Characterization of volatile organic compound emissions from animal manure and their ozone reactivity

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RESUME

Les composés organiques volatils (COV) sont importants pour la production d'ozone et des précurseurs critiques des aérosols organiques secondaires dans l'atmosphère. Les activités agricoles telles que l'utilisation d'engrais minéraux, l'élevage et l'épandage de fumier animal contribuent à la pollution atmosphérique. L'épandage de fumier animal sur le sol est associé à divers polluants tels que les aérosols primaires, l'ammoniac et le sulfure d'hydrogène, ainsi qu'aux émissions de COV. Dans ce contexte, une étude expérimentale a été menée sur différents types de fumier (vache, cheval, brebis et chèvre) collectés à Grignon (Paris, France). Les échantillons ont été placés dans des chambres de simulation atmosphérique et les émissions en phase gazeuse de composés organiques volatils et leurs produits d'oxydation résultant de réactions d'ozonolyse ont été caractérisés par spectrométrie de masse. Plus de deux cents COV ont été détectés et quantifiés. Les familles de COV détectées comprenaient des composés oxygénés, azotés, soufrés, des composés azotées et oxygénées et des hydrocarbures. Les composés oxygénés se sont avérés être les COV dominants dans tous les échantillons. Lorsqu'ils sont exposés à l'ozone, seuls les échantillons de fumier de vache ont montré une réactivité due à la présence du scatole (C_9H_9N). Cependant, aucune formation de particules n'a été observée dans nos conditions expérimentales. Cela est principalement dû aux faibles émissions de SO_2 des échantillons, car le SO_2 et le scatole jouent un rôle clé dans la formation d'aérosols organiques secondaires. Les données expérimentales obtenues dans le cadre de cette étude aideront à améliorer les inventaires des émissions par les activités agricoles et fourniront des informations sur les COV d'origine agricole qui peuvent servir de précurseurs d'aérosols organiques secondaires en présence de photo-oxydants, comme l'ozone.

ABSTRACT

Volatile organic compounds (VOCs) are significant to ozone production and critical precursors of secondary organic aerosols in the atmosphere. Agricultural activities such as the use of mineral fertilizers, livestock production and land application of animal manure contribute to atmospheric pollution. Land application of animal manure is associated with variety of pollutants such as primary aerosols, ammonia, and hydrogen sulfide as well as VOC emissions. In this context, an experimental study was carried out on different animal manures (e.g. cow, horse, sheep, and goat) taken from Grignon (Paris, France). The samples were placed in atmospheric simulation chambers and the gas phase emissions of VOCs and their oxidation products resulting from ozonolysis reactions were characterized using mass spectrometric tools. More than two hundred VOCs were detected and quantified. The detected VOCs families included oxygenated compounds, nitrogen-containing compounds, sulfur-containing compounds, nitrogen and oxygen containing compounds and hydrocarbons. Oxygenated compounds were found to be the dominating VOCs in all samples. When exposed to ozone, only cow manure samples showed reactivity due to skatole (C_9H_9N). However, no particle formation was observed in our experimental conditions. This is mainly explained by low SO_2 emissions from the samples, as SO_2 together with skatole play a key role in secondary organic aerosol formation. The experimental dataset obtained in this study will help to improve emission inventories for agricultural activities and provide deeper insights into potential VOCs that can serve as secondary organic aerosol precursors in the presence of photo-oxidants (e.g. ozone).

MOTS-CLÉS: produits résiduaires organiques, composés organiques volatils, réactivité à l'ozone, aérosol organique secondaire, spectrométrie de masse

KEYWORDS: organic waste products, volatile organic compounds, ozone reactivity, secondary organic aerosol, mass spectrometry

1. Introduction

Agricultural activities affect local, regional and global air quality by variety of pollutants. Air pollutants emitted from agricultural activities are either gaseous pollutants such as methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and ammonia (NH_3) (López-aparicio et al., 2013), volatile organic compounds (VOCs) (Rincón et al., 2019) or particulate pollutants (Erisman et al., 2008; Ciuraru et al., 2021; Kammer et al., 2020). VOCs contribute to atmospheric photochemistry and interfere in stratospheric ozone depletion (Atkinson, 2000), tropospheric ozone production and formation of secondary organic aerosols (SOA) (Atkinson et al., 2004; Zhao et al., 2015). The strong emissions of NH_3 (Yao et al., 2018) and VOCs could potentially lead to strong SOA (Atkinson et al., 2004; Ciuraru et al., 2021; Kammer et al., 2020).The most frequent agricultural activities are

the use of mineral fertilizers, livestock production and land application of animal manure. Livestock management is considered the most significant source of NH_3 in the atmosphere and contributes to 34-40% of global NH_3 emissions (Schmithausen et al., 2018). The contribution of animal manure to environmental pollution received a great interest (Ciganek & Neca, 2008; Feilberg et al., 2010, 2017; Kammer et al., 2020; Yuan et al., 2017). Land application of animal manure is associated with variety of pollutants such as dust, bacteria, mold, endotoxins, NH_3, and hydrogen sulfide (H_2S) (Feilberg et al., 2017; Woodbury et al., 2014) as well as VOC emissions (Feilberg et al. 2010; Liu et al. 2011, 2018; Ni et al. 2012; ; Sun et al. 2008; Woodbury et al. 2014).

A large number of VOCs with different physico-chemical properties are emitted from agricultural areas (Harrison et al., 2006). Those VOCs are diverse in their molecular formulas and chemical groups, including sulfur and nitrogen containing compounds, carboxylic acids, alcohols, indoles, phenols, aldehyde and ketones, etc. Our understanding of these VOCs is very limited compared to other agricultural pollutants, like NH_3 or hydrogen sulfide (Ni et al., 2012; Feilberg et al., 2017). The oxidation of VOCs by their reactions with photo-oxidants (such as ozone, NO_x and OH radicals) in the troposphere leads to the formation of lower volatile organic products (Atkinson, 2000). The addition of oxygen and nitrogen to organic compounds reduces their volatility to several orders of magnitude (Atkinson, 2000; Lee et al., 2006). These semi-volatile organic compounds can efficiently initiate particle formation. The ability of a VOC to form SOA depends on its concentration in the atmosphere, its chemical structure and reactivity and on the volatility of its oxidation products (Williams, 1995).

Several studies focused on the VOC emissions and evaluation of their emission factors from manure samples, however, no work has been addressed to date on the reactivity of the emitted VOCs from manure with photo-oxidants such as ozone under controlled laboratory experiments. Accordingly, investigations of VOCs reactivity to ozone are needed to better constrain the potential role of VOCs as aerosol precursor and suggest possible chemical mechanisms that lead to new particle formation. The aims of our study were to identify and quantify the VOCs emitted from different animal manure samples using mass spectrometric measurements and to investigate the reactivity of emitted VOCs to ozone and their potential role in new particle formation.

2.   Laboratory analysis of animal manure samples

Four animal manure samples (cow, horse, sheep and goat) collected from a farm located in Grignon, western region of Paris (France) were analyzed. Experiments were conducted using ECOSYS simulation chambers combined to online and offline analysis of the gas phase. The experimental setup consists of atmospheric simulation chamber made of poly (methyl methacrylate) with Teflon film covered walls in a temperature-controlled room (0.03 m^3 and 0.18 m^3 chambers). A high purity dry air or atmospheric concentrations of ozone sweep the chambers with a controlled flow rate. The emitted VOCs and their oxidation products were identified online by proton transfer reaction quadrupole ion guide time-of-flight mass spectrometry (PTR-Qi-ToF-MS) and off-line by thermal desorption gas chromatography coupled to mass spectrometry (TD-GC-MS). In addition, a continuous monitoring of the amount of SO_2 emitted by the sample (model 43C, Thermo Environmental Instruments), ammonia NH_3 (Picarro G2103), CO_2 and H_2O (LICOR LI-840A) and O_3 was performed. The particle number concentration and their size distribution were measured using scanning mobility particle sizer (SMPS).

3.   Identification and quantification of VOCs

A dataset consisting of online and off-line gas-phase analysis was obtained for each type of animal manure. A well-developed data analysis protocol was followed to extract the qualitative and quantitative information for each analyzed sample. Figure 1 summarizes the results obtained for VOCs analysis by PTR-Qi-ToF-MS and TD-GC-MS techniques. The identification of the compounds by PTR-Qi-ToF-MS was based on molecular formula. Accordingly, the performed offline analysis gave more complete picture of the VOC emissions from our samples. The number of common compounds between both techniques (Figure 1,d) underlines the consistency of the identification process considering that those measurement techniques are independent. Detected VOCs by PTR-Qi-ToF-MS were classified according to the following chemical groups: hydrocarbons, oxygenated compounds, nitrogen-containing compounds, sulfur containing compounds, nitrogen and oxygen containing compounds, and halogenated compounds.
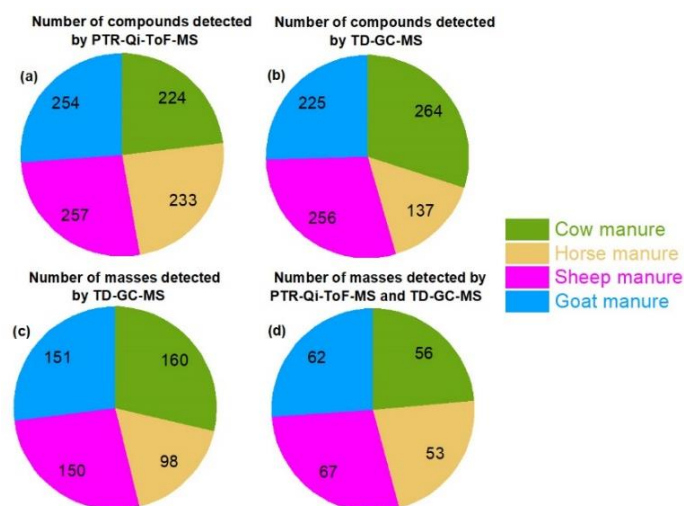
Figure 1: Results of animal manure gas-phase analysis. (a) Number of detected VOCs by PTR-Qi-ToF-MS, (b) number of detected compounds by TD-GC-MS, (c) number of detected masses by TD-GC-MS, (d) number of detected masses by both techniques.

The percentage contribution of each chemical group to total number of detected VOCs was estimated (Figure 2).The mixing ratio of detected VOCs by PTR-Qi-ToF-MS was calculated according to Cappellin et al., (2011). The results showed that oxygenated species dominated the detected VOCs. They represent the most abundant (Figure 2) and highest concentrated compounds in all manure samples. Accordingly, the oxygenated compounds are further classified by the number of oxygen atoms in the molecular formula. The obtained results demonstrated that cow manure is characterized by the highest contribution from oxygenated species containing two oxygen atoms, such as acids, esters, etc according to TD-GC-MS identification.
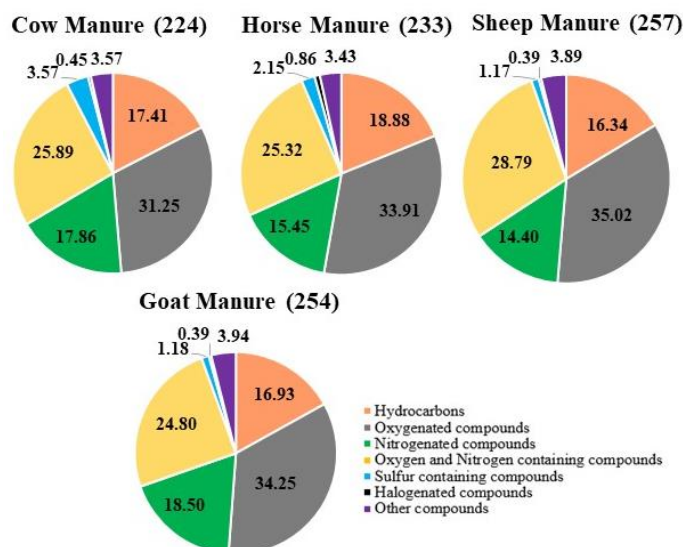

Figure 2: Percentage contribution of each chemical group to total number of detected VOCs by PTR-Qi-ToF-MS. The number between paranthesis represents the total number of detected compounds in each manure sample.

Principal component analysis (PCA) was applied to reduce the dimensionality of the data set and uncover hidden trends. We compared the gas phase emissions from all animal manure samples. The first two principal components account for ~ 89% of the variance and are enough to discriminate between all samples (Figure 3). The meaning of each component was derived using the contribution it receives from each detected species. We observe that cow manure is isolated from other manure types. The positive value of PC1 can be associated primarily with the contribution of oxygenated compounds "$C_nH_mO_p$" (e.g. alcohols, phenols, ketones, aldehydes, carboxylic acids, etc) and nitrogen containing compounds "$C_xH_yN_z$" (e.g. trimethyl amine and 3-methyl indole). It can be seen that the data points associated with cow manure samples are well separated by PC1 (~ 82 %) from the rest of manures. It is then possible to distinguish between the four types of manures based only on the contribution of oxygenated and nitrogen containing compounds. Horse and sheep manures seem to be very similar, while the goat manure is associated with an increased contribution of oxygen and nitrogen containing compounds "$C_nH_mO_pN_o$" and sulfur-containing compounds "$C_xH_yS_z$".
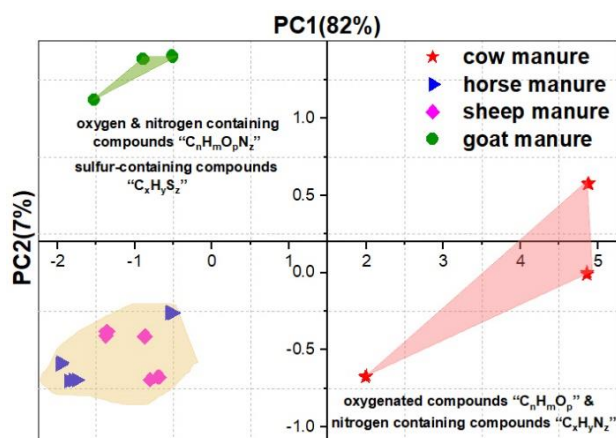
Figure 3: Score plot of the first two principal components (PC1_x-axis vs PC2_ y-axis) for gas phase emissions from animal manure samples. Each type of manure is designated by a color code. The chemical groups characterizing each component are highlighted.

4. VOCs reactivity to ozone

Among the analyzed samples, only the cow manure showed reactivity to ozone in our experimental conditions. Following the ozone addition into the chamber, the signal of 3-methyl indole (skatole) $C_9H_9NH^+$ at m/z 132.08 decreases within a few seconds of the initial exposure of cow manure to ozone. Along with, the signals of gas-phase oxygen and nitrogen containing molecules increased (m/z 136.07 $C_8H_9NOH^+$ and m/z 164.07 $C_9H_9NO_2H^+$). However, SMPS results showed no particle formation. It has been shown recently by Ciuraru et al., 2021 that the reaction of 3-methyl indole with ozone leads to new particle formation in the presence of SO_2. In our case, the absence of particle formation could be explained by the low amount of SO_2 emitted by the cow manure (i.e. ~ 4 ppb).Hydrocarbons represent around 13% of total VOCs mixing ratio in each manure sample. According to TD-GC-MS identification, most of hydrocarbons were unsaturated; some were alkenes, many aromatic hydrocarbons were detected, such as BTEX (benzene, toluene, ethylbenzene and xylene) and some polyclic aromatic hydrocarbons, as naphthalene and 1,7-dimethylnaphthalene for example. Typical hydrocarbons frequently attributed to biogenic origin (such as monoterpenes and sesquiterpenes) were also found reported in our samples. The structure of those hydrocarbons triggers their reactivity to ozone. However, under our experimental conditions, neither of emitted hydrocarbons showed notable reactivity to ozone. This might be linked either to low concentration of emitted compounds or to the short residence time in our chambers.

5. Conclusions

The chemical composition of VOCs strongly affects their ability to react with ozone and serve as aerosol precursors. It is therefore very important to identify the chemical nature of the VOCs emitted by organic waste products, animal manure in this work, in order to evaluate the aerosols formation. This study revealed that the four types of animal manure (cow, horse, sheep and goat) emitted a large spectrum of VOCs. The combination between different mass spectrometric techniques is essential to better characterize VOC emissions, especially from samples enriched with VOCs such as animal manures. The detected VOCs in all samples belong to different classes such as oxygenated compounds, nitrogen-containing compounds, sulfur-containing compounds, hydrocarbons, oxygen and nitrogen containing compounds, and halogenated compounds. Oxygenated VOCs were the most abundant compounds in all samples. The performed statistical analysis demonstrated that cow manure emissions are isolated from the other three types of manures. This separation is related to the contribution of oxygenated compounds and nitrogen containing compounds.

Concerning ozone reactivity, cow manure is characterized by the emissions of 3-methyl indole or skatole that showed reactivity to ozone unlike other types of animal manure analyzed. However, under these experimental conditions, no new particle formation was observed and this could be explained by low SO_2 emissions, which play a key role together with skatole in SOA formation. In addition, the detected hydrocarbons showed no reactivity to ozone which might be correlated to low concentrations or short reaction time under our experimental conditions. The experimental dataset obtained in this study will help to improve emission inventories for agricultural activities and provide deeper insights into potential VOCs that can serve as SOA precursors in the presence of photo-oxidants (e.g. ozone).

6. References and acknowledgements

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