Harmonization of sampling and chemical analysis for the study of Cr(VI) water contamination in aquifers of eastern Mediterranean and Oman- the CrITERIA project experience

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Abstract
The CrITERIA project aims to deliver a harmonized data base, to assist water resource management organizations and water users on decision making when coping with water scarcity, climate extreme events and contaminated water. Contamination by Cr(VI) is used as an example of a specific water pressure problem that has to be tackled. Comparative, collaborative research using real situation data from case study areas in each of the participating countries was the base of our methodology. Such areas had already been identified in Greece and Italy and were further monitored, evaluated and compared to potentially affected water bodies in Cyprus, Turkey, Jordan and Oman, suspect for Cr(VI) contamination due to either natural or industrial sources within the same time frame. To enable comparison a common protocol for water sampling has been developed. This served as the base for monitoring water quantity and quality aspects in the case study areas and verify if Cr(VI) contamination levels exceed regulatory levels. The analytical QA/QC has been facilitated by analyzing a proportion of the samples from each case study area in an external accredited laboratory. The paper presents the developed sampling protocol and discusses the challenges during the harmonization of data from sampling and analysis.
Keywords: hydrogeochemistry, database, quality control, measurement uncertainty.

1. Introduction

The countries of the Mediterranean have similar water resource problems but also share common cultural heritage and customs. This provides an opportunity to develop common approaches for tackling water resource management problems. The great experience of water management in several EU countries guided by the Water Framework Directive (WFD) and the tools provided by the Common Implementation Strategy (CIS) could be transferred to Southern and Eastern Mediterranean Countries in order to achieve Integrated Water Resources Management (IWRM).

Within this framework the CrITERIA project aims to deliver an optimization tool, including documentation and a database, to assist water resource management organizations and water users on decision making when coping with water scarcity, climate extreme events and contaminated water. Contamination by Cr(VI) as the central theme of the project is used as an example of a specific water pressure problem that has to be tackled through IWRM. Contaminated areas had already been identified in Greece and Italy and were further monitored, evaluated and compared to potentially affected water bodies in Cyprus, Turkey, Jordan and Oman, suspect for Cr(VI) contamination due to either natural or industrial sources within the same time frame.

2. Materials and Methods

2.1. Design of a common water sampling and analysis protocol

Designing a common protocol for sampling and analysis of water samples served as the base for monitoring water quantity and quality aspects in the case study areas and for verifying that Cr(VI) contamination levels exceed regulatory levels. At least two sampling campaigns one in the dry and one in the wet season took place in each study area during the first two years of the project. With respect to analysis, water contamination by Cr(VI) may lead to a failure to achieve the specified objective of water quality as a pressure on its own, or in combination with other pressures. Of major significance for the project was to ensure the chemical analysis of both major ion and trace element content in all collected samples. A combination of the following techniques were used, according to their availability in the laboratories of project participants: inductively coupled plasma mass spectrometry (ICP-MS) for trace elements, inductively coupled plasma atomic emission spectroscopy (ICP-AES) for major elements, ion chromatography (IC, anions), titration (alkalinity), photometric methods (Cr(VI)), potentiometric methods (pH) and conductometric methods (electrical conductivity). The output includes full documentation with detailed description of the protocol for water sampling and analysis in compliance with existing guidelines for best practice (e.g. ISO 5667-3:2012, ISO 5667-14:2014).

2.2. Quality control procedure

All data concerning the nature of water bodies were tested against the conceptual models, both to refine the models and to check for data errors. Quality assurance/control (QA/QC) is particularly important in the CrITERIA project because of the potential health implications of Cr(VI) contamination and the low concentrations expected in instances of geogenic origin of Cr. QA/QC has been facilitated by analyzing a proportion of the samples from each case study area and at least one sampling campaign in an external accredited laboratory. Specifically for measuring Cr(VI) concentrations, the US-EPA 218.7 method (US-EPA, 2011) with low detection limits has been employed during this exercise.

3. Results and Discussion

3.1. Performance of the common sampling protocol and limitations of chemical results harmonization

The developed sampling protocol provided detailed guidance with respect to the preparatory stage of planning the water sampling surveys as well as on water sampling procedures. Specific information for the planning stage included sampling frequency, sample containers, decontamination of equipment, selection of sampling locations and field preparations. Accordingly, information regarding water sampling procedures included the sampling quality assurance sample documentation and identification, chain of custody forms and field log information. Detailed instructions on purging, collection of field blanks and sampling replicates have also been included along with appropriate guidance on sample preservation, handling and transport.

The use of the common sampling protocol enabled all participants to collect water samples according to a prescribed methodology, thus ensuring harmonization during this research task. However, in the stage of chemical analysis such common protocol was not possible to be designed and implemented. In this instance the analytical protocols followed by each participant depended on available instrumentation and know-how on analytical methods. This fact, in combination with the wide range in natural variation of Cr(VI) concentrations in groundwater of the study areas has been a major challenge during research implementation.

Acknowledgments

The present work was co-funded by the European Union (ERDF) and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", under the ERANETMED 1st Joint Call on Water Resources (project acronym: CrITERIA/ project code: T3EPA-00004).

3.2. Results of inter-laboratory comparison

Inter-laboratory trials are common practice in order to ensure that performance of analytical laboratories is fit for purpose. In their typical form such trials include the analysis of common samples by the participants. In the present research, such trials would be difficult to implement due to logistic and financial constrains. Although participants were required to report detection limits and uncertainty values along with their results, harmonization was based on analysis of a proportion of the total samples by an external accredited laboratory. An example of the correlation plot based on Cr(VI) results reported for samples from Greece, Cyprus and Turkey is presented in Figure 1. It is clear that dispite the wide differences in measured Cr(VI) concentrations in each country, a high positive correlation is observed (R^2 = 0.99) taking into account the total range of reported values.

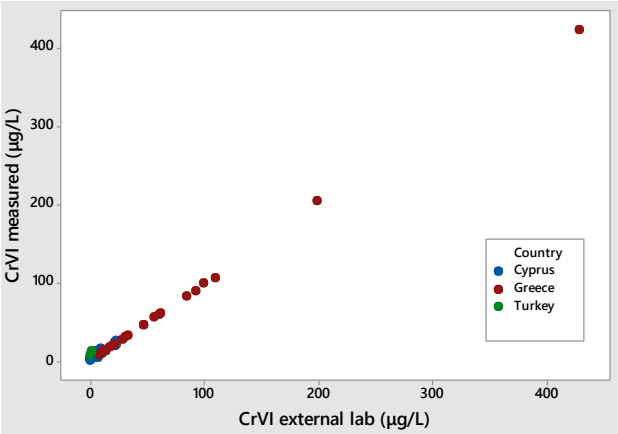

Figure 1. Scatter plot of measured Cr(VI) concentrations in water showing high correlation between results by the external laboratory and three participating countries.

4. Conclusions

The challenging task of harmonization of sampling and chemical analysis for the study of Cr(VI) water contamination within the CrITERIA project has been tackled through the design and implementation of a rigorous and detailed sampling protocol and through a modified inter-laboratory comparison of analytical data by involving an external referee laboratory. The developed methodology could be used in similar studies of pollution that are based on comparative research within the frame of IWRM.

References

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