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Distribution of Hydrogen Sulfide, Ammonia and volatile compounds in the ambient air surrounding a landfill facility

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The ambient concentration inside a landfill facility and its surroundings has been measured during two time periods (summer and autumn) in 24 selected spots within a radius of approximately 5 km. Organic volatile and semi-volatile compounds have been detected by MS-GC and the corresponding concentrations determined using passive samplers. 23 organic compounds have been detected and analyzed, in a wide range of concentration, from nil to 30 μg/Nm^3. Hydrogen sulfide and ammonia were also analyzed using passive samplers, and their concentration ranges are 0-22 μg/Nm^3 and 0.3-52 μg/Nm^3 respectively, corresponding the highest values to spots inside the landfill.

The hydrogen sulfide concentration has also been measured continuously in a spot inside the landfill for 28 days, in order to observe the corresponding variations under different weather conditions.

1. Introduction

The area studied in this paper corresponds to a landfill, sited in the Valencianne Community (Spain), where there are many small residential houses around a 5 km distance to the centre of the landfill. Odor is a normal problem around the landfill, so the first objective of the study carried out was to measure the concentration of hydrogen sulfide and ammonia. The second objective was to identify the organic volatile and semi-volatile compounds that are present in the area studied, in order to deduce if they are present with high concentrations.

2. Experimental Method

Initially a grid with 24 spots was selected considering the distance to the landfill, the geography of the zone and the windrose. Inside the landfill, 4 spots were selected: near the vessel front of fresh municipal waste, at the entrance of the landfill, near the pond of lixiviates and at one extreme of the internal landfill area. Outside the landfill, another 20 spots were selected, at different distances from the landfill, in an area with a distance around 5 km from the center of the landfill.

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Two campaigns were carried out, one at July 2009 (summer) and another in November 2009 (autumn) for a week. Passive samplers were used to measure the mean concentrations of the different compounds. The continuous measuring of hydrogen sulfide inside the landfill was carried out in winter.

2.1 Ammonia

For the analysis of ammonia, passive samplers type FERM (a small cylinder 10 mm high and 20 mm internal diameter) was used. These samplers are closed at one extreme with a polyethylene cap, where a glass fiber filter is introduced. At the other extreme, there is a cast iron mesh and a Teflon membrane. The filter is impregnated with a citric solution. The analysis is carried out by the reaction between the ammonia ion with phenol and sodium hypochlorite, which is intensified with sodium nitroprusiate, and the color produced is measured by spectrophotometer (indophenols method) (Roadmana et al, 2003).

2.2 Hydrogen sulfide

FERM samplers were also used for the retention of hydrogen sulfide. In this case, a silver nitrate solution impregnates the filter. The $AgNO_3$/FMA fluorimetric method was used. This method is very useful for determining very low hydrogen sulfide concentrations, but all precautions must be considered to minimize the reaction of the atmospheric oxygen with the FMA (Fluorescein Mercury Acetate) (Natusch et al., 1972)

2.3 Organic volatile and semi-volatile compounds

The retention of the volatile organic compounds (VOCs) was carried out by passive RADIELLO samplers (a cylindrical tube 5.5 cm length and 5.8 mm diameter). The adsorbent used was active carbon (5.3 mg, 35-50 mesh), placed inside the tube. Extraction was carried out with carbon disulfide.

The organic compounds were analyzed by GC/MS, with a SPB1 SULFUR column. The ionization potential was 70 eV. Library NIST was used to identify the most probable compounds and, on the other hand the relative volatility of the different compounds was also taken into account for the identification of the different compounds. Naphthalene D-8 was used as internal standard.

2.4 Continuous measuring of hydrogen sulfur inside the landfill

Automatic equipment, constituted by an SO_2 fluorescence analyzer and a furnace converting H_2S into SO_2, was used for measuring continuously the hydrogen sulfide inside the landfill. Temperature, wind velocity and direction data was used from a close meteorological station. All data correspond to a winter period of 26 days.

3. Experimental Results

Table 1 shows the experimental results corresponding to the different analyzed compounds, considering the two campaigns (summer and autumn), the maximum, minimum and median values of concentrations, and considering the 4 points inside the landfill and the remaining 20 spots outside the landfill within a radius of 5 km to the center of the landfill. Concentration calculations are based on Fick's first law. Temperature dependence is taken into account with the diffusion coefficient. The average temperature of the sampling period was used.

Table 1. Concentrations of different compounds inside and outside the landfill

Concentration (µg/Nm^3)	Summer						Autumn					
	Inside landfill			Outside landfill			Inside lanffill			Outside landfill		
Compound	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median
Hydrogen sulfide	22.7	4.99	10.1	5.96	0.24	1.10	12.3	3.48	6.09	4.02	0.01	0.50
Ammonia	31.8	1.62	6.01	6.96	0.28	1.26	53.3	2.65	4.73	21.2	0.33	1.52
Toluene	2.05	1.22	1.66	3.26	0.01	1.01	8.39	1.11	6.16	6.52	0.30	1.27
Butanoic acid, ethyl ester	0.20	0.09	0.20	0.03	0.03	0.03	1.48	0.05	0.29			
Tetrachloroe-thylene	0.19	0.07	0.14	0.08	0.03	0.06	0.88	0.07	0.34	0.23	0.02	0.07
Ethylbenzene	0.38	0.08	0.20	0.23	0,03	0.06	1.20	0.21	0.72	0.61	0.04	0.17
p/m- xylene	0.80	0.32	0.35	0.35	0.08	0.13	3.07	0.39	1.92	1.56	0.11	0.40
o-xylene	0.22	0.06	0.13	0.12	0.03	0.07	2.05	0.10	0.93	0.48	0.03	0.10
1R-α-Pinene	1.11	0.09	0.44	0.14	0.09	0.11	3.70	0.34	3.68	0.51	0.04	0.45
o/m/p-Cymen	1.64	0.23	0.77	0.29	0.01	0.02	2.65	0.49	1.87	0.83	0.02	0.14
psi-Cumene	0.22	0.08	0.15	0.11	0.03	0.06	2.79	0.08	0.65	0.31	0.03	0.12
D-Limonene	4.77	0.47	2.02	0.36	0.02	0.10	29.1	0.54	20.1	2.27	0.04	0.21
Propane, 2-ethoxy-2-methyl-	0.10	0.02	0.07	0.31	0.05	0.10						
Benzene	0.17	0.08	0.10	0.14	0.01	0.06	0.43	0.08	0.32	0.35	0.04	0.16
Trichloronitromethane	0.13	0,08	0,10	0.13	0.03	0.07	0.19	0.04	0.13	0.17	0.02	0.06
Cyclohexane	1.08	0,16	0,32	30.5	0.03	0.23	2.67	0.37	1.76	5.79	0.02	1.12
Decane	0.82	0,51	0,71	1.12	0.31	0.50	2.30	0.26	1.39	0.93	0.07	0.26
Isooctane	14.8	0,21	7,50	11.2	0.05	0.10	2.33	0.06	1.22	1.37	0.11	0.44
Heptane							0.59	0.09	0.46	0.25	0.02	0.12
Nonane							0.67	0.08	0.59	0.19	0.03	0.14
Undecane	0.24	0.13	0.19	0.21	0.01	0.12	0.51	0.05	0.31	0.30	0.03	0.09
Dodecane	2.05	1.45	1.61	3.52	0.79	1.47	1.71	0.23	1.12	1.84	0.12	0.51
Tridecane	1.44	1.24	1,38	6.08	0.12	1.17	1.05	0.11	0.69	1.83	0.06	0.29
Tetradecane	4.63	3.75	4.03	5.04	1.58	3.26	3.99	0.44	2.69	7.31	0.14	1.13

Hydrogen sulfide concentration varies in a wide range, with logically high concentrations inside the landfill. A great area around the landfill has an hydrogen sulfide concentration higher than 2 ppbv (3 µg/Nm^3), that is the limit considered for the odor threshold detection. There are two groups of compounds: a first group, with toluene, tetrachloroethylene ethybenzene, xylene 1R-α-pinene, psi-cumene, cymen and D-limonene with high variations of concentration in the 0-6 µg/Nm^3 range in surroundings, and 0.2-30 µg/Nm^3 inside the landfill, and a second group with benzene, trichloronitromethane (used as rat poison) , cyclohexane, isooctane, undecane, tridecane and tetradecane in a range concentration of 0.01-5 µg/Nm^3, but without a great difference between the spots inside and outside the landfill. Nevertheless, it must be stated that there are some values that not follows the general tendency. The values of concentrations determined are similar to those presented in literature.

As far as the continuous sulfide hydrogen concentration data are concerned, Figures 1 to 4 show the experimental values corresponding to different variables. Sulfide hydrogen values from continuous sampling are "ten minute average" in order to correlate them to meteorological fluctuations (wind speed and direction). They reach quite high values when emission plume is directly reaching the sampler (inside the landfill) in some specific conditions (low wind velocity, NW wind and night hours) and very low in others. The percentage of these values higher than 200 µg/m^3 is very low. To compare these measures to passive samplers, an average of seven days continuous sampling (more than thousand ten-minute data) must be done.

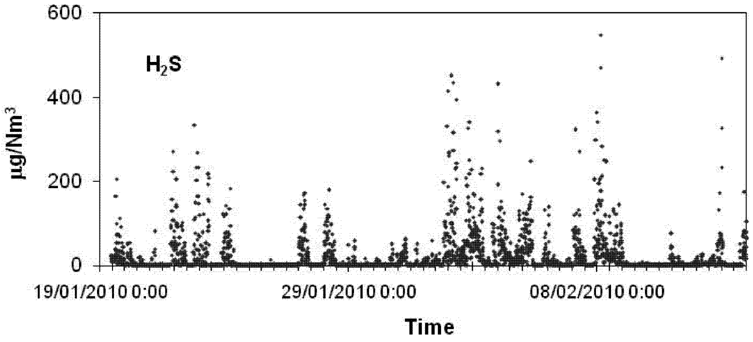

Figure 1. Variation of the hydrogen sulfide concentration vs. time

From Figure 1, a great variation of hydrogen sulfide concentration can be observed, from around 600 µg/Nm^3 to very low values. The mean value in the period studied is 14 µg/Nm^3, which is close to those observed with the passive samplers inside the landfill.

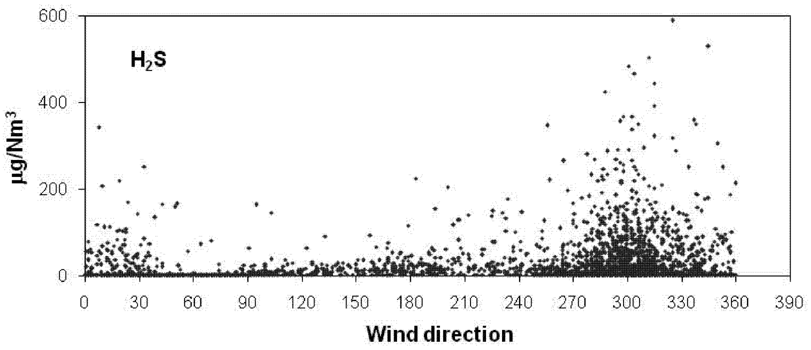

Figure 2. Variation of the hydrogen sulfide concentration vs. wind direction

From Figure 2, the direction of the main emission focus can be deduced, so this technique can be interesting when there are different areas or focus that can be responsible for the emission of hydrogen sulfide.

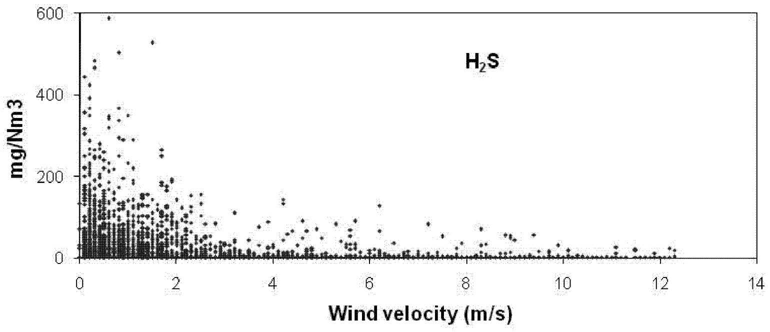

Figure 3. Variation of the hydrogen sulfide concentration vs. wind velocity

As it can be deduced from Figure 3, the concentration levels are high when the wind velocity is less than 4 m/s, causing an accumulation of hydrogen sulfide above and around the emission area.

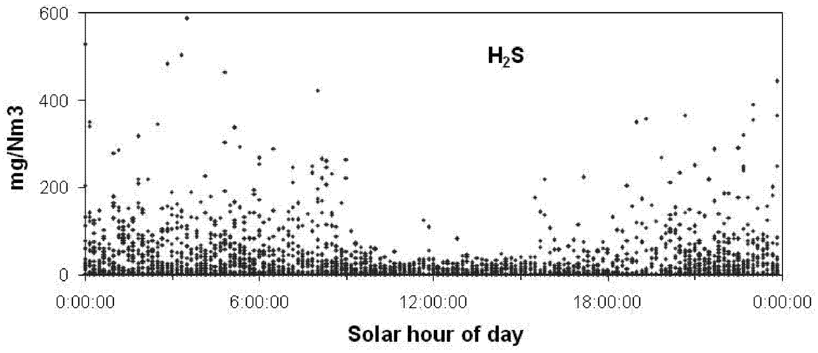

Figure 4. Variation of the hydrogen sulfide concentration vs. solar time of the day

Another interesting point is the variation of the concentration during the day. It can be deduced from Figure 4 that the highest values are recorded in the 16:00 to 10:00 solar hour range of the following day, so probably during the previous hours to 10:0 hydrogen sulfide is removed from the emission area to its surroundings. The low values of wind velocity during the night can cause an accumulation of hydrogen sulfide.

4. Conclusions

Twenty three organic compounds have been detected and analyzed, in a wide range of concentration, from nil to 14 µg/Nm^3. Hydrogen sulfide and ammonia were also analyzed, and their concentration ranges are 0-22 µg/Nm^3 and 0.3-52 µg/Nm^3 respectively. The highest values logically correspond to spots inside the landfill.

Using a continuous monitoring equipment for hydrogen sulfide, it was possible to determine the direction from where this compound is evolved, a critical velocity wind around 4 m/s which lead to a removal of the hydrogen sulfide above this value from the emission area, and the central solar time from 16:00 to 10:00 of the following day when the hydrogen sulfide accumulates on the emission area at the days with low values of wind velocity.

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