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journal homepage: www.elsevier.com/locate/envpolChlorate origin and fate in shallow groundwater below agricultural landscapes[☆]Micòl Mastrocicco^a, Dario Di Giuseppe^a, Fabio Vincenzi^b, Nicolò Colombani^{b,*},
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ABSTRACT

In agricultural lowland landscapes, intensive agriculture is accompanied by a wide use of agrochemical application, like pesticides and fertilizers. The latter often causes serious environmental threats such as N compounds leaching and surface water eutrophication; additionally, since perchlorate can be present as impurities in many fertilizers, the potential presence of perchlorates and their by-products like chlorates and chlorites in shallow groundwater could be a reason of concern. In this light, the present manuscript reports the first temporal and spatial variation of chlorates, chlorites and major anions concentrations in the shallow unconfined aquifer belonging to Ferrara province (in the Po River plain). The study was made in 56 different locations to obtain insight on groundwater chemical composition and its sediment matrix interactions.

During the monitoring period from 2010 to 2011, in June 2011 a nonpoint pollution of chlorates was found in the shallow unconfined aquifer belonging to Ferrara province. Detected chlorates concentrations ranged between 0.01 and 38 mg/l with an average value of 2.9 mg/l. Chlorates were found in 49 wells out of 56 and in all types of lithology constituting the shallow aquifer. Chlorates concentrations appeared to be linked to NO₃⁻, volatile fatty acids (VFA) and oxygen reduction potential (ORP) variations. Chlorates behaviour was related to the biodegradation of perchlorates, since perchlorates are favourable electron acceptors for the oxidation of labile dissolved organic carbon (DOC) in groundwater. Further studies must take into consideration to monitor ClO₄⁻ in pore waters and groundwater to better elucidate the mass flux of ClO₄⁻ in shallow aquifers belonging to agricultural landscapes.

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1. Introduction

Groundwater contamination by agricultural practices is considered a worldwide issue and conventionally, in most countries, agricultural practices are treated as a non-point source of pollution (Ongley, 1996). Runoff of highly soluble nutrients (such as nitrate, phosphate and ammonium) and pesticides (insecticides, herbicides, fungicides and bactericides) often pollute surface and groundwater of several areas in the EU, USA and China causing public health risks (CEC, 2000; Smith et al., 2017; Turral, 2012).

Moreover in recent times, due to the significant progress in the

analysis and detection of trace elements, some "emerging" contaminants have been discovered and quantified in groundwater and not a few of them are agriculture-related (Lei et al., 2015; Richardson and Ternes, 2005).

Recently, chlorate ions (ClO₃⁻) have been included among the inorganic substances in the list of emerging contaminants (Ader et al., 2001; Lei et al., 2015; Miraji et al., 2016). ClO₃⁻ is an oxy-anion of chlorine with strong oxidative capacity ($E^0 = +0.62$ V) and high water solubility. This anion, not common in nature, is almost entirely manmade and it is essentially manufactured for the production of bleaching agents (e.g. for paper industry), oxidants in explosives and weed-killers (Ader et al., 2001; Rao et al., 2010; Van Ginke et al., 1995).

Due to its high reactivity to the biological matters (Ali et al., 2016), ClO₃⁻ is a potentially toxic substance even at low concentrations; for example, women exposed to chlorate level >200 µg/l

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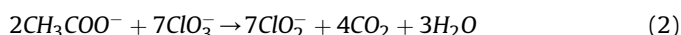
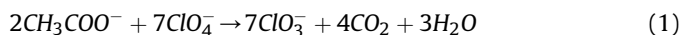
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may risk serious health damage to new-borns (Righi et al., 2012). Toxicological and epidemiological studies show that ClO_3^- exposure cause haematological damage and risk of congenital anomalies (Righi et al., 2012 and references therein). Moreover, some literature report cases of poisoning of animals associated to excessive application of chlorate-based herbicides (Smith et al., 2012). Therefore, ClO_3^- presence in water clearly gives rise to concerns, as to its effects for human health hazard and as an ecotoxicological agent. The 2005 WHO Guidelines for Drinking Water Quality established a provisional health-based guideline value of 0.7 mg/l for ClO_3^- in drinking water. In general, ClO_3^- environmental issue is due to their nature of “by-products”, in fact this ion is one of the main by-products of chlorination disinfection chemical reduction (Nieuwenhuijsen et al., 2000), by-products of weed-killer (Sutigoolabud et al., 2004) and by-product of the biological reduction of perchlorate (ClO_4^-) (Achenbach et al., 2001).

Chlorination disinfection agents, like chlorine dioxide (ClO_2) or hypochlorite (ClO_2^-), are strongly oxidizing agents used to sanitize water. These substances are powerful to eliminate harmful microorganisms but, when inserted into the water cycle during disinfection procedures, they decompose rapidly and form undesired disinfection by-products (for example ClO_2^- and ClO_3^-) (Hua and Reckhow, 2007; Lei et al., 2015; Righi et al., 2012). Favoured by oxidizing conditions, water treated with chlorination disinfectant can achieve ClO_3^- concentrations up to 9 mg/l (Boorman et al., 1999).

ClO_3^- , in the form of NaClO_3 is an active ingredient of several non-selective herbicides, used in the past, to kill weeds both in agricultural and in non-crop fields (Ali et al., 2016; US EPA, 2008). In literature, it is well known that ClO_3^- is produced by microbial reduction of ClO_4^- (Logan et al., 2001; Nerenberg et al., 2006; Xu et al., 2015). Specialized microorganisms (ClO_4^- -reducing bacteria) use ClO_4^- as an electron acceptor to oxidize a wide variety of organic dissolved species, e.g. acetate (Xu et al., 2015). These bacteria are ubiquitously distributed in the environment, and (thanks to specific enzymes) they can reduce ClO_4^- to Cl^- , producing ClO_3^- as by-product of the reaction.

The ClO_4^- -reduction pathway via acetate, where ClO_4^- is converted to ClO_3^- (1), then is reduced to ClO_2^- (2) using the (per) chlorate reductase and finally to Cl^- (3) using the chlorite dismutase. The reaction stoichiometry is modified from Nerenberg et al. (2006):



ClO_4^- contamination of groundwater came to an evident concern in the late 1990s with the development of a sensitive analytical technique that reduced its detection limit (Bardiya and Bae, 2011). ClO_4^- occurs both naturally and as a manufactured compound. Naturally occurring sources are geographically limited to arid environments (i.e. Chilean caliche), while man-made ClO_4^- has many fields of application, like oxidant for propellant, fireworks and explosives (Nerenberg et al., 2006). However, the main source of ClO_4^- contamination of soil are fertilizers; e.g. derived from Chilean saltpetre (Bardiya and Bae, 2011). Saltpetre may contain ClO_4^- in the range of 1.5–1.8 mg/g (Urbansky et al., 2001), in the form of KClO_4 (Schumacher, 1960; Susarla et al., 1999). The groundwater ClO_4^- contamination may occur as a result of percolation of rainwater through contaminated sediments or soils (Ma et al., 2016).

Though ClO_3^- is highly soluble and toxic, studies regarding groundwater contamination with residual ClO_3^- have been little

taken into account so far (Sutigoolabud et al., 2004).

In Italy, the most extensively investigated area with regard to agriculture-derived pollution (e.g. nitrate and herbicide) is the Po River plain (Balestrini et al., 2016; Castaldelli et al., 2013b; Meffe and De Bustamantea, 2014). However, to date, a study about ClO_3^- presence in groundwater has not been conducted.

The Po River plain is the largest Italian alluvial basin and its hydrological catchment covers an area of more than 71,000 km² (about a quarter of the national territory). Stretching over an area of 46,000 km², the Po plain includes 71% of all the flat areas in Italy, covering 15% of the Italian territory (Marchetti, 2002). The terminal part of this floodplain (Po Delta plain) has been reclaimed since Etruscan times with many subsequent works and is now an intensively cultivated lowland. Water draining and flow regulation keeps the depth of the water table of the unconfined aquifer near to the topographic surface. Due to many factors, such as preferential infiltration pathways (e.g. paleochannels), mud cracks or sub-surface drainage systems, the unconfined aquifers of the Po Delta plain are highly vulnerable to agrochemicals, especially in lowland areas where the flat topography minimizes the surface run-off. This causes serious environmental threats such as N compounds leaching and delivery towards surface waters, which in turn suffer from eutrophication (Onorati et al., 2006), and may also be responsible for the potential presence of ClO_3^- in shallow groundwater. Assessing the concentration of harmful ClO_3^- concentrations in the shallow groundwater is imperative in order to evaluate the potential risks to human health.

In this light, the present manuscript reports the first temporal and spatial variation of ClO_3^- and major anions concentrations in the shallow unconfined aquifer belonging to Ferrara province (in the Po River plain). The study was made in 56 different locations to obtain insight on groundwater chemical composition and its sediment matrix interactions. Thus, as far the authors are aware, the novelty of this study is the first recognition in Europe of groundwater ClO_3^- temporal and spatial variations in a shallow unconfined aquifer belonging to agricultural landscapes.

2. Site description

The Po River Delta plain (together with the City of Ferrara) belongs to the UNESCO World Heritage List and since its formation, it has played a fundamental role in the development of European civilization. The evolution of the hydrographic network of the Po river from the late Bronze Age until nowadays, created a delta that extends for more than 730 km², hosting one of the most important Italian agricultural areas (Stefani and Vincenzi, 2005). The geological setting of this floodplain is dominated by the Po River and by its ancient and present alluvial and delta deposits.

The Quaternary continental sediments deposited by the Po river are identified by a significant cyclicity with alternation between sandy bodies (aquifers) and silty-clay bodies (aquitards). These depositional structures were created by transgressive-regressive phases possibly connected to the eccentricity shift of the Earth's orbit, with a period of approximately 100 ka (Amorosi et al., 2008). At the top of the above mentioned Quaternary sequence, lay as series of silty clay sediments and sandy lenses, constituting the phreatic aquifer. Within the Ferrara province, sediments were mainly deposited by Po river branches and marginally by the Apennine (Amorosi et al., 2003).

The studied zone occupies an area extending from the city of Ferrara to the Adriatic Sea coast (Fig. 1a) at an altitude ranging from 21 to -4 m above sea level. The area consists of a fan-like delta, limited to the North by the actual Po up to the mouth of the Maistra branch and to the South by the Po di Primaro-Reno fluvial system, located just South of the Comacchio Lagoons. Within the floodplain

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