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# CO<sub>2</sub> and CH<sub>4</sub> Flux Measurements from Landfills – A Case Study: Gualeguaychú Municipal Landfill, Entre Ríos Province, Argentina

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## 1. Introduction

Municipal solid waste (MSW) landfills are used to dispose of household wastes: food and garden waste, paper, metal, glass, wood, textiles, rubber, leather, plastic, ash, dust and electronic waste (Meju 2000). Decomposition of landfilled MSW by long-term physicochemical, chemical and biological processes causes dissolution or decay of landfill materials and production of leachate and gases (Bjerg et al. 2005). In particular, bacterial decomposition of the biodegradable fraction of MSW generates mainly methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) as well as a wide variety of minor and trace components: hydrogen, water vapor, hydrogen sulfide, ammonia, and volatile organic compounds (Scottish Environment Protection Agency [SEPA], 2004). In spite of efforts being made to control landfill gases (LG) - gas containment, collection and utilisation, flaring and treatment-, these are usually released into the atmosphere directly and indirectly, from the ground or via sub-surface gas migration, respectively.

These LG emissions into the atmosphere represent potential hazards that are of concern locally, regionally and globally (UK Environment Agency, 2010). The trace components of LG pose an odour and toxicity risk (although CO<sub>2</sub> is also toxic if it is present in high enough concentrations). Explosion and asphyxia risk is related to sub-surface migration and accumulations in enclosed spaces. Root zone displacement of oxygen by landfill gas is the most likely cause of local ecotoxicity. In addition, volatile organic compounds (VOC) have detrimental effects on human health and they participate in photochemical pollution as precursors of tropospheric ozone. CO<sub>2</sub> and CH<sub>4</sub> are greenhouse gases and contribute to global warming. Landfills have been implicated as being the largest anthropogenic sources of atmospheric CH<sub>4</sub> in the world, comprising about 11% of the total anthropogenic global CH<sub>4</sub> contribution (Spokas et al., 2003).

Direct measurements of CH<sub>4</sub> and CO<sub>2</sub> emissions from ground to atmosphere are used as an effective tool to estimate the degassing rate of individual sources and to calibrate global Earth degassing estimates (Cardellini et al. 2003). Early studies of diffuse degassing, focus on the flow of CO<sub>2</sub> out of the soil, commonly called CO<sub>2</sub> “flux” or “efflux” and expressed as [mass] [area]<sup>-1</sup> [time]<sup>-1</sup>, they were developed in agricultural or ecological areas to measure soil respiration or the flux from soil of other gaseous species (Hanson et al. 1993; Kinzig and

Socolow, 1994; Norman et al. 1992; Parkinson 1981). Later, they were applied in active volcanic-geothermal environments where  $\text{CO}_2$  is derived from some geologic source at depth (Bergfeld et al. 2001; Chiodini et al. 1999, 2004; Gerlach et al. 2001) and also in landfills (Borjesson et al., 2000; Georgaki et al. 2008; Hedge et al., 2003; Jha et al., 2008; Mosher et al., 1999; Pier & Kelly, 1997).

In this chapter, we summarize all the steps involved in the process of the quantifying of  $\text{CO}_2$  and  $\text{CH}_4$  fluxes (background, measurement methods calibration, geostatistical treatment of results, presentation of data) from landfills, and its application in Gualaguaychú Municipal Landfill, Entre Ríos province, Argentina. The method of determining the biodegradation processes of solid wastes by extracting gases with a probe and analyzing carbon isotopes on those gases is also included in the text. In addition, the dissolution of these gases in shallow aquifers is evaluated since in the case study that we present the groundwater acts as a sink for the  $\text{CO}_2$  that is developing in the landfill.

## 2. Gases production during waste decomposition

The composition of LG will vary from one site to another, from one cell of a landfill to another, and will change over time. Because of this, it is possible to find varying amounts  $\text{CO}_2$ ,  $\text{CH}_4$  and trace components, plus nitrogen and oxygen derived from air that has been drawn into the landfill. LG production is a function of the composition (organic content), density of and moisture content of wastes, climate variables, particle size and thickness of landfill cover, air-filled porosity, pH, temperature, nutrient availability, methods of land filling (i.e. open dumping or sanitary landfill) and structural features of the site (Barlaz et al. 2004; Kumar et al. 2004).

In addition, LG composition depends on the predominant form of microbial activity (e.g. aerobic/anaerobic) within the landfill environment. Assuming that an anaerobic environment is achieved and maintained after waste placement, a pattern of five sequential stages for LG production or biodegradation stages (Figure 1) is proposed: aerobic, non-methanogenic anaerobic, unsteady methanogenic anaerobic, steady methanogenic anaerobic and mature phases (Farquar and Rovers 1973; (Scottish Environment Protection Agency [SEPA], 2004). During the initial stage of organic degradation within a landfill,  $\text{CO}_2$  is produced in molar equivalents to free  $\text{O}_2$  consumed. Once  $\text{O}_2$  concentration is low enough, anaerobic oxidation, hydrolysis and acidification reactions begin and  $\text{CO}_2$  concentration (up to 70%), hydrogen and organic acids such as acetic reach their peak. As anaerobic degradation continues, the concentrations of acetic and other organic acids decreases, associated with an increase in  $\text{CH}_4$  generation (methanogenesis).  $\text{CO}_2$  concentration declines and methanogenesis begins to prevail, establishing a phase of steady  $\text{CH}_4$  production: 50–70%  $\text{CH}_4$  (with 30 to 50%  $\text{CO}_2$ ). During the last stage (mature), there is not enough organic substrate required for microbial activity and the composition of interstitial gases becomes more similar to atmospheric air.

## 3. Landfill gases measurements

### 3.1 Accumulation chamber methods

To assess the impacts of anomalous emissions to the atmosphere, different accumulation chamber methods to measure  $\text{CO}_2$  and  $\text{CH}_4$  fluxes from individual sources have been used over recent years. Norman et al. (1997) described these methods as closed static chambers

(non-steady-state non-flow-through chamber), closed dynamic chambers (non-steady-state chamber flow-through) and open dynamic chambers (steady-state flow-through chamber).

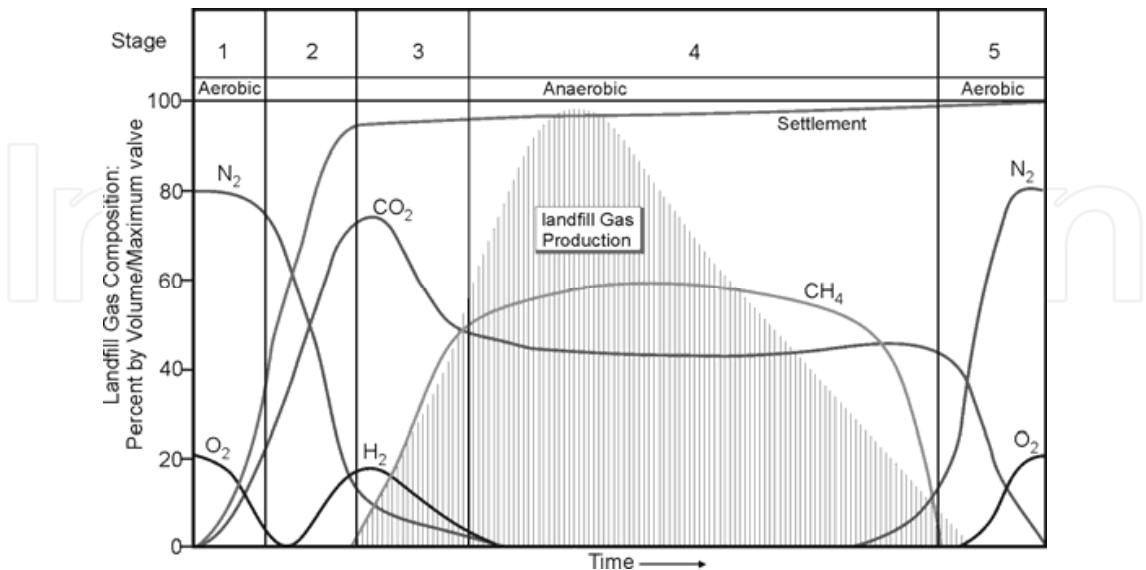


Fig. 1. Biodegradation stages during solid waste decomposition (Scottish Environment Protection Agency [SEPA], 2004): 1. aerobic, 2. non-methanogenic anaerobic, 3. unsteady methanogenic anaerobic, 4. steady methanogenic anaerobic, 5. mature.

In closed chamber methods (static and dynamic), the CO<sub>2</sub> flux is determined from the rate of concentration increase in a isolated chamber, that has been placed on the soil surface for a known period of time. In static chambers, samples are taken using disposable syringes which are transported and analyzed in laboratory. In dynamic chambers, the gas is extracted from the chamber, sent to an external infrared gas analyzer (IRGA), and then injected again into the chamber (Figure 2). In open chamber systems, described by Iritz et al. (1997), Moren and Lindroth (2000) and Rayment and Jarvis (1997), CO<sub>2</sub> flux is calculated from the difference between CO<sub>2</sub> concentration at the inlet and the outlet of the chamber.

None of these methods have yet been recognized as standard because experimental work has indicated differences in estimating fluxes among chamber types (Jensen et al. 1996) and has demonstrated limitations related with the chamber design (Hutchison and Mosier 1981; Welles et al. 2001). Consequently, some researchers have begun to carry out studies to determine the accuracy of measurements in comparison with a true flux through calibration systems to calculate the actual CO<sub>2</sub> flux and thus to estimate the real contribution to the global carbon cycle (Butnor and Johnsen 2004; Martin et al. 2004; Nay et al. 1994; Widen and Lindroth 2003). Likewise, Pumpanen et al. (2004) have determined correction factors for different chambers and specific soil types. The accumulation chamber method has also been tested under controlled laboratory conditions (Chiodini et al. 1998; Evans et al. 2001).

3.2 Other techniques to measure landfill gases

To characterize the biodegradation stages during waste decomposition, soil gas probes at different depths, made of stainless steel, are used to measure soil CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub> levels. Soil gases are brought to the vicinity of the tip of the probe by applying a vacuum and collected in TedlarTM bags (Figure 3). Samples are analysed in the laboratory by gas

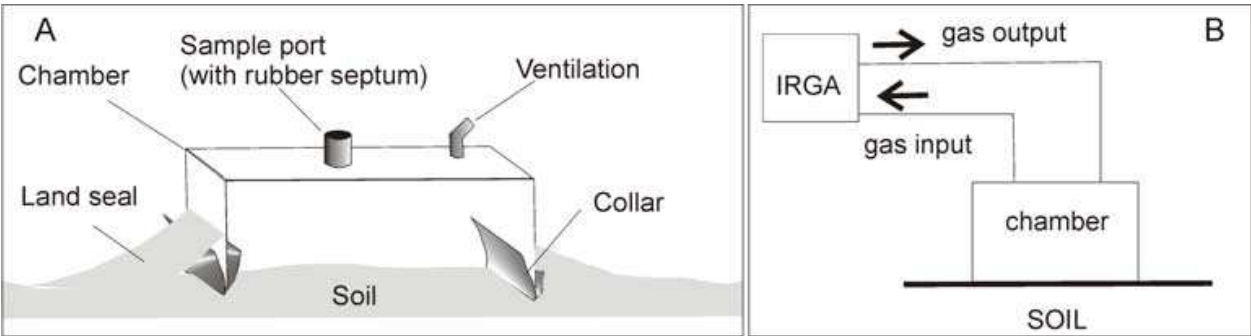


Fig. 2. Sketch of the instrument used to measure fluxes. A. Taken and modified from Kinzig and Socolow (1994). B. Taken and modified from Chiodini *et al.* (1998)

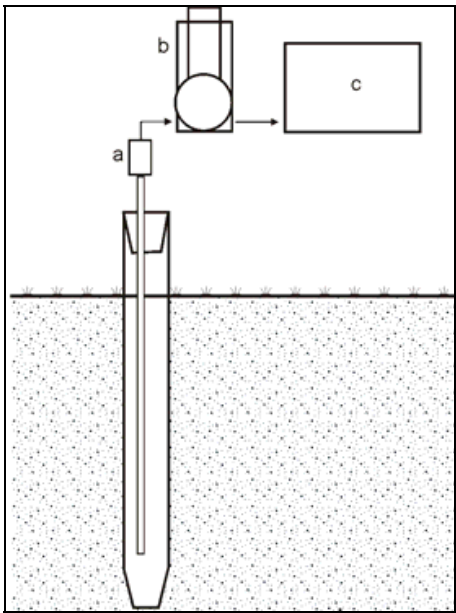


Fig. 3. Diagram of soil probe. A: filter, B: vacuum pump; C: Tedlar bags

chromatography. In addition, the determination of stable isotopes of carbon in CH<sub>4</sub> and CO<sub>2</sub> is an effective way to identify the different phases of biodegradation in a landfill (Coleman et al. 1993; Hackley et al. 1996). According to these authors, CO<sub>2</sub> is isotopically light during the initial aerobic and anaerobic oxidation phases of biodegradation with  $\delta^{13}\text{C}$  values that range from -35 to -10‰, which covers the range of most terrestrial plants. The initial input of isotopically light CO<sub>2</sub> associated with the earlier biodegradation phases is soon overcome during the methanogenesis phase by the constant input of isotopically heavy CO<sub>2</sub> associated with acetate fermentation and microbial CO<sub>2</sub> reduction (the two primary metabolic pathways by which microbial CH<sub>4</sub> is produced). During methanogenesis, CH<sub>4</sub> is enriched in the lighter carbon isotope (<sup>12</sup>C) and the CO<sub>2</sub> associated with microbial CH<sub>4</sub> production is enriched in the heavier isotope (<sup>13</sup>C). Thus, in a semiclosed environment such as a landfill, the  $\delta^{13}\text{C}$  of CO<sub>2</sub> is strongly affected by methanogenesis reactions with reported values between -10 and +20‰.

4. Data analysis

Flux measurements are distributed over regular grids, following Wang and Qi's (1998) statement that although three sampling patterns (regular grid, simple random and cellular

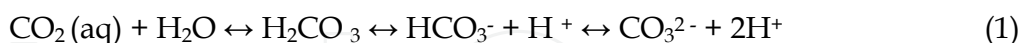


stratified sampling) are widely used in environmental studies, for a given sampling density, the regular grid provides better estimations than the other two. Histograms are plotted for the fluxes measured in the field and are log-transformed (ln) and fitted on a cumulative probability curve to verify the lognormal distribution and to identify different flux populations through changes in graph slope (Bergfeld et al. 2001; Cardellini et al. 2003; Chiodini and Frondini 2001; Gerlach et al. 2001).

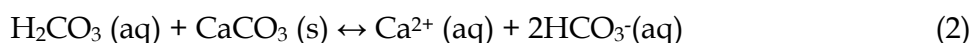
Since geospatial techniques are advisable to estimate the whole landfill surface flux from the spatially distributed chamber sites (Spokas et al. 2003), variograms are used to determine the level of spatial dependence of different sites. In experimental variograms (omnidirectional and directional) the semivariance  $\gamma(h)$  is plotted against the lag(h)—i.e. distance between sample sites (Webster & Oliver 1992). Since variograms may take several forms, different theoretical models are fitted to the data using the VARIOWIN software (Eddy & Paninatier 1996). Kriging is applied to generate contour maps, using the parameters of the variogram model that have been derived from the experimental variogram. Kriging is an interpolation method that takes advantage of the spatial dependence of a given variable. A number of papers compare spatial interpolation methods under different conditions, and kriging has proven to give the best estimations in numerous cases (Börjesson et al. 2000; Spokas et al. 2003).

## 5. Landfill gases effects on groundwater

LG contain a range of components that can dissolve in aqueous media, e.g. CO<sub>2</sub>, CH<sub>4</sub> and some traces. In landfills, CO<sub>2</sub> is the most water-soluble constituent of LG. The dissolution of this gas is partially responsible for observed variations in LG emissions to the atmosphere. CO<sub>2</sub> can dissolve in groundwater as described by Henry's law and react with water to form a balance of several ionic and nonionic species, collectively known as dissolved inorganic carbon -DIC- (Stumm & Morgan 1996). These species are free carbon dioxide (CO<sub>2</sub>(aq)), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>). The balance of these species, which ultimately affects CO<sub>2</sub> solubility, depends on the pH, amongst other things. CO<sub>2</sub> interacts with water as follows:



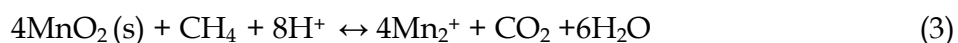
Moreover, adding CO<sub>2</sub> to groundwater changes the pH in the absence of interaction with aquifer solids. Kerfoot et al. (2004) calculated that landfill CO<sub>2</sub> may cause pH to drop to 4.7 in the absence of buffering reactions. However, carbonic acid can react with carbonate minerals (such as calcite) in the aquifer to buffer pH changes, according to the following reaction:



Although a rise in alkalinity suggests that groundwater is affected by the CO<sub>2</sub> generated in the landfill, it should be noted, that it might also be caused by leachates. Large amounts of CO<sub>2</sub> are produced in the landfill beneath the water table by organic matter decay into groundwater. Some of the CO<sub>2</sub> is retained as bicarbonate, part of it may be converted to CH<sub>4</sub> by microbes and the rest is released by outgassing (Baedeker and Back 1979).

CH<sub>4</sub> in water has the potential to act as a reducing agent, chemically reducing species and thereby potentially dissolving metal ions from aquifer solids (Kerfoot et al., 2004). An

example is the reaction with pyrolusite to produce soluble manganese (II) from insoluble insoluble manganese (IV):



In addition, carbon isotope analysis of DIC in groundwater is a useful tool to determine the sources of  $\text{CO}_2$  (soil gas, dissolution of calcareous material,  $\text{CO}_2$  produced by solid waste organic decomposition). Values of  $\delta^{13}\text{C}$ -DIC between -15‰ and -12‰ can be explained by isotope fractionation from the fixation of  $\text{CO}_2$  from soil respiration in the form of  $\text{HCO}_3^-$  within a process of calcite dissolution (Mook, 2000). In agreement with the explanation in section 3.2,  $\delta^{13}\text{C}$ -DIC values richer than -12‰ can be explained by the input of enriched  $\text{CO}_2$  from solid waste degradation which dissolves calcite (Kerfoot et al., 2003).

## 6. Isotopic analysis

As has been previously stated, the determination of stable isotopes of carbon in gases and groundwater is an effective way to identify solid waste biodegradation processes in a landfill. Samples of soil gas and groundwater are analyzed to determine the  $^{13}\text{C}/^{12}\text{C}$  ratio on  $\text{BaCO}_3$  obtained from precipitating  $\text{CO}_2$  and  $\text{HCO}_3^-$  with alkaline  $\text{BaCl}_2$ . In our laboratory experiments, the resulting  $\text{BaCO}_3$  is collected on an acid-washed glass fibre filter (GF/F) under a nitrogen atmosphere, rinsed with distilled water and dried to 60°C. Then, samples are reacted with  $\text{H}_3\text{PO}_4$  (100%) in vacuo, according to MacCrea (1950). The resulting  $\text{CO}_2$  is cryogenically purified; transferred with liquid  $\text{N}_2$  to a glass vial and measured against a working standard ( $\text{CO}_2$  from Carrara marble) in a dual inlet, triple collector mass spectrometer, Finnigan MAT Delta S. Carbon isotope composition is expressed as  $\delta^{13}\text{C}$ , according to:

$$\delta^{13}\text{C} = 1000 \left( \frac{\left[ \frac{^{13}\text{C}}{^{12}\text{C}} \right]_S - \left[ \frac{^{13}\text{C}}{^{12}\text{C}} \right]_R}{\left[ \frac{^{13}\text{C}}{^{12}\text{C}} \right]_R} \right) \text{‰} \quad (4)$$

where  $^{13}\text{C}/^{12}\text{C}$  is the carbon isotope ratio, suffix S corresponds to the sample and suffix R to the reference standard, Pee Dee belemnite (PDB), redefined in function of the NBS 19, TS-Limestone standard as V-PDB (Gonfiantini et al. 1995). Analytical uncertainty ( $2\sigma$ ) was  $\pm 0.2\%$ .

## 7. Case Study: Gualeguaychú Municipal Landfill, Entre Ríos Province, Argentina

### 7.1 Site description

The Gualeguaychú municipal landfill is located 3 km south of that city, in the southeast of the province of Entre Ríos, Argentina (Figure 4). The municipal facility was first exploited for mineral extraction, and waste was later disposed of in the depressions. One part of this facility was used for final disposal of MSW and closed in 2000 when it had filled up. Gas emissions were sampled there. There is no information regarding any environmental protection actions undertaken during the operation of the site, but visual observation of the site revealed that the topsoil cover is permeable and not compacted. So far, according to

geophysical studies (Pomposiello et al. 2009; Prezzi et al. 2005) in the filled-up disposal area, are of household origin and the filling depth does not exceed 2 m. Another part of the facility is currently being landfilled. There are no gas vents or recovery systems.

The Gualeguaychu municipal solid waste final disposal site (MSWDS) is located in the lower section of the Gualeguaychu River basin, which has a subhumid-humid climate (Sanci et al., 2009a). The Punta Gorda Group underlying the MSFDSW is the unit outcropping in the study area (Iriondo, 1980). Most of the sedimentary cover in the province of Entre Rios belongs to this group, which is composed mainly of brown, yellow and greenish silts (loess), clays and calcareous levels called “tosca”, composed of calcite. It was formed in lacustrine and aeolian environments and was assigned to Middle-Upper Pleistocene age (Iriondo, 1996). In addition, this group is intercalated by fluvial facies and silty levels, with abundant marine fossils from the marine ingression in the upper Pleistocene (Pereyra et al. 2002). The Punta Gorda Group contains a low-productivity phreatic aquifer, whose water is used for livestock farming and agriculture. This unit acts like a semi-confining layer for the underlying aquifer (Salto Chico) that is highly productive and has high quality of water, used for human consumption and irrigation.

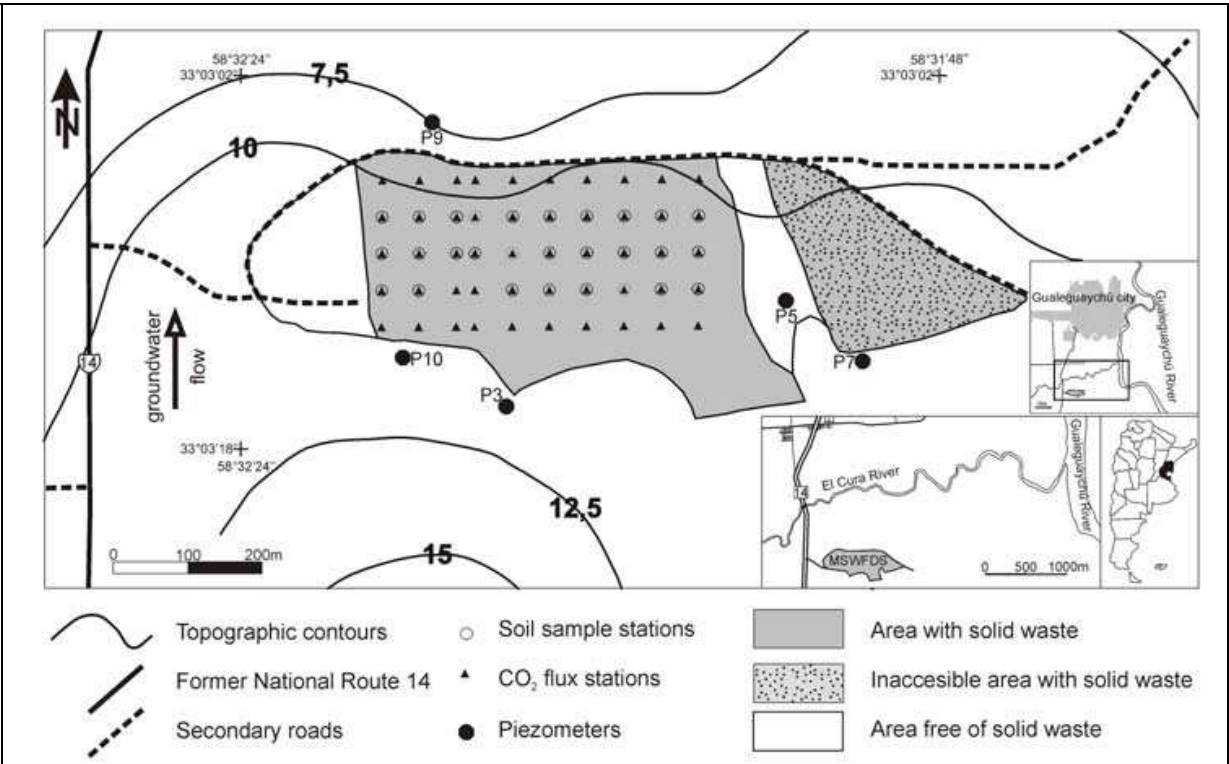


Fig. 4. Localization and description of MWSFDS

7.2 Measurement methods calibration

The accumulation chamber (0.26-m high and 0.30-m diameter) was placed on a collar that had been previously installed on the ground. The chamber also had outlet and inlet manifolds connected to the external pump in order to mix and distribute the air inside. A flow-meter was intercalated in order to regulate the mixing rate. There was also a port to test the temperature within the chamber. A pressure-relief vent was connected at the top of the chamber to



maintain the outside-inside pressure equilibrium. Flux rates were calculated by fitting linear regression to the variation of concentration (C) vs. time and adjusting for chamber volume (0.018 m<sup>3</sup>) and covered area (0.070 m<sup>2</sup>), according to the following equation:

$$F = \left( \frac{V}{A} \right) \left( \frac{dC}{dt} \right) \quad (5)$$

where F is the surface emission rate (g m<sup>-2</sup> day<sup>-1</sup>), V is the chamber volume and A is the soil area under the chamber and dC/dt is the variation of C with t within the chamber.

The dynamic and static closed chamber methods were applied during fieldwork, after calibration in the laboratory (Sanci et al. 2009b). This calibration consisted of a system where known CO<sub>2</sub> concentrations flowed through different porous materials, simulating CO<sub>2</sub> diffusion through the soil. This system allowed the determination of the differences between reference CO<sub>2</sub> flux values and experimental measurements under different sampling conditions. In the closed dynamic chamber method, soil gases are pumped for analysis from the accumulation chamber to a portable IRGA (PP Systems EGM-4) and subsequently returned to the chamber. The best fit (deviation smaller than 10%) was obtained taking short readings every 3 min during 12 min and mixing 25 s prior to CO<sub>2</sub> extraction (R<sup>2</sup> = 0.99). The best mixing rate was 250 ml min<sup>-1</sup>. The portable IRGA has an internal pump and a scale of (0–20,000) μmol mol<sup>-1</sup>. It allows the determining of CO<sub>2</sub> concentrations within an analytical uncertainty of ±1% of the reading. In the closed static chamber method, soil gases are extracted with syringes and analysed by gas chromatography (GC-TCD HP 5890 Series II). Although both methods allow measuring CO<sub>2</sub> fluxes directly, the static method allows the detection of another greenhouse gas, CH<sub>4</sub>, which proved to be useful in the exploratory surveys. The best fit (deviation <10%) was obtained taking three samples every 10 min during 20 min (R<sup>2</sup> = 0.99) and mixing 35 s prior to CO<sub>2</sub> sampling. The best mixing rate was 250 mL min<sup>-1</sup>.

### 7.3 Gas samples

The surveyed area covers about 150,000 m<sup>2</sup>. Measurements were distributed over regular grids: spacing was 100 m in the exploratory survey (March 2007, 14 sites), in the detailed surveys spacing was 50 m (50 sites) and 25 m (107 sites) respectively. Detailed surveys were carried out in July and October 2007. No measurements were made in the inaccessible part of the MSWFDS (Figure 4). Fieldwork was undertaken in dry and stable periods to avoid the influence of rainfall, soil humidity and atmospheric pressure on surface emissions. During the exploratory survey, CH<sub>4</sub> and CO<sub>2</sub> fluxes were measured with the static chamber method, whereas the dynamic chamber method was used during the detailed surveys for CO<sub>2</sub> flux measurements. Sampling density was increased taking into consideration the original location of the sites of the exploratory fieldwork.

In the exploratory survey, CO<sub>2</sub> fluxes ranged from 25 g m<sup>-2</sup> day<sup>-1</sup> to 194 g m<sup>-2</sup> day<sup>-1</sup>. CH<sub>4</sub> fluxes were not detected. In the detailed fieldwork, CO<sub>2</sub> fluxes in 50 and 107 stations ranged from 5 g m<sup>-2</sup> day<sup>-1</sup> to 214 g m<sup>-2</sup> day<sup>-1</sup> and from 31 g m<sup>-2</sup> day<sup>-1</sup> to 331 g m<sup>-2</sup> day<sup>-1</sup>, respectively. Irregularly spaced stations upstream of the MSWFDS were added to the study in October to measure the background values of soil respiration, which ranged from 29 g m<sup>-2</sup> day<sup>-1</sup> to 59 g m<sup>-2</sup> day<sup>-1</sup>. At all surveyed sites, soil temperature ranged from 21°C to 30°C (March), 12°C to 17°C (July) and 20°C to 30°C (October).

CO<sub>2</sub> flux data sets of the three campaigns are plotted in histograms (Figure 5). Distribution of measured CO<sub>2</sub> fluxes in the longest data set (107 sites) is log-normal, as can be seen in the linear cumulative probability plot of ln(CO<sub>2</sub>) flux of Figure 6a. Changes in slope indicate the presence of different populations within the data set, as follows: below 62 g m<sup>-2</sup> day<sup>-1</sup> (ln < 4.2) coinciding with measured background values beyond the MSWFDS; intermediate, between 67 g m<sup>-2</sup> day<sup>-1</sup> and 191 g m<sup>-2</sup> day<sup>-1</sup> (4.3 < ln < 5.3); and high values, above 219 g m<sup>-2</sup> day<sup>-1</sup> (ln>5.3). Mean CO<sub>2</sub> flux in the first population (23% of the data) at the 95% confidence level is (46 ± 4) g m<sup>-2</sup> day<sup>-1</sup> (or 13 g C m<sup>-2</sup> day<sup>-1</sup>). Mean CO<sub>2</sub> flux in the intermediate population (63% of the data) is (110 ± 9) g m<sup>-2</sup> day<sup>-1</sup> (or 30 g C m<sup>-2</sup> day<sup>-1</sup>). Mean flux in the third population (14% of the data) is (270 ± 22) g m<sup>-2</sup> day<sup>-1</sup> (or 74 g C m<sup>-2</sup> day<sup>-1</sup>). Extreme populations (high and low fluxes) correspond to a smaller number of sampling sites than the intermediate flux population. In addition, an estimation of CO<sub>2</sub> released to the atmosphere in tn day<sup>-1</sup> (Table 1) from MSWFDS was calculated taking into account the mean of each sub-population and their respective areas (sub-population mean × percentage of total population × total revealed area).

Since variogram reliability increases with the number of sites used in the model, the different regular sampling grids (14, 50 and 107 site surveys) were analysed until the geostatistical analysis indicated that an adequate sampling density had been achieved (Sanci et al. 2009a). Omni-directional and directional variograms were plotted, and spatial dependence was only observed between log-transformed data of CO<sub>2</sub> fluxes in the 107-site

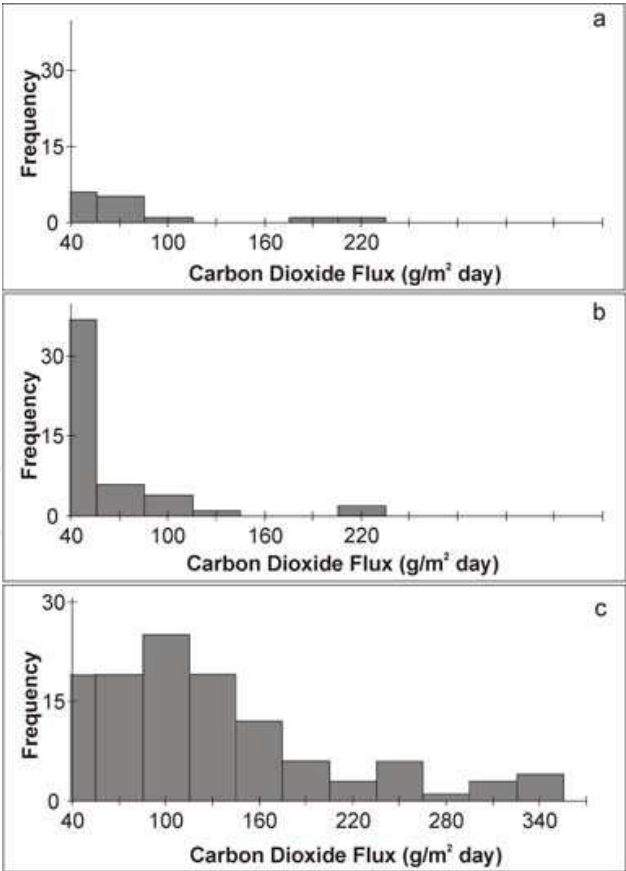


Fig. 5. Histograms of the CO<sub>2</sub> flux data from the three field campaigns: a. 14 stations (March); b. 50 stations (July); c. 107 stations (October).

Subpopulation	Percentage of total population (%)	Number points	Mean CO <sub>2</sub> Flux (g/m <sup>2</sup> día) with 95% confidence level	CO <sub>2</sub> released to atmosphere (tn day <sup>-1</sup> )
Background	23	25	46 (42-50)	1,59
Intermediate	63	67	110 (101-119)	10,39
High	14	15	270 (248-292)	5,67

Table 1. Statistical parameters of the sub-populations determined for the 107 stations sampled in October 2007.

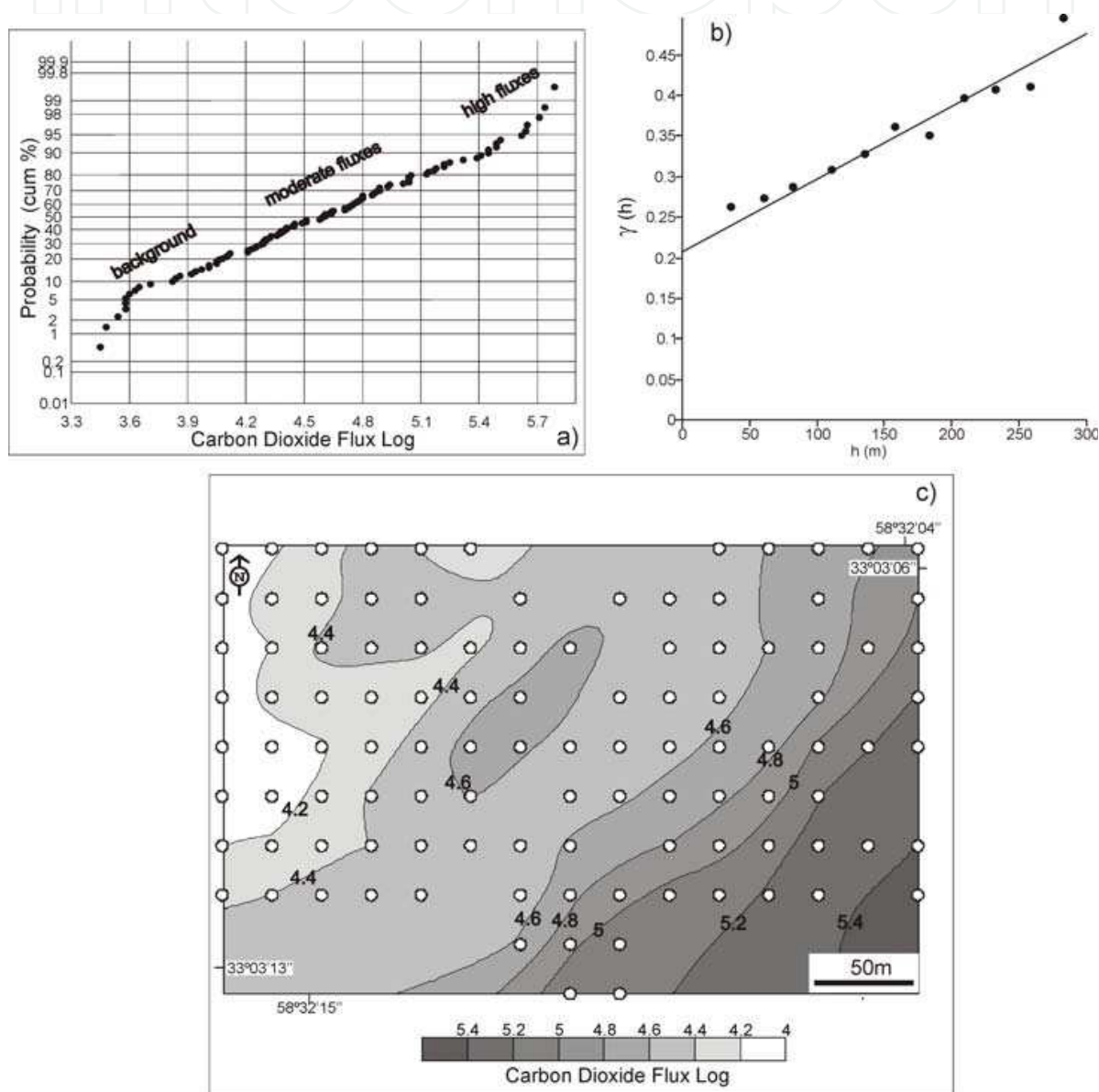


Fig. 6. A. Linear cumulative probability plot of  $\ln(\text{CO}_2)$  flux of 107 stations; B. Omnidirectional variogram; C. Contours map of  $\ln(\text{CO}_2)$  flux (Sanci et al., 2011).

survey (Sanci et al., 2011). The semivariance  $\gamma(h)$  plotted against a 30 m lag ( $h$ ) between sample points is shown in Figure 6a. This variogram is linear with nugget effect, and its

parameters were used to elaborate the contour map of  $\ln(\text{CO}_2)$  flux by kriging (Figure 6b). The distribution of  $\ln(\text{CO}_2)$  flux indicates that diffuse gas fluxes from the MSWFDS are not spatially homogeneous: values grow towards the southeast.

To characterize the biodegradation stages within MSFDSW, relative concentrations were analysed of CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub>, and the isotopic composition of CO<sub>2</sub> (<sup>13</sup>C/<sup>12</sup>C) was determined. A stainless steel probe was inserted to 20 cm and soil gases brought to the vicinity of the tip of the probe by applying a vacuum. Soil gas samples were taken at 28 locations spaced at 50 m, which coincide with sites where CO<sub>2</sub> fluxes were measured. Samples were collected in Tedlar<sup>TM</sup> bags and analysed in laboratory with a GC-TCD HP 5890 Series II. Volume fraction of CO<sub>2</sub> in soil gas samples ranged from ca. 0.01 to 0.103. In all cases, CH<sub>4</sub> fractions were <0.01, while those of O<sub>2</sub> and N<sub>2</sub> ranged from 0.165 to 0.209 and from 0.701 to 0.780, respectively, close to atmospheric concentrations. Isotope ratio <sup>13</sup>C/<sup>12</sup>C for CO<sub>2</sub> was determined by bubbling the sampled CO<sub>2</sub> into an alkaline BaCl<sub>2</sub> solution which precipitated as BaCO<sub>3</sub>. The  $\delta^{13}\text{C}\text{-CO}_2$  ranged from -34.2 to -17.6‰. The plot of CO<sub>2</sub> concentration versus  $\delta^{13}\text{C}\text{-CO}_2$  of Figure 7 (Sanci et al., 2011) shows two areas where different processes take place. One is related to normal soil respiration, about 0.01 of CO<sub>2</sub> (Welles et al. 2001). The second has values above 0.01, which may indicate the presence of anomalous concentrations of CO<sub>2</sub> from the biodegradation of urban solid waste (Pier & Kelly 1997) with a possible contribution of soil respiration. In the first group,  $\delta^{13}\text{C}$  ranges from -25.4 to -17.6‰, and in the second from -34.2 to -17.8‰.

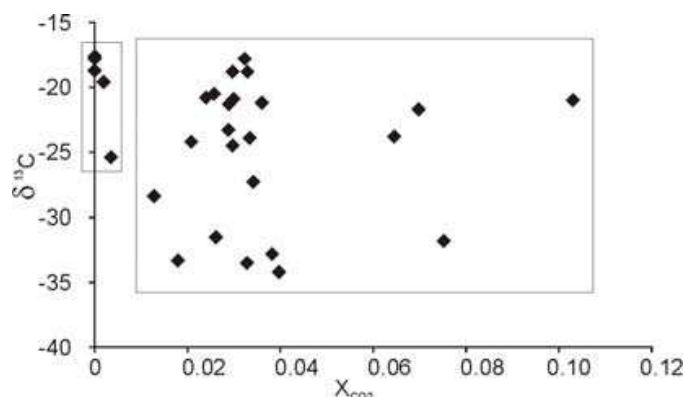


Fig. 7.  $\delta^{13}\text{C}\text{-CO}_2$  versus CO<sub>2</sub> concentrations (Sanci et al., 2011).

### 7.3 Groundwater samples

Considering that MSW were buried at the same depth as the water table (0.10 to 1.70 m below surface) groundwater samples for hydrochemical and isotopic analyses were taken in October 2007 to check whether the phreatic aquifer was acting as a sink for the CO<sub>2</sub> generated by waste biodegradation. Groundwater samples were filtered and stored in 1000-mL plastic bottles and cooled until analysis. pH, temperature, electrical conductivity and alkalinity were determined in the field. The latter was determined by titration with H<sub>2</sub>SO<sub>4</sub>. Major ion concentrations were measured in laboratory: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> by atomic absorption spectrometry (Buck Scientific 200 A); SO<sub>4</sub><sup>2-</sup>, as S, was quantified by inductively coupled plasma-atomic emission spectroscopy (BAIRD-ICP 2070) and Cl<sup>-</sup> by titration with AgNO<sub>3</sub>. Carbon isotopic analyses on groundwater were done according the procedure explained in section 6. Piezometers for groundwater observation were installed before

October 2007 to compare the electric conductivity measured in situ with that estimated by geoelectrical studies (Pomposiello et al. 2009). Wells were drilled to a depth of  $\leq 2.6$  m, along the main direction of the local groundwater flow (S–N): upstream (P3–P10), downstream (P9) and within the landfill (P7–P5).

Measured physical and chemical parameters are shown in Table 2 and the chemical classification of water in Figure 8a (sodium chloride and bicarbonate waters). Hydrochemical and isotope values varied in the different flow paths: P3 to P9; P10 to P9; P7 to P5 (Sanci et al., 2011). Alkalinity and  $\delta^{13}\text{C}$ -DIC tended to increase along the flow paths previously mentioned (Figure 8b). Values changed from 2.98 mmol L<sup>-1</sup>/–12.1‰ to 8.29 mmol L<sup>-1</sup>/4.4‰ (P3–P9), 2.44 mmol L<sup>-1</sup>/–15.0‰ to 8.29 mmol L<sup>-1</sup>/4.4‰ (P10–P9) and 8.18 mmol L<sup>-1</sup>/–8.1‰ to 41.45 mmol L<sup>-1</sup>/0.8‰ (P7–P5). Considering the results obtained for P3 and P10

Parameter	P3	P10	P9	P7	P5
Temperature (°C)	18.5	19	23.2	21.3	20.4
pH	6.9	6.9	7.1	6.9	7.0
Conductivity (μS/cm)	610	720	2440	1320	5450
Alkalinity (mmol/L)	2.98	2.44	8.29	8.18	41.45
Sulphate (mmol/L)	0.05	0.05	0.08	0.30	5.00
Chloride (mmol/L)	2.20	3.75	13.68	5.42	13.15
Sodium (mmol/L)	4.52	4.65	20.75	14.53	70.90
Potassium (mmol/L)	0.06	1.46	0.16	0.02	0.07
Calcium (mmol/L)	0.67	0.45	0.47	0.39	0.77
Magnesium (mmol/L)	0.23	0.30	1.60	0.33	1.81
$\delta^{13}\text{C}$ (‰ vs. PDB)	–12.1	–15.0	4.4	–8.1	0.8
Analytical error (%)					
$100 \cdot (\text{Cat} -  \text{An} ) / (\text{Cat} +  \text{An} )$	8.86	8.17	6.17	5.97	8.42

Table 2. Groundwater composition of piezometers

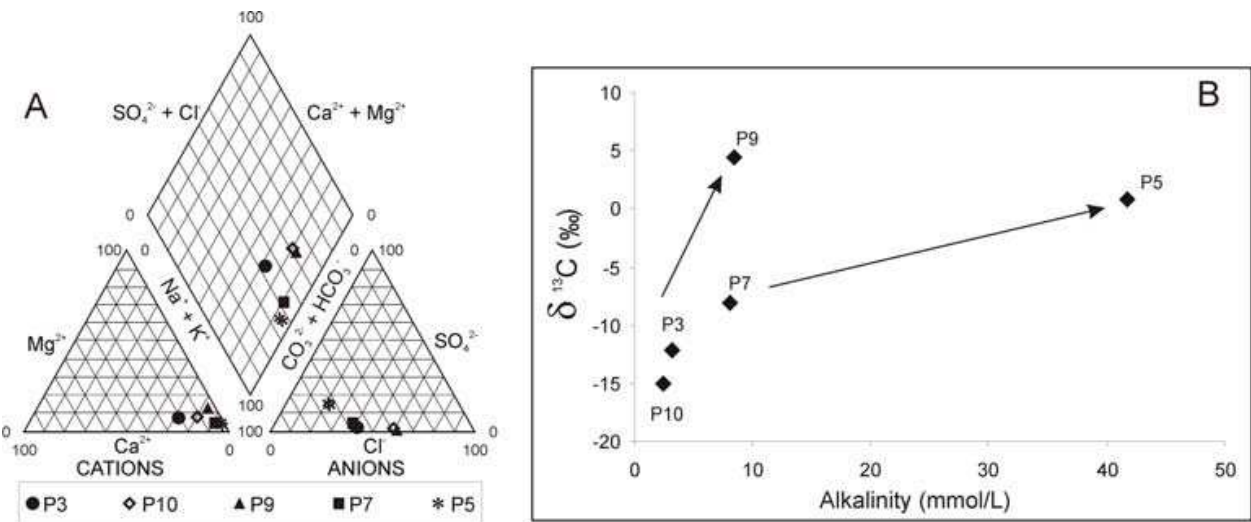


Fig. 8. A. Piper diagram showing the chemical classification of wells. P3, P7, P5: sodium bicarbonate groundwater; P10, P9: sodium chloride groundwaterchemical classification of groundwater; B. Alkalinity versus  $\delta^{13}\text{C}$ -DIC (Sanci et al., 2011).



as background (pristine water), and the evolution of groundwater flow along the MSFDSW, calcium concentrations downstream are similar to background values. On the other hand, concentrations of magnesium, sulphate, chloride and sodium are greater than background concentrations.

#### 7.4 Interpretation of results

The measurement of CO<sub>2</sub> fluxes in the MSWFDS with previous calibration in laboratory made it possible to reliably measure the spatial variability of the emissions in the field. CO<sub>2</sub> fluxes obtained (31–331 g m<sup>-2</sup> day<sup>-1</sup>) revealed the skewed distribution of the data (Figure 5c). This type of distribution (log-normal) was also observed in other soil CO<sub>2</sub> flux studies of natural and anthropic emission sources (Bergfeld et al. 2001; Cardellini et al. 2003; Chiodini and Frondini 2001; Gerlach et al. 2001). Logarithmic probability plots (Fig. 6b) show the polymodal distribution of CO<sub>2</sub> fluxes. They are a combination of three log-normal populations, which indicate that different processes of CO<sub>2</sub> generation take place. Low CO<sub>2</sub> fluxes are similar to the background values found around the MSFDSW and derive from soil respiration (Welles et al. 2001). The remaining values can be grouped into moderate and high fluxes. Values for both populations agree with those reported for biodegradation of solid waste in other sanitary landfills (Cardellini et al. 2003; Georgaki et al. 2008; Hedge et al. 2003; Jha et al. 2008; Pier & Kelly 1997). Spatial variations observed in surface CO<sub>2</sub> flux distribution (Figure 6c) are due to MSFDSW inhomogeneities. This variability may indicate that waste was buried in a NW-SE direction. Younger parts of the MSFDSW where biodegradation started later are more likely to have the highest CO<sub>2</sub> flux values.

Quantified anomalous CO<sub>2</sub> fluxes within the MSFDSW show that the site is still undergoing MSW biodegradation. Measured CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub> concentrations are similar to those described for an initial phase of aerobic oxidation or a posthumous stage of biodegradation (mature), and they are different from those described for anaerobic phases. Considering the time since the end of operations at the MSFDSW (about 10 years), the values obtained for these gases may indicate that the MSFDSW is in a mature stage. Moreover, the results obtained for C isotopes in the probe-sampled CO<sub>2</sub> (-34.2 to -17.6‰) suggest that the MSWFDS is in an aerobic phase of biodegradation.

Although concentrations of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub> and C isotope are indicators of the degree of maturity of sanitary landfills, in practice, the factors affecting gas generation need to be considered. These factors affect the duration of each particular biodegradation stage, as well as the degrees of phase overlap and phase omission. In this case, the shallow burial of waste (2 m), the absence of CH<sub>4</sub> and mainly the permeability of the top cover due to little compaction and inadequate materials, make it possible to assume that anaerobic conditions necessary for methanogenic reactions have not been achieved in the MSFDSW. Therefore, since MSW were first disposed, biodegradation was completely aerobic or the initial phase of aerobic oxidation might have been followed by another phase of anaerobic oxidation with no generation of CH<sub>4</sub>, arriving at the current maturation stage.

Data show that groundwater alkalinity grows across the MSFDSW in the direction of underground flow (Fig. 8). This suggests an input of C generated by anomalous CO<sub>2</sub>, which dissolves calcite from calcareous levels such as “tosca” in the MSFDSW. The interaction between carbonic acid and mineral carbonates might even buffer pH variations through

increased CO<sub>2</sub> (no changes are observed in the pH of the samples). Moreover, the expected effect of the MSWFDS CO<sub>2</sub> gas on groundwater chemistry could be an increase not only in alkalinity, but also in calcium. Calcium concentrations obtained in this study were similar to the background values. The presence of clays promoting the Ca/Na exchange reaction would explain this fact. In addition, the results of applying stable C isotopes on DIC ( $\delta^{13}\text{C}$  of -15.0 to 4.4 ‰) confirmed the changes observed in water alkalinity due to the anomalous ingress of CO<sub>2</sub>.  $\delta^{13}\text{C}$ -DIC values richer than -12‰ can be explained by the input of CO<sub>2</sub> from MSW degradation which dissolves calcite (a geologically feasible process). Another possibility is the decomposition of dissolved organic matter within the phreatic aquifer due to infiltration of leachates, given observable signs, such as previous geophysical studies (Pomposiello et al. 2009), subhumid/humid climate with annual rainfall of 1,077 mm, permeable cover, shallow phreatic aquifer and increased concentration of leachate associated constituents such as chlorides and sodium. Enrichment of  $\delta^{13}\text{C}$ -DIC in groundwater affected by leachates reached +13‰ (van Breukelen et al. 2003) and +20‰ (North et al. 2004). Future studies will examine and compare the hydrogeochemical changes caused by the dissolution of landfill gases with those produced by the presence of leachates.

## 8. Conclusions

According to the experiences obtained in the process of quantification of CO<sub>2</sub> and CH<sub>4</sub> fluxes, the two most important factors that had to be considered were the sampling methods and the sampling sites. In the first case, none of the accumulation chamber methods are nowadays considered to be standard because of differences in flux estimations between chamber types or chamber-specific limitations. Therefore, laboratory experiments were needed to achieve accurate flux measurements before applying those methods in the field. In addition, to assess a reliable spatial variability of fluxes, it was necessary to test different regular sampling grids until the geostatistical analysis indicated that an adequate sampling density had been achieved. The degree of spatial dependence between chamber sites was analyzed in experimental variograms.

In this way, direct measurements of CO<sub>2</sub> diffuse degassing from surface, with the accumulation chamber methodology tested in laboratory, allowed the detection of the spatial variability of CO<sub>2</sub> fluxes in the MSWFDS and the assessment of CO<sub>2</sub> released to atmosphere from this source. Different subpopulations were identified by the statistical and geostatistical analyses of CO<sub>2</sub> fluxes. Processes giving rise to the subpopulations are background values attributable to plant respiration and different anomalous values related to biodegradation of urban solid waste disposed in the MSWFDS.

Analysis of probe-sampled concentrations of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub>, as well as carbon isotope composition of the CO<sub>2</sub>, showed that the current process is an aerobic phase of biodegradation. However, other factors that affect the gas generation were also considered to determine the phase of biodegradation of MSWFDS. They were: the time since the end of operations in the MSWFDS, the characteristics of the environment where MSW were disposed (mainly permeability of capping due to little compaction and inappropriate cover material), the shallow depth of SW burial and the absence of CH<sub>4</sub>. All of these factors made it possible to assume that we are in the presence of a mature or posthumous stage of biodegradation, and allowed us to assume that biodegradation in the MSWFDS was

completely aerobic or that it may have gone through a period of anaerobic oxidation, without developing methanogenic processes.

Based on the increase in groundwater alkalinity as it flows across the MSWFDS and the DIC isotope composition, two different situations are possible: either CO<sub>2</sub> derived from MSW biodegradation is dissolving, or dissolved organic matter is decaying within the free aquifer due to the presence of leachates. Future research will be devoted to determining which of these possibilities best explains the process.

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## 10. References

- Baedecker, M. & Back, W. (1979) Hydrogeological processes and chemical reactions at a landfill. *Ground Water*, Vol. 17, N° 5, pp. 429–437
- Barlaz, M.; Green, R.; Chanton, J.; Goldsmith, C. & Hater, G. (2004) Evaluation of a biologically active cover for mitigation of landfill gas emissions. *Environ Sci Technol*, Vol. 38, pp. 4891–4899
- Bergfeld, D.; Goff, F. & Janik, C. (2001) Elevated carbon dioxide flux at the Dixie Valley geothermal field, Nevada; relations between surface phenomena and geothermal reservoir. *Chem Geol*, Vol. 177, pp. 43–66
- Bjerg, P.; Albrechtsen, H.; Kjeldsen, P. & Christensen, T. (2005) The groundwater geochemistry of waste disposal facilities. In: *Treatise on Geochemistry*, Volume 9, B. Sherwood Lollar (Ed.), pp. 579–612, Elsevier-Pergamon, Oxford
- Borjesson, G.; Danielson, A. & Svensson, B. (2000) Methane fluxes from a Swedish landfill determined by geostatistical treatment of static chamber measurements. *Environ Sci Technol*, Vol. 34, pp. 4044–4050
- Butnor, J. & Johnsen, K. (2004) Calibrating soil respiration measures with a dynamic flux apparatus using artificial soil media of varying porosity. *Eur J Soil Sci*, Vol. 55, pp. 639–647
- Cardellini, C.; Chiodini, G.; Frondini, F.; Granieri, D.; Lewicki, J. & Peruzzi, L. (2003) Accumulation chamber measurement of methane fluxes: application to volcanic-geothermal areas and landfills. *Appl Geochem*, Vol. 18, pp. 45–54
- Chiodini, G.; Cioni, R.; Guidi, M.; Raco, B. & Marini, L. (1998) Soil CO<sub>2</sub> flux measurement in volcanic and geothermal areas. *Appl Geochem*, Vol. 13, N° 5, pp. 543–552
- Chiodini, G.; Frondini, F.; Kerrick, D.; Rogie, J.; Parello, F.; Peruzzi, L. & Zanzari, A. (1999) Quantification of deep CO<sub>2</sub> fluxes from Central Italy. Examples of carbon balance for regional aquifers and soil diffuse degassing. *Chem Geol*, Vol. 159, pp. 205–222
- Chiodini, G. & Frondini, F. (2001) Carbon dioxide degassing from the Albani Hills volcanic region, Central Italy. *Chem Geol*, Vol 177, pp. 67–83
- Chiodini, G. ; Avino, R.; Brombach, T.; Caliro, S.; Cardellini, C. ; De Vita, S.; Frondini, F.; Granieri, D.; Marotta, E. & Ventura, G. (2004) Fumarolic and diffuse soil degassing west of Mount Epomeo, Ischia, Italy. *J Volcanol Geotherm Res*, Vol. 133, pp. 291–309

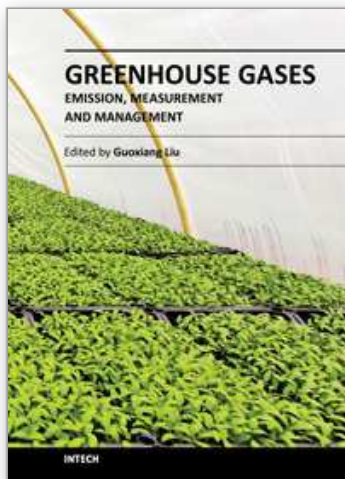
- Coleman, D.; Liu, C.; Hackley, K. & Benson, L. (1993) Identification of landfill methane using carbon and hydrogen isotope analysis, *Proceedings of 16th International Madison Waste Conference, Municipal & Industrial Waste*, pp. 303–314, Department of Engineering Professional Development, University of Wisconsin, Madison.
- Eddy, W. & Paninatier, Y. (1996) *Variowin: software for Spatial Data Analysis in 2-D*, Springer, New York
- Evans, C.; Sorey, M.; Kennedy, B.; Stonnestrom, D.; Rogie, J. & Shuster, D. (2001) High CO<sub>2</sub> emissions through porous media: transport mechanisms and implications for flux measurement and fractionation. *Chem Geol*, Vol. 177, pp. 15–29
- Farquar, G. & Rovers, F. (1973) Gas production during refuse decomposition. *Water Air Soil Pollut*, Vol. 2, pp. 483–495
- Georgaki, I.; Soupios, P.; Sacas, N.; Ververidis, F.; Trantas, E.; Vallianatos, F. & Manios, T. (2008) Evaluating the use of electrical resistivity imaging technique for improving CH<sub>4</sub> and CO<sub>2</sub> emission rate estimations in landfills. *Sci Total Environ*, Vol. 389, pp. 522–531
- Gerlach, T.; Doukas, M.; McGee, K. & Klessner, R. (2001) Soil efflux and total emission rates of magmatic CO<sub>2</sub> at the Horseshoe Lake tree kill, Mammoth Mountain California, 1995–1999. *Chem Geol*, Vol. 177, pp. 85–99
- Gonfiantini, R.; Stichler, W. & Rozanski, K. (1995) Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements, *Proceedings of a consultants meeting of reference and intercomparison materials for stable isotopes of light elements*, pp. 13–29, IAEA, Vienna.
- Hackley, K.; Liu, C. & Coleman, D. (1996) Environmental isotope characteristics of landfill leachates and gases. *Ground Water*, Vol. 34, N° 5, pp. 827–836
- Hanson, P.; Wullschleger, S.; Bohlman, S. & Todd, D. (1993) Seasonal and topographic patterns of forest floor CO<sub>2</sub> efflux from an upland oak forest. *Tree Physiol*, Vol. 13, pp. 1–15
- Hedge, U.; Chang, T. & Yang, S. (2003) Methane and carbon dioxide emissions from Shan-Chu-Ku landfill site in northern Taiwan. *Chemosphere*, Vol. 52, pp. 1275–1285
- Hutchison, J. & Mosier, A. (1981) Improved soil cover method for field measurements of nitrous oxide fluxes. *Soil Sci Soc Am J*, Vol. 45, pp. 311–316
- Iriondo, M. (1980) El Cuaternario de Entre Ríos. *Rev Asoc Cienc Nat Litoral*, Vol. 11, pp. 125–141
- Iriondo, M. (1996) Estratigrafía del Cuaternario de la cuenca del río Uruguay, *XIII Congreso Geológico Argentino y III Congreso de Exploración de Hidrocarburos*, pp. 15–25, AGAIAPG, Buenos Aires.
- Iritz, Z.; Lindroth, A. & Gardenas, A. (1997) Open ventilated chamber for measurements of H<sub>2</sub>O and CO<sub>2</sub> fluxes from the soil surface. *Soil Technol*, Vol. 10, pp. 169–184
- Jensen, L.; Mueller, T.; Tate, K.; Ross, D.; Magid, J. & Nielsen, N. (1996) Soil surface CO<sub>2</sub> flux as an index of soil respiration in situ: a comparison of two chamber methods. *Soil Biol Biochem*, Vol. 28, N° 10–11, pp. 1297–1306
- Jha, A.; Sharma, C.; Singh, N.; Ramesh, R.; Purvaja, R. & Gupta, P. (2008) Greenhouse gas emissions from municipal solid waste management in Indian mega-cities: a case study of Chennai landfill sites. *Chemosphere*, Vol. 71, pp. 750–758
- Kerfoot, H.; Baker, J. & Burt, D. (2003) The use of isotopes to identify landfill gas effects on groundwater. *J Environ Monit*, Vol. 5, pp. 896–901



- Kerfoot, H.; Baker, J. & Burt, D. (2004) Geochemical changes on ground water due to landfill gas effects. *Ground Water Monit Rem*, Vol. 24, N° 1, pp. 60–65
- Kinzig, A. P. y Socolow, R. H. (1994) Human impacts on nitrogen cycle. *Physics Today*, Vol. 47, N° 11, pp. 24–31
- Kumar, S.; Mondal, A.; Gaikwad, S.; Devotta, S. & Singh, R. (2004) Qualitative assessment of methane emission inventory from municipal solid waste disposal: a case study. *Atmos Environ*, Vol. 38, pp. 4921–4929
- MacCrea, J. (1950) On the isotopic chemistry of carbonates and paleotemperature scale. *J Chem Phys*, Vol. 18, N° 6, pp. 849–857
- Martin, J.; Bolstad, P. & Norman, J. (2004) A carbon dioxide flux generator for testing infrared gas analyser based soil respiration systems. *Soil Sci Soc Am J*, Vol. 68, pp. 514–518
- Meju, M. (2000) Geoelectrical investigation of old/abandoned, covered landfill sites in urban areas: mode development with a genetic diagnosis approach. *J Appl Geophys*, Vol. 44, pp. 115–150
- Mook, W. (2000) Natural abundance of the stable isotopes of C, H and O, In: *Environmental isotopes in the hydrological cycle: principles and applications*, W., Mook (Ed.), pp. 89–120, UNESCO, Paris
- Morén, A. & Lindroth, A. (2000) CO<sub>2</sub> exchange at the floor of a boreal forest. *Agric For Meteorol*, Vol. 101, pp. 1–14
- Mosher, B.; Czepiel, P. & Harriss, R. (1999) Methane emissions at nine landfill sites in the northeastern United States. *Environ Sci Technol*, Vol. 33, pp. 2088–2094
- Nay, S.; Matsson, K. & Bormann, B. (1994) Biases of chamber methods for measuring soil CO<sub>2</sub> efflux demonstrated with a laboratory apparatus. *Ecology*, Vol. 75, pp. 2460–2463
- Norman, J.; Garcia, R. & Verma, S. (1992) Soil surface CO<sub>2</sub> fluxes and the carbon budget of a grassland. *J Geophys Res*, Vol. 97, N° D17, pp. 18845–18853
- Norman, J.; Kucharik, C.; Gower, S.; Baldocchi, D.; Crill, P.; Rayment, M.; Savage, K. & Striegl, R. (1997) A comparison of six methods for measuring soil-surface carbon dioxide fluxes. *J Geophys Res*, Vol. 102, pp. 28771–28777
- North, J.; Russell, D. & Barrie, M. (2004) The use of carbon and nitrogen isotope ratios to identify landfill leachate contamination: Green Island Landfill, Dunedin, New Zealand. *Environ Int*, Vol. 30, pp. 631–637
- Parkinson, K. (1981) An improved method for measuring soil respiration in the field. *J Appl Ecol*, Vol. 18, pp. 221–228
- Pereyra, F.; Tchilinguirian, P. & Baumann, V. (2002) Hoja Geológica 3360-IV Gualeguaychú. Boletín No 335, Servicio Geológico Minero Argentino, Buenos Aires
- Pier, P. & Kelly, J. (1997) Measured and estimated methane and carbon dioxide emissions from sawdust waste in the Tennessee Valley under alternative management strategies. *Bioresour Technol*, Vol. 61, pp. 213–220
- Pomposiello, C.; Dapeña, C.; Boujon, P. & Favetto, A. (2009) Tomografías eléctricas en el Basurero Municipal Ciudad de Gualeguaychú, provincia de Entre Ríos. Evidencias de contaminación. *Rev Asoc Geol Arg*, Vol. 64, pp. 603–614
- Prezzi, C.; Orgeira, M.; Ostera, H. & Vazquez, C. (2005) Ground magnetic survey of a municipal solid waste landfill: pilot study in Argentina. *Environ Geol*, Vol. 47, N° 7, pp. 889–897



- Pumpanen, J.; Kolari, P.; Ivesniemi, H.; Minkkinen, K.; Vesala, N.; Lohila, A.; Larmola, T.; Morero, M.; Pihlatie, M.; Janssens, I.; Yuste, J.; Grünzweig, J.; Reth, S.; Subke, J.; Savage, K.; Kutsch, W.; Østreng, G.; Ziegler, W.; Anthoni, P.; Lindroth, A. & Hari, P. (2004) Comparison of different chamber techniques for measuring soil CO<sub>2</sub> efflux. *Agric For Meteorol*, Vol.123, pp. 159–176
- Rayment, M. & Jarvis, P. (1997) An improved open chamber system for measuring soil CO<sub>2</sub> effluxes in the field. *J Geophys Res*, Vol. 102, pp. 28779–28784
- Sanci, R.; Ostera, H. & Panarello, H. (2009a) Determinación del flujo de CO<sub>2</sub> en antrópicas: sitio de disposición final municipal, Gualeguaychú, Entre Ríos. *Rev Asoc Geol Arg*, Vol. 65, N° 3, pp. 533–544
- Sanci, R.; Panarello, H. & Ostera, H. (2009b) Assessment of soil moisture influence on CO<sub>2</sub> flux: a laboratory experiment. *Environ Geol*, Vol. 58, pp. 491–497
- Sanci, R.; Panarello, H. & Ostera, H. (2011) CO<sub>2</sub> emissions from a municipal site for final disposal of solid waste in Gualeguaychú, Entre Ríos Province, Argentina. *Environ Earth Sci* DOI 10.1007/s12665-011-1260-0
- Scottish Environment Protection Agency [SEPA] (2004) Guidance on the management of landfill gas. Available from: [http://www.sepa.org.uk/waste/waste\\_regulation/landfill.aspx](http://www.sepa.org.uk/waste/waste_regulation/landfill.aspx)
- Spokas, K.; Graff, C.; Morcet, M. & Aran, C. (2003) Implications of the spatial variability of landfill emission rates on geospatial analyses. *Waste Manage*, Vol. 23, pp. 599–607
- Stumm, W. & Morgan, J. (1996) *Aquatic chemistry*, Environmental Science and Technology, New York
- UK Environment Agency (2010). Guidance on monitoring landfill gas surface emissions. Available from: <http://www.environment-agency.gov.uk/business/sectors/108918.aspx>
- Van Breukelen, B.; Roling, F.; Groen, J.; Griffioen, J. & Van Verseveld, H. (2003) Biogeochemistry and isotope geochemistry of a landfill leachate plume. *J Contam Hydrol*, Vol. 65, pp. 245–268
- Wang, X. & Qi, F. (1998) The effects of sampling design on spatial structure analysis of contaminated soil. *Sci Total Environ*, Vol. 224, pp. 29–41
- Webster R, Oliver MA (1992) Sample adequately to estimate variograms of soil properties. *J Soil Sci* 43: 177–192
- Welles, J.; Demetriades-Shah, T. & McDermitt, D. (2001) Considerations for measuring ground CO<sub>2</sub> effluxes with chambers. *Chem Geol*, Vol. 177, pp. 3–13
- Widén, B. & Lindroth, A. (2003) A calibration system for soil carbon dioxide-efflux measurements chambers: description and application. *Soil Sci Soc Am J*, Vol. 67, pp. 327–334



## **Greenhouse Gases - Emission, Measurement and Management**

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Understanding greenhouse gas sources, emissions, measurements, and management is essential for capture, utilization, reduction, and storage of greenhouse gas, which plays a crucial role in issues such as global warming and climate change. Taking advantage of the authors' experience in greenhouse gases, this book discusses an overview of recently developed techniques, methods, and strategies: - A comprehensive source investigation of greenhouse gases that are emitted from hydrocarbon reservoirs, vehicle transportation, agricultural landscapes, farms, non-cattle confined buildings, and so on. - Recently developed detection and measurement techniques and methods such as photoacoustic spectroscopy, landfill-based carbon dioxide and methane measurement, and miniaturized mass spectrometer.

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Romina Sanci and Héctor O. Panarello (2012). CO<sub>2</sub> and CH<sub>4</sub> Flux Measurements from Landfills - A Case Study: Gualeguaychú Municipal Landfill, Entre Ríos Province, Argentina, Greenhouse Gases - Emission, Measurement and Management, Dr Guoxiang Liu (Ed.), ISBN: 978-953-51-0323-3, InTech, Available from: <http://www.intechopen.com/books/greenhouse-gases-emission-measurement-and-management/co2-and-ch4-flux-measurements-from-landfill-a-case-study-gualeguaych-municipal-landfill-entre-r-os-p>

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