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R Ciuraru[1*], J Kammer[1], C Decuq[1], M Vojkovic[2], K Haider[1, 2], Y Carpentier[2], F Lafouge[1], C Berger[1], M Bourdat-Deschamps[1], I K. Ortega[3], F Levavasseur[1], S Houot[1], B Loubet[1], D Petitprez[4], C Focsa[2]

[1]INRAE, Université Paris-Saclay, AgroParisTech, UMR ECOSYS, 78850, Thiverval-Grignon, France
[2]Univ. Lille, CNRS, UMR 8523, PhLAM – Laboratoire de Physique des Lasers Atomes et Molécules, F-59000 Lille, France
[3]Multi-physics for Energetics Department, ONERA Université Paris Saclay, F-91123, Palaiseau, France
[4]Univ. Lille, CNRS, UMR 8522, PC2A – Laboratoire de Physico-Chimie des Processus de Combustion de l'Atmosphère, F-59000 Lille, France

Abstract

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 aerosol 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, as skatole (C_9H_9N). The skatole emission and nucleation rates up to $1.1x10^6$ cm^{-3} s^{-1} due to ozone reactivity were measured in the laboratory. Our results show that SO_2 plays a key role in the oxidation of skatole and leads to intensive new particle formation. Products of the ozone reactions with skatole and the possible ozonolysis reaction mechanism are discussed. This novel nucleation mechanism might aid our understanding of the organic waste agricultural recycling contribution to the aerosol balance in the atmosphere. Based on the measured particle emission flux, the sewage sludge spread surface area in France and the time before sewage sludge incorporation into the soil, a rough estimation for the annual quantity of particles generated by this agricultural activity is on the range of one ton, which represents ~0.03% of the total $PM_{1.0}$ emissions from agriculture and forestry in France. As the spreading is concentrated on a few days (mid-summer), these emissions may punctually be of high concern for local and regional air quality during that period of the year.

Introduction

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 [1]. 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 [2].

As stated by different model simulation and laboratory studies, the most important source of atmospheric aerosols, in terms of their number concentration and of climate-relevant particles, is new particle formation (NPF) and growth [3]. However, the nucleation mechanism leading to new particle formation remains not well understood. Sulfuric acid has been identified as a key compound in atmospheric new particle formation[4], but its concentration in the atmosphere is too low to explain observed nucleation rates, so additional compounds are needed[4]. Base compounds such ammonia[5] or amines[6] have been proven to stabilize sulfuric acid clusters, leading to nucleation rates similar to those observed in the atmosphere. In addition, is has been shown that Highly Oxygenated Molecules (HOMs) coming from oxidation of VOCs, can as well stabilize sulfuric acid clusters[7]. Furthermore, a recent study[8] found that HOMs are able to form particles without the participation of sulfuric acid.

Measurements have quantified the formation of these compounds from ozonolysis of monoterpenes [9] and modelling studies have quantified their formation in the atmosphere and their role in air quality [10,11]. However, our understanding of the processes of formation and aging of organic aerosols remains very limited but entirely necessary to improve the robustness of the models [12].

It is now well known that agriculture and its activities affect local, regional and global air quality and global climate by its significant ammonia (NH_3) and greenhouse gases (GHG) emissions but also through VOC and aerosol emissions [13]. In some regions (e.g. eastern USA, Europe, Russia and East Asia) agricultural emissions are estimated to be the largest relative contribution to $PM_{2.5}$ [14]. Agriculture represents also a major ground-level ozone sink [15]. A wide variety of pollutants and GHGs, especially nitrogen containing compounds, are emitted to the atmosphere from agricultural activities, including fertilizers use, farm machinery or livestock manure spreading. In particular, in France, agriculture is estimated to generate about one third of the annual particle emissions (e.g. from livestock housing and tilling activities), a number still highly uncertain [16]. While great efforts have been made to estimate GHG and NH_3 emissions from agriculture and explore ways to abate them, knowledge about other pollutants emitted by this sector is still scarce, in particular on SOA and VOC precursors. Agricultural activities involving fertilizers or pesticides are also known to emit VOCs with high SOA forming potential [14]. However, the current knowledge mainly accounts for the effect of ammonia on PM formation. A recent study [17] testing reduction scenarios of agricultural emissions showed that in many densely populated areas, $PM_{2.5}$ aerosols formed from gases released by fertilizer application and animal husbandry can dominate over the combined contributions from all other anthropogenic pollution. The authors showed that the impact of livestock and fertilizers on air quality is

very pronounced in Europe, where agricultural $PM_{2.5}$ is responsible for 55% of air pollution linked to human activities [17].

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 [18]. 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 [19] and thereby improve soil chemical fertility, stimulate microbial activity or increase water retention [20]. It also improves the recycling of nutrients and can decrease the use of mineral fertilizers [21] 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 [22]. 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 [23]. Concerning the sludge final disposal, it has been shown that 53% of the production is used in agricultural application and composting [24].

In spite of the continuously increasing number of atmospheric new particle formation measurements, we are still lacking regional observations of NPF processes. This is the case for agricultural areas where we have only limited understanding of the biosphere-atmosphere exchange of agriculturally emitted trace gases other than NH_3, whilst their contribution to secondary aerosol is missing [13]. The importance of agriculture on atmospheric NPF is expected to vary regionally, as well as over the course of the year.

Some studies already showed VOC emissions from organic fertilizers by laboratory measurements or small wind tunnel experiments [25,26,27]. To our knowledge, no work addressed to date their contribution to SOA. For instance, there are few studies dealing with VOC measurements from livestock fertilizers [27,28] or urban waste products [29,30], although such data are essential for a better understanding of the formation and fate of SOA from agricultural practice. Research on VOC emissions was demonstrated to be very challenging due to the large number of VOCs and their variation in physicochemical properties [31]. Our understanding of the chemistry of these VOCs is very limited compared to other agricultural pollutants, like NH_3 or, more recently, hydrogen sulfide [32,33]. However, a certain number of VOCs observed in organic waste are now established precursors for SOA, such as: sulfur compounds (e.g. dimethyl and diethyl sulfide) [28,34], terpenes (alpha-pinene, limonene) [30], nitrogen containing compounds, ketones and aldehydes [35], aromatic compounds [29,31,36].

Simulations and atmospheric observations show that almost all nucleation processes involve ammonia or biogenic organic compounds in addition to sulfuric acid [3]. Up to now, the agricultural secondary aerosol formation is thought to be mainly induced by nucleation of ammonia emissions [14]. Here we report atmospheric particle formation solely from oxidized organic molecules and SO_2, both emitted by sewage sludge. The focus of this work is to identify the molecules that form new particles from sewage sludge and to understand the mechanism underlying particle formation and their initial growth. To the best of our knowledge, this is the first time these aerosol formation phenomena have been observed and quantified in an agricultural system.

Results

Evidence of new particle formation from sewage sludge

Sewage sludge samples from a sewage treatment plant were introduced into a Teflon coated reaction chamber and exposed to ambient levels of ozone (Supplementary Figure S1). Prior to each ozonolysis experiment, the chamber was carefully cleaned, and extremely low contaminant concentrations were established (Supplementary FigureS2). Upon the sample introduction into the chamber, a strong burst release of methylindole (m/z 132.087 $C_9H_9NH^+$) was observed. Following the initial burst, sewage VOC signals stabilized. A production of NH_3 and SO_2 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 O_3 in the chamber, the signal of m/z 132.087 $C_9H_9NH^+$ decreased and gas-phase oxygenated and nitrogen containing molecules increased, in particular m/z 136.075 $C_8H_9NOH^+$ and m/z 164.070 $C_9H_9NO_2H^+$ (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 O_3 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 lead to a particle nucleation rate up to $1.1x10^6$ cm^{-3} 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. This behavior of particle number concentration and size distribution was observed to be constant for experiments as long as five hours.

Interestingly, the ozone was not completely consumed during the experiment, which means that only around 20 ppb of O_3 were needed for the ozonolysis to form particles. Additional experiments performed in high excess of ozone (250 ppb) did not show any difference in particle number and size distribution. This may indicate that the reaction is limited by the residence time (5 min) inside the chamber. A fast but not complete consumption of m/z

132.087 $C_9H_9NH^+$ was also observed and the reaction products reached a plateau in less than 15 min. This may be due to the high kinetic rate constant of m/z 132.087 $C_9H_9NH^+$ reaction with ozone but might also indicate that the oxidation can occur in both gas and condensed phases (walls, sewage sludge surface or secondary aerosols).

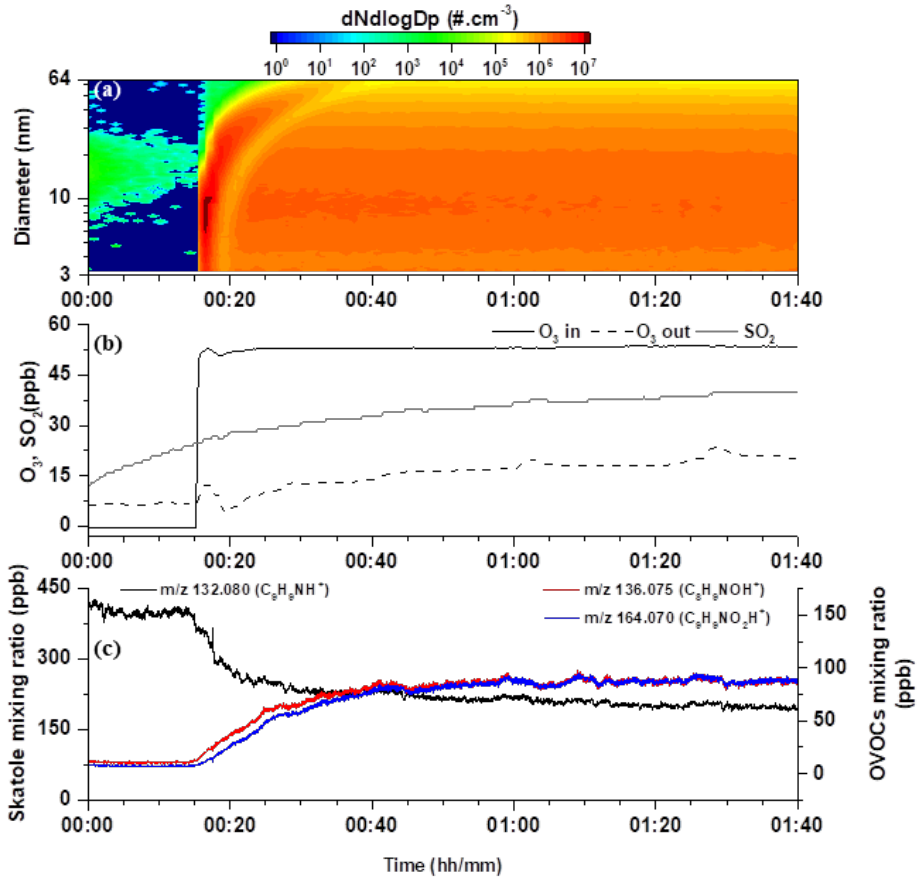


Figure 1. Typical sewage sludge ozonolysis experiment. (a) Temporal evolution of particle number concentration and size distribution. The ordinate represents the electrical mobility diameter (nm) and the color scale the particle number concentration. (b) Temporal evolution of O_3 entering the chamber (black line, O_3 in), O_3 measured at the exit of the chamber (black dotted line, O_3 out) and SO_2 (grey line). (c) Temporal evolution of m/z 132.080 $C_9H_9NH^+$ (black line, left axis), m/z 136.075 $C_8H_9NOH^+$ (red line, right axis) and m/z 164.070 $C_9H_9NO_2H^+$ (blue line, right axis).

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 $C_9H_9NH^+$ 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 [32,37]. Indoles belong to an important class of atmospheric VOCs with high emissions from land spreading of organic waste products to the atmosphere and contribute to odor nuisance [27,38].

It was reported that indoles and skatole are very reactive nucleophiles and easily undergo electrophilic substitution reactions [39]. Only one study reported the reaction rate constant in aqueous phase for skatole with ozone at pH=6.7 as being 4.5×10^6 M^{-1} s^{-1} [40]. The authors reported a stoichiometric factor of 0.9 meaning that 1 mol of ozone is needed for ozonation of 0.9 mol of skatole [40], the reaction rate constants of the indolic compounds in water increase with pH. A rough estimation of the rate constant, using skatole experiments, has been performed. We estimated the rate constant of 5×10^{-15} cm^3 mol^{-1} s^{-1}. Such a rate constant would confirm that skatole is a very reactive compound towards ozone, leading to a lifetime of around 3 minutes at typical ozone ambient concentrations. This is a higher reactivity than what was reported for indole (5×10^{-17} cm^3 mol^{-1} s^{-1})[41], or the well-known alpha-pinene system (1×10^{-16} cm^3 mol^{-1} s^{-1})[42], but lower than a few alkenes such as the alpha-terpinene or beta-caryophyllene.

As shown in Figure 1 c, two oxygenated products were observed in the gas phase (m/z 136.075 $C_8H_9NOH^+$ and m/z 164.070 $C_9H_9NO_2H^+$) 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 $C_9H_9NO_2H^+$ corresponds to 2-acetyl phenyl formamide.

Multiple other VOCs were emitted by the sewage sludge samples. For example, acids (e.g. formic acid), alcohols (e.g. methanol, butanol), aldehydes and ketones (acetone, butanone, acrolein) or sulfur containing compounds (e.g. dimethyl sulfide, hydrogen sulfide) were measured but most of these VOCs react very slowly with ozone. Isoprene and monoterpenes have been also measured by PTR-TOF-MS in our experiments. However, all the ion signals were carefully verified and the only decreasing ion that was observed, based on the PTR-TOF-MS measurements, was the one of skatole. We cannot fully exclude that other VOCs might play a role in the particle formation but, from our experiments, skatole is the only VOC that has been evidenced as aerosol precursor.

Proposed ozonolysis mechanism

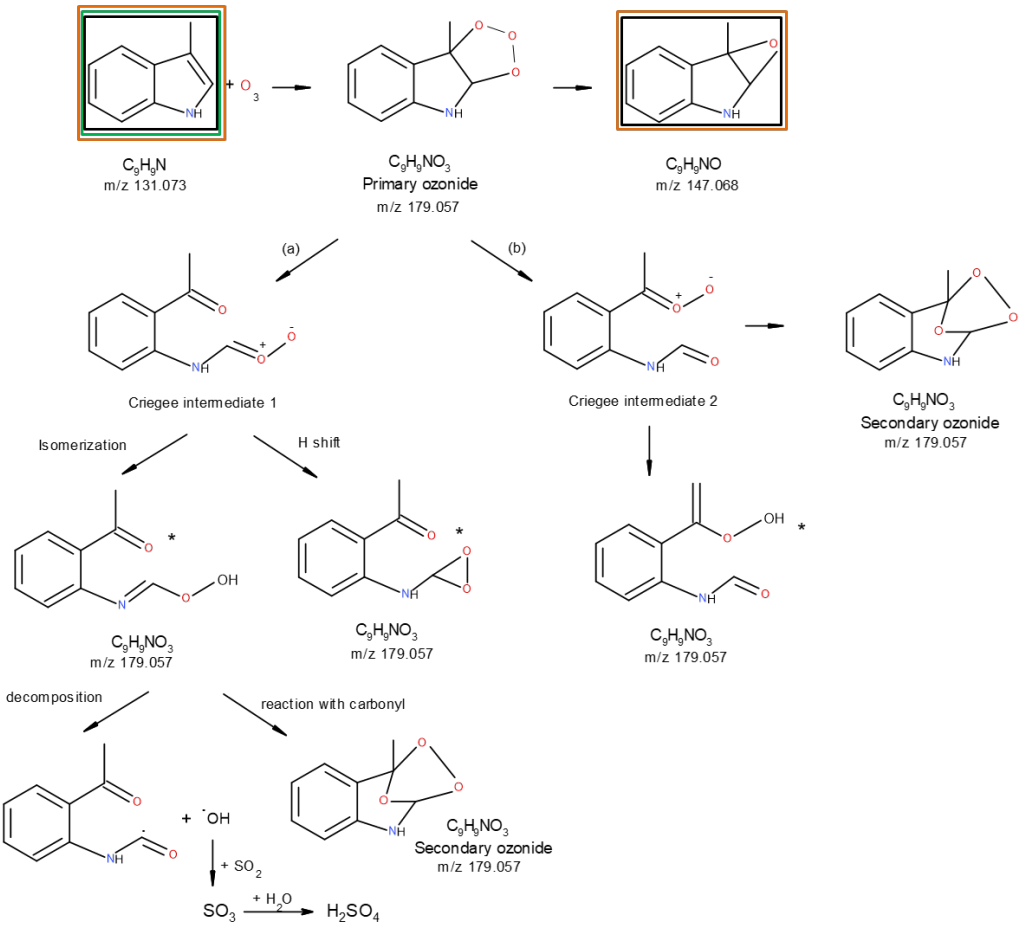
The reaction of ozone with skatole proceeds by the Criegee mechanism by an initial O_3 addition to the double bound to yield a primary ozonide which decomposes into two stabilized Criegee intermediates (Figure 2)[43]. Since the ozonolysis of skatole is taking place at the endocyclic double bound, the carbonyl oxide and carbonyl moieties that should be formed are attached together as part of the same molecule [44,45]. 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 [2].

The primary ozonide has two possible channels: decomposition by cycle cleavage of the O-O bond distal from the methyl group (a) or cleavage of the O-O bond proximal to the methyl (b). The first intermediate can undergo hydrogen shift reactions to form ketonic hydroperoxides or can isomerize to form a dioxirane[43]. The second intermediate leads to aldehydic hydroperoxides or cyclizes to form a secondary ozonide. Both can form a secondary ozonide via recyclization [43,45] (Figure 2). The further decomposition of of the O−OH bond in the hydroperoxides, which are thermally unstable[47], will lead to organic and OH radicals formation [48]. On the other hand, the Criegee intermediate 1 can react with a carbonyl and form the secondary ozonide $C_9H_9NO_3$ (m/z 179.057)[43]. The first intermediate can oxidize SO_2 and form the 2-acetyl phenyl formamide $C_9H_9NO_2$ (m/z 163.063) and SO_3. Hydrolysis of SO_3 leads to the further formation of H_2SO_4. It has been shown that reactions of Criegee intermediates formed in ozonolysis of certain alkenes with SO_2 can be significantly fast [49]. It has also been shown that this reaction is characterized by 97% collisional stabilization and only a few percent of ring opening and SO_3 formation[50]. The secondary ozonide ($C_9H_9NO_3$) can react with water to form a molecule possessing an aldehyde or a ketone group and a hydroxy-hydroperoxide group (Figure 2). The latter compound can lose H_2O_2 and form the 2-acetyl phenyl formamide. Further oxidation of this compound leads to an oxocarboxylic acid evidenced on the aerosol surface by two-step laser mass spectrometry (L2MS). Another possibility is that the hydroxy-hydroperoxide group loses water and thus 2-acetyl phenyl formamide is directly formed. Skatole oxide was also observed in the gas phase due to the ozonolysis reaction (m/z 148.075 $C_9H_9NOH^+$). It is now known that oxidation of SO_2 by stabilized Criegee intermediates represents a significant source for atmospheric sulfuric acid production via SO_3 formation. The SO_3 reacts very rapidly with water vapor to form H_2SO_4 [49] which is a key atmospheric nucleation species [45].. The production of OH radicals during the ozonolysis of the indole will drive further chemistry, including oxidation of SO_2 to H_2SO_4 [49]. Various field measurements and modeling studies showed that stabilized Criegee intermediates could make a significant contribution (from 10 to 70%) to SO_2 oxidation [44]. It has been shown that oxidation of SO_2 by stabilized Criegee intermediate is a significant source for atmospheric sulfuric acid production in VOC-rich environments [45]. The SO_2 emitted by the sewage sludge samples will react then with Criegee intermediates to produce sulfuric acid. Moreover, SO_2 can also partition into aerosol to form HSO_3^- that can further react with organic peroxides generated by skatole ozonolysis. This mechanism is consistent with literature data [51] and with the presence of this type of species on our collected particles. Secondary ion mass spectrometry (SIMS) surface analysis performed (in negative ion polarity) on the newly formed particles

collected on quartz filters during ozonolysis reactions revealed the presence of the characteristic H_2SO_4 peaks such as SO_3^- and HSO_4^- (Supplementary Fig. S4). We note that SO_3^- and HSO_4^- ions were also detected in the sewage sludge bulk samples by SIMS (Supplementary Fig. S5). No sulfur containing organic compounds were detected in the present study,but it cannot be excluded that organosulfates may have fragmented in the SIMS, contributing to the observed SO_3^- signal.

Another important channel is the reaction of stabilized Criegee intermediates with water, leading to the formation of α-hydroxy hydroperoxides, organic acids, ketones and aldehydes, SO_2, NOx, H_2O_2 [44]. These reactions may also represent a significant source of OH and HOx radicals [43]. The observed products can therefore arise from the reaction of both ozone and OH radicals with these compounds.



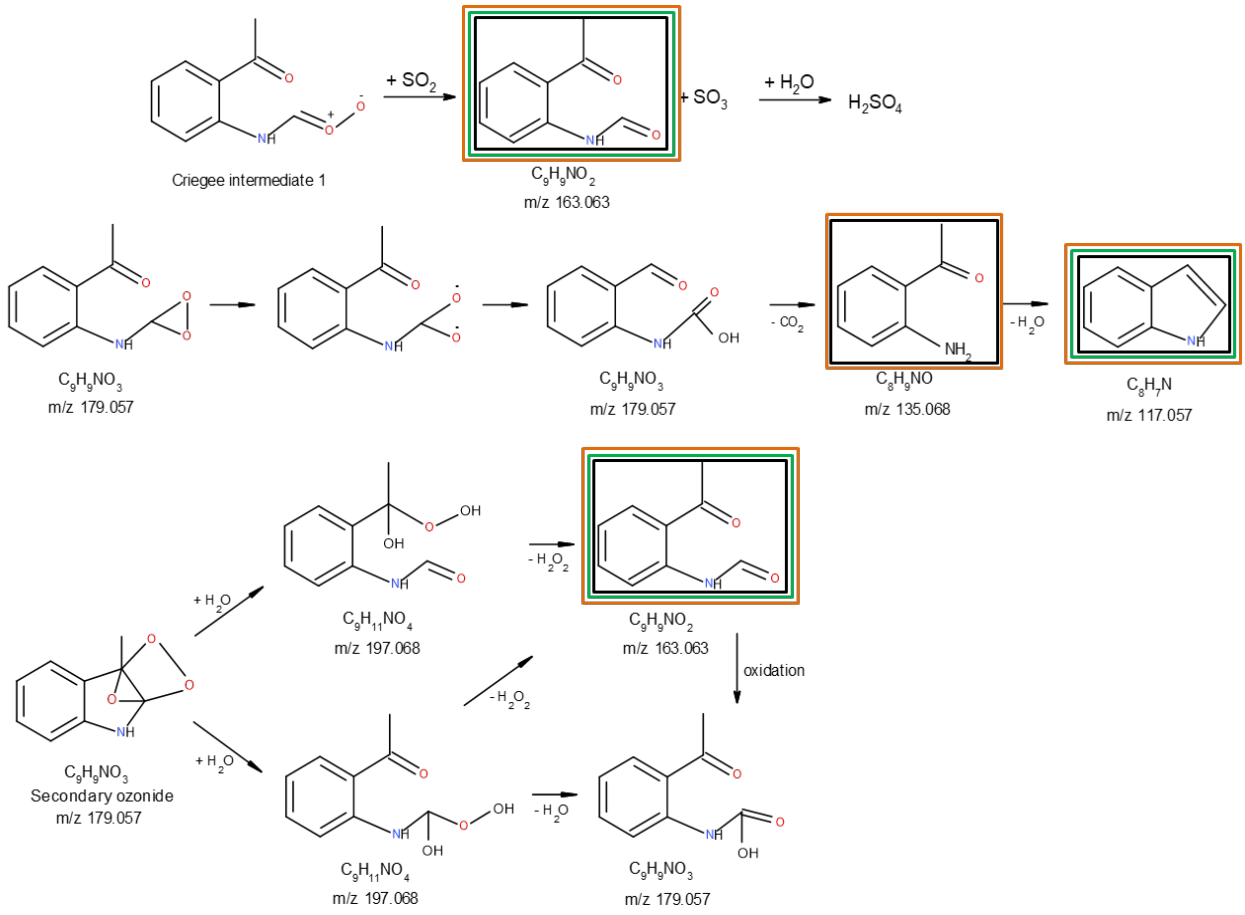


Figure 2. Proposed mechanism for skatole ozonolysis. The compounds detected by PTR-ToF-MS are framed with black, those detected by GC-MS with green and those by UHPLC-HRMS with orange in the mechanism.

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, $C_9H_9NO_2$, $C_9H_9NO_3$), 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. $C_9H_9N_2$, $C_{11}H_{20}N_2$, $C_{14}H_{21}N_2$) (Supplementary Fig. S6). 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.

Furthermore, some other experiments performed on non-SO_2 emitting sewage samples showed no particle formation following skatole ozonolysis (Figure 3). In light of these results, we are advancing a binary reaction mechanism of organics and SO_2 via sulfuric acid formation.

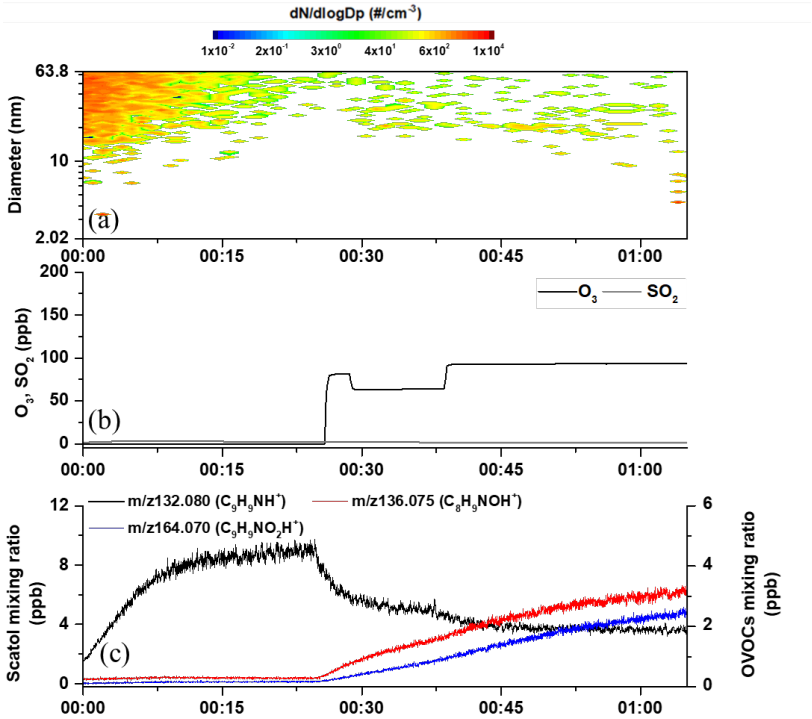


Figure 3. Non emitting SO_2 sewage sludge ozonolysis experiment . (a) Temporal evolution of particle number concentration and size distribution. The ordinate represents the electrical mobility diameter (nm) and the color scale the particle number concentration. (b) Temporal evolution of O_3 entering the chamber (black line, O_3 in), and SO_2 (grey line). (c) Temporal evolution of m/z 132.080 $C_9H_9NH^+$ (black line, left axis), m/z 136.075 $C_8H_9NOH^+$ (red line, right axis) and m/z 164.070 $C_9H_9NO_2H^+$ (blue line, right axis).

Several studies performed on sewage sludge samples or sewage sludge compost showed the presence of different inorganic and sulfur organic compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide) produced by anaerobic microorganisms. Sulfur-containing compounds are also produced by bacteria through the reduction of sulfate and S-containing amino acids[52,53]. Amino acids are the monomers of protein that have been shown to be present in protein extracted from activated sludges and anaerobically digested sludges. Organic sulfur compounds from dewatered biosolids can be generated by the degradation of sulfur-containing amino acids and methylation of sulfide and methanethiol. Furthermore, the thermal utilization of sewage sludge leads to the emission of pollutants in the form of sulfur dioxide[53] and it has also been shown that sewage sludge can contain high concentrations of sulphur compounds and emissions of sulphur dioxide (SO_2)[34]. H_2S reacts rapidly with OH radicals with a rate constant of 4.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}

and form SO_2. It is possible then that the SO_2 is formed by these reactions in our system. On the other hand, the reaction of H_2S with ozone is too slow to form SO_2 in our experiments[54].

Testing the skatole new particle formation hypothesis

To verify this hypothesis, we designed an experiment in which skatole reactivity was measured in the empty chamber. The goal was to test the effect of O_3, SO_2 and NH_3 on commercially available skatole. A pure skatole sample was introduced into the chamber and, as shown inFigure 4, the skatole signal drops dramatically after the O_3 introduction and is accompanied by a slow increase of m/z 136.075 $C_8H_9NOH^+$ and m/z 164.07 $C_9H_9NO_2H^+$. The reaction of ozone with skatole proceeds by initial O_3 addition to the double bound to yield a primary ozonide. However, no particle formation was observed following ozonolysis therefore, we can discard the pure biogenic nucleation mechanism Most likely the volatility of skatole oxidation products is not low enough. Upon SO_2 introduction into the chamber, the formation of m/z 146.060 $C_9H_7NOH^+$ was observed, which may represent the product of the hydroperoxide channel of the Criegee intermediate (Figure 2). The m/z 136.060 $C_8H_7NOH^+$, corresponding to the ester channel of the Criegee intermediate, was also observed in the gas phase after SO_2 introduction. The contribution of SO_2 in new particle formation is further illustrated in Figure 4, which shows the prompt NPF event only once the SO_2 is introduced into the chamber. This is consistent with sulfuric acid formation by reactions of sulfur dioxide with stabilized Criegee intermediates [45]. Most likely oxidation products of skatole are able to stabilize sulfuric acid clusters enhancing NPF event observed. Skatole itself is a base compound, with a similar proton affinity to the one for dimethyl amine (DMA), which has been found to be a key player in atmospheric nucleation[6]. From a molecular point of view, the key for stabilization of molecular clusters of bases with sulfuric acid is the proton transfer[55], as in the case of, e.g., ammonia and sulfuric acid clusters. Classical nucleation theory (CNT) use bulk properties, so it predicts a proton transfer from the very first cluster containing one sulfuric acid molecule and one ammonia molecule. However, quantum mechanics (QM) chemical calculations have shown that this is not the case, as one will need at least two molecules for the proton to be transferred. When translating it in terms of evaporation rates of cluster calculated by CNT and QM, this leads to differences of several orders of magnitude. In the case of DMA, the proton transfer happens from the very beginning, with just one molecule of sulfuric acid; this explains why DMA can enhance nucleation of sulfuric acid much more than ammonia[8],[55]. This is the reason why we compare DMA to skatole in terms of proton affinity. In addition, other important molecular feature for a base to be able to enhance nucleation effectively seems to be having an additional H atom attached to the N atom so it can form hydrogen bonds with more than one sulfuric acid molecule[55]. Skatole, as DMA, presents a hydrogen atom attached to the N atom, so we think that this might as well be an advantage for

skatole enhancing sulfuric acid nucleation as in the case of DMA. Dedicated quantum chemical calculations, out of the scope of this paper, might be interesting in this case and could confirm our hypothesis.

Other base compounds as indole are produced during skatole oxidation. Furthermore, all oxidation products of skatole keep the N atom in their structure, even if they might have as well a carboxylic acid group. From a molecular point of view, having both a NH group and a carboxylic acid group can facilitate the formation of clusters with several molecules of sulfuric acid. Indeed, the theoretical simulations done by Elm et al.[56] shows how small amino-acids can effectively stabilize sulfuric acids clusters, thus playing an important role in atmospheric NPF. Aerosol number concentration reaches its maximum when SO_2 is introduced. It is also interesting to observe the different particle size: smaller particles are formed in skatole controlled experiments compared to sewage sludge experiments, revealing the potential role of other VOCs that might contribute to particles growth. In a second step, ozone was introduced into the chamber while skatole and SO_2 mixing ratios were kept constant. Likewise, the skatole signal decreased shortly after O_3 was added (Figure 4f), accompanied by a concurrent new particle formation event (Figure 4b), confirming the need of sulfuric acid and oxidation products of skatole to produce new particles.

In a third step, water vapor was added into the chamber (from dry conditions to 90% RH). As shown in Figure 4f, the water introduction led to an increase of the m/z 136.075 $C_8H_9NOH^+$ and m/z 164.07 $C_9H_9NO_2H^+$ signals in the gas phase. The stabilized Criegee m/z 146.060 $C_9H_7NOH^+$ is slightly decreasing. It might then react with water vapor to form a carbonyl compound and H_2O_2. The increase of m/z 164.070 in presence of water indicates a possible competition between the water vapor and the Criegee intermediates. In the first set of experiments when RH is very low (Figure 4e), one can observe the formation of m/z 146.060 $C_9H_7NOH^+$ when introducing SO_2, while at high RH the formation of 2-acetyl phenyl formamide is detected. In contrast, water vapor showed no effect on the aerosol particle number concentration.

The same types of experiments were performed to test the NH_3 effect on the new particle formation. As in the case of SO_2, the NH_3 was injected into the chamber during skatole ozonolysis. No new particle formation was observed when injecting NH_3 (Figure S3). Seeing these results, we can conclude that most likely the NPF mechanism behind the observed nucleation evens consist in sulfuric acid nucleation enhanced by the oxidation products of skatole acting as a base, like in the case of ammonia or amine nucleation reported in literature [5,6].

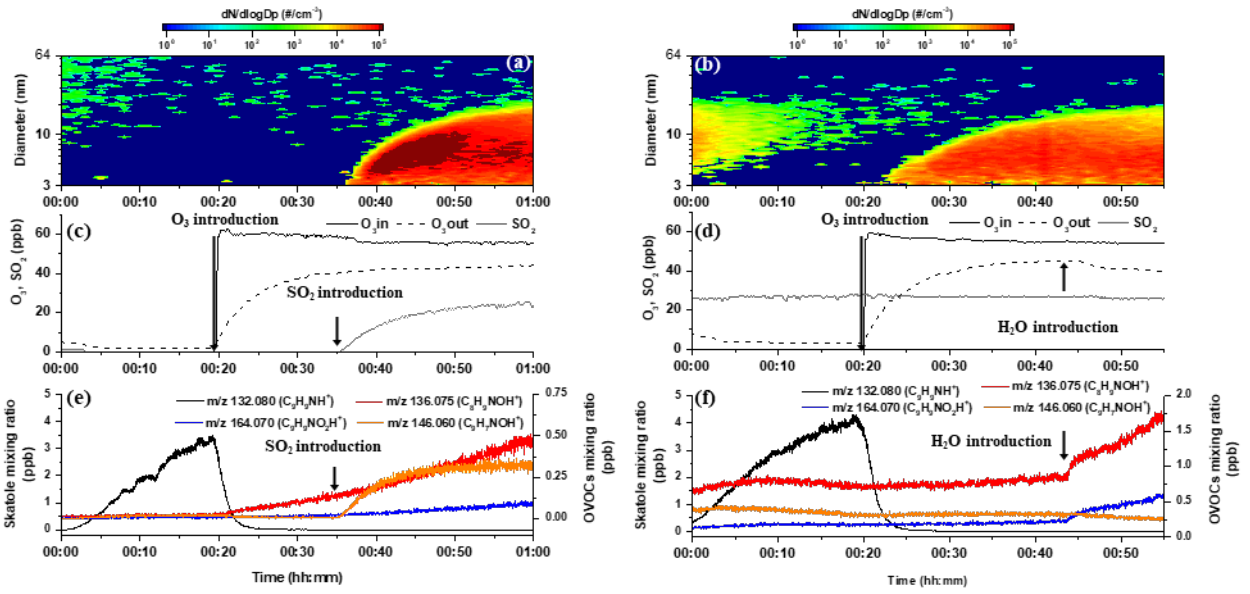


Figure 4. Skatole ozonolysis experiment. (a, b) Temporal evolution of particle number concentration and size distribution; (c, d) Temporal evolution of O_3 entering the chamber (black line), O_3 measured at the exit of the chamber (black dotted line) and SO_2 (grey line); (e, f) Temporal evolution of m/z 132.080 $C_9H_9NH^+$ (black line, left axis), m/z 136.075 $C_8H_9NOH^+$ (red line, right axis), m/z 146.060 $C_9H_7NOH^+$ (orange line, right axis) and m/z 164.070 $C_9H_9NO_2H^+$ (blue line, right axis). Left column: SO_2 introduction at 00:35 min; right column: H_2O introduction at 00:43 min.

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 PM_{10} emissions [13]. However, there is no estimate for the secondary organic aerosol formation from precursor gases emitted by agriculture [14]. 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 [14]. Moreover, agricultural particles were thought to be generated during the specific operations and processes or secondary formed due to NH_3 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 SO_2 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 µg m^{-2} min^{-1} following land spreading of pig slurry [27] or land application of swine manure slurry [57] have been shown in the literature. Our emissions are estimated at around 50

323 µg m^{-2} min^{-1} of skatole (details in Supplementary Information). Various reaction products were observed in the
324 gas and particulate phases. Among them, 2-acetylphenyl formamide was identified as the main skatole ozonolysis
325 product and formation pathways were proposed. Furthermore, the chemical analysis of particles shows that organic
326 compounds contribute to growth in this size range. All these statements are supported by chamber measurements
327 using commercially available skatole. The high reactivity of skatole towards ozone results in considerable
328 enhancement of condensable reaction products that might partition into the aerosol phase and potentially act as
329 cloud condensation nuclei [3].
330 The particle mass (2.9 µg m^{-3}) and number ($5x10^6$ # cm^{-3}) concentrations measured in our experiments exceed
331 some of field measurements conducted at various locations or other laboratory experiments performed on
332 agricultural samples. Our study shows a particle nucleation rate up to 1.1 10^6 cm^{-3} s^{-1} during the new particle
333 formation process. For example, the laboratory study of Joutsensaari *et al* [58] found aerosol number concentration
334 of $5.5x10^3$ # cm^{-3} from the ozonolysis of volatile organic compounds emitted by white cabbage living plants and
335 a particle formation rate of around 3 cm^{-3} s^{-1} (over the particle diameter range 5.5 - 70 nm). Our numbers are higher
336 than the particle formation rates observed in the atmosphere, which are often in the range of 0.01-10 cm^{-3} s^{-1} in the
337 boundary layer (for 3 nm particle). However, it has been shown that in urban, coastal areas or industrial plumes
338 the formation rates are higher, up to 100 cm^{-3} s^{-1} and 10^4-10^5 cm^{-3} s^{-1} respectively[12].. In our experiments,
339 emissions are constrained by the volume of the chamber. In the real atmosphere, they would be certainly more
340 diluted, leading to a lower concentration of precursors. However, in the chamber, the reaction time is limited to
341 the residence time (5 minutes). In the atmosphere, the ozonolysis of skatole will not be limited to 5 minutes, thus
342 oxidation will occur all along the emission plume. It is obvious that longer oxidation will conduct to more oxidized
343 compounds that will contribute to particle formation. Finally, even if our results are difficult to compare with real
344 atmospheric processes, they evidenced the huge potential of sludge emissions as a strong contributor to particle
345 formation.
346 Based on the particle emission flux in our experiments, on the sewage sludge spread surface area in France and on
347 the time before sewage sludge incorporation into the soil (48 h, according to the French legislation), our results
348 would yield a contribution of 0.94 tons particles per year. This value represents 0.03 % of $PM_{1.0}$ total emissions
349 from agriculture and forestry in France based on annual national emissions inventories (details in Supplementary
350 Information). Given that spreading of sewage sludge takes place only on a few days per year, usually in the middle
351 of the summer, the punctual contribution at this time of the year will not be negligible compared to other PM
352 emission sources. The emissions from agriculture may be of concern for local and regional of air quality during

353 the time after spreading. These numbers would be higher if particle number instead of particle mass is considered.
354 Indeed, high nucleation rates were observed, but the newly formed particles have a very low diameter and, as a
355 result, a low mass. New particle formation form organic waste product spreading contributes significantly to
356 atmospheric aerosol particle number concentrations that might be a significant source of cloud condensation nuclei
357 and altering cloud albedo, structure and lifetime.
358 The experiments carried out in this work, designed to match atmospheric conditions as closely as possible, might
359 be applicable to new particle formation and growth in the atmosphere, as ozone concentrations used in our study
360 approached tropospheric levels, even at remote locations during spring and summer. SOA yields were calculated
361 from the ratio of formed SOA amount to the amount of skatole reacted considering a density of the aerosol particles
362 of 1.0 g cm^{-3}. The SOA yields varied significantly between the experiments with an average of 2.45%. In the
363 literature, values for the SOA yield of skatole ozonolysis are not available. On the other hand, ozonolysis of
364 biogenic terpenes have already been characterized in simulation chambers and values of SOA yields varied over a
365 broad range: mass yields of 0.16 and 0.21 for α-pinene ozonolysis were found [59] while some other studies reported
366 SOA yields for the ozonolysis of monoterpenes between 0 and 76% [60]. Donahue et al. [61] explained the critical
367 factors for SOA yield from terpene ozonolysis. The authors showed that different competing factors could affect
368 the yield: the oxygenation that increases the absolute yield because the compounds are more polar and thus less
369 volatiles; the potential difference between gas phase and condensed phase oxidation and oligomerization. The
370 same authors suggested that SOA yields are likely to increase substantially through several generations of oxidative
371 processing of the semi-volatile products. It has also been shown that the SOA yields are 80 to 100% larger for
372 loadings above 2 μg m^{-3}. Our low SOA yields compared to some of the monoterpenes might be explained by the
373 aerosol mass loadings that were around 3 μg m^{-3} but also by the presence of oxygenated compounds and the
374 possible heterogeneous reactions at the sewage surface not taken into account in the yield calculations. Longer
375 reaction time, from experiments conducted in larger facility would also lead to more oxidation, and thus increase
376 the transfer from gas to particle phase. Our findings imply that during sewage sludge spreading, skatole is an
377 important potential contributor to the formation of new particles under atmospherically relevant conditions. Since
378 an increasing application of organic waste products is expected in continuously growing agricultural activities [13],
379 this additional VOC source may have a significant influence on atmospheric new particle formation and ozone
380 reactivity during the spreading period. This study shows a novel mechanism involving indols from agricultural
381 origin. Even though we cannot apply these values directly to the atmosphere, our results suggest that this skatole
382 emission can change the chemistry and oxidative capacity of the atmosphere by its contribution to local

concentrations. Even if not realistic for atmospheric conditions, these processes can have a qualitative contribution to particle number as the high nucleation rate can induce locally and punctually a significant annual source of particle formation.

Methods

The experiments were performed in a poly(methyl methacrylate) chamber with Teflon walls (0.03 m^3, 0.2 m height, 0.27 m width, 0.55 m length), built in a temperature-controlled room. A stainless steel container (0.52x 0.27x0.02 m^3) filled with the sewage sludge sample was used. High purity dry air (Air Liquide), passing through two Restek super clean gas filter kits for oxygen, moisture, and hydrocarbons removal (Restek, 22020) and an additional hydrocarbon trap (Restek 21991), was used for the experiments. Residence time of the air in the chamber was 5 min. Temperature and relative humidity in the chamber were 293 K and 40%, respectively. Before each experiment, the chamber was flushed with purified dry air for 30 min with a flow rate of 10 L min^{-1} until the particle number concentration in the chamber was lower than 1 particle cm^{-3}. When VOC concentrations reached an approximate steady state, ozone was injected reaching a chamber concentration of about 55 ppb. No OH or Criegee intermediates scavengers were added and no seed aerosol was used. Fifteen experiments with authentic sewage sludge samples (Supplementary Table S1) and two experiments with commercially available skatole (Sigma Aldrich >98.0% purity) were performed. Sewage sludge was sampled from the Colmar, France sewage treatment plant.

The gas and particle phases were continuously sampled. A high-resolution proton transfer reaction time-of-flight mass spectrometer [36] (HR-Qi-PTR-ToF-MS, Ionicon Analytik GmbH) was used to measure in real time the gas-phase VOC concentration (time resolution 1 s, m/z range 10–510). The drift tube pressure was set to 4 mbar, the temperature to 80 °C and the drift voltage to 1000 V, while the extraction voltage at the end of the tube (UDx) was 44 V. The E/N was 132 Td (1 Td = 10^{-17} V cm^2). Protonated water ($H_3{}^{18}O^+$, m/z 21.022) protonated acetone ($C_3H_7O^+$, m/z 59.049) and protonated diiodobenzene (PerMaSCal Ionicon, $C_6H_5I_2^+$) ions and fragments ($C_6H_4I_2H^+$, m/z 330.941 and $C_6H_5I^+$, m/z(203.943 respectively) were used for mass calibration. All data obtained by the PTR-ToF-MS were analyzed with the PTR-MS Viewer software (version 3.1.1, IONICON Analytik). O_3 was introduced into the chamber via an ozone generator (OSG-1, UVP) using purified dry air as carrier gas. The ozone at the entrance and at the exit of the chamber (41M, Environment SA), NO_x (model 42i-TL, Thermo Fisher Scientific, Inc.), SO_2 (model 43C, Thermo Environmental Instruments), NH_3 (Picarro G2103), CO_2 and H_2O (LICOR LI-840A) were continuously measured. VOCs were also trapped on Tenax TA cartridges for Thermal Desorption – Gas Chromatography – Mass Spectrometry (TD-GC-MS) analysis. The gas phase was sampled during 1 to 2 hours at 0.4 L min^{-1}, and regulated with a mass flow controller (Bronkhorst). Tubes were desorbed using a thermo-desorption unit (TDU, Gerstel). VOCs separation was carried out using an Agilent 7890B gas chromatograph on a capillary column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness, HP-5MS Ultra Inert, Agilent). VOCs detection was performed with an Agilent 5977A mass selective detector. Ozone, NO_x and SO_2 analysers have been calibrated before the experiments by the French air quality survey network. The PTR-ToF-MS has been calibrated using a Toluene standard of 102±10 ppb gas bottle diluted in zero air.

Particle number concentration and size distribution were measured using a scanning mobility particle sizer (SMPS 3938; TSI) consisting of a differential mobility analyzer (DMA; TSI 3085) and a condensation particle counter (CPC; TSI 3788), extensively described elsewhere[62]. Sample flow was fixed at 0.6 L min^{-1} and sheath flow at 6 L

min^{-1}, providing measurements of the particle number and size distribution between 2.64 and 64 nm electrical mobility diameter. In the present study it was assumed that the wall loss rate was constant during experiments. All the values are wall and tube loss corrected (a maximum of 5% wall loss correction was applied to lower diameters) based on Kulkarni *et al.* (2011) [63]. Particle number and size distribution measured with the SMPS has been used to estimate the nucleation rates following the methodology described by Kulmala et al[64]. The freshly formed secondary aerosols were collected during 3 – 5 hours on quartz fiber filters (Pall Tissuquartz QAT-UP 2500, 14 mm diameter) in order to be chemically characterized by mass spectrometry techniques and liquid chromatography. The pristine sewage sludge surface chemical composition before ozonolysis was also analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The TOF-SIMS analyses of bulk sewage sludge and filter-sampled particles were performed with an IONTOF TOF.SIMS$_5$ instrument equipped with a Bi_3^+ primary ion source. The energy of the Bi_3^+ ions was set to 25 keV and the used dose was ~ 2 10^{11} ions cm^{-2}, which matches the static mode in which only moderate fragmentation is expected [65]. Both positive and negative ion polarities were investigated with mass resolution $m/\Delta m$ of 2000 and 3000, respectively.

Two-step laser mass spectrometry (L2MS) measurements were done using a Fasmatech S&T instrument already described elsewhere [66] with an average mass resolution of $m/\Delta m$ ~ 8000. Desorption and ionization were achieved using two nanosecond Nd:YAG (Quantel Brilliant) pulsed lasers operated at 532 nm and 266 nm wavelength, respectively. Laser energies were adjusted to maximize the ion signal while limiting fragmentation of the parent species. Limit of detection as low as ~ 0.2 femtomole per laser pulse has been demonstrated in this configuration[67].

For UHPLC-HRMS analyses, the filters were extracted in methanol. 2 methyl indole, 5 methyl indole and 3 methyl indole (skatole) from Sigma Aldrich with >98.0% purity were used as analytical standards for UHPLC calibration. The UHPLC analyses were performed using an Acquity BEH C18 column (100x2.1mm, 1.7µm particle size, Waters). The mobile phase consisted in LC/MS grade acetonitrile/H_2O/0.1% formic acid circulating at 0.3 mL min^{-1} flowrate (gradient elution). The column temperature was set to 30°C and 10 µL of sample were used for injection. High-resolution mass spectrometry analysis was carried out with a Q-Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific) in positive mode with a Heated ElectroSpray Ionization (HESI) probe using a high resolution full scan. The mass resolution was 70,000 in the full range m/z 70 - 500.

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Author contribution

R.C. designed the study, performed chamber experiments and wrote the manuscript. J.K., C. B., F.La., D.P. performed chamber experiments and/or analyzed the PTR-ToF-MS and SMPS data. C. D. performed GC-MS

analysis and analyzed the data. M. V., K. H., Y. C., C. F. performed the L2MS and SIMS experiments and analyzed the resulting data. M. B-D. helped with the UHPLC-HRMS mass spectrometer data. F.Le. and S.H. provided expertise in organic waste recycling and contributed to the manuscript. B.L., D.P. and I.K.O. contributed to the manuscript. C.F. did data interpretation, critical editing and review of the manuscript. All authors commented on the manuscript.

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