

Chromium-manganese redox couple resulting in elevated Cr⁶⁺ concentration in groundwater of the Psachna basin, Central Euboea, Greece

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Chromium (Cr) includes two main species in natural aquatic systems, the trivalent (Cr³⁺) and the hexavalent (Cr⁶⁺) one (Richard and Bourg, 1991). The speciation of Manganese (Mn) in aquatic environment is controlled by the prevailing physical and chemical conditions, which includes mainly two oxidation states, the soluble divalent (Mn²⁺) and the insoluble tetravalent (Mn⁴⁺) manganese (Homocik *et al.*, 2010). Mn mobility, speciation and concentration are controlled by the physical parameters of pH, redox potential (Eh), dissolved oxygen (DO) and also by the aqueous solution chemistry (Homocik *et al.*, 2010).

Mn-oxide minerals, in which trivalent manganese (Mn³⁺) and/or Mn⁴⁺ is accommodated, such as birnessite (Fendorf *et al.*, 1992), pyrolousite (Eary and Rai, 1987), asbolane-type (Fandeur *et al.*, 2009), lithiophorite-type (Fandeur *et al.*, 2009) and cryptomelane (Feng *et al.*, 2007) have been reported to act in rocks and soils as natural oxidizing agents for the redox transformation of Cr³⁺ into Cr⁶⁺ in three (3) main steps (Amacher and Baker, 1982; Eary and Rai, 1987; Richard and Bourg, 1991):

- (1) Adsorption of Cr³⁺ on the surface sites of MnO₂,
- (2) Oxidation of Cr³⁺ to Cr⁶⁺ by surface Mn⁴⁺,
- (3) Desorption of the reaction products, Cr⁶⁺ and Mn²⁺ in the aqueous solution

The oxidation reaction takes place according to the following equation:



The amount and the surface area of Mn-oxides are crucial factors and control the oxidation rate of Cr³⁺, which is initially very fast, but through the time it slows down considerably (Eary and Rai, 1987). In addition, the oxidation rate of Cr³⁺ is highly dependent pH values (Amacher and Baker, 1982).

The aim of this research is to examine the speciation of dissolved Mn in groundwater of the Psachna basin, according to pH and Eh conditions, in order to investigate the oxidation of Cr³⁺ into Cr⁶⁺.

The Psachna basin - an ultramafic dominated environment- is located in the central part of Euboea Island; the main land use is agriculture. The geological formations of the Psachna basin are the carbonate rocks (limestones, dolomites), the ultramafic/mafic rocks (serpentinites, peridotites, diabases), the Fe-Ni ore deposits and post-Alpine sediments of Neogene and Quaternary age. The main aquifer system of the study area is developed into Quaternary sediments of ultramafic and carbonate origin. A large set of major ions and trace elements of thirty-four (34) groundwater samples were analysed and presented herein. The physical parameters (electrical conductivity-EC, DO, pH and Eh) were measured in-situ immediately after samples were collected according to YSI Professional Digital Sampling System (ProDSS); The analyses of major ions were determined by atomic absorption spectrometry (Ca²⁺, Mg²⁺, Na⁺ and K⁺), by titrimetry (Cl⁻ and HCO₃⁻) and by turbidimetry (SO₄²⁻) and the analyses of trace elements were performed at Analytical Laboratories of Bureau Veritas Commodities Canada Ltd, by means of inductively coupled plasma mass spectrometry (ICP-MS).

pH ranges from 7.21 to 8.27 (mean 7.64) indicating slightly alkaline conditions; Eh varies from 135.7 mV to 291 mV (mean 254.7 mV) suggesting an oxidative geological environment. The results of this study showed high concentrations of Cr (up to 161.5 µg L⁻¹), Cr⁶⁺ (up to 131.1 µg L⁻¹) and NO₃⁻ (up to 540 mg L⁻¹) in groundwater. The majority of the groundwater samples (70%) analysed herein, exceed the limit of 50 µg L⁻¹ for Cr concentration in drinking water of World Health Organization (WHO, 2011). The remarkable extreme values of NO₃⁻ are over 10 times higher than the guideline value of 50 mg L⁻¹ (WHO, 2011) and indicate the intense agricultural activities accompanied by extensive use of Nitrogen-bearing fertilizers. The concentrations of Mn (up to 25.53 µg L⁻¹) are below the guideline value (50 µg L⁻¹) for drinking water of WHO (2011). The oxidation of Cr³⁺ in natural aquatic environment is a process mainly attributed to the Mn oxides (Eary and Rai, 1987; Richard and Bourg, 1991). pH-Eh plots in the Pourbaix diagram for Mn (1966) revealed, that Mn²⁺ dominates, even at low concentration, in the groundwater samples of the Psachna basin (Fig. 1). Besides, Economou-Eliopoulos *et al.*, (2014) identified Mn-oxide minerals (birnessite, asbolane and cryptomelane) in the Euboea soils, which combined with the presence of Mn²⁺ in groundwater supports the natural oxidation mechanism of Cr³⁺ into Cr⁶⁺ by Mn oxides.

The weak to moderate correlation coefficients and the non-linear relationship between physical parameters (DO, EC, pH and Eh) and Mn concentrations indicate an unclear mechanism that is related to the Mn solubility and the spatial distribution of Mn concentrations in groundwater of the Psachna basin. The elevated concentrations of Cr⁶⁺ (up to 131.1 µg L⁻¹) may be attributed to the oxidation of Cr³⁺ by the redox couple of Mn²⁺/Mn⁴⁺. An additional external oxidant agent is likely to affect the water system synergistically with Mn redox couple increasing the Cr⁶⁺ concentrations.

Previous studies showed that DO could oxidize Cr^{3+} into Cr^{6+} , but the oxidation rate is very slow and enables Cr^{3+} to take part in faster reactions such as sorption or precipitation (Eary and Rai, 1987). Therefore, oxidation of Cr^{3+} by DO seems to be unlikely in soils. An additional potential redox couple except for $\text{Mn}^{2+}/\text{Mn}^{4+}$ is $\text{NO}_2^-/\text{NO}_3^-$, which could make possible the redox transformation of Cr^{3+} into Cr^{6+} in natural aquatic environments (Richard and Bourg, 1991; Stamatis *et al.*, 2011). Spatial distribution maps of Cr^{6+} and NO_3^- support a possible link between these two parameters; this hypothesis is strengthened by the strong correlation coefficient between NO_3^- and Cr^{6+} ($r=0.68$). However, the exact mechanism that the presence of NO_3^- results in increased Cr^{6+} concentration in groundwater has yet to be defined.

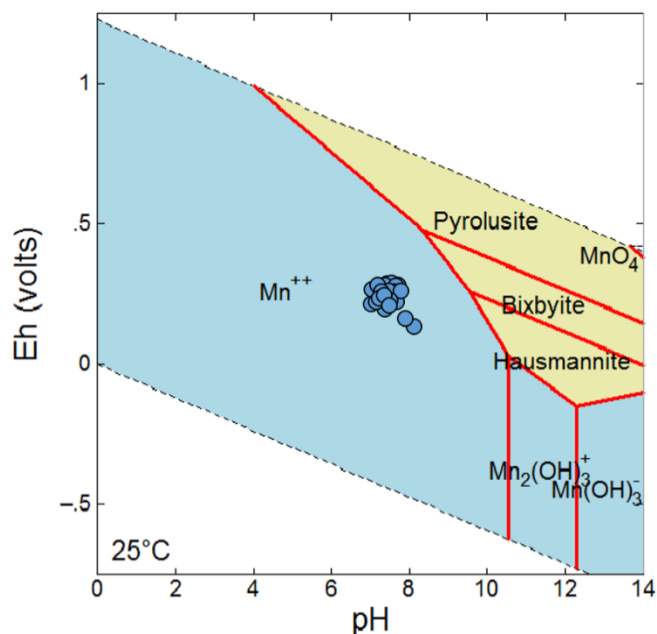


Figure 1. Eh-Ph diagram (Pourbaix, 1966) of the system Mn-O-H.

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