

On Odour Tolerability Criteria from Odorant Instrumental Monitoring

Sabina Licen^a, Nicola Pettarin^b, Gianpiero Barbieri^b, Pierluigi Barbieri^{a,*}

^aDept. of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

^b ARCO SolutionS s.r.l., spin-off company of the Dept. of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy
barbierp@units.it

At present one of the most accepted criteria for assessing tolerability for environmental odour impacts is based on a modelling approach that requires the characterizations of the odour flow rates from stationary sources, definition of both a digital terrain model of the studied area and of relevant meteorology during the considered period of time, so to provide an estimate of the areas where the number of hours exceeds specified hourly odour threshold (e.g. 1, 3 or 5 OUE). Often the 98th percentile of hourly peak odour concentration is considered at sensible receptors. In the case of complex odour sources or if the emitting entity is not collaborative, the experimental approach focused on receptor instrumental monitoring can provide a tool for the assessment of odour nuisance tolerability, so to foster or to force mitigation actions on odour emission sources. Since nowadays instruments allowing single (e.g. H₂S monitoring instruments) or multiple (e.g. e-noses) odorant concentration monitoring are available, and they are often positioned at sensible receptors, experimental measurement of the exceedance of odour threshold can be provided, if consensus odour threshold values for the odorant are available. Also for the experimental approach, the 98th percentile of hourly odour concentration can be provided. A case study based on H₂S monitoring is proposed; extension to e-noses application is possible, providing their active and efficient presence in the field 12 months a year. Pros and cons of different approaches and criteria will be discussed.

1. Introduction

Within odour regulations in force in different countries, impact criteria can be classified (Brancher, 2017) as belonging to one of five categories, i.e. maximum impact standard, separation distance standard, maximum emission standard, maximum annoyance standard, technology standard. Maximum impact standards - expressed as ambient air odour concentration and individual chemicals - have wide recognition. Commonly, ambient air odour concentrations are estimated from measurements of source odour emission rates (based on dynamic olfactometry), simulation of local meteorological conditions and dispersion modelling (Needham, 2009). Odour concentrations computed by simulation at sensitive receptors can be compared to normative numerical limit values to assess whether the odour levels predicted are acceptable or not. Such guidelines often take into account the fact that odour episodes relevant for human perceived nuisance can occur in seconds and this would not be represented by hourly mean concentrations simulated by dispersion models. Short-time peak concentrations, derived from 1-h mean values, can be incorporated into odour impact indicators (Schauberger, 2012), as it is done in New Zealand or in Italian Lombardy guidelines, where a fixed factor describing a peak-to-mean ratio multiplies average hourly odour concentration computed by a modelling chain. The availability of simulated 1-hour mean concentrations (ou/m³) for one year of simulation at sites of interest, corrected by the peak-to-mean ratio (e.g. 4), permit to identify the 98th percentile of the hourly concentrations. This indicator for the odour exposure corresponds to the estimated concentration that has been exceeded for one week during the year, a time length that can be considered to discriminate between limited/occasional and significant/frequent odour nuisance.

Despite the wide usage of the modelling approach, (Capelli, 2014) highlights how only few studies concerning validation of computational models have been published up to now, pointing at the need of improvement of

methodology, with the aim to provide sound regulations of odour disputes/conflicts. It must be noted how dispersion modelling results highly depend on representativeness of odour emission rates used as inputs; in case of significant variability of odour source emissions and close proximity among emission sources and receptors, few experimental odour emission rate measures at the sources could be not representative, and then predicted ambient air concentrations fail to describe the order of magnitude of odour nuisances as perceived by citizens. In these cases, an ambient air odour monitoring appears highly desirable or even necessary, in order to provide adequate tools for describing frequency, intensity, duration and offensiveness, parameters relevant in malodour characterization (Bull, 2014). The continuous monitoring of odour can be supported instrumentally by tailored sensor systems, i.e. e-noses, that can provide odour concentrations (odour units/m³) as output (Capelli, 2014; Giungato, 2016) and in Europe standardization of this approach is on the way (Romain, 2017); e-nose data can be effectively integrated with data from olfactometry and citizen reports (Licen, 2018). Otherwise, odorant compounds having known detection threshold can be measured by chemical analysis (Dincer, 2007; Wu, 2016) also by means of continuous analyzers, as it is the case for H₂S (hydrogen sulfide), allowing to estimate the odour concentration by computing the ratio of the odorant concentration to perception threshold obtained for the chemical species from literature (Kim, 2008). The odour detection threshold depends on individual sensitivities, age, and the conditions under which the odour is assessed, and different studies (Iremonger, 2012) identify H₂S thresholds between about 1 and 300 µg/m³. World Health Organization (WHO, 2000) and the New Zealand Ministry for the Environment (NZ MFE, 2002) proposed a range between 0,2 and 2,0 µg/m³, based on purity; in a report of the Italian agency for the environment APAT, (Laraia, 2003) indicates 1,4 µg/m³ as the value of 100% Odour Threshold (µg/m³); (Amoore, 1983; Collins, 2000; Chou, 2003) reported 8,0 ppb i.e. 11 µg/m³. Iremonger and colleagues (2012), focusing on two specific local communities in New Zealand, find a geometric average of 0,7 µg/m³. In absence of specific assessment of H₂S thresholds for the local population under study or definitive international agreements on the threshold, national indications can be considered for computing odour units (OU) as concentration (C) to threshold (T) ratio (OU=C/T). The monitoring of concentration of odorant as H₂S is based on robust metrology and it can provide data with minute frequency or even higher (e.g. 20 s); even if this approach underestimate odour episodes where other odorants play a role, it has the advantage of being based on robust evidence of environmental alteration. Having available continuous monitoring odorant data, and computing odour units as C/T, the 98th percentile for 1-hour mean odour concentrations criterium can be applied to the odour concentrations based on experimental monitoring, instead of more usual estimates from dispersion modelling. An evidence of impact on air quality related to odour perception is produced, without underestimation of odour nuisance due to unrepresentative odour emission rates that conditions modelling results. In the following, a case study is presented about the application of the hourly mean percentile for OU derived from H₂S measured for one year at three monitoring stations around an industrial plant.

2. Materials and methods

2.1 Site

The site considered as case study is located in the city of Trieste in Italy, a coastal city of 210000 inhabitants on the northernmost part of the Adriatic Sea. In close proximity of a densely inhabited district (8300 inh./km²) the biggest oil terminal of the Mediterranean Sea (42,4 million tons of crude oil unloaded in 2017), an integrated steel plant producing pig iron, with coke oven batteries and a blast furnace, as well as the city sewage treatment plant are located. Emissions from the steel plant have shown to alter the surrounding area from sediments (Adami, 2000) to outdoor and indoor air quality (Licen, 2016). Impacts are well evident in settlements at close distance from the plant (less than 0,5 km), but other emission sources appear to play a role on air quality at greater distances (Cozzi, 2010; Astel, 2010; Astel 2013). In the district, odour complaints recorded by the urban police are in number of several hundred a year and they were referred mainly to the iron works; recent studies have shown very high anomalies in the dwellings close to coke oven batteries (Licen, 2018). A study on perception of the life quality highlights how malodour is an issue impacting on citizen wellness in the district (Gabassi, 2017).

2.2 Instrumentation

The regional environmental protection agency, ARPA FVG, has a very articulate monitoring network around the steel plant and, since late 2016, three stations (San Lorenzo railway station-RFI, Pitacco-PIT, Ponticello-PON) are equipped with Teledyne Analytical Instruments T101 H₂S analyzers, measuring hydrogen sulfide (H₂S) as SO₂ by UV fluorescence after a catalytic conversion at 315°C and hydrocarbon kicking. The principle of the method has been proposed since 1981 (Harman, 1981) as a modification of the (Schwartz, 1974) method for SO₂ continuous monitoring method. US EPA has reported procedures for H₂S monitoring

using both Thermo (Diehl, 2006) and Teledyne (Kovacs, 2006; Office of Enforcement and Compliance Assurance, 2016) instruments. Recently (Bluhme, 2016) measured how humidity has an effect on H₂S monitoring data from Thermo instruments, generating underestimates of reported data; authors stated that a similar issue may also apply for Teledyne H₂S measuring devices, but no experimental evidences are available upto now.

Measurement range for H₂S spans from 0,4 to 50 ppb, that is 0,6 to 72 µg/m³; the selected frequency for reporting data within the institutional monitoring is of one hour, even if it could be lowered to less than one minute, allowing to detect short time odour peaks; in the present study this last option has not been implemented.

Periodic calibrations (Teledyne, 2016) are conducted within the institutional QA/QC program of the air quality monitoring network established for the IPPC authorization of the industrial plant.

2.3 Data set

The H₂S concentration data obtained from ARPA FVG and commented in the following were collected from 01 November 2016 to 31 October 2017 at three site PON, RFI and PIT. For each station 8760 (=24 H₂S hourly concentrations/day * 365 days) H₂S hourly concentration data are theoretically available. The hourly wind speed and direction data collected at a site (Molo Fratelli Bandiera, a synoptic weather station in an open position by the sea at 2 km from the plant – considered representative of the meteorological conditions of the city), were also obtained from the regional environmental protection agency (OSMER-ARPA) website. Graphic output of hourly H₂S concentration data handling has been performed by means of the openair package (Carslaw, 2012), running in the R statistical and graphic environment.

3. Results and discussion

3.1 Descriptive statistics for odorant

Basic statistics from instrumental monitoring of the odorant (H₂S) concentrations (µg/m³) as measured at the RFI railway station (RFI), via Pitacco (PIT) and via Ponticello (PON) stations are reported in table 1. RFI station appear as the most impacted receptor. Data above the odour threshold of 1.6 µg/m³ suggested by the Italian agency APAT/ISPRA for H₂S are displayed together with the value of the 98th percentile of the data collected during the considered 365 days; these hourly values represent the concentration that is surpassed on the whole for two weeks within that year; this duration of two weeks (2% of the hours in a year) represents the maximum period of malodour that is tolerated in a year, and it should not surpass odour tolerability criterium. The 98th percentiles are seven times the odour threshold (OT) for H₂S in RFI, four times the OT for PIT and two times the OT for PON. Distributions of H₂S concentrations at the three sites are represented as boxplot in figure 1.

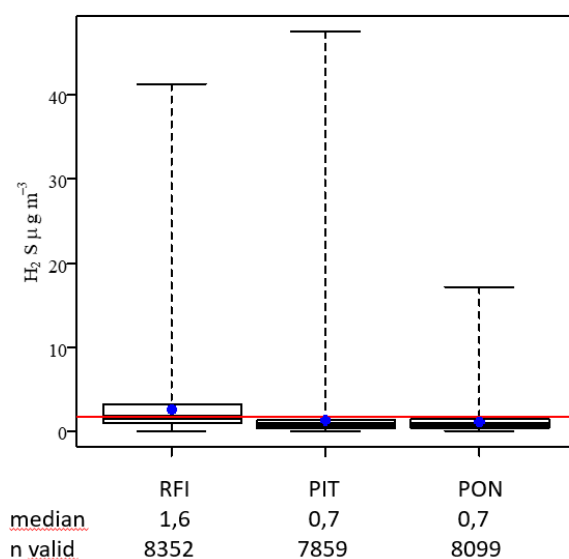


Figure 1: Boxplots for H₂S hourly concentrations (nov.2016- oct.2017) in RFI, PIT and PON; the red line is set at the H₂S odour threshold (1,4 µg/m³); the blue dots represent the mean value for each site.

Table 1: Univariate statistics for H_2S concentration ($\mu g/m^3$) at the RFI, PIT and PON monitoring stations (01/11/2016-31/10/2017)

	min	1st quartile	median	average	3rd quartile	98th percentile	max	valid n	$n > T_{it} (=1,4 \mu g/m^3)$	above/valid %
RFI	0,0	0,9	1,6	2,5	2,9	11,2	41,3	8352	4610	55,2
PIT	0,0	0,3	0,7	1,2	1,3	6,5	47,6	7859	1713	21,8
PON	0,0	0,3	0,7	1,0	1,4	3,7	17,1	8099	1926	23,8

Polar plots allow to display pollutant concentrations in polar coordinates showing concentration by wind speed and direction. They are presented for H_2S concentrations measured at the three stations in fig.2, posted on a map of the area. Warm tones in the color scale are referred to high values of concentration, and they identify the directions from where the wind is blowing from, when highest sulfide contamination occurs. Data from the three monitoring stations point all at the iron works area as the source of the odorant.

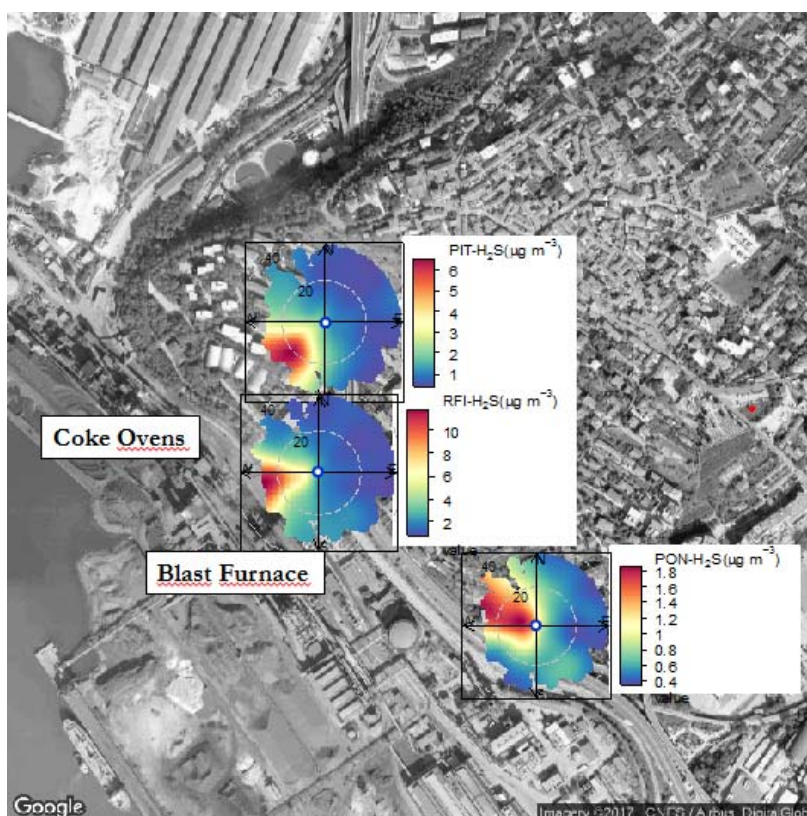


Fig. 2: Polar plots for H_2S hourly concentrations (nov.2016- oct.2017) in RFI, PIT and PON (note different maximum values for the three colour scales).

3.2 Odour concentrations and criteria

The odour impact criterium can be derived as the 98th percentile of hourly odour units computed as ratios of experimentally measured odorant (H_2S) concentrations to the odour detection threshold for the considered odorant. This indicator identifies the odour units that are exceeded for more than a week in a year at the considered receptor, and it should not exceed the value that is authorised in the area. The definition of the odour threshold is a very sensitive parameter for determining the odour units, as it is shown in Table 2, where the threshold reported in the document from the Italian environmental protection agency $T_{it} = 1,4 \mu g/m^3$ (Laraia, 2003), and two values reported by the World Health Organization $T_{WHOlow} = 0,2 \mu g/m^3$ and $T_{WHOhigh} = 0,2 \mu g/m^3$ (WHO,2000), are considered. More, a corrective factor can be applied to the 98th percentile indicator, so to account for the sensorial relevance of short time odour peaks, by applying a peak-to-mean ratio factor to the hourly OU in an analogous way as it has been applied to the dispersion modelling results. If short time odorant measures (e.g. 20 seconds or one minute frequency data) the introduction of this correction/bias would not be necessary.

Table 2: Odour Units computed as ratio of hourly Concentration to odour detection Threshold for H₂S (T_{It} (Laraia, 2003), T_{WHOlow} and $T_{WHOhigh}$ (WHO,2000)), at the 98th percentile in a year of measures (01/11/2016-31/10/2017) for the RFI, PIT and PON monitoring stations

	$T_{It} = 1,4 \text{ ug/m}^3$			$T_{WHOlow} = 0,2 \text{ ug/m}^3$			$T_{WHOhigh} = 2,0 \text{ ug/m}^3$		
	RFI	PIT	PON	RFI	PIT	PON	RFI	PIT	PON
98th percentile of OU=C/T hourly values	8,0	4,6	2,7	55,9	32,5	18,6	5,6	3,3	1,9
98th percentile of OU=C/T hourly values corrected by peak/mean factor = 4	32,0	18,6	10,6	223,7	130,0	74,2	22,4	13,0	7,4

Table 2 shows how in all the considered cases, the odour threshold even for a single odorant is exceeded at the 98th percentile of yearly hours, and especially if the peak-to-mean ratio is applied. Odour concentration is by far higher than odour detection threshold for more than one week per year, and instrumental measures can support complaints from citizens claiming recurrent and significative odour impacts.

Thresholds T_{It} and $T_{WHOhigh}$ provide comparable results, while the use of T_{WHOlow} implies an assessment showing a more severe scenario for almost an order of magnitude (e.g. for PIT: 98th percentile OU T_{It} corrected = 18,6 $\mu\text{g}/\text{m}^3$ vs 98th percentile OU T_{WHOlow} corrected = 130,0 $\mu\text{g}/\text{m}^3$).

4. Conclusions

The 98th percentiles of hourly odour concentrations based on yearly instrumental measures at three receptor sites have been computed in order to provide objective/instrumental evidence of odour impacts, in terms of experimental estimate of odour concentration in ambient air and of overall duration of significant odour impact within the year. The approach can be useful when there is relevant variability of odour emission rates of considered sources, hindering adequate dispersion modelling. It has been applied in the case of semi - continuous instrumental measures of a single odorant, i.e. hydrogen sulfide, but the approach has the potential for being applied to cases of multiple odorant monitoring and also in cases of explicit odour concentration monitoring by means of instrumental methods as the so called electronic noses. Further improvements could be done if four minutes' frequency data (Teledyne, 2016) would be selected and if a local threshold for the odorants (Iremonger, 2012) would be available. More, the obtained indicator could be matched with annoyance criteria, based on odour concentrations and acceptability assessment, as suggested by (Chaignaud, 2014).

Acknowledgements

Authors gratefully thank the "Agenzia per la Protezione Ambientale del Friuli Venezia Giulia" ARPA-FVG, and especially M. Bellini and F. Stel, for providing monitoring data about H₂S concentrations in ambient air in Trieste.

References

- Adami G., Barbieri P., Piselli S., Predonzani S., Reisenhofer E. 2000, Detecting and characterising sources of persistent organic pollutants (PAHs and PCBs) in surface sediments of an industrialized area (harbour of Trieste, northern Adriatic Sea), *Journal of Environmental Monitoring*, 2, 261-265.
- Amoore J.E., Hautala E. 1983, Odor as an aid to chemical safety: odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution, *Journal of Applied Toxicology*, 3, 272-290.
- Astel A., Cozzutto S., Cozzi F., Barbieri P., Tsakovski S., Simeonov V. 2010, Seasonal apportionment of the sources of ambient air particulates in the city of Trieste, *International Journal of Environment and Pollution*, 41, 70-89.
- Astel A., Giorgini L., Mistaro A., Pellegrini I., Cozzutto, S., Barbieri P. 2013, Urban BTEX spatiotemporal exposure assessment by chemometric expertise, *Water, Air and Soil Pollution*, 224(4),1503.
- Brancher M., Griffiths K.D., Franco D., de Melo Lisboa H. 2017, A review of odour impact criteria in selected countries around the world, *Chemosphere*, 168,1531-1570.
- Bull M., McIntyre A., Hall D., Allison G., Redmore J., Pullen J., Caird L., Stouling M., Fain R. 2014, Guidance on the Assessment of Odour for Planning. Institute of Air Quality Management (IAQM), London.
- Capelli L. Sironi S., Del Rosso R., Guillot J.M. 2013, Measuring odours in the environment vs. dispersion modelling: A review, *Atmospheric Environment*, 79, 731-743.

- Carlsaw D.C., Ropkins K. 2012, Openair – an R package for air quality data analysis, *Environmental Modelling Software*, 27–28, 52–61.
- Chaignaud M., Cariou S., Poette J., Fages M., Despres J.F., Fanlo J.L. 2014, A new method to evaluate odour annoyance potential, *Chemical Engineering Transactions*, 40, 13-18.
- Chou S.J. 2003, Hydrogen Sulfide: Human Health Aspects, WHO Concise International Chemical Assessment Document 53.
- Collins P., Lewis L. 2000, Hydrogen Sulfide: Evaluation of Current California Air Quality Standard with respect to Protection of Children, The California air resources board and California office of environmental health hazard assessment.
- Cozzi F., Adami G., Barbieri P., Reisenhofer E., Apostoli P., Bovenzi M. 2010, Toxic elements content in PM10 samples from a coastal area of the Northern Adriatic Sea, *Central European Journal of Chemistry*, 8, 1014-1026.
- Diehl C. A., Bogan B. W., Grant R. H., Boehm M. T. 2006, EPA Standard Operating Procedure G5: Measurement of Hydrogen Sulfide (H₂S) with the Thermo Electron Corporation Model 450I Pulsed-Fluorescence Analyzer, Tech. rep., Agricultural and Biological Engineering, Purdue University, IN, USA.
- Dincer F., Muezzinoglu A., 2007, Odor determination at wastewater collection systems: Olfactometry versus H₂S analyses, *Clean - Soil, Air, Water*, 35, 565-570.
- Gabassi P., Garzitto M., Sist P., Urbani R. 2016, Valutazione della qualità della vita e stress ossidativo in ambiente urbano limitrofo a insediamenti industriali, *Poliarchie/Polyarchies 2016/2*, Trieste, EUT Edizioni.
- Giungato P., de Gennaro G., Barbieri P., Briguglio S., Amodio M., de Gennaro L., Lasigna F. 2016, Improving recognition of odors in a waste management plant by using electronic noses with different technologies, gas chromatography–mass spectrometry/olfactometry and dynamic olfactometry, *Journal of Cleaner Production*, 133, 1395-1402.
- Guillot J.-M. 2016, E-noses: Actual limitations and perspectives for environmental odour analysis, *Chemical Engineering Transactions*, 54, 223-228.
- Harman J. N. 1981, Interference Reactor to Provide Selective SO₂ Measurement by Fluorescent Methodology, U.S. Patent No. 4, 272, 486.9 <https://patents.google.com/patent/US4272486>
- Iremonger S.D. 2012, Review of Odour Properties of H₂S: Odour Threshold Investigation 2012, Bay of Plenty Regional Council Environmental Publication 2012/06.
- Kim K.H., Park S.Y. 2008, A comparative analysis of malodor samples between direct (olfactometry) and indirect (instrumental) methods, *Atmospheric Environment*, 42, 5061–5070.
- Kovacs G.J., Reiter L.W. 2005 Ambient hydrogen sulfide analyzer application: measuring hydrogen sulfide concentrations at a swine finishing farm technology name: model 101E.
- Laraia R., Centola P., Il Grande M., Sironi S., Sberveglieri G., Pardo M. 2003, Metodi di misura delle emissioni olfattive, APAT Manuali e linee guida 19/2003.
- Licen S., Tolloi A., Briguglio S., Piazzalunga A., Adami G., Barbieri P. 2016, Small scale spatial gradients of outdoor and indoor benzene in proximity of an integrated steel plant, *Science of the Total Environment* 553, 524-531.
- Licen S., Barbieri G., Fabbris A., Briguglio S.C., Pillon A., Stel F., Barbieri P. 2018, Odor control map: Self organizing map built from electronic nose signals and integrated by different instrumental and sensorial data to obtain an assessment tool for real environmental scenarios, *Sensors and Actuators B: Chemical*, 263, 476-485.
- Needham C.E., Freeman T.J. 2009, Case studies in the use of source specific odour modelling guidelines. In: *Proceedings of the Water New Zealand's 51st Annual Conference & Expo. Water New Zealand Annual Conference, Rotorua, NZ.*
- New Zealand Ministry for the Environment 2002, Ambient air quality guidelines: 2002 update.
- Office of Enforcement and Compliance Assurance 2016, Appendix to Compendium of Next Generation Compliance Examples In Clear Air Act Programs, U.S. Environmental Protection Agency.
- Romain A.-C., Capelli L., Guillot J.-M. 2017, Instrumental odour monitoring: Actions for a new European standard (Conference Paper) ISOEN 2017 - ISOCS/IEEE International Symposium on Olfaction and Electronic Nose, Proceedings 5 July 2017, Article number 7968868.
- Schwarz F.P., Okabe H., Whittaker J.K. 1974, Fluorescence detection of sulfur dioxide in air at the parts per billion level, *Anal. Chem.*, 46 (8), pp 1024–1028.
- World Health Organization 2000, Air quality guidelines for Europe, 2nd ed. Chapter 6.6 Hydrogen Sulfide.
- Wu C., Liu J., Zhao P., Piringier M., Schaubberger G. 2016, Conversion of the chemical concentration of odorous mixtures into odour concentration and odour intensity: A comparison of methods, *Atmospheric Environment*, 127, 283-292.