ATMOSPHERIC PATTERN OF VOLATILE ORGANOCHLORINE COMPOUNDS AND HEXACHLOROBENZENE IN THE SURROUNDINGS OF A CHLOR-ALKALI PLANT

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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.

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., 2015; 2017; Minguillon et al., 2016; Oliveira et al., 2007; van Drooge et al., 2015; 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; Sanchez-Soberon 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 (Gari 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 (Figure 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. 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 adsorbents: a) 180 mg sorbent Carbopack B, 180 mg Carbopack and 180 mg Carbopack X (Supelco Inc., Bellefonte, PA) for the analysis of the compounds listed in Table 1, and b) 200 mg of Tenax TA 35/60 mesh (2,6-diphenyl-p-phenylene oxide; Markes International Ltd, Pontyclum, UK) for hexachlorobenzene. The sorbent cartridges were preconditioned with precleaned helium (5N grade) at 100 mL/min at 320°C for 2 hours and then at 335°C for 30 minutes with the same flow carrier gas. Then, the cartridges were sealed with brass Swagelock storage endcaps fitted with PTFE ferrules and stored in solvent-free clean environments.

2.2 Sampling

Air samples were collected for 30 min at 40 mL/min (1.2 L) in different sites around the chlor-alkali plant (Figure 1; the coordinates of the sampling sites are reported in the electronic supplementary information; SEM; Table S1) between 2013 and 2015. The sampling consisted in connecting two cartridges in parallel to a SKC Universal sampling pump Deluxe model (SKC Inc., USA) using an adjustable low flow adapter tube holder (SKC Inc., USA). The sampling pump was calibrated in the field with a Defender 510L Calibrator (BIOS, Butler, NJ) prior and after sampling in order to check the performance of the sampling pump. Each flow measurement encompassed ten successive determinations which were only accepted if the dispersion of values was lower than 5%. Then, the average (n = 10) was considered. Samples were only accepted as valid if the deviation in the flow measurements before and after sampling was lower than 10%. The average of the measurements before and after sampling was taken for calculation of the concentrations. After sampling the cartridges were sealed and transported to the laboratory for chemical analysis.

2.3. Instrumental analysis

The absorbed compounds in the cartridges samples were transferred with helium (5N grade; no inlet split flow) to a thermal desorption (TD) instrument equipped with a Unity Series 2 Thermal Desorber and an Ultra 50:50 Multi-tube Auto-sampler (Markes International Ltd). The compounds were desorbed from the cartridges at 300ºC for 5 min (desorption flow 40 mL/min) and re-concentrated in a graphitized carbon sorbent cold trap (U-T11GPC-2S for General Purpose; Markes International Ltd) cooled at -20ºC. This cold trap was heated to 300°C for 5 min while passing a helium flow of 7.5 mL/min (split flow 6 mL/min) in order to transfer the VOCs to an uncoated and deactivated fused-silica capillary transfer line of 1 m length (internal and outer diameters 0.25 and 0.35 mm, respectively) heated at 200ºC. The column flow was 1.5 mL/min. The total split ratios were 5:1 and 1:1 for the analysis of VOCs and hexachlorobenzene, respectively.

The transfer line introduced the compounds into a Gas Chromatograph 7890 (GC; Agilent Technologies Inc., Santa Clara, CA) coupled to a Mass Spectrometer 5975C Inert XL MSD. The GC was equipped with a DB-5MS UI capillary column (length 60 m; internal diameter 0.32 mm; film thickness 1 µm; Agilent J&W GC Columns). Helium (5N grade) was the carrier gas at a flow of 1.5 mL/min (constant flow mode). The GC oven temperature program for the VOCs started at 40°C (holding time 10 min) then it increased to 150ºC at 5°C/min and to 210°C at 15°C/min (final holding time 10 min). For hexachlorobenzene, the oven program also started at 40ºC with a holding time of 10 min, then it increased to 160ºC at 10ºC/min and to 225ºC at 20ºC/min (holding time 20 min).

A transfer line heated to 280ºC carried the compounds from the GC to the MS. The MS source and quadrupole temperatures were 230°C and 150°C, respectively. The MS operated in electron impact mode.

2.4. Qualitative and quantitative analysis

The mass spectrometer was scanned between 30 and 380 amu when operating in scan mode. It was also operated by selection ion monitoring (SIM) following the program described in Table 2 for VOC analysis. For hexachlorobenzene the monitoring program was focused on the m/z 284, 249, 214 and 142 ions. The calibration curves for the compounds in Table 2 were prepared from a VOC Mix Ultra Scientific Analytical solution containing these compounds at 2000 µg/mL (LGC standards, Teddlington, UK). The calibration curves for hexachlorobenzene were obtained from a hexachlorobenzene Pestanal ® neat standard (99.99% purity; Sigma-Aldrich, Darmstadt, Germany). All calibration curves encompassed nine solutions in methanol (Merck KGaA, Darmstadt, Germany) at different concentrations between 0.25 and 250 µg/mL for the compounds listed in Table 2 and between 0.01 and 5 µg/mL for hexachlorobenzene.

One µl aliquot of each standard solution was injected into a clean cartridge specific for either VOCs or hexachlorobenzene, as described above, using a Calibration Solution Loading Ring (CSLR™, Markes International Ltd., Llantrisant, UK) which allowed controlled vaporization and purging of the solvent (carrier gas flow at 50 mL/min during 3 min). These cartridges were subsequently analyzed in the TD-GC-MS. The VOCs were identified based on retention times of authentic standards and library identification of the mass spectra of each chromatographic peak (NIST2009, Mass Spectral Search Program, version 2.0f). Positive identification was only granted when all ratios of the compound under evaluation fulfilled those of the standard with less than

20% deviation. Authentic standards were used for the identification of the following compounds, trichlorofluoromethane, trans-1,2-dichloroethene, cis-1,2-dichloroethene, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, dichlorobenzenes, hexachloro-1,3-butadiene.

Quantification was performed by the external standard method. The quantification and qualification ions used for each compound in full scan and SIM modes are described in Table 2. The field blank levels are shown in Table 3.

2.5. Figures of merit

The calibration standards showed linearities in the range of 0.25 to 250 μg/mL for the VOCs and 0.05-5 μg/mL for HCB, with correlation coefficients between 0.994 and 1.000. The limits of detection (LODs) and quantification (LOQs) ranged between 0.02-0.05 $\mu g/m^3$ and 0.03-0.08 $\mu g/m^3$ for the VOCs, respectively and were 0.003 and 0.005 $\mu g/m^3$ for hexachlorobenzene, respectively (Table 3). They are lower than previously reported limits, e.g. 0.1 $\mu g/m^3$ for hexachlorobutadiene and 2.6 ng/m^3 (LOD) and 8.7 ng/m^3 (LOQ) for hexachlorobenzene (Dann 1997). For statistical calculations, half detection limit was assigned to non-detected VOC and intermediate values between LOQ and LOD, (LOD+LOQ)/2, were assigned to detected compounds at concentrations below limit of quantification.

The repeatability of the VOC analyses was 0.9-4.4% of the residual standard deviation and 7.1% for hexachlorobenzene (Table 3). The reproducibility of the VOC analyses was 1.1-6.5% of the residual standard deviation and 8.8% for hexachlorobenzene (Table 3).

3. Results and discussion

3.1. Qualitative composition

Figure 2 shows a representative chromatogram of the ambient air collected in the surroundings of the chlor-alkali plant (station No. 13; Figure 1). The most abundant compounds were trichloroethylene (peak No. 9) and tetrachloroethylene (peak No. 10). The former was manufactured in these installations between 1963 and 1990 and the synthesis of the latter started in 1972 (Torres, 1997). Other main constituents of this distribution, dichloroacetylene and 1,1,4,4-tetrachloro-1,3-butadiene, are by-products of the synthesis of organochlorine solvents. The mixture also contains other compounds that are not commonly found in environmental mixtures such as hexachloroethane and polychloro-1,3-butadienes. The dominance of these compounds shows a very distinct pattern from the VOC composition of rural or urban environments (Castellnou et al., 1997; Garzon et al., 2015; Lee et al., 2002; Mohamed et al., 2002).

Dichloroacetylene (peak No. 2 in Figure 2) has been identified by examination of the retention time and mass spectral fragments characteristic of this compound, e.g. m/z 47, 59, 94 and 96 (Figure 3). This compound can be formed after degradation of tri- and tetrachloroethylene (Greim et al. 1984, Reichert et al. 1983, Tobiszewski and Namiesnik 2006). Hexachloroethane (peak No. 21 in Figure 2) was manufactured between 1963 and 1992 (Torres, 1997) as it is used in the production of nitrocellulose, in the formulation of high pressure lubricants and anthelmintic in veterinary medicine (Snedecor, 1999). However, this compound may also be a by-product of industrial chlorination processes.

The polychloro-1,3-butadienes (peaks Nos. 12-15, 17-20, 22-27 and 28 in Figure 2) are also by-products of the synthesis of organochlorine compounds (Botta et al. 1996, Fattore et al. 1996, Zhang et al. 2015). The distributions of trichloro-, tetrachloro- and pentachloro-1,3-butadienes have been identified from the characteristic mass ions obtained from their mass spectra, m/z 50, 85, 121 and 156 for the trichloro-1,3-butadienes (Figure 3), m/z 119, 130, 155 and 192 for the tetrachloro-1,3-butadienes (Figure 4) and m/z 84, 156, 191 and 226 for the pentachloro-1,3-butadienes (Figure 4). The occurrence of 1,1,4,4-tetrachloro-1,3-butadiene has been identified from the specific mass spectral characteristics of this compound.

The three pentachloro-1,3-butadienes (*trans*-1H-pentachloro-1,3-butadiene, 2H-pentachloro-1,3-butadiene, *cis*-1H-pentachloro-1,3-butadiene) have been identified by comparison to the retention times reported elsewhere for a GC column of similar stationary phase polarity to the one used in the present study (Botta et al., 1996). These pentachloro-homologues had been found in waters contaminated by industrial effluents and in bottom fractions of rectification columns of tetrachloroethene (Botta et al., 1996). Now, they have been identified in atmospheric samples for the first time. Reductive dechlorination of hexachloro-1,3-butadiene in sediments by anaerobic microorganism can also lead to the formation of tri- and tetrachlorobutadiene isomers (Bosma et al.

1994; Field and Sierra-Alvarez 2004). The identification of these compounds shows that the exposure of populations to emissions from chlor-alkali plants is far more complex than it could be anticipated based on the available literature data. They could also originate from microbial transformation of hexachloro-1,3-butadiene present in the industrial residues dumped into the Flix water reservoir that were volatilized to the atmosphere during the dragging operations for river restoration. Specific studies on the toxicity of these compounds should be developed. Hexachloro-1,3-butadiene has also been identified from the specific mass spectral properties of this compound.

3.2. Air concentrations

The concentration ranges, average and median concentrations of the compounds detected in more than 50% of the samples are described in Table 3 and represented in the box plots of Figure 5. The median concentrations of trichloroethylene and tetrachloroethylene were 2.4 and 1.7 µg/m^3, respectively (Table 3). These two compounds were found in all samples constituting the most abundant VOC (Table 1). The median concentrations of trichloroethylene in sites No. 3 (5.1 µg/m^3), No. 7 (8.6 µg/m^3), No. 8 (14 µg/m^3), No. 9 (23 µg/m^3), No. 11 (20 µg/m^3) and No. 13 (87 µg/m^3) were higher than those in other locations from the same study area (0.09 – 3.4 µg/m^3). Some peak values were higher than 10 µg/m^3 in certain days, even higher than 100 µg/m^3. These later concentrations are around 10 times higher than those generally observed in urban and suburban areas (0.6 – 9.0 µg/m^3; EPA 2001). The high values may reflect remobilizations of organochlorinated solvents dumped into the Flix water reservoir that were exposed to open air as consequence of some solid residue dragging operations.

The concentrations of tetrachoroethylene had median values of 1.7 µg/m^3. The median values in most of the stations ranged between 0.10 µg/m^3 and 13 µg/m^3. Sites No. 11 and 13 are those in which highest median concentrations were found, 22 and 99 µg/m^3, respectively. These concentrations are high in comparison to other studies (EPA, 2001). As in the case of trichloroethylene, on certain days and sites the tetrachloroethylene concentrations peaked to 99 µg/m^3.

The overall median concentrations of carbon tetrachloride was 0.63 µg/m^3. This compound may be synthesized for use as solvent, which is at present highly restricted, and it may also be a by-product of the synthesis of other organochlorine compounds. The observed concentrations are similar to those found in the vicinity of manufacturing sites in the USA where average concentrations of 0.5 μg/m^3 were reported with peak concentrations of 1.6 μg/m^3 (ATSDR, 2005). Nevertheless, peak concentrations of 11 μg/m^3 were observed in the present study (Table 3).

Chloroform was found above limit of detection in 82% of the samples and could be quantified in 53% of them. The overall median concentration was 0.18 μg/m^3. The median concentrations in most of the sites ranged between 0.06 μg/m^3 and 1.1 μg/m^3. The highest median concentration was found in site No. 11, 1.8 μg/m^3.

Hexachloro-1,3-butadiene was detected in 77% of the samples but only in quantifiable amounts in 41% of them. The average and median concentrations of this compound were 0.21 and 0.10 μg/m^3, respectively (Table 3). This compound is used as solvent in the manufacture of plastics and is also an intermediate in the synthesis of lubricants (Verschueren, 1988; Yang, 1988). Atmospheric background concentrations below 0.1 μg/m^3 have been described but in some cases the concentrations of this compound are about 0.38 μg/m^3 (Shah and Singh, 1988). In site No. 6 (Figure 1) the average and median concentrations were 0.2 μg/m^3.

Hexachlorobenzene was detected in 50% of the samples and was above the LOQ in 17% of them. The median concentration was 5 ng/m^3, The median concentrations in the site with lower levels of this compound ranged between nd and 5.8 ng/m^3. Some sites showed high median values, e.g. Nos. 1, 2, 6, 7 and 8 with concentrations of 17, 13, 40, 22 and 100 ng/m^3. The levels in these sites Nos. 2 and 6 are close to the concentrations already observed in the atmosphere of Flix by high volume sampling in 1989-1992 (34 ng/m^3; Grimalt et al. 1994). These concentrations were much higher than those observed in urban background and remote mountainous areas, 0.05 ng/m^3, by high volume sampling (300-1000 m^3) and adsorption on polyurethane foam (Grimalt et al. 1994; van Drooge et al. 2004). This compound was used as fungicide in the past but it was included in the list of the banned organochlorine compounds of the Stockholm Convention. Once emitted to the atmosphere it has an average half-life of two years. The present observed level, 0.05 ng/m^3, seems to represent a general stable baseline of this compound in the northern hemisphere.

Trichlorofluoromethane was found above LOQ in nearly all samples. This compound, Freon 11, is very stable in the troposphere, with estimated half-lives between 55 and 207 years, which results in a general uniform global concentration of 1.4 μg/m^3 (Godish and Fu, 2003; Kaye and Penkett, 1994). This concentration is very similar to the median observed in the studied sites, 1.6 μg/m^3 (Table 3), indicating that the measured values probably reflect the overall tropospheric value and not specific inputs from the chlor-alkali installation despite these compounds were manufactured in the factory in the past (Torres, 1997). Most likely, the high volatility and low water solubility of these compounds avoided their accumulation in the solid residues dumped in the water reservoir.

Differences between the sampling sites located near the factory and in the surroundings, mostly encompassing the Flix village, may be observed (Table 3). However, these differences are not significant ($p > 0.05$) when the medians are evaluated with the Mann Whitney test. This lack of significance is consistent with an origin related with VOC volatilization from discharged materials during dredging in the water reservoir instead of direct emissions from the factory operations during the sampling period.

Likewise, median concentration differences between the cold (15 October-20 March) and the warm (21 March-14 Oct) periods can be identified (Table 3). For most VOCs and hexachlorobenzene they involve higher concentrations in the cold period but again these differences are not significant ($p > 0.05$) when evaluated from the Mann Whitney test.

3.3. Toxicity assessment

Trichloroethylene is classified as human carcinogen (Group 1) by IARC (2015) and (Group A) by USEPA IRIS (2012). The World Health Organization defines a threshold of 2.3 μg/m^3 for development of one cancer in one million over a 70 year-life period (WHO, 2010). The USEPA defines a reference value, RfC, of 2 μg/m^3 for no risk for any cause (USEPA IRIS, 2012). The RfC estimates the continuous inhalation exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime. This threshold includes sensitive subgroups and has an uncertainty spanning about one order of magnitude. Some samples show high values in relation to these thresholds (up to 140 μg/m^3; Table 3). However, they refer to chronic exposure. Since the observed median value in the area of study is 2.4 μg/m^3, 4.4 μg/m^3 in the factory surroundings (Table 3), the observed concentrations indicate that some health effects may occur in relation to the exposure of this compound. These effects cannot be assigned to specific sites since no statistically significant differences have been found between them when comparing the airborne VOCs and hexachlorobenzene concentrations.

Tetrachloroethylene is classified as probable human carcinogen, Group 2A by IARC (2015) and Group B1 by USEPA IRIS (2012). Different thresholds have been proposed by different organizations for no health effects, e.g. 40 µg/m^3 (RfC; USEPA IRIS, 2012), 250 µg/m^3 (WHO, 2010) and 4 µg/m^3 for no cancer effects (WHO, 2012). The observed median and average values, 1.7 µg/m^3 and 12 µg/m^3 (Table 3) suggest that limited health effects can be expected from exposure to this compound.

Carbon tetrachloride is a possible human carcinogen, Group 2B by IARC (2015) and Group B2 by USEPA IRIS (2012). The WHO defined 6.1 µg/m^3 as tolerable air concentration of this compound (WHO, 2000). For no cancer effects the threshold is set at 0.17 µg/m^3. The average and median results of Table 3, 1.5 and 0.63 µg/m^3, respectively, are well below the general threshold but above the reference level for no cancer effects.

Hexachloro-1,3-butadiene is classified as non-human carcinogen, Group 3 by IARC (2015) and Group C by USEPA IRIS (2012). This compound is included in the new list of 16 persistent organic pollutants (POPs) of the Stockholm Convention. No air concentration thresholds are indicated for this compound nor by the less chlorinated congeners from the WHO. The presence of polychloro-1,3-butadienes in the atmosphere is of concern due to the genotoxicity of these compounds (Brüschweiler et al. 2010, Reichert et al. 1984).

Hexachlorobenzene is a possible human carcinogen (Group 2B; IARC, 2015). This compound was included in the initial list of 12 POPs of the Stockholm Convention. According to EPA (2000) the threshold for non-carcinogen effects is 0.002 µg/m^3. This value is the same as the median value observed in the surrounding of the chlor-alkali plant (Figure 1) and lower than the average (0.013; Table 3).

4. Conclusions.

Trichloroethylene and tetrachloroethylene, the most abundant VOCs found in the atmosphere surrounding the chlor-alkali plant were related with synthetic processes of these installations. However, a substantial proportion of the concentrations of these compounds could originate from volatilitzation during extraction of previously dumped chlor-alkali residues developed within the environmental restauration program of the Flix water reservoir. Other compounds identified such as trichlorofluoromethane could reflect general environmental background levels.

The observed distributions of the airborne organochlorine compounds were also characterized by the occurrence of several by-products of the synthesis of organic solvents such as 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. The presence of pentachlorobenzenes and dichloroacetylene are identified in atmospheric samples for the first time. Some of these compounds, e.g. carbon tetrachloride, chloroform and tetrachloroethane, could have been manufactured in the past. In this respect, the tri-, tetra- and pentachloro-1,3-butadienes could also originate from microbial transformation in the solid residues accumulated in the water reservoir which were volatilized after extraction.

According to the WHO and USEPA recommendations, trichloroethylene is the VOC to be monitored more closely to avoid health risks to the population living in the surroundings of the installation since the observed median values are similar to the thresholds of no-risks described by these organizations.

Acknowledgements

We are thankful to the inhabitants of Flix for their help in VOC sampling. Financial support from the EU projects NEUROSOME (H2020-MSCA-ITN-2017-766251) and HEALS (FP7-ENV-2013- 603946) and projects GRACCIE_REDES (CTM2014-59111-REDC) and CTM2015-71832-P from the Spanish Ministry of Economy and Competitiveness is acknowledged.

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Table 1. Atmospheric volatile organochlorine compounds collected with the combined carbotrap multiadsorbents and identified by GC-MS in the surroundings of a chlor-alkali plant.

No.	Compound
1	Trichlorofluoromethane
2	Dichloroacetylene
3	1,1,2-Trichloro-1,2,2-trifluoroethane
4	Dichloromethane
5	trans-1,2-Dichloroethene
6	cis-1,2-Dichloroethene
7	Chloroform
8	Carbon tetrachloride
9	Trichloroethylene
10	Tetrachloroethylene
11	1,1,2,2-Tetrachloroethane
12	Trichloro-1,3-butadiene isomer
13	Trichloro-1,3-butadiene isomer
14	Trichloro-1,3-butadiene isomer
15	Trichloro-1,3-butadiene isomer
16	1,4-Dichlorobenzene
17	Tetrachloro-1,3-butadiene isomer
18	Tetrachloro-1,3-butadiene isomer
19	Tetrachloro-1,3-butadiene isomer
20	1,1,4,4,-Tetrachloro-1,3-butadiene
21	Hexachloroethane
22	Tetrachloro-1,3-butadiene isomer
23	Tetrachloro-1,3-butadiene isomer
24	Tetrachloro-1,3-butadiene isomer
25	*trans*-1*H*-Pentachloro-1,3-butadiene
26	2*H*-Pentachloro-1,3-butadiene
27	*cis*-1*H*-Pentachloro-1,3-butadiene
28	Hexachloro-1,3-butadiene

Table 2. Instrumental quantification conditions in SIM and full scan modes of the volatile organic compounds quantified.

		Selected ion monitoring			Full scan						
RT[a] (min)	Compound	TW[b] (min)	QF[c]	QL[d]1	QF	QL1	Ratio[e]1	QL2	Ratio2	QL3	Ratio3
5.130	Trichlorofluoromethane	W1: 2	101	103	101	103	64.7	105	10.5	66	10.5
5.850	1,1-Dichloroethene		61	96	61	96	76.4	98	48.8	63	32.9
7.350	trans-1,2-Dichloroethene		61	96	61	96	84.4	98	54.5	63	32.7
9.220	cis-1,2-Dichloroethene	W2: 8.5	61	96	61	96	94.1	98	60.0	63	32.5
10.200	Chloroform		83	85	83	85	65.7	47	17.9	87	10.9
12.730	Carbon tetrachloride		117	119	117	119	96.8	82	20.7	121	31.5
15.070	Trichloroethylene	W4:13.7	130	132	130	132	96.4	95	86.8	97	56.4
21.190	Tetrachloroethylene		166	164	166	164	78.1	129	66.4	131	64.3
30.100	1,3-Dichlorobenzene		146	148	146	148	64.0	111	36.2	75	23.9
30.430	1,4-Dichlorobenzene		146	148	146	148	64.0	111	34.9	75	23.4
31.180	1,2-Dichlorobenzene		146	148	146	148	64.6	111	38.2	75	23.7
35.970	Hexachloro-1,3-butadiene		225	227	225	227	64.3	223	62.2	190	41.8

[a] Retention time. [b] Initial retention time of the MS ion windows in SIM mode. [c] Quantification ion (m/z). [d] Qualifier ion (m/z).
[e] Ratio of the intensities of QF and QL (%).

Table 3. Concentrations of volatile organochlorine compounds (µg/m^3) measured in the outdoor ambient air of a chlor-alkali plant

Compound	All samples						Warm period	Cold period	Near factory	Factory surroundings					
	DET[a]	Min	Max	average	Standard deviation	Median	Median	Median	Median	Median	LOD[b]	LOQ[c]	R1[d]	R2[e]	Blank level
Trichlorofluoromethane	100	0.31	2.5	1.4	0.55	1.6	0.89	1.65	1.3	1.6	0.05	0.08	0.9	1.1	0.15
1,1-Dichloroethene	80	0.09	0.20	0.1	0.03	0.09	0.09	0.09	0.09	0.09	0.04	0.07	2.5	2.9	0.04
trans-1,2-Dichloroethene	52	0.09	0.42	0.1	0.11	0.09	0.09	0.09	0.20	0.09	0.04	0.07	2.0	2.8	0.04
cis-1,2-Dichloroethene	91	0.12	10	1.1	1.9	0.24	0.12	0.43	0.12	0.36	0.05	0.08	2.6	4.1	0.06
Chloroform	82	0.06	2.3	0.44	0.59	0.18	0.25	0.12	0.16	0.19	0.03	0.05	4.4	6.5	0.03
Carbon tetrachloride	100	0.05	11	1.5	2.2	0.63	0.68	0.59	0.66	0.63	0.02	0.03	3.4	5.2	0.02
Trichloroethylene	100	0.09	140	14	27	2.4	1.35	2.9	0.17	2.6	0.04	0.07	3.3	3.9	0.04
Tetrachloroethylene	100	0.06	99	12	20	1.7	1.2	4.5	0.88	4.4	0.02	0.03	1.3	1.6	0.03
1,3-Dichlorobenzene	73	0.05	1.0	0.1	0.17	0.05	0.05	0.05	0.05	0.05	0.02	0.03	2.0	2.4	0.02
1,4-Dichlorobenzene	80	0.04	15	0.65	2.6	0.06	0.12	0.08	0.04	0.1	0.02	0.03	2.7	3.3	0.02
1,2-Dichlorobenzene	66	0.04	14	0.67	2.5	0.07	0.16	0.06	0.04	0.08	0.02	0.03	2.0	2.5	0.02
Hexachloro-1,3-butadiene	77	0.04	1.8	0.21	0.31	0.1	0.14	0.14	0.10	0.14	0.02	0.03	2.7	3.3	0.02
Hexachlorobenzene	55	0.003	0.13	0.020	0.033	0.005	0.005	0.010	0.010	0.008	0.003	0.005	7.1	8.8	0.001

[a] DET: % of samples with values above LOQ. [b] LOD: límit of detection. [c] LOQ: límit of quantification. [d] Repeatability (%residual Standard deviation). [e] Reproducibility (%residual Standard deviation).

Figure captions.

Figure 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 Figure S1 (SEM). Images from the Catalan Institute of Geography and Geology (ICGC). Reconeixement Internacional 4.0, CC BY 4.0 License.

Figure 2. Representative chromatogram of the ambient air collected in the surroundings of the chlor-alkali plant and analyzed by thermal desorption-gas chromatography-mass spectrometry. The W1 and W2 boxes show the amplified signal of the retention time sections from the general chromatogram (top).

Figure 3. Fragmentograms of dichloroacetylene (peak 2), trichloro-1,3-butadiene isomers (peaks 12 – 15) and hexachloroethane (peak 21). The peak numbers correspond to those in Figure 2. The plots on top of each column show the mass spectra of these compounds.

Figure 4. Fragmentograms of tetrachloro-1,3-butadienes (peaks 17-20 and 22-24) and pentachloro-1,3-butadiene isomers (peaks 25-27). The peak numbers correspond to those in Figure 2. The plots on top of each column show the mass spectrum of these compounds.

Figure 5. Box plots of the VOC distributions of the ambient air collected in the surroundings of the chlor-alkali plant (Figure 1).