FINAL REPORT PROGRAM LEFE

Program LEFE - CHAT	Project Title: Emissions of Asphalt Pavements and Impacts to urban air quality (EmAPI)	Years 2020 – 2021

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Other funding sources :
IMT Nord Europe

Context

Outdoor air pollution is a major cause of chronic illnesses, and of mortality, with an estimated 4.5 million deaths every year. Its effects are amplified in urban areas, where the global population concentrates. Asphalt-covered surfaces dominate urban areas. Although asphalt's pollutant emissions have been investigated at temperatures above 120°C during laying, data on emissions at in-use temperatures are lacking.

Objectives / scientific questions

- To identify and quantify emissions of fresh and aged asphalt concrete under simulated atmospheric conditions. The speciated emissions from asphalt concrete surfaces have been estimated, employing temperature regulated atmospheric simulation chambers that can mimic the real conditions existing in the atmosphere (i.e. temperature, humidity, sunlight).
- To investigate the impact of atmospheric oxidants (i.e., O_3) on asphalt concrete emission composition and emission rates, and the possible concomitant formation of Secondary Organic Aerosol (SOA).
- To provide quantitative kinetic data regarding the heterogeneous interaction / reaction of asphalt concrete surfaces with O_3, NO and NO_2, under simulated atmospheric conditions, i.e., relevant pollutant concentrations, relative humidity (RH), sunlight radiation, temperature.

Main results

In this study, we applied a synergetic methodology combining laboratory experiments and numerical simulations (*not initially in the framework of EmAPI*) deploying a city scale model to assess the impact of asphalt emissions on the urban air quality. Laboratory experiments were carried out inside a temperature regulated atmospheric simulation chamber at in-use temperatures (23°C-60°C), humidity, and presence/absence of UV light. Two different classes of asphalt samples were studied: Fresh called STA (Short Term Aging) (i.e., provided by companies), and aged called LTA (Long Term Aging) (i.e., exposed for several years to ambient air pollution and traffic, collected from north of France). Samples were placed in the simulation chamber and their emissions were collected deploying a wide panel of analytical instrumentation, such as a high-resolution proton transfer reaction time of flight mass spectrometer (HR-PTR-ToF-MS) for the monitoring of non-methane volatile organic compounds (NMVOCs), a thermal desorption gas-chromatography flame ionization detector mass spectrometer (TD-GC-FID-MS) to detect C6-C16 alkanes/alkenes and aromatics, and a photolytic NOx analyzer to monitor specifically NOx emissions.

Regarding NMVOC emissions, over 100 different compounds, including important ozone and SOAs precursors, were identified and quantified. Individual and total emission factors (EFs, µg m^{-2} h^{-1}) were determined. 20 compounds (alkanes, aromatics, and 1 alcohol) contribute to more than 80% of the emissions. The results show that asphalt pavements significantly contribute to urban pollution, and therefore need to be included to emission inventories, and considered by models. VOC emissions by these extended surfaces are shown to be important contributors to ozone and SOA (PM_1) formed in urban areas. This study suggests that "net zero emissions" targets, such as the zero-pollution action plan of the European Green Deal, cannot be met until this new challenge is acknowledged, and tackled. Asphalt pavements were also found to emit NOx. Interestingly, aged samples produce much larger NOx emission than fresh samples. This could be attributed to the heterogeneous chemical transformations/oxidation of bitumen due to its exposure to atmospheric oxidants, and/or to additional NOx sources in vehicles gas exhaust.To evaluate the impact of laboratory-generated data to urban air quality, numerical simulations were performed with a high-resolution city scale Chemistry Transport Model (EPISODE-CityChem for NOx simulations). With this numerical model of NOx emissions in Athens, Greece, we show that this previously unknown source accounts for up to 20% of NOx emission in specific locations. Asphalt-covered surfaces can therefore significantly contribute to NOx urban pollution, and need to be included to emission inventories, and considered by models (Lasne et al. 2023).

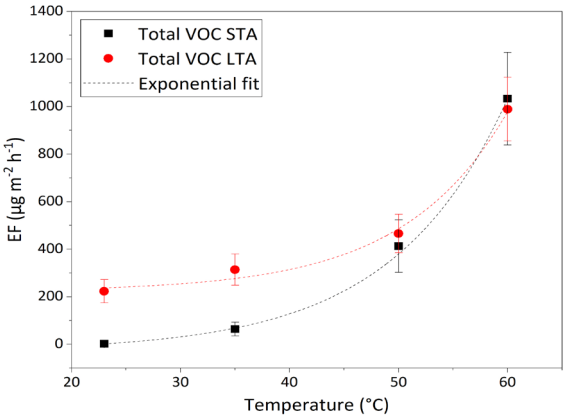

***Figure 1**: Evolution of the total EF (Emission Factor) of VOCs measured by PTR-ToFMS, as a function of temperature, under dry (RH = 0.1%) and dark conditions, for STA (black squares), and LTA (red circles), asphalt mixtures. Fits of the data are shown with dashed lines.*

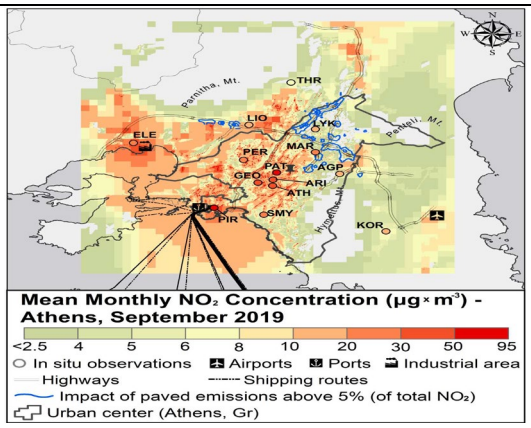

***Figure 2**: Mean monthly surface NO_2 concentrations (µg m^{-3}) over Athens (Greece), as modeled for September 2019. The measured values are shown in the color-coded circles. The blue isopleth corresponds to an impact of emissions from the paved surfaces higher than 5% of total NO_2 emissions.*

The total emission factors (EF) of VOCs detected with PTR-ToF-MS, emitted by STA and LTA asphalt mixtures annealed from 23°C to 35°C, 50°C, and 60°C, under dry (RH = 0.1%) and dark conditions, are illustrated in **Figure 1**. The evolution of the total VOC's EF_{PTR} values as a function of temperature in the 23°C – 60°C range can be accurately fitted with simple exponential functions for both STA and LTA asphalts. The results show that fresh and old asphalt mixtures emit more VOCs when temperature increases. LTA asphalt produces stronger total VOC emissions than STA asphalt, except at 50°C and 60°C, where they are similar. Generally, in the world, road pavements bear more similarities with LTA than with STA asphalt, because they have been aged and weathered, and have not been freshly deposited. Estimates of emissions based on STA asphalt mixtures' VOC emissions therefore largely underestimate emissions by road asphalt at relevant atmospheric temperatures of 23°C and 35°C.

The EF of speciated VOCs measured by GC-MS/FID and PTR-ToF-MS at different temperatures, RH and in the presence/absence of UV light, will be included in a CTM model run by CEREA (work in progress).

The EF of NO and NO_2, and NOx have been used in a city-scale model using Athens as a case study, based on emission kinetics determined at different temperatures to construct a daily profile that corresponds to atmospheric conditions of temperature. **Figure 2** shows the mapping of surface mean monthly NO_2 mass concentrations (µg m^{-3}), together with the mean monthly *in situ* values measured at the stations in Athens. The hotspot areas are the road network in the inner city, and the greater areas around the main industrial and port activity of the domain. The resulting changes due to NOx emissions from the asphalt surfaces are estimated through the normalized differences of the two model applications (with and without the emissions in study). Impacts above 5% to the total NO_2 mass during the hours of peak asphalt emissions (around midday) are shown by the blue isopleth in **Figure 2**, and can reach 20% over highway junctions (Lasne et al., 2023).

Future of the project : A project has been submitted to ADEME – AQACIA in autumn 2022, in collaboration with Université Gustave Eiffel and Nantes Métropole.

Publications, communications and theses

- Lasne J., Lostier A., Salameh T., Athanasopoulou E., Karagiannis D., Kakouri A., Vassaux S., Lesueur D., Romanias M.N. "NOx Emissions of Real-World Samples of Fresh and Old Asphalt Mixtures: Impact of Temperature, Relative Humidity, and UV-Irradiation". Urban Climate, Volume 49, 2023, https://doi.org/10.1016/j.uclim.2023.101457
- Lasne J., Lostier A., Romanias M.N., Vassaux S., Lesueur D., Gaudion V., Jamar M., Derwent R.G., Dusanter S., Salameh T. "VOC Emissions of Asphalt Mixtures: Impact of Temperature on Fresh and Old Road Coating". Submitted to « Environmental Science: Atmospheres », under revision.
- « Asphalt VOC and NOx emissions at in-use temperature: A game changer for urban atmospheric chemistry » oral presentation at 2022 Petersen Asphalt Research Conference, virtual.
- « Are asphalt pavements an important source of atmospheric particles precursors? » poster at IAC 2022, Athens – Greece.
- « How VOC Emissions by Asphalt Pavements under Service Conditions Impact Air Quality in Cities? » poster at EGU 2023, 23-28 April, Vienna – Austria.

- Two Master's thesis by Anais Lostier (Master 2) and Amir Ben Brik (Master 2) + 14-month post-doc of Jérôme Lasne (internal funding from IMT Nord Europe in the framework of the project IRAPAQ).

Data availability : upon request.