Determination of emission factors from a landfill through an inverse methodology: experimental determination of ambient air concentrations and use of numerical modelling

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The control of odor episodes potentially generated by waste treatment activities near urban areas requires the identification of their origin together with the compounds that generate the odorous annoyance. In many occasions, the shortness of the odor episodes makes incapable to track their origin without a stable system of continuous control and analysis of ambient air. Hence, the cost of a network of control in areas with high emission potential of odorous compounds is generally expensive. The application of numeric modeling techniques in order to determine the impact of potentially emitting activities, such as landfills, in its surroundings is a very valuable tool for facilities management. However, the superficial emission factors data to be included in the models has to be reliable. Therefore, the determination of superficial emission factors for each of the potential sources of a landfill is a key aspect.

In this line, our laboratory has developed a methodology for the characterization of the emission profiles of the different sources present in landfills for emission factors determination, applying an indirect methodology. An exemplification of the methodology has been done in Can Mata landfill, located in Els Hostalets de Pierola, Catalonia, Spain. Can Mata is a landfill where approximately 900.000 tons of municipal and non-hazardous waste is buried annually. Biogas is recovered from the process, generating more than 40 million of m^3 of raw biogas per year. Ambient air concentrations at 1 m above the ground of volatile organic compounds (VOCs), hydrogen sulfide (H_2S) and ammonia (NH_3) were determined in three potentially emission sources and in biogas for the determination of emission factors:

- Front abocador: the zone of the landfill where waste is being buried
- Zona pre-clausurada: pre-closed zone of the landfill
  - Zona plana (Flat area)
  - Talussos (Slopes)
- Bassa de lixiviats: lixiviate reservoir recovered from the process
- Biogàs

Several points for each emission source were measured during different days, in order to obtain solid data. Particularly, 8 representative sampling points were measured in Zona-pre clausurada, 4 representative sampling points in Front abocador, and 3 representative sampling points in Bassa de lixiviats. Biogas was analyzed before and after desulfurization.

Multi-sorbent bed tubes were used for VOCs sampling. They were custom packed and composed of Carbotrap (activated graphitized black carbon, weak sorption strength, 70 mg), Carbopack X (activated graphitized black carbon, medium sorption strength, 100 mg) and Carboxen 569 (spherical carbon molecular sieve, high sorption strength, 90 mg). They were developed in an earlier study and found to be highly versatile regarding polarity and volatility of a wide range of target VOCs (Ribes et al., 2007). Additionally, they have been used for analysis of a large number of these compounds in superficial emission, biogas and outdoor air for several years (Gallego et al., 2014, 2015, 2016, 2017, 2018, 2019, Polvara et al., 2023). VOCs analysis was conducted through thermal desorption (TD) coupled with gas chromatography (GC) and mass spectrometry (MS) for a wide range of chemical compounds form diverse families, i.e. 105 compounds were quantified individually. H_2S and NH_3 were sampled and analyzed using Radiello passive samplers. Additionally, with the application of odour thresholds to the concentrations obtained in ambient air, the most critic compounds regarding odour annoyances were determined.

The obtained ambient air concentrations were used for the indirect determination, through numerical modelling using a dispersion model, of the emission factors. The present approach to emission factors determination is an alternative methodology to the traditional one that uses chambers for the assessment of these values. The use of superficial emission chambers can be sometimes influenced by specific characteristics of the sampling points, such as the compaction of the terrain, the presence of vegetation, etc. Hence, the application of this indirect method allows a more realistic determination of the emission factors, as real concentrations in ambient air are measured. The Eulerian model employed (TAPM, SCIRO, Australia) solves the fundamental fluid dynamics and scalar transport equations, and calculates the distribution of the different contaminants' concentration in a 3D grid, according to the meteorological conditions during the sampling period.

Regarding ambient air concentrations, Front abocador presented the highest Total VOC (TVOC) concentrations (699-3480 $\mu g/m^3$), followed by Bassa de lixiviats (258-571 $\mu g/m^3$). Finally, zona pre-clausurada was the emission source presenting the lowest TVOC ambient air concentrations (77-165 $\mu g/m^3$). Alcohols (24-38%), ketones (12-22%), carboxylic acids (15-23%), aldehydes (5-14%), aromatic hydrocarbons (3-13%) and terpenes (1-12%) were the most important families contributing to TCOV for all four sampling points. Concerning odours related to VOCs concentrations, the most important compounds contributing to odorous nuisances were ethyl butyrate (ester), acetic acid (carboxylic acid), biacetyl (ketone), acetaldehyde (aldehyde) and ethyl mercaptan (sulfur compound). Total Odour Units (O.U.) in respect to VOCs were 253-1814 O.U., 12-16 O.U. and 4-18 O.U. in Front abocador, Bassa de lixiviats and Zona pre-clausurada, respectively.

Highest H_2S and NH_3 concentrations in ambient air were found in Bassa de lixiviats, 0.8-1.1 mg/m^3 and 1.7-1.8 mg/m^3, respectively. Front abocador was the second point regarding concentrations, with H_2S and NH_3 values of 8,5-49 $\mu g/m^3$ and 33-49 $\mu g/m^3$, respectively. Zona pre-clausurada presented variable concentrations concerning these two compounds, depending on the specific point sampled. H_2S and NH_3 figures for this emission source were 5.3-79 $\mu g/m^3$ and 7.3-57 $\mu g/m^3$, respectively. O.U. in respect to H_2S were 1129-1609 O.U., 12-69 O.U. and 7-113 O.U. in Bassa de lixiviats, Front abocador and Zona pre-clausurada, respectively. Regarding NH_3, O.U. generated from this compound were only found in Bassa de lixiviats, with a value of 1 O.U.

All the experimental data were included in the cited atmospheric dispersion model in order to obtain the emission factors in g/s for each emission source and obtain a global emission factor for all the landfill.

The inclusion of the calculated emission factors to the dispersion model in order to obtain the impact of the landfill generated several impact maps very valuable for the management of the possible emissions of the facility. These impact maps presented yearly and monthly average and maximum concentrations and odours to be expected in the surroundings of the facility. Additionally, figures regarding concentrations and odours to be expected during the different months of the year and hours of the day have been also studied for critical receptors located near the landfill. All these data is very useful in order to plan maintenance or works which are expected to produce higher emission during periods of the year/hours of the day with the lowest impacts in its nearby inhabited areas.

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