days. Measurements at fixed points over long periods of time reflect the seasonal variability of H_2S concentrations.

The meteorological information came from a tower installed at each plant. This infrastructure consists of a 15 m-tall mast with wind measures (speed and direction) at the highest level and temperature measures at two heights (3 and 15 m, thus providing a direct measure of the surface thermal gradient). The measurement system operates continuously and averages the data at 10-minute intervals.

2.2 Sampling and Analysis

Although full details of the optimization and validation of the procedure have been published (Llavador et al., 2010), they are summarised here.

Palmes-type diffusion tubes were used to sample H_2S (Shooter et al., 1995). They consisted of hollow acrylic tubes with length of 70 mm and internal diameter of 10 mm, fitted on one end with a polypropylene cap containing 2 stainless-steel meshes impregnated with 50 µL of a solution of 1% AgNO3, 10% glycerol in 20/80 EtOH/H2O. The samplers were mounted vertically, with the absorbent end upwards, on a holder with capacity for up to 4 tubes. In the case of ambient measurements, the holders with the exposed samplers were sheltered by a cylindrical frame at a height of approximately 2.5 m above the ground for ventilation and protection against bad weather. At each sampling point, 3 dosimeters and 1 blank were exposed for five days. During exposure, gaseous pollutants diffuse up the tube towards the support impregnated with $AgNO_3$. There, the H_2S molecules are specifically absorbed and converted into Ag_2S.

After the samples were collected, alkaline cyanide solutions were employed to extract Ag_2S from the absorbent because cyanide forms a complex with the silver releasing S^{2-}. In this work, 3 mL of 0.2 M NaCN/0.1 M NaOH were added to the tubes before treatment in an ultrasonic bath for 15 minutes. 2 mL of the extract were transferred to a stoppered quartz cell, 0.1 mL of 10^{-6} M FMA/0.1 M NaOH added, the solution mixed and the fluorescence intensity measured using a Hitachi F-4500 fluorescence spectrophotometer (λ_{ex} = 499 nm, λ_{em} = 519 nm). The quantification limit of the procedure, calculated as the ratio of 10 times the standard deviation of the blank and the slope of the calibration curve, is 0.61 ppb for a 5-day sampling.

3. Results

The above-described procedure was applied to evaluate the olfactory impact around four WWTPs; the impact is expressed as the time-weighted average H_2S concentration for a 5 day- sampling. Five days were selected for the exposure period because this amount of time was viewed as the best compromise between having relatively homogeneous atmospheric conditions and having enough time to quantify H_2S concentrations close to the olfactory threshold.

The Rincón de León WWTP, which is located relatively close to both the city of Alicante (Spain) and the coast, has been selected among the four studied facilities to illustrate the potential of this methodology, as summarized in Figure 1, Figure 2 and

Figure 3. It is a large facility with an inflow higher than 80000 m^3 per day, and it presents a markedly urban profile.

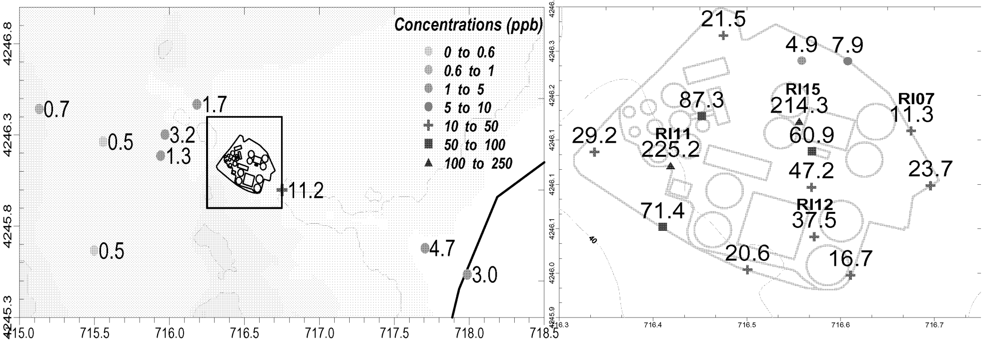

Figure 1. Location of sampling points and H_2S concentrations outside (a) and inside (b) the Rincón de León WWTP during the intensive campaign.

Outside the plant the concentrations ranged between 0.5 and 11.2 ppb. The only exceptions were 2 sampling points that presented concentrations lower than the LOQ but higher than the LOD. Figure 1 shows the normal concentration range as well as the estimated values of these two exceptions.

Markedly higher values, from 4.9 to 225.2 ppb, were found inside the WWTP, where there was also a strong concentration gradient between nearby points. Typical summer atmospheric conditions persisted throughout the intensive campaign, with a predominance of local breeze-type regimes. There is an axis of maximums in roughly the east-west direction, which coincides with the preferred air flow transport direction along the watercourse, as can be seen in the wind rose for the period, Figure 2(a).

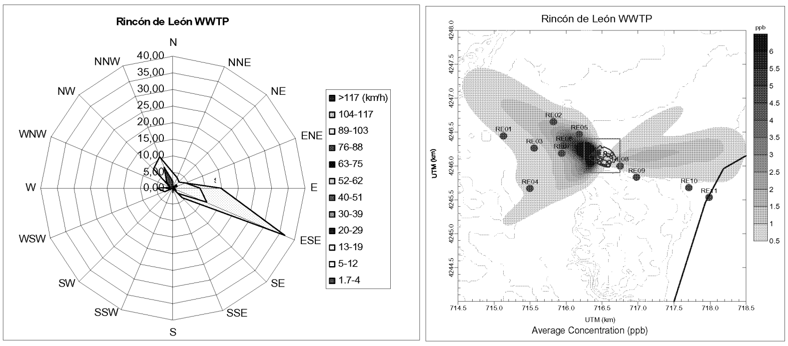

Figure 2. Wind rose registered during the intensive campaign (a) and simulated H_2S average concentration field (b).

Moreover, a clear gradient, which causes a decrease in concentrations with distance from the plant, can also be observed in Figure 1(b). This gradient is more intense leeward of the night flow. Therefore, the immission values considerably decrease as the distance from the potential emission sources increases, reaching the lower range of the low odour threshold. A puff-type dispersion model, based on a constant emission factor, was used to simulate the spatial structure of the H_2S average concentration field for this intensive campaign. Its output, Figure 2(b), depicts the average spatial distribution of H_2S concentrations under local wind dispersion. Ground-level concentrations show a characteristic "butterfly wing" distribution with a higher impact on-shore, due to predominant sea advection, and the highest concentrations are expected very close to the plant. This pattern fits quite well with the distribution of the sampling points.

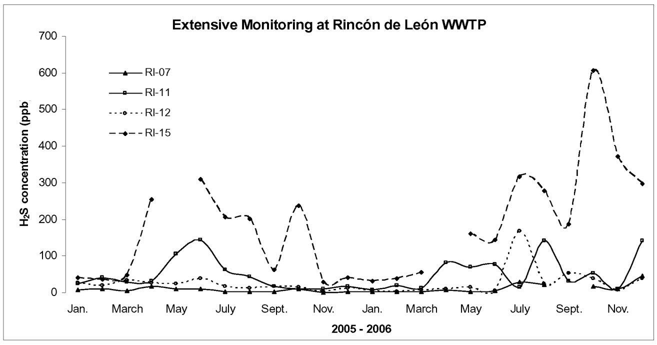

Figure 3. Monthly H_2S variation observed at ground level inside the plant during the two-year extensive campaign.

The two-year systematic measurements carried out at four points within the plant perimeter are shown in Figure 3. Important differences between nearby points, which were placed no further than several tenths of meters apart, were observed although the evolution of the time series shows a similar pattern with summer maximums and winter minimums. The highest concentrations were generally obtained for the summer and spring months during the extensive campaign, as can be seen in Figure 3, although the highest value was registered in October of the second year. This trend was more pronounced at the RI11 and RI15 points whereas RI07 and RI12 showed more homogeneous values. RI11 values ranged between 8.0 and 144.9 ppb, which are lower than the RI15 concentrations, ranging from 29.5 to 607.0 ppb, whereas RI07 and RI12 showed the lowest levels, from 1.2 to 45.1 ppb and from 2.3 to 168.0 ppb, respectively. All these concentrations were higher than 0.5 ppb, the low odour threshold. RI07 usually exhibited concentrations lower than 18 ppb, the standard detectable concentration, whereas all the RI15 monthly values were higher than 18 ppb. These results are logical since the samplers are located inside the influence area of the potential emission sources. RI11 is placed south of the sludge line and west of the dewatering facility whereas the primary clarifiers are very close to RI15, which is situated east of the sludge line. RI07 and RI12 are positioned to the east of the WWTP, rather far from the H_2S potential emissions.

4. Conclusions

The highest concentrations have been found at the points located inside the wastewater treatment plant. An important concentration gradient, even between nearby places, is also observed since H_2S concentrations decrease considerably as the distance from the potential emission sources increases. The values from interior points located near emission sources show a marked seasonal variation, with maximums in summer and minimums in winter, thus showing that the emission (production) mechanisms, which are more active during the warmest months, dominate over the dispersion processes, which are also more efficient in the summer season. Five-day sampling permits the quantification of H_2S concentrations close to the low odour threshold and exhibits the importance of meteorological conditions in emission-dispersion-immission processes. All the points exhibit concentrations within this threshold, from 0.5 to 300 ppb, although only the interior values are higher than the standard H_2S concentration detectable by the human nose, i.e., 18 ppb.

Thus, this procedure shows good potential for monitoring the olfactory impact from wastewater treatment plants, where H_2S emissions are dominant, and provides an ideal platform for a cost-efficient monitoring programme at either a large number of sampling points or a small number of points with high temporal frequency.

In consequence, this methodology is being applied at the present time in several WWTPs located in the Valencian Community (Spain), both in large and medium facilities with urban and seasonal profiles, to manage the olfactory impact associated with their presence.

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