Development of a "Deposition Box" for sampling Total Suspended Particles on not-filter substrates and to perform exposure studies for decay of materials.

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Atmospheric Particulate Matter can induce aesthetic damage and decay of materials as a consequence of its wet and dry deposition on surfaces. A typical approach to perform studies in this field, involves specimens exposure tests (Realini *et al*, 1995; Zappia *et al* 1998). Concerning the evaluation of the fluxes and the effects of dry depositions, repeatable samples are hardly obtainable due to the fact that particles deposition rates depend on several factors (Ferm *et al*; 2006; Maro *et al*. 2014).

In this work a new type of "deposition box" is presented (Figure 1). The "deposition box" can collect atmospheric particles directly deposed on any kind of surface of interest - stone, metal, glass, polymers -. The "deposition box" is made of a 50x50x20cm box covered by a pitched roof. The Air Exchange Rate in the exposure box is standardized at 7 min⁻¹ by means of a fan. Possible sampling size-artifacts have been evaluated by means of inter-comparison measurements carried out inside and outside the exposure box with Optical Particle Counters. An identical particles size distribution $(R^2 =$ 0,993) has been found. The box is made of PP and it can be placed in indoor or outdoor environments. Several specimens can be housed on the punctured sampling plate. Analysis and diagnostic surveys can be performed after the exposure, and different behaviour can be observed on inert and active surfaces, allowing the evaluation on particles-induced decay processes.

A three-months (23 December 2013 – 28 March 2014) exposure was performed in Milan involving four different substrates: PTFE and Quartz filters (used as passive surfaces), Aluminium foil and Marble specimens. Two identical "deposition box" were placed in two different site located in the urban area of Milan: Torre Sarca (45°31'19''N 9°12'46''E) and Villa Necchi Campiglio (45°28'08''N 9°12'08''E). The former is a high-traffic site while the latter is placed inside the Milan low emission zone "AreaC". Different deposition fluxes have been observed for the passive surfaces in the two sampling site: $48\pm4~\mu g~cm^{-2}~month^{-1}$ at Torre Sarca and $32\pm3~\mu g~cm^{-2}~month^{-1}$ at Villa Necchi. The dimensional distribution of the deposed particles has been evaluated by means of SEM analyses and it ranges

from around $100-150\mu m$ for the biggest particles to about $1\mu m$ for the smaller ones.

The obtained samples are suitable to perform several chemical analysis, both in bulk or at the surface. For example, Marble specimens, PTFE, Aluminium and Ouartz passive surfaces have been water-extracted in order to analyse the ionic fraction of the deposed particles. Ion chromatography results show that the ionic fraction accounts around the 10-15% of the total deposed mass. SO_4^{2-} , NO_3^{-} , Cl^- , Na^+ , K^+ , Ca^{2+} were found to be the prevalent ions. Especially regarding marble specimens, a significant presence of oxalates and other anions of carboxylic acids like i.e. acetates and formates, were found. SEM/EDS, XRD and IR analyses of the particles deposed on Marble surfaces shows the presence of gypsum, calcite and silicates. Concerning gypsum, its presence can be attributed to the deposition of dust particles as well as a sulphatation phenomenon of the marble surfaces. In any event the presence of gypsum suggests a potential decay hazard for the marble substrates.





Figure 1. Sketch and photo of the "Deposition Box".

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