

# A first semi-quantitative study of the emission of volatile organic compounds after the application of organic amendments in the field

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## Abstract

This paper presents a first study of volatile organic compounds (VOC) emissions occurring after organic waste field application. An experiment was carried out on the QualiAgro site (Yvelines, 78, France) for 3 urban composts and 1 dairy farm yard manure. Different air VOC concentrations were determined by dynamically sampling air through a cartridge filled with Tenax: air background, soil background, and on each amended plot after application. Tests were performed on both sampling and chemical analysis. First results exhibited increasing air concentrations after application of organic products. Depending on the concentration of the background air, fluxes can be calculated using the inverse modelling approach using the model FIDES

## Introduction

VOC belong to various chemical families and their emissions can lead to health and environmental impacts. For instance they are involved in the chemistry of ozone and aerosols. If some sources like forests have been largely studied, there are few data on VOC emissions by agricultural sources and especially following application of organic waste products on cultivated fields. VOC emissions have been studied during the composting of organic wastes [1], but their emissions after field application are still largely unknown. This paper presents a semi-quantitative study of the emission of selected VOC after the application of urban composts and farm yard manure in the field.

## Material and Methods

### *Experimental set-up and VOCs studied*

An experiment was carried out in the long-term field experiment named “Qualiagro”. This site is located in Feucherolles (Yvelines, France, 50 km West of Paris, lat 48°53’47”N, long 1°58’20”E, alt 175 m) and has been set up in 1998 to study the agronomical interest and the environmental impacts of municipal waste compost recycling in agriculture as amendment field application [2]. It is a 6 ha disposal consisting in 4 blocs of 10 plots (45m\*10m) crossed with 5 organic treatments. The organic fertilizer application occurs generally in early September following the wheat harvest and preceding the corn implantation the spring after. VOC concentrations were monitored for 3 urban composts and 1 dairy farm yard manure: (1) a compost obtained from the composting of residual municipal solid wastes after selective collect of “clean and dry” packaging (RMSW); (2) a biowaste compost obtained from the composting of yard wastes mixed with the source separated organic fraction of municipal solid wastes (BIO); (3) a compost made from either yard wastes or other kinds of green wastes co-composted with municipal treatment plant sewage sludge (YWSS); and (4) a dairy cow farm yard manure, considered here as the reference organic amendment (FYM). The measured selected compounds presented in Table 1 were chosen following 3 criteria: (i) abundance measured during the composting process [1], (ii) affinity for the same trapping adsorbent and (iii) separation using the same stationary phase for gas chromatography analysis. Immediately after each organic fertilizer application, air was sampled at three locations in a simultaneous way: (1) the first one was sampled at 20 cm above the applied field (Fertilizer Tube), (2) the second one was sampled at 20 cm above an untreated field (Soil background), and (3) the last one was sampled at 2 m above ground apart from the experimental area (Air background). The VOC were trapped by pumping air through stainless steel tubes (L 110 mm × ID 4 mm) filled with Tenax TA (250 mg, Supelco) at 1.3 L min<sup>-1</sup> over 4 hours. This setup was the best compromise to (a) maximise the concentration of studied compound on the trap tube and (b) avoid breakthrough volume. The air volume sampled was measured with volumetric controllers (Gallius, Schlumberger). After sampling each TENAX tube was placed in a container and

stored at 4°C. VOC were extracted at 300 °C during 10 minutes on a thermal desorption unit (ACEM 900, Dynatherm inc.), separated by gas chromatography with a VF-624ms column (ID 0.25mm \* OD 0.39mm L 30m) for stationary phase, helium gas for mobile phase and using a gradient temperature in order to optimize the separation. Finally VOC were detected by mass spectroscopy (GS/MS (VARIAN, 3800 / Saturn 2000)). This analysis system is also equipped with an autosampler allowing the liquid injection of standard solution, solution for which VOC concentration are known.

**Table 1. Chemical characteristics of VOCs selected**

Compound Name	Benzene	Dimethyl disulfide (DMDS)	Toluene	Ethyl benzene	m/p Xylene	Nonane	o-Xylene	Styrene
CAS Registry number	71-43-02	624-92-0	100-88-3	100-41-4	108-38-3	111-84-2	95-47-6	100-42-5
Chemical Abstracts Service					106-42-3			
Molar Mass (g.mol <sup>-1</sup> )	78	94	92	106	106	128	106	104
Formula	C <sub>6</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8</sub> H <sub>10</sub>
Vapor pressure (Pa) 20°C	10e4	5.32e4	2.9e3	1e3	8e2	4.2e2	8e2	7e2

#### *Flux calculation*

The VOC fluxes were estimated using an inverse modelling approach with the FIDES model [3] further developed for sensors integration with time [4]. In inverse mode FIDES predicts the volatilisation fluxes given the local meteorological conditions and the concentration at one or several height above the emitting field. It has been positively evaluated against measured ammonia fluxes with the aerodynamic gradient method and the REA method [5] as well as against pesticide volatilization rate measured with the aerodynamic gradient method after application on bare soil [6]. In this study, FIDES was used to estimate VOC volatilisation fluxes. The flux was estimated by least-square optimisation between the measured and the modelled concentrations at the locations simultaneously.

#### *Metrological tests: chemical analysis and measurement confidence*

Preliminary tests concerning quantification limits and repeatability of chemical analysis of the compounds were carried out. The evaluation of limit of quantification is based on the analysis of the compounds signal-to-noise ratio. They have been evaluated in two ways: using (1) the data given by the acquisition software data of mass and (2) by carrying out independent calculations. The repeatability of the analysis was evaluated with standard solution. 10 µL were injected and analyzed under the same conditions as the sample tubes. The standard deviation and the average of the chromatographic peak surfaces were used to calculate the coefficient of variation of analysis method. Concerning the sampling step carried out during the field experimentation, the uncertainty of 5 systems of pumps and volumetric controllers was assessed in the laboratory by measuring the flow sampled by the same pump with 5 different volumetric controllers, and then by measuring the flow with the same volumetric controller sampled by 5 different pumps.

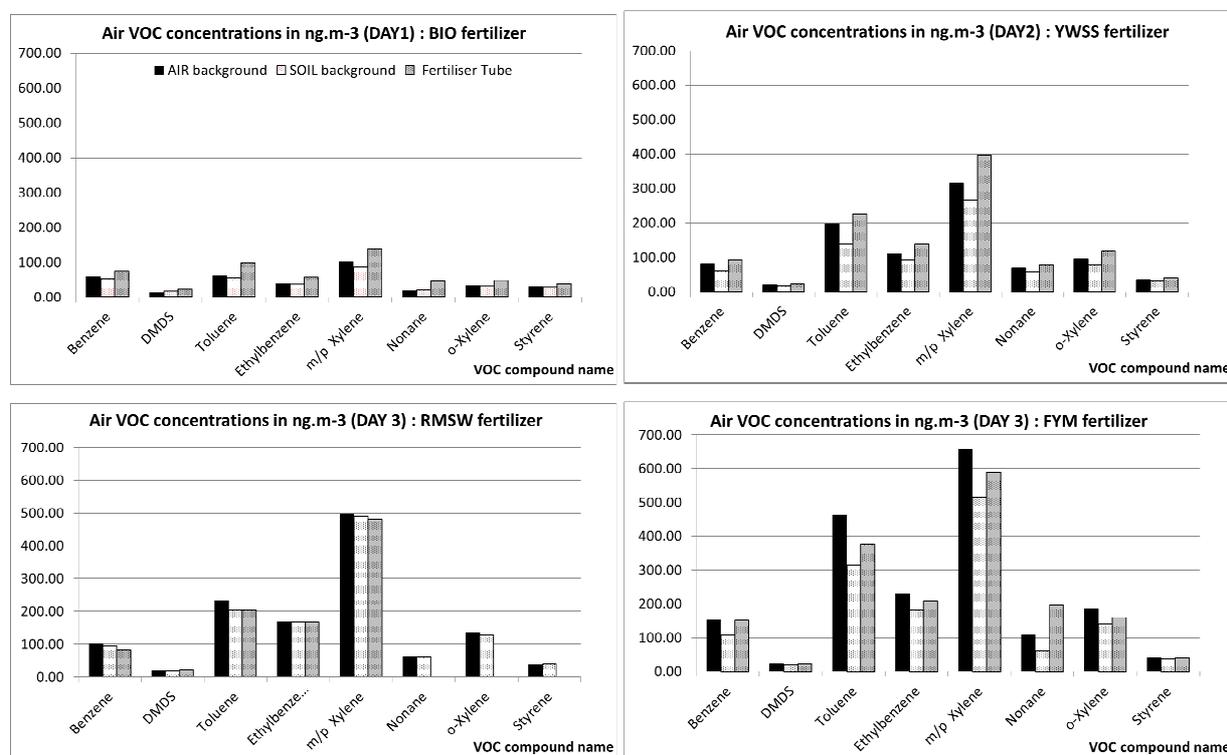
## **Results**

#### *Metrological results*

The repeatability of chemical analysis and the heterogeneity between sampling systems gave a percentage of confidence in the measurement ranging between 5 and 10% according to the studied compounds. About limits of quantification, the two calculating methods were in agreement, with limits of quantification after a liquid injection lower than 0.5 ng L<sup>-1</sup>.

## Experimental results

Air VOC concentrations obtained are showed in Figure 1.



**Figure 1. Air VOCs concentration (ng m-3) measured during Qualiagro experiment (Yvelines, France, 50 km West of Paris in September 2009)**

The Studied VOC were found in sample tube with concentration varying from 70 to 600 ng m<sup>-3</sup>. The level of VOC concentration at Soil and Air background locations were relatively high, with a Air background systematically higher than Soil background. The VOC concentrations were however higher in the Fertilizer Tube location than in background “Air and Soil” for the YWSS and BIO organic fertilizer. We therefore conclude that emissions of these studied VOC occurred during YWSS and BIO applications. We also note a significant concentration increase with time for the majority of compounds: the concentration was multiplied by a factor 4 for toluene for example between the first and third day following application. Compounds like DMDS or styrene showed constants concentrations with time. Thus, a different behavior depending on VOC membership of a chemical family can be observed. The fluxes data are still being analyzed, and will be presented at the conference.

## Conclusion and perspectives

First results exhibited increasing air concentrations following application of organic products. The accuracy of VOC concentration measurement was good enough to highlight differences between the 4 organic products applied. This study provides one of the first attempts to characterize VOC emissions after field application of organic amendments that would help to complete the environmental assessment of this practice. It helped identifying further required improvements for example : in the measurement chain as increasing the precision in doping tubes or integrating the thermal desorption process in the determination of the limits of quantification, in field sampling step modify the set up to better distinguish spatial and temporal emissions of each fertilizer organic application. It should be extended to other volatile organic compounds using a screening method and to other organic products recycled in agriculture in particular husbandry manure that produce nitrogenous VOC.

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