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Source identification of odours and VOCs from a composting plant by multivariate analysis of trace volatile organic compounds

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The analytical difficulties in odour measurements are related to the well known complexity of our olfactory sensory perception. Still the importance of such an analysis in environmental pollution is, in certain fields, of primary importance, and there is a strong need of instrumental analytical technologies to quantify the odour to define objective odour policy criteria. There is a lack in the actual legislation in specific odour control procedure and this paper discusses about the possibility of using instrumental analysis, in conjunction with sensorial analysis, to characterize odour emissions in order to detect malfunctions in the facilities and to prevent air pollution and olfactive nuisance in the environment. We present here results from a study, performed during environmental odour episodes, in the area surrounding a composting plant and a MSW landfill. Odour episodes were perceived as far as 3 km downwind, where ambient air has been sampled. Results seem to suggest that the main odour sources, responsible for this episode, were related to the bio-oxidation building area. The pattern of organic compounds emitted from the odour abatement systems and from the close-by landfill appears statistically different from ambient air samples and were well separated by statistical multivariate analysis.

1. Introduction

The composting process is an aerobic degradation of organic materials with complex interactions between biological and physical-chemical factors. The process takes place in different steps, characterized by different temperatures and oxygen availability to the microorganisms present. The whole process, starting from waste receiving, mechanical preparation, separation, shredding, as well as bio-waste and MSW composting process itself, results in different volatile organic compounds (VOC) emissions. The VOCs emitted, beside solvents and other anthropogenic organic compounds present in the MSW, are actually intermediates in the degradation of aminoacids, fats, carbohydrates, and are responsible for the typical composting odour produced. Odour emission are probably the major drawback of these plants, and general population concern is high, and sometimes this is the limiting factor for new plants realization.

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Although several odour emission control technologies have been developed, no odour monitoring system is readily available to give an useful feedback, for the process manager, to control odour emissions. Instrumental techniques in environmental odour impact assessment, like electronic noses (Sironi et. al. 2007) and GC-MS (Davoli et. al. 2003) are generally used to partially quantify the odour, while the definitive assessment method, for odour concentration, seems to be dynamic olfactometry. Here a panel of certified experts tests the presence of "odour" to a diluted environmental air sample. The sample dilution ratio is decreased until the panellists "feel" the odour. The dilution value is the odour units of the sample. Olfactometry is described in a CEN normative (UNI-EN 13725:2004) and is being introduced in other countries.
Our research aims to develop analytical technologies to support a comprehensive odour management, for plants operations, that will minimize the negative impacts of environmental odour pollution. A chemical characterization of odours, also, allows a comprehensive description of organic compounds, in emissions and ambient air, with a toxicological impact. And this is useful to describe ambient air quality. In Italy, recently, the guidelines published by Regione Lombardia (DGR 16 Apr. 2003 - N. 7/12764) about composting plants construction and operation, recommended this approach to describe odour emissions from composting plants. In this paper results from a study performed during environmental odour episodes in the area surrounding a composting plant and a MSW landfill are presented.

2. Methods

The composting plants site is located in east central Italy, and has been used as a case study for the research. This composting plant accepts organic fraction of municipal solid waste. All principal points of emission, as well as selected process areas, have been sampled. Ambient air has been collected downwind both close to the plant and approximately up to 3 km away (fig. 1) from the composting plant, during environmental odour pollution events.
Odour sampling has been performed following the UNI:EN 13725:2004 guidelines, with Nalophan bags, and a battery operated pump used to evacuate a container, which allows the initially deflated bag to inflate ("lung" principle). In the bags an internal standard (deuterated p-xylene) is added in order to increase the analytical accuracy. Solid phase microextraction (SPME) concentration has been performed with a 2 cm, 50-30 μm, DVB/Carboxen/PDMS fiber (Supelco) exposed for 20 min at room temperature to the air samples in the bags.
Gas chromatography/mass spectrometry (GC/MS) analysis have been performed on an Agilent 5975 instrument with a Supelco CP624 0.22 mm i.d., 60 m length, capillary column with a 1.2 μm film thickness. Oven temperature was 1 min 40°C isothermal, then 4 °C to 140°C with a final hold time of 1 min. Head pressure was 40 kPa. The mass spectrometer was operated in scan mode, with a 33-350 m/z mass range. Compounds were identified by the library and individually checked to validate results.
Chemometrics is used to reduce the complex data set to perform sample classification, by multivariate principal components analysis (PCA) (Davoli et al., 2003).

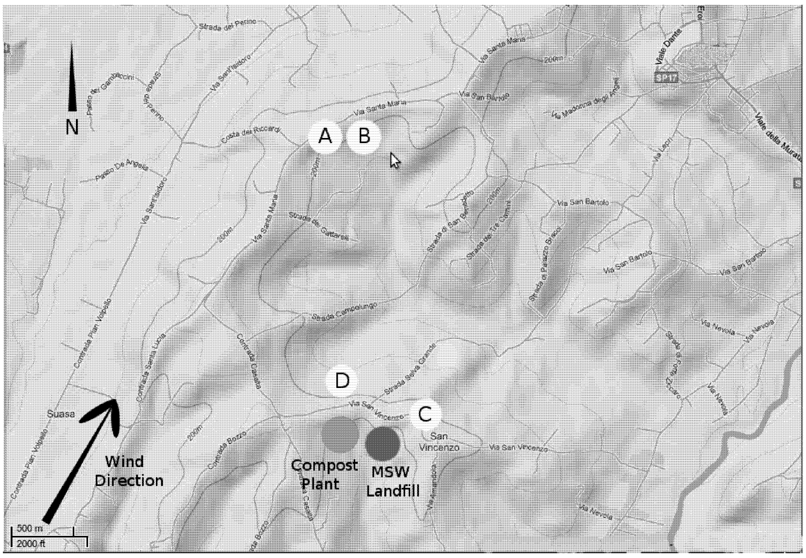

Fig. 1. Map of the area where the study has been carried out.

3. Results and discussions

VOCs analysis have been carried out in composting process samples (table 1), emissions and ambient air. Results show that total VOCs concentrations ranged from 11-46 ppbv in ambient air, to 478-2034 ppbv for process air and emissions (fig. 2), with the highest level in the bio-oxidation area and in the biofilter emissions. A large number of compounds has been identified in all samples, with concentrations ranging from 0.1 to 650 ppb. No carcinogenic compounds have been found at these levels. A chemical

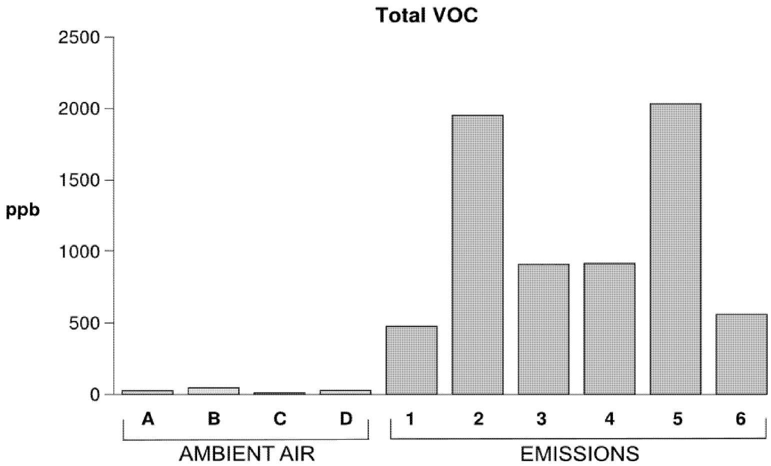

Fig. 2. Total VOCs concentration, expressed as ppbv, in all samples.

classification of all individual components identified (fig. 2) shows differences among samples. Main differences are about relative concentration of carbonyl compounds presence in process and emission samples, and hydrocarbons (both aliphatic and aromatic) in ambient air samples.

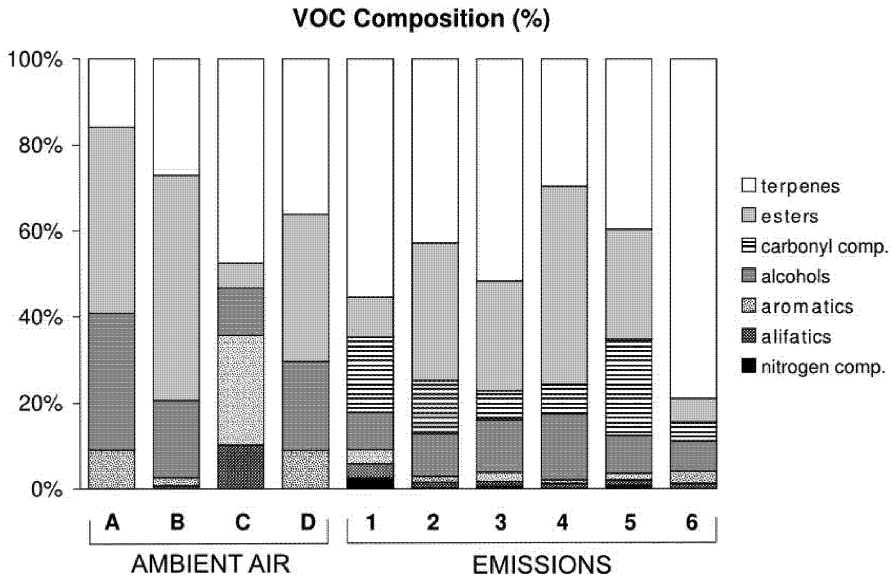

Fig. 3. Samples VOCs composition.

Principal component analysis, run on the data set as from fig. 3, shows how the first 2 components score plot separates sample from the blower area (air recycled inside the bio-oxidation building) is similar to all ambient air samples (A, B and D) and well separated from all other process steps.

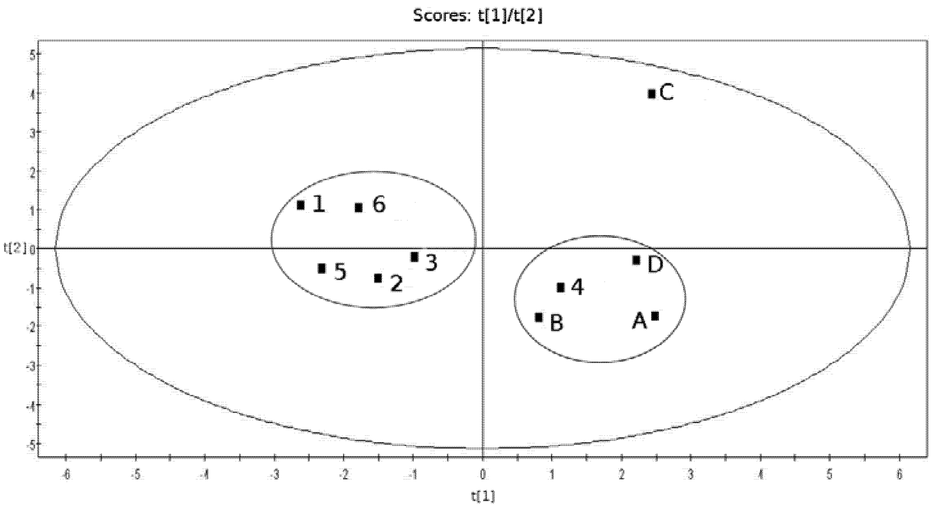

Fig. 4.. Principal component analysis of ambient air and emissions samples. Score plot for PC1 and PC2. For sample identification see Fig. 1 and Table 1.

Also ambient air collected just downwind the landfill (C) appears to be different from all collected samples, being separated both from the first and the second principal component (PC1 and PC2).
The loadings plot (fig. 3) shows how the variables (concentrations of classes of organic compounds) influenced the separation in the score plot.

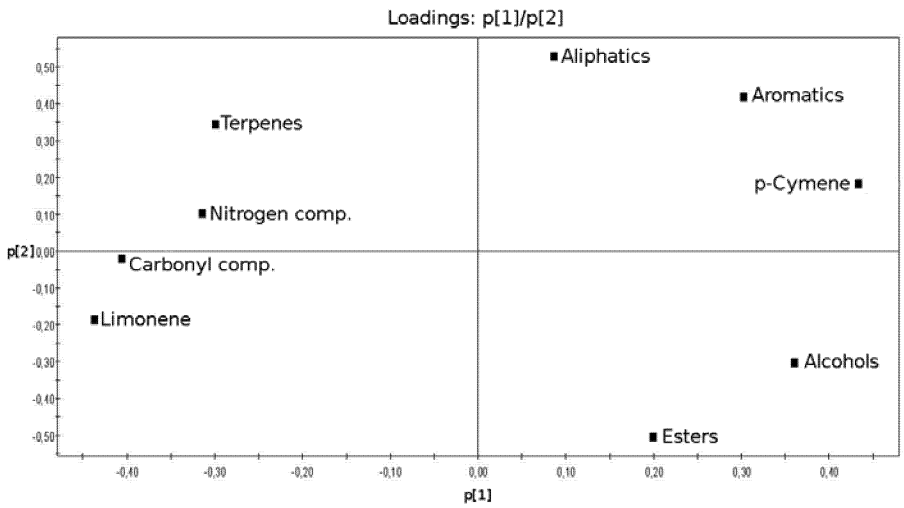

Fig. 5. Loading plots for the variables used.

Esters alcohols and terpenes, that represent the majority of the organic compounds produced in the aerobic process, are the variables that mainly influenced the separation between samples. The separation of the landfill air sample, on the second component, is due to the direct contribution of the variables p-cimene and, inversely, to limonene concentration. It is well known (6) that anaerobic fermentation (as in landfills, to produce landfill gas) is characterized by an high p-cymene to limonene concentration ratio, while in an aerobic process this ratio is very low, being limonene the main compound in the class of terpenes.
Looking at the second and third components (PC2 and PC3) score plot (fig. 4), again, all samples somehow related to the aerobic process, meaning the bio-oxidation building, the blowers and the biofilter inlets are similar to ambient air samples, while cured compost, biofilter emissions and landfill air are different and separated.

Table 1. Composting process emissions

Sample	*Process Description*
1	*OVERSCREEN STORAGE*
2	*BIO-OXIDATION BUILDING*
3	*BIO-OXIDATION CURING*
4	*BLOWERS BUILDING*
5	*BIOFILTERS INLETS*
6	*BIOFILTERS EMISSIONS*

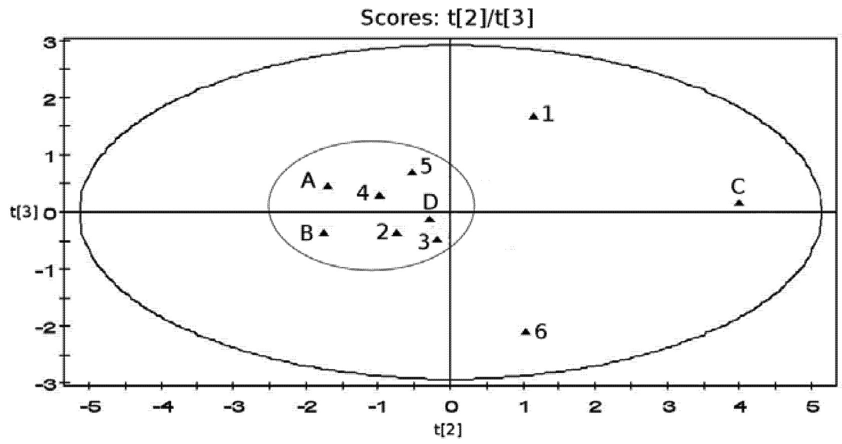

Fig. 6. Principal component analysis of ambient air and emissions, Score plot for PC2 and PC3.

The composting plant was new and a closer look at the bio-oxidation building, where the aerobic treatment and the first part of the curing process was taking place, showed that the roof of the building was not sealed with walls and air was freely flowing outside. As this air is the most contaminated with VOC, and the odour concentration is high (7) the idea is that this was the cause responsible for the environmental odour pollution episodes.

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