FINAL REPORT PROGRAM LEFE

Program LEFE/ CHAT	Heterogeneous INteraction of Volatile Organic Compounds with natural mineral dust under simulated atmospheric conditions (INVOC-dust)	Years 2018 – 2021
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Context : Mineral dust is a significant component of atmospheric aerosols that plays a crucial role in air quality and climate. Natural dust particles are mediums for pollutants uptake, transformation and transportation of VOCs in long distances.

***Objectives / scientific questions*:** INVOC-dust was based on three scientific questions: How efficiently VOC pollutants are taken up on natural dusts and what is the impact of environmental conditions such as relative humidity? How particle ageing influence VOC adsorption/reactivity or the hygroscopic/optical properties of mineral dust? Could the oxidation of primary VOCs on mineral dust particles explain part of the discrepancies observed between measured and modelled concentrations of OVOCs and SOA formation?

Main results: The heterogeneous interaction/reactivity of several VOCs with natural and synthetic mineral dusts was studied by means of laboratory studies and numerical simulations. Laboratory studies were carried out in micro-scale using optical cells and photochemical reactors to determine uptake coefficients and products, while large scale experiments were performed inside CESAM atmospheric simulation chamber reproducing a realistic dust event and the ageing of the dust particles by organic pollutants. Model simulations were performed with the INCA model.

1. Laboratory studies of model VOCs on mineral dusts in micro scale under simulated atmospheric conditions

The objective of laboratory studies at the micro scale was to obtain (i) crucial kinetic (uptake coefficients) and thermodynamic parameters (partitioning coefficients), (ii) mechanistic information regarding the interaction of model VOCs with natural mineral dusts evaluating the impact of atmospheric conditions and dusts chemical composition. Six different natural dusts samples were used, originating from the main arid regions of Earth, i.e. Sahara (Nefta from Tunisia and Mbour from Senegal), Gobi desert, Saudi Arabia (Rawdat) and Arizona. To correlate VOC reactivity and dust properties, in a first step a rigorous physicochemical characterization of dust properties was carried out. In particular, the specific surface area and the elemental composition (Zeineddine et al. 2018) was determined and it was found that **samples originating from Africa were found to be rich in Al while those from Asia continent were rich in Ca, in the form of calcite.** In addition, the identification of sulphite and sulphate species initially present in natural samples due to their atmospheric ageing, was achieved using a novel HPLC method (Urupina et al., 2020, 2021 and 2022).

The strategy followed to determine the uptake efficiency of VOCs was classified in the **screening and deepening phases.** In the screening phase, the uptake efficiency of several VOCs was tested using Gobi dust as "model" sample under fixed experimental conditions. The corresponding uptake coefficients determined were: 7×10^{-7} for isopropanol (IPA), 5×10^{-8} for isoprene (ISP), 1.3×10^{-7} for acetic acid (AcA) and 4×10^{-7} for methyl vinyl ketone (MVK) (Zeineddine thesis). In all cases, the uptake of the VOCs was found to be non-reactive **except for IPA and AcA, where the formation of multiple gas phase products was observed**. For that reason, these gases were further used for a more detailed analysis i.e. the deepening phase. In the deepening phase, the effect of gas phase concentration, relative humidity and dusts variability was evaluated. **In all cases, the uptake coefficients were found to be independent on gas phase concentration, and strongly dependent on relative humidity above 30% (Figure 1). This was attributed to the formation of water monolayer** (Ibrahim et al., 2018)**.** Furthermore, the uptake efficiency of IPA was depending on the chemical composition of the samples. **Under dry conditions, a linear increase of the uptake was noticed for the Al/SI and Fe/Si ratio,** however, under humid conditions (30%

RH) a saturation was observed for Al/Si and Fe/Si ratios above 5% and 3% respectively (Zeineddine et al. 2018).

2. Simulations of realistic dust storms in CESAM chamber and model simulations.

In the framework of INVOC-Dust, two intensive laboratory campaigns were conducted in the CESAM simulation chamber reproducing realistic dust events. The first campaign was dedicated to the establishment of experimental protocols and testing different VOC systems for the organic ageing of particles. **We have successfully achieved to create realistic dust events in the chamber establishing concentrations of dust particles in the range of 200 µg m^{-3} for several hours.** The second campaign was dedicated to the simulation of **the organic ageing of kaolinite (surrogate frequently used to simulate natural dust) and Gobi, using three different reaction systems**, i.e. the reaction of limonene with O_3 and NO_3, simulating a dust storm event impacting a biogenic environment during day-time and night-time respectively, and the reaction of toluene with OH radicals, simulating a dust event occurring in a polluted environment. In all cases, these sophisticated experiments were performed avoiding the formation of secondary particles. A wide panel of instrumentation was used to monitor in real time both gas and aerosol phases, i.e. PTR-MS, FTIR, NO_x, O_3, analysers for gas phase and CPC, SMPS, AMS, HTDMA and CAPS for monitoring particles number, size distribution, gas mixture chemical composition, hygroscopic and optical properties of particles. Figure 2 displays the modification of the hygroscopic properties of dust particles due to their ageing. It can be clearly seen that the organic ageing modified the hygroscopic properties of dust, leading to particle growth especially in case of reactions initiated by NO_3. These results are of high importance, since they improve our understanding for mineral dust aerosol ageing in real atmosphere. The results from the field campaign are still under analysis and soon will be published in high impact factor journals together with the model simulations.

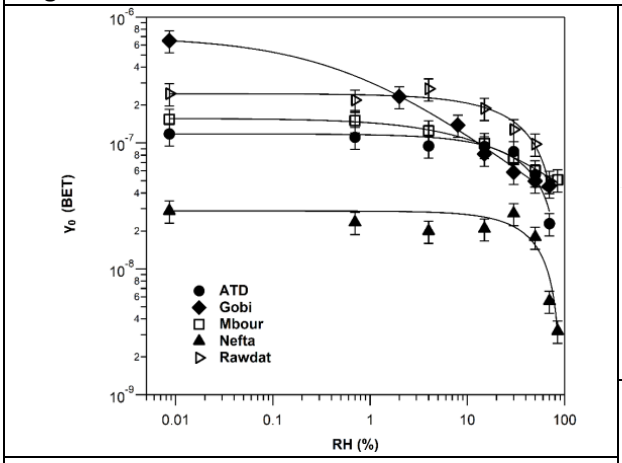

Figure 1. *Uptake coefficients of IPA as a function of RH for 5 natural dusts. The decrease of γ at 30% was attributed to the formation of water monolayer.*

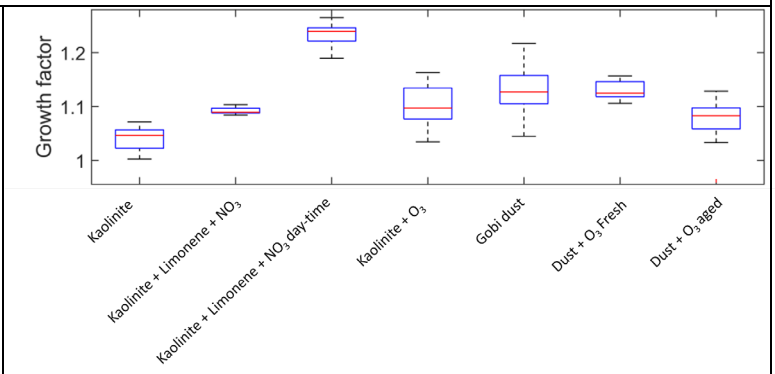

Figure 2. *Growth factors of kaolinite and Gobi dust due to their ageing by pollutants. The low volatility organic nitrates adsorbed on dust particles from the reaction of limonene with NO_3 increase the hygroscopicity of the particles. Pure ageing of particles with O_3 has negligible effects.*

Future of the project: ***In the framework of the INVOC-Dust, a strong and fruitful collaboration was established between the host institution and collaborators. On this basis, the ANR project CLIMDO (CLImate relevant processing of Mineral Dust by volatile Organic compounds) was created and financially supported by ANR (2019-2023) to continue the successful work initiated by the consortium members on VOC reactivity with dust surfaces.*** *Furthermore, the activities initiated in the framework of INVOC-Dust contributed to the WP2 of LabEx CaPPA project (https://www.labex-cappa.fr/) on the aerosol microphysical, chemical and optical properties from fundamental heterogeneous processes to remote sensing. Finally, INVOC-Dust enlarge the international network of PIs group with the establishment of long and fruitful collaborations.*

Publications, Communications and PhD theses:

- 5 articles already published (Zeineddine et al. 2018, Ibrahim et al. 2018, Urupina et al. 2020, Urupina et al. 2021, Urupina et al. 2022), and 3 under preparation
- 2 Thesis (M. N. Zeineddine, 2018, Urupina et al. 2021) and 1 master internship.
- 8 oral communications in national and international conferences, EGU (Giordano et al.) Dust 2018 (Zeineddine et al., Ibrahim et al., Romanias et al.) , Dust 2021 (Zogka et al., Wang et al., Romanias et al.), Labex (Thevenet et al.)