

TNA User Report

*The completed and signed form below should be returned by email to
eurochamp2020@lisa.u-pec.fr*

Project title	Secondary organic aerosol formation from volatile organic compounds degradation from Green Waste Products emissions
Name of the accessed chamber	ESC-Q-UAIC chamber - Integrated Centre of Environmental Science Studies in the North East Region of Romania (CERNESIM), Alexandru Ioan Cuza University of Iasi, Romania
Number of users in the project	Raluca CIURARU
Project objectives (max 100 words)	This project aims at providing new insights into fundamental processes involved in the formation and fate of secondary organic aerosols (SOA) formed as a result of the reactivity of volatile organic compounds (VOC) emitted by organic waste products (OWP) with photo-oxidants (O ₃ and OH). In this context, our objectives were to: (1) identify the VOC emissions from an urban OWP: the green waste (GW-OWP); (2) elucidate the mechanisms of production and degradation of these VOCs; (3) quantify the SOA formation potential.
Description of work (max 100 words):	The project entitled "Secondary organic aerosol formation from volatile organic compounds degradation from Green Waste Products emissions" performed at the Research Center- CERNESIM - from the Alexandru Ioan Cuza University of Iasi was focussed on studying SOA formation from the green waste emissions by using the ESCQ-UAIC facility, while employing in situ Fourier Transformed Infrared Spectroscopy, on-line proton transfer reaction mass spectrometry and scanning mobility particle analyser. For SOA chemical composition ongoing work is performed using offline liquid chromatography mass spectrometry (LC-MS) and laser desorption/ionization coupled with time-of-flight mass spectrometry (LD/LI-MS). A flow of GW from ECOSYS chamber has been added constantly to the ESC-Q-UAIC chamber for 20-30 min till pressure was reaching 1000 mbar. Reactions with OH and O ₃ have been performed and SOA size distribution has been recorded. At the end of the reaction the newly formed SOA has been collected on quartz filters for subsequent offline chemical analysis by LC-MS and LD/LI-MS.

Principal Investigator's and group's information	
First name	Raluca
Family name	CIURARU
Nationality	French
Activity domain ¹	Earth Sciences & Environment
Home institution	INRA - French National Institute for Agricultural Research
Institution legal status ²	RES
Email	raluca.ciuraru@inra.fr
Gender	Female
User status ³	Researcher
New user	Yes

¹ PLEASE CHOOSE ONLY ONE DOMAIN: Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

² RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

³ UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

Trans-National Access (TNA) Scientific Report

Name of the PI: Raluca CIURARU

Chamber name and location: ESC-Q-UAIC chamber - CERNESIM, ROMANIA

Campaign name and period: Secondary organic aerosol formation from volatile organic compounds degradation from Green Waste Products emissions, 30/08/2019 to 12/09/2019

Introduction and motivation

Volatile organic compounds (VOC) - emitted into the atmosphere from anthropogenic and biogenic sources or formed in situ as products of the atmospheric transformations of other VOCs - are of great interest because they participate to atmospheric photochemical reactions that contribute to ozone and secondary organic aerosols (SOA) formation¹. It is now established that agricultural activities, including fertilizers use or livestock manure spreading, affect air quality by its significant emission sources of ammonia and greenhouse gases (GHG) but also through VOC and aerosols emissions. While great efforts have been made to estimate GHG and ammonia emissions from agriculture and solutions to reduce them, knowledge about other pollutants is still scarce, in particular on SOA and its VOC precursors. 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. For urban wastes (e.g. green wastes), the European Union targeted a decrease in the amount disposed in landfills by 50% before 2050, mainly through their increased use in agricultural crops². It has been shown that these urban biowastes improve soil structure stability through their humidified organic matter³.

Oxidation reactions using a single gaseous parent VOC has been studied but the SOA potential forming using authentic OWP samples has never been explored. In the frame of this project, we propose to investigate the importance of the organic waste products as a source of VOCs and hence as an important source of new atmospheric secondary aerosols. We provide data describing SOA formation at the soil interface and explore the role of ozone and OH reactivity in order to assess the potential importance of these processes in providing new particle formation.

Scientific objectives

This project was aimed to investigate new particle formation by performing laboratory-based experiments using authentic green wastes samples (GW) to derive scientifically data on the chemistry of OWP with ozone and OH radicals and perform subsequent analysis of SOA chemical composition. The performed study helps in providing feasible evidences for developing a new mechanism describing the formation of SOA at the soil-atmosphere interface. The main scientific questions addressed by this project are: (1) what are the VOCs emitted by GW-OWP and what are the environmental drivers of their emission rates? and (2) what are the (photo)chemical mechanisms leading to the SOA formation from VOC emitted by OWP?

In this context, our objectives were to:

- (1) identify the VOC emissions from an urban OWP: the green waste (GW-OWP);
- (2) elucidate the mechanisms of production and degradation of these VOCs;
- (3) quantify the SOA formation potential.

Reason for choosing the simulation chamber

The ESC-Q-UAIC facility existent in Romania is a highly instrumented chamber. It allows performing investigations in the gas-phase under simulated atmospheric conditions at specific experimental conditions. A detailed description of the ESC-Q-UAIC chamber is presented elsewhere (see details on EUROCHAMP2020 website).

Method and experimental set-up

Three main tasks were proposed in this work:

Task 1: Identification of the gas phase composition from GW-OWPs emissions;

Task 2: Homogeneous oxidation involving selected VOCs from OWPs and photo-oxidants;

Task 3: SOA characterization.

The ESC-Q-UAIC chamber, ECOSYS soil simulation chamber and attached instrumentation were proposed as main investigation tools for this project (**Figure 1**).

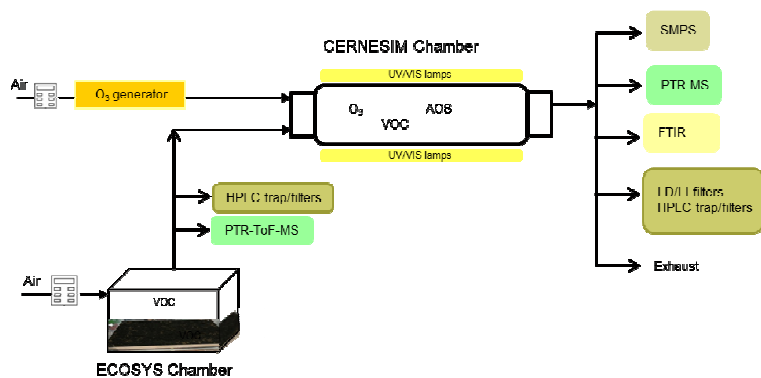


Figure 1. Experimental set-up used for laboratory experiments.

A high purity air flow was entering the ECOSYS soil chamber in order to transfer GW emitted VOCs to the ESC-Q-UAIC chamber. Subsequent reactivity of these VOCs towards O_3 and OH radicals was investigated in the ESC-Q-UAIC facility. The SMPS analyser was employed during experiments in order to investigate the concentration and size distribution of the new particle formation. Analysis of particle samples collected on filters will help identifying the main precursors of SOA formation and SOA chemical composition. Furthermore, from the GW-OWP emitted VOCs, a sesquiterpene – isolongifolene - has been selected for further investigations on the gas phase OH and O_3 initiated degradation mechanism and SOA formation potential in the ESC-Q-UAIC chamber. For ozonolysis experiments, the ozone was obtained by passing synthetic air through a handmade system allowing direct exposure to a 254 nm arc discharge lamp. OH radicals were obtained either by photolysis of methyl nitrite using 360 nm photolytic lamps with addition of NO to suppress ozone and nitrate radical formation or by photolysis of H_2O_2 at 254 nm.

Data description (in summary information)

In line with the scientific objectives, 2 types of experiments involving OH radical initiated degradation of GW and GW ozonolysis have been performed. Additionally, reactivity experiments and investigations of the gas phase chemical degradation mechanism have been performed for a selected sesquiterpene (isolongifolene).

Preliminary results

In line with the initial objective of the project chemical composition of GW-OWPs emissions was investigated. For this task, a flow of 1.5 l min^{-1} of air passing through the ECOSYS chamber was transferred to the ESC-Q-UAIC chamber until a total pressure of 1000 mbar (prior to the addition of GW, the chamber was filled at 950 mbar).

FTIR investigation on the GW emissions

Figure 2 presents an example of the initial FTIR spectrum recorded for GW transferred in the ESC-Q-UAIC facility. Unfortunately, the FTIR spectra for each performed experiment were affected by the huge amount of water contained in the authentic samples. Under this circumstance, the FTIR become unusable for potential identification of GW chemical composition. However, investigations performed by PTR-ToF-MS on the same GW-OWPs samples revealed details concerning monoterpenes and sesquiterpenes as potential released chemical compounds (**Figure 3**). Use of a cold trap prior GW emissions addition into the ESC-Q-UAIC chamber did not improved spectra quality. However, details in Figure 2 reveal only the existence of O_3 in a GWs ozonolysis experiment (signal at 1060 cm^{-1} after adding 2 ppmv into the ESC-Q-UAIC facility).

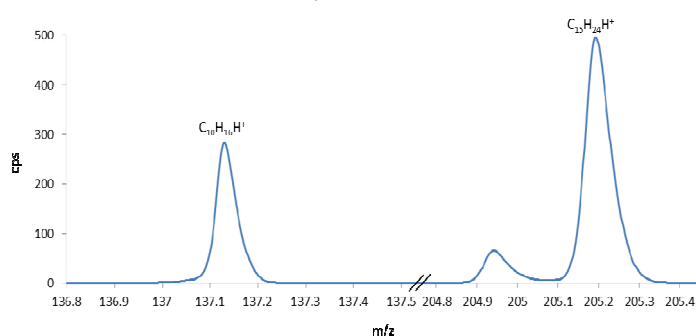
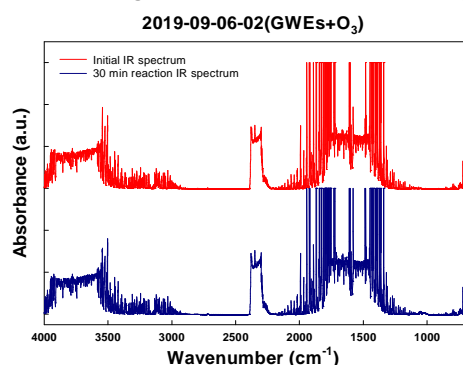


Figure 2. FTIR spectra recorded after GW addition into ESCQUAIC chamber and after 30 min of ozonolysis. **Figure 3.** PTR-ToF-MS spectra showing the emission of monoterpenes and sesquiterpenes by the GW sample.

SOA formation from the OH radical initiated oxidation of GW-OWPs emissions

The potential of GW-OWPs emissions to form SOA in the reaction with OH radicals has been investigated (using H₂O₂ and CH₃ONO as OH radical source; bi-replicate experiments). An air flow of 1.5 L min⁻¹ passing through the ECOSYS chamber was further transferred to the ESC-Q-UAIC facility. 10 ppmv of H₂O₂ has been added in the ESC-Q-UAIC facility in order to be used as OH radical precursor. The photooxidation process has been initiated by irradiating at 254 nm the gas mixture. The SMPS has been used at a sampling flow of 0.6 L min⁻¹. **Figure 4** clearly reveals evidences about the formation of SOA particles in the fine mode (small diameter). Most probably, initial formed small particles gets in larger particles due to the condensation process occurring in time. A mass concentration of ~ 6.5 µg m⁻³ SOA has been obtained for a reaction time frame of 30 min.

During the TNA project SOA formation from the OH radical initiated reaction formed by photolysis at 365 nm of 5 ppmv of CH₃ONO has also been investigated. Additionally, 2.5 ppmv NO were introduced into the reactor in order to suppress O₃ and NO₃ radical formation and to avoid secondary reactions of GW-OWPs emissions. **Figure 5** presents SOA mass concentration distribution when CH₃ONO photolysis has been used as OH radical source. A mass concentration of ~ 3.8 µg m⁻³ for SOA generated under NO_x conditions (reaction time frame of 30 min).

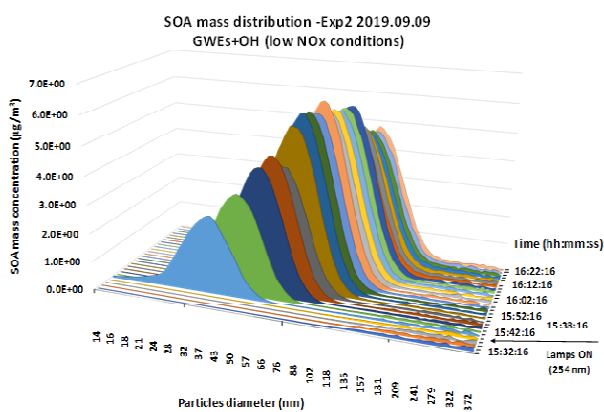


Figure 4. Secondary organic aerosol mass concentration distribution observed during the reaction of OH radicals with VOCs emitted by the investigated GW-OWPs (NO_x free conditions)

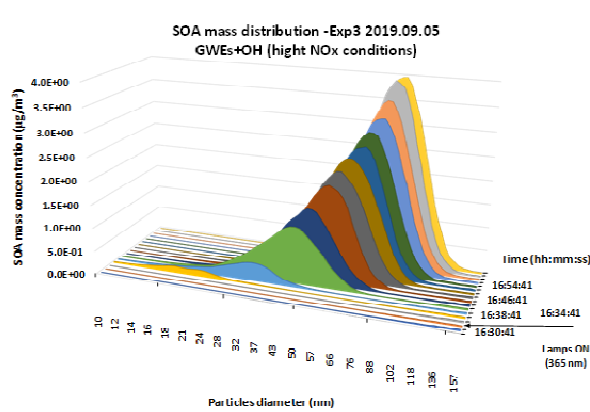


Figure 5. Secondary organic aerosol mass concentration distribution observed during the reaction of OH radicals with VOCs emitted by the investigated GW-OWPs (NO_x conditions)

SOA formation from the ozone-initiated oxidation of GW-OWPs emissions

Four ozonolysis experiments were performed for the reaction of GW-OWPs emissions with ozone. Ozone was introduced into the ESC-Q-UAIC facility at a concentration of 2 ppmv (2 min transfer process). Two experiments were performed in the presence of OH scavenger (4000 ppmv CO) to avoid possible reactions with OH radicals formed during ozonolysis process. The SMPS analyser has been used at a sampling flow of 0.6 L min⁻¹. **Figures 6 and 7** show SOA mass concentration distribution for ozonolysis experiments in both absence and presence of OH scavenger. Estimated SOA mass concentration show values around ~0.5 µg m⁻³ in the absence of OH radical scavenger and of ~0.3 µg m⁻³ in the presence of OH radical scavenger.

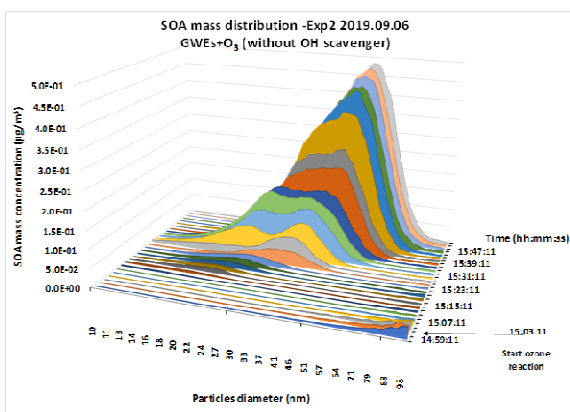


Figure 6. SOA mass concentration distribution during the ozonolysis of VOCs emitted by the investigated

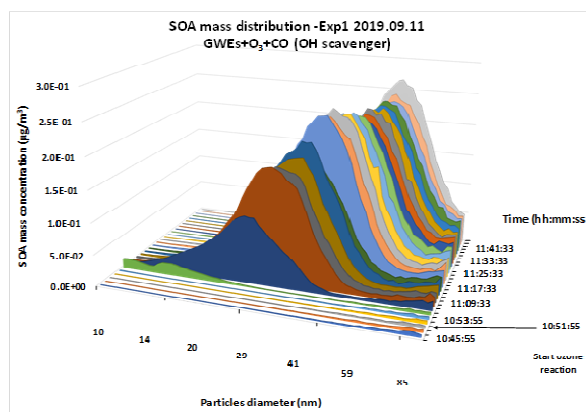


Figure 7. SOA mass concentration distribution during the ozonolysis of VOCs emitted by the investigated

GW-OWPs (no OH radical scavenger).

GW-OWPs (with CO as OH radical scavenger).

Additional ozonolysis experiments on the same GW samples were performed using only the ECOSYS chamber employing PTR-TOF-MS as measurement technique. **Figure 8** shows the time evolution of the $C_{15}H_{24}H^+$ ion corresponding to the signal of a sesquiterpene during an ozonolysis experiment.

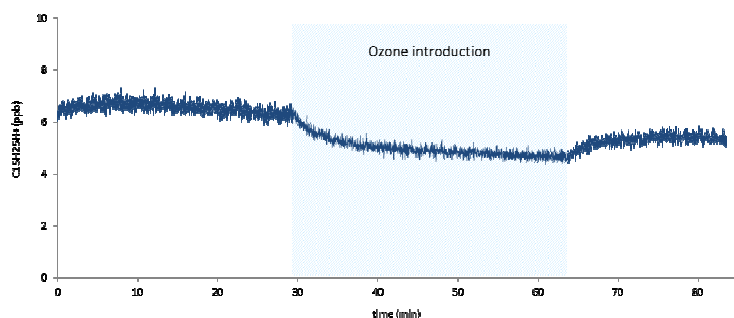


Figure 8. PTR-ToF-MS spectra showing the reactivity of the sesquiterpene signal with ozone over time using the ECOSYS chamber.

Isolongifolene gas phase chemistry

Isolongifolene has been selected as a representative sesquiterpene for the interest GW. Preliminary studies have been performed in this project in order to characterize the gas phase products resulted from the reaction of isolongifolene with OH radicals and ozone. Fast reactivity of isolongifolene with OH radicals is expected. To the best of our knowledge, no literature data are available for the rate coefficient determination, $k_{(O_3+isolongifolene)} = (1.1 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is reported⁴. Preliminary experimental work on the product studies indicates evidences about the formation of acetone and unidentified carbonyl compounds as shown in **Figure 9**. From the product spectrum recorded after 30 min of reaction time, the methyl nitrite and NO together with isolongifolene have been subtracted in order to obtain the residual product spectrum. After acetone subtraction, **Figure 10** shows a highlight of carbonyl area where at least two carbonyl products formation can be observed. IR absorption features at $1290 \text{ cm}^{-1} - 1300 \text{ cm}^{-1}$ could be attributed to the formation of a gas phase product. No product studies have been performed to date for the isolongifolene reaction with OH radicals.

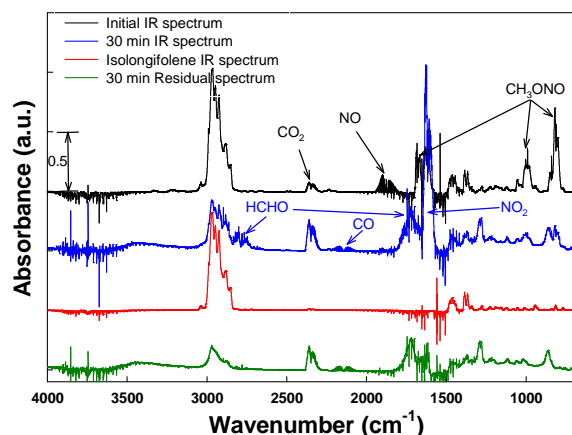


Figure 9. Infrared spectral data: (black) spectrum before the reaction; (blue) after 30 min of reaction; (red) isolongifolene reference spectrum and (green) residual spectrum.

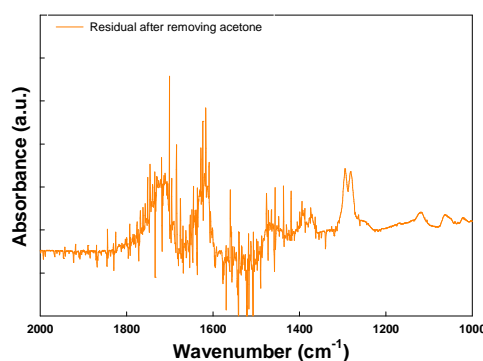


Figure 10. Infrared spectral data from 1000 cm^{-1} to 200 cm^{-1} for the residual product spectrum of the reaction of isolongifolene with OH radicals.

SOA quartz filter characterization

The work is in progress for the offline filters characterization using LD/LI-MS and LC-MS techniques.

Conclusions

TNA project has successfully achieved all the objectives. SOA size distribution from the GW products of the OH radicals-initiated reactions has been determined using two different OH source. Preliminary results show a faster formation of SOA when OH radicals are generated by H_2O_2 photolysis relative to a slower SOA formation process when OH radicals are generated by CH_3ONO photolysis. Similarly, at 30 min reaction time for all the reaction investigated in this study, more SOA mass concentration has been observed when H_2O_2 photolysis was used as OH radical source if compared to the case when CH_3ONO photolysis was used to generate OH radicals. Within this TNA project the ozonolysis of GW in the presence and absence of OH scavenger was also investigated. In the

absence of OH scavenger a faster formation process of SOA was observed when compared to GW degradation in the presence of OH scavenger. Analysis of the SOA chemical composition by LD/LI-MS and LC-MC is still in progress. Isolongifolene behaviour in the gas phase has also been investigated within this action. Gas phase reactivity studies and chemical degradation mechanism investigations for the reaction initiated by OH radicals are in progress.

Outcome and future studies

The final data evaluation is still in progress. After the final results evaluation and interpretation, a first publication on the SOA characterization from the GW concerning the reaction with OH radicals and ozone is expected. Preliminary SOA size distribution and future evaluation of SOA composition by LC-MS and LD/LI-MS from filters collected during the TNA project will be included in this first article.

Additionally, a study on the gas phase reactivity and degradation mechanism investigation will be finalized after the evaluation of all the data collected from the TNA project.

References

1. Guenther, A. *et al.* A global-model of natural volatile organic compound emissions. **100**, 8873–8892 (1995).
2. Kumar, A. *et al.* Volatile organic compound emissions from green waste composting: Characterization and ozone formation. *Atmos. Environ.* **45**, 1841–1848 (2011).
3. Annabi, M., Le Bissonnais, Y., Le Villio-Poitrenaud, M. & Houot, S. Improvement of soil aggregate stability by repeated applications of organic amendments to a cultivated silty loam soil. *Agric. Ecosyst. Environ.* **144**, 382–389 (2011).
4. Richters, S., Herrmann, H. & Berndt, T. Gas-phase rate coefficients of the reaction of ozone with four sesquiterpenes at 295 ± 2 K. *Phys. Chem. Chem. Phys.* **17**, 11658–11669 (2015).