Emission of non CO$_2$ greenhouse gases from landfills of different age located in central Italy

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Abstract
Landfill gas is a product of the natural biological decomposition of organic material contained in wastes deposited in landfills. This denomination generically indicates a gas mixture made of methane and carbon dioxide. These gases are produced until most of the organic material in the waste has been degraded. Emissions from municipal landfill sites are therefore potentially harmful to both local and global air quality; the global emissions of an important greenhouse gas such as methane are estimated to be between 20 and 70 Tg year^{-1}. Moreover, landfills have been shown to be a major source of anthropogenic halogenated greenhouse gases such as chlorofluorocarbons (CFCs) and their hydrogenated substitutes (HCFCs, HFCs). These long-living gases are emitted into the atmosphere as a consequence of leakage occurring in landfills where chlorine containing equipment and materials have been dumped. In this study, municipal landfills of different ages located in Tuscany (central Italy) have been investigated. Grab samples, collected at gas collection facilities, were analysed in gas chromatography with flame ionization detection for major gas measurements and in gas chromatography-mass spectrometry for halocarbon measurements. Furthermore, fluxes from the landfill surface were measured by means of a flux chamber. This approach allows an estimation of the total yearly emissions of non-CO$_2$ greenhouse gases from a landfill.

Keywords: *Landfills, greenhouse gases, halocarbons, fluxes, global change*

1. Introduction

Landfills are a major source of gases that can seriously affect air quality and at the same time can contribute to global change phenomena. The emitted gases are essentially of two different origins: those emitted by the anaerobic decomposition of the organic matter of wastes and those coming from the volatilization of the gases contained in wastes.

CO$_2$ and CH$_4$ belong to the first category and alone account for almost 100% of landfill gas, their relative abundance being equal to 40–50% and 50–60%, respectively.

Halogenated hydrocarbons, including fluorinated gases (CFCs, HCFCs and HFCs) and chlorinated solvents are essentially emitted after volatilization by the waste itself. Moreover, landfill gas contains a number of VOCs (aromatic compounds, alcanes, alkenes, sulphurated

compounds), produced by both the anaerobic decomposition and the volatilization of the waste. VOCs, besides their impact on human health, are someway involved in global change, having an important role as ozone precursors.

All VOCs (halogenated and non-halogenated) account for $1-2\%$ of total landfill emissions: nevertheless their impact both on climate and air quality is significant (Eklund et al. 1998, Schuetz et al. 2003a, Hodson et al. 2004). Notwithstanding problems related to emissions and to the impact on landscape, in Italy landfill remains the prevalent disposal method; about 62% of Municipal Solid Waste (MSW) is disposed in landfills. According to the last report from the Italian Environmental Protection Agency (APAT 2003), in Italy there are more than 600 landfills for MSW disposal.

2. Sites and sampling approach

In this study three different municipal landfills of different ages located in central Italy were considered. Landfill 1 extends over an area of 38 000 m^2 and has a waste volume of about 385 000 m^3. Operative from 1976 to 2000, the gas collection system of this landfill consists of three torches. Landfill 2 extends over an area of 64 000 m^2 and has a waste volume of about 430 000 m^3. Operative since 1994, it is composed of completed sections, capped and not yet receiving wastes, and of active sections, where wastes are currently dumped. The landfill gas produced at this site is collected by a system of wells and is used to produce energy. Landfill 3 extends over an area of 120 000 m^2 and has a waste volume of about 1 900 000 m^3. Operative since 1992, the gas collection facility of this landfill is made up of individual extraction wells; collected biogas is used to produce energy.

A preliminary campaign, involving the three landfills, took place in November 2004 and was essentially aimed at a preliminary survey and at an optimization of the analytical procedure. A second campaign (May 2005) involved Landfill 1 and Landfill 2 only.

Samples from Landfill 1 were collected from the three torches. All the samples (from Torch 1, Torch 2 and Torch 3) are representative of 'old age' landfill gas. From Landfill 2, samples were collected from three different extraction wells of the gas collection system. The samples are representative of different age landfill gases. In fact, Well 1 is pertinent to the most recently capped section of the landfill; Well 2 to an intermediate section and Well 3 to the oldest section of the landfill.

3. Method

3.1. Main landfill gas components

Glass ampoules (100 ml) were used for collecting gaseous samples, which were subsequently analysed in gas chromatography (GC) with thermo conductibility detection (TCD). Using this method main landfill gas components, i.e. CO_2, O_2, Ar, N_2 and CH_4, were determined.

3.2. Halocarbons

Passivated 850 ml stainless-steel canisters (Biospheric Research Corporation, Hillsboro, OR, USA) were filled with biogas at gas collection facilities. Air was drawn into the canisters by means of a portable ultra clean air pump (model FC-1121, Biospheric Research), the air-contact surfaces of which were all in stainless steel to eliminate release of organic compounds. Sample aliquots of 30 ml were pre-concentrated on an adsorption tube (length 10 cm; inner diameter 0.4 cm), filled with 50 mg of Carbograph 1 (sa 90 m^2 g^{-1}) and 350 mg of

Carbograph 5 (sa 560 m^2 g^{-1}) and kept at a temperature of 4°C. The adsorbed compounds were subsequently introduced into the gas cromatographic column by thermal desorption by means of a CP-4020 TCT Thermal Desorber (Chrompack International, Middelburg, The Netherlands) at a temperature of 250°C for 10 min and the desorbed analytes were transferred to the gas chromatographic system at a flow rate of 8 ml min^{-1}, by reversing the direction of carrier gas flow relative to the direction of flow during sampling. To cryofocus the analytes at the head of the column, a fused silica cold trap capillary was set at −150°C for 5 min. The gas chromatograph was equipped with a 30 m × 0.32 mm inner diameter J&W GS-GASPRO column (Mangani et al. 2000). A quadrupole Mass-Selective Detector was used as the detector. Samples are calibrated against 'working secondary standards' currently linked to two absolute calibration scales for halocarbons which reside at the Scripps Institution of Oceanography (SIO98 scale, La Jolla, CA, USA) and at Bristol University (UB98 scale, University of Bristol, UK).

3.3. CO$_2$ and landfill gas fluxes

Together with CH$_4$, CO$_2$ is the most abundant component of gas emanations from MSW landfills. Therefore, the measurements of CO$_2$ fluxes from the surface of MSW landfills represent the basis to estimate the overall fluxes of biogas (Rogie et al. 1998, Cardellini et al. 2003).

In this study, CO$_2$ flux measurements were obtained by using a static non-stationary accumulation chamber method (Cossu et al. 1997), as diffusively applied already for flux surveys in volcanic and geothermal areas, as well as for preliminary landfill applications (Rogie et al. 1998, Cardellini et al. 2003). In detail, the instrument (developed by West Systems$^{®}$, Pontedera, Italy) consists of three combined units: (1) an accumulation chamber (with surface area 0.0314 m^2 and two possible volumes, either 0.003 m^3 or 0.006 m^3), equipped with a specific, internal device for proper gas mixing into the chamber volume; (2) a flux-meter equipped with an IR (infrared) spectrometer detector (LICOR 800 IR); and (3) a palmtop computer for on-site data collection and processing.

During on-site landfill measurements, the accumulation chamber was directly placed on the ground (either cover, lateral slope or surrounding landfill areas), and soil gas emanations from the ground were collected in the chamber headspace and drawn into the IR detector by a pump, passing before through a water trap for moisture separation.

Measurements of CO$_2$ concentration, revealed by the IR detector, were recorded and simultaneously displayed by the palmtop, as concentration variations over time. Due to a specific mathematical software (Palm Flux$^{®}$) based on linear interpolation, the corresponding slope of temporal changes in CO$_2$ concentration was directly evaluated on-site. Then, according to local measurement conditions (chamber volume, and mainly temperature and atmospheric pressure), the corresponding CO$_2$ mass emission flux was derived in g m^{-2} day^{-1}.

4. Results and discussion

4.1. Evaluation of the landfills total CO$_2$ emission

In order to evaluate the total CO$_2$ emission, a set of onsite flux measurements were randomly collected from the surface of each MSW landfill with a mean linear density of 1/25 m. Each data point was located using a GPS receiver and referred to metric UTM grid coordinates (Capaccioni et al. 2004).

First, starting from the measured values a regular, rectangular array of values (grid) were calculated. To obtain a grid of values from irregularly spaced data several methods of interpolation or extrapolation exist. Ordinary Kriging and the Inverse Distance of Power (IDP) are among the most commonly used geostatistical gridding methods whose detailed characteristics are described elsewhere (Davis 1986, Cressie 1990). To avoid smoothing at the grid node, we adopted the IDP method because it is an 'exact' interpolator, i.e. the grid node is assigned the value of the coincident observation. Moreover the IDP method seems to be less affected by the density of the sampling points.

Since CO_2 fluxes are expressed as weight per unit time per square meter, the net volume between the upper computed surface and a lower surface taken as reference level provides the total weight emitted daily from the whole investigated area. These elaborations result in landfill CO_2 flux maps as illustrated in Figures 1, 2 and 3. The total volume of the CO_2 emitted by surface uncontrolled dispersion depends on many parameters such as: the age and
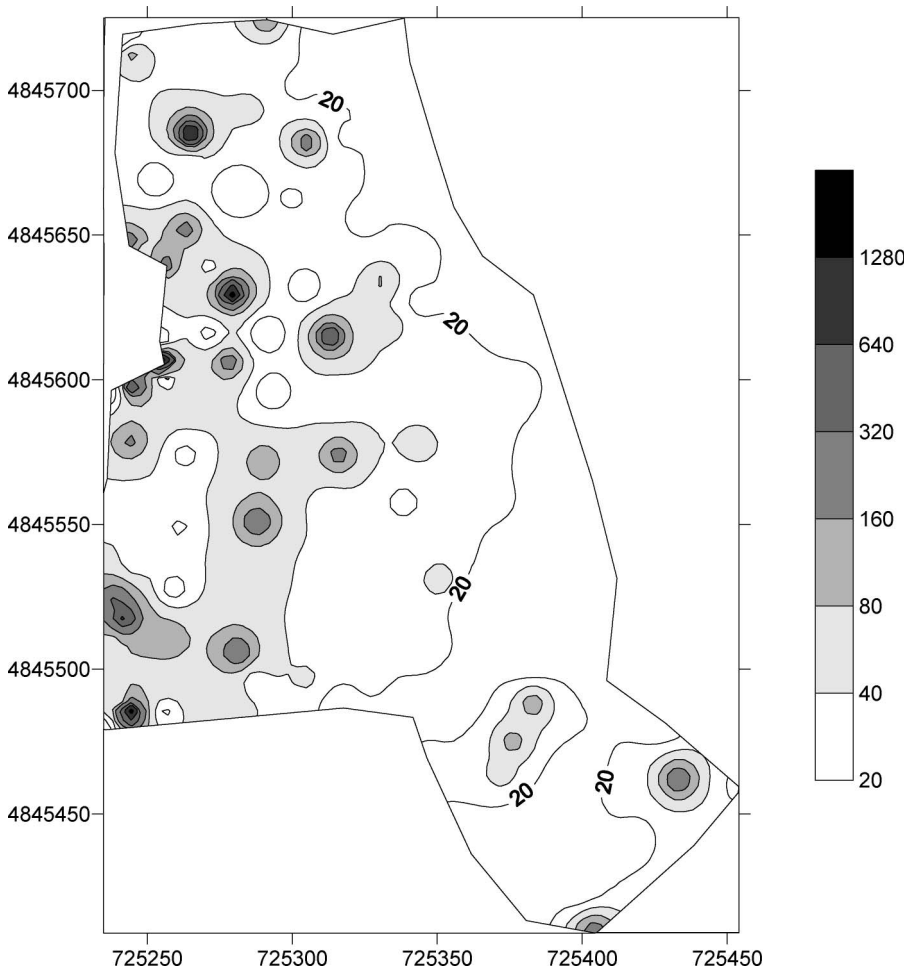

Figure 1. Landfill 1 CO_2 flux map (May 2004); fluxes are expressed in $g\ m^{-2}\ d^{-1}$, axes refer to UTM coordinate system. The estimated total CO_2 flux from Landfill 1 is 2.2 tons day^{-1}.
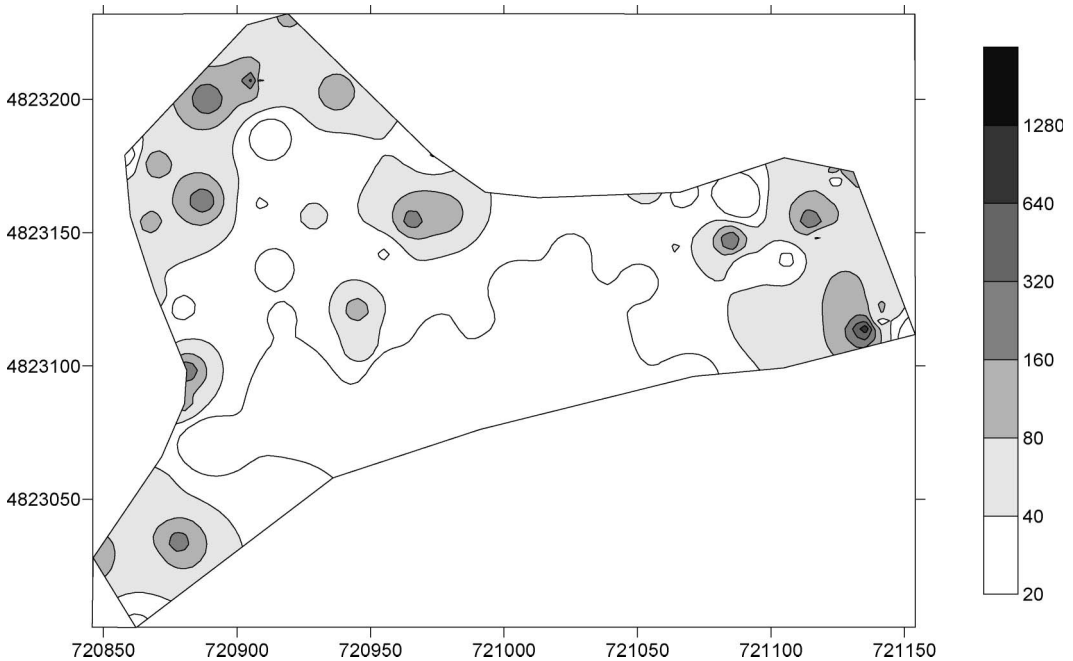
Figure 2. Landfill 2 CO_2 flux map (June 2005); fluxes are expressed in g m^{-2} d^{-1}, axes refer to UTM coordinate system. The estimated total CO_2 flux from Landfill 2 is 2.5 tons day^{-1}.

dimension of the landfill; the efficiency of the biogas extraction; thickness, composition and moisture content of the covering soil; waste disposal methods.

The evaluated CO_2 volumes emitted from inactive landfill sections range from less than 1 ton day^{-1} to more than 25 tons day^{-1}. The detected emissions display quite different geometries being usually concentrated along the flanks and corners of the landfill inactive sectors, suggesting the existence of horizontal impervious layers.

Simultaneous measurements of CH_4 fluxes suggest the significant removal of this component from the gas mixture which, according to the observed increase in CO_2 fluxes, can be referred to partial or total oxidation on passing throughout the covering soil. Such a removal mechanism seems to be effective also for selected halogenated species (Scheutz & Kjeldsen 2003). These phenomena appears particularly evident at flux rates lower than 50–100 g m^{-2} day^{-1}.

4.2. Halocarbons emissions

Our first interest was in trying to investigate any possible difference between emissions from 'aged' and recent landfills and, within the same landfill, among sections of different age. To this regard, Landfill 1 is representative of 'old age' landfill gas, meanwhile in Landfills 2 and 3 the age of emissions depends on the section, and corresponding well, where the sample was collected. A list of the halocarbons detected in landfill gas is reported in Table I, together with information on their background atmospheric concentration, lifetime, year of introduction, and use.

Major gas quantitative analysis, in this study, was finalized at providing information to be used to support halocarbon analysis. As a matter of fact, data obtained can help in
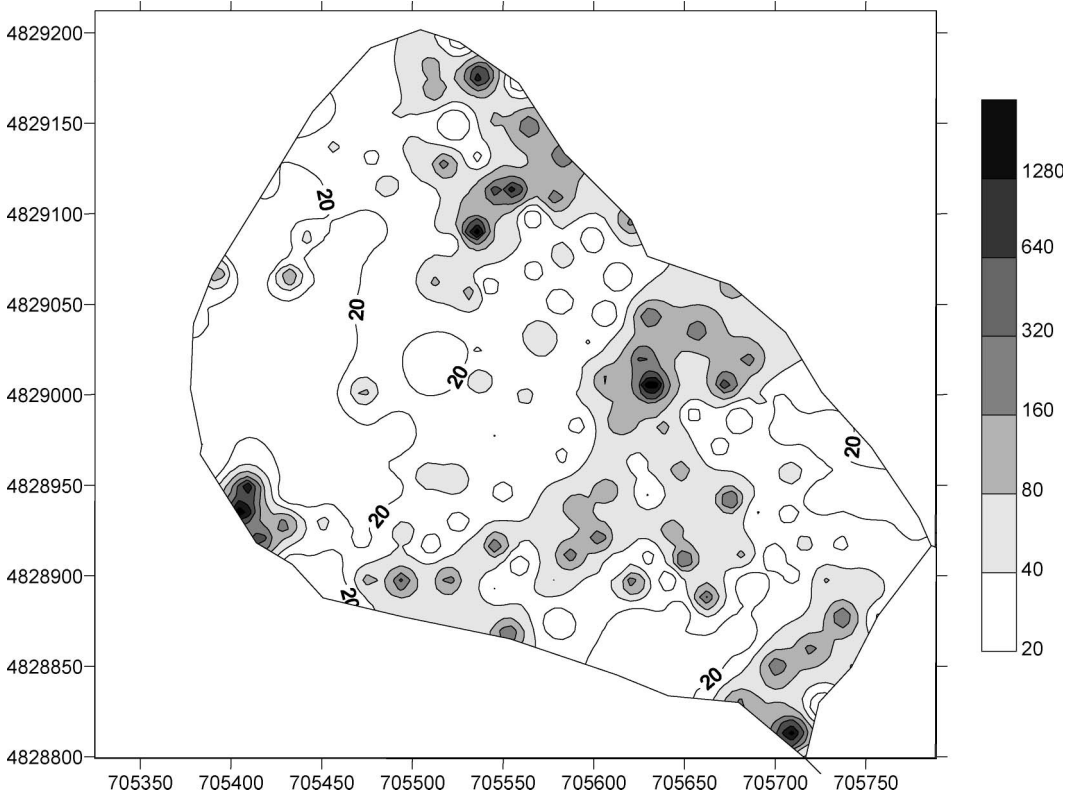
Figure 3. Landfill 3 CO_2 flux map (July 2005); fluxes are expressed in g m^{-2} d^{-1}, axes refer to UTM coordinate system. The estimated total CO_2 flux from Landfill 3 is 2.03 tons day^{-1}.

Table I. List of the halocarbons detected and their main characteristics.

Compound	Background atmospheric concentration (ppmv)	Lifetime (years)[a]	Year of introduction[b]	Use
CFC 11	0.254	45.0	1934	blowing agent
CFC 12	0.546	100.0	1931	refrigerant
CFC113	0.080	85.0	1979	solvent
CFC 114	0.017	300.0	1979	refrigerant
HCFC 22	0.174	12.0	1970	refrigerant
HCFC 142b	0.018	17.9	1981	blowing agent
HFC 134a	0.035	14.0	1990	refrigerant
HFC 152a	0.006	1.4	1990	blowing agent

[a]IPCC (2001).
[b]AFEAS (2005).

understanding if some dilution of the landfill gas with ambient air occurred, shown whenever a relatively high percentage of N_2, O_2 and Ar is found. This clearly demonstrates the occurrence of ambient air intrusion, likely to occur along the pipeline. Other information is related to the age of the section: high percentages of CH_4, indicating more anaerobic conditions, usually correspond to 'mature' waste sections.

An example is reported in Table II, where concentrations measured from samples L2W1 and L3W2 reflect the usual landfill gas composition, meanwhile samples L1T3 and L3W1 are representative of diluted gas, and sample L2W3 is representative of emission from 'mature' waste.

In Table III the halocarbon concentrations measured in the samples collected during the second campaign are reported. Such concentrations are up to several orders of magnitude higher than the atmospheric background.

The first consideration concerns the extremely high variability in concentration levels measured. Such variability was noticed not only in samples collected from different landfill sites, but also in samples collected from the same landfill. Taking into consideration the fully halogenated hydrocarbons, already phased out under Montreal Protocol, the high CFC12/ CFC11 ratio (much higher than that found in background atmosphere) could be ascribable to the habit of dumping domestic refrigeration equipments (main use of CFC12 was in domestic refrigeration) without any previous gas recycling or gas collection procedure. In fact, another refrigerant used in domestic equipment, HCFC22, is among the most abundant species detected, together with HFC134a, the fluorinated gas used as a replacement for CFC12 since the 1990s. The relatively high abundance of CFC12 with respect to CFC11 can also be explained with its longer lifetime (i.e. higher stability). Moreover, it has been reported (Scheutz & Kjeldsen 2003) that, in particular conditions, CFC11 could undergo degradation by mathanotrophic bacteria. Such organisms have been showed to be much more efficient in removing CFC11 than CFC12. Degradation processes seem to especially occur in older landfills where gas production is lower.

Table II. Major gas composition of samples collected at different sites. Concentration expressed in %.

Compound	Background atmospheric concentration[a]	Sample L1/T3	Sample L2/W1	Sample L2/W3	Sample L3/W1	Sample L3/W2
CO_2	0.0360	22.693	40.503	29.537	22.270	37.101
O_2	21	8.253	0.010	–	7.975	0.010
Ar	0.9	0.364	0.001	0.001	0.351	0.001
N_2	78	28.841	0.040	0.010	27.860	0.052
CH_4	0.000172	39.847	59.446	70.452	41.377	62.834

[a]Seinfeld and Pandis (1998).

Table III. Fluorinated gases in landfill gas. Concentration expressed in ppmv.

Compound	Background (ppmv)	Landfill 1			Landfill 2		
		Sample T1	Sample T2	Sample T3	Sample W1	Sample W2	Sample W3
CFC 11	0.254	24.697	28.869	8.991	20.488	0.938	0.562
CFC 12	0.546	313.931	308.110	71.982	177.720	90.670	175.129
CFC 113	0.080	0.844	3.357	0.447	0.079	0.389	0.116
CFC 114	0.017	13.554	15.581	9.367	8.416	17.267	11.449
HCFC 22	0.174	415.591	254.655	41.058	185.099	187.134	31.967
HCFC 142b	0.018	555.272	457.893	100.366	30.227	39.316	9.865
HFC 134a	0.035	559.248	762.890	37.644	304.867	273.255	18.454
HFC 152a	0.006	27.636	17.898	2.869	4.112	1.199	0.231

Concentrations of the already phased out Montreal gases are significant also in samples collected from the 'younger' and still operative section (i.e. that corresponding to well 1 in Landfill 2), which was opened only in 2004, suggesting a persistency of the use/dumping of materials and equipment containing these compounds.

The rather low amount of CFC113 (also if compared with background concentrations) is consistent with the fact that this solvent is not as common in domestic waste as it is in trade and industrial wastes.

The extremely high variability in halocarbon concentrations can be only partially explained through the major gas percentage composition of the landfill gas. Nevertheless, in those samples in which higher amounts of N_2, O_2 and Ar were found, and which can be considered as diluted with ambient air, halocarbon concentrations are to some extent lower than in other samples.

As stated above, the composition of samples collected within the same landfill but from different age sections was compared. Since the first campaign no particular trends were noticed when considering the fully halogenated species, meanwhile for the hydrogenated species lower concentrations were usually found in the mature sections. This is also confirmed by concentration data measured in samples collected during the second campaign (Table III), where the hydrogenated gases are up to an order of magnitude less concentrated in the mature sections. This could be ascribed to their being not phased out, their higher reactivity, and their relatively recent introduction.

Estimates on the contribution of landfills emissions to the release of fluorinated gases into the atmosphere were calculated on the basis of the measured CO_2 fluxes from the total landfill surface.

The calculation of halocarbon fluxes are based on the assumption that CO_2 accounts for about 50% of the landfill gas and that the capping soils are not able to absorb the halogenated compounds. For such calculation, and in order to give worst-case estimates, the highest concentration values measured in each sampling site were used. In Table IV and V a rough estimation of the maximum amount of fluorinated gases that could potentially be emitted in a year from two sites is given. Comparing our flux estimates with those calculated in a similar study conducted in the UK (Allen et al. 1997), it seems that, in our study, the amount of fluorinated gases that can be potentially emitted by a landfill in a year has been underestimated. That because our calculation took into account that gas caption systems are available in all the investigated sites. Therefore, fluxes are referred only to the fraction of biogas which is actually emitted by the surface.

Table IV. Estimated halocarbon fluxes, Landfill 1.

Flux CO_2 (tons day^{-1})	Flux CO_2 (moles day^{-1})	Flux CO_2 (l day^{-1})	Total biogas flux (l day^{-1})
2.20	50000.00	1120700.00	2241400.00

Compound	Flux (ml day^{-1})	Flux (kg year^{-1})
CFC 11	20.15–55.36	up to 0.45
CFC 12	161.34–703.65	1.40
CFC113	1.00–7.52	0.23
CFC 114	21.00–34.92	0.95
HCFC 22	92.03–931.51	1.30
HCFC 142b	224.96–1244.59	2.03
HFC 134a	84.38–1709.94	2.84
HFC 152a	6.43–61.94	0.67

Table V. Estimated halocarbon fluxes, Landfill 2.

Flux CO_2 (tons day^{-1})	Flux CO_2 (moles day^{-1})	Flux CO_2 (l day^{-1})	Total biogas flux (l day^{-1})
2.50	56 818.18	1 273 522.73	2 547 045.45

Compound	Flux (ml day^{-1})	Flux (kg year^{-1})
CFC 11	1.43 – 52.18	up to 0.16
CFC 12	230.94 – 452.66	0.87
CFC 113	0.20 – 0.99	0.003
CFC 114	21.44 – 43.98	0.12
HCFC 22	81.42 – 476.64	0.67
HCFC 142b	25.13 – 100.14	0.16
HFC 134a	47.00 – 776.51	0.04
HFC 152a	0.59 – 10.47	0.01

5. Conclusions

The issue related to a possible degradation of halocarbons in landfill capping soil is undoubtedly central in the evaluation of total emissions from landfill sites. Apart from laboratory studies, field measurements of halocarbon fluxes by means of an off-line accumulation chamber, which will be the next step of this investigation, seem to be necessary to provide further insights into such phenomena.

Nevertheless, the problem related to the extremely high variability in the halocarbon content remains, which makes an accurate evaluation of the strength of landfills as halocarbon sources difficult even if it is clear their contribution to total emissions is not negligible. The variability is due to a number of factors such as waste composition, waste age and meteorological conditions that can clearly affect the landfill gas composition and emission, which make a systematic study of this complex environment necessary.

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