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Original Citation:				
A - 11-1-114				
Availability:				
This version is available	http://hdl.handle.net/2318/1659571	since 2	2018-02-05T18:05:13Z	
Publisher:				
Università di Salerno				
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## Development Of A Suitable Sequential Extraction Procedure For The Assessment Of The Availability And Reactivity Of Metal Species In Arctic PM<sub>10</sub> Samples

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Most of the studies on the atmospheric particulate matter (PM) trace metal content consist of the determination of the total concentrations, without distinguishing between the various chemical forms of each element. This procedure does not give any information on the different sources of PM and often provides an overestimate of potential metal toxicity, as only the soluble fraction is likely to interact with the environment and living beings. Unfortunately, the chemical complexity of PM, the extremely small particle sizes and the small quantity of sample typically collected can pose significant problems for metal speciation. In many cases the exact distribution of an element among well-defined chemical species is impossible to determine, due to the large numbers of individual species and to the lack of a universal analytical technique able to both identify and quantify all of them. Alternatively, fractionation procedures are often applied, and the classification of analytes is made according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties. This kind of classification is a valid instrument for both the identification of emission sources<sup>1</sup> and the evaluation of health and environmental impact<sup>2</sup>.

Many researchers have worked on the design of extraction schemes for the sequential solubilization of metals from sediments, leading to the development of the commonly accepted three-steps BCR protocol. The adaptation of this extracting scheme to PM samples led to the development of two-steps procedures, considered a good compromise among costs, analytical times and achievable information. However, different extracting solutions, different extraction methods (ultrasounds, microwave, stirring, prolonged contact) and different techniques for the separation of the extract from the solid residue (filtration, centrifugation) are used, thus reducing the possibility to compare the results<sup>3</sup>.

In this study the most common extracting solutions for PM fractionation have been compared: i) deionized water, due to its high representativeness of the natural solubility processes taking place in the environment; ii) diluted acetic acid, also reported in the BCR fractionation protocol, allowing a good control of the external factors that could influence the extraction and iii) a buffer solution, (ammonium acetate buffer, pH 4.5), able to maintain a good pH control throughout the extraction; the selected pH is very similar to the PM spontaneous one, in order to mime the interactions naturally occurring in the environment<sup>4</sup>. A two-step sequential extraction scheme was optimized by using three Certificate Reference Materials (BCR176 "City waste incineration ash", NIST1648a "Urban particulate matter" and BCR701 "Lake sediment") and comparing the results obtained applying different extraction methods and different extracting solutions. The optimized procedure was then applied to some Arctic PM<sub>10</sub> samples.

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