

The Aristeia (“Excellence”) Project for the “Integrated study of trace metals biogeochemistry in the coastal marine environment”

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Abstract

Trace Metals have attracted significant scientific interest due to their wide dispersal in the environment, their provenance from a variety of natural and anthropogenic sources, and their toxicity to biota and humans. European Environmental issues and related policies, such as, the Marine Strategy Framework Directive (MSFD), the Water Framework Directive (WFD), the Integrated Coastal Zone Management (ICZM) Adaptation protocol, the Horizon 2020, the REACH EU regulatory framework etc., refer to trace metal distributions, speciation and behavior. The understanding the environmental biogeochemical cycling of metals that include their sources and sinks, as well as their transport and interaction patterns requires sound knowledge of their chemical speciation which is also useful for assessing the impacts of pollutants to the overall ecosystem functioning including their toxicity and bioavailability. The *Aristeia* (“Excellence”) project aimed to elucidate the trends in trace metal pollution of a notorious hot spot coastal areas (The Gulf of Elefsis as well as the Evoikos Gulf) and evaluate the effectiveness of measures and policies that have been applied for the reduction/prevention of pollution of the coastal zone. Furthermore we aimed to identify in detail the current environmental status of these areas including potential risks for the ecosystem and human health and compare them with past records. Finally through the Dissemination Actions we aimed to communicate these results to local stakeholders and the general public.

Keywords: trace metals, biogeochemistry, coastal, Aristeia.

1. Introduction

The Laboratory of Environmental Chemistry (LEC) of the National and Kapodistrian University of Athens-NKUA) was established by Prof. M. Scoullas who is considered to be a pioneer among Greek Academia in the field of Marine Chemistry and introduced the study of different chemical forms of metals in waters and sediments as early as the late seventies. Since then LEC - NKUA has a demonstrated excellence in trace metal analysis in a wide variety of environmental media and has used a large variety of speciation methodologies and techniques. During this time the staff of LEC-NKUA have published over 200 scientific papers, more than 300 other types of publications and a very long list of conference presentations. Furthermore more than 160 doctorate and master degrees have been awarded based on research carried out in the LEC. LEC has also compiled the monitoring of the most industrialized coastal areas of Greece since 1986 and is now holding one of the most complete time series of trace metal levels in waters and sediments of the Gulf of Elefsis and Evoikos Gulf. LEC has effective close collaboration with other high level research institutions (e.g. HCMR) and is also working in Public Awareness, Environmental Education (EE) and Education for Sustainable Development (ESD) and has successfully transformed the produced scientific outcomes into public knowledge used for education, awareness and informed decision making on environmental issues to benefit society.

2. Materials and methods

Aristeia aimed to undertake speciation studies combined with total trace metal analysis in water, sediment and biota samples with existing protocols used in our research efforts and with new protocols that developed during the project from the scientific team. In order to successfully undertake the above mentioned studies LEC purchase an analytical instrument (ICP-MS) through this project (Fig.1). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is arguably the most versatile trace elemental analysis technique available today. Depending on the individual instrument configuration, sample types ranging from sea waters and rock digests to ultra-pure semiconductor grade chemicals can be routinely analysed, for almost all the elements in the Periodic Table, from low pg/mL (in most cases) to high µg/mL concentration levels.

The utilization of the highly sensitive, multi- elemental technique ICP-MS system with collision cell technology to remove interferences in conjunction with the existing infrastructure of LEC (a clean room, atomic absorptions spectrometers, environmental sampling equipment) allowed the integrated study of trace metal distributions, exchange between phases and compartments, sources and sinks etc in polluted coastal marine environments and in special intermittently anoxic conditions.

LEC carried out in depth study of almost all aspects of distributions in the aquatic environment for the most common trace metals (Cd, Cr, Cu, Zn, Ni, Fe, Mn, Al, Pb) for which there were already an extensive background research. Furthermore the utilization of the proposed ICP-MS gave LEC-NKUA the opportunity to measure for the first time a larger number of other trace elements i.e. As, Ga, Se, V, Rb, Sr, Cs and other rare earths.

Since the ICP-MS was used for the first time in the LEC-NKUA one aspect of this research was to focus on analytical methodology i.e. to plan the analytical protocols and validate them.



Fig. 1: Inductively Coupled Plasma Mass Spectrometry (model iCAP-Qc)

The *Aristeia* project focused on two coastal areas of Greece facing increased environmental pressures and pollution problems. The first area (Gulf of Elefsis) is affected by industrial activities and increased ship traffic and suffers from intermittently anoxic conditions during summer. The other one (Evoikos Gulf) was also under significant environmental pressure from industrial and urban sources for several decades and it is also affected by a strong tidal current which is rare for a Mediterranean area. The research activities of the project included:

- In situ measurements of physicochemical and hydrological parameters.

- Samplings of seawater – sediments – particulate matter – organisms in all parts and depths of the selected areas.
- Determinations of total metal concentrations and various metal forms using speciation methodologies and measurements with ICP-MS.
- Use of numerical models and statistical programmes for the handling of research results, as well as construction of specific databases.

The trace elements determined were divided into four categories; a) elements of high priority in the Mediterranean Region (Pb, Cd, As), b) essential for the organisms' elements (Fe, Cu, Se, Zn), c) elements with high concentrations in the sediments of the studied areas due to geological singularity (Ni, Cr, Mn) and d) metals deriving from anthropogenic activities with few toxicity data (V, Rb, Sr).

The project assisted the staff of LEC to strengthen existing collaborations and form new ones in the areas of trace metal speciation and analysis. The collaborating researchers and institutes were: Ruder Boskovic Institute of Zagreb (Assoc. Prof., Dr. Marta Plavsic), Marine Environmental Studies Laboratory (MESL-IAEA, Director Dr. Agelidis, Dr Emilia Vassileva), Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, (Assoc. Prof., Dr. Diana Rabadjieva), Priority Action Program/ Regional Activity Centre (PAP/RAC) (Split, Croatia) and Institute of Atmospheric Pollution Research of the National Research Council of Italy (CNR-IIA).

3. Scientific Team - Work packages

The proposed research carried out by the following scientific team members:

- Experienced Academic Staff – Steering Committee: 1) Prof. M. Scoullas (Principal Investigator), 2) Prof. M. Dassenakis 3) Prof. Ath. Valavanidis.
- Experienced LEC - Researchers: 1) Dr. S. Karavoltos, 2) Dr. F. Botsou, 3) Dr. A. Sakellari, 4) Dr. V. Paraskevopoulou, 5) Dr. E. Stathopoulou.
- New members: 1) Dr. G. Katsouras (post doctorate researcher), 2) E. Louropoulou (doctorate candidate), 3) N. Kapetanaki (doctorate candidate), 4) O. Chalkiadaki (MSc student), 5) N. Mpoura (MSc student).

In order to achieve the project aims, the next working packages were followed:

WP1 – Purchase and installation of scientific equipment - Set up of equipment - Analytical protocols - Test runs (Month 0-30): After setting the technical characteristics of the requested equipment and have an indication of the requirements and the costs, an ICP-MS and the Hg-fluxes modules purchased. The development of analytical protocols took place by the experienced researchers of LEC in collaboration with all the new members of the scientific team and under the supervision of the Academic Staff of LEC.

WP2 – Samplings and Analysis (Month 13-36): This work package included the main part of the experimental work for this project, i.e samplings in the selected hot spot coastal areas (Gulf of Elefsis and Evoikos Gulf) and the analysis of samples. All LEC members (old and new) with their experience were involved in designing and carrying out sampling campaigns and did the analyses of all.

WP3 Collaborations with other Institutes (Month 4-36): This work package covered the exchange visits of LEC staff to the European Institutes mentioned above and the travel of European researchers to Athens.

WP4: Dissemination actions (Month 18-36): This WP included the organization of the Final Conference of the project as dissemination actions as well as the presentation of the research outcomes of the project in National and International conferences and scientific journals.

4. Conclusions

In conclusion through all the measures mentioned above the following specific objectives of the *Aristeia* project achieved during 9/2012 to 9/2015:

a) The study of metal pollution trends and the evaluation of the effectiveness of measures and policies that have been applied for the reduction/prevention of pollution in the coastal zone of Elefsis and Evoikos Gulf,

b) The investigation of the biogeochemical cycles and speciation of metals that have newly emerged as pollutants, by means of new sophisticated methodologies and techniques (ICP-MS). The operation of the unique ICP-MS equipment in NKUA, on its own has already led to research collaborations with other departments of NKUA for biological, geological, pharmaceutical and medicinal applications,

c) The vision of Laboratory of Environmental Chemistry, to become a robust Centre of Excellence which will be able to contribute effectively to the improvement of the Mediterranean Coastal Environment by employing better environmental and analytical chemistry, improving inter-disciplinarity, and disseminating useful knowledge through collaborations with governmental and scientific bodies, education and public awareness.

At the same period (2012 – 2015) the research strategy of LEC/NKUA, linked to several current marine policy issues and research initiatives. The ones presenting greater synergy possibilities were: The *Marine Strategy Framework Directive*, the *2000 Water Framework Directive*, the *European ICZM*, the *Strategic Action Program (SAPMED of the UNEP MEDPOL)*, the *2009 European Commission White Paper* and the relative *HORIZON 2020 Initiative* and the UNEP Mercury Partnership.

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