MAPPING OF CHROMIUM IN THE GREATER AREA OF ASOPOS RIVER BASIN

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EXTENDED ABSTRACT

The greater area of the Asopos river, situated at the Region of Sterea Ellada, north of Athens is a unique case of combined anthropogenic and geogenic origin of chromium contamination. The high concentrations of chromium and hexavalent chromium found at the groundwater system of Asopos have resulted in an increased public concern, since part of the groundwater is used for water abstraction for human consumption and most of it for irrigation purposes.

The objective of this work was to organize all available data pertinent to the groundwater flow and chromium transport modeling of the area into maps, using geographical information systems, geotechnical graphics software and geostatistical techniques. The data was collected from various sources such as field campaigns, existing reports, data logs etc. One of the most important parameters that affect chromium transport is the geology of the area, thus a digitized geological map of the main formations encountered in the upper layers of the subsurface of the region was generated. In addition, geological boring logs for a large number of wells were created (using a geotechnical graphics software) and then combined in order to create vertical cross-sections, at various locations in the greater area, that define the geological characteristics of the deeper layers. The combination of the above defines the 3-D representation of the geological stratification of the physical system. Another parameter of interest in the area is the groundwater level and flow direction. In order to create a hydraulic head map of the area, the locations of more than 1000 shallow and deep wells that have been documented in the greater area of the Asopos river basin were defined using GIS software. A kriging technique was then applied to the available data in order to produce hydraulic head contours and consequently define the general groundwater flow direction. The same technique was applied for the generation of chromium concentration contours that provide an indication of the most problematic locations as well as a general chromium background level in the greater area.

KEYWORDS: hexavalent chromium, geographical information systems, geostatistics, geological mapping, hydraulic head contouring, chromium concentration contouring

1. INTRODUCTION

The river basin of Asopos is located at the Region of Sterea Ellada and the River Basin District of East Sterea Ellada. The groundwater system of Asopos presents high concentrations of chromium and hexavalent chromium both in surface and groundwater and as a result there is an increased public concern, since part of the groundwater is used for water abstraction for human consumption and most of it for irrigation purposes. Chromium (Cr) is a metal used primarily as a coating or alloy by the metal finishing industry, because of its unique properties that include high resistance to corrosion and hardness. Other Cr uses include leather tanning, refractory bricks in furnaces and fireplaces, wood treatment and pigment processing (Jacobs and Testa, 2005). Cr exists under various oxidation states, the most important being its trivalent (Cr(III)) and...
hexavalent (Cr(VI)) forms. The geochemical behavior and biological toxicity of chromium in these two common oxidation states are profoundly different. Cr(III) is almost immobile in natural systems (because it precipitates out of solution at pH > 5), while Cr(VI) exhibits high toxicity, mobility and water solubility, resulting in the contamination of soil, surface water and groundwater reserves (Hellerich and Nikolaidis, 2005; Moraetis et al., 2012). The different toxicity and mobility of the two oxidation states makes the assessment of potential human health risks a difficult task. The extensive use of Cr in industrial activities has resulted in thousands of soil and groundwater contaminated sites in Europe and North America. This has rendered Cr(VI) the focus of scientific discussion, regulatory concern, and legal posturing (Jacobs and Testa, 2005, Nikolaidis and Shen, 2000). It has also motivated research on the fate and transport of chromium compounds in the environment (Hellerich and Nikolaidis, 2005).

Until recently, high levels of hexavalent Cr in the environment were always attributed to anthropogenic pollution. However, over the past 10 years there have been reports in the literature demonstrating that relatively high levels of hexavalent Cr may be attributed to natural geogenic processes, especially in areas where there are relatively high levels of naturally occurring Cr(III) or Cr (VI) in the sediments, and natural processes that can convert Cr(III) to Cr(VI). Such cases have been reported in California (Oze et al., 2004; Morrison et al., 2009), Zimbabwe (Cooper, 2002), Mexico (Villalobos-Aragón et al., 2012), Italy (Fantoni et al., 2002), New Caledonia (Becquer et al., 2003) and Greece (Moraetis et al., 2012).

The Asopos river basin studied in this work is a unique case of combined anthropogenic and geogenic origin of Cr contamination. Previous studies in the same area were conducted by Bolsou et al. (2011), Economou-Eliopoulos et al. (2011; 2012) and Moraetis et al. (2012).

This work is part of the project “CHARM: Chromium in Asopos groundwater system: remediation technologies and measures” that aims to provide solutions to technical, social and administrative problems related to the issue of water resources management as a whole, and particularly to the chromium contamination management. Given the fact that predicting Cr(VI) mobility is one of the critical elements in remediating the multitude of sites, part of this project focuses on the development of a modelling methodology to assess the extent of Cr(III) and Cr(VI) transport in soil and groundwater environments.

The objective of this work was to organize all available data pertinent to the groundwater flow and chromium transport modelling of the area into maps, using geographical information systems, geotechnical graphics software and geostatistical techniques. The data was collected from various sources such as field campaigns, existing reports, data logs etc. This data includes detailed information regarding the geology of the area of study based on existing geological maps as well as on well profiles (boring logs). This information will be used for the determination of the geological stratification and 3-D representation of the physical system, the determination of the porosities, the hydraulic conductivities etc. Secondly, a map of groundwater levels and flow direction was created that will contribute to the determination of the initial hydraulic head conditions and the boundary conditions such as locations of steady head or charging/discharging points of the subsurface system. The third important source of data involves chromium concentrations distributed in space and time. This information will provide an indication of the most problematic locations as well as a general chromium background level in the greater area.

2. METHODOLOGY

2.1. Geographical information systems

For the definition of the geology of the area all relevant geologic maps (6 maps created by the Institute of Geology and Mineral Exploration) were scanned in order to be
converted into digital form. Subsequently, they were imported into the GIS software where they were geo-referenced to the LAEA (Lambert Azimuthal Equal-Area) coordinate system using the corresponding map coordinates.

For the creation of the hydraulic head and chromium concentration maps of the area all available data from deep and shallow wells were imported into the GIS software and the geostatistical interpolation technique of kriging was applied to create hydraulic head contours and chromium isoconcentration maps. The kriging interpolation method available on the GIS software was used. According to previous studies the kriging method in GIS software produces the most accurate interpolation for groundwater level and contaminant concentration estimation (Dash et al., 2010) compared to other interpolation methods such as splines, inverse distance methods etc, this is why it was chosen in this work.

2.2. Geotechnical graphics

Geological information for a large number of wells in the area was organized into boring logs, which were then combined in order to create vertical cross-sections at various locations in the greater area, in order to define the geological stratification of the physical system. This was done using the M-Tech Geotechnical Groundwater Graphics software. For the creation of boring log diagrams and geologic cross-sections the modules QuickLog and QuickCross were used, respectively.

The boring log diagrams contain information about the well such as general data (location, client, well completion details etc), lithologic descriptions, depths and symbols for each geologic layer, pumping rate information, water level measurements etc. The geologic cross sections are generated using the created boring log diagrams of selected wells and information about the distances between consecutive wells.

3. RESULTS

3.1. Geology

One of the most complex factors that control the movement of contaminants in the subsurface is the geology of the area, thus a detailed description of the type, location and depth of the geological formations encountered in the area is a very important step towards the development of an accurate transport model. To this end, a digitized geological map of the main formations encountered in the upper layers of the subsurface of the region was firstly generated (Figure 1). In this figure the Asopos river basin is depicted with an orange curve and the river reaches with blue curves. As observed from the map, the main geologic formations encountered in the greater area of the Asopos river basin are limestones and dolomitic limestones, neogenic deposits (marls, sands, conglomerates etc), quaternary deposits (clay, alluvial, talus cones etc), shales, sandstones and ultrabasic rocks. Ultrabasic rocks (peridotites and pyroxenites) are the main geogenic origin of Cr(VI). Common minerals that host Cr as Cr(III) are spinels (chromite and magnetite) and silicate minerals (pyroxene and olivine) (Moraetis et al., 2012). The process of serpentination (alteration by hydrothermal fluids) in mantle rocks is a common process that introduces new mineral phases to ultramafic rocks. Some of these are serpentine (lizardite, crysolite and antigorite), chlorite, talc and actinolite, which exhibit high Cr(III) content (Oze et al., 2004). It is observed that there are several areas with ultrabasic rocks located especially on the eastern part of the Asopos river basin, providing evidence of the geogenic origin of chromium contamination in the area.

In addition, geological boring logs for a large number of wells (Figure 2) were created (using a geotechnical graphics software) and then combined in order to create vertical cross-sections, at various locations in the greater area, that define the geological
characteristics of the deeper layers. The combination of the geologic map information (upper layers) and cross section information (deeper layers) defines the 3-D representation of the geological stratification of the physical system.

Figure 1. Geology of the greater Asopos River Basin area

Figure 2 shows the locations of all the wells for which vertical geological information exist. Boring logs were created for all of these wells. Subsequently, some of them were combined in order to create a large number of cross-sections; only three of which are presented here (Figure 3), for brevity. Their location on the map of the area is shown in Figure 2. From the vertical cross-sections it is observed that an upper layer of clay is prominent in many parts of the basin, followed by interchanging layers of sand, gravel or conglomerates. In some cases a second layer of clay is observed between these layers. Limestone is also found in the deeper layers in some locations.
3.2. Groundwater level and flow direction

Another parameter of interest in the area is the groundwater level and flow direction. In order to create a hydraulic head map of the area, the locations of more than 1000 shallow and deep wells that have been documented in the greater area of the Asopos river basin were defined using GIS software. Their locations are shown in Figure 4. Information regarding the groundwater depth was available for about half of these wells (544 wells). A kriging interpolation technique was applied to the available data in order to produce hydraulic head contours and consequently define the general groundwater flow direction.
as shown in Figure 5. According to this map the maximum hydraulic heads are observed on the southern part of the basin and reach the value of 360 m.a.s.l. The general groundwater flow direction is also from the southern to the northern parts of the basin.

Figure 4. Existing pumping wells of the area (the different colours correspond to different sources of data)

Figure 5. Hydraulic head contours and general groundwater flow direction

3.3. Chromium concentrations

In order to provide an indication of the most problematic locations as well as a general chromium background level in the greater area a chromium isoconcentration map was generated with the same interpolation technique (kriging), using the available concentration information from 115 wells shown in Figure 6. From this map, an initial general chromium background level estimate could be defined below 20 μg/l. In addition, there are several problematic zones in the area with chromium concentration levels
reaching 175 μg/l in locations outside the river basin boundaries but in the greater area, which may require immediate remediation efforts. Inside the river basin area the maximum chromium concentrations measured exceed the level of 100 μg/l in some cases, which is also very high, considering that the parametric value for total chromium is 50 μg/l in Europe.

Figure 6. Chromium concentration contours in the extended study area

4. CONCLUSIONS

The groundwater system of Asopos presents high concentrations of chromium and hexavalent chromium in groundwater and as a result there is an increased public concern regarding the quality of drinking water in the region. In this work all available data pertinent to the groundwater flow and chromium transport in the area were organized into maps. These maps include: 1) a digitized geologic map of the upper layers of the area, 2) boring logs and cross-sections that define the stratigraphy of the area 3) a hydraulic head contour map that defines groundwater flow direction and 4) a chromium isoconcentration map to represent the natural and anthropogenic contaminant sources as well as define the extension of the contaminant plume and the problematic areas.

The main geologic formations encountered in the greater area of the Asopos river basin are limestones and dolomitic limestones, neogenic deposits, quaternary deposits, shales, sandstones and ultrabasic rocks. Ultrabasic rocks (peridotites and pyroxenites) constitute the main geogenic source of Cr(VI), providing evidence that the Asopos river basin is a unique case of both anthropogenic and geogenic origin of chromium in the subsurface.

According to the hydraulic head contour map, the general groundwater flow direction in the basin is from the south to the north and the maximum hydraulic heads are observed on the southern part of the basin reaching the value of 360 m.a.s.l. Using the chromium isoconcentration map, an initial general chromium background level estimate could be defined below 20 μg/l. In addition, there are several problematic zones in the area with chromium concentration levels inside the basin exceeding 100 μg/l in some cases and reaching 175 μg/l in locations outside the river basin boundaries, strongly indicating the need for immediate remediation efforts for the aquifer restoration.
REFERENCES


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