Occurrence and distribution of hexavalent chromium in ground and surface waters in Cyprus under the CrITERIA project

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Abstract
The origin and distribution of hexavalent chromium, Cr (VI) over four seasonal cycles was investigated through a conceptual model that included three aquifer systems in Cyprus. An extensive water sampling grid covered two sea water intruded coastal aquifers, namely the **Kokkinochoria** (**A1**) and **Kiti-Pervolia** (**A2**) aquifers and the **Troodos massif** (**A3**). Analytical results give a first insight to the presence of Cr (VI). Areas A1 and A2 exhibit high conductivity and nitrate concentrations (due to NPK fertilisers and seawater intrusion). The highest Cr (VI) value of 26 μg/l is observed in the Troodos area (A3) where Cr(VI) is detected in all water systems sampled (surface, ground and spring). Nonetheless, the highest mean value of 7 μg/l is exhibited in Kiti-Pervolia (A2). Stable isotope analyses show strong deuterium and Cr (VI) correlation with distinct differentiation between water systems. Troodos shows two distinct groups of meteoric and near meteoric waters whereas isotopically enriched water is shown to correspond to the Kiti and Kokkinochoria area.
Keywords: Cyprus, Cr(VI), hexavalent chromium, water, sampling, climate

1. Introduction

Recent studies have demonstrated that Cr(VI) can be of geogenic origin specifically in areas of ultramafic lithologies (Dermatas 2012, Bompoti 2015). Cyprus is an island in the north-eastern Mediterranean Sea and its geology is dominated by the Troodos Ophiolite. The island has a rich mining history especially for copper, chromite and asbestos, all directly linked to the ultramafic units of Troodos at some 2000 m above sea level.

2. Generic Conceptual Model

This study was conducted based on a generic conceptual model which assumes the dissolution of chromium bearing minerals, such as chromite, occurring in ultramafic and mafic rocks of the Troodos massif (Wilson, 1959). Such weathering can either take place in-situ affecting the ground and surface waters of Troodos and/or in coastal clastic or alluvial aquifers comprising of igneous clasts with chromium content reported in soil geochemical studies (Cohen 2012). In addition to the Troodos area, the coastal aquifers of Kokkinochoria and Kiti have also been selected to test such a scenario.

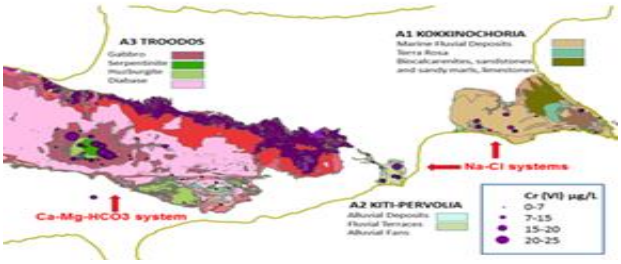

Figure 1. Study areas vs geology

3. Water Sampling

Sampling was conducted by the Geological Survey Department utilizing the existing national water quality monitoring network. Surface and groundwater sampling stations cover the three hydrogeologically distinct sampling areas (Figure 1). **A1** is situated in the southeast. The land is predominantly agricultural (~ 91%) with coastal towns of touristic importance. The surficial geology is dominated by Pliocene and Pleistocene gravels, sands, silts, calcareous sandstones, sandy marls and “terra rosa” soils. Limited recharge and high water demand resulted to a negative water balance while nitrate pollution from agriculture consists a major pressure on groundwater (Geological Survey Department of Cyprus 2000). In total 13 water samples have been collected from A1. **A2** is a small phreatic aquifer situated in the southern part of Cyprus. Geology is dominated by Pleistocene marine terraces and Holocene alluvial sediments. The area is affected by both point and diffuse pollution sources thus deteriorating groundwater quality. Sea water intrusion and nitrate pollution (agriculture and animal husbandry) are the main pressures. In total 8 water samples have been collected from A2. **A3** consists of the Troodos massif in the central part of the island. Land use is evenly divided between agricultural and forested areas whereas only about 1.4% of the total area is urbanized. In total 32 samples have been collected from Study Area 3 during each sampling campaign.

4. Results and Discussion

Analytical results under the CrITERIA project (verified by both UV-VIS and ICP MS techniques) give a good insight to the presence of Cr(VI) (Figures 1 & 2). The highest maximum value of 26 μg/l is observed in area A3 along with the wider ranges of redox values. The highest Cr(VI) mean value of 7 μg/l is observed in area A2. Groundwater samples in areas A1 and A2 exhibit high conductivity and elevated nitrate concentrations. The latter is attributed to the excessive use of NPK fertilizers (Figure 2). In area A3, Cr(VI) is observed in surface, ground and spring waters.

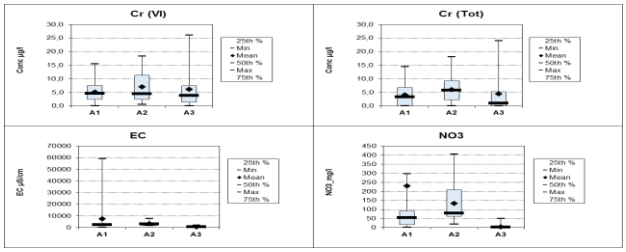

Figure 2. Box plots for Cr(VI), Cr (Tot), Electrical Conductivity (EC)and NO_3 measurements per study area. A1: Kokkinochoria, A2: Kiti-Pervolia and A3: Troodos

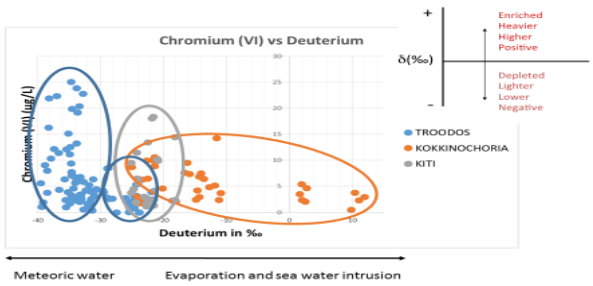

Figure 3. Stable isotope characterisation of water samples

Stable isotope analyses were performed for all CrITERIA samples. Deuterium versus Cr(VI) shows distinct differentiation between the water systems and origin in terms of their isotopes (Figure 3). Area A1 exhibits two distinct groupings of meteoric and near meteoric waters (in blue) whereas "heavier" more enriched water is shown in areas A2 and A1. The waters of Area A3 show low to fairly higher Cr(VI) concentrations which cluster around the ultramafic rocks of Troodos massif and have the isotopic composition of meteoric water thus confirming the generic model of geogenic source. The near meteoric group suggests slight evaporation as it is frequently seen in the cases of surface waters and base flow. In area A2, Cr(VI) concentration ranges are close to that of Troodos although slightly lower (Figure 3). Groundwater in this aquifer is isotopically enriched reflecting infiltration from heavier precipitation, the effect of return irrigation and/or mixing with seawater as it is suggested by the hydrochemistry of these waters (Figure 1). In area A1, Cr(VI) concentrations are lower than in areas A2 and A3 (Figure 3). The isotopic composition of groundwater samples from the local aquifer clearly indicate the effect and extend of seawater intrusion. One can discern the increasing participation of seawater mixing as illustrated by the shifting of the isotopic composition of groundwater to that of seawater. Samples with positive deuterium values most likely reflect return irrigation of evaporated saline groundwater. Nonetheless, the influence of other water sources such as treated water or even sewerage water cannot be excluded.

5. Conclusions

The presence of Cr(VI) in ground and surface waters in Cyprus is mostly related to geogenic factors associated with ultramafic rocks of the Troodos ophiolite. The concentrations detected are by no means considered harmful or dangerous but Cr(VI) from anthropogenic sources on the island have to be investigated further. Cr(VI) is also detected in the planes of areas A1 and A2. Its presence is also attributed to mostly geogenic factors but in some instances anthropogenic factors could not be excluded.

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