SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CA17136 – Indoor Air Pollution Network
STSM title: Categorization of the oxidative potential of fine aerosols from different types of environments by using the DTT method
STSM start and end date: 01/05/2022 to 28/05/2022
Grantee name: Nuno Henrique Varela Canha

PURPOSE OF THE STSM:

The main purpose of this STSM was for the grantee acquire know-how regarding the technique for characterization of the oxidative potential (OP) of aerosols, using the dithiothreitol method (OP^{DTT}), in a reference laboratory in the field, as the DiSTeBA (Università del Salento - Lecce, Italy). The ultimate goal was that the acquired knowledge would be implemented in the near future in the research center where the grantee is based (C^2TN, Instituto Superior Técnico, University of Lisbon, Portugal), which would make it the first Portuguese laboratory performing such type of analysis.

This STSM was also proposed in order to foster the start of a scientific collaboration between the grantee and the host institution focusing on the OP of aerosols, which is expected to translate in joint research projects (which includes calls for new projects and also collaborations on going projects) and joint future publications.

For its implementation, the STSM target to characterize the oxidative potential of fine aerosols from different types of environments, whose samples were gathered by the grantee in Portugal.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

Before the STSM, the applicant gathered PM2.5 samples (sampled in 47mm quartz filters) from different environments and sources, including: 1) indoor – office, 2) outdoor: urban-industrial area, and, 3) emission sources: traffic, traditional cigarettes, and incense. However, changes were made regarding the initial plan of the STSM since it was not possible to perform the sampling as expected. The grantee started the acquisition of two silent PM2.5 samplers to use exclusively indoors (to avoid interference on the occupants' activities due to the noise of the samplers) in January 2022. However, the equipments were not delivered in time (the deliver will happen only by July 2022), which impossibilitated the sampling of the initial foreseen samples.

Overall, the grantee collected the following PM2.5 samples prior to the start of STSM: 3 x Dust storm, 3 x cigarrete smoke, 3 x incense smoke, and 1 x traffic (total of 10 samples plus their respective blanks).

Due to the problem of lower indoor samples than expected due to the unavailability of sampling equiments, a set of 30 filters (plus blanks) was selected. This set of filters (from a total of 128 samples) corresponds to a 24h sampling (typically 4 times per week) that occurred in between December 2019 and November 2020, in a urban-industrial area of the Lisbon Metropolitan area. Chemical characterization of the filters was previously done, including source apportionment by PMF that identified 7 different sources: soil, secondary sulphate, fuel-oil combustion, sea, vehicle non-exhaust, vehicle exhaust and industry. The 30 samples were chosen considering the samples with the highest load for each source (both massic or %), which could eventually allow to understand the impact of each source regarding its associated OP.

Considering the limited time (4 weeks) and the homogeonity of the 30 samples described above, this set of samples was selected to be analised.

The following tasks were implemented:

Task 1 (Week 1):
Training step-by-step on the OP analysis was done by using test filters (both blanks and sampled) made available by the host institution. The methodology applied was similar to the one described by Chirizzi et al. (2017). A step-by-step technical protocol (eg., reagents/equipments/consumables needed, details about the procedure, including data analysis) was written to be used as a living tool/document (with continuous updating) during the rest of the STSM and for latter implementation in Portugal. During the first week, all solutions needed were also prepared.

Task 2 (Week 2 – two days):
Preparation and extraction of 30 PM2.5 quartz filters (with additional 4 blanks filters) to be analysed in Task 3 was done. Shortly, water-soluble content was extracted from 1/4 of each filter in 15 mL of deionized water via sonication in a water bath for 30 min. Extracts were filtered using PTFE (polytetrafluoroethylene) 0.45 µm pore syringe filters to remove insoluble materials and residual fibers.

Task 3 (Weeks 2, 3 and 4):
OP determination of the water-soluble fraction of the selected PM2.5 filters using the DTT assay was done. Samples were incubated at 37 ºC with DTT (100 µM) in 0.1 M potassium phosphate buffer at pH 7.4 (5 mL total volume) for times varying from 5 to 90 min. At designated times (5, 10, 15, 20, 30, 45, 60 and 90 minutes), a 0.5 mL aliquot of the incubation mixture were picked up and 0.5 mL of 10% trichloroacetic acid was added to stop the reaction. The reaction mixture was mixed with 2 mL of 0.4M Tris-HCl, pH 8.9 containing 20 mM EDTA and 25 µL of 10 mM DTNB. The concentration of the formed 5-mercapto-2-nitrobenzoic acid was measured by its optical density absorption at 412 nm using a UV-Vis spectrophotometer. DTT consumption rate (δ_{DTT}, pmol/min) was determined from the slope (δ_{ABS}) and intercept (ABS_0) of the linear regression of measured absorbance versus time as $\delta_{DTT} = \delta_{ABS} (N_0/ABS_0)$, where N_0 was the initial moles of DTT used. A total of 57 samples were analised (including some replicates).

Task 4/5 (Week 4):
Data analysis of all results was done (with final DTT activity normalised in terms of sampled air volume and in terms of collected aerosol mass) and additional analysis of the PM2.5 filters for determination of organic (OC) and elemental carbon (EC) via thermo-optical method, using a Sunset OC/EC Analyser and following the EUSAARII protocol, was also done.
On 25th May, the grantee presented an one hour seminar entitled “Integrated human exposure to air pollutants - the role of sleeping environments” in DiSTeBA to present his research work to the local researchers, professors and students.

Reference: Chirizzi D., Cesari D., Guascito M.R., Dinoi A., Giotta L., Donateo A., Contini D. (2017) Influence of Saharan dust outbreaks and carbon content on oxidative potential of water-soluble fractions of PM2.5 and PM10. Atmospheric Environment 163, 1-8. DOI: http://dx.doi.org/10.1016/j.atmosenv.2017.05.021

DESCRIPTION OF THE MAIN RESULTS OBTAINED

During weeks 2, 3 and 4, a total of 30 different samples were analysed, along with 4 different blanks.
Replicates were done for all blanks and for 10 samples. Mean activity of blank filters (average of 6 analysis of a total of 4 different filters’ quarters) was 1012 ± 169 pmol/min, which were latter discounted from the samples. One sample presented lower levels than the blanks.
Figure 1 presents the levels of DDT activity (normalized to the mass) of the analised samples, where a mean value of 11.9 ± 6.8 pmol/min*µg was found, with samples ranging from 2.6 to 26.1 pmol/min*µg.

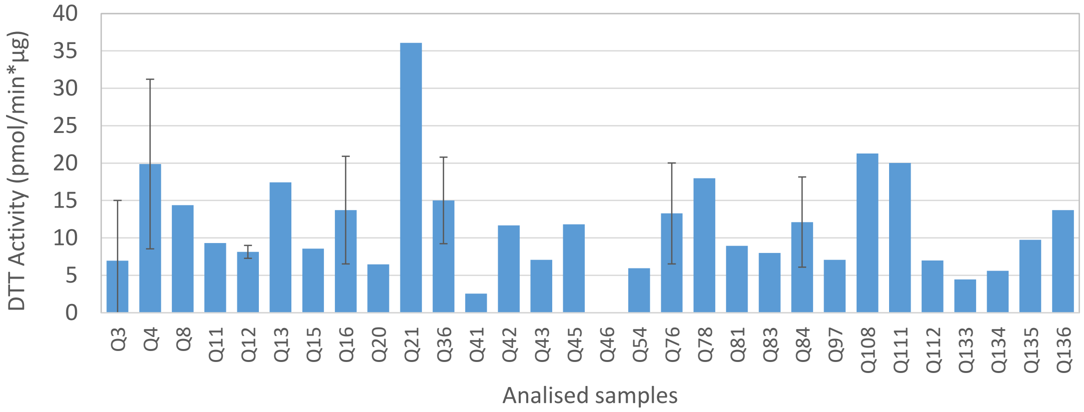

Figure 1. Levels of DDT activity (normalized to the mass) of the analised samples.

The DDT activity (normalized to the sampled volume) showed to have an association with the PM2.5 concentrations, as shown by Figure 2.

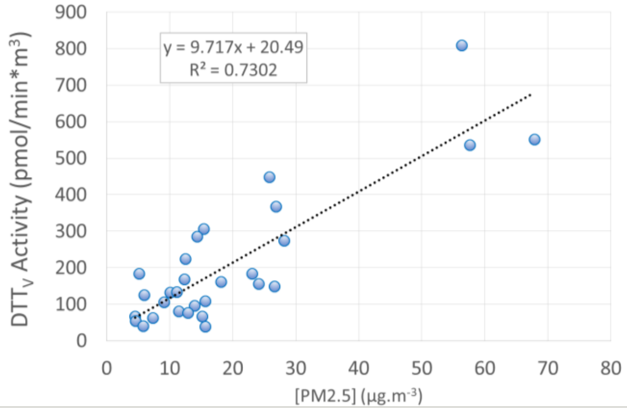

Figure 2. Correlation between PM2.5 concentrations and their DTTv activity.

Considering that the contribution in mass of the different sources was known to the PM2.5 levels, spearman correlations were conducted and it was found significant correlations between DTTv and two different sources: vehicle exhaust (R^2= 0.651, p-value = 0.001) and fuel-oil combustion (R^2 = 0.510, p-value = 0.016).

In discussion with Dr. Rachele Guascito, it was decided that, in Portugal, after the implementation of the DTT technique using the created protocol applied to test filters, the remaining samples of the set of 128 samples from the urban-industrial area would be analysed and those results would be used for the preparation of a manuscript to submit to a ISI scientific journal (naturally, the acknowledgment to the support of CA17136 – Indoor Air Pollution Network for this STSM will be made). Afterwards, the indoor samples will also be analysed (including new samplings will be done in between) and future collaboration works will be conducted. The submission of other manuscripts will be fostered.

FUTURE COLLABORATIONS

This STSM enable and fostered a scientific collaboration with the host institution, which is reflected by:

1) The application to a scientific project's call of the Portuguese Foundation of Science and Technology by the grantee (focusing on OP), with the host responsible as an associated partner.

2) The collaboration of the host institution in the implementation of the OP technique in the grantee' institution, with collaboration in the OP analysis of aerosols from different projects conducted by the grantee.

The planning of writing joint manuscripts regarding the work done during this STSM (complemented with additional analysis that will be done in the coming months) and future OP analysis done in Portugal.