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► **To cite this version:**

Olivier Bour, K. Favereaux, M. Sylvain. Case study of sulphur compounds emissions characterization. 10. International waste management and landfill Symposium (Sardinia), Oct 2005, Sardinia, Italy. pp.NC, 2005. <ineris-00972504>

**HAL Id: ineris-00972504**

**<https://hal-ineris.archives-ouvertes.fr/ineris-00972504>**

Submitted on 3 Apr 2014

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# CASE STUDY OF SULPHUR COMPOUNDS EMISSIONS CHARACTERIZATION

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**SUMMARY :** In order to manage the methane and sulphur compounds emissions of a landfill area with deposits of plasterworks, a flux measurements study was conducted with a mobile laboratory, portable analysers and different chambers. The static chamber was first used in order to locate the methane hot spots. The funnel and the Total Reduced Sulphur (TRS) analyser allow the comparison between emissions of methane and hydrogen sulphide which represent the predominant sulphur compound. In a second stage, the variability of the hydrogen sulphide emissions was monitored with two dynamic chambers and a period of several days. Hydrogen sulphide emissions by cap are much lower than those predicted by the methane flux and the concentration of hydrogen sulphide in landfill gas (LFG).

## 1. INTRODUCTION

Accurate field emissions measurements of sulphur compounds such as hydrogen sulphide is a decisive step in assessing their environmental impact. The use of funnels and flux chambers is a simple method for locating and measuring emission rate under field conditions (Savanne D. & al, 1997).

The goal was to study the temporal and spatial emission variability in order to give information for the characterization methodology of sulphur compounds surface emission fluxes. The spatial distribution of the surface emissions was studied with a static flux chamber and a funnel, in order to do a preliminary quick survey of methane and sulphur compounds fluxes and air concentrations. The static flux chamber offers a relatively quick quantitative methane flux measurement in approximately five minutes with a Flame Ionisation Detector (FID). The funnel (an open chamber, 0.7 m diameter), which needs approximately half an hour of time diffusion stabilization in the chamber, was used in the second stage of the preliminary survey. This equipment provides a semi-quantitative measurement of the methane and sulphur compounds concentrations with the mobile laboratory TRS and FID analysers. In the second stage of the survey the daily variations of methane and sulphur compounds was monitored with two dynamic chambers and a constant flow rate, which was controlled by two flowmeters.

## 2. LOCATION AND EMISSION RATE CHARACTERIZATION

### 2.1 Determination of the location of the sulphur compounds emissions

A first survey of LFG hydrogen sulphide concentration in the wells of the collection system was used to delimit a specific area, approximately 2 ha (Figure 1). The LFG hydrogen sulphide concentration of that area ranged between 7 to 380 ppmv. During the exploitation of the landfill, deposits of plasterworks were noticed by the operators in this specific area.

A preliminary survey of the methane concentration above the cap was done with an FID analyser in order to identify the methane “hot spots”.

### 2.2 The sorting of the sulphur compounds emissions

The studied area was divided into 20 points. The funnel used with TRS and FID analysers and the static chamber used with another FID analyser have measured 11 significant positive methane and H<sub>2</sub>S surface emissions rate. Due to the wind funnel sensibility and some LFG leakage from wells it was necessary to eliminate the influenced measurements for the interpretation. This method permitted to delete measurement points, due essentially to wind velocities peaks which have reached 6 m/s during the survey. The funnel measurement provided sufficient information in order to make a first sorting of the sulphur compounds emissions.

The comparison of methane surface emission rate measurements permitted to notice a good correlation for the two methods (funnel and static chamber), as previously reported (Fécil B. & al, 2003). Nevertheless, we observed no correlation between methane flux and sulphur compounds concentration in the studied area (Figure 2). The high heterogeneity of the H<sub>2</sub>S source term was probably linked with the heterogeneity of the plasterworks deposits in a small spatial scale.

A gas chromatograph with a flame photometric sensor was used to verify during the survey that the predominant sulphur compound was hydrogen sulphide.

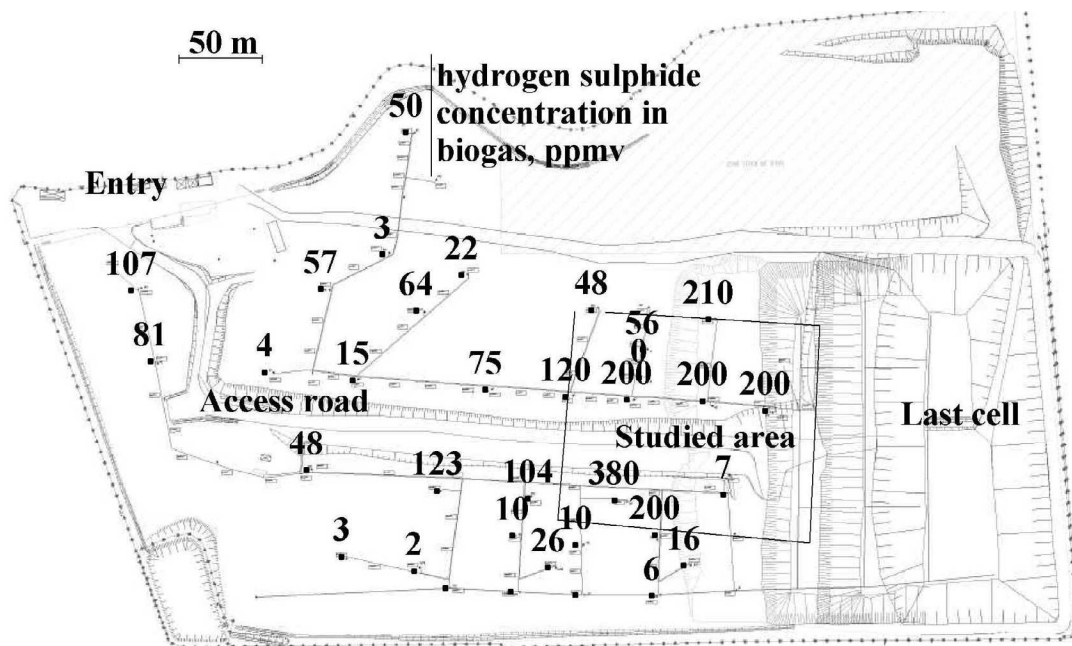


Figure 1. Scheme of LFG hydrogen sulphide concentration locations in the landfill area

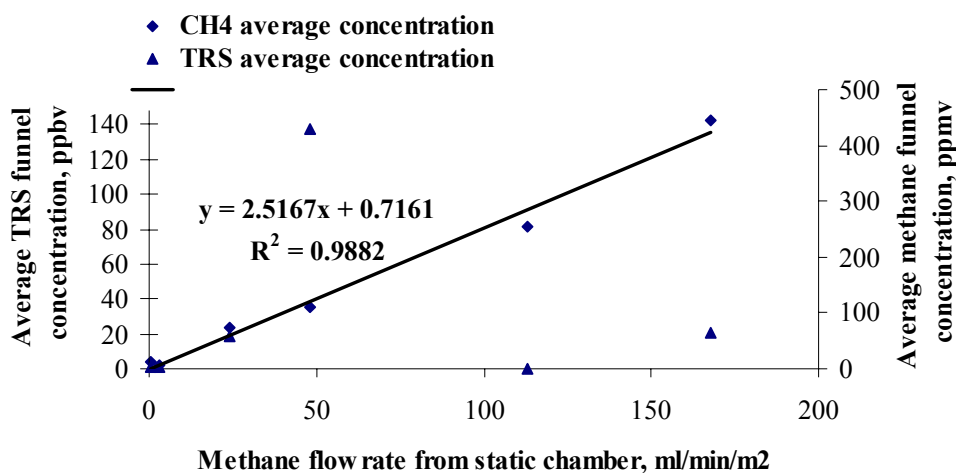


Figure 2. Methane flowrate from static chamber and concentration of methane and TRS from funnel

### 3. HYDROGEN SULPHIDE EMISSION RATE AND TEMPORAL EMISSION VARIATION CHARACTERIZATION

#### 3.1 Hydrogen sulphide emission rate characterization

A new selection of 10 measurement locations was made in order to focus on the central area which represents all the statistical distribution of the methane concentration measurements on the surface of the landfill.

The goal was to monitor the methane and sulphur compounds surface emission rate. Two dynamic chambers were used with a synthetic gas entry and exit line of approximately 0.4 m<sup>3</sup>/h.

The H<sub>2</sub>S fluxes were relatively low on the cap : the TRS concentration peaks in the dynamic chambers varied from 1 to 135 ppbv. In order to simplify the interpretation of the large data set of two weeks continuous concentration measures with 3 analysers on different locations, different periods were identified at each location. The sum of the periods for all the 10 points range from 2-3 hours to 5 days. The interpretation permits to notice periods with low and high variations on the sulphur fluxes emissions. The H<sub>2</sub>S surface flux values, which were calculated from the average TRS concentrations over a few hours periods without high winds, varied between 0,03 to 1 µl H<sub>2</sub>S /min/m<sup>2</sup>. The median H<sub>2</sub>S surface flux on the 43 defined measurement periods on the 10 selected points is approximately 0,15 µl H<sub>2</sub>S /min/m<sup>2</sup>. In fact, the highest hydrogen sulphide surface flux measured has reached punctually 4 µl H<sub>2</sub>S /min/m<sup>2</sup> (Figure 3).

Considering LFG with 50% methane content and a typical intermediary cover methane surface flux of 100 ml/min/m<sup>2</sup>, the predicted hydrogen sulphide surface flow should reach at least 1,4 µl H<sub>2</sub>S /min/m<sup>2</sup> with the assumption of no H<sub>2</sub>S oxidation and the minimal LFG H<sub>2</sub>S concentration of 7 ppmv. The contribution of the temporary clay cap for the measured odour production rate has a real significance, depending of the thickness and permeability of the cover and of uncontrolled LFG emissions (Karnik M. & Parry C., 2001). That low flow indicates that a high oxidation rate occurs in the rather thin silty clay cover (50 cm) of the intermediary cover. During the survey period (June-July 2004), the relatively high air temperature promoted the oxidation.

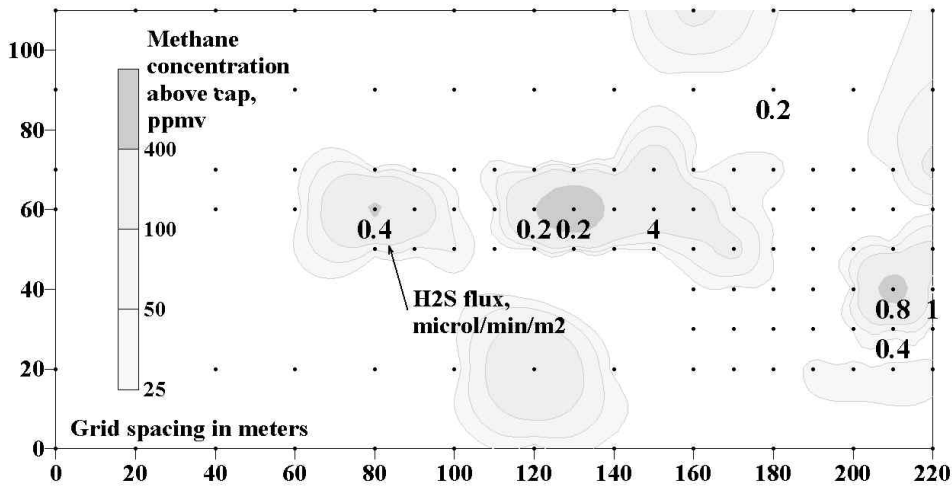


Figure 3. Methane concentration on the cap from the preliminary survey and low but significant hydrogen sulphide surface emission fluxes

### 3.2 Hydrogen sulphide temporal emission characterization

The general trend of the TRS and FID concentration versus time plots are similar for the period without high winds. We also notice the minor occurrence of periods with sulphur peaks which could not be directly explained by the simple wind directions and velocities. The only variation of the TRS concentration on some minor parts of the curves seems to indicate that we had encountered some adsorption, which was often observed with sulphur compounds (Cossu R. & al, 2003). We needed in fact to use a relatively long (up to 200 meters) air line to drive the pumped air from the supply gas to the dynamic chamber and from the dynamic chamber to the mobile laboratory. These relatively quick H<sub>2</sub>S concentration variations were also encountered for the dynamic chambers.

The proximity of the access road could also be a minor factor of the emissions variability. For the measured points with high methane and medium to high H<sub>2</sub>S dynamic chamber concentrations, the variations with stable atmospheric pressure conditions were generally explained by the high winds periods (Figure 5).

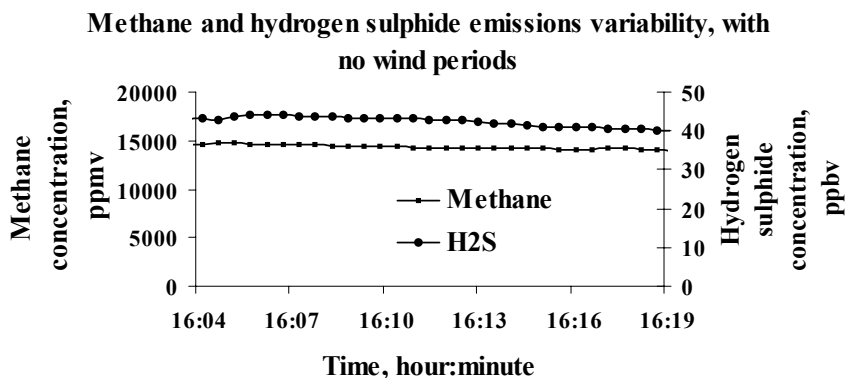


Figure 4. Methane and H<sub>2</sub>S emissions variability with high methane emission and no high wind periods.

### Methane and hydrogen sulphide emissions variability, with wind periods

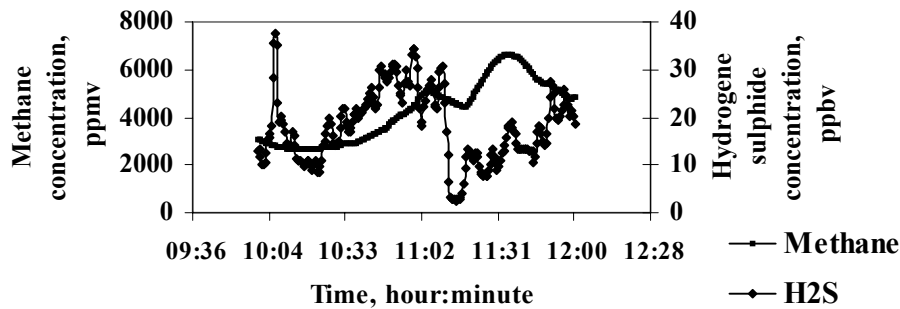


Figure 5. Methane and H<sub>2</sub>S emissions variability with high to medium methane emissions and high wind periods.

With no high wind periods, the variability of H<sub>2</sub>S and methane emission was rather low (10% of the measured value, Figure 4). Due to the low emissions and consequently the low air velocity used in order to avoid another dilution in the dynamic chamber, the influence of the winds generally hides the H<sub>2</sub>S source term variability.

We also have used a Jerome Hydrogen sulphide analyzer (Model 631-X Arizona Instrument, Phoenix) with a static chamber for complementary measurements. This method allows to measure H<sub>2</sub>S surface fluxes from 0,3  $\mu\text{l}/\text{min}/\text{m}^2$  to 4  $\mu\text{l}/\text{min}/\text{m}^2$ . The quick saturation of the sensor for high hydrogen sulphide concentration (higher than 300 ppb) limits the use in the confined volume of a static chamber. For low H<sub>2</sub>S fluxes, the use of this analyser was also limited by the landfill ground level hydrogen sulphide air concentration, which could limit the response precision in the sensor middle range (100 ppb – 1 ppm). Due to the different surface areas covered with the two type of chambers used, we could not make a real correlation between the results of the two types of chambers.

A comparison between the portable analyser and the TRS was made for different LFG samples and with a calibration gas. The Jerome analyser exhibits a rather good selectivity with the measured value of 270 ppb of hydrogen sulphur for a 200 ppb hydrogen sulphur, 400 ppb dimethyl sulphide and 340 ppb methyl mercaptan calibration gas. The differences between the TRS and Jerome analyser measurements for more than 30 samples of diluted LFG were lower than 20% for all the samples. There are generally less than 10% of variability between TRS and Jerome 631-X results.

## 4. CONCLUSIONS

The methane and sulphur emissions of the landfill were studied in a two stages survey. Firstly, the survey of hydrogen sulphide concentration in the collection system and methane concentrations above the intermediary cap was used in a preliminary stage to define the studied area for the second characterization stage.

TRS measurements on the cap with funnel, flux box and dynamic chambers allow to provide an evaluation of the range of the hydrogen sulphide emissions for the studied site, namely 0.03 to 4  $\mu\text{l}/\text{min}/\text{m}^2$ . The monitored temporal variations were linked to the influence of high wind.

The studied area exhibits relatively low emissions of hydrogen sulphide by the cap. The relative low surface H<sub>2</sub>S rate source limits efficiency of the monitoring for the study of the temporal variation of the source term. The high daily air temperature which promotes oxidation in the cover and the relative weakness of the H<sub>2</sub>S source could explain the low emissions. The heterogeneity of the deposits of plasterworks on the waste also provide a large variation of H<sub>2</sub>S in a small spatial scale. The predominant sulphur compounds was the hydrogen sulphide, also the portable Jerome 631-X analyser used for complementary measures provides results which could be compared with the measurements given by the mobile laboratory TRS analyser.

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