PhD Research Project Proposal

Applicant: Eleonora Renzi

1. Title

A combination of ambient and vacuum ionization mass spectrometry techniques applied to environmental organic phosphorus compounds and other contaminants

Keywords: eutrophication, cyanobacteria, organic phosphorus compounds, liquid-chromatography, tandem mass spectrometry, extractive-liquid sampling electron ionization.

2. Research Area

Research Methods in Science and Technology – Analytical Chemistry CHEM-01/A

3. General presentation of the project and state of the art

Eutrophication is one of the most widespread environmental problems of inland waters and represents their enrichment by nutrients (*e.g.*, N and P containing compounds) leading to an accelerated growth of cyanobacteria (see *Figure 1*).[1,2]

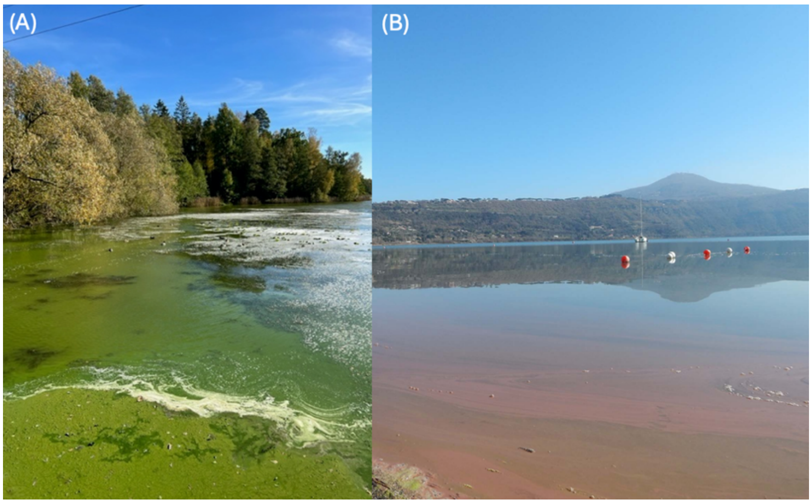

Figure 1. Algae blooms from (A) Lake Norra Bergundasjön, Sweden and (B) Lake Albano, Italy.[3,4]

Such phenomenon is spread worldwide and a number of publications can be found in the literature, with a focus on organic phosphorus (OP) compounds analyses.[2,5–22] Nevertheless, little is known about OP compounds in south European countries, where Italy represents one example.[23–31]

Taking into account that OP compounds accumulate in sediments,[2,21] the project will aim to get a deeper understanding of OP compounds in environmental samples and their relationship with other contaminants.

4. Research Objectives

Inositol phosphates (IPs) are a class of OP compounds which are widely found in aquatic systems, see one example in *Figure 2*.[32]

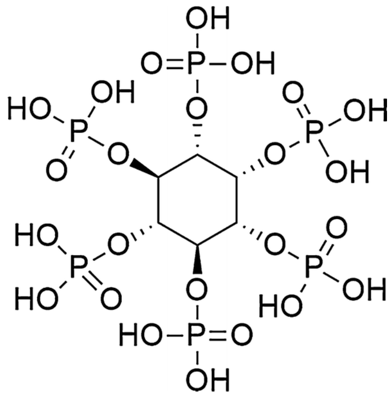

Figure 2. Chemical structure of inositol hexakisphosphate, also known as phytic acid.[33]

In turn, IPs can be classified depending on the number of phosphate groups attached to the inositol ring, as well as depending on the stereoisomeric forms found in the environment.[34] Hence, the project will aim to get a deeper insight of IPs in aquatic systems, with a combination of liquid chromatography-mass spectrometry (LC-MS) and direct mass spectrometry (DMS). In the former case, chromatography will help to reduce sample complexity and an appropriate mass analyzer/analyzers will allow detection of the gas phase ions. In the latter case, DMS will be performed with the technique "extractive-liquid sampling electron ionization-mass spectrometry" (E-LEI-MS), allowing real-time analyses without sample preparation steps. Thus, a combination of hard and soft ionization techniques (*i.e.*, electron and electrospray ionizations) will be combined to get complementary and/or comparative results.

5. Methodology and Expected Results

Real time analysis will be performed with E-LEI-MS and as it employs electron ionization (EI), the reproducible mass spectra allow immediate comparison with commercially available libraries.[35] Furthermore, E-LEI-MS has shown to overcome most of the matrix effects observed with other ionization techniques and will be further assessed to a complex environmental matrix, as sediments are.[35,36] Additionally, E-LEI-MS provides the ability to perform multilayer analyses permitting the sample mapping in three dimensions, hence both surface and spatial analyses can be performed.[37]
Nevertheless, for certain class of compounds the ionization efficiency with electrospray (ESI) was found to be more sensitive than EI, for this reason a LC

system hyphenated to a tandem mass spectrometer will aid to compare the ionization efficiencies of these compounds.[36] Furthermore, as EI lack of molecular ions information, they will be detected with ESI.[36]
The above-mentioned techniques will allow OP compounds quantification in aquatic systems, aiming to get a deeper insight of nutrients overloading and if their presence and abundance can be modified by the concurrent contamination of other compounds. A general workflow schematic is depicted in *Figure 3*.

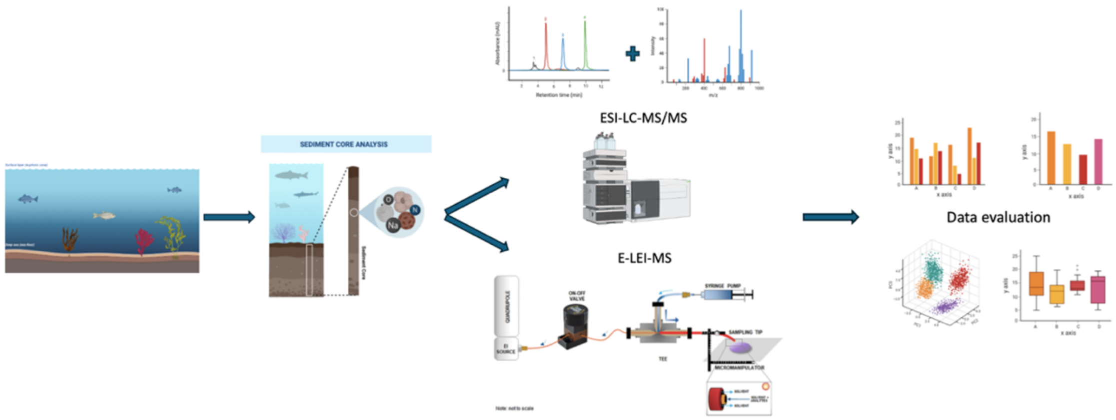

Figure 3. Research project proposal workflow schematic.[37,38]

6. Bibliography

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7. Description of the research in the three-year period (feasibility)

The primary goal is to enhance the detection, identification and quantification of the analytes in various environmental samples, such as water, soil and sediment.

Year 1: Method Development and Optimization

Develop and optimize ambient MS techniques to detect OP compounds.
Integrate these methods with vacuum ionization MS techniques to improve sensitivity and accuracy. The candidate techniques are direct infusion MS, LC-MS, GC-MS with a previous investigation of the optimal analytes extraction conditions.
Conduct initial experiments to validate the combined techniques using standard samples.

Year 2: Application to Environmental Samples

Apply the optimized methods to real environmental samples collected from different sources, including animals and plants.
Focus on identifying and quantifying organic phosphorus compounds and other relevant contaminants.
Compare the performance of the combined techniques with traditional methods.

Year 3: Data Analysis and Environmental Impact Assessment

Analyze the collected data to understand the distribution and concentration of organic phosphorus compounds and contaminants.
Assess the environmental impact of these compounds, focusing on their sources, pathways, and potential risks.

Publish the findings and provide recommendations for monitoring and mitigating environmental contamination.

This research will contribute to a better understanding of environmental contaminants and support the development of advanced analytical techniques for environmental monitoring and protection.