

## CO<sub>2</sub> emissions from a municipal site for final disposal of solid waste in Gualeguaychu, Entre Rios Province, Argentina

Romina Sancí · Héctor O. Panarello ·  
Héctor A. Ostera

Received: 13 September 2010 / Accepted: 18 July 2011 / Published online: 7 August 2011  
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**Abstract** This paper estimates CO<sub>2</sub> fluxes in a municipal site for final disposal of solid waste, located in Gualeguaychu, Argentina. Estimations were made using the accumulation chamber methods, which had been calibrated previously in laboratory. CO<sub>2</sub> fluxes ranged from 31 to 331 g m<sup>-2</sup> day<sup>-1</sup>. Three different populations were identified: background soil gases averaging 46 g m<sup>-2</sup> day<sup>-1</sup>, intermediate anomalous values averaging 110 g m<sup>-2</sup> day<sup>-1</sup> and high anomalous values averaging 270 g m<sup>-2</sup> day<sup>-1</sup>. Gas samples to a depth of 20 cm were also taken. Gas fractions, XCO<sub>2</sub> < 0.1, XCH<sub>4</sub> < 0.01, XN<sub>2</sub> ~ 0.71 and XO<sub>2</sub> ~ 0.21, δ<sup>13</sup>C of CO<sub>2</sub> (−34 to −18‰), as well as age of waste emplacement, suggest that the study site may be at the final stage of aerobic biodegradation. In a first approach, and following the downstream direction of groundwater flow, alkalinity and δ<sup>13</sup>C of dissolved inorganic carbon (−15 to 4‰) were observed to increase when groundwater passed through the disposal site. This suggests that the CO<sub>2</sub> generated by waste biodegradation dissolves or that dissolved organic matter appears as a result of leachate degradation.

**Keywords** CO<sub>2</sub> fluxes · Solid waste · Carbon isotopes · DIC groundwater

### Introduction

Municipal solid waste (MSW) landfills are used to dispose of household wastes: food and garden, 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 gases and leachate (SEPA 2004). These gas and liquid emissions represent environmental hazards such as explosions, vegetation damage, anomalous emissions to the atmosphere that contribute to global warming, and groundwater pollution or changes in its quality due to the presence of carbonic acid (Bjerg et al. 2005).

Bacterial decomposition of the biodegradable fraction of MSW generates mainly carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), as well as a wide variety of minor and trace components (Spokas et al. 2006). The production rate of these landfill gases (LG) is a function of the composition (organic content), age (or time since placement) 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 refuse placement, a pattern of five sequential stages for LG

R. Sancí (✉) · H. O. Panarello  
Instituto de Geocronología y Geología Isotópica, Universidad de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Pabellón INGEIS, Ciudad Universitaria, C1428EHA Ciudad Autónoma de Buenos Aires, Argentina  
e-mail: romina@ingeis.uba.ar

H. A. Ostera  
Departamento de Geología, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II, Ciudad Universitaria, C1428EHA Ciudad Autónoma de Buenos Aires, Argentina

production or biodegradation stages is proposed: aerobic, non-methanogenic anaerobic, unsteady methanogenic anaerobic, steady methanogenic anaerobic and mature phases (Farquar and Rovers 1973; SEPA 2004).

To assess the impacts of landfill gases (LG) on the atmosphere, several authors have quantified CO<sub>2</sub> and CH<sub>4</sub> surface emissions (CO<sub>2</sub> and CH<sub>4</sub> fluxes) (Pier and Kelly 1997; Mosher et al. 1999; Börjesson et al. 2000; Cardellini et al. 2003; Hedge et al. 2003; Georgaki et al. 2008; Jha et al. 2008) using different accumulation chamber methods, namely closed dynamic chambers, closed static chambers and open dynamic chambers (Norman et al. 1997). Also, to characterize the biodegradation stages within the municipal site for final disposal of solid waste (MSFDSW), other authors such as Coleman et al. (1993) and Hackley et al. (1996) measured the contents of CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub> from gas samples collected with a sampling probe and quantified the carbon (C) isotope ratio (<sup>13</sup>C/<sup>12</sup>C) on CO<sub>2</sub> and CH<sub>4</sub>.

The main objective of this study was to quantify the LG released to the atmosphere from an old inactive MSFDSW located in Gualeguaychu, Argentina, by measuring CO<sub>2</sub> and CH<sub>4</sub> fluxes. In the process, two important factors such as the sampling methods and the sampling sites were considered. This is because in the first case, none of the accumulation chamber methods is nowadays considered a standard because of the differences in flux estimations among chamber types or chamber-specific limitations (Pumpanen et al. 2004). Therefore, laboratory experiments were needed to achieve accurate flux measurements before applying those methods to the field (Sanci et al. 2009a). In addition, since geospatial techniques are advisable to estimate the whole landfill surface flux from the spatially distributed chamber sites (Spokas et al. 2003), variograms were used to determine the level of spatial dependence of the different sites. Since variogram reliability increases with the number of sites used in the model, different regular sampling grids were analysed until the geostatistical analysis indicated that an adequate sampling density had been achieved (Sanci et al. 2009b).

Complementarily, gas probe and underground water samples were taken. 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. Bearing in mind that the gases generated in a solid waste landfill may dissolve in groundwater and that water levels and SW were at a similar depth (Kumar et al. 2004), the possibility was considered of the free aquifer acting as a CO<sub>2</sub> sink. During the first preliminary survey, the concentrations of common inorganic constituents in groundwater that could be affected by LG were measured. Carbon isotope ( $\delta^{13}\text{C}$ ) of dissolved inorganic carbon (DIC) was analysed to obtain complementary information about possible changes in groundwater solute concentrations.

## Surveyed site

### Site description

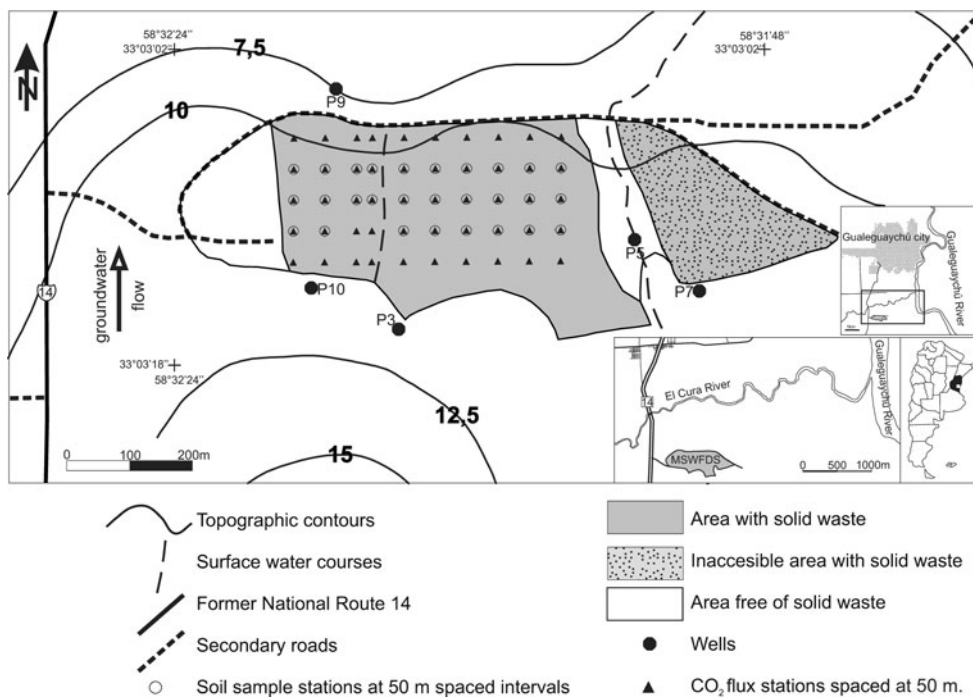
The Gualeguaychu municipal waste landfill is located 3 km south of that city, in the southeast of the province of Entre Rios, Argentina, next to the confluence of the Cura Stream and the Gualeguaychu River (Fig. 1). The municipal facility was first exploited for mineral extraction, and waste was later disposed of in the depressions. One part of this facility was used for final disposal of urban solid waste. It was closed in 2000 when it filled up. Gas emissions were sampled there. Another part of the facility is currently being landfilled. So far, according to geophysical studies (Prezzi et al. 2005; Pomposiello et al. 2009) in the filled-up disposal area, SWs are of household origin; the filling depth does not exceed 2 m and the site has not been recycled previously. There is no information regarding any environmental protection actions undertaken during the operation of the site. Visual observation of the MSFDSW revealed that the topsoil cover is permeable and not compacted. There are no gas vents or recovery systems.

### Geological and hydrogeological setting

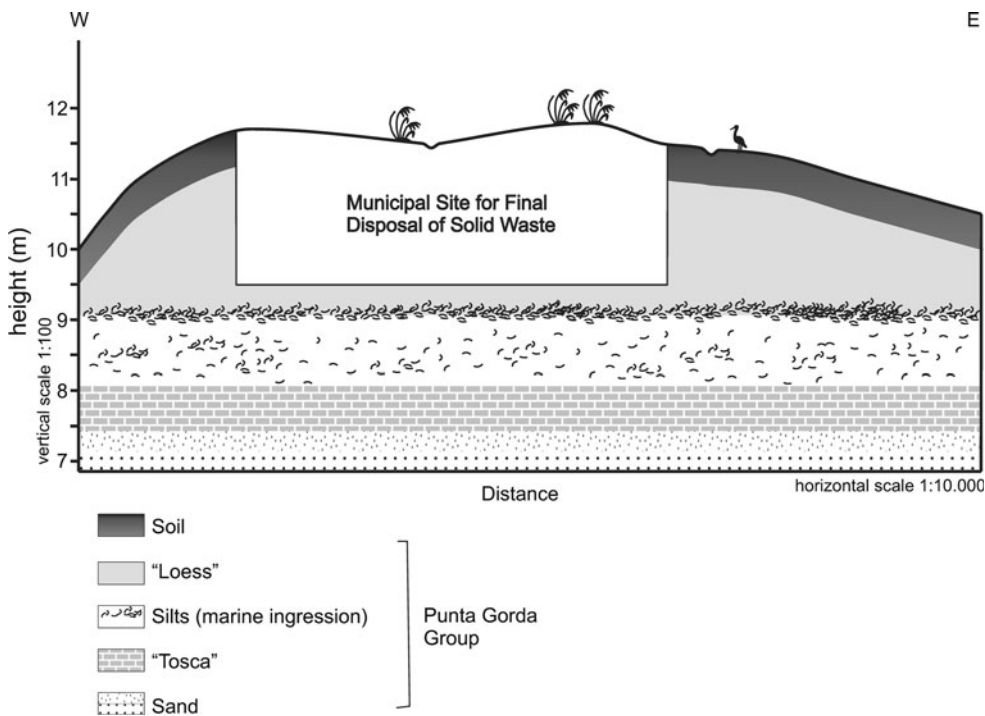
The Gualeguaychu municipal waste disposal site is located in the lower section of the Gualeguaychu River basin, which has a subhumid–humid climate (Thorntwaite and Matter 1957) according to rainfall and temperature data from Aero Gualeguaychu Station of the Argentinean National Weather Service (Servicio Meteorológico Nacional SMN) for the 1969–2005 period. For that period, mean annual rainfall was 1,077 mm, and mean temperature, 17.6°C. The region belongs to the Chaco-Paranaense basin. The Punta Gorda Group underlying the MSFDSW is the unit outcropping in the study area (Iriondo 1980) (Fig. 2). 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 (Ituzaingó) that is highly productive and has high quality of water, used for human consumption and irrigation.

**Fig. 1** Location and description of the MWSFDS



**Fig. 2** Depth of SW, topography and geology of the site



**Methods and procedures**

**Gas samples**

Closed chamber methods were used to measure surface emissions. These methods are independent of the physical properties of soil and allow measuring the CH<sub>4</sub> and CO<sub>2</sub>

released to the atmosphere. The dynamic and static closed chamber methods were applied during fieldwork, after calibration in laboratory (Sanci et al. 2009a). Previous studies (Nay et al. 1994; Chiodini et al. 1998; Evans et al. 2001; Widén and Lindroth 2003; Butnor and Johnsen 2004; Martin et al. 2004) demonstrated the importance of using calibration systems to test the accumulation chamber methods.

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. Surface emissions were estimated as the increase of CO<sub>2</sub> and CH<sub>4</sub> concentrations over time. Flux rates were calculated by fitting linear regression to the variation of concentration ( $C$ ) over 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:

$$F = \left(\frac{V}{A}\right) \left(\frac{dC}{dt}\right) = 0.257 \text{ m} \left(\frac{dC}{dt}\right) \quad (1)$$

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.

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 (Sanci et al. 2009a). This system allowed determining 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 infrared gas analyser (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 ( $R^2 = 0.99$ ). 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 determining 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 one allows detecting 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 ( $R^2 = 0.99$ ) and mixing 35 s prior to CO<sub>2</sub> sampling. The best mixing rate was 250 mL min<sup>-1</sup>.

A soil gas probe was used to measure soil CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub> levels. The stainless steel probe was inserted to 20 cm and soil gases brought to the vicinity of the tip of the probe by applying vacuum. Soil gas samples were taken at 28 locations spaced at 50 m. (Fig. 1), which coincide with sites where CO<sub>2</sub> fluxes were measured. Samples were collected in Tedlar™ bags and analysed in laboratory with a GC-TCD HP 5890 Series II. 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>. BaCO<sub>3</sub> for isotopic analysis of carbon was treated with H<sub>3</sub>PO<sub>4</sub> as described in “Groundwater samples”.

## Data analysis

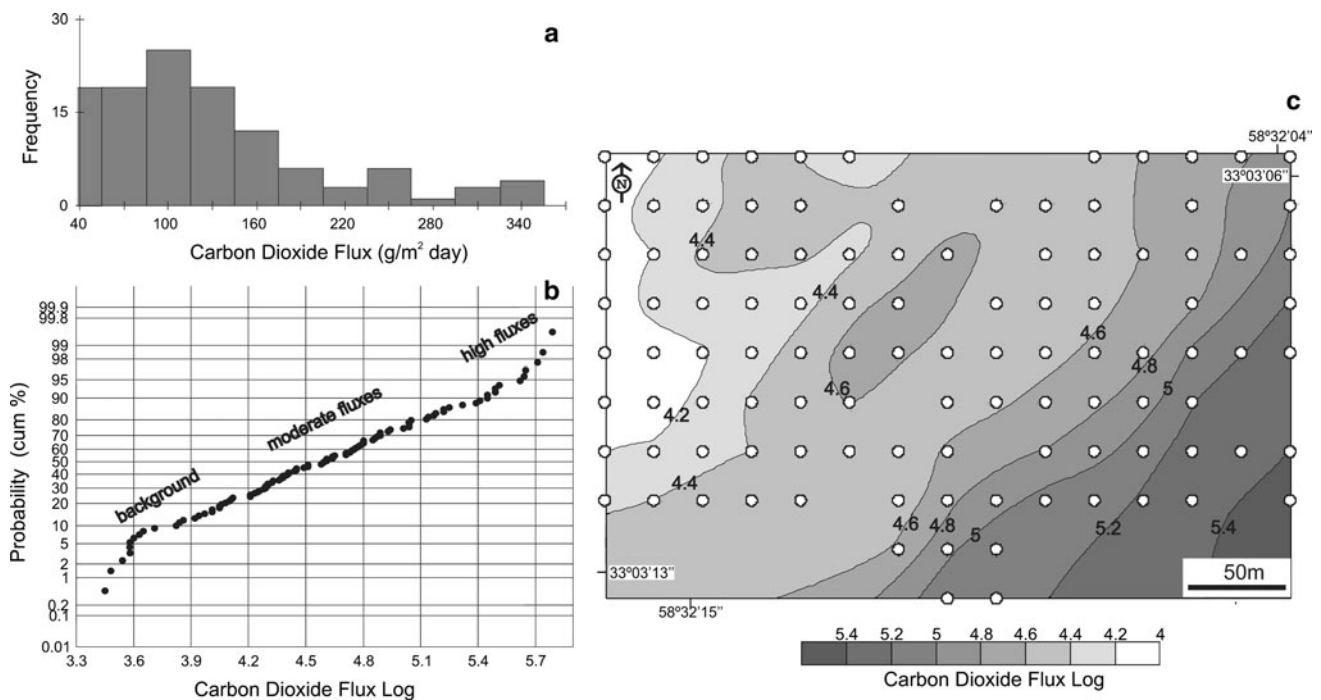
Measurements were distributed over regular grids, following Wang and Qi's (1998) statement that although three sampling patterns (regular grid, simple random and cellular stratified sampling) are widely used in environmental studies, for a given sampling density, the regular grid provides better estimations than the other two. Histogram was plotted for the CO<sub>2</sub> fluxes measured in the field (October 2007). CO<sub>2</sub> fluxes were log-transformed (ln) and fitted on a cumulative probability curve to verify the log-normal distribution and to identify different flux populations through changes in graph slope (Bergfeld et al. 2001; Chiodini and Frondini 2001; Gerlach et al. 2001; Cardellini et al. 2003).

Geostatistical techniques were used to assess the spatial variability of fluxes. The degree of spatial dependence between samples was analysed in experimental variograms (essential tool for this type of techniques) in which the semivariance  $\gamma(h)$  was plotted against the lag( $h$ )—i.e. distance between sample sites (Webster and Oliver 1992). The sampling density of CO<sub>2</sub> fluxes was increased (14, 50 and 107 site surveys) taking into consideration the original location of the sites of the exploratory fieldwork. Omnidirectional and directional variograms were plotted for the data obtained in the 14, 50 and 107 site surveys, and spatial dependence was only observed between the data of CO<sub>2</sub> flux sites spaced at 25 m for the 107 sites (Sanci et al. 2009b). Since variograms may take several forms, different theoretical models were fitted to the data using the VARIOWIN software (Eddy and Paninatier 1996). It is worth mentioning that because in the exploratory survey, CH<sub>4</sub> fluxes were not detected, geospatial analysis was only applied on CO<sub>2</sub> flux measurements.

Kriging was applied to generate contour maps, using the parameters of the variogram model that had 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).

## Groundwater samples

Groundwater samples were filtered and stored in 1000-mL plastic bottles 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



**Fig. 3** **a** Histogram of the CO<sub>2</sub> flux data from 107 stations; **b** cumulative probability of the natural logarithm of the CO<sub>2</sub> flux for 107 stations showing a log-linear distribution of flux data; **c** spatial distribution of the natural logarithms of CO<sub>2</sub> fluxes of three populations

spectroscopy (BAIRD-ICP 2070) and Cl<sup>-</sup> by titration with AgNO<sub>3</sub>. Saturation indices were calculated with the PHREEQC software (Parkhurst and Appelo 1999) used for speciation, batch reaction, one-dimensional transport and inverse geochemical calculations. Piezometers for groundwater observation were installed before October 2007 to compare the electric conductivity measured in situ with the one estimated by geoelectrical studies (Pomposiello et al. 2009). Wells were drilled to a depth of ≤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).

**Isotopes**

Samples of soil gas and groundwater were analysed to determine the <sup>13</sup>C/<sup>12</sup>C ratio on BaCO<sub>3</sub> obtained from precipitating CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> with alkaline BaCl<sub>2</sub> (Taylor and Fox 1996). The resulting BaCO<sub>3</sub> was 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 were reacted with H<sub>3</sub>PO<sub>4</sub> (100%) in vacuo, according to MacCrea (1950). The resulting CO<sub>2</sub> was cryogenically purified; transferred with liquid N<sub>2</sub> to a glass vial and measured against a working standard (CO<sub>2</sub> from Carrara marble) in a dual inlet, triple collector mass spectrometer, Finnigan MAT Delta S. Carbon isotope composition is expressed as δ<sup>13</sup>C, according to:

$$\delta^{13}C = 1,000 \frac{[^{13}C/^{12}C]_s - [^{13}C/^{12}C]_R}{[^{13}C/^{12}C]_R} \text{‰} \tag{2}$$

where <sup>13</sup>C/<sup>12</sup>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 (2σ) was ±0.2‰.

**Results**

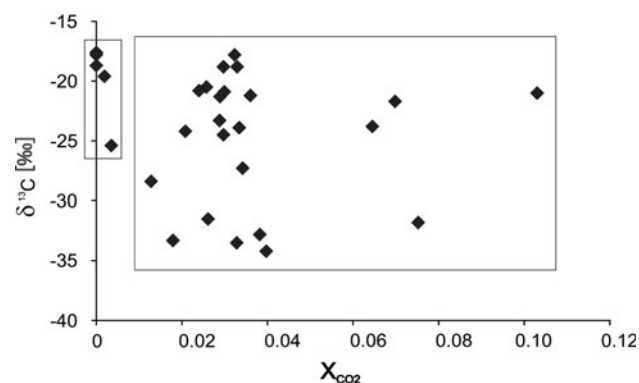
**Gas measurements**

The surveyed area covers about 150,000 m<sup>2</sup>. No measurements were made in the inaccessible part of the MSFDSW (Fig. 1). Fieldwork was undertaken in dry and stable periods to avoid the influence of rainfall, soil humidity and atmospheric pressure on surface emissions. Measured CO<sub>2</sub> fluxes spaced at 25 m (107 stations) ranged from 31 to 331 g m<sup>-2</sup> day<sup>-1</sup>. The CO<sub>2</sub> flux histogram (Fig. 3a) shows that fluxes are low to moderate in most of the sites, with only a few sites having very large CO<sub>2</sub> fluxes. Irregularly spaced stations upstream of the MSFDSW were added to the study to measure the background values of soil respiration, which ranged from 29 to 59 g m<sup>-2</sup> day<sup>-1</sup>. Soil temperature ranged from 20 to 30°C.

Distribution of measured CO<sub>2</sub> fluxes is log-normal, as can be seen in the linear cumulative probability plot of ln(CO<sub>2</sub>) flux (Fig. 3b). 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 the measured background values beyond the MSFDSW; intermediate, between 67 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.

Since fluxes had an almost log-normal distribution, experimental variograms and kriging were calculated for the ln-transformed CO<sub>2</sub> fluxes. The variogram model (linear with nugget effect), obtained from the data set of the 107 site surveys, and its parameters were used to elaborate the contour map of ln(CO<sub>2</sub>) flux by kriging (Fig. 3c). The distribution of ln(CO<sub>2</sub>) flux indicates that diffuse gas fluxes from the MSFDSW are spatially inhomogeneous: values grow towards the southeast.

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. The δ<sup>13</sup>C–CO<sub>2</sub> ranged from –34.2 to –17.6‰. The plot of CO<sub>2</sub> concentration versus δ<sup>13</sup>C–CO<sub>2</sub> (Fig. 4) 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 and Kelly 1997) with a possible contribution of



**Fig. 4** δ<sup>13</sup>C versus CO<sub>2</sub> concentration (volume fraction)

soil respiration. In the first group, δ<sup>13</sup>C ranges from –25.4 to –17.6‰, and in the second from –34.2 to –17.8‰.

#### Groundwater samples

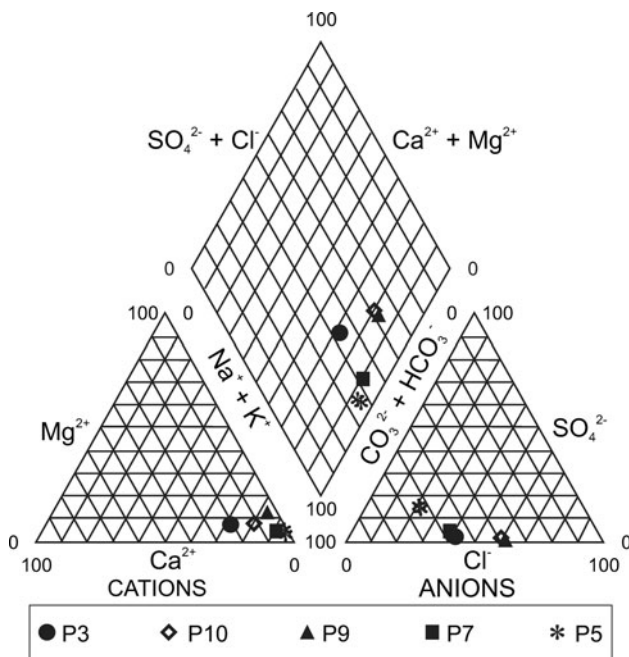
Water tables from five piezometers were measured. Levels ranged from 0.10 to 1.70 m below surface. Considering that SWs were buried at these depths, groundwater samples for hydrochemical and isotopic analyses were taken in October 2007 to check whether the phreatic aquifer was acting as a sink for the CO<sub>2</sub> generated by waste biodegradation. Measured physical and chemical parameters are shown in Table 1 and the chemical classification of water in Fig. 5 (sodium chloride and bicarbonate waters). Hydrochemical and isotope values varied in the different flow paths: P3 to P9; P10 to P9; P7 to P5. Alkalinity and δ<sup>13</sup>C–DIC tended to increase along the flow paths mentioned before (Fig. 6). 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 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.

#### Discussion

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 (Fig. 3a). 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; Chiodini and Frondini 2001; Gerlach et al. 2001; Cardellini et al. 2003). Logarithmic probability plots (Fig. 3b) 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 (Pier and Kelly 1997; Cardellini et al. 2003; Hedge et al. 2003; Georgaki et al. 2008; Jha et al. 2008). Spatial variations observed in surface CO<sub>2</sub> flux distribution (Fig. 3c) are due to MSFDSW inhomogeneities. This variability may

**Table 1** Groundwater composition of piezometers

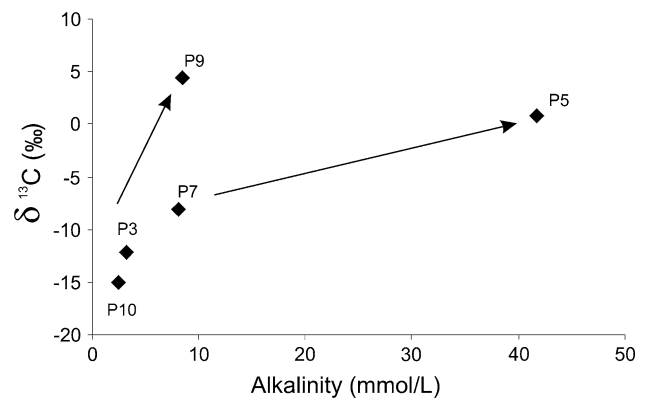
| Parameter  | P3    | P10   | P9    | P7    | P5    |
|--|-------|-------|-------|-------|-------|
| Temperature (°C)   | 18.5  | 19    | 23.2  | 21.3  | 20.4  |
| pH   | 6.9   | 6.9   | 7.1   | 6.9   | 7.0   |
| Conductivity (μS/cm)   | 610   | 720   | 2,440 | 1,320 | 5,450 |
| Alkalinity (mmol/L)  | 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  |
| SI calcite   | -0.95 | -1.20 | -0.53 | -0.80 | -0.02 |
| $\delta^{13}\text{C}$ (‰ vs. PDB)                                  | -12.1 | -15.0 | 4.4   | -8.1  | 0.8   |
| Analytical error (%)   | 8.86  | 8.17  | 6.17  | 5.97  | 8.42  |
| $100 \times (\text{Cat} -  \text{An} )/(\text{Cat} +  \text{An} )$ |       |       |       |       |       |



**Fig. 5** Piper diagram showing the chemical classification of wells. P3, P7, P5: sodium bicarbonate groundwater; P10, P9: sodium chloride groundwater

indicate that waste was buried in the 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.

Several authors have proposed a pattern for landfill gas production (five biodegradation stages) based on the assumption that an anaerobic environment would be attained and maintained after refuse placement (Farquar and Rovers 1973; Farquhar 1989; SEPA 2004). During the initial stage of organic degradation within a landfill, CO<sub>2</sub> is



**Fig. 6** Alkalinity versus  $\delta^{13}\text{C}$ -DIC

produced in molar equivalents to free O<sub>2</sub> consumed. Once O<sub>2</sub> concentration is low enough, anaerobic oxidation, hydrolysis and acidification reactions begin and CO<sub>2</sub> concentration (up to 70%) and organic acids such as acetic peak. As anaerobic degradation continues, the concentrations of acetic and other organic acids decrease, associated with an increase in CH<sub>4</sub> generation (methanogenesis). CO<sub>2</sub> concentration declines and methanogenesis begins to prevail, establishing a phase of steady CH<sub>4</sub> production: 50–70% CH<sub>4</sub> (with 30 to 50% CO<sub>2</sub>). 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.

In addition, the analysis of stable isotopes of carbon and hydrogen 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;  $\delta^{13}\text{C}$  values range from -35 to -10‰, which covers the

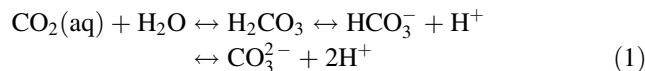
range of most terrestrial plants. The initial input of isotopically light CO<sub>2</sub> associated with the earlier biodegradation phases will soon be overcome during the methanogenesis phase by the constant input of isotopically heavy CO<sub>2</sub> associated with acetate fermentation and microbial 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 δ<sup>13</sup>C of CO<sub>2</sub> is strongly affected by methanogenesis reactions with reported values between −10 and +20‰ (Coleman et al. 1993; Hackley et al. 1996).

Quantified anomalous CO<sub>2</sub> fluxes within the MSFDSW show that the site is still undergoing SW 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.

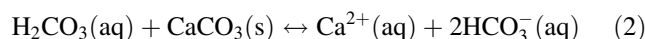
Although concentrations of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub> and C isotope are indicators of the degree of maturity of sanitary landfills, in practice, they rarely go through the whole sequence of development stages. In addition, the factors affecting gas generation need to be considered: differences in waste composition and pre-treatment, age and depth of waste emplacement, capping, compaction, gas management regime or the hydraulic characteristics of the site (Meju 2000). These factors affect the duration of each particular stage, as well as the degrees of phase overlap and phase omission (SEPA 2004). In this case, the shallow burial of waste (2 m) 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 SWs were first disposed before the present stage, 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.

In landfills, CO<sub>2</sub> is the most water-soluble constituent of MSW gas. 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 DIC (Stumm and Morgan 1996). These species are free carbon dioxide (CO<sub>2(aq)</sub>), 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, among others. Carbon dioxide 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, a part may be converted to CH<sub>4</sub> by microbes and the rest is released by outgassing (Baedecker and Back 1979).

Data show that groundwater alkalinity grows across the MSFDSW in the direction of underground flow (Fig. 6). 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. Even the interaction between carbonic acid and mineral carbonates might 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 can 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 confirmed the changes observed in water alkalinity due to the anomalous ingress of CO<sub>2</sub>. Values of δ<sup>13</sup>C-DIC between −15 and −12‰ can be explained by isotope fractionation from the fixation of CO<sub>2</sub> from soil respiration in the form of HCO<sub>3</sub><sup>−</sup> within a process of calcite dissolution (Mook 2000), but δ<sup>13</sup>C-DIC values richer than −12‰ can be explained by the input of CO<sub>2</sub> from SW degradation which dissolves calcite (a geologically feasible process). Specifically, values close to −8‰ can be explained by the dissolution of landfill-generated CO<sub>2</sub> (with values close to −17‰) and fixation as HCO<sub>3</sub><sup>−</sup> with an isotopic enrichment of +9‰. 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.

### Conclusions

1. Direct measurements of  $\text{CO}_2$  diffuse degassing from surface, with the accumulation chamber methodology tested in laboratory, allowed detecting the spatial variability of  $\text{CO}_2$  fluxes in the MSWFDS.
2. Three subpopulations were identified by the statistical and geostatistical analyses of  $\text{CO}_2$  fluxes. Processes giving rise to the subpopulations are background values attributable to plant respiration ( $46 \text{ g m}^{-2} \text{ day}^{-1}$ ) and different anomalous values (110 and  $270 \text{ g m}^{-2} \text{ day}^{-1}$ ) related to biodegradation of urban solid waste disposed in the MSWFDS.
3. Probe-sampled concentrations of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$  and  $\text{O}_2$ , as well as carbon isotope composition of the  $\text{CO}_2$ , show that the process underway is an aerobic phase of biodegradation. In particular, the time since the end of operations in the MSWFDS makes it possible to assume that we are in the presence of a mature or posthumous stage of biodegradation.
4. The characteristics of the environment where SWs were disposed (mainly permeability of capping due to little compaction and inappropriate cover material), the shallow depth of SW burial and the absence of  $\text{CH}_4$  allow assuming that biodegradation in the MSWFDS was completely aerobic or that it may have gone through a period of anaerobic oxidation, though not developing methanogenic processes.
5. Based on the increase in groundwater alkalinity while it flowed across the MSWFDS and the DIC isotope composition, two different situations are possible: either  $\text{CO}_2$  derived from SW 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.

**Acknowledgments** This research was supported by the Instituto de Geocronología y Geología Isotópica (UBA-CONICET) and PICT 2002 No 12243. The authors are grateful to Eduardo Llambías, Anibal Tricarico and Gabriel Giordarengo for their collaboration in the field.

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