CRITERIA

Cr(VI) Impacted water bodies in the Mediterranean: Transposing management options for Efficient water Resources use through an Interdisciplinary Approach

Mid-term Report

UNIROMA1

Part 3 – Hexavalent chromium natural occurrence in Italy

The naturally occurring content of hexavalent chromium has been verified in different areas of the Italian peninsula, most of them being concentrated on the northern arch of Apennines range. In some cases, concentrations up to 5000 mg kg^{-1} in soil sample and up to 73 µg L^{-1} in water sample have been reported thus exceeding the required limit for drinking water of 50 µg of Cr(VI) per liter.

Major source of Cr(VI) natural contamination is related to the presence of ultramafic rocks and serpentinites of ophiolite complexes.

Ophiolites are slivers of ancient oceanic brought to surface by the action of strong tectonic forces at convergent plate boundaries for example during orogeny of mountain belts. Due to the prolonged compression stress, these rocks are often very deformed. From a mineralogical point of view, ophiolites are mainly composed by peridotite, pyroxenes and amphiboles. Some of these minerals contain notable amount of chromite [$FeCr(III)_2O_4$]. Though recalcitrant to weathering, diagenesis, and low-grade metamorphic reactions, chromite represents the primary source of Cr(III). Trivalent chromium, as known, exhibits scarce solubility under a wide range of conditions. However, some transitions metals such as manganese can act as oxidizing agents thus transforming the harmless Cr(III) into the very dangerous Cr(VI). Some authors include birnessite and brucite, among the minerals suspected of oxidizing Cr(III) and resulting in hazardous levels of aqueous Cr(VI) in surface and groundwater. The prevailing Cr(VI) species in solution is CrO_4^{2-}; however, som authors report that $CaCrO_4°$ and $MgCrO_4°$ neutral complexes can represent significant percentages (up to 42 %) thus suggesting that the mobility and consequently the bioavailability of Cr(VI) can be significantly enhanced by the charge exhibited

especially because they are not involved in adsorption/desorption processes (Lelli et al, 2014).

Fig.1 Sites contaminated by naturally occurring chromium

More in detail:

SITE	GEOLOGY	DATA	REFERENCE
1) Verrayes and Pontay, Val d'Aosta region, Province of Aosta 	Ophiolites	Content of Chromium (VI) in groundwater and surface water above the limit for drinking water.	Rotiroti, M., Fumagalli, L., Frigerio, M.C., Stefania, G.A., Simonetto, F., Capodaglio, P., Bonomi, T. Natural background levels and threshold values of selected species in the alluvial aquifers in the Aosta Valley Region (N Italy) (2015) Rendiconti Online Societa Geologica Italiana, 35, pp. 256-259 Bonomi, T., Fumagalli, L., Stefania, G.A., Rotiroti, M., Frigerio, M.C.,Pelliccioli F., Simonetto, F., Capodaglio, P., Ground water contamination by Cr(VI) in tha Aosta Plain (northern Italy) : characterization and preliminary modeling (2015) Rendiconti Online Societa Geologica Italiana, 35, pp. 21-24
2)	Ultramafic rocks, usually	Analysis of 58 samples	Fantoni, D., Brozzo, G., Canepa, M., Cipolli, F., Marini, L., Ottonello,

Liguria region, Province of La Spezia 	affected by extensive serpentinnizati on, .	(September-October 2000): Cr(III) undected, dissolved Cr is present in toto as Cr(VI), with concentrations up to 73 ppb. source for	G., Vetuschi Zuccolini, M. Natural hexavalent chromium in groundwaters interacting with ophiolitic rocks (2002) Environmental Geology, 42 (8), pp. 871-882.
3) Emilia Romagna region, Province of Parma 	Serpentinites consisting of weathering phases, mostly smectite and Fe-xides/hydroxid es; with serpentinite, mostly lizardite and minor chlorite and chrysotile.	Cr content in spring water up to 20 ppb.	Venturelli, G., Contini, S., Bonazzi, A., Mangia, A. Weathering of ultramafic rocks and element mobility at Mt. Prinzera, Northern Apennines, Italy (1997) Mineralogical Magazine, 61 (6), pp. 765-778
4) Valpadana, Emilia Romagna region 	High chromium and nickel content in soils and sediments of the Po River Plain deriving from the weathering of femic and ultrafemic rocks.		Bianchini, G., di Giuseppe, D., Natali, C., Beccaluva, L. Ophiolite inheritance in the Po Plain sediments: Insights on heavy metals distribution and risk assessment (2013) Ofioliti, 38 (1), pp. 1-14.
5) Cecina, Tuscany region, Province of Livorno	Extensive outcrops of serpentinized ultramafic rocks where the oxidizing agent of Cr(III) is supposed to be brucite $Mg(OH)_2$ as well as Mg–HCO_3.	High lev- els of Cr and Ni often exceeding law limit in sediments collected in the Possera Creek a left tributary of the Cecina River.	Langone A., Baneschi I., Boschi C., Dini A., Guidi M, and Cavallo A., (in press), Serpentinite-water interaction and chromium (VI) release in spring waters: examples from Tuscan ophiolites, Ofioliti, 38(2013). Laterza V., Franceschini F, Influence of ophiolitic rocks on the spatial distribution of Chromium and Nickel in stream sediments of the Cecica river Basin (Tuscany, Italy), ofioliti, 38(2013), 59-73.

		Concentration of Cr(VI) in groundwater up to 49 µg/L.	Lelli, M. Grassi, S. Amadori, M. Franceschini, F, Natural Cr(VI) contamination of groundwater in the Cecina coastal area and its inner sectors (Tuscany, Italy), Environmental Earth Sciences 71(2014) 3907–3919 .
6) Pollino, Basilicata region, Province of Potenza 	Ophiolites, serpentinated ultramafic rocks, and crystalline rocks of continental origin naturally rich in chromium and nickel.	6 of the 43 spring waters analyzed, in a first study exhibited Cr(VI) values up to 20 ppb. In the MoGeSPol project Cr concentrations in soils above 3000 mg / kg always associated with nickel contents in the order of 2000 mg / kg, were found while the content of Chromium (VI) in the analyzed waters was always close to the threshold of 5 ppb with maximum value of 45 ppb in 2013 for Fontana Altosano).	Margiotta S., Mongelli G., Summa V., Paternoster M., Fiore S.– Trace element distribution and Cr(VI) speciation in Ca-HCO3 and Mg-HCO3 spring waters from the northern sector of the Pollino massif, southern Italy. Journal of Geochemical Exploration 115(2012), 1-12. Boccia P, Meconi C, Sturchio E, Margiotta S, Ragone P and Summa V (2015). Natural geochemical risk in the Pollino Massif: a case-study of chromium. Front. Genet. Conference Abstract: ICAW 2015 - 11th International Comet Assay Workshop. doi: 10.3389/conf.fgene.2015.01.00023