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Occurrence of volatile organic compounds in shallow alluvial aquifers of a Mediterranean region: Baseline scenario and ecological implications

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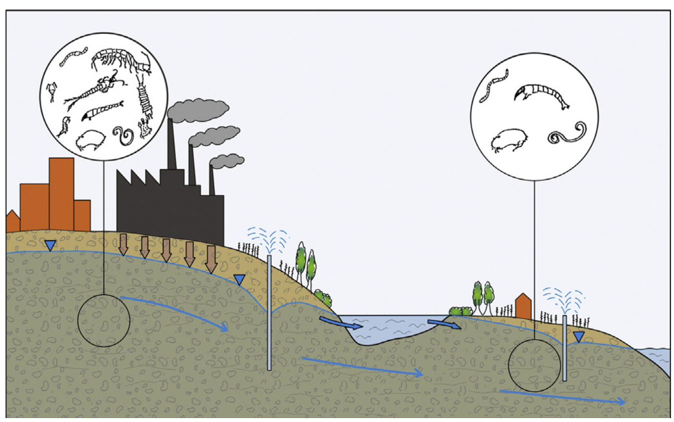
HIGHLIGHTS

- The occurrence of eight VOCs was investigated in alluvial aquifers in Southern Italy.
- Benzene, toluene, ethylbenzene and p-xylene concentrations were not detected.
- We detected persistent contamination by chloroform (CHL) and tetrachloroethene (PCE).
- The detected PCE and CHL contaminations may be lethal to groundwater organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

A regional survey of eight volatile organic compounds (VOCs), namely BTEX (benzene, toluene, ethylbenzene and p-xylene) and four chlorinated aliphatic hydrocarbons (CAHs: chloroform, 1,2-dichloroethane, trichloroethene and tetrachloroethene), was carried out at 174 sites, in 17 alluvial aquifers of Abruzzo, a Mediterranean region of southern Italy, from 2004 to 2009. Frequency of detection, concentration range, spatial distribution pattern, and temporal trend of contaminant concentration in each aquifer were analyzed as well as the relationships between VOC concentrations and the total amount of precipitation during the 90 days preceding each sampling date. A review of published ecotoxicological data, providing an indication of the biological risk associated with the observed levels of VOC contamination, was presented and discussed. BTEX concentrations were under detection limits in all the investigated aquifers, indicating absence of contamination. In contrast, CAH contamination occurred in 14 out of 17 aquifers. The two most frequently detected compounds were chloroform and tetrachloroethene. No significant temporal trend was observed for chloroform and tetrachloroethene concentrations during the six years of observation, indicating the persistence of stable contaminations, except for some slightly decreasing trends observed in three out of 17 aquifers. In four aquifers chloroform and tetrachloroethene concentrations increased with precipitations in the preceding months. Spatial patterns of contamination differed among aquifers, indicating highly complex contaminant distributions at aquifer scale not related to single-plume

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geometries. Patterns of contamination by chloroform and tetrachloroethene in the most urbanized aquifers were likely associated with multiple sources of VOCs not clearly detectable at the scale used in this study. In five out of 17 aquifers, chloroform and tetrachloroethene co-occurred at concentrations that are lethal to groundwater-dwelling organisms under a short exposure period (four days). Future studies should therefore consider the possibility that in the other aquifers groundwater-dwelling organisms might be physiologically damaged by sub-lethal VOC concentrations.

1. Introduction

Volatile organic compounds (VOCs), such as chlorinated aliphatic hydrocarbons (CAHs) and BTEX (benzene, toluene, ethylbenzene and xylene), are a class of highly toxic contaminants commonly found in groundwater, which may pose a substantial threat to human health, and to soil, freshwater and marine ecosystems (van Leeuwen and Vermeire, 2007). Because of their chemical characteristics, VOCs find a wide application in both urban activities and industrial processes, such as metal-degreasing (Kuney, 1986), textiles and paper treatment (Verschueren, 1983), paint and pesticide production, and as refrigerants (Lewis, 2001). Due to improper use and disposal practices, VOCs are common organic contaminants in North America, Europe and other industrialized areas of the world (Hunkeler and Aravena, 2000; Kao and Lei, 2000; Kueper et al., 2003; Parker et al., 2003; Rivett and Feenestra, 2005; Cortés et al., 2011; Balderacchi et al., 2014).

VOCs usually occur at trace levels in surface water, as a result of their volatility. On the contrary, they may be found at high concentrations in groundwater, and are considered the main contaminants of this resource (Falcó and Moya, 2007). Due to their liquid nature, with a limited miscibility and dissolution rate in water, they may occur in underground in different phases: as a main separate one (non-aqueous phase liquid: NAPL) and frequently as a residual one, but also as dissolved or vapor phase (Pankow and Cherry, 1996; Parker et al., 2003). VOCs degradation, both biotic and abiotic, is often incomplete and yields more toxic intermediates, especially in anoxic contaminated groundwater (Zhang and Bennett, 2005; Loffler and Edwards, 2006; Guan et al., 2013, 2014). Hence, VOC NAPL tends to persist in groundwater for decades after the original spillage and, whether present as free or residual phase, it may continue to feed groundwater plumes in the saturated zone or vapor plumes in the unsaturated zone for ages (Johnson et al., 1999; U.S. Environmental Protection Agency, 1998).

Frequently, VOC distribution in groundwater is not traceable as proceeding from a single plume evolution. Especially in urbanized areas, VOCs may be considered ubiquitous, due to enormous number of local sources and to the persistence of secondary residual sources (Balderacchi et al., 2014). Finally, the aquifer heterogeneity also influences their distribution in groundwater, leading to a very complex and widespread distribution scenario in the alluvial and phreatic aquifers of industrial regions (Petitta et al., 2013; Balderacchi et al., 2014).

Differently from BTEX, which float on the water table and have a high rate of vaporization (Lawrence, 2006), pollution from CAHs is considered persistent and more difficult to remediate, due to the high density of these chemicals, that favors their distribution across the entire aquifer thickness. Through a gravity-driven and predominantly vertical infiltration, CAHs reach the water table, enter groundwater and seep deep down into the aquifer, up to the aquiclude top (Leighton and Calo, 1981; Thomas, 1990). From there, they may continuously dissolve into the water body (Leighton and Calo, 1981; Thomas, 1990). Recent studies showed that there is an increasing risk of appearance of these contaminants in surface water due to the connectivity between surface water and groundwater (Lorah and Voytek, 2004). This represents a serious threat for freshwater cyanobacteria and eukaryotic algal species (Lukavsky et al., 2011), because VOCs strongly affect density and chlorophyll content of phytoplankton (Ward et al., 1986; Bácsi et al., 2012), and for aquatic organisms overall, due to the carcinogenic potential of these compounds (Ramos et al., 1999; Xue and Warshawsky, 2005). Indeed, studies on vertebrates showed that CAHs cause oxidative stress in different organisms (Mitoma et al., 1985). However, the effect of VOCs on groundwater-dwelling organisms has been poorly investigated to date, and we are aware of only a single study on this topic (Avramov et al., 2013).

In a recent communication, the European Commission stated that the status of EU waters is not doing well enough because the ecological and chemical status of EU waters is threatened, and water ecosystems, whose services our societies depend on, are becoming more and more vulnerable (EC, 2012). Preservation of groundwater, one of the basic resources for life, nature and economy, is a main topic for EU member states (EC, 2012), but necessitates a detailed assessment of groundwater impact.

To this end, we investigated CAHs and BTEX occurrence in the alluvial aquifers of Abruzzo, a Mediterranean region of southern Italy. Contamination from CAHs and BTEX of surface water and groundwater in Italy has been poorly investigated, particularly in southern Italy (Meffe and de Bustamante, 2014). We analyzed data collected at 174 sites, sampled twice per year, from 2004 to 2009. Specifically, we assessed the frequency of VOC detection, the concentration range, and the extent of areas involved by contamination, as well as temporal trend of VOC concentrations in each aquifer and the relationship with the total amount of precipitation during the 90 days preceding each sampling. A geostatistical system was developed to create a large-scale spatial model of contaminant distribution in the most polluted alluvial aquifers. Finally, ecotoxicological data, providing an indication of the biological risk associated with the level of VOC contamination found in the alluvial aquifers of Abruzzo, were presented and discussed.

2. Study area

Abruzzo is characterized by a large abundance of groundwater, mainly stored in fractured and karstified carbonate aquifers that feed low-altitude alluvial inner and coastal aquifers, through groundwater seepage and surface/groundwater interactions. The alluvial aquifers, usually developing along a W–E direction, are narrow and fragmented along many river valleys, as in the intramontane basins, due to the recent tectonic (Desiderio et al., 1999). As a consequence, they host a significant amount of groundwater with active flow towards the coastline. Generally, permeability ranges from medium to high, thanks to the prevalence of gravel and sand portions, due to the recent Quaternary filling-up of these low-altitude areas (Celico, 1983). Hydrogeological maps are available at the website of Abruzzo Region (Regione Abruzzo, 2010). Nevertheless, low-permeability lenses and levels can locally be predominant, mainly in the center of each valley and closer to the shoreline. As a result, groundwater flow shows a predominantly eastward direction following the direction of the river valleys towards the Adriatic Sea, but it is locally influenced by lateral and vertical heterogeneity (Celico, 1983; Caschetto et al., 2014). Moderate but significant marine intrusion is frequent (Desiderio and Rusi, 2003; Desiderio et al., 2003; Di Lorenzo et al., 2012).

The study was carried out in 17 alluvial aquifers (overall extent of the aquifer outcrops: 1508 km^2; Table 1) of the Abruzzo Region (10,763 km^2). Abruzzo was awarded the title of the “Greenest Region of Europe” due to one third of its territory, the largest proportion in Europe, being protected by national and regional parks and reserves. The aquifer outcrops are used mainly for farming (Table 1; Fig. 1a),