

New particle formation from agricultural recycling of organic waste products

R Ciuraru^{1*}, J Kammer¹, C Decuq¹, M Vojkovic², K Haider^{1,2}, Y Carpentier², F Lafouge¹, C Berger¹, M Bourdat-Deschamps¹, I K. Ortega³, F Levavasseur¹, S Houot¹, B Loubet¹, D Petitprez⁴, C Focsa²

¹INRAE, Université Paris-Saclay, AgroParisTech, UMR ECOSYS, 78850, Thiverval-Grignon, France

²Univ. Lille, CNRS, UMR 8523, PhLAM – Laboratoire de Physique des Lasers Atomes et Molécules, F-59000 Lille, France

³Multi-physics for Energetics Department, ONERA Université Paris Saclay, F-91123, Palaiseau, France

⁴Univ. Lille, CNRS, UMR 8522, PC2A – Laboratoire de Physico-Chimie des Processus de Combustion de l'Atmosphère, F-59000 Lille, France

raluca.ciuraru@inrae.fr

Secondary organic aerosols (SOA) are one of the main uncertainty sources in the current understanding of the Earth's Climate. It is known that agriculture contributes to primary aerosols emissions but there is no estimate for the secondary organic aerosol formation from precursor gas phase. Organic waste products like sewage sludge are applied to cropland as fertilizers. In this work we show that sewage sludge is an unaccounted source of nucleation precursors (skatole, C₉H₉N). The skatole emission and nucleation rates due to ozone reactivity were determined in the laboratory. Based on our results, SO₂ plays a key role in the oxidation of skatole and leads to new particle formation. The results presented here provide new insights into this novel nucleation mechanism and aid our understanding of the organic waste agricultural recycling contribution to the aerosol balance in the atmosphere.

KEYWORDS: new particle formation, organic waste products, agricultural secondary organic aerosols, ozone reactivity

1.1. Evidence of new particle formation from sewage sludge

Atmospheric aerosols constitute a major concern for human health and impact Earth's radiative balance both directly and indirectly, through their influence on cloud properties. Atmospheric aerosols act as cloud condensation nuclei, thus altering cloud albedo, structure, and lifetime. They also represent a major health and economic issue since the particulate pollution is responsible for approximately 3 million premature deaths per year and projected to increase to 6 million in 2050 (Burnett et al., 2018). Volatile organic compounds (VOC), emitted into the atmosphere from anthropogenic and biogenic sources, are major players in atmospheric photochemical reactions that contribute to ozone formation. VOCs are also responsible for secondary organic aerosol (SOA) formation in the presence of photo-oxidants (Kroll & Seinfeld, 2008).

The recycling of different types of organic waste products (OWP) from livestock, urban or industrial sources is currently being promoted as a substitute for mineral fertilizers for agricultural land. The recycling of OWP represents also an alternative to waste management by landfilling or incineration. The OWP recycling in agriculture can increase the organic matter stocks in soil (Peltre et al., 2012) and thereby improve soil chemical fertility, stimulate microbial activity or increase water retention (Diacono & Montemurro, 2010). It also improves the recycling of nutrients and can decrease the use of mineral fertilizers (Gutser et al., 2005) which are non-renewable resources. However, the application of OWP to agricultural soils can present different health and environmental risks: some contaminants can accumulate in the soil, degrade water quality or be emitted into the atmosphere (Houot et al., 2002). In a peri-urban context, where the number of municipal wastewater treatment plants is continuously increasing through urbanization, the sewage sludge production increased by 50% in European countries from 1992 to 2005 and a further increase of the total sludge production is being expected in the upcoming years. Concerning the sludge final disposal, it has been shown that 53% of the production is used in agricultural application and composting (Kelessidis & Stasinakis, 2012).

Sewage sludge samples from a sewage treatment plant were introduced into a Teflon coated reaction chamber and exposed to ambient levels of ozone. Prior to each ozonolysis experiment, the chamber was carefully cleaned, and extremely low contaminant concentrations were established.

Upon the sample introduction into the chamber, a strong burst release of methylindole (m/z 132.087 C₉H₉NH⁺) was observed. Following the initial burst, sewage VOC signals stabilized. A production of NH₃ and SO₂ was also observed. NO_x mixing ratios were low (2-3 ppb) during the experiments. Within a few seconds of the initial exposure of sewage sludge samples to O₃ in the chamber, the signal of m/z 132.087 C₉H₉NH⁺ decreased and gas-phase oxygenated and nitrogen containing molecules increased, in particular m/z 136.075 C₈H₉NOH⁺ and m/z 164.070 C₉H₉NO₂H⁺ (Figure 1c). The ozone mixing ratio was continuously monitored into the chamber and remained at around 55 ppbv at the entrance of the chamber during each experiment. Particles appeared almost instantaneously after O₃ injection. The particle number and size distributions (Figure 1a) span the entire

measured size range from 2 to 64 nm electrical mobility diameters, therefore showcasing newly formed particles. During these experiments, the particle number concentration reached a maximum of 10^6 particles cm^{-3} within less than 2 min. This led to a particle nucleation rate up to $1.1 \cdot 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ during the new particle formation process. At longer reaction times, the particles grew in size and their number remained constant thereafter or slightly decreased probably due to coagulation and/or losses by adsorption to the walls.

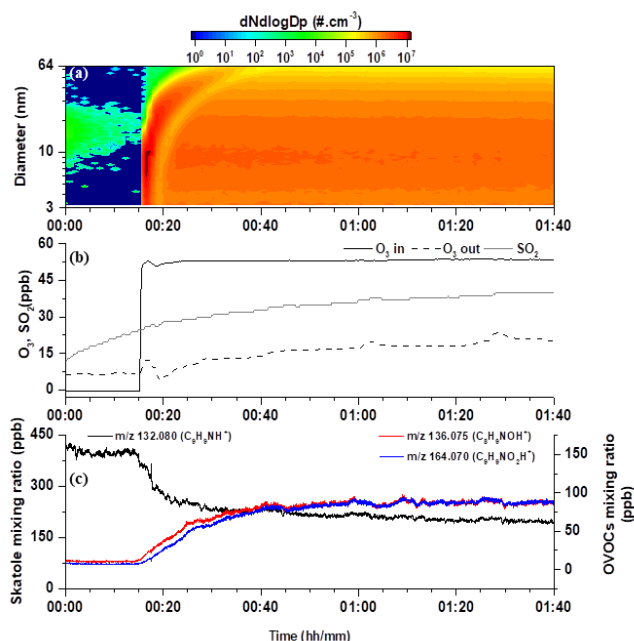


Figure 1. Typical sewage sludge ozonolysis experiment. (a) Temporal evolution of particle number concentration and size distribution. The ordinate represents the electrical mobility diameter (nm) and the color scale the particle number concentration. (b) Temporal evolution of O₃ entering the chamber (black line, O₃ in), O₃ measured at the exit of the chamber (black dotted line, O₃ out) and SO₂ (grey line). (c) Temporal evolution of m/z 132.080 C₉H₉NH⁺ (black line, left axis), m/z 136.075 C₈H₉NOH⁺ (red line, right axis) and m/z 164.070 C₉H₉NO₂H⁺ (blue line, right axis).

1.2. Identification of key players in new particle formation

A comparison of the VOC data measured with three independent techniques (proton-transfer reaction mass spectrometry - PTR-ToF-MS; gas chromatography coupled to mass spectrometry - GC-MS and ultra-high performance liquid chromatography coupled to high-resolution mass spectrometry - UHPLC-HRMS) was performed to identify the detected ions. The identification was based on each compound retention time and mass spectrum. The m/z 132.08 C₉H₉NH⁺ was identified as skatole. Skatole has been showcased as one of the major malodorous compounds contributing to the odor problem of animal production facilities and sewage treatment plants being emitted by bacterial degradation in slurry.

As shown in Figure 1 c, two oxygenated products were observed in the gas phase (m/z 136.075 C₈H₉NOH⁺ and m/z 164.070 C₉H₉NO₂H⁺) subsequent to ozonolysis reactions. These oxidation products contain the carbon skeleton of their precursor skatole. Gas chromatography analysis performed before and after ozonolysis and liquid chromatography performed on collected particles revealed that m/z 164.070 C₉H₉NO₂H⁺ corresponds to 2-acetyl phenyl formamide.

1.3. Ozonolysis mechanism

The reaction of ozone with skatole proceeds by the Criegee mechanism by an initial O₃ addition to the double bond to yield a primary ozonide which decomposes into two stabilized Criegee intermediates (Figure 2) (Donahue et al., 2011). Since the ozonolysis of skatole is taking place at the endocyclic double bond, the carbonyl oxide and carbonyl moieties that should be formed are attached together as part of the same molecule (Khan et al., 2018). The ozonolysis of endocyclic compounds may add several functional groups with no loss in carbon number leading further to the formation of secondary ozonides which has been shown to have an important contribution to SOA.

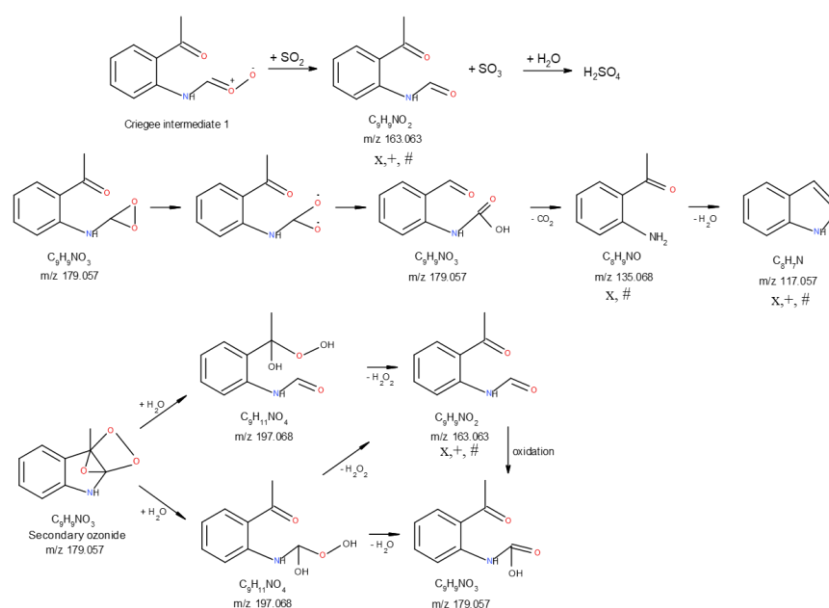


Figure 2. Proposed mechanism for skatole ozonolysis. The compounds marked with an x were detected by PTR-ToF-MS, those with + by GC-MS and those with # by UHPLC-HRMS.

1.4. Aerosol chemical composition

Generated aerosol chemical composition was studied using L2MS, SIMS and UHPLC-HRMS. A high number of oxidized and bifunctional species was detected on the filter-sampled particles. Overall, L2MS revealed the formation of oxidized compounds, not detected in the gas phase by PTR-ToF-MS or GC-MS. The observed compounds can be classified in different groups: a first group containing the carbon skeleton of skatole with insertion of oxygen atoms (e.g. C_9H_9NO , $C_9H_9NO_2$), a second one resulting from the ring opening due to successive oxidation processes (e.g. $C_9H_{17}NO$, $C_{11}H_{22}NO_2$), a third class with oxygen attached to the 6-member ring (e.g. $C_8H_{13}NO_2$) and finally a fourth one with nitrogenated compounds (e.g. $C_9H_9N_2$, $C_{11}H_{20}N_2$). Due to the presence of multiple double bonds in skatole, multiple ozonolysis reactions are possible and consistent with the observation that SOA continue to grow. All these reaction products might continue to evolve chemically leading to a decrease of organic volatility and a rapid partitioning to the particulate phase. The 2-acetyl phenyl formamide ($C_9H_9NO_2$) was also detected in the particulate phase by L2MS and UHPLC-HRMS and accounted for a large fraction of the identified products in the gas phase.

1.5. Atmospheric implications

This study gives new insights into the gaseous emissions and aerosol formation from organic waste products. It clearly points toward an impact of the processes at the air - soil interface.

It has been shown that the agriculture contributes to about 16% of the PM_{2.5} primary emissions and to ~18% of the PM₁₀ emissions (Aneja et al., 2009). However, there is no estimate for the secondary organic aerosol formation from precursor gases emitted by agriculture (Lelieveld et al., 2015). Recent studies show that aerosol formation in regions of intensive ammonia emission may have been underestimated. A large part of the gap between modeled and measured aerosol concentrations might be explained by these underestimated agricultural sources. Moreover, agricultural particles were thought to be generated during the specific operations and processes or secondary formed due to NH₃ emissions. In this study, a new particle formation mechanism from agriculture that does not involve ammonia is highlighted.

This study shows that indoles, and more specifically skatole, together with SO₂ emitted by sewage sludge, are the species pertinent to initiate reactions with atmospheric relevant ozone mixing ratios leading to particle nucleation and growth events. The indole compounds are present at field scale during spreading on agricultural surfaces. For example, skatole production and release of 4.91 - 8.3 $\mu\text{g m}^{-2} \text{min}^{-1}$ following land spreading of pig slurry (Liu et al., 2018) or land application of swine manure slurry (Parker et al., 2013) have been shown in the literature. Our emissions are estimated at around 50 $\mu\text{g m}^{-2} \text{min}^{-1}$ of skatole. Various reaction products were observed in the gas and particulate phases. Among them, 2-acetylphenyl formamide was identified as the main skatole ozonolysis product and formation pathways were proposed. Furthermore, the chemical analysis of particles shows that organic compounds contribute to growth in this size range. All these statements are supported by chamber measurements using commercially available skatole. The high reactivity of skatole towards ozone results in considerable enhancement of condensable reaction products that might partition into the aerosol phase and potentially act as cloud condensation nuclei (Kirkby et al., 2011).

1.6. Références et remerciements

This work was supported by the French national programme LEFE/INSU (ENGRAIS) no 1762C0001, INRA EA department programme “Pari Scientifique” and ADEME (RAVISA, no 1762c0006). This work also benefited from the support of the ANAEE-FR services 592 (ANR project n°11-INBS-0001).

- Aneja, V. P., Schlesinger, W. H., & Erisman, J. W. (2009). Effects of Agriculture upon the Air Quality and Climate: Research, Policy, and Regulations. *Environmental Science & Technology*, 43(12), 4234–4240. <https://doi.org/10.1021/es8024403>
- Burnett, R., Chen, H., Szyszkowicz, M., Fann, N., Hubbell, B., Pope, C. A., Apte, J. S., Brauer, M., Cohen, A., Weichenthal, S., Coggins, J., Di, Q., Brunekreef, B., Frostad, J., Lim, S. S., Kan, H., Walker, K. D., Thurston, G. D., Hayes, R. B., ... Spadaro, J. V. (2018). Global estimates of mortality associated with long-term exposure to outdoor fine particulate matter. *Proceedings of the National Academy of Sciences*, 115(38), 9592–9597. <https://doi.org/10.1073/pnas.1803222115>
- Diacono, M., & Montemurro, F. (2010). Long-term effects of organic amendments on soil fertility. A review. *Agronomy for Sustainable Development*, 30(2), 401–422. <https://doi.org/10.1051/agro/2009040>
- Donahue, N. M., Drozd, G. T., Epstein, S. A., Presto, A. A., & Kroll, J. H. (2011). Adventures in ozoneland: down the rabbit-hole. *Physical Chemistry Chemical Physics*, 13(23), 10848. <https://doi.org/10.1039/c0cp02564j>
- Gutser, R., Ebertseder, Th., Weber, A., Schraml, M., & Schmidhalter, U. (2005). Short-term and residual availability of nitrogen after long-term application of organic fertilizers on arable land. *Journal of Plant Nutrition and Soil Science*, 168(4), 439–446. <https://doi.org/10.1002/jpln.200520510>
- Houot, S., Clergeot, D., Michelin, J., Francou, C., Bourgeois, S., Caria, G., & Ciesielski, H. (2002). Agronomic Value and Environmental Impacts of Urban Composts Used in Agriculture. In U. D. D. H. Insam, N. R. M. Sc, & M. S. Klammer (Eds.), *Microbiology of Composting* (pp. 457–472). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-662-08724-4_38
- Kelessidis, A., & Stasinakis, A. S. (2012). Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. *Waste Management (New York, N.Y.)*, 32(6), 1186–1195. <https://doi.org/10.1016/j.wasman.2012.01.012>
- Khan, M. a. H., Percival, C. J., Caravan, R. L., Taatjes, C. A., & Shallcross, D. E. (2018). Criegee intermediates and their impacts on the troposphere. *Environmental Science: Processes & Impacts*, 20(3), 437–453. <https://doi.org/10.1039/C7EM00585G>
- Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., ... Kulmala, M. (2011). Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature*, 476(7361), 429–433. <https://doi.org/10.1038/nature10343>
- Kroll, J. H., & Seinfeld, J. H. (2008). Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmospheric Environment*, 42(16), 3593–3624. <https://doi.org/10.1016/j.atmosenv.2008.01.003>
- Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., & Pozzer, A. (2015). The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature*, 525(7569), 367–371. <https://doi.org/10.1038/nature15371>
- Liu, D., Nyord, T., Rong, L., & Feilberg, A. (2018). Real-time quantification of emissions of volatile organic compounds from land spreading of pig slurry measured by PTR-MS and wind tunnels. *The Science of the Total Environment*, 639, 1079–1087. <https://doi.org/10.1016/j.scitotenv.2018.05.149>
- Parker, D. B., Gilley, J., Woodbury, B., Kim, K.-H., Galvin, G., Bartelt-Hunt, S. L., Li, X., & Snow, D. D. (2013). Odorous VOC emission following land application of swine manure slurry. *Atmospheric Environment*, 66, 91–100. <https://doi.org/10.1016/j.atmosenv.2012.01.001>
- Peltre, C., Christensen, B. T., Dragon, S., Icard, C., Kätterer, T., & Houot, S. (2012). RothC simulation of carbon accumulation in soil after repeated application of widely different organic amendments. *Soil Biology and Biochemistry*, 52, 49–60. <https://doi.org/10.1016/j.soilbio.2012.03.023>