FINAL REPORT PROGRAM LEFE

Program LEFE/ CHAT	**Project Title : DATAbASE** ***Do Anthropogenic Terpenoids matter in Atmospheric Chemistry ?***	**Years 2019 – 2021**

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Contribution to :

Other funding sources :

Context

Terpenoids are highly reactive Volatile Organic Compounds (VOCs) toward major atmospheric oxidants known for decades for their biogenic origin. While some studies suggest an anthropogenic origin for those compounds such as fossil fuel combustion, biomass burning or, more recently, volatile chemical product usage emissions, the quantification of their anthropogenic emissions remains poorly representative in space. Here, we discuss the nature and magnitude of the anthropogenic emissions of terpenoïds by compiling and reanalyzing fourteen datasets of in-situ VOC observations in urban areas from mid-latitudes to subtropical regions collected over the last decade.

Objectives / scientific questions

- To search for the systematic presence of anthropogenic terpenoids from observations in the analyzed datasets.
- To quantify the anthropogenic emissions of terpenoids by coupling observations and emission inventories
- To evaluate their atmospheric impact on the oxidative capacity of the atmosphere (i.e. ozone production) by a modeling approach

Main results

We have determined the anthropogenic emission ratios of terpenoïds through the re-analyses of fourteen VOC datasets and by selecting conditions where chemistry and biogenic emissions are negligible. We demonstrate the ubiquity of anthropogenic terpenoids in the atmosphere of urban areas worldwide though their significant levels in winter and their correlations with anthropogenic tracers.. Despite the recent evidence of monoterpene emissions from household solvent use in North American cities, we estimate that traffic may represent up to 40% of monoterpene levels in other urban areas. Although low in quantity at urban and national scales (less than 1% in mass of emissions of other anthropogenic VOCs), anthropogenic emissions of terpenoids may play a role in urban nighttime and wintertime chemistry through their reactivity with the nitrate radical and ozone. The first results of 0D box modelling using the Master Chemical Mechanism v3.3.1 made it possible to test the sensitivity of photooxidants to emissions of anthropogenic terpenoids under a high NOx polluted ideal urban scenario. We show that the addition of anthropogenic terpenoïd emissions leads to an increase of + 15 ppb in ozone and 15% in the OH radical at midday (after 84h). The implementation of 0D box modeling in three contrasting cities in terms of emissions and climatic conditions (Paris - Beirut-Dunkirk) will be carried out to confirm this importance Finally, on a global scale, we propose a mapping of anthropogenic isoprene emissions thanks to their indirect quantification from the determination of terpenoïd anthropogenic emission ratios. The quantities newly estimated in DATAbASE are about 4 times greater than the ones provided by EDGAR.

Ultimately, this project provides a scientific basis for evaluating the need or not to take these emissions into account in the emission inventories used in regional and global atmospheric models. The project sets the scientific framework of a doctoral thesis jointly supervised by France and Lebanon.

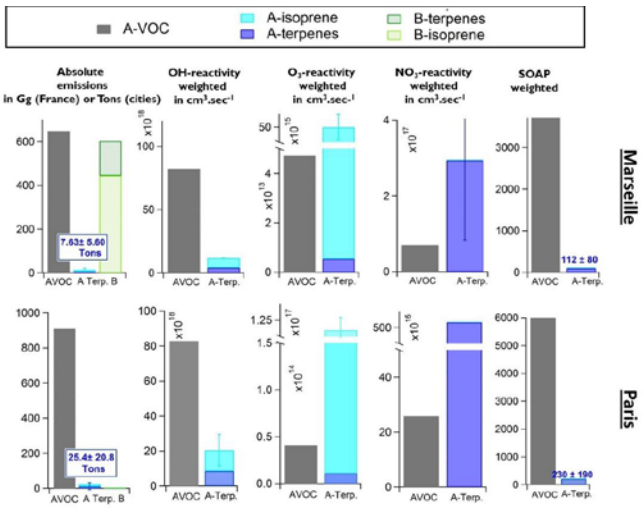
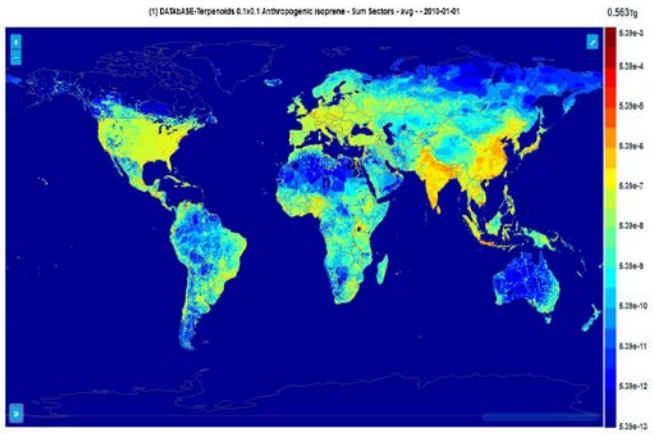


Figure 1 *: Urban emissions of anthropogenic terpenoids estimated for Marseille and Paris and weighted by their reactivity.*



DATAbASE : 0.56 Tg/year of isoprene

Figure 2 *: Mapping of global anthropogenic isoprene emissions estimated in DATAbASE.*

The calculated urban anthropogenic emissions of terpenoids are plotted on Figure 1 and compared to the ones from common anthropogenic VOC precursors (alkenes, aromatics). While the absolute anthropogenic emissions of terpenoids appear negligible, a different picture arises when weighting those emissions by their atmospheric reactivity (second to fourth column of figure 2). While the OH-reactivity from anthropogenic terpenoids accounts for 20% of the total AVOC reactivity, the OH-reactivity of terpenoids remains dominated by their biogenic component, especially during the day at the maximum of photochemistry and biogenic emissions. Remarkably, the ozone- and NO_3-reactivity from anthropogenic terpenoid emissions exceed by three orders of magnitude and by one order of magnitude, respectively, the ones from other AVOC, a difference even greater than potential analytical bias from the measurement. Indeed, isoprene and monoterpenes react a million times faster with ozone and NO_3 than other alkenes and aromatics, respectively.

Spatially resolved emissions are mapped in Figure 2. They are compared to anthropogenic isoprene emissions from the Edgar 4.3.2 inventory. Isoprene emissions by the DATAbASE inventory are estimated at 0.56 Tg per year in 2010 (0.54 Tg in 2020) (max: 0.813 Tg and min: 0.290Tg). They are 3.7 times greater than those of the reference inventory Edgar (0.14 Tg), well beyond the 40% uncertainty. It should also be noted that Edgar takes into account a greater number of sectors. This first estimate suggests that the traditional inventory underestimates anthropogenic isoprene emissions.

Future of the project :

The implementation of 0D modeling in three contrasting cities in terms of emissions and climatic conditions (Paris – Beirut - Dunkirk) will confirm this importance. It is the scope of Mariana Farhat's PhD co-supervised by France and Lebanon. Some on-going discussion with group of Colette Heald at MIT (USA) will promote the global estimation of the impacts with the GEOS CHEM model.

Publications, Communications and PhD theses

Borbon et al., 2022. Paper under review for JGR : *Ubiquity of anthropogenic terpenoids in cities worldwide: emission ratios, emission quantification and implication for urban atmospheric chemistry*

Farhat et al., Highlighting the Industrial Origin of Terpenoids in a Coastal City in Northern France: a Source - Apportionment Approach of Volatile Organic Compounds (VOCs). AGU Virtual Fall Meeting – December 2021.

Page 3 : Informations à destination des instances LEFE uniquement (ne seront pas rendues publiques)

Nombre d'ETP mobilisés par le projet, montant du financement LEFE et des cofinancements :

Financement LEFE : 13.63 k€ // 33 ETP //

Financement complémentaire : 76k€ (dont une gratification de stage) incluant les campagnes sur lesquelles le projet s'appuie

Avenir du projet (ANR, européen, … Thèse et exploration de l'origine des terpénoïdes dans ACROSS

Quel impact ce projet a-t-il eu sur la communauté (structuration, innovation ?, …)? Mise en synergie de différents jeux de données. Valorisation de jeux de données.