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Groundwater deterioration: the simultaneous effects of intense agricultural activity and heavy metals in soil

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Abstract

Groundwater deterioration due to agricultural activity is mainly attributed to intense fertilization, groundwater overpumping and seawater intrusion being more pronounced in coastal areas. Irrigation return water is one of the main sources of aquifers enrichment and it is expected to become the main source due to the simultaneous reduction of the amount/frequency of precipitation for many areas in Greece and the Mediterranean. The reduction of groundwater quantity and the simultaneous deterioration due to enhanced concentrations of fertilizer residues, such as nitrates, is well documented. Moreover, heavy metals of both anthropogenic and natural origin may be present in soils where agricultural activity takes place. As a result, groundwater is enriched in soluble species of heavy metals and this enrichment is a serious problem added on top of the above mentioned problems of groundwater deterioration. The relationship between heavy metals mobilization from soils to groundwater and the content of irrigation return water in solutes that influence the generation rates and mobility of heavy metals soluble species are discussed in this work. Data from groundwater samples taken in Psachna, Evia, a region characterized by elevated geogenic Cr in soils and intense agricultural activity, are presented. Two aspects of the problem are discussed: 1. The intense use of ammonium fertilizers: The pH reduction from the nitrification of ammonium fertilizers may be a serious factor influencing Cr(III) mobility. 2. The role of the ionic strength of the water (enhanced concentrations of cations due to seawater intrusion in the aquifer) in the mobility of Cr(III) by mechanisms of cation exchange.

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1. Introduction

Groundwater deterioration due to agricultural activity is mainly attributed to intense fertilization, groundwater overpumping and seawater intrusion being more pronounced in coastal areas. The recharge of aquifers occurs through atmospheric precipitation and irrigation return water. In many regions, the quantity of water recharging aquifers, originating from atmospheric precipitation, has been significantly reduced and more than half of groundwater quantity can be attributed to irrigation return water [1]. The reduced recharge of groundwater with fresh water from atmospheric precipitation and groundwater overpumping for irrigation are main reasons for the elevated NO_3^- concentrations in groundwater. Thus, the observed deterioration of groundwater due to enhanced concentrations of fertilizer residues, such as nitrates, is well documented for many regions where agriculture is a main activity.

Heavy metals of both anthropogenic and natural origin may be present in soils where agricultural activity takes place. The metals may be present in soils under different insoluble forms, such as metal oxides, hydroxides, carbonates and phosphates, or may be adsorbed in soils by inorganic colloids, such as clays, and other insoluble metal species. The metals may then be mobilized forming soluble species and redistributed between soil and water. Main parameters influencing the formation of soluble species are: soil type, metal speciation, metal concentration, soil pH, solid/solution mass ratio and contact time [2, 3]. In general, greater metal retention and lower solubility occur at high soil pH [4, 5, 6].

Heavy metals mobilization from soils to groundwater appears to be significantly influenced by agricultural activity [1, 7, 8]. Both ammonium- and phosphate-based fertilizers have been shown to increase the mobility of Cr(VI) in ultramafic areas [1, 3, 8]. Field and laboratory simulations data are very recent, appearing in literature during the last decade. The elucidation of the mechanisms responsible for hexavalent chromium mobilization from soils is actually subject of international effort of high priority due to Cr(VI) toxicity.

Studies on the properties of ophiolites and associated metal mobility in different regions in Greece have been recently published [9, 10, 11, 12]. Recent data on ophiolithic aquifers in Vergina (northern Greece) [13], where agriculture is the main anthropogenic activity, have shown that there is a relationship between fertilization and the enhanced Cr(VI) concentration in groundwater.

The present paper focuses on Cr(VI) content in groundwater in Psahna plain in Central Evia, a region characterized by ophiolithic formations and alluvial deposits of clastic ophiolite material, where agriculture is the main activity. The paper reports preliminary results on the investigation of the relationship between Cr mobilization from soils to groundwater and the content of irrigation return water in solutes originating from intense fertilization. Apart from intense fertilization, seawater intrusion in the aquifer, resulting from groundwater overpumping, is evident in the region. The influence of seawater intrusion on Cr mobilization is also discussed.

2. Methodology

2.1. Sampling

Two data sets of groundwater are included in the present study. The first set (samples P1 to P19) corresponds to the November 2012-April 2013 period whereas the second set (samples M1 to M11) corresponds to April 2015. Three sample types are included in the present work: samples from irrigation drills, drills and springs. Two samples were also taken from mining pits. The sampling positions are presented in Table 1 and Figure 1. Three different samples were taken from each sampling position: one sample was used for the determinations of anions and cations; another for the determinations of heavy metals (after filtration and acidification of the sample by nitric acid) and another for