Proceedings of the 9ICEG
9th International Congress on Environmental Geotechnics
25-28 June, 2023 | Chania, Greece
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https://doi.org/10.53243/ICEG2023-243

Use of Field Measurements of Mercury Vapour Emissions from soil in risk assessment procedure for a polluted site

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ABSTRACT

In a Tier 2 application of the RBCA (Risk Based Corrective Action) procedure for polluted sites, the application of common analytical volatilization models may lead to an overestimation of vapour emissions. The use of site-specific parameters of soil and specifically measured physico-chemical parameters of contaminants are sometimes not able to mitigate this overestimation. The present note describes the results of measurements of mercury vapour emission from soil at an actual contaminated italian site. Several surveys were carried out over one year, in order to take into account possible seasonal variations. Both the vapour flux from soil and the concentration in open air were measured by means of open dynamic flux chambers (FC) and through direct measurements in outdoor air, respectively. For a given investigation point, the predictions of volatilization models were compared with direct measurements. The actual emissions were found to be significantly lower than those estimated by the models, seasonal variation did not cause high differences among measured concentration and flux values. The use of an experimentally determined soil-water partition coefficient helped in obtaining a less unrealistic output of the model and information about the effect of using default parameters can be retrieved by combining results from both FC and direct measurements in outdoor air.

Keywords: Polluted site, risk assessment, migration models, volatilization, flux chambers, vapour emissions

1 INTRODUCTION

The Italian Legislative Decree 152/06 defines the risk assessment (RA) for polluted sites as an estimate of the effects of prolonged exposure to the contaminated environmental media (soil, subsoil and groundwater) on human health. The RA procedure was initially developed in the United States (USEPA, 1996-a; USEPA, 1996-b), standardized by ASTM (E2081-00 reapproved in 2010) and then adopted in Europe (CONCAWE, 2003) with the growing number of contaminated sites to be remediated. In Italy risk assessment was allowed by regulations on contaminated sites since 1999 (Legislative Decree 471) and the first handbook for the implementation was published by UNICHIM (2002). The Italian National Environmental Protection Agency (now named SNPA) has published the latest revision of the guidelines for RA for contaminated sites in 2008 with some integration by the Ministry of Environment in 2014.

In the RBCA method, the RA can be performed following a tiered approach (tier 1 to 3) in which each tier requires an increasing level of modelling complexity. Tier 2, that consists in the use of analytical models and site-specific parameters to simulate the contaminant migration, is the tier recommended by Italian Regulations. The RA for polluted sites starts from the definition of the Conceptual Site Model (CSM), i.e. the description of its three components: source of contamination, migration paths and targets of contamination. Based on the CSM, calculations of risk (for carcinogenic effects) or hazard index (for toxic non-carcinogenic effects) can be carried out (USEPA, 1996-a).

Contaminant migration (from the source to the target) represents the core of the RA procedure, its aim is to estimate the concentration at the point where receptors are located (C_{POE}), named "point of exposure". Site-specific determination of parameters (i.e. measured on soil samples or derived from in-situ investigations) has the aim of making model results as close as possible to reality (Di Sante et al., 2011).

With regard to volatilization of contaminants from soil, some widely used migration models may significantly overestimate vapour emission from the soil and the exposure of the human targets despite the use of site-specific parameters (e.g., Verginelli et al., 2014; Bretti et al., 2014). In these cases, the site-specific determination of additional parameters (e.g., k_d), besides those strictly required by the guidelines, or the direct measurement of in-situ vapour emissions can help in achieving a more realistic estimate of risks.

Direct measurements of vapour emissions were therefore standardized from the Italian Protection Agency (SNPA) in 2018 (SNPA, 2018). Three different types of measurement are included in the guidelines:

- soil gas survey, SGS, that is the measurements of the concentration of pollutant in the pore air of the unsaturated soil;
- flux chamber, FC, that is an instrumentation to measure the emission of vapours from the soil;
- outdoor air measurements, OAM, that is contaminant concentration measurements directly in open air.

This note describes and discusses the comparison between the predictions of different volatilization analytical models and direct measurements carried out in an abandoned industrial site, contaminated by various heavy metals, including mercury. Measures of mercury vapour emissions were performed by open dynamic flux chambers and direct measurements of contaminant concentration in open air, in order to have multiple lines of evidence. The two set of data are also combined in order to retrieve information about the effect of the use of default values of parameters.

2 ANALYTICAL VOLATILIZATION MODELS OF CONTAMINANTS AND DIRECT IN-SITU MEASUREMENTS

2.1 Volatilization models

Analytical models of volatilization from the unsaturated zone of the soil to the outdoor air are based on the following assumptions:

- homogeneous soil properties;
- uniformly distributed concentration of contaminants throughout the source;
- constant contaminant concentration in the source and constant contaminant flux across the ground surface over the exposure period;
- no attenuation or chemical/biological degradation along the path,
- constant wind speed;
- no variation in atmospheric stability.

In general, volatilization models consist of three steps (Figure 1), briefly described in Table 1.

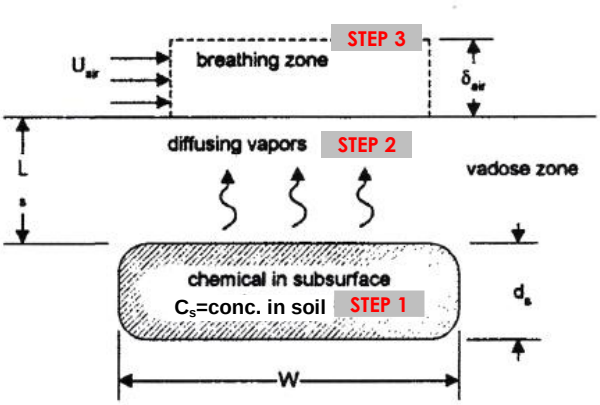

Figure 1. *Schematics of volatilization models from unsaturated soil zone to outdoor air (modified from ASTM E2081-00)*

Table 1. *Steps of common volatilization models and ability of direct measurement techniques to by-pass each step*

Step	Volatilization model Description	By-passed by:
1	Linear equilibrium partitioning of the contaminant in the three phases (solid-liquid-gas) present in the subsoil within the source	SGS, FC and OAM
2	Migration of the contaminant from the source to the ground level by diffusion.	FC and OAM
3	Final mixing in the outdoor air above the source of contamination, according to a box model of perfect mixing.	OAM

The volatilization model recommended in the guidelines to simulate the volatilization from the surface soil (from ground level to 1m of depth) is the Jury's model (Jury et al., 1990 – eq.1). Models are usually applied in the risk assessment procedure in terms of transport factors. C_{POE} can be obtained by multiplying the representative source concentration, Cs (Figure 1), by the volatilization factor (VF) that derives from the analytical model of concern. VF from Jury's model can be calculated by the following equation (the symbols included are explained in Table 2).

$$VF_{Jury} = \frac{2W\prime\rho_s}{U_{air}\delta_{air}} \cdot \sqrt{\frac{D_s^{eff}H}{3.14\tau(\vartheta_w + k_d\rho_s + H\vartheta_a)}} \quad (1)$$

2.2 Direct in-situ measurements

Each type of in situ direct measurement of vapour emission cited in section 1 shows advantages and limitations.

2.2.1 SGS

It gives the values of concentration of contaminants in pore air of the unsaturated soil portion, which correspond to the output of step 1 (see Figure 1 and Table 1). The remaining steps of the models must still be applied therefore it only partially overcomes the limitations imposed by the hypotheses listed in section 2.1. This type of measurement is the one suggested by Italian SNPA due to their high expertise and familiarity with this type of measurements, gained during years.

2.2.2 FCs

They are able to give the value of the flux, F, (i.e. mass of pollutant per unit emissive area and time); replacing the output of step 2 but still requiring the application of the box model of step 3 (Figure 1 and Table 1). The use of FC allows overcoming all the assumptions except for those related to the mixing according to the box model (perfect mixing in air, constant wind speed and atmospheric stability). They also offer the advantage of being independent of other external emission sources. For all these reasons, recent studies have been developed in Italy with relation to FCs and to the optimization of its technical protocols (e.g., Careghini et al., 2014; Verginelli et al., 2018).

In the case of FC, the value of F, was used in the following formula (eq.2) to determine C_{POE}, other symbols are explained in Table 2.

$$C_{POE} = (F \cdot W') / (U_{air} \cdot \delta_{air}) \quad (2)$$

2.2.3 OAM

This last type of measurements is directly performed in the open air with air samplers which gave the value of the concentration of the contaminant in air, Cair, that represent itself the value of CPOE (i.e., Cair=CPOE). In this case all the steps of the volatilization models are overcome with all the related hypotheses. They can be directly entered in the calculation of exposure and therefore of risk. However, OAM can be affected by the contribution of other sources of contamination, different from the considered soil source, this is the reason why a blank test (i.e., out of the considered site) is always required. It is important to underline that this problem does not occur with FC or SGS because they are “isolated” systems. In any case, blank tests are always recommended in order to take into account possible natural emissions.

2.3 Case Study

Four surveys of vapour emissions with open dynamic flux chambers and three surveys of measurements of concentration in open air (both shown in Figure 2) were carried out in an actual italian contaminated site for taking into account possible seasonal variations (Poissant et al., 2004). The first one, carried out in July 2014, consisted of 15 measurements with flux chambers only. In the following surveys (January, May and September 2015) the measurement stations were 22 across an area of 15 ha. At each station, a flux chamber and an air analyser were coupled (as requested by the environmental protection agencies). In 5 locations out of 22 continuous 24 h monitoring of the air concentration were carried out due to the proximity to the site boundary (next to a residential area). In the remaining 17 location, 8 h air sampling was performed. The number of measurement stations with FCs that gave values greater than the detection limit (DL) are 2 during the first 3 surveys and 12 in the fourth.

The FC used in the study are open dynamic flux chambers, the sampling was preceded by a purging stage by pushing nitrogen for one hour (flow rate=4 L/min) in the chamber and letting the air flow out (temperature and humidity measured with a sensor). During sampling, which lasted 5 h in the first survey and 8 h in the others (due to the request of the local Environmental Protection Agency), inflow of nitrogen continued and the gas acted as a carrier fluid. Nitrogen was induced to flow through a vial full of carulite® (i.e. a material capable of accumulating mercury) by aspirating it with a pump (flow rate=0.2 L/min), following the American Standard NI OSH 6009. The ratio between the outflow and the inflow rates was equal to 0.05, that is sufficiently low value to minimize errors in the flux estimate as demonstrated by several studies (e.g., Gao and Yates, 1998; Reichman et al., 2002).
In the 8 h OAM sampling was carried out by vacuum air pumping (0.2 L/min) through the same vial of flux chambers, stating from 8:00-8:30am until 4:00-4:30pm.

The 24 h OAM was carried out according to European standard UNI EN 15852 and gave C_{air} (concentration in outdoor air) as output. The standard refers specifically to air quality and consists of a continuous measurement by means of an in-situ analyser located at a height of 1 m from g.l., that gave the total gaseous mercury in air, registering values in ng/m^3. A portable atomic absorption spectrometer was used, with Zeeman correction to remove background interfering impurities. Measurements start from 8:00-8:30 in the morning until the same hour of the next day. Blank level (=1.72 ng/m^3) was measured out of the site of concern and subtracted from each concentration value measured on site.

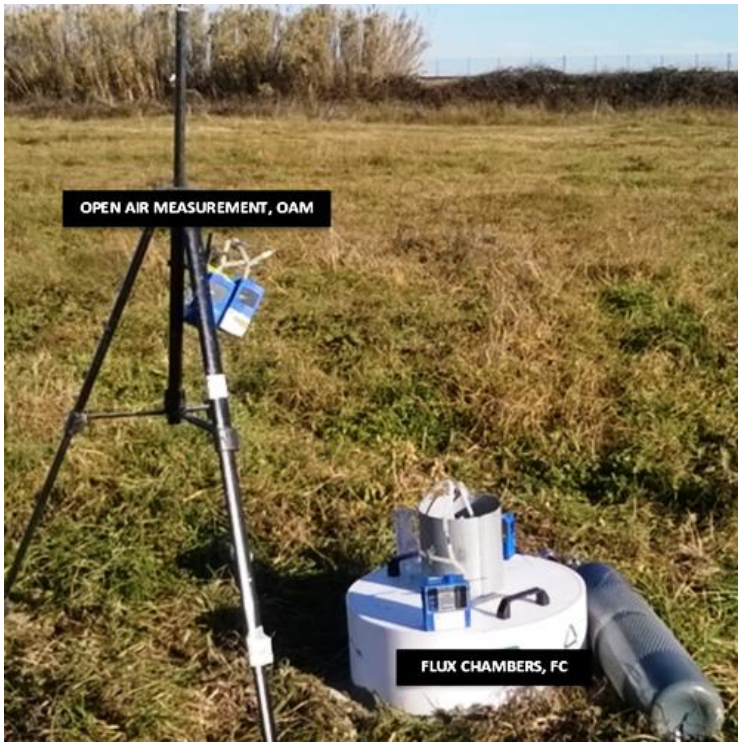

Figure 2. *In-situ measurement with flux chambers and air samplers (photos shown by courtesy of THEOlab - THEAREN Laboratories)*

In particular, among the 22 locations and across the four surveys, a single measurement station (indicated as SN16) gave values of flux greater than the DL and is coupled with 24 h OAM. With relation to SN16, concentrations of mercury in soil samples were also available from characterization data. The maximum concentration of mercury in soil, C_s = 69.5 mg/kg was detected within 0.4m of depth and was used as input data in the volatilization model previously described (eq.1). A square of 50mx50m was the area of influence of each boreholes and therefore considered as the size of emitting source.

The site-specific data and physico-chemical parameters of the considered contaminant (mercury) used in the volatilization modelling are summarized in Table 2.

Besides the use of the solid-liquid partition coefficient, k_d, suggested for mercury in the ISS-INAIL database of contaminant properties, 2014 (k_d = 52 L/kg), the experimental determination of k_d was performed on a soil sample taken next to the SN16 location and it was found to be equal to 603 L/kg (Table 2).

The mean daily values of wind speed, U_{air}, were retrieved from a near weather station (elevation=10 m) for each day of measurement, and were used as input in the simulations. Given that in the box model used for the outdoor volatilization the height of the mixing zone in air is considered by default equal to 2 m, wind speed at an elevation of 2 m was calculated using eq.3 (Hanna et al., 1982):

$$\frac{U_{air}(z_1)}{U_{air}(z_2)} = \left(\frac{z_1}{z_2}\right)^p \qquad (3)$$

where z_1 and z_2 are different heights, U_{air} (z_1) and U_{air} (z_2) are the corresponding speeds and p is a coefficient that takes into account the atmospheric stability class and the type of area (urban or rural). Atmospheric stability class was established based on the weather data of each day of measurement. The calculated wind speed values at a height of 2 m, used in each of the four simulations, are listed in Table 2.

Table 2. *Site-specific data and parameters used in the calculations for SN16*

Parameter	Symbol	Value	unit
Soil bulk density	ρ_s	1.7	g/cm³
Total porosity*	θ_t	0.43	-
Volumetric air content*	θ_a	0.36	-
Volumetric water content*	θ_w	0.068	-
Effective diffusion coefficient	D_s^{eff}	calculated (ISPRA, 2008)	cm²/s
Diffusion coeff. in air (b)	D_a	0.0307	cm²/s
Diffusion coeff. in water (b)	D_w	0.0000063	cm²/s
Wind speed (a)	U_{air}	2.62 (Jul) 1.96 (Jan) 1.75 (May) 1.96 (Sept)	m/s
Height of mixing zone in air	δ_{air}	2	m
Length of soil source in wind direction (O-E) (a)	W'	60.5	m
Henry's Law Constant (b)	H	0.467	-
Soil-water partition coeff.	k_d	52 (database) 603 (experimental)	l/kg
Duration of vapor emission	τ	25	years

* derived by grain size characteristics, (a) directly measured, (b) database physico-chemical properties of contaminants ISS-INAIL (2015)

The models of Jury was applied by a spreadsheet, SMARTrisc, programmed in Visual Basic and Excel at the Technical University of Marche, in order to perform risk assessment and develop sensitivity analyses (Di Sante et al., 2013) for research and study purposes. The results of this model have been compared with those resulting from the calculations (eq.2) using FC data and measurement of concentration in air.

3 RESULTS AND DISCUSSION

3.1 Comparison of direct measurements and results of theoretical models of contaminant volatilization

In Figure 3 the output of a 24 h OAM is shown (SN16 during the January survey). The measurement starts at 8:00 in the morning and a marked difference between the day-time (i.e. until 43200 s) and the night-time trends is observable. During the first 12 hours the mean value of concentration in air is 5.5 ng/m³ with a peak value of 17.5 ng/m³ while, during the night, the mean value of C_{air} is 2.9 ng/m³ without significant variations. The higher day-time concentration is probably due to the evaporation caused by the higher day-time temperatures. It is important to underline that for the 8 h OAM locations (see section 2.3) the sampling was carried out during the day-time hours and therefore it was expected to give values of concentration higher than those of the night hours, thus cautionary.

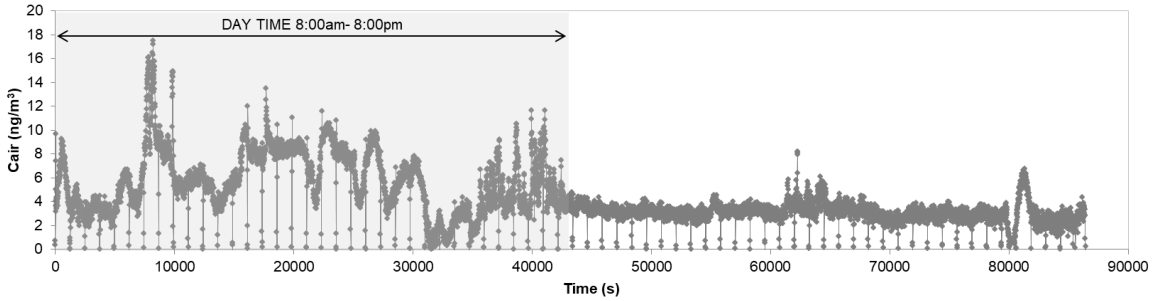

Figure 3. *24 hours open air monitoring (SN16, January 2015)*

The direct measurements in SN16 location were compared with the results of the application of Jury volatilization model starting from the concentration values measured in the soil in SN16 and using parameters in Table 2.

The results obtained both in terms of C_{POE} for each of the four surveys and the corresponding Hazard Index are displayed in Figure 4 and Figure 5 respectively. In the graphs, results from direct measurements in air (Cair bar, in black) and from Flux chambers (Flux chamber bar, in grey) are compared with predictions of volatilization models implemented by SMARTrisc spreadsheet: Jury model with k_d value from ISS database (Jury SMART bar, in red) and Jury model with experimental determined k_d (Jury SMART k_d bar, in blue), see Table 2 for k_d values.

The values of concentration obtained both from direct measurements and estimated from FC, are significantly lower than those predicted by the volatilization models and hazard indexes follow the corresponding trend, switching from acceptable (<1) to unacceptable values (>1) when using in-situ measurements.

High values of C_{POE} concentration given by volatilization models (3-4 orders of magnitude greater than those obtained with direct measurements) can be explained by two main reasons:

- the highly simplified and precautionary hypothesis of analytical models (see section 2.1) that lead to an overestimation of vapour emissions;
- mercury is a contaminant that can be found in nature in various forms; among them, elemental mercury is the most volatile form (Cantarutti et al., 2006; Calace, 2012). The calculations implemented in analytical models assume that the entire amount of mercury detected in the soil is in the volatile form not distinguishing between volatile and non-volatile fractions (unless a speciation test is preliminarily run). On the contrary, the direct measurement takes into account the fraction of mercury that is actually capable of reaching the ground level, only.
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Anyway, in this case, the use of in-situ measurements of vapour emissions was decisive for the risk assessment results, influencing also the remediation actions to be undertaken.

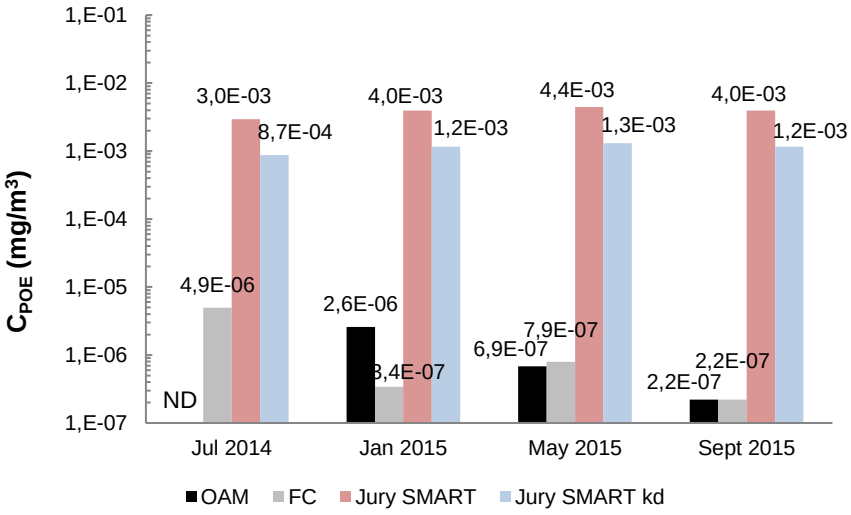

Figure 4. *Concentrations at point of exposure, C_{POE}*

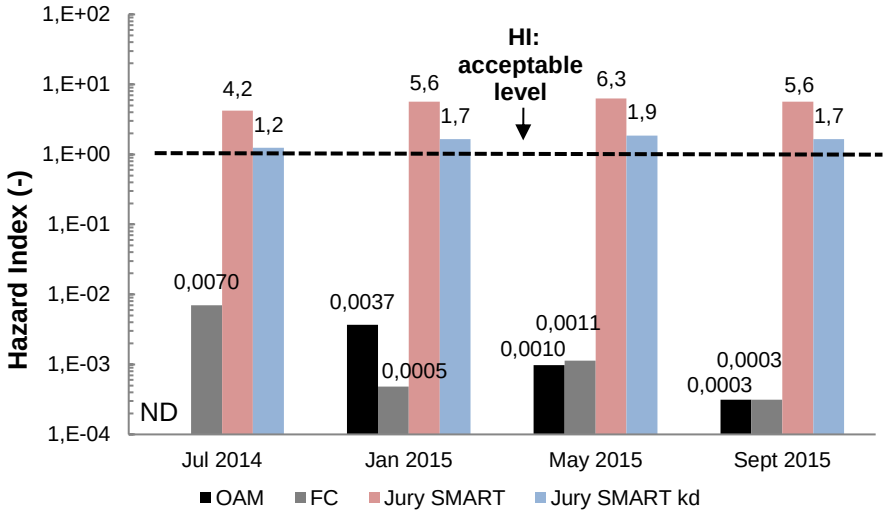

Figure 5. *Hazard Index results, HI*

In addition, the difference between the concentration in air obtained from direct measurement and that derived from FC is within one order of magnitude; this data matching corroborates the consistency of both types of measurement. In the case of concern, the measured value of vapour emissions vary within one order of magnitude across the different surveys.

3.2 Evaluation of default settings

The two set of measured data (by FC and OAM), simultaneously taken in each location, can also be combined in order to retrieve information about the effect of the use of default values of parameters in the box model (STEP3 in Table 1). In particular, eq.2 represents the box model dilution with outdoor air. In particular, the parameter δ_{air} represents the height of the mixing zone in air and is commonly assumed equal to 2m as a default value. From eq.4 it is possible to determine δ_{air} by posing C_{POE} equal to C_{air} measured by OAM, inserting the flux value, F, correspondingly measured by FC and using the site specific measured values of U_{air} and W' (wind speed and length of soil source in wind direction (O-E), see Table 2). This calculations were performed for SN16 location across the last three surveys (in the first one only FC was used). Results are displayed in Figure 6 They demonstrates that the assumption of a defult value of 2 m is in agreement with the survey of September while in May a slightly higher value of δ_{air} is required to match the mixing model, meaning that the volume of the box model that well suit the actual dilution should be slightly higher. On the contrary, in January, a value of one order of magnitude lower than the default is derived for δ_{air}, this is probably due to the low solar radiation of the winter period, and the consequent high atmospheric stability that does not facilitate the dilution process with outdoor air.

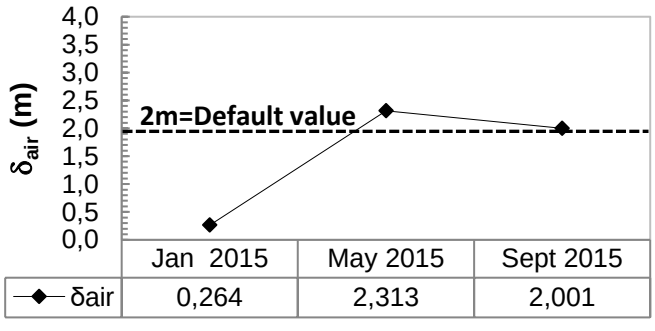

Figure 6. *Values of the height of mixing zone in air, δ_{air}, derived by eq.4 combining flux values by FC and OAM*

4 CONCLUSIONS

The present paper compares the predictions from Jury volatilization model with the results of measurements of mercury vapour emission from soil at an actual contaminated site, carried out by means of flux chambers and open air analysers. The two set of data are also combined in order to retrieve information about the effect of the use of default values of parameters in risk assessment procedure. In light of the obtained results, the following conclusions can be drawn.

- The 24hours trend of open air measurements showed that concentrations are significantly higher during the day-time period.
- The values of measured air concentrations and those calculated from FC results were significantly lower than those obtained with the volatilization models, strongly influencing risk assessment outcomes, thus the remediation strategies to be undertaken.
- It is recommended, whenever possible, to carry out experimental determination of soil-water partition coefficient for a less unrealistic output of the models.
- Direct measurements provided a more realistic assessment of emissions as they only take into account the fraction of total mercury that is actually capable of reaching the ambient air, under the site-specific conditions.
- In the case of concern, the use of the default value of the height of the mixing zone in air (2 m) fits the actual level of mixing with outdoor air in the spring and summer surveys while, in the winter season, the actual dilution was lower than that predicted by applying the default volume of the mixing box.

Possible future developments of the present research work are the evaluation of the volatilization of other contaminants (e.g. VOCs) and of the effect of an interposed layer between the soil and the measurement device, such as a clayey layer or a barrier made by Geosynthetic materials.

5 ACKNOWLEDGEMENTS

The authors would like to thank Immobiliare Del Poggio (IT) for allowing the publication of the data and THEAREN (Ex THEOlab) laboratories (IT) for the images of measurement devices.

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