15th International Congress of the Geological Society of Greece
Athens, 22-24 May, 2019 | Harokopio University of Athens, Greece
Bulletin of the Geological Society of Greece, Sp. Pub. **7** Ext. Abs. GSG2019-253

Detection of Engineered, Incidental, and Natural Nanoparticles in Marine Waters in the Proximity of Islands

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In the past few decades, there has been a strong drive towards understanding the potential environmental impact of nanotechnology (Wiesner *et.al.,* 2006), which has produced a vast number of publications studying the eco-toxicity and, to a lesser extent, the reactivity and transformation of nanoparticles (NPs) in the environment. Although size distributions and number concentrations of the NPs are of paramount importance in such studies, these parameters are often neglected (Baalousha *et.al.,* 2013). Experimental studies for the determination of real-world size distributions and number concentrations of nanoparticles and their dynamics are still scarce. Furthermore, scientific interest is focused on the potential environmental impact of engineered nanoparticles (ENPs), following their release from nano-enabled products; e.g., Ag, Cu, TiO_2 ENPs. In comparison, less attention is being given to incidental nanoparticles (INPs), i.e., nanoparticles that are unintentionally produced due to anthropogenic activities; e.g., plastic particles. In contrast, naturally occurring colloids (particles in the size range of 1 to 1000 nm) have been studied for decades. However, natural nanoparticles (NNPs), such as iron oxides, have been detected and characterised either as a few individual particles, or as part of the 'colloidal fraction' in natural samples. Therefore, there is a shortage of information on the abundance of ENPs, INPs, and NNPs. Identifying differences in their physicochemical characteristics would allow proper source appointment to nanoparticles, facilitate risk assessment and regulation of the nanotechnology industry, and improve our understanding of the role of nanoparticles in the global cycling of elements. Moreover, recent regulatory recommendations (2011/696/EU and EPA-HQ-OPPT-2010-0572) call for the need to characterise nanoparticles based on number concentrations and size distributions; a paradigm-shift away from the conventional mass-based evaluation of solid materials. As a result, the occurrence of natural and anthropogenic nanoparticles in the environment need to be re-evaluated on the basis of population dynamics, i.e., changes of particle number and size with time. The lack of standardised protocols for measuring these properties is weakening regulatory efforts and has created an uneven playing field for nanoparticle manufacturers and processors, hindering investments in research and development. It is, therefore, necessary to develop measurement protocols that will simplify the regulatory field, and thus unlock investment spending for nanoparticles manufacturers, which in turn will help create job opportunities, support the production of environmentally responsible nano-enabled products, and contribute towards the economic growth of the EU.

Nanometrology is critical for enforcing regulations on nano-enabled products and for determining their environmental impact. Environmental nanometrology unavoidably deals with materials of poorly-defined properties and in complex matrices (von der Kammer *et.al.,* 2012), in which nanoparticles may undergo significant transformations (Louie *et.al.,* 2014). It is, therefore, imperative to develop appropriate sampling and analysis protocols to understand the environmental dynamics of these materials. Stabilising agents and separation techniques may be necessary to prevent artefacts, such as aggregation, dissolution, and loss of material. Furthermore, analysis of nanoparticles in an environmental matrix is a challenging task for two reasons: first, the complexity of the matrix may hinder the performance of analytical equipment and second, there are no straightforward guidelines to distinguish ENPs from NNPs or INPs (Wagner *et.al.,* 2014).

In order to differentiate between ENPs, NNPs, and INPs, two approaches can be followed. First, analysis of the bulk solid material and use of specific handles (such as elemental ratios, crystal phases, isotope ratios, etc.) to identify the material in question. This approach requires the presence of significantly high amounts of nanoparticles in the sample. Second, nanometrology offers information specifically for nanoparticles, however it is hindered by the complexity of sample handling. Recent technological advancements have drastically improved nanometrology. For example, efforts to minimise artefacts for electron microscopy analysis (e.g., by using stabilisers), the development of single-particle inductively coupled plasma – mass spectrometry (spICPMS) (Pace *et.al.,* 2011), and single particle chronoamperometry (Tschulik *et.al.,* 2013) for the determination of particle number concentrations and size distributions. These analytical techniques, although not yet developed to their full potential, make it possible to measure composition, number concentrations, and size distributions of nanoparticles suspensions. In combination with appropriate sampling and sample treatment methods, these techniques will be applied to the characterisation of nanoparticles in a real-world environment in this work. Such information would be essential for (1) the regulation of ENPs, (2) studying the environmental implications of ENPs and INPs, and (3) understanding the role of NNPs in the global cycle of elements and pollutants.

The overarching goal of this project is to compare the physicochemical characteristics and population dynamics of engineered, incidental, and natural nanoparticles in the marine environment, in the proximity of an island. Marine waters and sediments are hosts to several potential sources of nanoparticles, both anthropogenic and natural. A few examples are the release of nanoparticles from ship paints, wastewater, food, sunscreens, and cosmetics, the precipitation of particles from volcanic and hydrothermal vent activity, and the deposition of particulate fuel combustion by-products and atmospheric particles on the water column. Although several nano-enabled products for use in the marine environment are already commercialised (e.g., ship paints), information of the fate of nanoparticles in marine water systems is limited. The primary objective of this research project is to produce analytical handles for detecting and characterising ENPs, INPs, and NNPs, while exploring the applicability of advanced environmental nanometrology techniques in marine water systems. It is aimed to (1) optimise sampling techniques for the marine environment, (2) develop methods of analysis, which will tackle difficulties posed by the characteristics of the system (e.g., high salinity, low concentration), (3) measure element-specific nanoparticle populations, (4) identify key descriptors for differentiating nanoparticles based on their source, taking advantage of seasonal variations of these sources, and (5) integrate the gathered information into large-scale databases that will facilitate risk assessment of ENPs. For the purposes of this project, a unique location, the Island of Santorini, Greece, has been identified, which hosts an unusually large variety of sources for ENPs, INPs, and NNPs in a partially enclosed system.

Santorini is part of the active Aegean Volcanic Arc in the South Aegean Sea (Megalovassilis *et.al.*, 2015), a volcano-tectonic line along the subduction zone between the European and African plates. It is the top part of a volcano that is submerged under water and its circular shape forms a natural barrier that partially isolates the waters of the volcanic Caldera from the rest of the Aegean Sea (Nomikou *et.al.*, 2014); there exist only three shallow openings on the North-West and South-West parts of the Caldera with a maximum depth of 390 m. Its unique seabed morphology is likely to act as a natural trap for anthropogenic and natural nanoparticles. In addition, the island has a relatively small area (approx. 20 km^2), but receives an excessive number of tourists during the summer season. Tourist arrivals by cruise ships, ferry boats, or airplanes lie in the range of 1,500,000 – 2,000,000 per tourist season (April – October), while permanent population on the island is less than 25,000 people. The drastic population increase during the tourist season offers an opportunity to study natural sources of nanoparticles, prior to the tourist season, and anthropogenic sources during the tourist season.

Environmental concentrations of nanoparticles are currently being modelled based on information of their production and use. However, these models have not been validated due to the lack of real-world environmental measurements (Nowack *et.al.*, 2015). Such measurements are scarce and typically focus on one element of interest. This work aspires to set a standard for detecting nanoparticles in natural waters and applying state-of-the-art environmental nanometrology techniques for measuring time-resolved number concentrations and size distributions of these materials. High-frequency recorded CTD data in the water column over the Santorini caldera will be used to create depth profiles of oceanographic properties such as conductivity, temperature and salinity. These data will be combined with NP measurements to determine the particle population dynamics, i.e., changes of number and size over time and space.

Acknowledgements

This project has received funding from the Hellenic Foundation for Research and Innovation (HFRI) and the General Secretariat for Research and Technology (GSRT), under grant agreement No 1317.

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