



## Attenuation of methane, PAHs and VOCs in the soil covers of an automotive shredded residues landfill: A case study

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### ABSTRACT

The article shows the results of a research carried out on a landfill of automotive shredded residues, with the aim to assess the attenuation effects of a multilayer soil cover (clay, gravel and vegetable top soil layer) on the outwards migration of methane, VOCs and PAHs present in the biogas. As a consequence of the fixation and biodegradation phenomena the concentration of methane undergoes a reduction from 480,000 ppm<sub>v</sub> in the raw biogas to 22.51 ppm<sub>v</sub> in the outside air just above the soil cover. All VOCs, due to their good solubility in water and their bioavailability, have undergone a drastic reduction, while crossing the landfill cover, as much as to be detected in the outside air at a concentration lower than the limit of analytical detection. PAHs found in raw biogas have a chemical structure with four or five aromatic rings and a number of C atoms from 16 to 20 so that they have a very low water solubility and low biodegradability. They are present in biogas as particulate, so that the more significant removal mechanism appears the complex process of biogas filtration while crossing the multilayer cover. For them it stands out the remarkable reduction in the concentration of chrysene, from 48.5 ngNm<sup>-3</sup> in the raw biogas to 3.0 ng Nm<sup>-3</sup> in outdoor air. In any case, all the PAHs were detected in the outside air at concentrations lower than 5 ng Nm<sup>-3</sup>.

**Keywords:** automotive shredded residue, car fluff, landfill biogas, PAHs, VOCs.

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### INTRODUCTION

The treatment of end-of-life vehicles (ELVs) involves the manual separation of the most hazardous materials (e.g., batteries, fuel, and lubricating oil) and the subsequent mechanical recovery of recyclable parts (e.g., iron, other metals, plastic, and paper). The remainder material, typically termed as Automotive Shredded Residue (ASR) or "car fluff", amounts to approximately 25% in weight and it is generally disposed of in landfill, resulting in relevant environmental and health issues [1-2]. However, several thermal treatment plants are known [3-5]. The separation of hazardous components is not always performed with the proper care. However, even operating at maximum efficiency, hazardous inorganic compounds (particularly lead, cadmium, and copper) remain in the residue, along with organic compounds derived from fuels, lubricating oils, paints, combustion residues, and solvents used in vehicle maintenance and cleaning [6]. The composition of the ASR and the presence of hazardous inorganic compounds are well documented in the literature [2][4-5] [7-8]. The leachate of ASR landfills is characterized by a significant presence of organic compounds and heavy metals and its treatment is carried out in a manner similar to the leachate from municipal waste landfills; in particular physical-chemical processes [9] and biological activated sludge processes, also MBR, are applied [10-11].

The biogas production from ASR landfills represents a small share of the total production of biogas from different sources, which in Europe amounts approximately to 10 Mtoe y<sup>-1</sup>[12-14]. However, the biogas from ASR landfills is

characterized by the presence of a broad spectrum of hazardous organic compounds in the categories of VOCs and PAHs, which are typically ubiquitous and their presence is normally found also in urban areas [15-19].

With reference to hazardous organic compounds found in biogas of ASR landfills a recent research has evidenced the level of presence of 16 PAHs and 35 VOCs[2].

The objective of the present research is focused on the verification of the attenuation effects of the top soil cover on the migration of methane, PAHs and VOCs towards the outside atmosphere. The research was conducted on a real scale landfill, with 250.000 ton ASRs deposited. As regards to this attenuation effects the scientific literature reports different mechanisms of action, from adsorption to solubilisation and biological degradation, whose efficiency depend strongly from the molecular structure of the specific compound, the quality of soil, temperature, moisture and the presence of oxygen [20-25].

## EXPERIMENTAL SECTION

### Landfill characteristics

The landfill object of this research is located in north Italy. It was filled with 250,000 tons of ASRs which average composition (of total 70 samples) was as follows: fines (<20 mm) 42.9%; rubber 18.7%; plastics 14.0%; paddings 8.1%; fabrics 5.0%; metals 3.2%; other fractions (mainly paper, rope, wood and leather) 8.1%. The landfill is equipped with 24 wells of biogas equally distributed over the entire area (1.8 ha), each discharging into a manifold connected to two enclosed flares. The total flow rate of collected biogas is  $720 \text{ Nm}^3 \text{ h}^{-1}$ .

The landfill, after being filled with waste, was covered by a multilayer system composed as shown in Figure 1. The average composition, on a dry base, of the clay layer is: 68% clay; 32% by other minerals (calcite, dolomite, quartz, feldspar). In turn, the clay composition is: 43% montmorillonite, 21% illite, 39% kaolinite, chlorite 7%. The average composition, on a dry base, of the vegetable top soil is: sand 65%; silt 15%; clay 8%; humus 7%; limestone 5%.

In order to assess the attenuation effects of the landfill cover on the migration of methane, PAHs and VOCs into the atmosphere, 9 control positions uniformly distributed over the landfill surface have been defined, with the addition of a further (10<sup>th</sup>) control position, before the flares, for assessing the quality of raw biogas. In correspondence with each control position, the sampling of biogas and outside air was carried out in 5 points (see Figure 1):

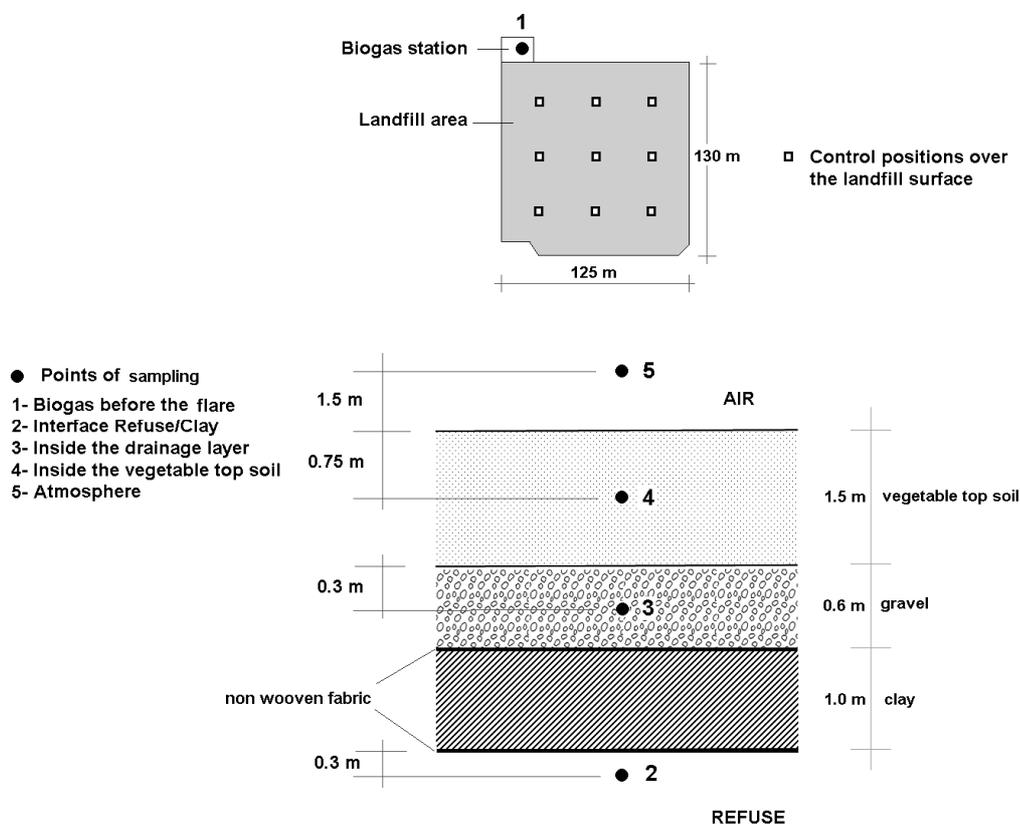


Figure 1. Characteristics of the landfill cover with the 5 sampling points (above are indicated the 9 control positions over the landfill surface, with in addition the position 1 for the sampling of biogas before the flares)

The research program was started 4 years after the closure of the landfill and it consisted of three analytical campaigns carried out in a period of 6 months. 37 samples were collected for each campaign (total 111 samples throughout the whole research) The samples were collected on days with good atmospheric stability (Pasquill Stability Classes: F and G) in order to minimize the effects of dilution of contaminants (point 5). The results of the analysis in every single point were processed in order to determine, on a statistical base, the average level of attenuation of the landfill cover. The attenuation performance was evaluated for the whole cover with respect to PAHs and VOCs (comparison between the average concentration in point 1 and in point 5); instead, for methane and other parameters the analysis were extended to all 5 point of measure (comparison of average concentration resulted in points 1, 2, 3, 4 and 5).

### **Analysed compounds**

The research program was started 4 years after the closure of the landfill and it consisted of three analytical campaigns carried out in a period of 6 months.

The following compounds were analysed:

- CH<sub>4</sub>, CO<sub>2</sub> and O<sub>2</sub> (in all 5 sampling points);
- 16 PAHs and 35 VOCs (in point 1 and point 5).

Temperature, Relative Pressure and Relative Humidity were also determined (soil moisture was also determined inside the clay layer and the vegetable top soil).

### **Methods of sampling and analysis**

Biogas in point 1: Measurement of CH<sub>4</sub>, CO<sub>2</sub> and O<sub>2</sub> with infrared analyzer LFG 20 (resolution 0.01%). Pressure measurement with micro-electronic manometer (accuracy  $\pm 1\%$  of full scale). Temperature and humidity measurement with thermo-hygrometer (accuracy: T  $\pm 0.45$  °C; RU  $\pm 1\%$  of full scale). The sampling and analysis of PAHs and VOCs were performed with specific procedures for each class of compounds after separation of particulate on filter membrane, separation of condensate and adsorption of the organic compounds present in the vapour phase, on a vial ORBO 43. The determination of PAHs was obtained by HPLC with fluorescence detection so as to combine a high sensitivity to a sufficient selectivity. VOCs, halogenated or not, have been identified and quantified by gas chromatography with flame ionization detector.

Biogas in points, 2, 3 and 4: Sampling by means of two coaxial hollow probes, 1 m long, prolonged with extensions of 1m. Measurement of CH<sub>4</sub>, CO<sub>2</sub> and O<sub>2</sub>, pressure humidity and temperature as in point 1. Soil moisture measurement with hygrometer (1% resolution), equipped with adaptable probes 75 mm, 120 mm and 250 mm lengths

Outside air (point 5): Sampling and analysis of PAHs and VOCs as for biogas in point 1. Measurement of CH<sub>4</sub>, CO<sub>2</sub> and O<sub>2</sub>, pressure, humidity and temperature, as in point 1.

## **RESULTS AND DISCUSSION**

### **Attenuation of methane emission**

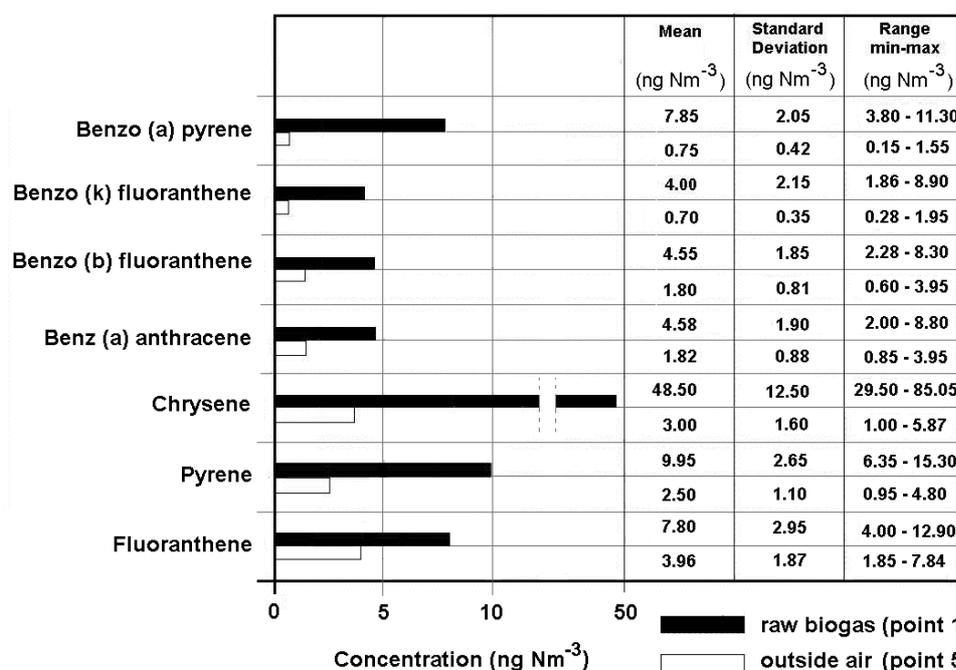
Table 1 shows the values of the concentrations of CH<sub>4</sub>, CO<sub>2</sub>, and O<sub>2</sub> in the five sampling points. The table also shows the values of temperature, pressure and humidity of biogas and outside air (with in addition the moisture content of the soil), as these parameters can greatly influence the migration of methane and others contaminants through the landfill cover.

It can be observed that the depression maintained in the main suction pipe of the biogas (-115 mm H<sub>2</sub>O) has determined a vast range of action affecting also the various layers of the landfill cover. In fact, an average depression of -22.8 mm H<sub>2</sub>O resulted at the waste-clay interface and an average depression of -13.9 mm H<sub>2</sub>O was measured inside the upper layer of vegetable soil. These data demonstrate an extensive and efficient collection of biogas, such as to determine a noticeable effect of air intake into the landfill. However it is important to note that the depression measured in the cover layers has strong variations around the average values, as demonstrated by the standard deviation values and the range min-max.

**Table 1.** Concentration of methane, carbon dioxide, oxygen and values of temperature (*T*), relative pressure (*p*) and relative humidity (*RU*) in the five point of measure. In addition is the soil moisture (*M*) inside the clay and vegetable layers). Data are represented as mean, standard deviation (*SD*) and range min-max (n. of samples: 27 for each point of measure)

Point of sampling	Parameter Significance	CH <sub>4</sub> (ppm <sub>v</sub> )	CO <sub>2</sub> (ppm <sub>v</sub> )	O <sub>2</sub> (ppm <sub>v</sub> )	<i>T</i> (°C)	<i>p</i> (mm H <sub>2</sub> O)	<i>RU</i> (%)	<i>M</i> (%)
1	Mean	480000	387000	15200	58.0	-115.0	96.5	
	(SD)	(98400)	(68230)	(5600)	(3.3)	(3.2)	(3.5)	
2	Mean	324000	97750	143700	22.9	-22.8	85.8	48.0
	(SD)	(38480)	(17300)	(28640)	(2.6)	(9.3)	(8.3)	(8.7)
3	Mean	52.900	16500	167800	21.9	-16.8	75.6	
	(SD)	(9255)	(3890)	(18900)	(3.1)	(11.1)	(9.2)	
4	Mean	2956	32475	178900	21.7	-10.6	68.1	42.6
	(SD)	(388)	(6310)	(8300)	(4.0)	(6.0)	(16.8)	(8.5)
5	Mean	2251	1316	209000	21.8	0	59.8	
	(SD)	(5.9)	(141)	(810)	(4.4)	(4.4)	(17.0)	

This situation determines an alternation of zones of the soil cover characterized by infiltration of outside air with zones characterized by the potential migration of biogas outwards. It must be stressed that the fresh air intake is inevitable in order to achieve a high efficiency in biogas collection and preventing the outwards migration; however, any excess must be avoided in order to limit the risk of fire and explosion.



**Figure 2.** Attenuation effect of soil cover on PAHs. Data are represented as mean, standard deviation and range min-max (total n. of samples: 30)

Just because of the intrusion of outside air, an average concentration of methane of 324,000 ppm<sub>v</sub> (32.4%), was measured, at the waste-clay interface (point 2); this value is much lower than the average concentration measured at the biogas station (point 1). In the vegetable layer (point 3) the concentration is significantly reduced, down to the average value of 2,956 ppm<sub>v</sub> (2.95%). This reduction is not justified by the simple dilution with air, but it is reasonable to assume that, crossing the cover layers, methane has undergone the effects of adsorption, solubilisation and biodegradation. In fact, it is well known that clay exerts an effective adsorption action and the sorption capacity depends on the type of clay with the following hierarchy: montmorillonite>illite/smectite mixed layer> kaolinite> chlorite>illite[22]. BET surface area is the main factor affecting CH<sub>4</sub> adsorption capacity[22]. The contribution of solubilisation in soil moisture is connected to the methane solubility in water (17-20 mg L<sup>-1</sup> at 20°C and atmospheric pressure). With reference to methane biodegradation, it takes place through a biochemical oxidative reaction so that only soil penetrated by oxygen is concerned. Methanotrophic bacteria are responsible for methane oxidation to carbon dioxide and water. There are only a few values for the methane uptake rate in soils; values have been found with reference to soil weight, between 0.024 and 0.112 mgCH<sub>4</sub> g<sup>-1</sup> h<sup>-1</sup>[24]. As a consequence of the fixation and degradation phenomena and also dilution with air the mean concentration of methane in point 5 (outside air) has been found at 22.51 ppm<sub>v</sub>.

### Attenuation of PAHs emission

Figure 2 shows the results of attenuation with reference to PAHs, by comparing the concentrations in raw biogas (point 1) and in the outside atmosphere, just above the cover (point 5). The figure reports the PAHs effectively found in the biogas: benzo(a)pyrene, benzo(k)fluoranthene, benzo(b)fluoranthene, benz(a)anthracene, chrysene, pyrene, fluoranthene. All other PAHs were found at concentrations below the limit of analytical detection of  $0.1 \text{ ngNm}^{-3}$ .

In particular stands out the remarkable reduction in the concentration of chrysene, from  $48.5 \text{ ngNm}^{-3}$  in the raw biogas to  $3.0 \text{ ng Nm}^{-3}$  in the outdoor air (more than 16 times reduction). In any case, all the PAHs were detected in point 5 at concentrations lower than  $5 \text{ ng Nm}^{-3}$ .

As known, PAHs are organic compounds with two or more aromatic rings in several structural configurations, and they are attributed carcinogenic, mutagenic and toxic characteristics. Table 2 shows the main physical-chemical properties of PAHs found in biogas, which have a chemical structure with four or five aromatic rings and a number of C atoms from 16 to 20.

**Table 2. Physical-chemical properties of PAHs (US-DHHS, 1995)**

PAH	Formula	n. rings	Mol. Wt.	Melting point (°C)	Boiling point (°C)	Vapour Pressure at 25°C (mm Hg)	Solubility in water at 25°C ( $\mu\text{g L}^{-1}$ )
<i>Benzo[a]pyrene</i>	$\text{C}_{20}\text{H}_{12}$	5	252.3	179	495	$5.6 \cdot 10^{-9}$	2.3
<i>Benzo[k]fluoranthene</i>	$\text{C}_{20}\text{H}_{12}$	5	252.3	215.7	480	$9.59 \cdot 10^{-11}$	0.76
<i>Benzo[b]fluoranthene</i>	$\text{C}_{20}\text{H}_{12}$	5	252.3	168.3		$5.0 \cdot 10^{-7}$ (at 20°C)	1.2
<i>Benz[a]anthracene</i>	$\text{C}_{18}\text{H}_{12}$	5	228.3	158-162	438	$2.2 \cdot 10^{-8}$ (at 20°C)	10
<i>Chrysene</i>	$\text{C}_{18}\text{H}_{12}$	4	228.3	255-256	448	$6.3 \cdot 10^{-7}$	2.8
<i>Pyrene</i>	$\text{C}_{16}\text{H}_{10}$	4	202.1	156	404	$2.5 \cdot 10^{-6}$	77
<i>Fluoranthene</i>	$\text{C}_{16}\text{H}_{10}$	4	202.3	108.8 *	384	$5.0 \cdot 10^{-6}$	200-260

\* [26]

All PAHs have a high melting point, so that they are normally in a solid state and in biogas are present as fine particulate. They are also characterized with a low water solubility and in particular PAHs with four or more rings are considered practically insoluble (only Fluoranthene shows a water solubility in the range  $0.2\text{-}0.26 \text{ mg L}^{-1}$  at 25°C, anyway small but higher than others PAHs).

Due to this very low solubility in water the removal by dissolution in soil moisture can be considered negligible. Also sorption mechanisms have little consideration, even if PAHs are characterized by their hydrophobic nature and consequently, these species could be adsorbed on the organic fraction of soil. The more significant removal mechanism appears the complex process of filtration while crossing the multilayer cover and in particular the fine texture of the top vegetable layer. In this sense the leakage of the only finer particles of the various PAHs would lead to the very small concentrations detected in the outside air.

Some importance is also attributed to the mechanism of biodegradation. High-molecular-weight PAHs (HMW-PAHs), such as the ones found in biogas, are generally considered recalcitrant and resistant to microbial attack so that there is currently a lack of knowledge regarding their biodegradation [21]. The very low solubility in water and the complex chemical structure are the main causes of their low bioavailability, high persistency in the environment and bioaccumulation in organisms. Instead, the biodegradation of PAHs with fewer than three aromatic rings has been the subject of several publications. Studies on the ability of microorganisms to degrade the various PAHs are of particular interest in the field of bioremediation of contaminated sites. In fact, microorganisms with the capacity to degrade PAHs were identified in areas chronically polluted by these compound. A recent study[25] reports the ability to degrade PAHs by lignin-degrading white-rot fungi that produce a set of extracellular enzymes, such as oxidases and peroxidases. Although less extensively than fungi, the PAHs degradation capacity of bacteria has also been reported for genera such as *Pseudomonas* *Actinobacteria*, *Bacillus* and *Ralstonia* [25].

### Attenuation of VOCs

Figure 3 shows the results of cover attenuation with reference to VOCs, by comparing the average concentrations measured in raw biogas (point 1) and in the outside air (point 5).

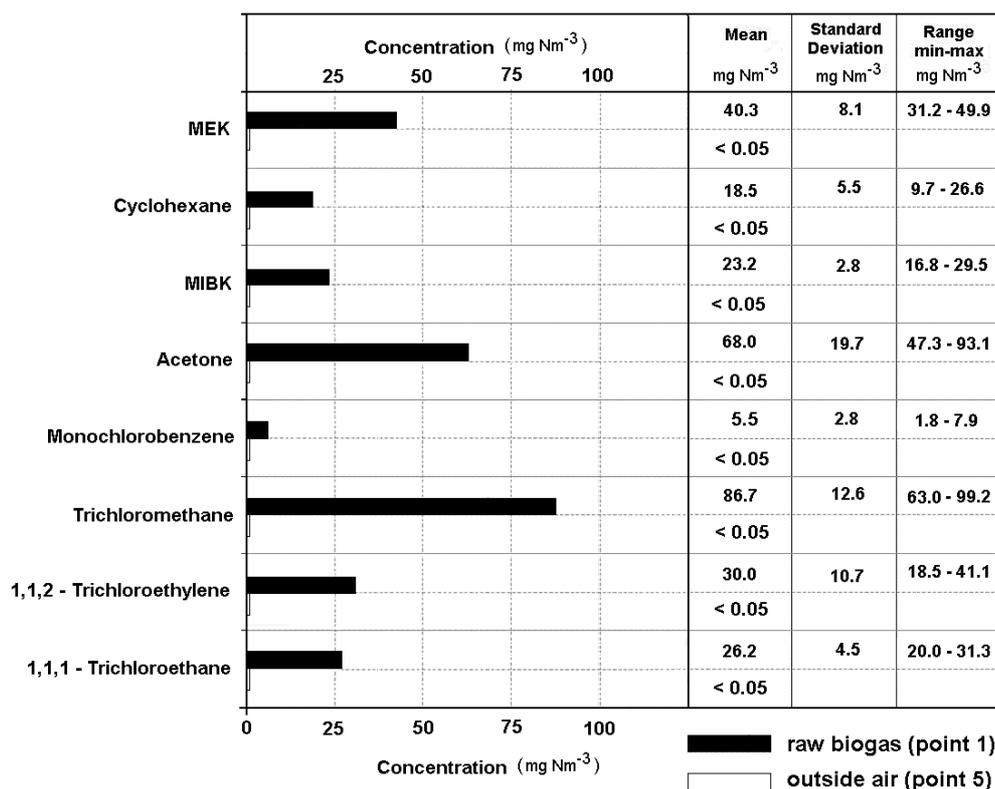


Figure 3. Attenuation effect of soil cover on VOCs. Data are represented as mean, standard deviation and range min-max (total number of samples: 30)

This figure reports the VOCs effectively found in the biogas, while others were found at concentrations below the limit of analytical detection ( $0.05 \text{ mg Nm}^{-3}$ ). Table 3 shows the main physical-chemical properties of VOCs found in raw biogas.

It stands out that all VOCs undergo a drastic reduction while crossing the landfill cover, as much as to be detected in the outside air (point 5) at a concentration lower than the limit of analytical detection ( $0.05 \text{ mg Nm}^{-3}$  for each compound). In this sense the removal of VOCs while crossing the soil cover shows results almost parallel to that of methane. This kind of result was also evidenced in a previous research [24] for any VOCs, even chlorinated.

The main mechanisms of VOCs removal are condensation, sorption and biodegradation. Condensation is determined by the effective lowering of biogas temperature while crossing the multilayer cover. Sorption is mainly determined by solubilization in the soil moisture which is expected relevant for methyl-ethyl-ketone, the most soluble in water ( $275 \text{ g L}^{-1}$  at  $20^\circ\text{C}$ ), but noticeable are also the solubility values of other VOCs.

Table 3. Physical-chemical properties of VOCs found in raw biogas [27-28]

VOCs	formula	Mol. Wt	Boiling point at 760 mm Hg ( $^\circ\text{C}$ )	Vap. Pressure at $25^\circ\text{C}$ (mm Hg)	Solubility in water at $25^\circ\text{C}$ ( $\text{g L}^{-1}$ )
MEK	$\text{C}_4\text{H}_8\text{O}$	79.6	56.2	77.5 ( $20^\circ\text{C}$ )	275 ( $20^\circ\text{C}$ )
Cyclohexane	$\text{C}_6\text{H}_{12}$	84.1	80.7	96.9	0.055
MIBK	$\text{C}_6\text{H}_{12}\text{O}$	100.16	116.2	14.9 ( $20^\circ\text{C}$ )	17 ( $20^\circ\text{C}$ )
Acetone	$\text{C}_3\text{H}_6\text{O}$	58.08	56.2	231.06	0.020
Monochlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	112.6	132	12.49	0.293
Trichloromethane	$\text{CHCl}_3$	119.38	61.3	159.6 ( $20^\circ\text{C}$ )	7.5-9.3
1,1,2 Trichloroethylene	$\text{C}_2\text{HCl}_3$	131.4	86.7	57.8 ( $20^\circ\text{C}$ )	1.07 ( $20^\circ\text{C}$ )
1,1,1 Trichloroethane	$\text{C}_2\text{H}_3\text{Cl}_3$	133.4	74.1	99.7	0.3

With reference to VOCs biodegradation, many researches has highlighted its importance. In the treatment of waste air of composting processes and many industrial processes the efficient removal of different VOCs by biotrickling and biofiltration processes is well documented [20][23] [29].

Good level of biodegradability in soil has been verified, even for chlorinated VOCs [24]. Bio-oxidation rates in soil for the halogenated aliphatic VOCs were found between 0.03 and 1.7  $\mu\text{g g}^{-1} \text{h}^{-1}$ . Even better rates were found for aromatic VOCs which demonstrate to rapidly degrade with high oxidation rates in the range 0.17-1.4  $\mu\text{g g}^{-1} \text{h}^{-1}$  [24].

### CONCLUSION

A landfill of automotive shredded residues of a 250.000 ton capacity and a surface of 1.8 ha was covered by a multilayer system composed as follow:

- Base layer of compacted clay with a thickness of 1.0 m, placed over the waste (with an interposed sheet of non-woven fabric);
- Intermediate porous layer, made of coarse gravel (3-6 cm), with a thickness of 0.6 m, placed over the clay layer (with an interposed sheet of non-woven fabric);
- Vegetable top soil layer with a thickness of 1.5 m.

Four years after the closure of the landfill a research programme has been developed, over a period of six months, in order to assess the attenuation effects of the top soil cover with respect to methane, PAHs and VOCs. A total of 16 PAHs and 35 VOCs were searched in the biogas. PAHs effectively found were benzo(a)pyrene, benzo(k)fluoranthene, benzo(b)fluoranthene, benz(a)anthracene, chrysene, pyrene, fluoranthene. VOCs effectively found where MEK (Methyl-Ethyl Ketone), cyclohexane, MIBK (Methyl-Isobutyl-Ketone), acetone, monochlorobenzene, trichloromethane, 1,1,2-trichloroethylene and 1,1,1-trichloroethane.

The depression maintained in the main suction pipe of biogas (average -115 mm  $\text{H}_2\text{O}$ ) has determined its extensive and efficient collection, such as to determine a noticeable effect of air intake into the landfill. However it is important to note that the depression measured in the cover layers had a strong variations around the average values, such as to allow a potential migration of biogas outwards.

The attenuation effects were evaluated by comparing the quality of raw biogas with the quality of the outside air (in 9 control points, 1.5 m above the top cover, equally distributed over the landfill surface). As a consequence of the fixation (mainly sorption) and biodegradation phenomena (and also dilution with air) the mean concentration of methane in raw biogas (480.000  $\text{ppm}_v$ ) has undergone a drastic decrease down to 22.51  $\text{ppm}_v$  in the outside air, just above the cover.

With concern to PAHs, it stands out the remarkable reduction of chrysene concentration, from 48.5  $\text{ng Nm}^{-3}$  in the raw biogas to 3.0  $\text{ng Nm}^{-3}$  in outdoor air (reduction of more than 16 times). In any case, all the PAHs were detected in outside air, at average concentrations lower than 5  $\text{ng Nm}^{-3}$ . Due to their very low solubility in water the removal of PAHs by absorption in soil moisture can be considered negligible. Also adsorption mechanisms has little consideration. Instead, the more significant removal mechanism appears the complex process of filtration while crossing the multilayer cover, in particular the fine texture of the top vegetable layer. In this sense the leakage of the only finer particles of the various PAHs would lead to the very small concentrations detected in the outside air. A contribute of biodegradation cannot be excluded as species of fungi and bacteria were found able to decompose different kind of PAHs (mainly with two or three rings), but it should be noted that PAHs found in the biogas have four to five aromatic rings, so as to severely limit their bioavailability.

It stands out that all VOCs have undergone a drastic reduction while crossing the landfill cover, as much as to be detected, in the outside air above the cover, at a concentration lower than the limit of analytical detection (0.05  $\text{mg Nm}^{-3}$  for each compound). The mechanisms of VOCs removal are condensation, sorption and biodegradation. Condensation is determined by the effective lowering of biogas temperature while crossing the multilayer cover. Sorption is mainly determined by solubilisation in the soil moisture which is expected relevant for MEK, the most soluble in water (275  $\text{g L}^{-1}$  at 20°C), but noticeable are also the solubility values of other VOCs. Also the mechanism of biodegradation has great importance in VOCs removal, even for chlorinated and aromatic VOCs, which both have shown in many experiences a good level of biodegradability in soil.

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### REFERENCES

[1] US-DHHS (United States - Department of Health and Human Services). Toxicological profile for polycyclic aromatic hydrocarbons (PAHs), Agency for Toxic Substances and Disease Registry, Atlanta, 1995, 487.

- [2] M Raboni; V Torretta; G Urbini; P Viotti. *Waste Manage. Res.*, **2014**, (in press).
- [3] L Ciacci; L Morselli; F Passarini; A Santini; I Vassura. *Int. J. Life Cycle Assess.*, **2010**, 15(9), 896-906.
- [4] A Santini; F Passarini; L Vassura; D Serrano; J Dufour; L Morselli. *Waste Manage.*, **2012**, 32(5), 852-858.
- [5] G Mancini; P Viotti; A Luciano; M Raboni; D Fino. *Waste Manage.*, **2014**, 34(11), 2347-2344.
- [6] EA Torres; GS Cerqueira; TM Ferrer; CM Quintella; M Raboni; V Torretta; G Urbini. *Waste Manage.*, **2013**, 33(12), 2670-2674.
- [7] R Cossu; S Fiore; T Lai; G Mancini; B Ruffino; P Viotti; MC Zanetti. *Proc. of Int. Conf. Crete 2012 on Ind. and Haz. Waste Manage.*, **2012**, Crete (Greece).
- [8] L Morselli; A Santini; F Passarini; I Vassura. *Waste Manage.*, **2010**, 30(11), 2228-2234.
- [9] M Raboni; V Torretta; P Viotti; G Urbini. *Rev. Amb. & Agua*, **2013**, 8(3), 22-32.
- [10] M Pirbazari; V Ravindram; BN Badriyha; SH Kim. *Water Res.*, **1996**, 30(11), 2691-2706.
- [11] V Torretta; G Urbini; M Raboni; S Copelli; P Viotti; A Luciano; G Mancini. *Sustain.*, **2013**, 5(4), 1501-1509.
- [12] Eurobserv'Er. Biogas barometer, *Le Journal des Énergies Renouvelables*, Paris, **2012**, 67-79.
- [13] M Raboni; G Urbini. *Rev. Amb. & Agua*, **2014**, 9(2), 191-202.
- [14] M Raboni; P Viotti; AG Capodaglio. *Rev. Amb. & Agua*, **2015**, 10(1), 37-47.
- [15] E Menichini. *Sci. Total Environ.*, **1992**, 116(1-2), 109-135.
- [16] MF Mohamed; D Kang; VP Aneja. *Chemosphere*, **2002**, 47(8), 863-882.
- [17] K Rawindra; R Sokhi; R Van Grieken. *Atmos. Environ.*, **2008**, 42(13), 2895-2921.
- [18] V Torretta; M Raboni; S Copelli; EC Rada; M Ragazzi; G Ionescu; T Apostol; A Badea. *U. Politeh. Buch. Ser. D*, **2013**, 75(4), 221-228.
- [19] B Yuan; M Shao; J De Gouw; DD Parrish; S Lu; M Wang; L Zeng; Q Zhang; Y Song; J Zhang; M Hu. *J. Geophys. Res.-Atmos.*, **2012**, 117(D24), 15-24.
- [20] S Copelli; V Torretta; M Raboni; P Viotti; A Luciano; G Mancini; G Nano. *Chem. Eng. Trans.*, **2012**, 30, 49-54.
- [21] RA Kanaly; S Harayama. *Microb. Biotechnol.*, **2010**, 3(2), 136-164.
- [22] L Ji; T Zhang; KL Milliken; J Qu; X Zhang. *Appl. Geochem.*, **2012**, 27(12), 2533-2545.
- [23] EC Rada; M Raboni; V Torretta; S Copelli; M Ragazzi; P Caruson; IA Istrate. *Rev. Chim. Bucharest*, **2014**, 65(1), 68-70.
- [24] C Scheutz; H Mosbaek; P Kjeldsen. *J. Environ. Qual.*, **2004**, 33(1), 61-71.
- [25] R Simarro; N Gonzalez; LF Bautista; MC Molina. *FEMS Microbiol. Ecol.*, **2013**, 83(2), 438-449.
- [26] A Mrozik; Z Piotrowska; S Labuzek. *Pol. J. Environ. Stud.*, **2003**, 12(1), 15-25.
- [27] SJ Lawrence. Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water - A Review of Selected Literature. USGS (United States Geological Survey), Reston, **2006**; 54.
- [28] W Wang, JL Schnoor, J Doi. Volatile Organic Compounds in the Environment – STP1261, 1<sup>st</sup> ed, ASTM, Philadelphia, **1996**; 282.
- [29] V Torretta; M Raboni; S Copelli; P Caruson. *WIT Trans. Ecol. Envir.*, **2013**, 176, 225-233.