CHEMICAL ENGINEERING TRANSACTIONS
VOL. 54, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Selena Sironi, Laura Capelli
Copyright © 2016, AIDIC Servizi S.r.l.,
**ISBN** 978-88-95608-45-7; **ISSN** 2283-9216

# Dynamic Olfactometry and Sample Toxicity. A Case Study for a MSW Incinerator Odour Assessment Project

Enrico Davoli[a]*, Ettore Zuccato[a], Giancarlo Bianchi[a], Massimiliano Il Grande[b], Simone Bonati[b], Andrea N. Rossi[b], Clemente Porporato[c], Massimiliano Pereno[c], Simona Soldati[d]

[a]Environmental Health Science Department, IRCCS Istituto Mario Negri, Via La Masa 19, 20156 Milano
[b]Progress S.r.L., Via Porpora 147, Milano
[c]ARPA Piemonte Dipartimento Territoriale Nord-Ovest
[d]ARPA Piemonte Dipartimento Tematico di Epidemiologia e Salute Ambientale
enrico.davoli@marionegri.it

The study reported in this paper is focused on occupational exposure to potential toxic compounds for employees working in dynamic olfactometry, following EN 13725:2003 standard procedures.

Municipal solid waste (MSW) incineration plants, typically, have authorized stack emissions for primary pollutants (like CO, NOx, particulate), for selected trace organics (polycyclic aromatic hydrocarbons (PAHs) or dioxins), metals or for total organic compounds (TOC). Odour control is limited on recommendations of good practices for the waste receiving areas and storage, generally on the air management systems.

In Italy there is an increasingly number of requests, to environmental inspection authorities, Agenzia Regionale per la Protezione Ambientale (ARPA), Regional Environment Agency, to quantitatively describe possible odour annoyance effects from different industrial plants, including MSW incineration plants. Recently ARPA Piemonte has been asked to perform one odour survey for the newly incinerator for the city of Torino, that burns 500,000 t/y of MSW recovering energy through cogeneration. The plant is equipped with a pollutant's automated measuring system (AMS) to assess the compliance with the emission limit values, but not to measure odour emissions. For this reason, it is necessary to assess odour emissions as well, in order to prepare an exhaustive environmental odour scenario for the whole area.

We recently presented a risk assessment approach, to evaluate non-carcinogenic and carcinogenic compounds for different sample types, based on STEL or TWA data, or EPA slope factors values respectively. It has been decide to follow this approach to define potential sample toxicity (PT), using the different risk occupational scenarios proposed, before odour concentration analysis of stack emissions samples. Using emission limit values that are set in the permit, PT has been defined. Since samples are presented to assessors in an ascending concentration series, workers exposure has been limited to acceptable levels defining the specific minimum dilution value to be used in the ARPA Piemonte olfactometric laboratory standard procedures.

## 1. Introduction

Environmental odour pollution is a complex problem that is producing an increasing number of complaints. Individuals living near confined animal facilities, wastewater treatment plants and biosolids recycling operations have primary complaints associated both with annoyance caused by odours and concerns about health risks from exposure to the odorants. The problem of environmental odour pollution and health is obviously not limited to few activities, and is not new. In the mid 1800s “smellscapes” or olfactory maps of New York City were constructed for “navigating the city to avoid odors and protect health” (Kiechle 2015) and sanitarian, concern about stenches, encouraged the creation of Metropolitan Board of Health responsible for urban breathing. With the global increase of environmental regulations in the 1970’s, United States followed by European countries began to develop standards of evaluation for odours, to go beyond personal experience of Board of Health members. Some examples of these standards are: US-ASTM D-1391 (1978), ASTM E679 - 91(1991), VDI 3881 (1980, Germany), AFNOR X-43-101 (1986, France), NVN2820 (1996, Netherlands). Standardized methods that are dependable, reproducible, objective, and quantitative are the basis for a correct governance of odour nuisance.

Municipal solid waste (MSW) management is one of the most critical activity in this respect for communities. For example landfills are identified as a hazardous air pollutant source under the Urban Air Toxic Strategy (EPA, 1999) and there is an increased attention from the population for toxicological aspects due to municipal solid waste (MSW) landfilling. Several hazardous air pollutants (HAP) are present in landfill gas, some of these being known carcinogen for humans. Environmental air quality can be assessed with analytical instrumentation but environmental odour measurement is still a challenge. Several instruments are now available for the environmental odour scientist, starting from single solid-state sensors (Chiu, 2013), to electronic noses (Capelli, 2014), up to laboratory-grade analytical methods based on gas chromatography/mass spectrometry with different pre-concentration approaches and devices (Davoli, E., 2003; Dincer, 2006; Durmusoglu, 2010; Kleeberg, 2005). The use of dedicated instruments, sensors, or chemical analysis to measure odour concentrations is still not possible mainly due to the synergy, inhibition and masking phenomena between different compounds in our sense of olfaction. There is still a strong need of instrumental analytical technologies to characterize and quantify the odour to define objective solutions, to describe the environment and the health effects. European Union (EC, 2003) stated that determination of odour concentration can be made, at least until now, only by dynamic olfactometry and EN 13725:2003 method were finally published in order to standardize the methodology within the Member States. As no instruments are available to measure the effects of a mixture of odorants, a panel of qualified human assessors tests the presence of “odour” to a diluted sample. The sample dilution ratio is decreased until the assessors “feel” the odour. By applying this procedure, when samples contain chemicals of potential concern (COPCs), a potential health issue is present (Davoli, E., 2010; Orzi, 2010; Scaglia, 2011; Ying, 2012; Zhao, 2015). This standard was published ten years ago now, and is necessary to revise it in order to improve aspects. The working group WG2 of CEN/TC264 was reactivated at the end of 2012 to start the revision. Within this revision, the Task Group 9: Health and safety issues has been created to discuss procedures to warranty safety for the assessors (panellists).

Recently guidelines for a safe occupational health have been proposed. ARPA Piemonte is preparing a proposal of a technical reference procedure (fig. 1) for dynamic olfactometry where an occupational health management system will be defined for workers involved in dynamic olfactometry. Samples that arrive in laboratories involved in odour assessment have more and more different origins, and presence of COPCs is real. The olfactometric laboratory of ARPA Piemonte has been asked to perform a MSW incinerator odour assessment study and an occupational health concern was present due to the fact that for this study the determination of the odour concentration of gas samples of the stack emissions should be undertaken, but COPCs presence in those stack emissions is well known and documented. In this work we present results of the use of this approach to present a case study for this MSW incinerator odour assessment project feasibility in an EN13725:2003 operating laboratory.

## 2. Methods

### 2.1 Samples description

The MSW incinerator under study is located in Torino, Italy. The plant installation has been authorised, with an Integrated Environmental Authorisation (Autorizzazione Integrata Ambientale, AIA) in 2006 (n. 309 – 557341) with modifications during the years. The emission limit values set out in the permit for emissions into air are reported in table 1a-c http://www.cittametropolitana.torino.it/cms/. Metals and organometallic compounds emissions has been set as well, to 0.05 mg/m$^3$ (Cd, Tl and Hg) and 0.5 mg/m$^3$ (Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn) (1 hour average).

Arpa Piemonte
Agenzia Regionale per la Protezione Ambientale

**Procedura Tecnica**
Realizzazione del prodotto

**Determinazione della concentrazione di odore mediante olfattometria dinamica**

**U.RP.T122**

| Revisione | Data | Oggetto Revisione |
|---|---|---|
| 1 | | Prima emissione |
| 2 | | Seconda emissione |

*Figure 1: ARPA Piemonte will be publishing a proposal for technical reference procedures for the olfactometric laboratory operating under EN 13725:2003 standard procedures.*

*Table 1a: Authorized stack emissions for the MSW under study*

| | Emission values | | |
|---|---|---|---|
| Parameter | daily average mg/m$^3$ | 30 min average (100%) mg/m$^3$ | 30 min average (97%) mg/m$^3$ |
| Total suspended particles (TSP) | 10 | 30 | 10 |
| Total organic compounds (TOC) | 10 | 20 | 10 |
| Chlorine and total inorganic chlorine compounds as HCl | 10 | 60 | 10 |
| Fluorine and total inorganic chlorine compounds as HF | 1 | 4 | 2 |
| Sulphur oxides as SO2 | 50 | 200 | 50 |
| Nitrogen oxides as NO2 | 200 | 400 | 200 |
| Ammonia ($NH_3$) | 5 | 15 | 5 |

*Table 1b: Authorized stack emissions for the MSW under study*

| | Emission values |
|---|---|
| Parameter | 8 hour average |
| Dioxins and furanes (PCDD + PCDF) | 0.1 ng/m$^3$ |
| Polycyclic aromatic hydrocarbons (PAHs) | 0.01 mg/m$^3$ |

*Table 1c: Authorized stack emissions for the MSW under study*

| | Emission values | |
|---|---|---|
| Parameter | daily average mg/m$^3$ | 30 min average mg/m$^3$ |
| Carbon monoxide (CO) | 50 | 100 |

## 2.2 Risk Assessment

Workers considered are those in the laboratory, the assessors and the panel leader, while the sampling operators have not been considered here. Assessors' exposure is only through the sniffing port, of diluted samples. For this reason the exposure pathways considered are limited to inhalation. The panel leader works remote from the sniffing ports, and his main potential exposure is during connection of sample bags to the olfactometer. His exposure might therefore be considered only accidental, due to non-appropriate operations with the bags if sample, and no assessments of risk have been estimated in this work.

Exposure assessment was based on two different scenarios, to analyze a "commercial" olfactometric laboratory (owned by a private company) and an "institutional" olfactometric laboratory (owned by an environmental inspection authority). It has been based on a large, 7 years database, with close to 10,000 samples analyzed, available from the commercial olfactometric laboratory, and to a limited database, with a provisional sample estimates, coming from the institutional olfactometric laboratory of ARPA Piemonte.

For the first case, the commercial laboratory, the majority of assessors were exposed to a number of samples in the range of 10-50 per month. Assuming a conservative value of 60 samples/month, with 8 samples/day, assessors are exposed 90 days/year (EF). Assuming a number of rounds in the odour measurement equal to 3, assuming an average number of presentations in the dilution series equal to 5 and assuming an inhalation time (evaluation time according to EN 13725:2003 clause 8.2) equal to 2.2 seconds, we derive an exposure time, ET, of 0.073 hours. ED is imposed to 10 years.

For the second case, the ARPA institutional laboratory, EF is limited to 10 days/year. An average of 9 samples/day has been assessed, with with 9 dilution series in average and 3 number of rounds, with 2.3 sec inhalation time. In this case ET is 0.17 hours out of 24 hours and an averaging time of 365 days for 70 years. ED is imposed by the procedure, being 7 years.

Risk assessment (RA) has been performed both for carcinogenic (Fig. 2) and non carcinogenic (fig. 3) risk for all COPCs authorised in stack emissions. These values have been monitored during the years and are all well documented. As an input, the maximum authorised values were used.

Carcinogenic excess lifetime risk were calculated as follows (1):

$$Inhalation\ Risk = \ CDI\ *\ IUR \tag{1}$$

where inhalation exposure (2), CDI is:

$$CDI_{iw-air-ca}\left(\frac{\mu g}{m^3}\right) = \frac{C_{air}\ \left(\frac{\mu g}{m^3}\right)\ EF_{iw}\left(\frac{250\ days}{year}\right) ED_{iw}(25years)\ ET_{iw}\left(\frac{8\ hours}{day}\right)\left(\frac{1\ day}{24\ hours}\right)}{AT_{iw}\left(\frac{365\ days}{year}\right) LT\ (70\ years)} \tag{2}$$

Non-carcinogenic effects were calculated as follows (3):

$$HQ = \ \frac{CDI}{RfC} \tag{3}$$

where inhalation exposure (4), CDI is:

$$CDI_{iw-air-ca}\left(\frac{\mu g}{m^3}\right) = \frac{C_{air}\ \left(\frac{\mu g}{m^3}\right)\ EF_{iw}\left(\frac{250\ days}{year}\right) ED_{iw}(25years)\ ET_{iw}\left(\frac{8\ hours}{day}\right)\left(\frac{1\ day}{24\ hours}\right)}{AT_{iw}\left(\frac{365\ days}{year}\right) ED_{iw}(25\ years)\left(\frac{1000\ \mu g}{1mg}\right)} \tag{4}$$

RA calculations have been performed using the RAIS Risk Exposure Models for Chemicals available from The Risk Assessment Information System (https://rais.ornl.gov/) using the default RAIS Chemicals Toxicity and Properties. In the model, indoor workers equations inputs for Air have been used. As stated in the RAIS web pages “although the toxicity values presented in the formal and condensed toxicity profiles were correct at the time they were produced, the toxicity values are subject to change”. The advantage of this approach is the use of a public domain system, with updated and standardized toxicity profiles. The calculator tool is ready to use and it performs a complete RA study for specific problems. More refined RA studies can be performed in case of particular situations, using different exposure scenarios or locally regulated toxicity values, with an overview of a trained risk assessor.

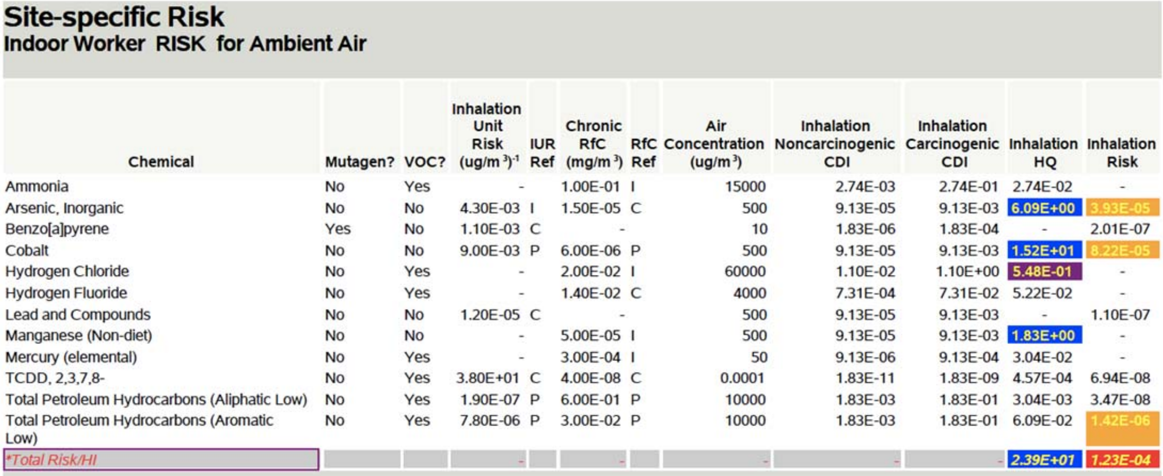
### 2.3 COPCs considered

In compliance with EN 13725:2003 clause 7.3.1, particulate materials are removed from the sample flow, so the presence of particulate in samples has not been considered. All other compounds emitted to air and mentioned in the permit have been considered, including metals. In fig. 2 and 3 all different COPCs considered are listed, along with their toxicity values used in calculations.

## 3. Results and conclusions

Figure 2 and 3 report the results obtained with using the default RAIS PRG Calculator. The method proposed defined sample PT with respect to different pollutants. This allows the laboratory manager, risk assessors or others involved in decision making, to determine, if necessary, a minimum dilution factor, to protect workers/panellists health. To protect employees working in dynamic olfactometry tests, is therefore important to define a minimum dilution value to guarantee an acceptable carcinogenic risk level (risk < $10^{-6}$ for a single compound and $10^{-5}$ as a total in case of mixtures) and an acceptable non-carcinogenic risk level (HQ < 1). It must be stressed that the purpose of this approach is to assist the olfactometric laboratory manager to set a safe minimum dilution value for panellist, therefore, in case of complex, site specific risks, it might be appropriate to adopt more restrictive parameters. This with respect to default acceptable risk values especially for the cumulative carcinogenic risk for all actual and potential carcinogenic contaminants when the carcinogenic risk exceeds $10^{-5}$.

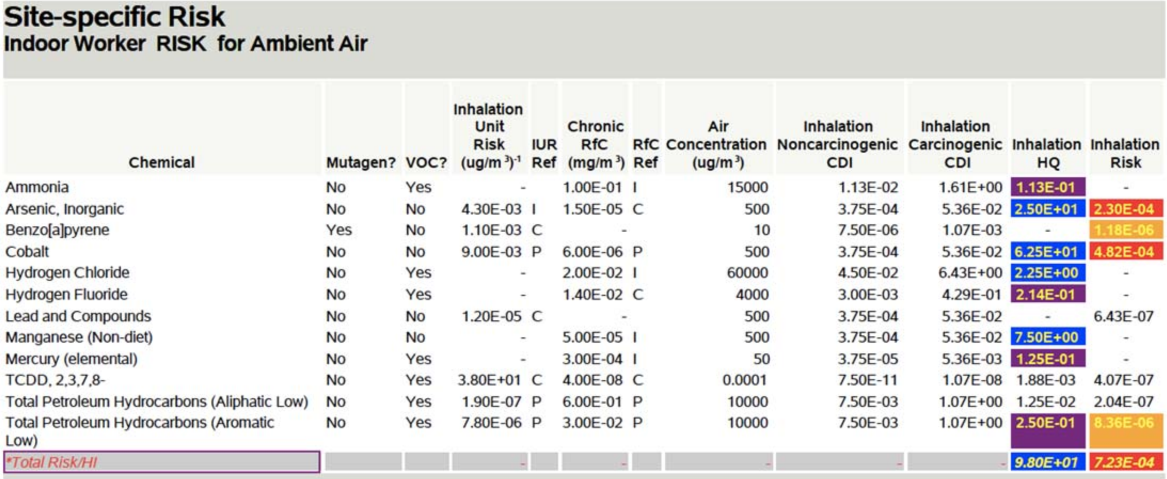
For this MSW incinerator plant samples a **minimum dilution value** should be set at least to 73 for the commercial and to 24 for the institutional laboratory in order to guarantee a safe occupational level for panellists.



**Site-specific Risk**
**Indoor Worker RISK for Ambient Air**

| Chemical | Mutagen? | VOC? | Inhalation Unit Risk $(ug/m^3)^{-1}$ | IUR Ref | Chronic RfC $(mg/m^3)$ | RfC Ref | Air Concentration $(ug/m^3)$ | Inhalation Noncarcinogenic CDI | Inhalation Carcinogenic CDI | Inhalation HQ | Inhalation Risk |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ammonia | No | Yes | - |  | 1.00E-01 | I | 15000 | 2.74E-03 | 2.74E-01 | 2.74E-02 | - |
| Arsenic, Inorganic | No | No | 4.30E-03 | I | 1.50E-05 | C | 500 | 9.13E-05 | 9.13E-03 | 6.09E+00 | 3.93E-05 |
| Benzo[a]pyrene | Yes | No | 1.10E-03 | C | - |  | 10 | 1.83E-06 | 1.83E-04 | - | 2.01E-07 |
| Cobalt | No | No | 9.00E-03 | P | 6.00E-06 | P | 500 | 9.13E-05 | 9.13E-03 | 1.52E+01 | 8.22E-05 |
| Hydrogen Chloride | No | Yes | - |  | 2.00E-02 | I | 60000 | 1.10E-02 | 1.10E+00 | 5.48E-01 | - |
| Hydrogen Fluoride | No | Yes | - |  | 1.40E-02 | C | 4000 | 7.31E-04 | 7.31E-02 | 5.22E-02 | - |
| Lead and Compounds | No | No | 1.20E-05 | C | - |  | 500 | 9.13E-05 | 9.13E-03 | - | 1.10E-07 |
| Manganese (Non-diet) | No | No | - |  | 5.00E-05 | I | 500 | 9.13E-05 | 9.13E-03 | 1.83E+00 | - |
| Mercury (elemental) | No | Yes | - |  | 3.00E-04 | I | 50 | 9.13E-06 | 9.13E-04 | 3.04E-02 | - |
| TCDD, 2,3,7,8- | No | Yes | 3.80E+01 | C | 4.00E-08 | C | 0.0001 | 1.83E-11 | 1.83E-09 | 4.57E-04 | 6.94E-08 |
| Total Petroleum Hydrocarbons (Aliphatic Low) | No | Yes | 1.90E-07 | P | 6.00E-01 | P | 10000 | 1.83E-03 | 1.83E-01 | 3.04E-03 | 3.47E-08 |
| Total Petroleum Hydrocarbons (Aromatic Low) | No | Yes | 7.80E-06 | P | 3.00E-02 | P | 10000 | 1.83E-03 | 1.83E-01 | 6.09E-02 | 1.42E-06 |
| **Total Risk/HI* |  |  | - |  | - |  | - | - | - | ***2.39E+01*** | ***1.23E-04*** |

*Figure 2: Simulation for the Institutional laboratory. Output of the RAIS PRG Calculator used for this study. For this MSW incinerator plant a **minimum dilution value should be set at least to 24** in order to guarantee a safe occupational level for panellists. In this case the limiting factor is the non carcinogenic risk with an **Inhalation HQ** value of 2.39 E+01 while the acceptable non-carcinogenic risk level is HQ < 1.*



**Site-specific Risk**
**Indoor Worker RISK for Ambient Air**

| Chemical | Mutagen? | VOC? | Inhalation Unit Risk $(ug/m^3)^{-1}$ | IUR Ref | Chronic RfC $(mg/m^3)$ | RfC Ref | Air Concentration $(ug/m^3)$ | Inhalation Noncarcinogenic CDI | Inhalation Carcinogenic CDI | Inhalation HQ | Inhalation Risk |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ammonia | No | Yes | - |  | 1.00E-01 | I | 15000 | 1.13E-02 | 1.61E+00 | 1.13E-01 | - |
| Arsenic, Inorganic | No | No | 4.30E-03 | I | 1.50E-05 | C | 500 | 3.75E-04 | 5.36E-02 | 2.50E+01 | 2.30E-04 |
| Benzo[a]pyrene | Yes | No | 1.10E-03 | C | - |  | 10 | 7.50E-06 | 1.07E-03 | - | 1.18E-06 |
| Cobalt | No | No | 9.00E-03 | P | 6.00E-06 | P | 500 | 3.75E-04 | 5.36E-02 | 6.25E+01 | 4.82E-04 |
| Hydrogen Chloride | No | Yes | - |  | 2.00E-02 | I | 60000 | 4.50E-02 | 6.43E+00 | 2.25E+00 | - |
| Hydrogen Fluoride | No | Yes | - |  | 1.40E-02 | C | 4000 | 3.00E-03 | 4.29E-01 | 2.14E-01 | - |
| Lead and Compounds | No | No | 1.20E-05 | C | - |  | 500 | 3.75E-04 | 5.36E-02 | - | 6.43E-07 |
| Manganese (Non-diet) | No | No | - |  | 5.00E-05 | I | 500 | 3.75E-04 | 5.36E-02 | 7.50E+00 | - |
| Mercury (elemental) | No | Yes | - |  | 3.00E-04 | I | 50 | 3.75E-05 | 5.36E-03 | 1.25E-01 | - |
| TCDD, 2,3,7,8- | No | Yes | 3.80E+01 | C | 4.00E-08 | C | 0.0001 | 7.50E-11 | 1.07E-08 | 1.88E-03 | 4.07E-07 |
| Total Petroleum Hydrocarbons (Aliphatic Low) | No | Yes | 1.90E-07 | P | 6.00E-01 | P | 10000 | 7.50E-03 | 1.07E+00 | 1.25E-02 | 2.04E-07 |
| Total Petroleum Hydrocarbons (Aromatic Low) | No | Yes | 7.80E-06 | P | 3.00E-02 | P | 10000 | 7.50E-03 | 1.07E+00 | 2.50E-01 | 8.36E-06 |
| **Total Risk/HI* |  |  | - |  | - |  | - | - | - | ***9.80E+01*** | ***7.23E-04*** |

*Figure 3: Simulation for the commercial laboratory. Output of the RAIS PRG Calculator used for this study. For this MSW incinerator plant a **minimum dilution value should be set at least to 73** in order to guarantee a safe occupational level for panellists. In this case the limiting factor is the carcinogenic risk with an **Inhalation Risk** value of 7.23 E-04 while the acceptable carcinogenic risk level is < $10^{-6}$.*

This study shows that Risk Assessment is a valid and reliable approach to evaluate carcinogenic and non-carcinogenic effects related to potential sample toxicity, before dynamic olfactometry exposure. In this specific case study, Risk Assessment method results highlight both a carcinogenic and non-carcinogenic inhalation risk from MSW stack emission, using emission limit values set out in the permit.

Moreover, the use of default RAIS PRG Calculator allows risk assessment calculations to be performed in every laboratory, without the need of trained personnel. Risk assessors might be involved for selected cases where either emission scenarios are complex or when pollutants are significative and are not listed in standard databases and expert opinion is necessary.

## References

Chiu, S.W., & Tang, K.T. (2013). Towards a chemiresistive sensor-integrated electronic nose: a review. Sensors (Basel), 13(10), 14214-14247.

Capelli, L., Sironi, S., & Del Rosso, R. (2014). Electronic noses for environmental monitoring applications. Sensors (Basel), 14(11), 19979-20007.

Davoli, E., Gangai, M.L., Morselli, L., & Tonelli, D. (2003). Characterisation of odorants emissions from landfills by SPME and GC/MS. Chemosphere, 51(5), 357-368.

Davoli, E., Fattore, E., Paiano, V., Colombo, A., Palmiotto, M., Rossi, A.N., Il Grande, M., & Fanelli, R. (2010). Waste management health risk assessment: a case study of a solid waste landfill in South Italy. Waste Management, 30(8-9), 1608-1613.

Davoli, E., Zuccato, E., Bianchi, G., Palmiotto, M., Il Grande, M., Bonati, S., & Rossi, A.N. (2012). Dynamic Olfactometry and Potential Sample Toxicity. Guidelines for a Safe Occupational Health Approach. Chem. Eng. Trans., 30, 7-12.

Dincer, F., Odabasi, M., & Muezzinoglu, A. (2006). Chemical characterization of odorous gases at a landfill site by gas chromatography-mass spectrometry. J Chromatogr A, 1122(1-2), 222-229.

Durmusoglu, E., Taspinar, F., & Karademir, A. (2010). Health risk assessment of BTEX emissions in the landfill environment. J Hazard Mater, 176(1-3), 870-877.

EN 13725: 2003. Air Quality - Determination of odour concentration be dynamic olfactometry, CEN.

Kiechle, M. (2015) Navigating by Nose: Fresch Air, Stench Nuisance, and the Urban Environment, 1840, 1880. J. Urb. History, 1-19

Kleeberg, K.K., Liu, Y., Jans, M., Schlegelmilch, M., Streese, J., & Stegmann, R. (2005). Development of a simple and sensitive method for the characterization of odorous waste gas emissions by means of solid-phase microextraction (SPME) and GC-MS/olfactometry. Waste Manag, 25(9), 872-879.

Orzi, V., Cadena, E., D'Imporzano, G., Artola, A., Davoli, E., Crivelli, M., & Adani, F. (2010). Potential odour emission measurement in organic fraction of municipal solid waste during anaerobic digestion: Relationship with process and biological stability parameters. Bioresour Technol, 101(19), 7330-7337.

Scaglia, B., Orzi, V., Artola, A., Font, X., Davoli, E., Sanchez, A., & Adani, F. (2011). Odours and volatile organic compounds emitted from municipal solid waste at different stage of decomposition and relationship with biological stability. Bioresour Technol, 102(7), 4638-4645.

Ying, D., Chuanyu, C., Bin, H., Yueen, X., Xuejuan, Z., Yingxu, C., & Weixiang, W. (2012). Characterization and control of odorous gases at a landfill site: a case study in Hangzhou, China. Waste Manag, 32(2), 317-326.

Zhao, Y., Lu, W., & Wang, H. (2015). Volatile trace compounds released from municipal solid waste at the transfer stage: Evaluation of environmental impacts and odour pollution. J Hazard Mater, 300, 695-701.