ENGLISH

Topic/Title

Geochemical and isotopic characterization (Chromium and Magnesium) in environmental matrices: MDBA Bacoli case study.

Proposer (Tutor)

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Research proposal[1]

Chromium, a heavy metal in trace amounts, has two prevalent oxidation states, Cr(III) and Cr(VI), which show completely antithetical characteristics in terms of toxicity, behaviour in soil and in plants. Cr(III) is a micronutrient for mammals and humans, while Cr(VI) is carcinogenic. Cr isotopes (^{50}Cr , ^{52}Cr, ^{53}Cr, ^{54}Cr) have been engaged to distinguish between geogenic and anthropogenic Cr(VI) contamination and to further study the natural attenuation of toxic Cr(VI) in the environment. During the natural reduction of Cr(VI) to Cr(III) by organic material, sulfides, and ferrous species, the reaction rates of the ^{52}Cr are faster, and therefore, the remaining Cr(VI) is isotopically enriched in ^{53}Cr . On the other hand, hydrolyzed Cr(III) can be slowly oxidized to the toxic and mobile Cr(VI) by Mn oxides, resulting in Cr isotopic fractionation, with a residual Cr(III) depleted in ^{53}Cr and a mobile Cr(VI) enriched in heavy isotopes.

Magnesium, a metal that constitutes 2.3% of the lithosphere by weight, is found on the market with purities that exceed 99.8%, but, in industrial applications, it is rarely used in its pure state. Amalgamated with other elements, it forms alloys renowned for their low density, high resistance, notable elastic modulus, shock absorption capacity, resistance to corrosion by organic substances and alkalis. Exposure to the vapor of magnesium oxide, following combustion, welding or fusion from metal processing, can cause fever, cold, nausea, vomiting and muscle pain.

The chosen case study is a plant located in the Municipality of Bacoli (NA) which main production concerns the construction of electronic equipment and falls within the perimeter of the former area of national interest "Litorale Domitio Flegreo ed Agro Aversano". In August 2007 the Characterization Plan was presented and in May 2011 the results showed that the

[1] *Project possibly financed with other research funds*

parameters Chromium and Chromium VI were higher than the CSC (threshold contamination concentrations) in groundwaters. In February 2016, the Phase 1 of the Remediation Project was approved and in 2017, given the positive results of the pilot remediation interventions carried out, the Full Scale Operational Remediation Project was presented and approved, starting on 02/21/18. Since February 2021 the remediation is active and hydrochemical monitoring has been carried out approximately on a monthly basis. Monitoring results have highlighted: in some areas pinkish colorations of the water due to the incomplete consumption of the injected permanganate; the continuation of the injection interventions has also led to an increase in the formation of unwanted products such as Chromium VI in the area of Building 13; in cell A, where the abiotic dechlorination intervention is underway, the achievement of the remediation objectives for Chromium VI in all 9 control points; in cell B where the biological reductive dechlorination intervention is underway, the CrVI is found to be stably compliant with the CSC in all points.

For the PhD project samples of lacustrine sediments will be analysed together to groundwaters and soils in opportunely selected points of the plant area. New chemical data (Cr content, Mg content, Cr speciation) on sediments, soils and groundwaters will be compared with previous analyses available in Regional Agency for Environmental Protection of Campania (ARPAC) databases. The setting of Cr isotopic systematic at the DiSTAR laboratories and its application, togheter with the using of Mg isotopes systematic at INGV laboratories, to opportunely selected samples of different matrices will be performed. The chemical and isotopic dataset will be processed in order to identify the geological and antropogenic factors that control the Cr (VI) and the Mg chemical and isotopic variation on different environmetal matrices.

Research Plan

The PhD project work will be divided into several phases.

I° year

- **POINT 1** During the first year, a bibliographic study will be carried out to study the area under investigation from both a geological and chemical point of view, recording in specially created databases the results of studies conducted during and after the remediation operations. The results of this preliminary activity will allow us to identify the major or trace elements that can be considered tracers of environmental pollution processes.

- **POINT 2** Samples of the different environmental matrices (lacustrine sediments, solis, groundwater) will be selected for which Cr speciation data will be obtained and, where possible, Mg content.
- **POINT 3** Once the chemical elements of interest have been identified and the most suitable sites for the PhDl project have been defined, the phase of inspection and sampling of soils and waters in an area of approximately 15km^2 will begin, based on the results of bibliographic research and ARPAC monitoring data.

II° year

- **POINT 1** During the second year, or in any case as soon as the sampling phase is concluded, the speciation analyses of Cr will be carried out and the procedures for the preparation and analysis of Cr isotopes will be systematized at the Clean Room and Mass Spectrometry laboratories of DiSTAR. The latter includes: 1) preparation of ion exchange chromatographic columns with appropriate resins; 2) preparation of high purity reagents; 3) set up of the Cr extraction procedures and analysis of its isotopic composition by thermoionization mass spectrometry.
- **POINT 2** At the same time, both the preparation of samples for chemical analysis and Mg isotopic analysis will be carried out at the INGV-OV laboratories.

- **POINT 3** In the second half of the year, an algorithm based on the Python programming language will be implemented in order to process the large amount of data that will be produced during the PhD work.

III° year

- **POINT 1** During the last year, the activities of implementing the algorithm and processing the data produced during the PhD work will continue.
- **POINT 2** The publication of two or more scientific articles in high-impact scientific journals could be possible as early as the end of the second year of activity.
- **POINT 3** The last months of the PhD will be dedicated to writing the thesis and presenting the results obtained at national and international conferences.

Additional notes:

A preliminary timetable of activities over the three years is reported below.

Activity	1-2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	23-24	25-26	27-28	29-30	31-32	33-34	35-36
Bibliographic research	x	x	x	x	x													
Geochemical data database of studied	x	x	x	x	x													
Field activities to identify sampling areas			x	x	x	x												
Set up of sample preparation and procedures for Cr speciation and Cr isotopic analyses					x	x	X	X	x	x	x	x						
Sample preparation for chemical and isotopic analysis of Mg							x	x	x	x	x	x						
Chemical data and isotopic data acquisition								x	x	x	x	x						
Preliminary data elaboration										x	x	x	x					
Algorithm for statistical data processing										x	x	x	x					
Courses	x	x					x	x										
Participation in conferences										x	x			x	x			
Preparation of scientific papers										x	x	x	x	x	x	x	x	x
Final work thesis															x	x	x	x