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**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 $\mu$g/m$^3$ and 1.7 $\mu$g/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 $\mu$g/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 $\mu g/m^3$ 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

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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.

116    *2.2 Sampling*

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118    Air samples were collected for 30 min at 40 mL/min (1.2 L) in different sites around the

119    chlor-alkali plant (Figure 1; the coordinates of the sampling sites are reported in the

120    electronic supplementary information; SEM; Table S1) between 2013 and 2015. The

121    sampling consisted in connecting two cartridges in parallel to a SKC Universal

122    sampling pump Deluxe model (SKC Inc., USA) using an adjustable low flow adapter

123    tube holder (SKC Inc., USA). The sampling pump was calibrated in the field with a

124    Defender 510L Calibrator (BIOS, Butler, NJ) prior and after sampling in order to check

125    the performance of the sampling pump. Each flow measurement encompassed ten

126    successive determinations which were only accepted if the dispersion of values was

127    lower than 5%. Then, the average (n = 10) was considered. Samples were only accepted

128    as valid if the deviation in the flow measurements before and after sampling was lower

129    than 10%. The average of the measurements before and after sampling was taken for

130    calculation of the concentrations. After sampling the cartridges were sealed and

131    transported to the laboratory for chemical analysis.

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133    *2.3. Instrumental analysis*

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135    The absorbed compounds in the cartridges samples were transferred with helium (5N

136    grade; no inlet split flow) to a thermal desorption (TD) instrument equipped with a

137    Unity Series 2 Thermal Desorber and an Ultra 50:50 Multi-tube Auto-sampler (Markes

138    International Ltd). The compounds were desorbed from the cartridges at 300ºC for 5

139    min (desorption flow 40 mL/min) and re-concentrated in a graphitized carbon sorbent

140    cold trap (U-T11GPC-2S for General Purpose; Markes International Ltd) cooled at -

141    20ºC. This cold trap was heated to 300°C for 5 min while passing a helium flow of 7.5

142    mL/min (split flow 6 mL/min) in order to transfer the VOCs to an uncoated and

143    deactivated fused-silica capillary transfer line of 1 m length (internal and outer

144    diameters 0.25 and 0.35 mm, respectively) heated at 200ºC. The column flow was 1.5

145    mL/min. The total split ratios were 5:1 and 1:1 for the analysis of VOCs and

146    hexachlorobenzene, respectively.

147        The transfer line introduced the compounds into a Gas Chromatograph 7890

148    (GC; Agilent Technologies Inc., Santa Clara, CA) coupled to a Mass Spectrometer

149    5975C Inert XL MSD. The GC was equipped with a DB-5MS UI capillary column

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150 (length 60 m; internal diameter 0.32 mm; film thickness 1 μm; Agilent J&W GC

151 Columns). Helium (5N grade) was the carrier gas at a flow of 1.5 mL/min (constant

152 flow mode). The GC oven temperature program for the VOCs started at 40°C (holding

153 time 10 min) then it increased to 150ºC at 5°C/min and to 210°C at 15°C/min (final

154 holding time 10 min). For hexachlorobenzene, the oven program also started at 40ºC

155 with a holding time of 10 min, then it increased to 160ºC at 10ºC/min and to 225ºC at

156 20ºC/min (holding time 20 min).

157 A transfer line heated to 280ºC carried the compounds from the GC to the MS.

158 The MS source and quadrupole temperatures were 230°C and 150°C, respectively. The

159 MS operated in electron impact mode.

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161 *2.4. Qualitative and quantitative analysis*

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163 The mass spectrometer was scanned between 30 and 380 amu when operating in scan

164 mode. It was also operated by selection ion monitoring (SIM) following the program

165 described in Table 2 for VOC analysis. For hexachlorobenzene the monitoring program

166 was focused on the m/z 284, 249, 214 and 142 ions. The calibration curves for the

167 compounds in Table 2 were prepared from a VOC Mix Ultra Scientific Analytical

168 solution containing these compounds at 2000 μg/mL (LGC standards, Teddlington, UK).

169 The calibration curves for hexachlorobenzene were obtained from a hexachlorobenzene

170 Pestanal ® neat standard (99.99% purity; Sigma-Aldrich, Darmstadt, Germany). All

171 calibration curves encompassed nine solutions in methanol (Merck KGaA, Darmstadt,

172 Germany) at different concentrations between 0.25 and 250 μg/mL for the compounds

173 listed in Table 2 and between 0.01 and 5 μg/mL for hexachlorobenzene.

174 One μl aliquot of each standard solution was injected into a clean cartridge

175 specific for either VOCs or hexachlorobenzene, as described above, using a Calibration

176 Solution Loading Ring (CSLR™, Markes International Ltd., Llantrisant, UK) which

177 allowed controlled vaporization and purging of the solvent (carrier gas flow at 50

178 mL/min during 3 min). These cartridges were subsequently analyzed in the TD-GC-MS.

179 The VOCs were identified based on retention times of authentic standards and library

180 identification of the mass spectra of each chromatographic peak (NIST2009, Mass

181 Spectral Search Program, version 2.0f). Positive identification was only granted when

182 all ratios of the compound under evaluation fulfilled those of the standard with less than

183 20% deviation. Authentic standards were used for the identification of the following

184 compounds, trichlorofluoromethane, trans-1,2-dichloroethene, cis-1,2-dichloroethene,

185 chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, 1,1,2,2-

186 tetrachloroethane, dichlorobenzenes, hexachloro-1,3-butadiene.

187        Quantification was performed by the external standard method. The

188 quantification and qualification ions used for each compound in full scan and SIM

189 modes are described in Table 2. The field blank levels are shown in Table 3.

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191 *2.5. Figures of merit*

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193 The calibration standards showed linearities in the range of 0.25 to 250 µg/mL for the

194 VOCs and 0.05-5 µg/mL for HCB, with correlation coefficients between 0.994 and

195 1.000. The limits of detection (LODs) and quantification (LOQs) ranged between 0.02-

196 0.05 µg/m$^3$ and 0.03-0.08 µg/m$^3$ for the VOCs, respectively and were 0.003 and 0.005

197 µg/m$^3$ for hexachlorobenzene, respectively (Table 3). They are lower than previously

198 reported limits, e.g. 0.1 µg/m$^3$ for hexachlorobutadiene and 2.6 ng/m$^3$ (LOD) and 8.7

199 ng/m$^3$ (LOQ) for hexachlorobenzene (Dann 1997). For statistical calculations, half

200 detection limit was assigned to non-detected VOC and intermediate values between

201 LOQ and LOD, (LOD+LOQ)/2, were assigned to detected compounds at concentrations

202 below limit of quantification.

203        The repeatability of the VOC analyses was 0.9-4.4% of the residual standard

204 deviation and 7.1% for hexachlorobenzene (Table 3). The reproducibility of the VOC

205 analyses was 1.1-6.5% of the residual standard deviation and 8.8% for

206 hexachlorobenzene (Table 3).

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209 **3. Results and discussion**

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211 *3.1. Qualitative composition*

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213 Figure 2 shows a representative chromatogram of the ambient air collected in the

214 surroundings of the chlor-alkali plant (station No. 13; Figure 1). The most abundant

215 compounds were trichloroethylene (peak No. 9) and tetrachloroethylene (peak No. 10).

216 The former was manufactured in these installations between 1963 and 1990 and the

217 synthesis of the latter started in 1972 (Torres, 1997). Other main constituents of this

218   distribution, dichloroacetylene and 1,1,4,4-tetrachloro-1,3-butadiene, are by-products of

219   the synthesis of organochlorine solvents. The mixture also contains other compounds

220   that are not commonly found in environmental mixtures such as hexachloroethane and

221   polychloro-1,3-butadienes. The dominance of these compounds shows a very distinct

222   pattern from the VOC composition of rural or urban environments (Castellnou et al.,

223   1997; Garzon et al., 2015; Lee et al., 2002; Mohamed et al., 2002).

224        Dichloroacetylene (peak No. 2 in Figure 2) has been identified by examination

225   of the retention time and mass spectral fragments characteristic of this compound, e.g.

226   $m/z$ 47, 59, 94 and 96 (Figure 3). This compound can be formed after degradation of tri-

227   and tetrachloroethylene (Greim et al. 1984, Reichert et al. 1983, Tobiszewski and

228   Namiesnik 2006). Hexachloroethane (peak No. 21 in Figure 2) was manufactured

229   between 1963 and 1992 (Torres, 1997) as it is used in the production of nitrocellulose,

230   in the formulation of high pressure lubricants and anthelmintic in veterinary medicine

231   (Snedecor, 1999). However, this compound may also be a by-product of industrial

232   chlorination processes.

233        The polychloro-1,3-butadienes (peaks Nos. 12-15, 17-20, 22-27 and 28 in Figure

234   2) are also by-products of the synthesis of organochlorine compounds (Botta et al. 1996,

235   Fattore et al. 1996, Zhang et al. 2015). The distributions of trichloro-, tetrachloro- and

236   pentachloro-1,3-butadienes have been identified from the characteristic mass ions

237   obtained from their mass spectra, $m/z$ 50, 85, 121 and 156 for the trichloro-1,3-

238   butadienes (Figure 3), $m/z$ 119, 130, 155 and 192 for the tetrachloro-1,3-butadienes

239   (Figure 4) and $m/z$ 84, 156, 191 and 226 for the pentachloro-1,3-butadienes (Figure 4).

240   The occurrence of 1,1,4,4-tetrachloro-1,3-butadiene has been identified from the

241   specific mass spectral characteristics of this compound.

242        The three pentachloro-1,3-butadienes (*trans*-1H-pentachloro-1,3-butadiene, 2H-

243   pentachloro-1,3-butadiene, *cis*-1H-pentachloro-1,3-butadiene) have been identified by

244   comparison to the retention times reported elsewhere for a GC column of similar

245   stationary phase polarity to the one used in the present study (Botta et al., 1996). These

246   pentachloro-homologues had been found in waters contaminated by industrial effluents

247   and in bottom fractions of rectification columns of tetrachloroethene (Botta et al., 1996).

248   Now, they have been identified in atmospheric samples for the first time. Reductive

249   dechlorination of hexachloro-1,3-butadiene in sediments by anaerobic microorganism

250   can also lead to the formation of tri- and tetrachlorobutadiene isomers (Bosma et al.

251   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 $\mu g/m^3$, 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 $\mu g/m^3$), No. 7 (8.6 $\mu g/m^3$), No. 8 (14 $\mu g/m^3$), No. 9 (23 $\mu g/m^3$), No. 11 (20 $\mu g/m^3$) and No. 13 (87 $\mu g/m^3$) were higher than those in other locations from the same study area (0.09 – 3.4 $\mu g/m^3$). Some peak values were higher than 10 $\mu g/m^3$ in certain days, even higher than 100 $\mu g/m^3$. These later concentrations are around 10 times higher than those generally observed in urban and suburban areas (0.6 – 9.0 $\mu g/m^3$; 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 $\mu g/m^3$. The median values in most of the stations ranged between 0.10 $\mu g/m^3$ and 13 $\mu g/m^3$. Sites No. 11 and 13 are those in which highest median concentrations were found, 22 and 99 $\mu g/m^3$, 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 $\mu g/m^3$.

The overall median concentrations of carbon tetrachloride was 0.63 $\mu g/m^3$. 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

286    sites in the USA where average concentrations of 0.5 μg/m$^3$ were reported with peak

287    concentrations of 1.6 μg/m$^3$ (ATSDR, 2005). Nevertheless, peak concentrations of 11

288    μg/m$^3$ were observed in the present study (Table 3).

289          Chloroform was found above limit of detection in 82% of the samples and could

290    be quantified in 53% of them. The overall median concentration was 0.18 μg/m$^3$. The

291    median concentrations in most of the sites ranged between 0.06 μg/m$^3$ and 1.1 μg/m$^3$.

292    The highest median concentration was found in site No. 11, 1.8 μg/m$^3$.

293          Hexachloro-1,3-butadiene was detected in 77% of the samples but only in

294    quantifiable amounts in 41% of them. The average and median concentrations of this

295    compound were 0.21 and 0.10 μg/m$^3$, respectively (Table 3). This compound is used as

296    solvent in the manufacture of plastics and is also an intermediate in the synthesis of

297    lubricants (Verschueren, 1988; Yang, 1988). Atmospheric background concentrations

298    below 0.1 μg/m$^3$ have been described but in some cases the concentrations of this

299    compound are about 0.38 μg/m$^3$ (Shah and Singh, 1988). In site No. 6 (Figure 1) the

300    average and median concentrations were 0.2 μg/m$^3$.

301          Hexachlorobenzene was detected in 50% of the samples and was above the LOQ

302    in 17% of them. The median concentration was 5 ng/m$^3$, The median concentrations in

303    the site with lower levels of this compound ranged between nd and 5.8 ng/m$^3$. Some

304    sites showed high median values, e.g. Nos. 1, 2, 6, 7 and 8 with concentrations of 17, 13,

305    40, 22 and 100 ng/m$^3$. The levels in these sites Nos. 2 and 6 are close to the

306    concentrations already observed in the atmosphere of Flix by high volume sampling in

307    1989-1992 (34 ng/m$^3$; Grimalt et al. 1994). These concentrations were much higher than

308    those observed in urban background and remote mountainous areas, 0.05 ng/m$^3$, by high

309    volume sampling (300-1000 m$^3$) and adsorption on polyurethane foam (Grimalt et al.

310    1994; van Drooge et al. 2004). This compound was used as fungicide in the past but it

311    was included in the list of the banned organochlorine compounds of the Stockholm

312    Convention. Once emitted to the atmosphere it has an average half-life of two years.

313    The present observed level, 0.05 ng/m$^3$, seems to represent a general stable baseline of

314    this compound in the northern hemisphere.

315          Trichlorofluoromethane was found above LOQ in nearly all samples. This

316    compound, Freon 11, is very stable in the troposphere, with estimated half-lives

317    between 55 and 207 years, which results in a general uniform global concentration of

318    1.4 μg/m$^3$ (Godish and Fu, 2003; Kaye and Penkett, 1994). This concentration is very

319    similar to the median observed in the studied sites, 1.6 μg/m$^3$ (Table 3), indicating that

320　the measured values probably reflect the overall tropospheric value and not specific

321　inputs from the chlor-alkali installation despite these compounds were manufactured in

322　the factory in the past (Torres, 1997). Most likely, the high volatility and low water

323　solubility of these compounds avoided their accumulation in the solid residues dumped

324　in the water reservoir.

325　　　　Differences between the sampling sites located near the factory and in the

326　surroundings, mostly encompassing the Flix village, may be observed (Table 3).

327　However, these differences are not significant ($p > 0.05$) when the medians are

328　evaluated with the Mann Whitney test. This lack of significance is consistent with an

329　origin related with VOC volatilization from discharged materials during dredging in the

330　water reservoir instead of direct emissions from the factory operations during the

331　sampling period.

332　　　　Likewise, median concentration differences between the cold (15 October-20

333　March) and the warm (21 March-14 Oct) periods can be identified (Table 3). For most

334　VOCs and hexachlorobenzene they involve higher concentrations in the cold period but

335　again these differences are not significant ($p > 0.05$) when evaluated from the Mann

336　Whitney test.

337

338　*3.3. Toxicity assessment*

339

340　Trichloroethylene is classified as human carcinogen (Group 1) by IARC (2015) and

341　(Group A) by USEPA IRIS (2012). The World Health Organization defines a threshold

342　of 2.3 $\mu g/m^3$ for development of one cancer in one million over a 70 year-life period

343　(WHO, 2010). The USEPA defines a reference value, RfC, of 2 $\mu g/m^3$ for no risk for

344　any cause (USEPA IRIS, 2012). The RfC estimates the continuous inhalation exposure

345　to the human population that is likely to be without an appreciable risk of deleterious

346　effects during a lifetime. This threshold includes sensitive subgroups and has an

347　uncertainty spanning about one order of magnitude. Some samples show high values in

348　relation to these thresholds (up to 140 $\mu g/m^3$; Table 3). However, they refer to chronic

349　exposure. Since the observed median value in the area of study is 2.4 $\mu g/m^3$, 4.4 $\mu g/m^3$

350　in the factory surroundings (Table 3), the observed concentrations indicate that some

351　health effects may occur in relation to the exposure of this compound. These effects

352　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 $\mu g/m^3$ (RfC; USEPA IRIS, 2012), 250 $\mu g/m^3$ (WHO, 2010) and 4 $\mu g/m^3$ for no cancer effects (WHO, 2012). The observed median and average values, 1.7 $\mu g/m^3$ and 12 $\mu g/m^3$ (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 $\mu g/m^3$ as tolerable air concentration of this compound (WHO, 2000). For no cancer effects the threshold is set at 0.17 $\mu g/m^3$. The average and median results of Table 3, 1.5 and 0.63 $\mu g/m^3$, 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 $\mu g/m^3$. 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

387 chlor-alkali residues developed within the environmental restauration program of the
388 Flix water reservoir. Other compounds identified such as trichlorofluoromethane could
389 reflect general environmental background levels.

390      The observed distributions of the airborne organochlorine compounds were also
391 characterized by the occurrence of several by-products of the synthesis of organic
392 solvents such as dichloroacetylene, carbon tetrachloride, hexachloroethane,
393 hexachlorobutadiene, *trans*-1H-pentachloro-1,3-butadiene, 2H-pentachloro-1,3-
394 butadiene, *cis*-1H-pentachloro-1,3-butadiene, tetrachloro- and trichloro-butadienes and
395 hexachlorobenzene. The presence of pentachlorobenzenes and dichloroacetylene are
396 identified in atmospheric samples for the first time. Some of these compounds, e.g.
397 carbon tetrachloride, chloroform and tetrachloroethane, could have been manufactured
398 in the past. In this respect, the tri-, tetra- and pentachloro-1,3-butadienes could also
399 originate from microbial transformation in the solid residues accumulated in the water
400 reservoir which were volatilized after extraction.

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

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407 **Acknowledgements**

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544

545 Table 1. Atmospheric volatile organochlorine compounds collected with the combined

546 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 |

547

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

550

| | | | 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 |

551 [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).

552 [e]Ratio of the intensities of QF and QL (%).

553

554

555

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

| Compound | DET[a] | All samples | | | | | Warm period | Cold period | Near factory | Factory surroundings | LOD[b] | LOQ[c] | R1[d] | R2[e] | Blank level |
| | | Min | Max | average | Standard deviation | Median | Median | Median | Median | Median | | | | | |
| 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 |

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

558    [e]Reproducibility (%residual Standard deviation).

559

561    **Figure captions.**

563    **Figure 1.** Sampling sites for VOC near the chlor-alkali plant. The industrial complex is

564    situated along the Ebro River. The sampling sites coordinates are reported in Table S1

565    in the electronic supplementary information (SEM). An amplified figure of the area

566    around the village and the chlor-alkali plant is reported in Figure S1 (SEM). Images

567    from the Catalan Institute of Geography and Geology (ICGC). Reconeixement

568    Internacional 4.0, CC BY 4.0 License.

570    **Figure 2.** Representative chromatogram of the ambient air collected in the surroundings

571    of the chlor-alkali plant and analyzed by thermal desorption-gas chromatography-mass

572    spectrometry. The W1 and W2 boxes show the amplified signal of the retention time

573    sections from the general chromatogram (top).

575    **Figure 3.** Fragmentograms of dichloroacetylene (peak 2), trichloro-1,3-butadiene

576    isomers (peaks 12 – 15) and hexachloroethane (peak 21). The peak numbers correspond

577    to those in Figure 2. The plots on top of each column show the mass spectra of these

578    compounds.

580    **Figure 4.** Fragmentograms of tetrachloro-1,3-butadienes (peaks 17-20 and 22-24) and

581    pentachloro-1,3-butadiene isomers (peaks 25-27). The peak numbers correspond to

582    those in Figure 2. The plots on top of each column show the mass spectrum of these

583    compounds.

585    **Figure 5.** Box plots of the VOC distributions of the ambient air collected in the

586    surroundings of the chlor-alkali plant (Figure 1).