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#### Applied Geochemistry xxx (2014) xxx-xxx





**Applied Geochemistry** 

journal homepage: www.elsevier.com/locate/apgeochem

# Human Health Risk Assessment of a landfill based on volatile organic compounds emission, immission and soil gas concentration measurements

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#### ARTICLE INFO

Article history: Available online xxxx

#### ABSTRACT

A Human Health Risk Assessment (HHRA) was required for a closed landfill located in Cerdanyola del Vallès (Barcelona, Spain). The HHRA had two objectives, to evaluate the present risk of the identified receptors in the area and to safely develop the future urban planning of the area, therefore 3 scenarios for the current situation and 4 for the future situation were developed.

After reviewing the existing data and exploring the needs of information, the assessment in this study was focused on the measurement of volatile organic compounds (VOCs) fluxes from the subsoil (emission from the landfill at 5 points), concentrations of VOCs in the air (immission in 4 urban sites) and concentration of VOCs in soil–gas (measurements at 5 m below ground surface outside the landfill at 8 sites). Around 70 VOCs were analyzed by using multi-sorbent tubes and Thermal Desorption Gas Chromatogra-phy (TD–GC–MS). The VOCs that were detected and quantified include alkanes, aromatic hydrocarbons, alcohols, ketones, halocarbons, aldehydes, esters, terpenoids, ethers and some nitrogenated and sulfur compounds, furans and carboxylic acids. Specific mercury flux measurements were performed in a hot spot by using carulite tubes, that were also analyzed by using Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry.

Results showed average values of volatile emission fluxes ranging from non-detected to 331  $\mu$ g m<sup>-2</sup> day<sup>-1</sup> (dichlorodifluoromethane). In the case of immission, the concentration of VOCs measured in the air of populated area surrounding the landfill ranged values from non-detected to 42.0  $\mu$ g m<sup>-3</sup> (acetic acid). The soil–gas measurements in piezometers around the landfill showed individual VOC values with a maximum 830  $\mu$ g m<sup>-3</sup> for dichlorodifluoromethane.

With the obtained fluxes and concentrations in air and soil–gas, USEPA methodology and modeling was used to evaluate equivalent concentration in the scenarios considered. Toxicity values from IRIS database were used to finally obtain chemical risk indicators. Admissible risk indicators were obtained in all scenarios. The VOCs that contributed more to risk indexes in RH2 were trichloroethylene, trimethylbenzene, chloroform, 1,2-dichloroethane and carbon tetrachloride. The carcinogenic risk in RH7 was linked to the presence of benzene and chloroform. The comparison of the measurements of the present work with other landfills evidence that HHRA in ambient air would be needed in order to perform a correct landfill management.

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#### 1. Introduction

http://dx.doi.org/10.1016/j.apgeochem.2014.06.018 0883-2927/© 2014 Elsevier Ltd. All rights reserved. The presence of VOCs and other trace contaminants in subsoil due to landfills, contaminated soils or contaminated groundwater is an important source of risk, as these contaminants could remain after an incomplete remediation of these sites for new uses.

In the case of the landfills, the characterization of emitted trace gases is an important topic for Risk Assessment (Butt et al., 2008) and measurements have to be focused on trace pollutants like VOCs,

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mercury and sulfur species, depending on the kind of waste buried and the processes (aerobic, anaerobic) involved in the landfill.

Mercury is directly linked to wastes with batteries, fluorescents and thermometers and is usually characterized as elemental vapor form (Kim et al., 2001; Kim and Kim, 2002). Methylated species can also be characterized (Lindberg et al., 2005) but usually represent small percentage of total mercury (Lindberg et al., 2001).

Volatile sulfur compounds (VSCs) or reduced sulfur compounds (RSCs) are sometimes most dominant components in air other than trace carbon compounds (Kim et al., 2006b) and this predominance is usually linked to malodorous problems (Kim et al., 2005).

The emission of VOCs from the landfills allows to describe the release of these contaminants from a specific source, a landfill, to air. As HHRA of VOCs finally needs to evaluate the indoor and out-door concentrations in defined scenarios, the direct immission measurements or modeled concentrations in air are needed. Emission and soil–gas measurements could be used for the modeling of air quality in scenarios linked to the landfill, while immission values in air could be directly used for HHRA and include not only the landfill emission, but also other sources of contamination that influence in these points.

In the case of contaminated soils studies, the calculation of indoor and outdoor concentrations is usually performed by modeling from the concentrations of VOCs in soil and groundwater located at a specific depth. From these concentrations equilibrium is assumed of each VOC with soil, water and soil–gas by using simple models as Henry's law or linear adsorption in soil (ASTM, 1995; WHI, 2001). From these equilibrium values, diffusion models through porous media are usually applied to finally calculate fluxes and indoor and outdoor concentrations.

In the case of a landfill, it is difficult to locate a single source of contaminants at a specific depth because the contamination could be diffuse. Furthermore, compared with contaminated soil, the material of the landfill could be more heterogeneous and cracks could be present, thus other mechanisms of transport, such as direct advection of contaminated soil–gas with VOCs could happen and make difficult the application of porous models.

In order to evaluate the concentration of VOCs in landfills, traditional approaches include the measurement of concentration of trace gases emitted from the landfill (Brosseau and Heitz, 1994) and the quality of air on the landfill (Durmusoglu et al., 2010; Kim et al., 2006a; Ding et al., 2012; Lee et al., 2002; Zou et al., 2003). From these two alternatives the second approach can be used for HHRA, but concentrations could be very dependent on the atmospheric conditions and some contaminant values could be very low. This implies that the sampling time has to be high enough to determine these low values and, thus, the equipment needs very high autonomy.

A good alternative for HHRA could be the measurement of fluxes from the landfill by using flux chambers, that have been used in some references (EI-Fadel et al., 2012; Barlaz et al., 2004; Scheutz et al., 2008; Gallego et al., 2014). VOCs determination in landfills using a flux chamber consists in accumulating the emitted flux of VOCs in a chamber and displacing them to the adsorption beds by using an inert gas. The measurement of fluxes allows knowing the release of specific contaminants to the air and can be obtained in few hours, since the VOCs released are captured in the chamber. In this way the measured concentrations are more precise and higher compared with immission. Using this approach, the complex modeling of VOCs in the subsurface is avoided and flux values could be combined with single box models to estimate the concentration of VOCs on the landfill or use these data as inputs in dispersion models to evaluate the impact outside the landfill area.

The direct measurement of VOCs in outdoor air (immission) allows obtaining a value ready for HHRA. In order to be representative, these measurements have ideally to cover several moments

of the day, several days and several seasons. The VOCs obtained by using these methods are representative of all the sources that impact in the point of immission.

The measurement of VOCs in soil–gas at a specific depth is a good approach to evaluate points outside the landfill. From these VOCs values in soil–gas, the transport models based on diffusion through soil and structures around the building could be applied and, thus, air quality for future uses of soil could be calculated (Johnson and Ettinger, 1991).

All these three approaches need to use sampling devices for adsorbing VOCs into multi-sorbent tubes and release of these compounds to Gas Chromatography equipped with Mass Spectrometer to identify and quantify the individual compounds. Several applications allow determining a wide range of VOCs in air at very low concentrations (Ribes et al., 2007; USEPA, 1999).

In the proposed landfill case study, the concentration of measurements of VOCs in soil, soil–gas and groundwater from 1995 to 2008 was reviewed (IDOM, 2008a,b). These VOCs included contaminants as alkanes, aromatic hydrocarbons, halocarbons, alcohols and mercury at specific points and showed and important spatial heterogeneity, but most of the samples were measured in the landfill as concentrations and do not help to define the emission in terms of flux. Furthermore, several gaps were found as there were no immission measurements in the surrounding air of the landfill and soil–gas measurements in the subsoil outside the landfill were not determined.

In the present study, measurements of VOCs emission fluxes combined with concentrations in air and soil–gas were performed in order to obtain more accurate input values for the HHRA with respect to the typical approach. The application of this new approach will avoid all the uncertainties linked to number and type of sources, heterogeneity of the landfill subsoil and transport mechanisms.

#### 2. Materials and methods

#### 2.1. Case study and sampling strategy

The landfill consists of a former clay extraction activity area that caused the existence of three 16–40 m deep holes which were later filled with industrial waste during the 80s: melting salts, industrial sewage sludge, polluted soils and non-hazardous wastes. After its closure in 1995, several studies were performed in the area (IDOM, 2008a) to assess the effect of the buried wastes on the environment and concluded that VOCs were relevant. Fig. 1 shows the landfill and surroundings. The landfill has limited access to the public and is very close to a working industrial area (in SE) and to the city of Cerdanyola del Vallès (NE).

More detailed characteristics of this landfill and atmospheric conditions can be found in Gallego et al. (2014).

The determination of VOCs was planned to be quantified as emission fluxes in 5 points placed on the landfill designed as FG samples in Fig. 1. Outdoor air stations for immission measurements were placed at 4 urban sites around the landfill (PI samples in Fig. 1) that include the closest urban and industrial use of land. The composition of soil–gas was determined at 5 m below ground surface using old and new wells placed outside the landfill (8 sites designed as SG samples).

The sampling campaign was complemented by taking superficial soil samples on the landfill (SS samples) and groundwater in new wells (see Fig. 1).

#### 2.2. Air sampling and analytical methods

The procedures for sampling were different for each approach, but they use the same elements and the same procedure of

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Fig. 1. Sampling strategy for the study of VOCs in the landfill (black contour). PI: Immission measurements; SG: Soil-gas measurements and FG: Flux emission measurements. SS corresponds to Soil sample and pZ, N and SP corresponds to groundwater samples.

analysis. VOCs were sorbed into multi-sorbent tubes (Pyrex tubes, 6 mm  $\times$  9 cm length with Carbotrap (20/40 mesh, 70 mg), Carbopack X (40/60 mesh, 100 mg) and Carboxen 569 (20/45 mesh, 90 mg) using a pumping system patented by Universitat Politècnica Catalunya (Ribes et al., 2007). VOCs were analyzed by means of a TD–GC–MS system (Desorption with ATD-400 Perkin Elmer and analysis with GC/MS Thermo Quest Trace with a column DB-624 (60 m  $\times$  0.25 mm  $\times$  .1.4 µm)).

Multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569) coupled to TD-GC/MS was chosen as a reference methodology as it has been validated for a wide range of VOCs, giving excellent results for selectivity, sensitivity, linearity, precision, accuracy, total desorption of the studied compounds, artefact formation, breakthrough, and stability during storage (Gallego et al., 2010; Ribes et al., 2007). Glass material used in sorbents avoided the problem of loss of Fatty Volatiles Acids, as acetic acid, due to the use of stainless steel (Kim and Kim, 2013).

The Quality Assurance of the method was established by the validation of this analytical method and the quality control was established by using blanks and evaluating the response of certified standards supplied by Supelco (Bellefonte, PA, USA) and Accustandard (New Haven, CT, USA).

The quantitation of the studied VOCs was performed by using external standards and showed repeatabilities (% relative standard deviation values)  $\leq 25\%$ , accomplishing the USEPA performance criteria (USEPA, 1999). The limits of detection were determined by applying a signal-to noise ratio of 3 and ranged from 0.001 to 10 ng (Gallego et al., 2014).

The measurement of VOCs fluxes was determined by using a cylindrical chamber of 0.18 m<sup>2</sup> of section attached to soil to collect the emission. Helium gas was used for the displacement of the contaminants from the chamber to the multi-sorbent tubes by using the described pumping systems. Detailed information about the measurement of these specific fluxes and the analysis can be found in (Gallego et al., 2014) as refers to the same case study and analysis.

Mercury flux was also measured in FG4, as previous results showed levels of 1000 mg kg<sup>-1</sup> in soil close to these sampling point (IDOM, 2008b). Volumes from 6 to 101 of air coming from the chamber were adsorbed into Carulite-Hydrar tubes (SKC). Samples ranging 200–238 mg of loaded Carulite were analyzed by using Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry with AMA254 Advanced Mercury Analyzer (Leco). Quality Assurance of this method was established by the validation of the method and quality control was established by using instrumental blanks and reference solutions of 10, 100 and 1000 µg/l, that showed repeatabilities from 15% to 20%.

The concentration of VOCs in outdoor air was quantified by directly sampling the air at 80–120 ml/min continuously for 24 h to the multi-sorbent tubes by using the mentioned pump. The procedure was repeated for 12 days in each of the mentioned 4 stations from 16 to 31th May 2012.

In the case of soil–gas air, samples were taken from piezometers at 100–105 ml/min by using the same described pump. This procedure was repeated 3 or 4 times in different dates between 17 and 23th June 2012.

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#### 2.3. HHRA methods and modeling applied

Table 1 shows the scenarios considered in the HHRA. All scenarios, except RH1, RH3 and RH6, include a child and an adult as separated receptors.

The scenarios correspond to the uses of the site in the present (RH1–RH3) and in the future (RH4–RH7). Samples considered in each scenario are shown in Table 1. The column n indicates the numbers of separate measurements that were used to calculate the average values for each scenario. The scenarios RH1 and RH7 included oral, dermal and inhalation of particles and VOCs due to direct contact with landfill (soil concentration values were not included in the present article) while the rest of scenarios only include the pathway linked with indirect VOCs contact. The last column indicates the modeling procedure that was applied from the data obtained from samples to finally obtain the concentration of VOCs in the air that was in contact with the receptors.

The models applied to HHRA are recommended by normative (ASTM, 1995) and implemented in software packages (WHI, 2001). Box models and Johnson & Ettinger models are simple and has the objective of a "worst case approach" to calculate a conservative value for HHRA instead an exact value.

Single box models consider a receptor inside a box placed in the surface of the landfill. The box receives all the flux from soil surface and mixes the contaminants with the air to obtain the outdoor concentration. A simple mass balance with no lateral losses are considered, thus is the most conservative approach to calculate the concentration on the landfill. In the present study a height of 1.5 m, a length of 427 m and a wind speed of 1 m s<sup>-1</sup> (average representative from the zone) were considered for this modeling to finally obtain the concentration in outdoor air,  $C_a$ .

Johnson and Ettinger one-dimensional model (Johnson and Ettinger, 1991) is implemented in Risc Workbench software (WHI, 2001) and was used to obtain an attenuation factor from the soil-gas concentration at 5 m to the indoor concentration. These models are also recommended by normative (ASTM, 1995) and (USEPA, 2014) to perform HHRA. The input for the model was the soil-gas composition measured in the field. The building characteristics were a volume of 245 m<sup>3</sup> with a cross-sect with area of basement of 98 m<sup>2</sup> with a fraction of cracks equal to  $10^{-3}$ and with a foundation thickness of 0.2 m. The air of the building was renewed 12 times per day and a pressure difference of  $10 \text{ g cm}^{-1} \text{ s}^{-2}$  between the soil-gas and the indoor air was used. Permeability of soil to vapors was  $10^{-9}$  cm<sup>2</sup> and viscosity of air vapor was assumed to be  $1.8 \times 10^{-4} \text{ g cm}^{-2}$ . These parameters have been selected according to the case study and the references (ASTM, 1995; Johnson and Ettinger, 1991) and give a final attenuation factor (ratio indoor concentration to soil-gas concentration) of  $2.64 \times 10^{-5}$  for RH4, RH5 and RH6.

In the case of immission measurements, the concentration in outdoor air,  $C_a$  was directly the value obtained from the measurements. It should be noticed that the contribution of the contaminants to these samples was not only from the landfill, but also

from several other sources in the zone (traffic, industrial activities among others).

Inhalation of VOCs was the most important pathway considered in the different scenarios and, thus, USEPA specific exposure methodology (USEPA, 2009) was used. In order to calculate the risk indicators linked to VOCs, the equivalent concentration  $C_e$  was calculated by using the expression

$$C_{e} = \frac{C_{a} \cdot ET \cdot FE \cdot DE}{T \cdot 365 \cdot 24}$$

where  $C_e$  is the equivalent concentration in air for each contaminant (µg m<sup>-3</sup>),  $C_a$  is the contaminant concentration in the air (µg m<sup>-3</sup>), ET is the exposure Time (h day<sup>-1</sup>), FE is the exposure frequency (day year<sup>-1</sup>), DE is the exposure duration (year) and *T* is the average time considered (year). For systemic effects DE = T, while for carcinogenic effects DE and T are separate values.

Toxicity assessment was performed using the Reference concentration, RfC ( $\mu$ g/m<sup>3</sup>) and Unit Risk Factors, URF (m<sup>3</sup>  $\mu$ g<sup>-1</sup>) from RAIS (Risk Assessment Information System) (RAIS, 2012) database. Hazard Index (HI) and Carcinogenic Risk (*R*) were obtained from the following expressions by integrating all the contaminants

$$HI = \sum C_{e,i} / RfC_i$$

 $R = \sum C_{e,i} \cdot URF_i$ 

where the subscript *i* refers to the individual contaminants analyzed.

In the case of soil ingestion and dermal contact, dose expressions with reference doses and oral slope factors were used to calculate equivalent indicators as described elsewhere (ASTM, 1995). For these exposure pathways, data from chemical characterization of superficial soil samples were used. Specifically, contaminants considered were metals and Polycyclic Aromatic Hydrocarbons (PAHs).

#### 3. Results and discussion

#### 3.1. Analytical results

Tables 2–4 show the analytical results grouped according to Table 1. Results include measurements as fluxes (Table 2), concentration in outdoor air (Table 3) and concentration in soil gas (Table 4).

In the case of Table 2 and 15 values were used to obtain average values and its standard deviation (SD) for scenarios RH1 and RH7. Most of the results showed a coefficient of variation CV (%) ranging from 20% to 40%. In the case of mercury, 6 samples placed in FG4 showed values of  $0.20 \pm 0.16 \,\mu g \,m^{-2} \,day^{-1}$  that were much lower than observed in other landfill (Kim et al., 2001; Kim and Kim, 2002). The average fluxes of VOCs and mercury were used as inputs of the box model to finally obtain outdoor concentration data for the HHRA.

Table 1

Scenario	Description	Samples considered	n VOCs	Pathways	Model VOCs
RH1	Trespasser on the landfill	Average FG1-FG5	15	Oral, Dermal, Inhalation particles, Inhalation VOCs	Box
RH2	Inhabitants of Cerdanyola	Average PI4	11	Inhalation VOCs	None
RH3	Workers PTV	Average PI1-PI3	36	Inhalation VOCs	None
RH4	Residential use	Average SG13 <sup>a</sup>	4	Inhalation VOCs	J & E
RH5	Kinder garden	Average SG18 <sup>a</sup>	3	Inhalation VOCs	J & E
RH6	Industrial/commercial	Average SG13 <sup>a</sup>	4	Inhalation VOCs	J & E
RH7	Recreation on the landfill	Average FG1-FG5	15	Oral, dermal, Inhalation particles, Inhalation VOCs	Box

J & E, Johnson & Ettinger model.

<sup>a</sup> Selected as a most conservative value from the influence points.

In Table 3, RH2 and RH3 scenarios were considered. As RH2 includes 36 measurements from 3 different stations and RH3 11 measurements from a single station, the air concentration values of SD from RH2 are more disperse. In the case of RH2 and RH3, the measurements of the average concentration of air were directly used.

Table 4 includes soil-gas measurements of the points that showed higher levels of VOCs (SG13 and SG-18). Starting from soil-gas measurements and groundwater concentration values of contaminants, Johnson-Ettinger model was applied to estimate indoor concentration in buildings for future scenarios RH4, RH5 and RH6.

#### 3.2. HHRA results

Results of systemic and carcinogenic risk indicators are summarized in Tables 5 and 6. As it could be seen, all the indicators of risk are acceptable (HI < 1 and  $R < 10^{-5}$ ) in all scenarios.

The highest total systemic risk indicator corresponds to the children in scenario RH7 (HI = 0.775) and include oral, dermal and inhalation pathways with a important contribution of oral pathway. In general, risk indexes of inhalation of VOCs in all scenarios are low, with a maximum value for adults in RH2 (HI = 0.436 and R = 8.75E - 06).

As RH2 scenario has been evaluated with immission measurements, many sources, not only the landfill, may contribute to the presence of VOCs in air. The VOCs that contribute more to the systemic risk index in RH2 include trichloroethylene (HI = 8.6E-02) and 1,2,4-trimethylbenzene (HI = 7.8E-02) and the VOCs linked to carcinogènic effects are chloroform (R = 3.4E - 06), 1,2-dichloroethane (R = 2.4E-06) and carbon tetrachloride (R = 1.3E-06).

Summary of systemic effects indicators (HI values) for the studied scenarios.

In the case of RH1 and RH7, oral pathway is the most important route of contaminants intake and it is linked to metal and PAHs present in the surface of the landfill. Inhalation of VOCs from landfill is the second important pathway for systemic effects with HI close to 0.01 and R close to 1E–07 (see Tables 5 and 6). The VOCs that contribute more to *R* in RH7 adult are benzene (R = 6.9E - 08) and chloroform (R = 1.4E - 08).

The VOCs that contribute more to risk indexes, together with the contaminants found at higher concentrations in the present case study are summarized and compared with other references in Table 7.

As it could be seen, the values for the immission of trichloroethylene, 1,2,4-trimethylbenzene,chloroform, and carbon tetrachloride are lower than in the case of other landfill air references. 1,2-dichloroethane shows slightly higher values than the reference (Ding et al., 2012).

These means that if scenarios like RH2 (risk to people living close to a landfill) are considered in these landfills, HHRA need to be performed as admissible risk indexes could be exceeded. As it could be seen, trichloroethylene in air from (Lee et al., 2002; Zou et al., 2003) could be more than 12 times the value of the present study and thus would imply non-admissible systemic risk.

From the same table, it could be seen that emission fluxes of benzene and chloroform are in the same order of magnitude than in the case of other landfills. This means that in the case of carcinogenic R for scenarios like RH7 (Recreation on the landfill) similar risk could be obtained attending to these contaminants.

The present work shows a high flux of dichlorodifluoromethane (CFC-12) when the values are compared with other landfill references but moderate values in soil gas outside the landfill. Acetic acid immission is high compared with levels of other air close to

9.08E-03

Scenario	Exposure pathway	Oral	Dermal	Inhalation particles	Inhalation VOCs	Total
RH1	Child	1.90E-01	4.30E-04	5.73E-04	1.13E-03	1.92E-01
RH1	Adult	4.00E-02	ni	1.15E-03	2.27E-03	4.34E-02
RH2	Child	ni	ni	ni	2.13E-01	2.13E-01
RH2	Adult	ni	ni	ni	4.36E-01	4.36E-01
RH3	Adult	ni	ni	ni	1.01E-04	1.01E-04
RH4	Child	ni	ni	ni	1.22E-03	1.22E-03
RH4	Adult	ni	ni	ni	9.63E-03	9.63E-03
RH5	Child	ni	ni	ni	2.61E-04	2.61E-04
RH5	Adult	ni	ni	ni	2.06E-03	2.06E-03
RH6	Adult	ni	ni	ni	2.11E-03	2.11E-03
RH7	Child	7.60F - 01	1 70F-03	4 63F-03	9 08F-03	7 75F-01

4.63E-03

ni

ni, not included.

#### Table 6

RH7

Table 5

Summary of carcinogenic effects indicators (R values) for the studied scenarios.

8.10E-02

Adult

Scenario	Exposure pathway	Oral	Dermal	Inhalation particles	Inhalation VOCs	Total
RH1	Child	7.70E-07	1.00E-07	1.93E-09	2.32E-09	8.74E-07
RH1	Adult	5.50E-07	ni	1.29E-08	1.55E-08	5.78E-07
RH2	Child	ni	ni	ni	3.70E-06	3.70E-06
RH2	Adult	ni	ni	ni	8.75E-06	8.75E-06
RH3	Adult	ni	ni	ni	3.32E-06	3.32E-06
RH4	Child	ni	ni	ni	1.17E-09	1.17E-09
RH4	Adult	ni	ni	ni	5.89E-09	5.89E-09
RH5	Child	ni	ni	ni	3.52E-11	3.52E-11
RH5	Adult	ni	ni	ni	3.53E-10	3.53E-10
RH6	Adult	ni	ni	ni	1.28E-09	1.28E-09
RH7	Child	3.10E-06	4.00E-07	1.54E-08	1.86E-08	3.53E-06
RH7	Adult	1.60E-06	ni	7.71E-08	9.28E-08	1.77E-06

ni, not included.

Please cite this article in press as: Martí, V., et al. Human Health Risk Assessment of a landfill based on volatile organic compounds emission, immission and soil gas concentration measurements. Appl. Geochem. (2014), http://dx.doi.org/10.1016/j.apgeochem.2014.06.018

9.47E-02

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#### Table 7

Comparison of relevant VOCs measurements (see Tables 2–4) with other references.

Contaminant	Measurement	Present work	Other works	Reference
Trichloroethylene	Immission ( $\mu g m^{-3}$ )	0.26 (RH2)	0.27-84.5	Lee et al. (2002)
			0.4-50.8	Zou et al. (2003)
1,2,4-Trimethylbenzene	Immission (µg m <sup>-3</sup> )	0.81 (RH2)	0.1-614	Zou et al. (2003)
Chloroform	Immission ( $\mu g m^{-3}$ )	0.8 (RH2)	0.66-1.13	Lee et al. (2002)
			0.5-29	Zou et al. (2003)
	Flux (µg m <sup>-2</sup> day)	4.7 (RH7)	4.2-17	Barlaz et al. (2004)
			Max 44,6	Scheutz et al. (2008)
1,2-Dichloroethane	Immission (µg m <sup>-3</sup> )	1.0 (RH2)	0.14-0.44	Ding et al. (2012)
Carbon tetrachloride	Immission (µg m <sup>-3</sup> )	1.1 (RH2)	0.2-6	Zou et al. (2003)
Benzene	Flux (µg m <sup>-2</sup> day)	4.9 (RH7)	1.4-93	Barlaz et al. (2004)
			Max 3,6	Scheutz et al. (2008)
Dichlorodifluoromethane	Flux (µg m <sup>-2</sup> day)	331 (max.)	7.1-66	Barlaz et al. (2004)
			0.02-1.1	Scheutz et al. (2008)
	Soil-gas (µg m <sup>-3</sup> )	827 (max.)	1600-3100	Scheutz et al. (2008)
Acetic acid	Immission ( $\mu g m^{-3}$ )	42 (max.)	0.12-2.22	Ding et al. (2012)

landfills and could be correlated with the high emission value, but could not be concluded that the contribution is only from the landfill.

#### 4. Conclusions

A new approach by combining VOC's concentrations from three different sources related to a closed landfill such as emission fluxes from the landfill, air measurements and soil–gas measurements was performed. This approach allowed to perform a realistic calculation of risk indicators for VOCs in the HHRA. Results showed admissible risk indexes in both systemic and carcinogenic indicators in all studied scenarios. The methodology could be applied to other landfills to assess the most important contaminants in order to control them and perform a Risk-Based Landfill Management.

#### Acknowledgements

The present project was funded by the entity Consorci Urbanístic del Centre Direccional de Cerdanyola del Vallès. The Local Government of Cerdanyola del Vallès is acknowledged for its interest in this work. Thanks are due to LCMA (Laboratori del Centre de Medi Ambient (UPC)) and Centro Nacional de Condiciones de Trabajo (INSHT) for supplying details of VOCs analysis. The reviewers are also acknowledged for their comments, which significantly improved the quality of the original manuscript.

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014. 06.018.

#### References

- ASTM, 1995. Emergency Standards Guide for Risk-Based Corrective Action Applied at Pretroleum Release Sites, ASTM 1739-95.
- Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., Hater, G.R., 2004. Evaluation of a biologically active cover for mitigation of landfill gas emissions. Environ. Sci. Technol. 38, 4891–4899.
- Brosseau, J., Heitz, M., 1994. Trace gas compound emissions from municipal landfill sanitary sites. Atmos. Environ. 28, 285–293.
- Butt, T.E., Lockley, E., Oduyemi, O.K.K., 2008. Risk assessment of landfill disposal dites – state of art. Waste Manage. 28, 952–964.
- Ding, Y., Cai, C., Hu, B., Xu, Y., Zheng, X., Chen, Y., Wu, W., 2012. Characterization and control of odorous gases at a landfill site: a case study in Hangzhou, China. Waste Manage. 32, 317–326.

Durmusoglu, E., Taspinarb, F., Karademira, A., 2010. Health risk assessment of BTEX emissions in the landfill environment. J. Hazard. Mater. 176, 870–877.

- El-Fadel, M., Abi-Esber, L., Salhab, S., 2012. Emission assessment at the Burh Hammoud inactive municipal landfill: viability of landfill gas recovery under the clean development mechanism. Waste Manage. 32, 2106–2114.
- Gallego, E., Roca, F.J., Perales, J.F., Guardino, X., 2010. Comparative study of the adsorption performance of a multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569) and a Tenax TA adsorbent tube for the analysis of volatile organic compounds (VOCs). Talanta 81, 916–924.
- Gallego, E., Perales, J.F., Roca, F.J., Guardino, X., 2014. Surface emission determination of volatile organic compounds (VOC) from a closed industrial waste landfill using a self-designed static flux chamber. Sci. Total Environ. 470– 471, 587–599.
- IDOM, 2008a. Estudi de delimitació i activitat de l'abocador de Can Planas. Anàlisi de solucions. Definició de la solució adoptada a nivell d'avantprojecte. Fase I. Diagnòstic preliminar i proposta d'investigació. Internal report.
- IDOM, 2008b. Estudi de delimitació i activitat de l'abocador de Can Planas. Anàlisi de solucions. Definició de la solució adoptada a nivell d'avantprojecte. Fase II. Treballs d'investigaciói diagnòstic mediambiental, Internal report.
- Johnson, P.C., Ettinger, R.A., 1991. Heuristic model for predicting the intrusion rate of contaminant vapors into buildings. Environ. Sci. Technol. 25, 1445–1452.
- Kim, K.-H., Kim, M.-Y., 2002. Mercury emissions as landfill gas from a large-scale abandoned landfill site in Seoul. Atmos. Environ. 36, 3475–3493.
- Kim, M.-Y., Kim, K.-H., 2013. Extent of sample loss on the sampling device and the resulting experimental biases when collecting Volatile Fatty Acids (VFAs) in air using sorbent tubes. Anal. Chem. 85, 7818–7825.
- Kim, K.-H., Kim, M.-Y., Lee, G., 2001. The soil-air exchange characteristics of total gaseous mercury from a large-scale municipal landfill area. Atmos. Environ. 35, 3475–3493.
- Kim, K.-H., Choi, Y.-J., Jeon, E.-C., Sunwoo, Y., 2005. Characterization of malodorous sulfur compounds in landfill gas. Atmos. Environ. 39, 1103–1112.
- Kim, K.-H., Baek, S., Choi, Y.-J., Sunwoo, Y., Jeon, E.-C., Hong, J.H., 2006a. The emission of major aromatic VOC as landfill gas from urban landfill sites in Korea. Environ. Monit. Assess. 118, 407–422.
- Kim, K.-H., Choi, Y.J., Oh, S.I., Sa, J.H., Jeon, E.C., Koo, Y.S., 2006b. Short-term distributions of reduced sulfur compounds in the ambient air surrounding a large landfill facility. Environ. Monit. Assess. 121, 343–354.
- Lee, S.C., Chiu, M.Y., Ho, K.F., Zou, S.C., Wang, Xinming, 2002. Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong. Chemosphere 48, 375–382.
- Lindberg, S.E., Wallschlaeger, D., Prestbo, E.M., Bloom, N.S., Price, J., Reinhart, D., 2001. Methylated mercury species in municipal waste landfill gas sampled in Florida, USA. Atmos. Environ. 35, 4011–4015.
- Lindberg, S.E., Southworth, G., Prestbo, E.M., Wallschlaeger, D., Bogle, M.A., Price, J., 2005. Gaseous methyl-and inorganic mercury in landfill gas from landfills in Florida, Minnesota, Delaware, and California. Atmos. Environ. 39, 249–258.
- Ribes, A., Carrera, G., Gallego, E., Roca, X., Berenguer, M.J., Guardino, X., 2007. Development and validation of a method for air-quality and nuisance odors monitoring of volatile organic compounds using multi-sorbent adsorption and gas chromatography/mass spectrometry thermal desorption system. J. Chromatogr. A 1140, 44–55.
- Risk Assessment Information System. <http://rais.ornl.gov/> (consulted in May 2012).
- Scheutz, C., Bogner, J., Chanton, J.P., Blake, D., Morcet, M., Aran, C., Kjeldsen, P., 2008. Atmospheric emissions and attenuation of non-methane organic compounds in cover soils at a French Landfill. Waste Manage. 28, 1892–1908.
- USEPA, 1999. Compendium of methods for the determination of toxic organic compounds in ambient air. Method TO-15, EPA/625/R-96/010b. Cincinnati: Center for Environmental Research Information, Office of Research and Development.

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- USEPA, 2009. Risk Assessment Guidance for Superfund, vol. I, Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment) EPA-540-R-070-002.
- USEPA, 2014. <http://www.epa.gov/athens/learn2model/part-two/onsite/JnE\_lite\_ forward.htm> (visited in May 2014).
- Waterloo Hydrogeologic Inc., 2001, Risc4 User's Manual: Human Health Risk Assessment Software for Contaminated Sites.
- Zou, S.C., Lee, S.C., Chan, C.Y., Ho, K.F., Wang, X.M., Chan, L.Y., Zhang, Z.X., 2003. Characterization of ambient volatile organic compounds at a landfill site in Guangzhou, South China. Chemosphere 51, 1015–1022.