Science of the Total Environment 628–629 (2018) 782–790

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Atmospheric pattern of volatile organochlorine compounds and hexachlorobenzene in the surroundings of a chlor-alkali plant

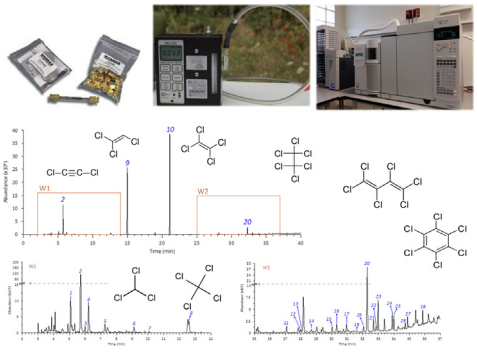
Barend L. van Drooge, Esther Marco, Joan O. Grimalt *

Institute of Environmental Assessment and Water Research (IDÆA-CSIC), Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain

HIGHLIGHTS

- The volatile airborne pollutants released from a chlor-alkali plant were identified.
- The polychloro-1,3-butadienes from chlor-alkali plant emissions were identified.
- Dichloroacetylene was the main by-product from the chlor-alkali plant air emissions.
- Trichloroethylene was the dominant volatile compound emitted to the atmosphere.
- Trichloroethylene was the VOC involving higher health risk for the nearby population.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 November 2017
Received in revised form 7 February 2018
Accepted 8 February 2018
Available online xxxx

ABSTRACT

The outdoor atmospheric distributions of chlorinated volatile organic compounds (VOCs) from locations receiving the emissions of a chlor-alkali plant have been studied. Trichloroethylene and tetrachloroethylene (medians 2.4 μg/m^3 and 1.7 μg/m^3, respectively) were the most abundant compounds, which was in accordance with the production processes from these installations. The concentrations of trichlorofluoromethane, median 1.6 μg/m^3, are rather similar to the average levels described in general in the troposphere and cannot be attributed to this specific source.

Several by-products involving dichloroacetylene, carbon tetrachloride, hexachloroethane, hexachlorobutadiene, *trans*-1H-pentachloro-1,3-butadiene, 2H-pentachloro-1,3-butadiene, *cis*-1H-pentachloro-1,3-butadiene, tetrachloro- and trichloro-butadienes and hexachlorobenzene were also identified. Some of these compounds, e.g. carbon tetrachloride, chloroform and tetrachloroethane, could also have been manufactured during some periods. The occurrence of these manufactured compounds and by-products in the atmosphere could also reflect, at least in part, volatilization during the extraction of previously discharged chlor-alkali residues developed within the environmental restoration program of the Flix water reservoir. In this respect, the tri-, tetra- and pentachloro-1,3-butadienes could also originate from microbial transformation in the solid deposits accumulated in the water reservoir which were volatilized after extraction.

Among all identified VOCs, trichloroethylene showed the highest health risks considering the measured airborne concentrations and the WHO and USEPA recommendations.

* Corresponding author.
E-mail address: joan.grimalt@idaea.csic.es (J.O. Grimalt).

https://doi.org/10.1016/j.scitotenv.2018.02.088
0048-9697/

1. Introduction

Atmospheric pollution is at present one of the main causes of human health deterioration. Pollutants in the atmosphere are the second and ninth causes of health disease and injury identified in the global study of the 2000–2010 period (Lim et al., 2012). Furthermore, the World Health Organization (WHO) estimates that ambient air pollution is responsible for 3.7 million premature deaths per year worldwide (WHO, 2014).

Important efforts are addressed to minimize or decrease these health problems. Comprehensive characterization of the airborne pollutants is mandatory for implementation of adequate remediation strategies. Most of these efforts have been centered in the study of urban areas and the pollution problems related to traffic (van Drooge and Grimalt, 2015; Bi et al., 2008; Mesquita et al., 2014; 2017; Minguillon et al., 2016; Oliveira et al., 2007; van Drooge et al., 2017). While these efforts are justified by the large numbers of individuals exposed to these emissions, there are other pollution processes that may also be influential on the populations' health that need to be characterized, e.g. source apportionment of pollutants in the surroundings of cement plants (Karstensen, 2008; Mari et al., 2016; Sánchez-Soberón et al., 2016), petrochemical areas (Ras et al., 2009; Tiwari et al., 2010) and other industrial activities.

Chlor-alkali plants are also specific sources of atmospheric pollutants to the atmosphere. While diverse studies have assessed the relevance of some of the problems related with these installations (Garí et al., 2014; Grimalt et al., 1994), a comprehensive approach for the characterization of the total burden of pollutants released from these plants and the possible effects into the population are still to be developed.

Many of the organic pollutants released to the atmosphere from these factories are volatile organic compounds (VOCs), some of them are manufactured and others constitute by-products of the synthetic processes. An analytical method has been developed and implemented to identify and quantify airborne VOCs in the low μg/m^3 range from the surroundings of a chlor-alkali plant and the nearby village (Flix, Catalonia, Spain) that is taken as representative example of these installations. This factory is located in a rural area and is the only manufacturing industry in a surrounding area of at least 10 km of radius. The volatile products sampled nearby, most of the sampling sites in distances shorter than 1 km from the factory, represent inputs from the installation. The released VOC mixtures are representative of chlor-alkali plants devoted to the synthesis of a wide diversity of organochlorine compounds such as polychlorobiphenyls, DDT and other semivolatile products in the past, e.g. 1960–1987, and organochlorine solvents in recent decades (Torres, 1997). The volatile organochlorine compounds manufactured in the factory included chlorofluorocarbons, chloroform, methylene chloride, trichloroethylene, tetrachloroethylene, hexachloroethane, chlorobenzene, carbon tetrachloride (Torres, 1997) which provide a good reference case of study of the possible VOC emissions from chlor-alkali installations.

Sampling was performed in different sites (Fig. 1) in 2013–2015 (n = 44). During this period, remediation works to remove industrial residues that had been previously discharged into the Flix water reservoir were performed (EU, 2007). These works may have partially mobilized dumped VOCs from the chlor-alkali installation enhancing their release into the atmosphere. The atmospheric content of these compounds reflects inputs from the installation in which they were synthesized. Hexachlorobenzene is also a by-product of the synthesis of some of these solvents and has also been included in the present study. The qualitative and quantitative information generated from these analyses is discussed in the context of airborne concentrations and available toxicity data.

2. Methods and materials

2.1. Materials

Stainless steel sorbent cartridges (8.9 cm long and 0.64 cm outer diameter) were used. These cartridges were filled with different

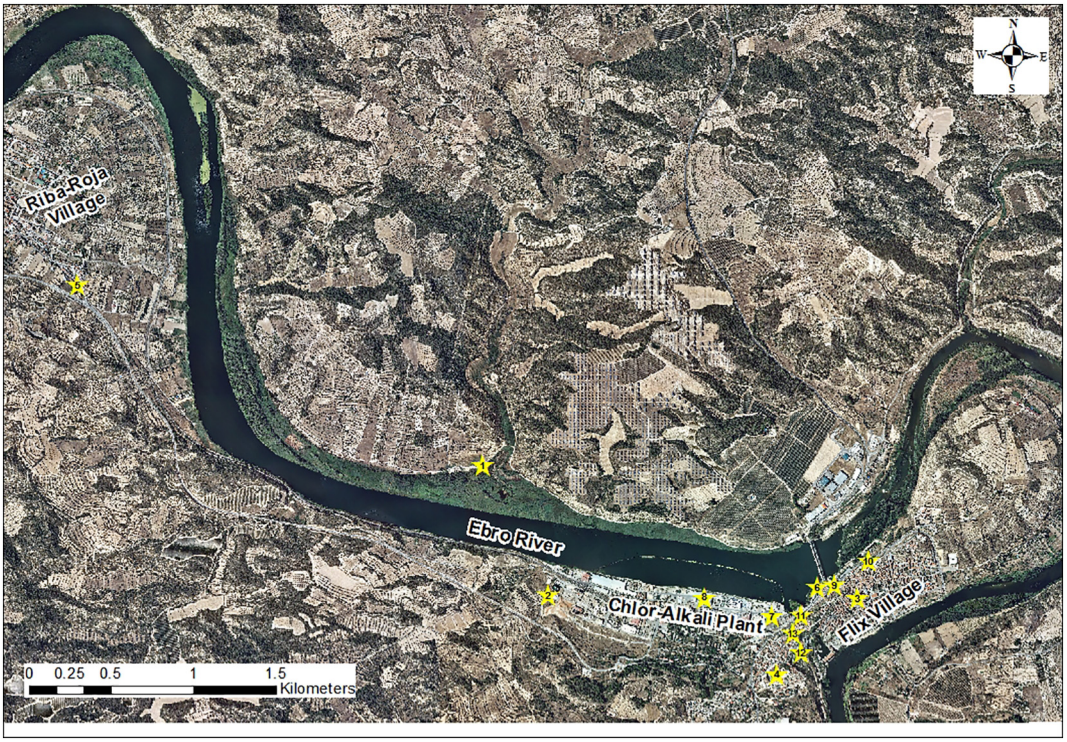


Fig. 1. Sampling sites for VOC near the chlor-alkali plant. The industrial complex is situated along the Ebro River. The sampling sites coordinates are reported in Table S1 in the electronic supplementary information (SEM). An amplified figure of the area around the village and the chlor-alkali plant is reported in Fig. S1 (SEM). Images from the Catalan Institute of Geography and Geology (ICGC). Reconeixement Internacional 4.0, CC BY 4.0 License.