

CO₂ FLUX FROM LANDFILL SOIL: A METHODOLOGY TO ESTIMATE THE DIFFUSE BIOGAS

Roberto Cioni¹, Massimo Guidi¹, Brunella Raco¹ ✉, Marco Guercio², Riccardo Corsi³

1-Istituto di Geoscienze e Georisorse CNR, Via Moruzzi 1, 56127Pisa - Italy

2-AMIAT Via Germagnano 50 10156 Torino – Italy

3-STEAM Srl, Via Rismondo 28, 56127 Pisa- Italy

Abstract

In 1998, in the framework of environment certification according to the requirements of the standard UNI EN ISO14001 and the CEE 1836/93 Regulations (EMAS), the AMIAT Spa (Azienda Municipalizzata di Igiene Ambientale di Torino) charged Steam Srl to carry out a survey of biogas flux from soil to estimate the amount of biogas lost in the atmosphere. A total of 380 measurements sites have been distributed over an area of 400000 m². The accumulation chamber method to measure CO₂ and CH₄ flux from soil has been utilized. The estimation of total diffuse biogas flux was 375 ton/day with a specific flux of 0.93 kg/m² day. Moreover anomalous zones, mainly surrounding wells, have been recognized.

A second survey has been performed in 2001 in order to verify the effectiveness of the remedial measures adopted by AMIAT to reduce the biogas flux to the atmosphere. These actions have been provided within the environmental management plan of the “Basse di Stura” site, whose objective is to cut the impacts on significant environmental facets.

A total of 950 measurement sites were distributed over an area of 498000m². A total diffuse flux estimation of 118 ton/day was obtained for the air-soil interface. This estimation corresponds to a specific flux of 0.23 kg/m²day, with a 75% reduction as compared to specific fluxes gauged in 1998.

These figures strictly correspond to the difference between the theoretical amount of biogas yielded by the landfill, obtained by mathematical model, and actual total biogas burned in the plant to produce electric power.

This result strongly supports the idea that this kind of biogas flux survey may allow to obtain optimum management conditions for the exploitation of landfills to produce electric power and minimize the amount of biogas lost in the atmosphere.

Introduction

The municipal solid waste (MSW) landfills are often regarded as very important sources of atmosphere contamination: this is due to the escape of biogas from landfill body even when biogas collection and combustion systems are present. Nevertheless no protocols have been yet utilized to quantify pollutant flow from landfill area.

It is well-known that methane and carbon dioxide are produced in landfills from anaerobic decomposition of organic matter by methanogenic bacteria (Kirshop, 1984; Whitman, 1985). In landfill, wastes are first subjected to aerobic degradation processes until the oxygen is totally consumed; wastes are in fact compacted and covered to avoid oxygen penetration. Therefore wastes are decomposed by non methanogenic bacteria (Boone and Bryant, 1980; McInerey and Bryant, 1980, 1981a, 1981b), which convert organic compound in organic acid provided with a simple structure. These simple substances are further transformed in CO₂ e CH₄ by those bacteria that are present in the leachate (Mah and Smith, 1981). These gases are generally called biogas.

Biogas is mainly a mixture of approximately 55% methane and 45% carbon dioxide, which are gaseous species liable for the greenhouse effect. Landfills participate to increase the amount of CH₄ lost in the atmosphere. As a matter of facts the estimations of Krause et al., (1989) indicate that the CH₄ emission from landfills is about 10% of the total methane present in the atmosphere, while the U.S Protection Agency (2001) indicates that percentage reach about 22%.

Several organic compounds are present in traces in biogas.

A lot of numerical models, able to foresee biogas production from MSW landfill, are available (Damiani and Gadolla,1984; Manna et al., 1999) This technology is mostly used to size the plant that should be feed by biogas. The main problem is to perform appropriate covering works for the landfill in order to avoid the biogas escapes to the atmosphere and improve the efficiency of exploitation. Nevertheless no protocol exists to quantify the biogas leakage from landfill soil. This problem could be solved by using the methods of soil gas survey; anyway we should remember that this technique uses the Fick law to correlate the gradient to the flux by knowing the diffusion coefficient (Thorstenson and Polloch, 1989).

In the landfill we preferred using the direct flux measurement because the advective component is relevant due to the high gas pressure.

Measurements of CO₂ and/or CH₄ fluxes from landfills soil and contextual chemical analyses of biogas allow the estimation of the pollutant flow. At the same time, they may be used to verify the actual characteristics of the impervious cover and to assess the possible presence of anomalous degassing zones or fractures. These latter can act as preferential path for biogas escaping.

If the aim of the work is to quantify the total CH₄ emission from landfill soil towards the atmosphere, it is then more correct to measure the CH₄ flux. On the other hand if the task is to highlight the presence of anomalous degassing zones or fractures on the covering, to measure the CO₂ flux would be more appropriate, due to the fact that in the shallower layers of the soil, under oxidation processes, CH₄ can be transformed into CO₂ (Czepiel et al., 1996a, 1996b). In this case it is possible to estimate the total biogas flux from landfill soil by determining the CH₄/CO₂ ratio. This estimation can help optimize the drainage and collecting systems where biogas is being exploited to produce heat and/or energy.

This paper shows the data obtained from two biogas flux surveys carried out in the municipal landfill of Turin with the technical support of the organization A.M.I.A.T. (Azienda Municipalizzata di Igiene Ambientale Torinese). This MSW landfill named “Basse di Stura” collects biogas by means of some vertical and slanting drainpipes and has been employing it to produce electric power since 1985, with a progressive installed capacity increase which has reached, at present, 7.0 MW. The landfill is made up of several lots, which are often cultivated simultaneously, sometimes by following a predetermined sequence. Because of this reason the morphological aspect of landfill changes year by year.

Measurements of CO₂ flux from soil have been done to underline high permeability zones and fractured areas.

Where the CO₂ flux values were relatively high, also the CH₄ flux from soil were gathered. In order to characterize the biogas composition some samples from soil gas and from drainpipes have been collected and analyzed. The estimation of biogas flux has been extrapolated from the CH₄/CO₂ ratio.

Instrumentation and method

The accumulation chamber method has been utilized to measure the CO₂ flux from soil. This method allows the determination of the rate of increase in the CO₂ concentration within an inverted chamber placed on the soil surface. This static technique has been successfully used in agricultural science to determine soil respiration (Witkamp, 1969; Kucera and Kirkham, 1971; Kanemasu et al., 1974; Parkinson, 1981), to measure the flux from soil of other gaseous species, e.g., N₂O (Kizing and Socolow, 1994) to evaluate total diffuse CO₂ output in volcanic and geothermal areas (Tonani and Miele, 1991; Chiodini et al., 1996; 1998).

The instrument used (the Flux Meter by West Systems Srl) consists of (Fig.1):

- a circular chamber 10 cm high;
- an IR spectrophotometer
- an analogic-digital converter
- a hand-size computer.

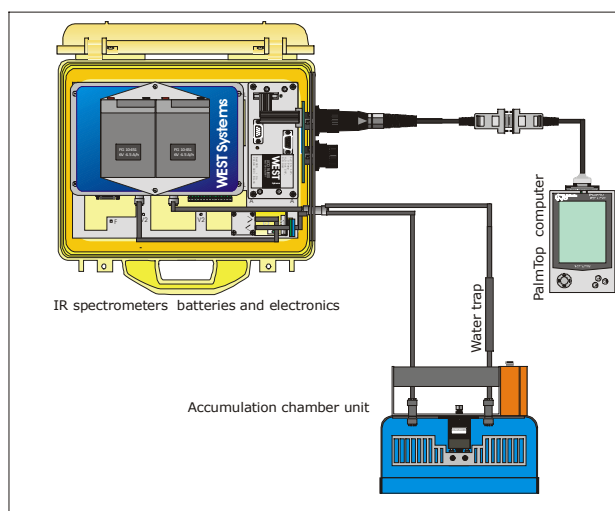


Fig. 1. Sketch of the instrument used to measure ϕ_{soilCO_2} (from West System, 2001).

The apposite software package, developed by West Systems, gives the operator the evaluation of the initial slope of the CO₂ – t line, which is carried out directly on the field. The initial slope is proportional to CO₂ flux from soil (ϕ_{soilCO_2}). The reliability of this instrument is known (Chiodini et al., 1996; 1998), and it is also rapid (a measurement takes approximately 1 minutes).

This strategy allows not only to estimate the total output of CO₂, but also to recognize very high emission zones. Moreover the accumulation chamber method is less dependent on weather conditions than other methods, i.e., airborne infrared thermometry, trace gas, micrometeorological, mass balance, Eddy correlation (Tregoures et al., 1999).

However the influence of meteorological conditions such as rain and soil humidity has been avoided by working in dry seasons. The influence of barometric pressure on soil gas concentration and fluxes is generally high (Reimer, 1980, Hinkle and Ryder 1987 ;1988 ;Hinkle, 1994; King and Minissale 1994; Pinoult and Baubron, 1996), so, in order to evaluate the influence of P_{atm}, repeated measurements were carried out in some sites located in the landfill area and characterized by different fluxes. However these measurements, carried out during 20-26 April 1998, did not show significant variations.

Application

Carbon dioxide fluxes have been mapped after data processing with ISATIS program, employing the Kriging method (Krige 1951; Matheron, 1962; 1965; 1969; 1970; Clark, 1979) to extrapolate values where the measures had not been taken.

From the experimental variogram, the extrapolation requires the construction of the ideal variogram and the singling out of the best neighborhood to be considered for the interpolation process.

Moreover, the Kriging methods assures that the interpolated value is unbiased as compared to the mean value and the minimum variance (Chauvet, 1982; 1991; 1993; Armstrong, 1984; Wackernagel, 1995).

Nevertheless the global estimation of biogas has not been done by utilizing the kriging technique. The global mean would in fact very rarely be kriged directly due to two main reasons (Journel and Huijbregts, 1978):

- It is not usually possible to assume stationarity or a single drift of known form over the entire area, but only over limited neighborhoods (local quasi-stationarity).
- Even if stationarity could be verified over the entire investigated area, there are usually too many data to construct a kriging matrix and then to solve the kriging system.

Moreover, the construction of such a kriging matrix would imply that the structural function, $C(h)$ or $\gamma(h)$, is known for distance h of the order of dimensions of the area and the limit of reliability of an experimental semi-variogram is a distance $L/2$, half of the field dimensions.

In order to estimate the total biogas output from soil the Sinclair (1974, 1991) procedure and the Sichel's estimator (Sichel, 1966, David, 1977) has been used. For all the investigated zones (in the two surveys) the logarithmic probability plots show that FCO_2 soil have a polymodal distribution, consisting of combination of 2, 3, sometimes 4 populations, which are log-normally distributed.

The area covered by each population was evaluated by the following relation:

$$A_i = P_i * A_{tot}$$

where A_{tot} is the total investigated area. The total CO_2 flux from soil from the surveyed area was estimated by summing the contributions of each population:

$$F_{tot}CO_2 = \sum FCO_{2,i} * A_i$$

where $FCO_{2,i}$ represents the average CO_2 flux of the i -th population.

This mathematical procedure needs objective criterion to verify the reliability of the partitioning population.

Moreover, in order to estimate the total biogas flux from the landfill soil some gas samples have to be collected and analysed to calculate the CH_4/CO_2 ratio.

Usually, every investigated zone is characterized by a different CH_4/CO_2 ratio depending on the age and nature of wastes. The CH_4 flux was calculated multiplying the CO_2 flux from soil (estimated for each zone) by its characteristic CH_4/CO_2 ratio. The contribution of these two major components allows the estimation of the total biogas flux from soil.

1998 field survey

In 1998, in the framework of environment certification according to the requirements of the standard UNI EN ISO14001 and the CEE 1836/93 Regulations (EMAS), a survey of CO_2 flux from soil was carried out to estimate the amount of biogas lost in the atmosphere in the AMIAT landfill. The accumulation chamber method to measure CO_2 flux from soil has been utilized.

In 1998 the AMIAT landfill was made up of 8 lots (1A, 2A, 3A, 1B, 2B, 1C, 2C and the old landfill zone). During the survey period, lot 3A was utilized as composting unit and lot 1C was realized but not cultivated, a total of 501 measurements sites were distributed over the remaining lots and covered an area of approximately 700000 m^2 (Fig. 2). The ϕ_{soilCO_2} range from 0.12 to 392 mol/m^2day with a standard deviation of 39.2.

The data processing has been carried out for every single lot which represents a zone with homogeneous features.

Inspection of Fig. 3, where isoflux maps for each lot have been reported, elicits the following remarks:

- *lot 2C*: High- ϕ_{soilCO_2} fluxes had been recognized in the S and in the NE sectors of the zone. The anomalous zone located in the S sector coincided with the boundary slope between lots 2C and 2B, while the small zone located in the NE sector coincided with the boundary slope between lots 2C and 1C. The low- ϕ_{soilCO_2} value measured in the north sector were due to an impervious cover present in this area. At the time of the survey the cultivation of this lot was terminated, but no impervious cover was installed.
- *lot 1B* : High- ϕ_{soilCO_2} zones were present in the N in the S and in the W sectors of the area, these zones represented the boundary slopes between lots 1C, 2A and 1A, respectively. These slopes were not covered by impervious layer. Very low- ϕ_{soilCO_2} values clustered in the eastern part of the zone. In this zone a slope with an effectiveness impervious cover was present. Moreover low- ϕ_{soilCO_2} flux was recognized in the central sector. These low values were probably due to the fact that the soil is over compacted by heavy trucks transit. During the survey this lot was under cultivation.
- *Lot 2B*: High fluxes were found in the surroundings of some wells, in the E and in the N sector of the zone. This lot was equipped with a capping, but such capping did not cover the E sector.
- *lots 1 and 2A* - Anomalous high ϕ_{soilCO_2} zones, mainly surrounding wells, had been recognized. In the central sector of the area the high fluxes were due to small shallow fractures observed during the field work. In these lots the definitive drainage systems was realized, but they did not equipped with capping.
- *Old landfill zone* - In this area the ϕ_{soilCO_2} values had a mean of 0.5 mol/m^2day , typical of soil characterized by grass cover. These fluxes are mainly due to biological and radical activity (Lundengard, 1924; Leith and Ouellette, 1962). Only five measured sites localized near old wells had high ϕ_{soilCO_2} values, but they were not taken into account during the mean calculation. Moreover no map has been drawn for this area. This old landfill was under exploitation during 50's and the end of 70's.

As mentioned above, the Sinclair procedure and the Sichel estimator have been taken into account in order to estimate the total diffuse CO_2 flux from soil.

A total diffuse CO_2 output of 250 ton/day is estimated for the entire area, with upper and lower limits at 90% confidence of 556 and 160 ton/day, respectively.

In order to characterize the biogas composition 10 samples from wells and 10 samples from gas soil have been collected and analyzed. The CH_4/CO_2 molar ratio in well gas samples ranges from 1.64 to 1.45 with an average value of 1.53 and a standard deviation of 0.065, the CH_4/CO_2 molar ratio in soil gas sample is quite similar to that of well except for sample in which the amount of air is too high to consider them as representative samples, while the CH_4/CO_2 values of 1.10 and 0.76 are probably due to the different age of lots. It is well-known that in the first phases of conversion of organic substrate the dominant gas specie is CO_2 .

In Tab.1 the values of CH_4/CO_2 ratio for each lot are reported together with the relative biogas flux. A total diffuse biogas flux of 375 ton/day was estimated for the entire investigated area.

In order to explain, at least in part, this high flux we should take into consideration that during the survey:

- a) the biogas extraction system, of lots 1A, 2A and 2B, was repeatedly stopped for maintenance problems.
- b) In the lots 2C and 1B the biogas was not collected to feed the plant, but it was conveyed to the flares.

However, as a consequence of the results obtained in the 1998 survey, the AMIAT has provided a project aimed to optimise the drainage system and minimise the biogas lost in the atmosphere.



Fig. 2. Location of the measurement sites in the AMIAT landfill in 1998.

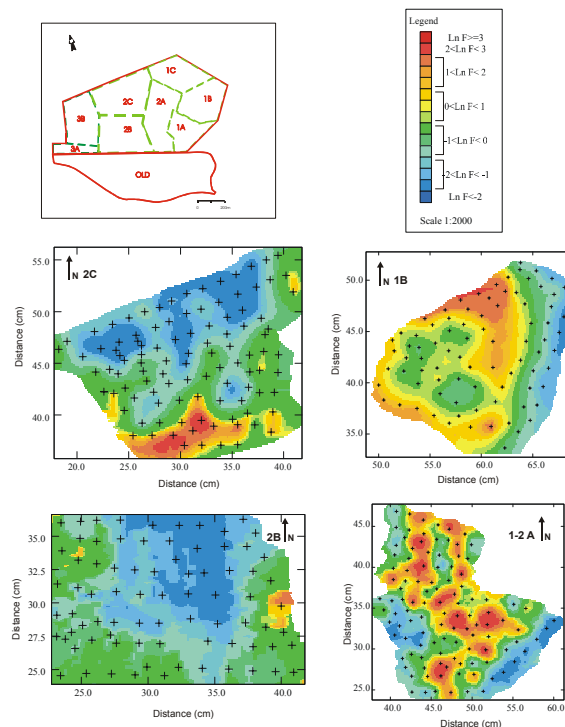


Fig. 3. Isoflux CO_2 maps of lots 2C, 1B, 2B and 1-2A in 1998. For each map also the location of the measurement sites is shown.

Tab. 1. Values of CH₄/CO₂ ratio chosen for each lot and relative biogas flux.

	Average CH ₄ / CO ₂	CO ₂ flux Ton/day	CH ₄ flux Ton/day	Biogas flux Ton/day
Lot 1-2 A	1.46	162	85	247
Lot 2 C	1.23	24	11	35
Lot 2 B	1.38	42	21	63
Lot 1 B	0.98	22	8	30

2001 field survey

To verify the effectiveness of the actions foresaw by the project a second survey of CO₂ flux from soil has been carried out in 2001. In this period the AMIAT landfill was made up of 4 lots (north zone, 2B, 1A and the southern part of 2A, hereunder named ex 1-2A). A total of 944 measurement sites were distributed over an area of 500000 m² (Fig. 4). The $\phi_{\text{soil CO}_2}$ range from 0.00088 to 184 mol/m²day with a standard deviation of 18.2.

Isoflux maps (Fig. 5) have been constructed, inspection of them allow one to deduce the following:

- *North (lots 1B, 1C, extra storey of 2A and 2C)* - Two high $\phi_{\text{soil CO}_2}$ zones were present in the N and in the S sector of the area. These two zone were located near the fresh waste management area. High CO₂ flux value have been measured in the northern boundary slopes. These high values were limited at the areas surrounding wells. The other sectors of the area are characterized by low flux. During the survey this zone was under cultivation.
- *Lot 2B* – high $\phi_{\text{soil CO}_2}$ were present on the southern slope, covered by impervious material. Other high CO₂ flux values have been measured in small and limited zones surrounding wells.
- *Lot ex1- 2A* - All the area was characterized by low flux, except for small and limited zone surrounding wells.

A total diffuse soil CO₂ output of 76.5 ton/day, with upper and lower limits at 90% confidence of 89.6 and 66.8 ton/day, respectively, has been estimated for the entire surveyed area.

In order to characterize the biogas composition 7 sample from wells and 10 samples from gas soil have been collected and analyzed. The CH₄/CO₂ molar ratio in the biogas wells range between 1.59 and 1.40 with a mean value of 1.48 and standard deviation of 0.076, while the CH₄/CO₂ molar ratio presents in soil gas sample range between 0.01 and 1.74. For samples with an high CO₂ flux the CH₄/CO₂ ratio assumes values near to those measured for wells. A sample shows a CH₄/CO₂ ratio of 1.2, even if the CO₂ flux is quite low. Moreover some samples are not representative owing to the high amount of air present in the sample. On the other hand there is a sample that shows a CH₄/CO₂ ratio of 0.87 in spite of the high CO₂ flux and the low content of air. This fact can be due to a different age of waste and/or different nature. In the zone where grass is present the CH₄/CO₂ molar ratio is very low (0.1), then such areas do not contribute to the methane emission.

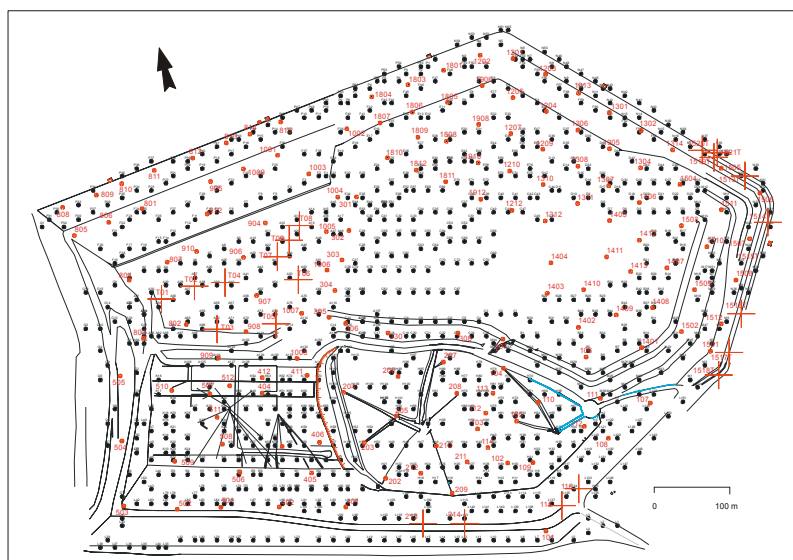


Fig. 4. Location of the measurement sites in the AMIAT landfill in 2001

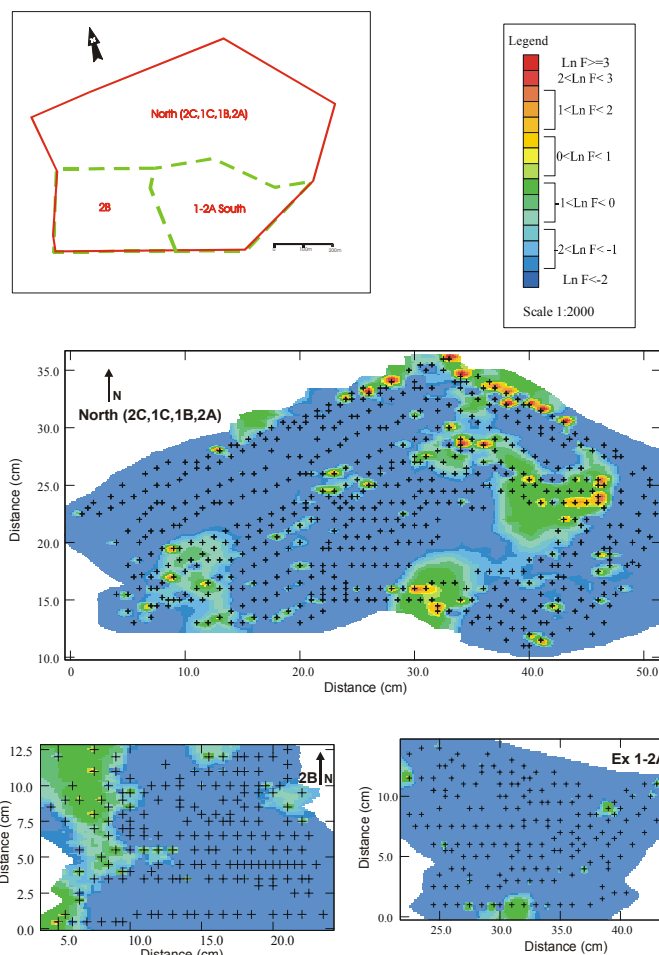


Fig. 5. Isoflux CO₂ maps of North zone, lot 2B and lot ex1-2A in 2001. For each map also the location of the measurement sites is shown.

The mean value representative of the CH₄/CO₂ molar ratio for the entire investigated area has been calculated averaging the value of wells and the values of soil gas sample with low oxygen content. In this way we have obtained a CH₄/CO₂ molar ratio of 1.49

Finally, a total diffuse biogas flux estimation of 118 ton/day was obtained for the air-soil interface (Tab. 2).

Tab. 2. Values of CH₄/CO₂ ratio and relative biogas flux (2001 survey).

	Average CH ₄ /CO ₂	CO ₂ flux Ton/day	CH ₄ flux Ton/day	Biogas flux Ton/day
<i>Nord</i>	1.49	71.1	38.2	109.3
1 e 2A	1.49	1.2	0.6	1.8
2 B	1.49	4.3	2.3	6.6
Total		76.6	41.1	117.7

Comparison between the two surveys

In order to evaluate the amount of diffuse emissions Tab. 3 has been drawn. This table also shows the summarizing results obtained in another MSW landfill – which we will name landfill A- where similar measurements have been carried out. These data are reported in Tab. 3 together with the specific fluxes measured in the “Basse di Stura” landfill in 1998 and in 2001:

Tab. 3. Comparison between 1998 and 2001 surveys.

Average specific flux (g m ⁻² g ⁻¹)	% of surface of landfill A	% of surface of Torino landfill in 1998	% of surface of Torino landfill in 2001
< 22	63.9	51.16	81.14
440	29.6	9.94	16.52
880	0	14.43	0.64
1320	6.53	7.03	0
1760	0	0	0

>1760	0	17.44	1.69
-------	---	-------	------

- a medium specific flux lower than 440 g/m²/day was emitted by 97.66% of soil in 2001 and by 60% of the same soil in 1998, while in landfill A that percentage of soil reached the value of 93.5% ;
- a medium specific flux in the range 880-1320 g/m²/day was emitted only by 7% of soil in 1998. No percentage has been pointed out in 2001, while in landfill A that percentage of soil reached the value of 6.5%. This range of medium-high specific flux is due to high permeability zones where usually fractures are present ;
- a specific flux higher than 1760 g/m²/day was emitted only by 1.7% of soil in 2001, while in 1998 the same flux was emitted by 17.4 % of soil.

Moreover we have taken into account that the high fluxes measured during the 2001 survey were recognized in a cultivated area and near several wells. These wells were not collected to the drainage system due to the heavy trucks transit.

The above presented and discussed comparison between the 1998 and the 2001 surveys prove the effectiveness of the remedial measures actions carried out in the framework of the AMIAT environmental program. These actions have required the increase the number of wells. In particular several slanting wells together with new pumping station have been realized. These latter allow to apply the correct depression on the whole available landfill body, thus also in areas under cultivation.

Conclusions

The whole "Basse di Stura" landfill area exhaled into the atmosphere 250 ton/day of CO₂ in 1998 and 76.5 ton/day of CO₂ in 2001. These results correspond, within bounds fixed by some inexactitudes of the various calculation methods, to a maximum quantity of biogas equal to 375 ton/day (300000 Nm³/day) in 1998 and 118 ton/day (96600 Nm³/day) in 2001.

As regards Torino landfill, some mathematical models theoretically foresaw a biogas production quantifiable to 250000 Nm³/day in 1998 and 277000 Nm³/day in 2001 (on the basis of AMIAT data). Data gathered in 1998 coincide, quantitatively, with those estimated with the accumulation chamber method.

Moreover, for what concern data collected in 2001, the difference among the biogas estimated by mathematical model (about 277000 Nm³/day) and the amount of biogas captured (152200 Nm³/day), is about 124400 Nm³/day; The estimation carried out with the accumulation chamber method points out that about 96600 Nm³/day was lost into the atmosphere.

Inspection of CO₂ flux distribution in a landfill soil carried out with this methodology allow to obtain very detailed maps in a very short time also in widespread areas as "Basse di Stura" landfill. Therefore this methodology appear to be very useful for monitoring biogas escape from soil.

Moreover this methodology allow to obtain useful information for optimum management conditions for the exploitation of biogas. In fact, during the two surveys, several anomalies in the capping around wells have been recognised and some of these wells have been drilled again.

In synthesis this monitoring method allow to highlights, with least effort, the areas where is possible to operate for reducing the amount of pollutant substances that can be responsible of health damage and greenhouse effect.

Acknowledgement- The instrument presented in this paper was realised by Institute of Geosciences and Earth Resources, CNR, Pisa, and Earth Sciences Department, Perugia University in co-operation with West Systems. The Authors wish to thank Giorgio Virgili of West System for his technical support.

References

- Armstrong M. (1984). Problems with universal Kriging. *Math. Geol.*, 16, n. 1, 101 – 108.
- Boone D.R., Bryant M.P., (1980). Propionate – degrading bacterium, *Syntrophobacter wolinii*, from methanogenic ecosystems. *Appl. Environ. Microbiol.*, 40, 626 – 632.
- Chauvet P., (1982). The variogram cloud. Johnson TB & Barnes RJ (Ed.) 17th APCOM, Society of Mining Engineers, New York, 757 – 764.
- Chauvet P. (1991). Aide mémoire de géostatistique linéaire. *Chaiers de Géostatistique, Fascicule 2. Ecole des Mines de Paris, Fontainebleau*, 210p.
- Chauvet P. (1993). Processing data with a spatial support: geostatistics and its method. *Chaiers de Géostatistique, Facicule n. 4, Ecole des Mines de Paris, Fontainebleau*, 57p.
- Chiodini G., Frondini F., Raco B. (1996). Diffuse emission of CO₂ from the Fossa crater, Vulcano Island (Italy). *Bull. Volcanol.*, 58, 41-50.
- Chiodini G., Cioni R., Guidi M., Marini L., Raco B. (1998). Soil CO₂ flux measurements in volcanic and geothermal areas. *Applied Geochemistry*, 13, 543-552.
- Clark I. (1979). *Practical Geostatistics*. Department of Mineral Resources Engineering, Royal School of Mines, Imperial College of Science and Technology, London, 129p.
- Czepiel P.M. Mosher B., Harriss R.C., Shorter J.H., McManus J.B., Kolb C.E., Allwine E., Lamb B.K. (1996a). Landfill methane emissions measured by enclosure and atmospheric tracer methods. *Journ. Geophys. Res.*, 101, 16711-16719.
- Czepiel P.M., Mosher P., Crill P.M., Harriss R.C. (1996b). Quantifying the effect of oxidation on landfill methane emissions. *Journal of Geophysical Research*, 101, n. D11, 721 – 729.
- Damiani A. and Gadolla M. (1984) "Gestione del biogas da discariche controllate" Ed. Istituto Per l' Ambiente

- David M. (1977). Geostatistical ore reserve estimation. Elsevier Amsterdam.
- Hinkle M. (1994). Environmental conditions affecting concentrations of He, CO₂, O₂ and N₂ in soil gases. *Applied Geochemistry*, 9, 53 – 63.
- Hinkle M., Ryder J.L., (1987). Meteorological variables and concentrations of helium, carbon dioxide, and oxygen in soil gases collected regularly at a single site for more than a year. U.S. Geol. Surv.. Open-File report. 87-449.
- Hinkle M., Ryder J.L., (1988). Effect of meteorological changes on concentration of helium, carbon dioxide and oxygen, in soil gases. *Soc. Mining Eng., SME Ann. Mtg. Phenix, Arizona Preprint number 88-9*.
- Journel A.G., Huijbregts Ch. J., (1978) Mining geostatistics, Academic Press.
- Kanemasu E.T. Power W.L., Sij J.W. (1974). Field chamber measurements of CO₂ flux from soil surface. *Soil Science*, 118,4, 233-237
- King C.Y., Minissale A. (1994). Seasonal variability of soil gas radon concentration in central California. *Radiat. Meas.*, 23, 683-692.
- Kirshop B.H., (1984). Methanogenesis. *CRC Critical Rev. In Biotech.*, 1, 109 – 159.
- Kising A.P., Socolow R.H. (1994). Human impact on the nitrogen cycle. *Physics Today*, 47-11, 24-31.
- Koch G.S. and Link R. (1970). Statistical analysis of geological data. Dover Publication, Inc., New York.
- Krause F., Bach W., Koomey J., (1989) . Energy Policy in the greenhouse, Vol1, IPSEP-EEB
- Krige D.G., (1951). A statistical approach to some basic mine valuation problems on the Witwatersrand. *J. Chem. Metall. Min. Soc. S. Afr.*, 52, 119 – 139.
- Kucera C., Kirkham D. R., (1971). Soil respiration studies in tall grass Prairie in Missouri. *Ecology*, 52, 912 – 915.
- Lieth H., Oullette R. (1962). Studies of the vegetation of the Gaspé peninsula II. The soil respiration of some plant communities. *Can. J. Bot.*, 40, 127-140.
- Lundengard H. (1924). Carbon dioxide evolution of the soil and crop growth. *Soil Science*, 23, 417-454.
- Mah R.A., Smith M.R., (1981). The methanogenic bacteria. *The Prokaryotes: A Handbook on Habitats, Isolation and Identification of Bacteria*, 1, 948 – 977.
- Manna L., Zanetti M.C., Genon G. (1999). Modeling biogas production at landfill site. *Resources, Conservation and Recycling*, 26, 1 – 14.
- Matheron G. (1962). *Traité de géostatistique appliquée*. Technip, Paris.
- Matheron G., (1965). Les variables Regionalisées et leur estimation. Masson, Paris, 305p.
- Matheron G., (1969). Le Krigeage universel. Fascicule n. 1, Les Cahiers du Centre De Morphologie Mathématique, Ecole des Mines de Paris, Fontainebleau, 83p.
- Matheron G., (1970). The theory of regionalized variables and its applications. Fascicule n. 5, Les Cahiers du Centre De Morphologie Mathématique, Ecole des Mines de Paris, Fontainebleau, 211p.
- McInerney M.J., Bryant M.P., (1980). Syntropic associations of H₂ utilizing methanogenic bacteria and H₂ producing alcohol and fatty acid – degrading bacteria in anaerobic degradation of organic matter. *Anaerobes and Anaerobic Infections*, Gustav Fisher Verlag, New York, 117 - 126.
- McInerney M.J., Bryant M.P., (1981a). Basic principles of bioconversions in anaerobic digestion and methanogenesis. *Biomass Conversion Processes for Energy and Fuels*. Plenum, New York, 277 – 296.
- McInerney M.J., Bryant M.P., (1981b). Review of methane fermentation fundamentals. *Fuels and Gas Production from Biomass*. Chemical Rubber Co. Press. West Palm Beach, Florida, 19 – 46.
- Parkinson K.J. (1981). An improved method for measuring soil respiration in the field. *J. Appl. Ecology*, 18,,221-228.
- Pinoul J.L., Baubron J.C. (1996). Signal processing of soil gas radon, atmospheric pressure, moisture, and soil temperature data: a new approach for radon concentration modeling. *J. Geophys. Res.*, 101, 3157-3171.
- Reimer G.M. (1980). Use of soil gas helium concentration for earthquake prediction: limitation imposed diurnal variation. *J. Geophys. Res.*, 85B, 3107-3114.
- Sichel H.S., (1966). The estimation of means and associated confidence limits for small samples for lognormal population. *Proc. 1966 Symp. South African Institute of Mining and Metallurgy*.
- Sinclair A.J., (1974). Selection of threshold values in geochemical data using probability graphs. *Journal of Geochemical Explorat.*, 3, 129 – 149.
- Sinclair A.J., (1991). A fundamental approach to threshold estimation in exploration geochemistry: probability plots revisited. *Journal of Geochemical Explorat.*, 41, 1 – 22.
- Thorstenson D.C., Polloch D.W., (1989). Gas transport in unsaturated porous media: adequacy of Fick's law. *Reviews of Geophysics*, 27, n. 1, 61 – 78.
- Tonani F., Miele G. (1991). Methods for measuring flow of carbon dioxide through soils in volcanic setting. Napoli '91. International Conference on Active Volcanoes and Risk Mitigation. Napoli, 27 August-1 September. (abstract).
- Trégourès A. et al., (1999). Comparison of seven methods for measuring methane flux at a municipal solid waste landfill site. *Waste Management Research*, 17, 453 – 458.
- U.S. Environmental Protection Agency, (2001). EPA-430-R01007 december 2001. www.epa.gov/outreach/ghginfo
- Wackernagel H., (1995). *Multivariate geostatistics*. Springer – Verlag, Berlin, 256p.
- West System Carbon dioxide flux meter handbook, release 3.0 (2001). www.westsystems.com
- Witkamp M., (1969). Cycles of temperature and carbon dioxide evolution from litter and soil. *Ecology*, 50, 922 – 924.
- Witman W.B., (1985). *Methanogenic bacteria. Archaeobacteria*. Academic Press, New York, 3 – 84.