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Origin of VC-only plumes from naturally enhanced dechlorination in a peat-rich hydrogeologic setting

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ABSTRACT

The occurrence of vinyl chloride (VC) is often a main concern at sites contaminated with chlorinated solvents due to its high degree of toxicity and carcinogenicity. VC occurrence in aquifers is most often related to the degradation of higher chlorinated ethenes or ethanes and it is generally detected in plumes along with parent contaminants. However, specific combination of stratigraphic, hydrogeologic and geochemical conditions can enhance the degradation of parents and lead to the formation of plumes almost entirely composed of VC (i.e. VC-only plumes). This paper investigates the causes of VC-only plumes in the aquifers below the city of Ferrara (northern Italy) by combining multiple lines of evidence. The City of Ferrara is located on an alluvial lowland, built by the River Po, and is made up of alternating unconsolidated sandy aquifer and silt-clay aquitard deposits of fluvial origin. This region has been strongly impacted by prior industrial activities, with the occurrence of chlorinated compounds at several sites. VC-only plumes with uncertain source location were found at two contaminated sites. The source zone of a third plume composed of chloroethenes from PCE to VC was investigated for high resolution depositional facies architecture and contaminant distribution (contaminant concentration and Compound Specific Isotope Analysis – CSIA). The investigation suggested that degradation of PCE and TCE takes place during contaminant migration through peat-rich (swamp) layers related to the Holocene transgression, which locally act as a "reactor" for stimulating degradation with the accumulation of VC in the strongly reducing environment of the peat. Regional-scale stratigraphic architecture showed the ubiquitous occurrence of swamp layers at distinct stratigraphic levels in the investigated system and their apparent linkage to the in situ creation of the VC-only plumes.

1. Introduction

Chlorinated hydrocarbons are the most prevalent organic contaminants found in groundwater (Stroo et al., 2003). Among them, Vinyl Chloride (VC) is often of greater concern than higher chlorinated compounds, since it is more mobile in liquid and gas phases (Mackay et al., 2006) and is a known human carcinogen (IARC, 2007). VC can be found in aquifers as result of direct dumping or most often as the product of partial biotransformation of high chlorinated ethenes and ethanes (Barrio-Lage et al., 1986; Bradley and Chapelle, 2010; Chen et al., 1996; Lorah and Olsen, 1999; Vogel and McCarty, 1985). VC from partial dechlorination generally occurs in groundwater along with its associated high chlorinated parent compounds. However, under certain biogeochemical conditions the dechlorination of parents can be enhanced and lead to the formation of plumes composed almost entirely of VC (i.e. VC-only plumes). The occurrence of VC-only plumes can pose severe human health concerns related to groundwater quality and vapor intrusion. It is therefore essential to identify the kinds of settings where the phenomenon might be expected. A robust stratigraphic model based on distinct depositional environments and consideration of contaminant constituents and concentrations can help identify zones where dechlorination of contaminants and potential production of hazardous metabolites (e.g. VC) occurs or is likely to occur. The association between chlorinated hydrocarbon constituents, isotopic composition, hydrochemical and depositional environments is particularly relevant in the case of unconsolidated porous settings comprising layered sediments (e.g. alluvial plains) where the contaminants have intimate and pervasive contact with the lower permeability and organic-rich matrix and average groundwater flow rates are relatively low (e.g. Allen-King et al., 2006; Chapman and Parker, 2005; Guilbeault et al., 2005; Kalinovich et al., 2012; Parker et al., 2004; Ritzi et al., 2013). Gilmore (2010) and Sale et al. (2013) observed the importance of studying contaminant mass storage in depositional zones corresponding to

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lower K sediment layers, where contrasting hydrochemical conditions and strongly variable physicochemical properties of sediments can influence contaminant degradation. Detailed investigation of contaminant distribution in low permeability layers was recently performed by Damgaard et al. (2013a); Damgaard et al. (2013b); Manoli et al. (2012); Scheutz et al. (2010) in the context of enhanced biodegradation of chloroethenes in clayey tills. Takeuchi et al. (2011) showed occurrence of natural attenuation of chloroethenes in an organic-rich clay aquitard and reported that the organic-rich clay may also play an active role in the natural attenuation in adjacent aquifers.

The main objective of this study was to identify factors that contributed to the origin of VC-only plumes in an unconsolidated alluvial setting. To achieve the main objective, sub-aims of the research were to carry out detailed reconstructions of stratigraphy (i.e. depositional facies architecture) and contaminant distribution in a complex multilayered aquifer system (southeastern sector of the Po Plain, Ferrara, northern Italy), where contamination by chlorinated ethenes occurs at several sites, showing peculiar accumulations of the degradation product VC in plumes that lack of the parent compounds suspected to have been released as DNAPLs decades ago. In particular, two VC-only plumes with uncertain source locations were detected at contaminated sites "A" and "B" (Fig. 1). The study focused at the known source of contamination of a third site ("Caretti site") where the whole series of chloroethenes (from PCE to VC) occurs in groundwater at concentrations up to 1×10^4 μg/L. Detailed depositional facies analysis and high-resolution vertical hydrogeological investigations (i.e. reconstruction of contaminant architecture, in the same manner as Adamson et al., 2015; Guilbeault et al., 2005; Parker et al., 2003) have been carried out along with an investigation of groundwater geochemical conditions and the application of Compound-Specific Isotope Analyses (CSIA). A detailed conceptual model developed at the Caretti source zone explains the accumulation of by-products in relation to the regional stratigraphy, and provides insights on the genesis of VC enriched plumes in the Ferrara region.

2. Geological and hydrogeological setting

The Po Plain, one of the largest alluvial plains in Europe, has been widely investigated during the last three decades in terms of basin formation and evolution (Dalla et al., 1992; Dondi and D'Andrea, 1986; Muttoni et al., 2003; Pieri and Groppi, 1981). These early studies showed the Po Plain as a rapidly subsiding foreland basin bounded by two mountain chains, the Alps to the north and the Apennines to the south.

South of the Po River, the large-scale stratigraphic architecture of the Pliocene-Quaternary basin fill displays vertically stacked, third-order depositional sequences (sensu Mitchum et al., 1977), identified on a seismic basis and mapped as unconformity-bounded stratigraphic units (UBSU - Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998). A tectonic unconformity within the uppermost unit (Emilia-Romagna Supersynthem) allows its subdivision into two lower-rank units: Lower and Upper Emilia-Romagna Synthems. The latter shows the characteristic alternation of continental/marine deposits (Amorosi et al., 2004; Amorosi et al., 1999) or distinctive fluvial-channel stacking patterns (Amorosi et al., 2008). The Upper Emilia-Romagna Synthem is subdivided into four fourth-order depositional cycles (subsynthems), 50 to 100 m thick, which have been interpreted to reflect transgressive-regressive (T-R) cycles falling in the Milankovitch band (ca. 100 kyr), and that are inferred to represent regional hydrostratigraphic units (aquifer systems A0 to A4 of Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998; Regione and ENI Divisione AGIP, 2002).

In the study area (Fig. 1), landward of the maximum marine ingression, the T-R cycles are made up entirely of continental deposits. Above basal, overbank clays and silts with highly lenticular fluvial sand bodies, each fourth-order cycle exhibits increasingly amalgamated and laterally extensive channel-belt sand bodies (Amorosi et al., 2008). The sheet-like fluvial bodies represent the major aquifer systems, while the overbank fines are considered low permeability barriers. The youngest

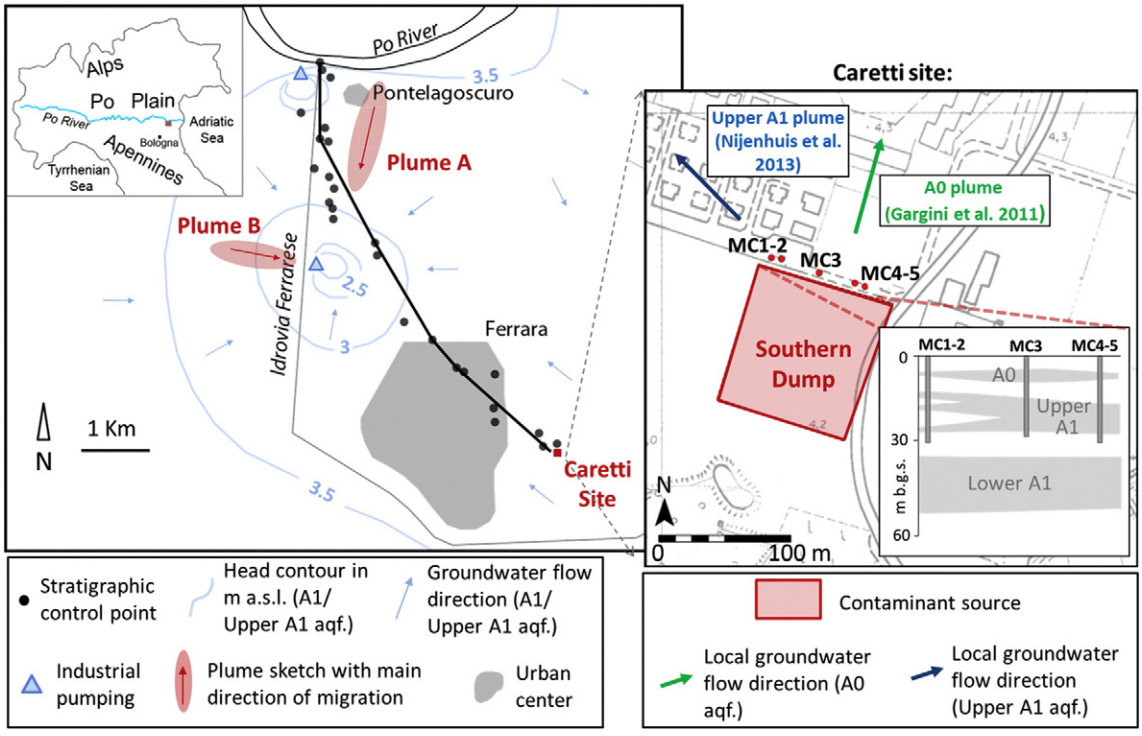

Fig. 1. Location of the study area. The left box depicts sketches of the VC-only plumes A and B, their main migration direction and the points used for stratigraphic reconstruction across the Ferrara region. Regional head contours of A1/upper A1 aquifer (Nijenhuis et al., 2013) are in m a.s.l. with 0.5 m spacing. Details about the Caretti site (configuration of the monitoring cross-section in relation with the source of contamination) are sketched on the right. Contaminant plumes originated from the Southern Dump in the A0 aquifer (northward migration) and upper A1 aquifer (northwestward migration) were investigated by Gargini et al. (2011) and Nijenhuis et al. (2013), respectively.