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# Exploring the link between sulphur-containing compounds and noxious odours at waste management facilities: implications for odour monitoring and mitigation strategies

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With this study we challenge the widely held assumption that sulphur-containing compounds in ambient air are good indicators of the presence noxious odours near waste management facilities. We analysed an extensive set of olfactometric data and data on the concentrations of hydrogen sulphide and trace sulphur compounds (TSCs) near a waste management facility in Croatia in 2021. The results show that the presence of noxious odours significantly correlates only with the concentrations of hydrogen sulphide and methyl mercaptan in ambient air but not with other measured TSCs. Thus, in addition to the measurement of pollutants in ambient air, Integrated Pollution and Prevention Control (IPPC) permits should mandate olfactometric measurements to detect and mitigate noxious odours near waste management facilities.

**KEY WORDS:** bioreactor landfill; Integrated Pollution Prevention and Control (IPPC); odour measurements; trace sulphur compounds

Waste management facilities are often a source of noxious odours which can cause nuisance to neighbouring communities (1–4). Compounds containing sulphur such as hydrogen sulphide ( $H_2S$ ), methyl mercaptan ( $CH_3SH$ ), ethyl mercaptan ( $C_2H_6S$ ), dimethyl sulphide ( $CH_3)_2S$ , and dimethyl disulphide ( $CH_3)_2S_2CH_3$ ) are believed to be the primary cause of noxious odours (5). These gases are produced during the decomposition of the organic fraction of waste and are eventually released into the atmosphere during the handling, processing, and landfilling of waste.

Their impact on human health has been studied extensively.  $H_2S$  is known to be highly toxic and cause respiratory problems, nausea, headaches, and even death at high concentrations (6).  $CH_3SH$  has a strong, unpleasant odour similar to that of rotten eggs, and exposure to high concentrations can irritate the eyes, nose, and throat (7).  $(CH_3)_2S$  and  $CH_3)_2S_2CH_3$  have a pungent odour and are also known for causing respiratory irritation and nausea (8). In addition to causing adverse health effects, these gases contribute to environmental pollution.  $H_2S$  can react with other pollutants in the air to form sulphur dioxide ( $SO_2$ ), a major contributor to acid rain (9), whereas  $CH_3SH$  and  $(CH_3)_2S$  promote the formation of volatile organic compounds (VOCs), known to affect air quality (10, 11). To protect neighbouring communities from noxious odours, the

Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (12) sets the framework for monitoring these compounds in ambient air under the assumption that if hydrogen sulphide and trace sulphur compounds (TSC) concentrations are kept low, noxious odours will be kept in check. The directive sets the context for environmental emission limits for various industries, yet only the waste management sector is required to provide limits on odour concentrations. These limits are based on the concept of Best Available Techniques (BAT) and the corresponding BAT reference documents (BREFs), which are periodically reviewed and updated. They are not legally binding and leave to local authorities to set odour limits, which are based both on BREFs and site-specific characteristics. Some EU27 countries, such as France, Germany, Austria, Hungary, Spain, the Netherlands, Italy, and Belgium, have their own specific odour regulations and guidelines, but not Croatia. To date, there are three waste management centres in Croatia that handle residual municipal solid waste with mechanical-biological treatment (MBT). All MBT plants are equipped with scrubbers and biofilters to treat their exhaust air before being released into the environment. Two of these facilities, located in the north-western part of Croatia, landfill the organic

fraction separated during mechanical treatment, which is the main source of odour emissions. Efforts have been made to control odours by reducing the active area of the landfills with cover-up membranes and an active collection system that extracts landfill gas under negative pressure generated by a central blower. The extracted gas is eventually flared. The third centre, in the southern part of Croatia near the city of Zadar, stabilises the organic fraction aerobically in a closed system. When the microbiological activity in the organic fraction has ceased and the waste has become inert, it is disposed of in a landfill.

There are several common techniques to measure odours. These include gas chromatography, sensor arrays, dynamic olfactometry, and chemical sensors. Recent advances in odour measurement include two-dimensional gas chromatography, which offers improved separation capabilities and better identification of volatile compounds contributing to unpleasant odours. Furthermore, high-resolution olfactometric systems have been developed which allow for a more accurate assessment of the presence of odours. These advances in odour measurement techniques will help to better understand the relations between noxious odours and specific compounds in ambient air.

The aim of our study was to test the assumption that ambient air concentrations of sulphur-containing compounds are a good proxy indicator of odour nuisance by investigating how well their concentrations correlate with advanced olfactometric measurements of noxious odours at one of the three waste managements centres in Croatia.

## MATERIALS AND METHODS

### Site description and data collection

Olfactometric and ambient air concentration data for hydrogen sulphide ( $H_2S$ ), methyl mercaptan ( $CH_3SH$ ), ethyl mercaptan ( $C_2H_6S$ ), dimethyl sulphide ( $(CH_3)_2S$ ), and dimethyl disulphide ( $CH_3S_2CH_3$ ) were collected near a residential area situated close to the waste management centre (WMC) Marišćina in 2021 (Figure 1). This WMC consists of a mechanical biological treatment plant (MBT) with a treatment capacity of 100,000 t of municipal solid waste (MSW) per year. The plant produces solid recovered fuel (SRF) using biological treatment and mechanical processing of residual waste. After sieving, the fine fraction, consisting mainly of organic material, gets landfilled in a bioreactor landfill to produce landfill gas, which is currently flared but will eventually be used for energy recovery. In addition, the centre operates a state-of-the-art wastewater treatment plant (WWTP).

### Olfactometric analyses

The main principle of olfactometry is based on human olfactory perception. It involves the use of trained testers who evaluate and quantify odours by smelling samples. The aim is to provide an

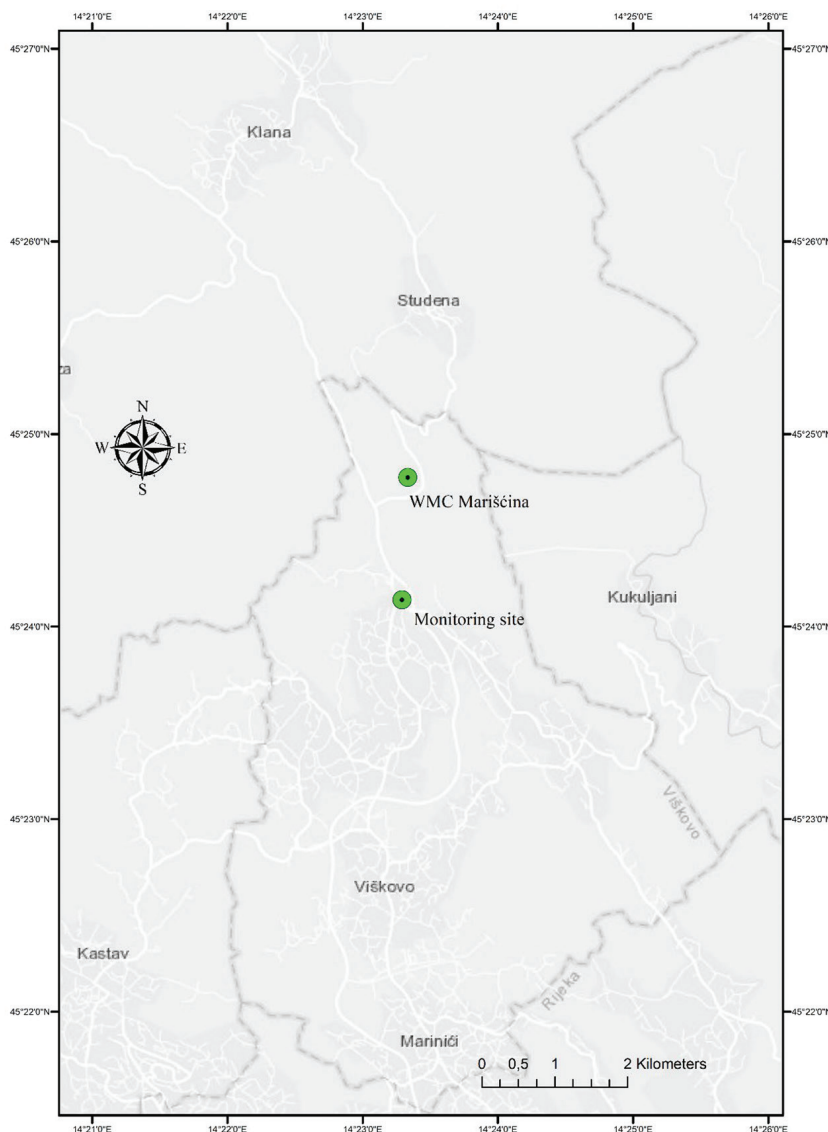
objective and standardised measurement of odour concentration, intensity, and character. Odour concentration is usually measured in odour units (OU), which represent the dilution ratio required to reach the detection limit of the odorant. One OU corresponds to a volume of an odorous gas diluted with clean air to the point where the tester can still detect the odour. This standardised scale allows for objective comparisons of odour emissions from different sources and facilitates regulatory compliance (13).

Typically, odour nuisances are evaluated based on the EN 13725:2022 standard: Emissions from stationary sources – Determination of odour concentration by dynamic olfactometry and odour emission rate (13). In this study, we took olfactometric measurements approximately three times a week with a field olfactometer (Scentroid SM100, Stouffville, Ontario Canada), which relies on the dilution-to-threshold method to measure the concentration of odorous compounds in the air. The main difference between the two methods is in that a field olfactometer is operated by a single tester and it quantifies ambient odour strength in OU by drawing in and diluting ambient air using a Venturi pump and fresh, odourless air which the operator inhales in order to assess the level at which noxious odours are sensed. The operator controls the air ratio with an adjustable slider, and the sample strength is displayed on the instrument in OU. Dynamic olfactometry according to the EN 13725:2022 standard, on the other hand, relies on a panel of trained human testers who evaluate the intensity of odours by sniffing samples in a controlled environment. The results are then used to calculate the odour concentration. Regardless of the differences, the results obtained by a field olfactometer and the EN 13725:2022 standard correlate well ( $R^2=0.855$ ) (14).

Hydrogen sulphide concentrations were measured using the automatic Horiba AP5A-370/CU-1 (HORIBA Instruments Incorporated, Irvine, CA, USA) ambient hydrogen sulphide monitor. The device measures the concentration of  $SO_2$  after conversion from  $H_2S$  using ultraviolet (UV) fluorescence. The data are collected in real-time and averaged over one hour. Data on  $CH_3SH$ ,  $C_2H_6S$ ,  $(CH_3)_2S$ , and  $CH_3S_2CH_3$  were obtained using the Chromatotec airmoMEDOR analyser (Chromatotec Group, Houston, TX, USA), which works on the principle of gas chromatography with isothermal separation through a Teflon microcolumn with detection using a wet electrochemical cell with chromic acid.

### Statistical analyses

Olfactometry data and concentrations of the four compounds of interest were summarised descriptively. Multiple regression analysis, run on Minitab v 20 statistical software (Minitab, State College, PA, USA), was used to assess the contribution of the tested pollutants to odour nuisance. The normality of the data was not an issue due to a large sample ( $N=103$ ). Stepwise regression was used to determine the most significant predictors of odour nuisance, with the significance level set at  $p<0.01$ .



**Figure 1** Location of the WMC Mariščina and the environmental monitoring site, with residential area of Viškovo south of the monitoring site. WMC – waste management centre

The basic model is described by the following formula:

$$F(x) = \beta_0 + \sum_i \beta_i X_i + \sum_i \beta_{ii} X_i^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad [1]$$

The stepwise model allows terms to be entered at one step and removed later if necessary, depending on other terms included in the model. Terms were entered or removed based on  $\alpha=0.1$ . Predictors were standardised by subtracting the mean and dividing it by the standard deviation to remove most of the correlation between linear and square terms, which reduces the chance of unnecessary adding higher order terms. To detect possible covariance between predictors, we calculated the variance inflation factor (VIF) and found no issues. The goodness of fit ( $R^2$ ) for multiple regression is reported in Table 3.

### Quality assurance and control

The quality assurance and control (QA/QC) procedures involved the following: daily automatic verification of instruments and zero span adjustments; bi-weekly visit to the station; fine-tuning of the instruments at the station (as needed); annual servicing and calibration of instruments and verification of working characteristics according to relevant standards; instrument calibration (as necessary); and regular participation in intercalibration exercises.

The detection limits for the instruments were as follows: hydrogen sulphide: 0.00028 mg/m<sup>3</sup>; methyl mercaptan: 0.00039 mg/m<sup>3</sup>; ethyl mercaptan: 0.0005 mg/m<sup>3</sup>; dimethyl sulphide: 0.0005 mg/m<sup>3</sup>; dimethyl disulphide: 0.00004 mg/m<sup>3</sup>; and olfactometric analysis: 2 OU. The concentrations are expressed at a temperature of 25 °C and 1 atm (101 kPa).

The Horiba APSA 370/CU-1 and the Chromatotec airMoMEDOR analysers were calibrated periodically using a certified reference gas. The Scentroid 100 SM field olfactometer, on the other hand, uses fixed orifice dilution control and requires annual re-calibration.

## RESULTS

Table 1 shows hourly concentration averages ( $\mu\text{g}/\text{m}^3$ ) for hydrogen sulphide ( $\text{H}_2\text{S}$ ), methyl mercaptan ( $\text{CH}_3\text{SH}$ ), ethyl mercaptan ( $\text{CH}_3\text{CH}_2\text{SH}$ ), dimethyl sulphide [ $(\text{CH}_3)_2\text{S}$ ], and dimethyl disulphide ( $\text{CH}_3\text{S}_2\text{CH}_3$ ) measured at the monitoring site in 2021. Hydrogen sulphide had the highest concentrations (mean  $0.76 \mu\text{g}/\text{m}^3$ ; 95 % CI  $0.64\text{--}0.88 \mu\text{g}/\text{m}^3$ ) and dimethyl disulphide the lowest (mean  $0.08 \mu\text{g}/\text{m}^3$ ; 95 % CI  $0.041\text{--}0.12 \mu\text{g}/\text{m}^3$ ).

Figure 2 shows the time series data for the five sulphur compounds averaged over one hour. These concentrations were time-aligned with olfactometric data, collected approximately three times a week. In other words, only the time points with both sulphur compounds concentrations and olfactometric data were included in the analysis. The hourly environmental limit value (ELV) is mandated only for hydrogen sulphide ( $7 \mu\text{g}/\text{m}^3$ ) in Croatia (15) and has not been exceeded during the observed period.

Table 2 shows olfactometric data measured at the monitoring site in 2021, and Figure 3 their time series. Most of the time, noxious odours were below the detection limits save for a relatively small number of measurements, probably due to the stable atmosphere, which favours the accumulation of pollutants in the troposphere, including odorous VOCs.

Multiple regression analysis shows that only  $\text{H}_2\text{S}$  and methyl mercaptan significantly correlate with noxious odours determined by olfactometric measurements ( $p < 0.01$ ).

The final model equation is as follows:

$$OU = -0.78 + 4.87 * X1 - 4.16 * X2 - 0.917X1^2 + 1.761X2^2 \quad [2]$$

where  $X1 = \text{H}_2\text{S}$  ( $\mu\text{g}/\text{m}^3$ ) and  $X2 = \text{methyl mercaptan}$  ( $\mu\text{g}/\text{m}^3$ ).

The tested predictor variables were able to explain only 12.5 % of the variation, which means that approximately 87.5 % of response variation is owed to factors not included in this model.

Figure 4 shows the time series of olfactometric data. Most of the time, noxious odours were low or undetectable, save for the beginning of 2021, when they soared once, possibly due to plant operation coupled with extremely unfavourable atmospheric conditions.

## DISCUSSION

Our olfactometric measurements did detect noxious odours at the monitoring site, but these did not exceed the environmental limits for sulphur-containing pollutants. The main finding of our study is that only a small part of variation in odour can be explained by regularly monitored compounds. Of these, only hydrogen sulphide and methyl mercaptan significantly correlated with noxious odours. Our results are corroborated by Liu et al. (16), who singled out methyl mercaptan as the only dominant odorous compound but did not study the contribution of hydrogen sulphide ( $\text{H}_2\text{S}$ ). Its contribution to noxious odours at landfill sites has been reported by other studies (17–21).

Dimethyl sulphide showed seasonal variations, with higher concentrations in the warmer months. This may be owed to increased microbial activity and organic decomposition of waste materials and increased volatility and air movement.

The fact that the chemical compounds measured at the monitoring site account for only a small variation in noxious odours is not surprising considering that the main sources of odour in the landfill gas are styrene, toluene, xylene, acetone, methanol, *n*-butanone, *n*-butylaldehyde, acetic acid, dimethyl sulphide, dimethyl disulphide, and ammonia (22), none of which are mandated for monitoring by the current IPPC permit. Capelli et al. (23) also report poor correlation between chemical compounds measured at the site and odour concentration measured by dynamic olfactometry.

**Table 1** Hourly concentration averages ( $\mu\text{g}/\text{m}^3$ ) of sulphur-containing compounds measured at the monitoring site south of the Waste Management Centre Marišćina in 2021

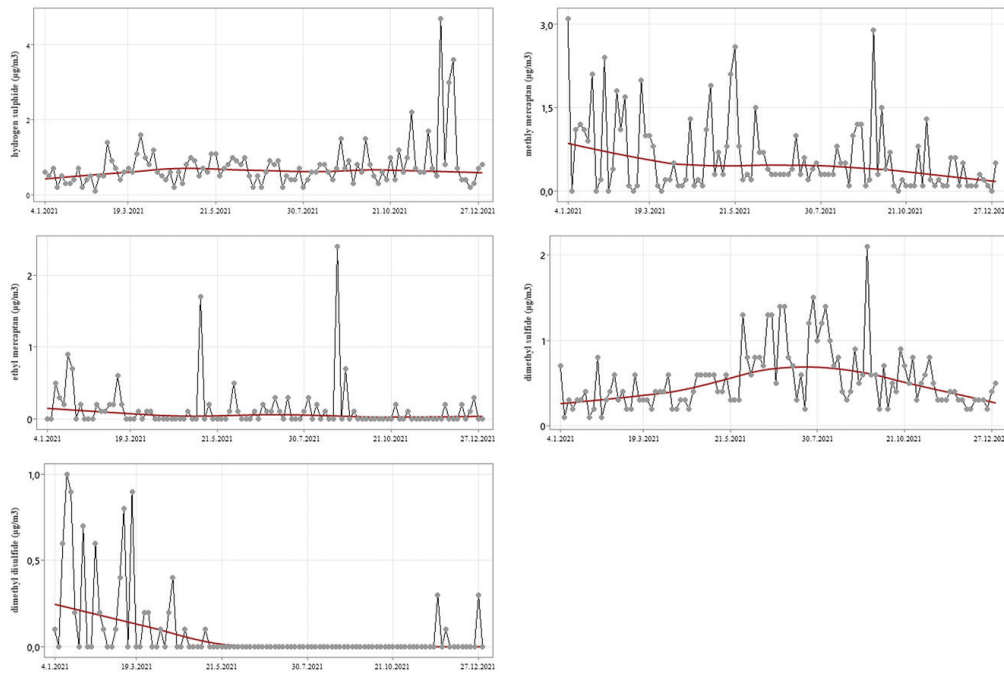
Parameter	N	Mean	SD	Min	Q1	Median	Q3	Max	Range	Mode
Hydrogen sulphide	106	0.76	0.63	0.1	0.40	0.60	0.83	4.70	4.60	0.60
Methyl mercaptan	106	0.60	0.67	0.00	0.10	0.30	0.83	3.10	3.10	0.10
Ethyl mercaptan	106	0.13	0.32	0.00	0.00	0.00	0.10	2.40	2.40	0.00
Dimethyl sulphide	106	0.54	0.36	0.10	0.10	0.30	0.70	2.10	2.00	0.30
Dimethyl disulphide	106	0.08	0.21	0.00	0.00	0.00	0.00	1.00	1.00	0.00

Q1 – first quartile; Q3 – third quartile; SD – standard deviation

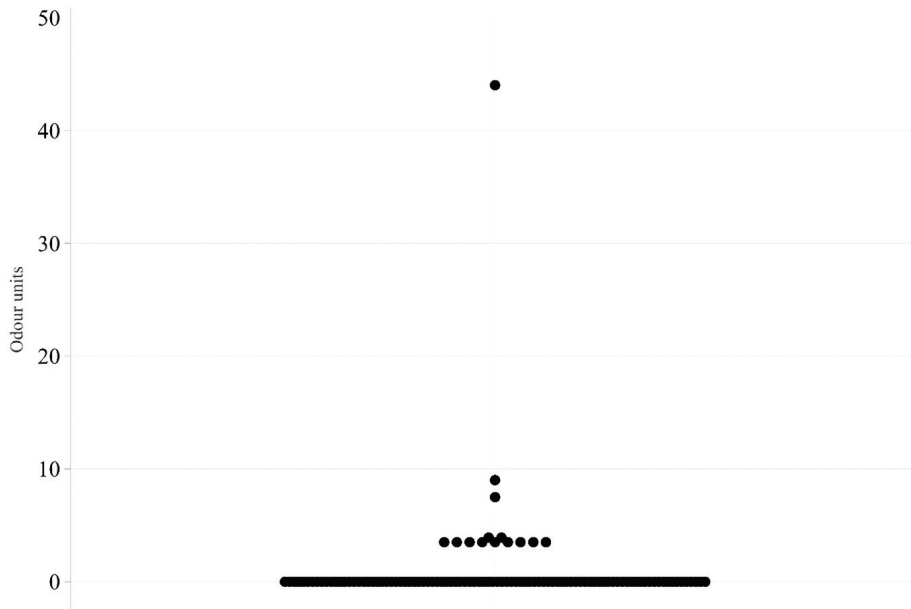
**Table 2** Olfactometric results at the monitoring site south of the Waste Management Centre Marišćina in 2021

Parameter	N	Mean	SD	Min	Q1	Median	Q3	Max	Range	Mode
Odour ( $\text{OU}/\text{m}^3$ )	106	0.94	4.49	0.00	0.00	0.00	0.00	44.00	44.00	0.00

Q1 – first quartile; Q3 – third quartile; SD – standard deviation



**Figure 2** Time series for hydrogen sulphide, methyl mercaptan, ethyl mercaptan, dimethyl sulphide, and dimethyl disulphide for 2021



**Figure 3** Individual value plot for olfactometric analyses at the monitoring site

**Table 3** Goodness of fit for multiple regression analysis

Parameter	R <sup>2</sup>
Hydrogen sulphide	8.86
Methyl mercaptan	17.74
Ethyl mercaptan	12.12
Dimethyl sulphide	15.62
Dimethyl disulphide	29.29

Hydrogen sulphide and methyl mercaptan significantly correlated with noxious odours ( $p < 0.01$ ), whereas the correlation of other parameters was not significant

In our study, the main source of odorous compounds at the site was the bioreactor landfill. The exhaust air from the MBT plant passes through a flue gas cleaning system with bag filters, scrubbers, and biofilters, which effectively removes odorous VOCs (24–26).

Odour complaints by neighbouring residents were more frequent in the summertime (data not shown), which is consistent with the finding by Wu et al. (27), who reported a positive correlation between odour concentrations and air temperature. These complaints mostly refer to the smell in the evening and early morning and seem to reflect the dominant northwesterly wind, especially in the summertime. This is similar to the report by Wenjing et al. (28), who found that 2:00 am, 6:00 am, 2:00 pm, and 10:00 pm were the “most probable times” for odour occurrence.

Odour characterisation is complex and involves different factors, including offensiveness, intensity, frequency, duration, and personal experience and bias among the residents affected by the odours (29). Therefore, mandating a certain environmental limit in terms of odour units to waste management facilities may not resolve the issue, as there are other factors affecting the perception of odour

nuisance that are very hard, if not impossible, to quantify and regulate. However, even in the absence of environmental limits, complementing environmental monitoring near waste management facilities with olfactometric analyses will improve the protection of nearby residents and help to design odour mitigation strategies.

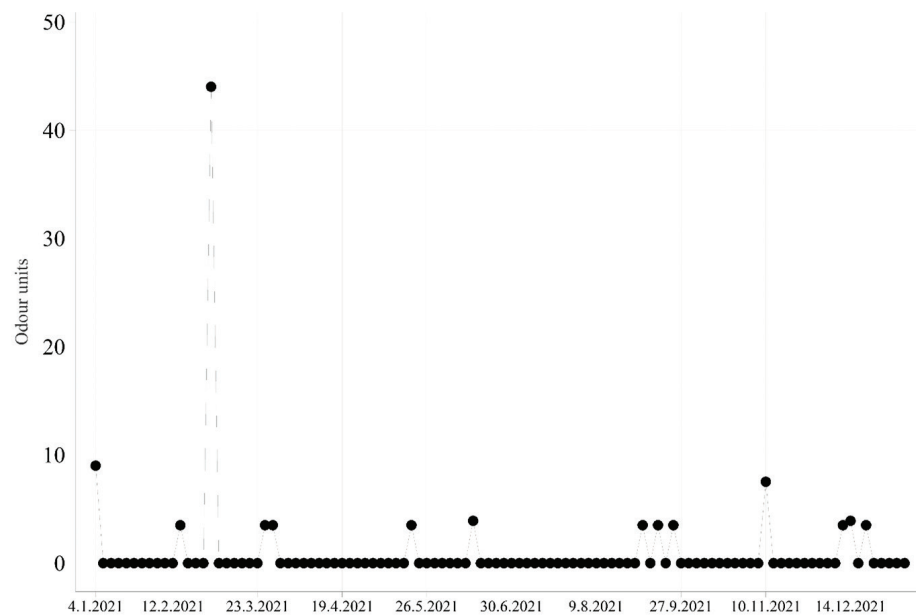
Our study also shows that measuring hydrogen sulphide and methyl mercaptan at waste management facilities may be useful, as they significantly correlate with the presence of noxious odours, whereas measuring ethyl mercaptan, dimethyl sulphide, and dimethyl disulphide is of questionable value, since their concentrations do not correlate with the presence unpleasant odours.

## CONCLUSION

Our study provides a few new insights into the relationship between sulphur-containing compounds in the ambient air and the presence of unpleasant odours, as it rejects the commonly held assumption that ambient air concentrations of sulphur compounds are a good proxy indicator of odour nuisance. In addition, it evidences that only a small fraction of the variation in odour nuisance is owed to sulphur compounds in ambient air, more specifically to hydrogen sulphide and methyl mercaptan, whereas other sulphur compounds do not correlate with unpleasant odours.

Our findings are therefore relevant not only to the scientific community but also to regulators and bodies responsible for the protection of the environment and human health.

In this respect, both organisational and technical solutions can be used to minimise odour emissions from waste treatment facilities. Organisational measures include covering the landfill with soil and/or alternative materials such as geotextiles, foam, or other materials.

**Figure 4** Time series of olfactometric analysis in 2021

If the organic fraction is composted, the compost pile should be properly aerated to minimise anaerobic conditions. Engineering solutions include landfill gas collection systems to capture and control the gas generated during organic waste decomposition. These systems typically include gas extraction wells, collection pipes, and gas treatment equipment such as gas flares. Other effective solutions include the use of advanced odour control technologies such as biofilters or activated carbon filters to treat collected gas before it is released into the atmosphere (30, 31).

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### Istraživanje veze između spojeva koji sadrže sumpor i prisutnosti neugodnih mirisa u okolici postrojenja za gospodarenje otpadom: implikacije za praćenje prisutnosti i ublažavanje neugodnih mirisa

U ovom je radu istražena povezanost između koncentracija spojeva koji sadrže sumpor, a koji se tradicionalno koriste kao tzv. *proxy* indikatori prisutnosti neugodnih mirisa u blizini postrojenja za gospodarenje otpadom, i prisutnosti neugodnih mirisa detektiranih olfaktometrijskim mjerenjima. Podatci su dobiveni u blizini centra za gospodarenje otpadom u kojem se provodi mehaničko-biološka obrada otpada i u sklopu kojega je i bioreaktorsko odlagalište na kojem se odlaže izdvojena organska komponenta preostalog miješanog komunalnog otpada. U rad se problematizira pretpostavka da je koncentracija spojeva koji sadrže sumpor u okolnom zraku dobar pokazatelj prisutnosti neugodnih mirisa. U tu svrhu analizirali smo opsežnu bazu podataka kemijskih i olfaktometrijskih mjerenja provedenih u okolici lokacije centra tijekom 2021 godine. Rezultati pokazuju da se samo male varijacije u neugodnim mirisima mogu objasniti spojevima sumpora u okolnom zraku. Statistički značajna korelacija s prisutnošću neugodnih mirisa dokazana je samo za sumporovodik i metil merkaptan, a za ostale testirane spojeve, koji su uključivali etil merkaptan, metil sulfid, dimetil sulfid i dimetildisulfid, nije bilo statistički značajne korelacije. Iako je praćenje sumporovodika i metil merkaptan sulfida opravdano kao *proxy* metoda za mjerenje prisutnosti neugodnih mirisa, okolnom bi dozvolom, osim kemijskih analiza onečišćujućih tvari u vanjskom zraku, trebala biti propisana i olfaktometrijska mjerenja radi što kvalitetnije zaštite okoliša i zdravlja ljudi koji obitavaju u okolici centra.

KLJUČNE RIJEČI: bioreaktorsko odlagalište; centri za gospodarenje otpadom; spojevi sumpora; spojevi sumpora u tragovima; štetni mirisi