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1 Categorizing chlordecone potential degradation products to explore their
2 environmental fate

3

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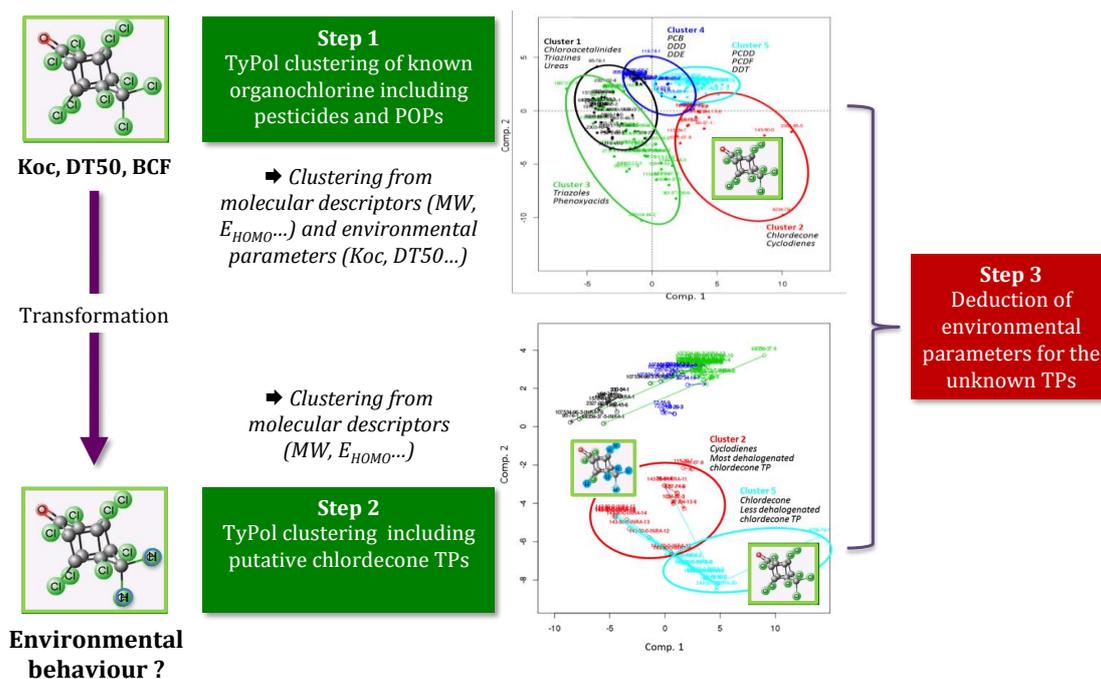
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18

19 **GRAPHICAL ABSTRACT**

In silico categorization of putative transformation products (TPs) of chlordecone using TyPol (Typology of Pollutants) tool



20

22 **ABSTRACT**

23 Chlordecone (C₁₀Cl₁₀O; CAS number 143-50-0) has been used extensively as an
24 organochlorine insecticide but is nowadays banned and listed on annex A in The
25 Stockholm Convention on Persistent Organic Pollutants (POPs). Although experimental
26 evidences of biodegradation of this compound are scarce, several dechlorination
27 products have been proposed by Dolfing et al. (2012), using Gibbs free energy
28 calculations to explore different potential transformation routes. We here present the
29 results of an *in silico* classification (TyPol - Typology of Pollutants) of chlordecone
30 transformation products (TPs) based on statistical analyses combining several
31 environmental endpoints and structural molecular descriptors. Starting from the list of
32 putative chlordecone TPs and considering available data on degradation routes of other
33 organochlorine compounds, we used different clustering strategies to explore the
34 potential environmental behaviour of putative chlordecone TPs from the knowledge on
35 their molecular descriptors. The method offers the possibility to focus on TPs present in
36 different classes and to infer their environmental fate. Thus, we have deduced some
37 hypothetical trends for the environmental behaviour of TPs of chlordecone assuming
38 that TPs, which were clustered away from chlordecone, would have different
39 environmental fate and ecotoxicological impact compared to chlordecone. Our findings
40 suggest that mono and di-hydrochlordecone, which are TPs of chlordecone often found
41 in contaminated soils, may have similar environmental behaviour in terms of
42 persistence.

43

44 *Keywords: Organochlorine pesticides, Biodegradation, Molecular modeling, Partial*
45 *least squares*

46

47 **HIGHLIGHTS**

- 48 • TyPol, an *in silico* typology, was used to categorize 170 organochlorine molecules
- 49 • Clustering used both molecular descriptors and environmental behaviour
- 50 • Parent and transformation products represented various chemical families
- 51 • 20 chlordecone putative transformation products (TPs) were categorized
- 52 • Combining two clustering allowed assessing the potential fate of chlordecone TPs

53

54 |

55 **1. Introduction**

56 In the French West Indies (FWI), chlordecone (C₁₀Cl₁₀O; CAS number 143-50-0 -
57 decachlorooctahydro-1,3,2-metheno-2Hcyclobuta[c,d]pentalen-2-one) has been largely
58 used on banana plantations over the 1978–1993 period to control banana weevil. Its
59 persistence in the agricultural soils of the FWI (i.e., 20,000 ha that represent up to 25 %
60 of the agricultural surface of the FWI) was estimated to last for several decades in
61 Nitisol, centuries in Ferralsol, and half a millennium in Andosol soils (Cabidoche et al.,
62 2009).

63 This organochlorine insecticide is now banned and listed in annex A of the
64 Stockholm Convention on Persistent Organic Pollutants (POPs) but its former use has
65 induced a general and important contamination of rivers, springs, and drinking water as
66 well as coastal ecosystems of the FWI (Coat et al., 2011) as revealed by investigation of
67 the French National Action Plan for chlordecone (PNAC 2008–2010). In such context,
68 finding strategies to remediate and/or mitigate this contamination on the very long-term
69 is a great challenge and, from this point of view, the FWI represent an open field for
70 remediation (Cabidoche and Jeannot, 2011; Levillain et al., 2012).

71 There is no clear cut evidence of microbial chlordecone degradation under aerobic
72 conditions. Indeed Orndorff and Colwell (1980) proposed that *Pseudomonas*
73 *aeruginosa* strain KO3 and a bacterial consortium isolated from Hopewell plant sewage
74 sludge under aerobic conditions transform chlordecone into monohydro-chlordecone
75 and di-hydro-chlordecone. However, these results have been criticized by Cabidoche et
76 al. (2009) because the initial contents in mono-hydro- and di-hydro-chlordecone, known
77 to be by-products of the synthesis contaminating the chlordecone, have not been
78 measured. This lack is compromising the proposed results because detection of
79 chlordecone TPs can be the result of incomplete chlorination of chlordecone during
80 synthesis and not to microbial biodegradation. Later on, George and Claxton (1988)
81 studied chlordecone degradation catalyzed by three *Pseudomonas* spp. showing that
82 after two weeks of incubation chlordecone reached only 15–25% of initial concentration
83 with a relatively high uncertainty of 10% on chlordecone HPLC concentration
84 measurements. In addition, in non-inoculated control, mono- and dihydro chlordecone
85 were detected as well. A poor bacterial growth was recorded and, consequently, the
86 authors concluded that due to its important chlorination, chlordecone was a poor carbon
87 source for bacterial growth. However, a recent study based on a large data set of 881
88 field soils of the FWI showed a significant increase of the

89 5bhydrochlodecone/chlordecone ratio in the soils 25 times greater than in commercial
90 formulations which suggested that natural transformation into 5b-hydrochlodecone over
91 the long term occurred in these soils (Devault et al., 2016).

92 Under anaerobic conditions, a pure culture of *Methanosarcina thermophila* grown on
93 acetate was shown to convert chlordecone to polar and nonpolar products (Jablonski et
94 al., 1996). Interestingly, similar pattern of soluble chlordecone decomposition products
95 were obtained with reduced vitamin B12 and reduced coenzyme F430 isolated from *M.*
96 *thermophila*. More recently, *Pseudonocardia* sp. KSF27 isolated from a soil repeatedly
97 treated with endosulfan was shown to also degrade dieldrin and other organochlorine
98 insecticides such as chlordecone but without providing information on the degradation
99 pathway (Sakakibara et al., 2011).

100 In France, giving the environmental and health problem caused by chlordecone
101 contamination in the West Indies, several research programs have recently been carried
102 out on soil bioremediation. Search for chlordecone-degrading microorganisms under
103 anaerobic and aerobic conditions remains a big challenge due to the lack of
104 experimental evidences of degradation products in soil environment. Indeed, only few
105 measured data on the identification of chlordecone TPs are available showing traces of
106 the TP 5b-hydrochlodecone in some Andosol, Nitisol, and Ferralsol soil samples
107 (Devault et al., 2016; Martin-Laurent et al., 2014). Recently, Fernandez-Bayo et al.
108 (2013) gave evidence for a weak but measurable mineralization of ^{14}C -chlordecone in
109 an Andosol from Guadeloupe in aerobic conditions reaching 4.9% of the ^{14}C -
110 chlordecone initially added in the topsoil (0-20 cm) and 3.2% in the below horizon (30-
111 60 cm) over a 230d period of incubation. The absence of $^{14}\text{CO}_2$ evolution in sterile soil
112 microcosms led the authors to conclude that chlordecone mineralization was biotic
113 being most likely catalyzed by microorganisms (Fernandez-Bayo et al., 2013).

114 Dolfing et al. (2012) conducted a theoretical study using Gibbs free energy
115 calculations to explore the thermodynamic feasibility of different chlordecone potential
116 degradation routes. By performing ab initio quantum chemical calculations to estimate
117 molar values of $\Delta_f H_m^\circ$ and $\Delta_f G_m^\circ$ for chlordecone and selected dechlorination
118 products, they have estimated the energetics of the degradation and dechlorination of
119 chlordecone under a variety of redox conditions. They ended up with the proposal of a
120 list of 20 potential TPs and concluded that there were no thermodynamic reasons why
121 chlordecone-respiring or -fermenting organisms should not exist.

122 Complementary information could be brought by clustering approaches based on the
123 relationships between molecular properties and environmental fate of organic
124 compounds. With this aim, we recently developed ‘TyPol’ (Typology of Pollutants), a
125 classification method based on statistical analyses combining several environmental
126 endpoints (i.e. environmental parameters such as sorption coefficient, degradation half-
127 life or bioconcentration factor), and structural molecular descriptors (number of atoms
128 in the molecule, molecular surface, dipole moment, energy of orbitals...). This approach
129 also allows to focus on TPs present in different classes and to infer possible changes in
130 environmental fate consecutively to different degradation processes (Servien et al.,
131 2014). Starting from the list of chlordecone TPs proposed by Dolfing et al. (2012) and
132 considering available literature data on degradation routes of other organochlorine
133 compounds, we conducted a study using TyPol to explore the potential environmental
134 behaviour of chlordecone TPs based on their molecular properties.

135

136 **2. Materials and methods**

137 *2.1. Clustering methodology*

138 The TyPol tool permits to classify organic compounds, and their transformation
139 products, according to both their behaviour in the environment and their molecular
140 properties. The calculation of molecular descriptors is performed using an *in silico*
141 approach, while the environmental endpoints (i.e. environmental parameters) are
142 extracted from several available databases and literature. The strategy relies on partial
143 least squares analysis and hierarchical clustering (see below 2.5. Statistical treatments).
144 The robustness of the TyPol method was assessed on a list of 215 organic compounds
145 using a cross-validation algorithm. The information system is based on a management
146 system for relational database MySQL DBMS-R (version 5.1), an Apache web server
147 (version 2.2), and the statistical R software (also used for graphs). More details
148 concerning TyPol can be found in Servien et al. (2014).

149

150 *2.2. Environmental parameters*

151 Seven environmental parameters are considered in TyPol in order to cover the main
152 processes involved in the behaviour of organic substances: water solubility (S_w) and
153 octanol-water partition coefficient (K_{ow}) to describe dissolution; vapor pressure (P_{vap})
154 and Henry’s law constant (K_H) for volatilization from soil and plant, and water,
155 respectively; adsorption coefficient normalized to soil carbon organic content (K_{oc}) for

156 adsorption; half-life (*DT50*) for degradation; and bioconcentration factor (*BCF*) for
157 ecotoxicity (Servien et al., 2014).

158

159 *2.3. Molecular descriptors*

160 Forty relevant molecular descriptors are considered in TyPol. They have been selected
161 from a literature review of QSARs (Quantitative Structure Activity Relationships)
162 developed to predict different environmental processes (Mamy et al., 2015). We focused
163 on QSARs only built with structural molecular descriptors (number of atoms, molecular
164 surface, dipole moment, energy of the orbitals...) rather than characteristics such as *Sw*
165 or *Kow*. Molecular descriptors are calculated using several software (ChemOffice Ultra
166 12.0, Dragon 5.5).

167

168 *2.4. Database implementation*

169 A literature survey was done to provide a list of compounds (parent and transformation
170 product) representing different mechanisms - i.e reductive dechlorination,
171 hydroxylation, oxidation, epoxidation, photolysis, hydrolysis - involved in their abiotic
172 or biotic transformations. In total, 170 chlorinated compounds were listed and added to
173 the TyPol database by implementing data on environmental parameters when available
174 (130 compounds). The idea was to cover a broad spectrum of compounds such as
175 organochlorine pesticides but also PCB, PCDD and PCDF so that clustering could
176 segregate chlorinated compounds according to their molecular properties and
177 environmental behaviour. TPs were looked for these different chemical families (Hester
178 and Harrison, 1996; Roberts and Hudson, 1999). Molecular descriptors were calculated
179 and inserted for each compound. For chlordecone, 20 dechlorinated TPs proposed by
180 Dolfing et al. (2012) as well as chlordecol were considered.

181

182 *2.5. Statistical treatments*

183 In TyPol, the PLS (Partial Least Squares) model is carried out to find the
184 multidimensional directions in the X observable variables (i.e. molecular descriptors)
185 space that explains the maximum multidimensional variance direction in the Y
186 predicted variables (i.e. environmental parameters) space. The optimal number of PLS
187 components to perform clustering is selected according to Wold rules (Wold, 1978). In
188 addition, we use the NIPALS (Non-linear Iterative PARTial Least Squares) algorithm,
189 which allows performing PLS without removing the individuals with missing values

190 and without estimating these missing values (Tenenhaus, 1998). After PLS analysis, a
191 hierarchical clustering algorithm is used on the X and Y PLS axes to categorize the
192 molecules by assignment of similar compounds into one cluster. At each step, the final
193 number of clusters is chosen by comparison of heights in the dendrogram, a statistical
194 map resuming Ward clustering. Minimization of intra-variability and maximization of
195 inter-variability are the parameters retained to choose the most appropriate number of
196 clusters (Servien et al., 2014).

197 We used TyPol in two manners. In a first approach, TyPol was used to identify
198 relationships between molecular descriptors and environmental fate processes among
199 several clusters of organochlorine molecules by considering molecular descriptors and
200 available environmental parameters. In a second approach, TyPol clustering was
201 performed by including chlordecone TPs and using only the molecular descriptors as
202 their environmental parameters are unknown. In this case the observable and the
203 predicted variables are the same (i.e the molecular descriptors) and the PLS is
204 equivalent to a Principal Component Analysis (PCA). The clustering was further used to
205 estimate trends for the environmental parameters of chlordecone TPs clusters by
206 comparing molecular descriptors of chlordecone TPs to those of 113 other
207 organochlorine compounds of the database and 16 organochlorine TPs for which
208 environmental parameters such as sorption coefficient or degradation half-life were
209 known. The dataset generated allowed discussing and proposing hypothetical
210 environmental behaviour of the different chlordecone TPs.

211

212 **3. Results and discussion**

213

214 *3.1. Degradation routes of organochlorine pesticides*

215 As reviewed by Roberts and Huston (1999), organochlorine insecticides such as DDT
216 and cyclodienes were historically among the first major classes of synthetic chemicals
217 that have been restricted because of their high persistence, high potential of
218 bioaccumulation and ubiquitous contamination. Main degradation pathways of these
219 compounds reported in literature are oxidation, epoxidation and dechlorination reactions
220 (Table 1).

221 The most important transformation reactions in soils of DDT are dehydrochlorination
222 to DDE and reductive dechlorination to DDD. Due to their recalcitrance, these two TPs
223 are still frequently found in environmental samples although they can also undergo

224 reductive dehalogenation (Subba-Rao and Alexander, 1985) or hydroxylation of
225 aliphatic moieties (Bumpus and Aust, 1987).

226 Cyclodiene insecticides share few structural similarities with the bishomocubane
227 structure, which constitutes the skeleton of chlordecone and of its derivatives (Francis
228 and Metcalfe, 1984). Chlordane has a variety of metabolic pathways including
229 oxidation, reductive dechlorination, hydroxylation and epoxidation in soils leading to
230 TPs such as dichlorchlordene, oxychlordane, heptachlor, heptachlor epoxide or
231 chlordene chlorohydrin (Table 1). Endosulfan is readily hydrolysed in water to the diol
232 form but it is moderately persistent in soil where the major TP is the endosulfan sulfate,
233 which is more persistent than the parent compound.

234 Up to now, mostly 5b-hydrochlordene and dihydrochlordene have been identified
235 as chlordecone TPs mostly concerned (Martin-Laurent et al., 2014; Orndorff and
236 Colwell, 1980) suggesting that in the soil environment hydroxylation and dechlorination
237 are the most probable transformation reactions. The bishomocubane structure (typical
238 for chlordecone and congeners) provides a great stability due to the 10 Cl atoms which
239 promotes electron delocalization and limits the possibilities of oxidation of the C atoms,
240 explaining the great recalcitrance of chlordecone in aerobic conditions. On the contrary,
241 the high chlorine content of the chlordecone molecule makes anaerobic dechlorination
242 the most likely mode of initial transformation reaction (Table 1) as already shown for an
243 important number of different aromatic and aliphatic compounds, including chlorinated
244 ethylenes, PCBs, dioxins and furans, which are degraded by reductive dechlorination
245 (Field and Alvarez, 2008 a and b; Schanke and Wackett, 1992). Dechlorination of
246 chlordecone may occur in reductive environmental conditions and is the most probable
247 route according to thermodynamic approach based on Gibbs free energy calculations
248 (Dolfing et al., 2012).

249

250 *3.2. Clustering using molecular descriptor and environmental parameters*

251 One hundred and thirty organochlorine compounds were used in this first clustering
252 (Fig.1, Table A1). The number of PLS components was chosen equal to four according
253 to Wold rules (Wold, 1978). The PLS model was characterized by the following
254 statistical results: $R^2_X = 0.62$, $R^2_Y = 0.70$ and $Q^2_Y = 0.40$ indicating that it was a
255 satisfactory model representative for the different compounds included in TyPol. The
256 main characteristic of the first component, which explains 34% of the variance of the
257 molecular descriptors and 47% of the variance for the environmental parameters, is the

258 strong positive loadings for all the geometric and topological descriptors, and
259 constitutional descriptors like the number of chlorine or halogen atoms (Fig. 2). A
260 contrario, the dipole moment and the total energy have strong negative effects therefore
261 have an opposite effect. The second axis explains 28% of the variance of the molecular
262 descriptors and 23% of the variance for the environmental parameters. On this axis,
263 variables such as the number of chlorine or halogen atoms have a positive loading
264 whereas the number of rotatable, double or simple bonds or the number of hydrogen,
265 oxygen or total atoms have a negative loading (Fig. 2). Fig. 2 also shows that many
266 variables seem to be correlated, mainly the different connectivity and valence
267 connectivity indices.

268 The selection of the number of clusters was performed by plotting the heights of the
269 dendrogram's node and looking for a break. The results showed that the best choice,
270 minimizing intra-variability and maximizing inter-variability, was to classify the
271 compounds in 5 clusters. The size of the five clusters varied from 15 to 32 compounds
272 (Fig. 1, Table A1), each cluster being characterized by specific features. Fig. 3 shows
273 the range of variations of the values of the 7 environmental parameters for each of the 5
274 clusters. The trigger value of P_{vap} is indicated to differentiate volatile and non-volatile
275 compounds (there is no trigger value for K_H , FOCUS, 2008), that of Koc to differentiate
276 mobile and non-mobile compounds (Mackay, 2006), that of $DT50$ to differentiate
277 persistent and non-persistent compounds (1107/2009 EC, 2009), and that of BCF to
278 differentiate compounds having or not a potential of bioaccumulation (1107/2009 EC,
279 2009) (Fig. 3). Depending on the values of P_{vap} , Koc , $DT50$ and/or BCF , each of the five
280 clusters aggregate various organochlorine compounds having (or not) risks for air, water
281 and/or soil contamination and/or high ecotoxicity. The importance of the different
282 environmental parameters in the clustering can be evaluated on the correlation circle
283 (Fig. 2) showing that BCF , Kow (positive loadings) and Sw (negative loading) are
284 strongly related to the first component. P_{vap} and K_H have a positive loading on the
285 second axis. $DT50$ and Koc are the parameters which have low influence on the two
286 main PLS components of the clustering (Fig. 2)

287 The cluster 1 contains 31 molecules and groups together chloroacetanilides,
288 chlorinated *s*-triazines, ureas and triallates inputted in TyPol. This cluster is made of
289 compounds characterized by an important dipole moment and high values of total
290 energy, whereas polarizabilities and the different connectivity indices are low (Table
291 A2). These compounds have low number of chlorine atoms, low molecular weight and

292 low Connolly molecular surface area. Median values of S_w are high (median $\log_{10}S_w =$
293 1.55) although K_{oc} have medium to relatively high values (median $\log_{10}K_{oc} = 2.34$).
294 They have low $DT50$ (Fig. 3) suggesting that they have a low persistence in the
295 environment (Regulation EC 1107/2009, 2009). They also have relatively low BCF
296 suggesting that these compounds are not susceptible to bioaccumulate in living
297 organisms (i.e. low ecotoxicity, Regulation EC 1107/2009, 2009). Finally, compounds
298 gathered in cluster 1 have medium K_H values (i.e. a medium volatility from water) but
299 relatively high values of P_{vap} so high volatility from soil and plant, and potential of
300 transfer to atmosphere (FOCUS, 2008). Few compounds of this cluster are closed to
301 those of cluster 2 in the two X-axes of the PLS, but differences between these molecules
302 are more easily noticeable in the Y-axes of the PLS.

303 The cluster 2 contains mirex, kelevan and chlordecone as well as other
304 organochlorine pesticides such as aldrin, chlordane, endosulfan, heptachlor and their
305 known TP's such as oxychlordan, heptachlor epoxide, endosulfan sulfate. The 3
306 bishomocubanes (chlordecone, mirex and kelevan) are relatively detached from the
307 other molecules in the PLS projection. As discussed above, these three compounds have
308 a very particular chemical structure (bishomocubane family) responsible for their high
309 persistence (high $DT50$) in the environment. They have very high values of connectivity
310 or valence connectivity indices, polarizability, molecular weight, number of chlorine
311 and other halogen atoms; and low values of number of multiple bonds, total energy,
312 HOMO energy, dipole moment and medium value for LUMO energy (Table A2). The
313 number of rotatable and aromatic bonds is extremely low. Considering the
314 environmental parameters, they have low S_w but rather low K_{oc} (median $\log_{10}K_{oc} =$
315 1.76), medium to high BCF indicating their that is high ecotoxicity towards living
316 organisms, and high K_H (Dolfing et al., 2012; PPDB, 2013) (Fig. 3).

317 The cluster 3 is composed of 32 compounds with several chemical families
318 represented: triazoles, phenoxyacids, strobilurins, ketones. These compounds have high
319 dipole moment, high polarizability and low total energy. The number of Cl atoms is low
320 whereas the number of O and N atoms is the highest of all clusters. Valence
321 connectivity indices and connectivity indices for zero and first order are high as well as
322 the Connolly molecular surface area (Table A2). These compounds also have low $DT50$
323 (rapid dissipation and low persistence), medium K_{oc} (medium mobility), high S_w (and
324 low K_{ow}), and low BCF suggesting their low ecotoxicity (Fig. 3).

325 The cluster 4 is composed of 25 compounds, most of them being the PCBs inputted
326 in TyPol and some degradation products of DDT (DDE, DDD). This cluster is
327 characterized by low polarizability, low dipole moment and low connectivity indices.
328 The number of Cl atoms is low as well as the number of O and N atoms. The number of
329 aromatic bonds is high (Table A2). It has the lowest DT50 of the five clusters indicating
330 their relatively low persistence in the environment. Compounds of cluster 4 have high
331 values of BCF indicating their high ecotoxicity. They also have high Kow and low Sw ,
332 high P_{vap} and K_H , indicating their high potential for volatilization.

333 The cluster 5 contains 27 molecules with all PCDD and PCDF and few
334 organochlorine insecticides such as DDT. They have high values of polarizability and
335 valence and connectivity indices, whereas the total energy, LUMO energy and the
336 dipole moment are very low. This group is characterized by low number of N and O
337 atoms and by contrast high number of Cl atoms (Table A2). This feature, in
338 combination with high molecular weights and low number of hydrogen atoms is related
339 to low values of Sw (the lowest among the 5 clusters) and high values of Kow , and to
340 the highest values of BCF . The compounds of cluster 5 also have the highest DT50
341 among the 5 clusters, which means very high persistence in soils (Regulation EC
342 1107/2009, 2009) (Fig. 4). Finally, they have low values of P_{vap} and K_H indicating a
343 moderate risk of transfer to the atmosphere (Fig. 3).

344

345 3.3. Clustering using molecular descriptors only

346 We have added to the 130 organochlorine compounds inputted in TyPol, the 19 TPs of
347 chlordecone proposed by Dolfing et al. (2012) as well as 21 putative TPs of
348 tebuconazole containing Cl atoms recently screened by Storck et al. (2016) (Table 2).
349 With this new dataset a second TyPol clustering was carried out and four PLS
350 components were selected as described above. The PLS model had good statistical
351 results: $R^2 = 0.65$, and $Q^2 = 0.81$. It has to be noted that the PLS analysis was only
352 performed on the molecular descriptors. Therefore, the X observable variables are also
353 the Y predicted variables. Nevertheless, obtained results showed that the PLS was a
354 good model for the different compounds included in TyPol. The first and second
355 components explained 39% and 26% of the variance, respectively. The second PLS is
356 sharing some similarities with the first one. The main characteristic of component 1 was
357 also the strong positive loadings for some topological descriptors such as the different
358 connectivity indices as well as the polarizability and strong negative loading of the total

359 energy. However, by comparison with the first PLS, the dipole moment and number of
360 chlorine and halogens had no influence on this first component. On the contrary, these
361 variables are well distributed along the second component. On this second axis,
362 variables such as the number of chlorine or halogen atoms have this time a negative
363 loading whereas HOMO energy, the number of hydrogen, oxygen, the number of
364 multiple, aromatic and rotatable bonds have a positive loading (Fig. 4). As for the first
365 PLS, the LUMO energy has a poor influence on the 2 first components.

366 The size of the five clusters varied from 12 to 50 compounds (Fig. 5, Table A3).
367 Compared to the first classification, several compounds moved from one group to
368 another one most likely due to the fact that environmental parameters were not taken
369 into account. For instance, the cluster 1 still contains phenylureas, triallates and s-
370 triazine pesticides but includes also phenoxyacids and few TPs of tebuconazole and
371 small biphenyls. Also, clustering on molecular descriptors separated better chlordecone
372 and analog cyclodienes (mirex, kelevan) and a large part of the putative TPs from the
373 other organochlorine compounds (Fig. 5; Table A3). All these compounds are now
374 found in cluster 5 whereas they were associated to other organochlorine insecticides in
375 the first classification (cluster 2). This more homogeneous composition of cluster 5
376 around compounds characterized by a bishomocubane skeleton is probably due to the
377 fact that classification was done only with the molecular descriptors. In comparison to
378 the other organochlorine pesticides (still in cluster 2), the chlordecone cluster has
379 several features in common: low number of multiple bound, no rotatable bound, low
380 dipolar moment and high polarizability (Table A4). But the chlordecone cluster was
381 made of compounds characterized by typical values of the following molecular
382 descriptors: they have the lowest total energy and HOMO energy, the highest
383 connectivity indices, the highest number of Cl atoms and the highest molecular weight
384 of all clusters. Such specificities are in accordance with (i) the results of our first
385 clustering which has shown that such trends of molecular descriptors were associated
386 with high values of *DT50* and *BCF* (clusters 2 and 5 of the first clustering) and (ii) the
387 low biodegradation of chlordecone observed in the environment (Cabidoche et al.,
388 2009; Dolfing et al., 2012; Fernandez-Bayo et al., 2013; Martin-Laurent et al., 2014).

389 An important result was that the main features of molecular descriptors remain quite
390 similar from one classification to another one. As in the first classification, cluster 1 was
391 characterized by low polarizability values, low connectivity and valences indices, low
392 number of Cl atoms and molecular weight (Table A4). Total energy and dipole moment

393 had high values. Cluster 2 still contained the organochlorine insecticides and
394 additionally, the more dechlorinated TPs of chlordecone. It kept the main features for
395 the molecular descriptors: high values of connectivity or valence connectivity indices,
396 polarizability, molecular weight, number of chlorine and other halogen atoms; and low
397 values of number of multiple and rotatable bonds, low values of total energy and
398 HOMO energy (Table A4). The dipole moment value was a bit higher than in the first
399 classification. Cluster 3 containing triazoles has now incorporated most of the
400 tebuconazole TPs (Table A3). This group is characterized by high dipole moment, high
401 polarizability and low total energy. The number of Cl atoms was low whereas the
402 number of O and N atoms was the highest of all clusters. Valence connectivity indices
403 and connectivity indices for zero and first order were high as well as the Connolly
404 molecular surface area (Table A4). Cluster 4 now gathered all PCDD, PCDF and the
405 majority of PCBs and DDT (Table A3). Molecular descriptors have kept the main
406 features: low polarizability; low dipole moment; low number of Cl, O and N atoms;
407 high number of aromatic bonds. Compared to the first clustering, polarizability as well
408 as the connectivity indices had now medium values in the cluster 4 (Table A4).

409

410 *3.4. Exploring the environmental fate of putative chlordecone transformation products*

411 The similarities of molecular descriptors distribution values in the two clustering can be
412 used to deduce parameters for compounds for which environmental parameters are
413 unknown. This is done assuming that compounds gathered in the same cluster on the
414 basis of their molecular descriptors have similar environmental parameters (Storck et
415 al., 2016).

416 Sixty-two parent-TP couples have been used for the TyPol clustering using only
417 molecular descriptors. 74% of TPs were found in the same cluster than their parent
418 molecule suggesting that most of the TPs may have similar behaviour in the
419 environment than parent compounds from which they derived. For organochlorine
420 pesticide such as DDT and chlordane, TPs were always found in the cluster of the
421 parent molecule (Figure 6). This suggests that their transformation changed neither their
422 molecular properties nor their environmental behaviour.

423 Concerning chlordecone and its potential TPs, we can notice that TPs gathered in
424 different clusters according to the extent of their dechlorination. When more than 4 Cl
425 atoms were replaced by OH then putative TPs gathered to cluster 2 (penta-
426 hydrochlordecone) or cluster 1 (hepta to nona-hydrochlordecone) and not to cluster 5

427 like parent compound. In the first case, cluster 2 regrouped organochlorine pesticides
428 such as DDT and chlordane but also compounds such as chlorinated dioxin, furans and
429 high molecular weight PCBs whereas cluster 1 was containing low molecular weight
430 PCBs and pesticides such as 2,4D, dicamba, atrazine and chlortoluron. Less
431 dechlorinated compounds as well as chlordecol, remained in cluster 5 suggesting that
432 mono-hydro to tetra-hydrochlordecone could have strong similarities with chlordecone,
433 mirex and kelevan.

434 Looking more carefully into the analysis of molecular descriptors of the
435 corresponding clusters of chlordecone (cluster 5), organochlorine insecticides (cluster 2)
436 and low molecular weight and more polar pesticides (cluster 1) showed that median
437 values of molecular descriptors were quite discriminant for these 3 groups (see 3.3.
438 Clustering using molecular descriptors only). Clusters 5 and 2 shared common features
439 such as low dipole moment and high polarizability, low number of multiple bound, no
440 rotatable bound, low total energy and HOMO energy, high connectivity indices, high
441 number of Cl atoms and high molecular weight. But, as pointed out before, the
442 chlordecone cluster had more extreme values for the total energy, connectivity indices,
443 dipole moment and Cl atoms number. On the opposite, molecules of cluster 1 had
444 higher dipole moment, higher total energy, lower polarizability, much lower values of
445 connectivity and valence indices, lower number of Cl atoms and lower molecular
446 weight.

447 Using the results of the first clustering resulting from the analysis of both
448 environmental parameters and molecular descriptors we deduced some trends by linking
449 molecular descriptors features to values of environmental parameters such as *DT50*,
450 *Koc*, *P_{vap}* and *BCF* for the clusters obtained for chlordecone, organochlorine insecticides
451 and low molecular weight and more polar pesticides. Based on this deductive approach
452 one could hypothesize that the most dechlorinated chlordecone TPs (hepta to nona-
453 hydrochlordecone) may have environmental properties similar to that of low molecular
454 weight and more polar pesticides: low *DT50* (rapid dissipation), medium *Koc* (medium
455 mobility), high *Sw* (and low *Kow*), and low *BCF* so low ecotoxicity. On the contrary,
456 TPs less heavily dechlorinated such as penta-hydrochlordecone may have like its parent
457 compound very high values of *BCF* and high *DT50*, which means a very long
458 persistence in soils and very high risk for bioaccumulation and transfer all along the
459 food chain. Finally the lowly dechlorinated TPs are close to the parent compound and
460 consequently are expected to exhibit similar trends in terms of environmental fate and

461 ecotoxicological impacts. They would be characterized by a very long persistence in
462 soils and very high risk for the transfer in the food chain but also in the environment *via*
463 mobility from soil to water compartment through slow leaching processes since the
464 chlordecone cluster is characterized by relatively low *K_{oc}*. As pointed out by Dolfing et
465 al. (2012), reductive dechlorination of chlordecone is thermodynamically favorable, but
466 whether this reaction can proceed at environmentally significant rates and/or at rates,
467 which can sustain growth of organisms catalyzing such reactions, remains unproven yet.
468

469 **4. Conclusion**

470 We used *in silico* molecular typology to explore the potential fate of putative
471 chlordecone TPs. The TyPol approach applied implied two steps. A first clustering step
472 served to search for possible correlations between molecular descriptors of
473 organochlorine compounds and their environmental parameters covering
474 biodegradation, mobility and bioaccumulation processes. From the calculation of
475 molecular descriptors for a series of existing or putative TPs, we performed a second
476 clustering where the filiation between parent and TPs was accounted for. By comparing
477 the two clustering results, we deduced environmental parameters for chlordecone TPs
478 and discussed hypothetical trends for their environmental behaviour.

479 Recent experimental studies exploring the degrading capacities of different type of
480 soils and of different soil microorganisms have confirmed that biodegradation of
481 chlordecone is very low and slow. Our findings suggest that lowly dechlorinated TPs
482 such as mono and di-hydrochlordecone, often found in chlordecone-contaminated soils,
483 may have similar environmental behaviour than chlordecone in terms of persistence and
484 transfer in the environment, bioaccumulation and transfer all along the food chain. By
485 contrast, more heavily dechlorinated TPs may have very different environmental
486 parameters more favorable than those of chlordecone but unfortunately, to our best
487 knowledge, the conditions leading to their formation remain unknown.

488

489

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496

497 **References**

498 Bristeau S., Amalric L., Mouvet C., 2014. Validation of chlordecone analysis for native
499 and remediated French West Indies soils with high organic matter content. *Anal*
500 *Bioanal Chem*, 406,1073–1080

501 Bumpus J.A., Aust S.D., 1987. Biodegradation of DDT 1,1,1-dichloro-2,2-bis-4-
502 (chlorophenyl)ethane by the white rot fungus *Phanerochaete cryosporium*. *Appl*
503 *Environ Microbiol* 53, 2001–2008.

504 Cabidoche Y-M., Lesueur-Jannoyer M., 2011. Long term pollution of soils in French
505 West Indies: how to manage chlordecone contamination? *Innov Agron*, 16, 117–133.

506 Cabidoche Y-M., Achard R., Cattan P., Clermont-Dauphin C., Massat F., Sansoulet J.,
507 2009. Long-term pollution by chlordecone of tropical volcanic soils in the French
508 West Indies: a simple leaching model accounts for current residue. *Environ Pollut*
509 157, 1697–1705.

510 Coat S., Monti D., Legendre P., Bouchon C., Massat F., Lepoint G., 2011.
511 Organochlorine pollution in tropical rivers (Guadeloupe): role of ecological factors
512 in food web bioaccumulation. *Environ Pollut* 159,1692–1701.

513 Devault D.A., Laplanche C., Pascaline H., Bristeau S., Mouvet C., Macarie H., 2016.
514 Natural transformation of chlordecone into 5b-hydrochlordecone in French West
515 Indies soils: statistical evidence for investigating long-term persistence of organic
516 pollutants. *Environ Sci, Poll Res*, 23, 81-97.

517 Dolfing J., Novak I., Archelas A., Macarie H., 2012. Gibbs free energy of formation of
518 chlordecone and potential degradation products: implications for remediation
519 strategies and environmental fate. *Environ Sci Technol* 46, 8131–8139.

520 Fernández-Bayo J.D., Saison C., Voltz M., Disko U., Hofmann D., Berns A.E., 2013.
521 Chlordecone fate and mineralisation in a tropical soil (andosol) microcosm under
522 aerobic conditions. *Sci Total Environ* 463–464, 395–403.

523 Field J.A., Sierra-Alvarez R., 2008a. Microbial degradation of chlorinated dioxins
524 *Chemosphere* 71, 1005–1018.

525 Field J.A., Sierra-Alvarez R., 2008b. Microbial degradation of polychlorinated
526 biphenyls. *Environmental Pollution* 155, 1-12

527 Francis B.M., Metcalf R.L., 1984. Evaluation of mirex, photomirex and chlordecone in
528 the terrestrial aquatic laboratory model ecosystem. *Environ Health Perspect*, 54, 341–
529 346.

530 George, S.E., Claxton, L.D., 1988. Biotransformation of chlordecone by *Pseudomonas*
531 species. *Xenobiotica* 18, 407–416.

532 Hester R.E., Harrison R.M., 1996. Chlorinated Organic Micropollutants. *Issues in*
533 *Environmental Science and Technology*, 6. The Royal Society of Chemistry,
534 Information Services Cambridge, UK.

535 Jablonski P.E., Pheasant D.J., Ferry J.G., 1996. Conversion of Kepone by
536 *Methanosarcina thermophila*. *FEMS Microbiol Lett* 139(2–3), 169–173.

537 Levillain J., Cattan P., Colin F., Voltz M., Cabidoche Y-M., 2012. Analysis of
538 environmental and farming factors of soil contamination by a persistent organic
539 pollutant, chlordecone, in a banana production area of French West Indies. *Agric*
540 *Ecosyst Environ* 159, 123–132.

541 Mackay, D.S.-C., 2006. Handbook of physical-chemical properties and environmental
542 fate for organic chemicals. CRC Press Taylor and Francis.

543 Mamy L., Patureau D., Barriuso E., Bedos C., Bessac F., Louchart X., Martin-Laurent
544 F., Miege C., Benoit P., 2015. Prediction of the Fate of Organic Compounds in the
545 Environment From Their Molecular Properties: A Review. *Critical Reviews in*
546 *Environmental Science and Technology* 45, 1277-1377.

547 Martin-Laurent F., Sahnoun M.M., Merlin C., Vollmer G., Lübke M., 2014. Detection
548 and quantification of chlordecone in contaminated soils from the French West Indies
549 by GC-MS using the $^{13}\text{C}_{10}$ -chlordecone stable isotope as tracer. *Environ Sci Pollut*
550 *Res*, 21, 4928–4933

551 Orndorff S.A., Colwell RR., 1980. Microbial transformation of kepone. *Appl Environ*
552 *Microbiol*, 39, 398–406.

553 PPDB (Pesticide properties database), 2013.
554 <<http://sitem.herts.ac.uk/aeru/footprint/index2.htm>>.

555 Regulation EC 1107/2009, 2009. Regulation (EC) No 1107/2009 of the European
556 Parliament and of the Council of 21 October 2009 concerning the placing of plant
557 protection products on the market and repealing Council Directives 79/ 117/EEC and
558 91/414/EEC.

559 Roberts T.R., Huston D.H., 1999. Metabolic Pathways of Agrochemicals Part 2
560 Insecticides and Fungicides. The Royal Society of Chemistry Information Services
561 Cambridge, UK.

562 Servien R., Mamy L., Li Z., Rossard V., Latrille E., Bessac F., Patureau D., Benoit P.,
563 2014. TyPol – A new methodology for organic compounds clustering based on their
564 molecular characteristics and environmental behaviour. Chemosphere, 111, 613-622.

565 Sakakibara F., Takagi K., Kataoka R., Kiyota H., Sato Y., Okada S., 2011. Isolation and
566 identification of dieldrin-degrading *Pseudonocardia* sp strain KSF27 using a soil-
567 charcoal perfusion method with aldrin trans-diol as a structural analog of dieldrin.
568 Biochem Biophys Res Commun, 411(1), 76–81.

569 Schanke C.A., Wackett L.P., 1992. Environmental reductive elimination reactions of
570 polychlorinated ethanes mimicked by transition-metal coenzymes. Environ. Sci.
571 Technol. 26: 830-833.

572 Subba-Rao R.V., Alexander M., 1985. Products formed from analogs of 1,1,1-trichloro-
573 2,2-bis-(p-chlorophenyl)ethane (DDT) TPs by *Pseudomonas putida*. Appl Environ
574 Microbiol 33:101–108.

575 Tenenhaus M., 1998. In: La regression, P.L.S. (Ed.), Théorie et Pratique. Technip,
576 Paris.

577 Wold S., 1978. Cross-validation estimation of the number of components in factor and
578 principal component analysis. Technometrics 24, 397– 405.

579

Parent compound (PC)	CAS PC	Transformation product (TP)	CAS TP	OX	EpOX	HyOX	Rdn	Hygn	Hys	DeX	R-DeCl	Dehys	Phos	ReAm	
Chlordane	57-74-9	Heptachlor	76-44-8							x	x				
		Heptachlor epoxide	1024-57-3	x	x										
		1-chloro-2-hydroxychlordene chlorohydrin	57-74-9-INRA-1			x				x	x				
		1-chloro-dihydrochlordene	57-74-9-INRA-2						x		x				
		3,4,5,6,7,8,8-heptachloro-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoindene-1,2-diol	57-74-9-INRA-3			x									
		1,2-dichlorochlordane	57-74-9-INRA-4										x		
		1-exo-hydroxy-2-chlorochlordene	57-74-9-INRA-5			x									
		Chlordene chlorohydrin	37571-87-2						x						
		Oxychlordane	27304-13-8	x	x										
Biphenyl	92-51-3	2-hydroxybiphenyl	90-43-7	x	x	x									
		3-hydroxybiphenyl	580-51-8	x	x	x									
		2,3-dihydro-2,3-dihydroxybiphenyl	34244-66-1	x						x					
		2,3-dihydroxybiphenyl	1133-63-7				x								
Heptachlor	76-44-8	1-hydroxychlordene	24009-05-0							x					
		Chlordene	3734-48-3								x				
		Chlordene epoxide	6058-23-7	x	x										
		Heptachlor epoxide	1024-57-3	x	x										
		3,4,5,6,7,8,8-heptachloro-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoindene-1,2-diol	57-74-9-INRA-3								x				
		1-hydroxy-2,3-epoxychlordene	1024-57-3-INRA-1								x				
g-HCH	608-73-1	Pentachlorocyclohexene	643-15-2				x			x	x				
		1,2,4-trichlorobenzene	120-82-1				x			x	x				
		1,4-dichlorobenzene	106-46-7								x				
		1,2,3-trichlorobenzene	87-61-6				x			x	x				
		1,2-dichlorobenzene	95-50-1								x				
		2,4,6-trichlorophenol	88-06-2								x	x			
		1,2,3,4-tetrachlorobenzene	634-66-2								x	x			

Parent compound (PC)	CAS PC	Transformation product (TP)	CAS TP	OX	EpOX	HyOX	Rdn	Hygn	Hys	DeX	R-DeCl	Dehys	Phos	ReAm		
Chlordecone	143-50-0	10-hydrochlordecone	143-50-0-INRA-1				x				x					
		9-hydrochlordecone	143-50-0-INRA-2				x				x					
		6-hydrochlordecone	143-50-0-INRA-3				x					x				
		8-hydrochlordecone	143-50-0-INRA-4				x					x				
		cis-8,10-dihydrochlordecone	143-50-0-INRA-5				x					x				
		3,7-dihydrochlordecone	143-50-0-INRA-6				x					x				
		8,10,10-trihydrochlordecone	143-50-0-INRA-7				x					x				
		3,7,10-trihydrochlordecone	143-50-0-INRA-8				x					x				
		3,7,10,10-tetrahydrochlordecone	143-50-0-INRA-9				x					x				
		r-3,7,8,10-tetrahydrochlordecone	143-50-0-INRA-10				x					x				
		3,7,8,10,10-pentahydrochlordecone	143-50-0-INRA-11				x					x				
		2,3,7,8,10,10-hexahydrochlordecone	143-50-0-INRA-12				x					x				
		2,3,7,8,9,10,10-heptahydrochlordecone	143-50-0-INRA-13				x					x				
		1,2,3,7,8,9,10,10-Octahydrochlordecone	143-50-0-INRA-14				x					x				
		1,2,3,4,6,7,8,9,10-nonahydrochlordecone	143-50-0-INRA-15				x					x				
		2,3,4,6,7,8,9,10,10-nonahydrochlordecone	143-50-0-INRA-16				x					x				
		1,2,3,6,7,8,9,10,10-nonahydrochlordecone	143-50-0-INRA-17				x					x				
		1,3,4,6,7,8,9,10,10-nonahydrochlordecone	143-50-0-INRA-18				x					x				
		Decahydrochlordecone		143-50-0-INRA-19				x				x				
		Chlordecol		143-50-0-INRA-20		x		x					x			

Table 2

Chlorinated compounds inputted in TyPol with CAS numbers, names, chemical formulae and chemical families. The parent CAS is given in case of transformation products (PCB: polychlorinated biphenyls, PCDF: polychlorinated dibenzofurans, PCDD: polychlorinated dibenzodioxins).

CAS	Name	Chemical formula	Chemical family	Parent CAS
115-29-7	Endosulfan	C ₉ H ₆ C ₁₆ O ₃ S	Organochlorine	
1031-07-8	Endosulfan sulfate	C ₉ H ₆ C ₁₆ O ₄ S	Organochlorine	115-29-7
118-74-1	Hexachlorobenzene	C ₆ Cl ₆	Organochlorine	
143-50-0	Chlordecone	C10C110O	Organochlorine	
143-50-0-INRA-1	10-Hydrochlordecone	C10HC19O	Organochlorine	143-50-0
143-50-0-INRA-10	r-3,7,8,t,10-Tetrahydrochlordecone	C10H4C16O	Organochlorine	143-50-0
143-50-0-INRA-11	3,7,8,10,10-Pentahydrochlordecone	C10H5C15O	Organochlorine	143-50-0
143-50-0-INRA-12	2,3,7,8,10,10-Hexahydrochlordecone	C10H6C14O	Organochlorine	143-50-0
143-50-0-INRA-13	2,3,7,8,9,10,10-Heptahydrochlordecone	C10H7C13O	Organochlorine	143-50-0
143-50-0-INRA-14	1,2,3,7,8,9,10,10-Octahydrochlordecone	C10H8C12O	Organochlorine	143-50-0
143-50-0-INRA-15	1,2,3,4,6,7,8,9,10-Nonahydrochlordecone	C10H9C11O	Organochlorine	143-50-0
143-50-0-INRA-16	2,3,4,6,7,8,9,10,10-Nonahydrochlordecone	C10H9C11O	Organochlorine	143-50-0
143-50-0-INRA-17	1,2,3,6,7,8,9,10,10-Nonahydrochlordecone	C10H9C11O	Organochlorine	143-50-0
143-50-0-INRA-18	1,3,4,6,7,8,9,10,10-Nonahydrochlordecone	C10H9C11O	Organochlorine	143-50-0
143-50-0-INRA-19	Decahydrochlordecone	C10H10O	Organochlorine	143-50-0
143-50-0-INRA-2	9-Hydrochlordecone	C10HC19O	Organochlorine	143-50-0
143-50-0-INRA-20	Chlordecol	C10H2C110O	Organochlorine	143-50-0
143-50-0-INRA-3	6-Hydrochlordecone	C10HC19O	Organochlorine	143-50-0
143-50-0-INRA-4	8-Hydrochlordecone	C10HC19O	Organochlorine	143-50-0
143-50-0-INRA-5	cis-8,10-Dihydrochlordecone	C10H2C18O	Organochlorine	143-50-0
143-50-0-INRA-6	3,7-Dihydrochlordecone	C10H2C18O	Organochlorine	143-50-0
143-50-0-INRA-7	8,10,10-Trihydrochlordecone	C10H3C17O	Organochlorine	143-50-0
143-50-0-INRA-8	3,7,10-Trihydrochlordecone	C10H3C17O	Organochlorine	143-50-0
143-50-0-INRA-9	3,7,10,10-Tetrahydrochlordecone	C10H4C16O	Organochlorine	143-50-0
2385-85-5	Mirex	C10C112	Organochlorine	
4234-79-1	Kelevan	C17H12C110O4	Organochlorine	
50-29-3	p,p'-DDT	C14H9C15	Organochlorine	
72-54-8	DDD	C14H10C14	Organochlorine	50-29-3
72-55-9	DDE	C14H8C14	Organochlorine	50-29-3
58-89-9	Lindane	C6H6C16	Organochlorine	
608-73-1	Hexachlorocyclohexane	C6H6C16	Organochlorine	
107534-96-3	Tebuconazole	C16H22CIN3O	Triazole	
107534-96-3-INRA-1	M1-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-10	M10-Tebuconazole	C16H22CIN3O3	Triazole metabolite	107534-96-3
107534-96-3-INRA-11	M11-Tebuconazole	C16H20CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-12	M12-Tebuconazole	C16H20CIN3O2	Triazole metabolite	107534-96-3

107534-96-3-INRA-13	M13-Tebuconazole	C16H20CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-14	M14-Tebuconazole	C16H20CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-16	M16-Tebuconazole	C16H20CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-2	M2-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-24	M24-Tebuconazole	C15H20CIN3O	Triazole metabolite	107534-96-3
107534-96-3-INRA-25	M25-Tebuconazole	C13H16CIN3O	Triazole metabolite	107534-96-3
107534-96-3-INRA-26	M26-Tebuconazole	C12H14CIN3O	Triazole metabolite	107534-96-3
107534-96-3-INRA-3	M3-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-4	M4-Tebuconazole	C16H22CIN3O3	Triazole metabolite	107534-96-3
107534-96-3-INRA-5	M5-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-6	M6-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-65	M65-Tebuconazole	C15H21CIN2O	Triazole metabolite	107534-96-3
107534-96-3-INRA-67	M67-Tebuconazole	C15H21CIN2O	Triazole metabolite	107534-96-3
107534-96-3-INRA-7	M7-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-76	M76-Tebuconazole	C7H5ClO2	Triazole metabolite	107534-96-3
107534-96-3-INRA-8	M8-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
107534-96-3-INRA-9	M9-Tebuconazole	C16H22CIN3O2	Triazole metabolite	107534-96-3
119446-68-3	Difenoconazole	C19H17Cl2N3O3	Triazole	
131983-72-7	Triticonazole	C17H20CIN3O	Triazole	
131983-72-7-INRA-1	(1R,3R,E)-3-(4-chlorobenzylidene)-5,5-dimethyl-1-((1H)-1,2,4-triazol-1-ylmethyl)-cyclopentan-1,3-diol	C17H20CIN3O2	Triazole metabolite	131983-72-7
131983-72-7-INRA-2	(E)-2-(4-chlorobenzylidene)-5,5-dimethyl-1-((1H)-1,2,4-triazol-1-ylmethyl)-cyclopentan-1,3-diol	C17H20CIN3O2	Triazole metabolite	131983-72-7
133855-98-8	Epoxiconazole	C17H13ClFN3O	Triazole	
94361-06-5	Cyproconazole	C15H18CIN3O	Triazole	
14168-01-5	Dilor	C10H7Cl7	Chloro-bicycloheptene	
1715-40-8	Bromocyclene	C8H5BrCl6	Chloro-bicycloheptene	
2550-75-6	Chlorbicyclene	C9H6Cl8	Chloro-bicycloheptene	
297-78-9	Isobenzane	C9H4Cl8O	Chloro-bicycloheptene	
309-00-2	Aldrine	C12H8Cl6	Chloro-bicycloheptene	
465-73-6	Isodrine	C12H8Cl6	Chloro-bicycloheptene	
57-74-9	Chlordane	C10H6Cl8	Chloro-bicycloheptene	
27304-13-8	Oxychlordane	C10H4Cl8O	Chloro-bicycloheptene metabolite	57-74-9
60-57-1	Dieldrine	C12H8Cl6O	Chloro-bicycloheptene	
76-44-8	Heptachlore	C10H5Cl7	Chloro-bicycloheptene	
1024-57-3	Heptachlore epoxide	C10H5Cl7O	Chloro-bicycloheptene	76-44-8, 57-74-9
8001-35-2	Toxaphene	C10H8Cl8	Chloro-bicycloheptene	
15972-60-8	Alachlor	C14H20ClNO2	Chloroacetamide	
1918-16-7	Propachlor	C11H14ClNO	Chloroacetamide	
34256-82-1	Acetochlor	C14H20ClNO2	Chloroacetamide	
51218-45-2	Metolachlor	C15H22ClNO2	Chloroacetamide	
67129-08-2	Metazachlor	C14H16ClN3O	Chloroacetamide	
122-34-9	Simazine	C7H12ClN5	Triazine	

1912-24-9	Atrazine	C8H14ClN5	Triazine	
21725-46-2	Cyanazine	C9H13ClN6	Triazine	
5915-41-3	Terbutylazine	C9H16ClN5	Triazine	
15545-48-9	Chlortoluron	C10H13ClN2O	Urea	
1746-81-2	Monolinuron	C9H11ClN2O2	Urea	
330-55-2	Linuron	C9H10Cl2N2O2	Urea	
555-37-3	Neburon	C12H16Cl2N2O	Urea	
330-54-1	Diuron	C9H10Cl2N2O	Phenylurea	
95-76-1	3,4-dichloroaniline	C6H5Cl2N	Phenylurea metabolite	330-54-1
2327-02-8	3,4-dichlorophenyl urea	C7H6Cl2N2O	Phenylurea metabolite	330-54-1
3567-62-2	1-(3,4-dichlorophenyl)-3-methylurea	C8H8Cl2N2O	Phenylurea metabolite	330-54-1
52315-07-8	Cypermethrin	C22H19Cl2NO3	Pyrethroid	
52645-53-1	Permethrin	C21H20Cl2O3	Pyrethroid	
68359-37-5	Cyfluthrin	C22H18Cl2FNO3	Pyrethroid	
68359-37-5-INRA-1	3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid	C8H10Cl2O2	Pyrethroid metabolite	68359-37-5
32809-16-8	Procymidone	C13H11Cl2NO2	Dicarboximide	
36734-19-7	Iprodione	C13H13Cl2N3O3	Dicarboximide	
63637-89-8	N-(3,5-dichlorophenyl)3-isopropyl-2,4-dioxoimidazoline-1-carboxamide	C17H20ClN3O2	Dicarboximide metabolite	36734-19-7
7085-19-0	Mecoprop	C10H11ClO3	Aryloxyalkanoic acid	
94-74-6	MCPA	C9H9ClO3	Aryloxyalkanoic acid	
1570-64-5	2-methyl-4-chlorophenol	C7H7ClO	Aryloxyalkanoic acid metabolite	94-74-6
1698-60-8	Chloridazon	C10H8ClN3O	Pyridazinone	
27314-13-2	Norflurazon	C12H9ClF3N3O	Pyridazinone	
23576-24-1	Desmethyl norflurazon	C11H7ClF3N3O	Pyridazinone metabolite	27314-13-2
133-06-2	Captan	C9H8Cl3NO2S	Phthalimide	
133-07-3	Folpet	C9H4Cl3NO2S	Phthalimide	
175013-18-0	Pyraclostrobin	C19H18ClN3O4	Strobilurin	
361377-29-9	Fluoxastrobin	C21H16ClFN4O5	Strobilurin	
2303-16-4	Di-allate	C10H17Cl2NOS	Thiocarbamate	
2303-17-5	Tri-allate	C10H16Cl3NOS	Thiocarbamate	
1897-45-6	Chlorothalonil	C8Cl4N2	Chloronitrile	
1897-45-6-INRA-1	4-hydroxy-2,5,6-trichloroisophthalonitrile	C8HCl3N2O	Chloronitrile metabolite	1897-45-6
335104-84-2	Tembotrione	C17H16ClF3O6S	Triketone	
99105-77-8	Sulcotrione	C14H13ClO5S	Triketone	
94-75-7	2,4-D	C8H6Cl2O3	Alkylchlorophenoxy	
709-98-8	Propanil	C9H9Cl2NO	Anilide	
51338-27-3	Diclofop-methyl	C16H14Cl2O4	Aryloxyphenoxypropionate	
23950-58-5	Propyzamide	C12H11Cl2NO	Benzamide	
1918-00-9	Dicamba	C8H6Cl2O3	Benzoic acid	
101-21-3	Chlorpropham	C10H12ClNO2	Carbamate	
74070-46-5	Aclonifen	C12H9ClN2O3	Diphenyl ether	
16672-87-0	Ethephon	C2H6ClO3P	Ethylene generator	
126833-17-8	Fenhexamid	C14H17Cl2NO2	Hydroxyanilide	

110488-70-5	Dimethomorph	C21H22ClNO4	Morpholine
135410-20-7	Acetamiprid	C10H11ClN4	Neonicotinoid
5598-13-0	Chlorpyrifos-methyl	C7H7Cl3NO3PS	Organophosphate
1918-02-1	Picloram	C6H3Cl3N2O2	Pyridine
64902-72-3	Chlorsulfuron	C12H12ClN5O4S	Sulfonylurea
13029-08-8	2,2'-Dichlorobiphenyle	C12H8Cl2	PCB
16605-91-7	2,3-Dichlorobiphenyle	C12H8Cl2	PCB
2050-67-1	3,3'-Dichlorobiphenyle	C12H8Cl2	PCB
2050-68-2	4,4'-Dichlorobiphenyle	C12H8Cl2	PCB
2051-24-3	Decachlorobiphenyle	C12Cl10	PCB
2051-60-7	2-Chlorobiphenyle	C12H9Cl	PCB
2051-61-8	3-Chlorobiphenyle	C12H9Cl	PCB
25569-80-6	2,3'-Dichlorobiphenyle	C12H8Cl2	PCB
2974-90-5	3,4'-Dichlorobiphenyle	C12H8Cl2	PCB
2974-92-7	3,4-Dichlorobiphenyle	C12H8Cl2	PCB
33146-45-1	2,6-Dichlorobiphenyle	C12H8Cl2	PCB
33284-50-3	2,4-Dichlorobiphenyle	C12H8Cl2	PCB
34883-39-1	2,5-Dichlorobiphenyle	C12H8Cl2	PCB
34883-41-5	3,5-Dichlorobiphenyle	C12H8Cl2	PCB
34883-43-7	2,4'-Dichlorobiphenyle	C12H8Cl2	PCB
35065-30-6	2,2',3,3',4,4',5-Heptachlorobiphenyle	C12H3Cl7	PCB
35694-08-7	2,2',3,3',4,4',5,5'-Octachlorobiphenyle	C12H2Cl8	PCB
37680-66-3	2,2',4-Trichlorobiphenyle	C12H7Cl3	PCB
38380-07-3	2,2',3,3',4,4'-Hexachlorobiphenyle	C12H4Cl6	PCB
38444-78-9	2,2',3-Trichlorobiphenyle	C12H7Cl3	PCB
38444-93-8	2,2',3,3'-Tetrachlorobiphenyle	C12H6Cl4	PCB
40186-72-9	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyle	C12HCl9	PCB
52663-59-9	2,2',3,4-Tetrachlorobiphenyle	C12H6Cl4	PCB
52663-62-4	2,2',3,3',4-Pentachlorobiphenyle	C12H5Cl5	PCB
52663-71-5	2,2',3,3',4,4',6-Heptachlorobiphenyle	C12H3Cl7	PCB
52663-78-2	2,2',3,3',4,4',5,6-Octachlorobiphenyle	C12H2Cl8	PCB
52663-79-3	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyle	C12HCl9	PCB
55215-18-4	2,2',3,3',4,5-Hexachlorobiphenyle	C12H4Cl6	PCB
60145-20-2	2,2',3,3',5-Pentachlorobiphenyle	C12H5Cl5	PCB
39001-02-0	OCDF	C12Cl8O	PCDF
51207-31-9	2,3,7,8-TCDF	C12H4Cl4O	PCDF
55673-89-7	1,2,3,4,7,8,9-HpCDF	C12HCl7O	PCDF
57117-31-4	2,3,4,7,8-PeCDF	C12H3Cl5O	PCDF
57117-41-6	1,2,3,7,8-PeCDF	C12H3Cl5O	PCDF
57117-44-9	1,2,3,6,7,8-HxCDF	C12H2Cl6O	PCDF
60851-34-5	2,3,4,6,7,8-HxCDF	C12H2Cl6O	PCDF
67562-39-4	1,2,3,4,6,7,8-HpCDF	C12HCl7O	PCDF
70648-26-9	1,2,3,4,7,8-HxCDF	C12H2Cl6O	PCDF

72918-21-9	1,2,3,7,8,9-HxCDF	C12H2Cl6O	PCDF
1746-01-6	2,3,7,8-Tetrachlorodibenzo-p-dioxine	C12H4Cl4O2	PCDD
19408-74-3	1,2,3,7,8,9-HxCDD	C12H2Cl6O2	PCDD
3268-87-9	OCDD	C12Cl8O2	PCDD
35822-46-9	1,2,3,4,6,7,8-HpCDD	C12HCl7O2	PCDD
39227-28-6	1,2,3,4,7,8-HxCDD	C12H2Cl6O2	PCDD
40321-76-4	1,2,3,7,8-PeCDD	C12H3Cl5O2	PCDD
57653-85-7	1,2,3,6,7,8-HxCDD	C12H2Cl6O2	PCDD

Figure captions

Fig. 1.

Graphical representation of the obtained clusters in the two X-axes of the PLS with the molecular descriptors and environmental parameters on all organochlorine compounds – with exception of the putative transformation products of chlordecone for which environmental parameters are unknown.

Fig. 2.

Circles of correlations of the ‘environmental parameters’ (in blue) and ‘molecular descriptors’ (in red) variables on the two main components of the PLS (Comp 1 and Comp 2). C.i-i stands for the connectivity index C.i of order i ($i = 0$ to 5), and V.c-i stands for the valence connectivity index V.c of order i ($i = 0-5$).

Fig. 3.

Range of variation (box-and-whisker plots) of the values of the seven ‘environmental parameters’ considered into TyPol (water solubility S_w , octanol–water partition coefficient K_{ow} , vapor pressure P_{vap} , Henry’s law constant K_H , adsorption coefficient normalized to soil carbon organic content K_{oc} , half-life $DT50$, and bioconcentration factor BCF) for each cluster after analysis of the 130 chlorinated compounds. Dotted lines represent the limits between: volatile ($\log P_{vap} > 1$) and non-volatile compounds ($\log P_{vap} < 1$) ([FOCUS, 2008](#)); mobile ($\log K_{oc} < 2.7$) and non-mobile compounds ($\log K_{oc} > 2.7$) ([McCall et al., 1980](#)); persistent ($\log DT50 > 2.25$) and non-persistent compounds ($\log DT50 < 2.25$) ([Regulation EC 1107/2009, 2009](#)), and compounds having ($\log BCF > 2$) or not ($\log BCF < 2$) a potential of bioaccumulation ([Regulation EC 1107/ 2009, 2009](#)).

Fig. 4.

Circles of correlations of the ‘molecular descriptors’ (in red) variables on the two main components of the PLS (Comp 1 and Comp 2). C.i-i stands for the connectivity index C.i of order i ($i = 0$ to 5), and V.c-i stands for the valence connectivity index V.c of order i ($i = 0-5$). PLS realized with the molecular descriptors only – considering all organochlorine compounds including the putative metabolites of chlordecone.

Fig. 5.

Graphical representation of the clusters obtained with the ‘molecular descriptors’ only – considering all organochlorine compounds including the putative metabolites of chlordane.

Fig. 6.

Filiation’s parents-TPs shown on the cluster representation obtained with the molecular descriptors only

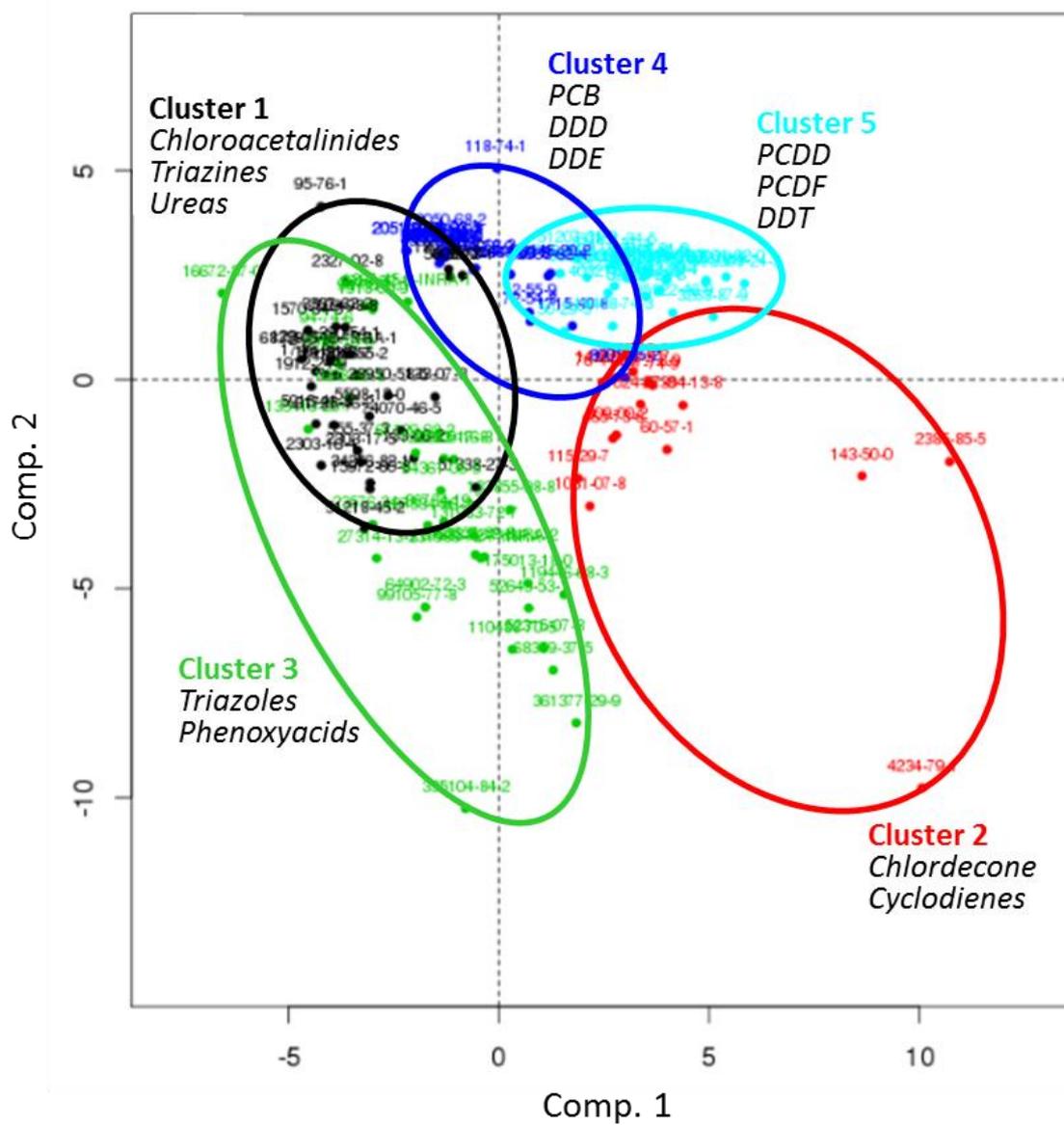


Fig. 1

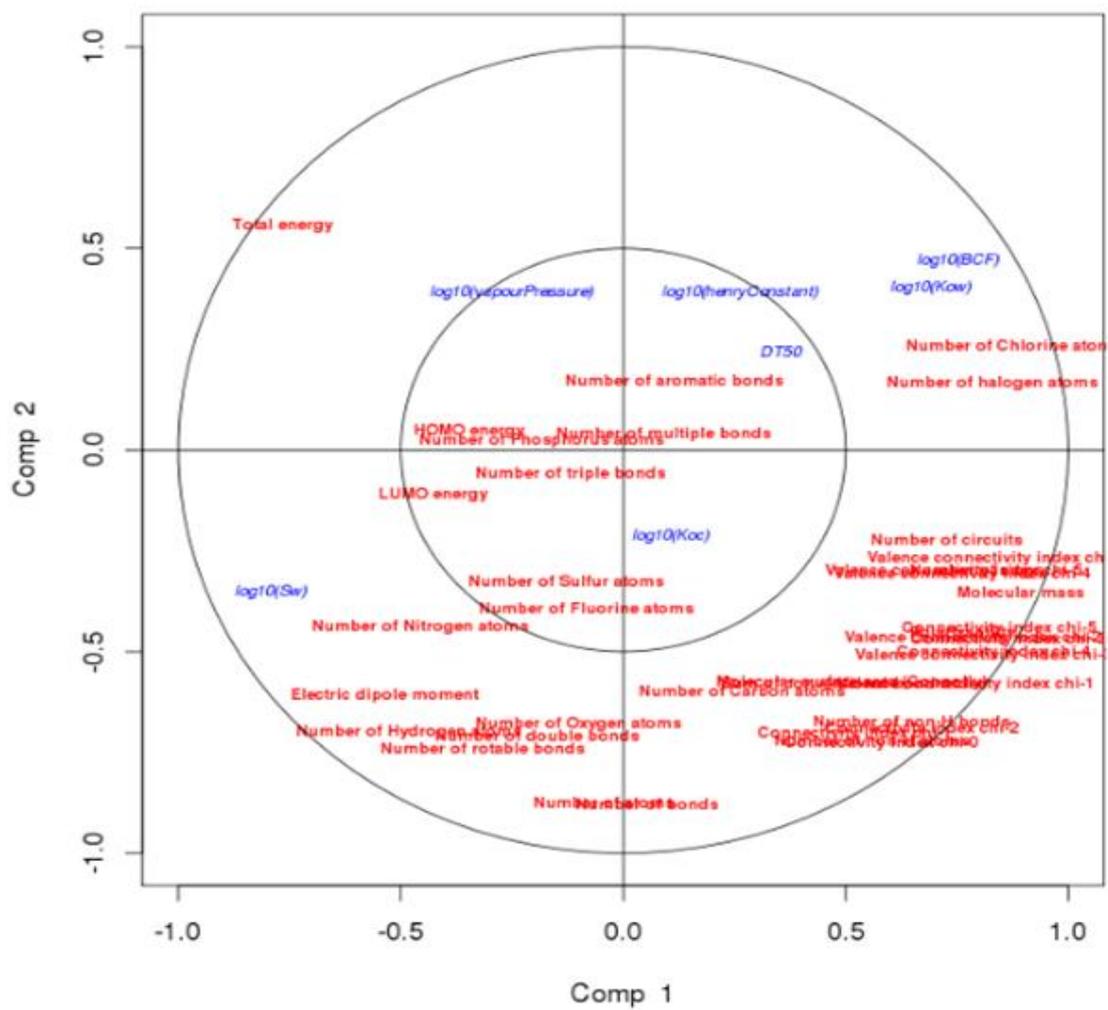


Fig. 2

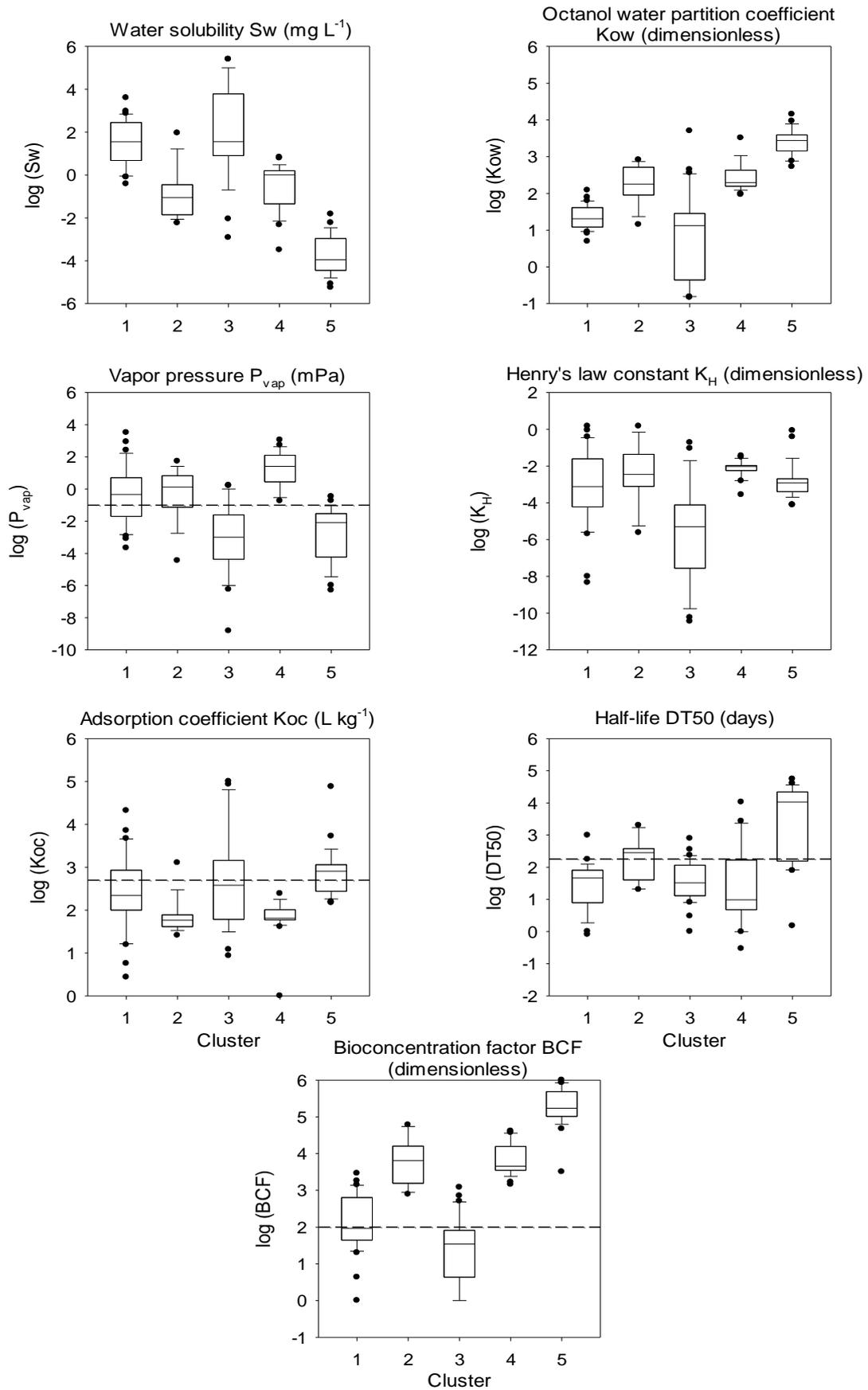


Fig. 3

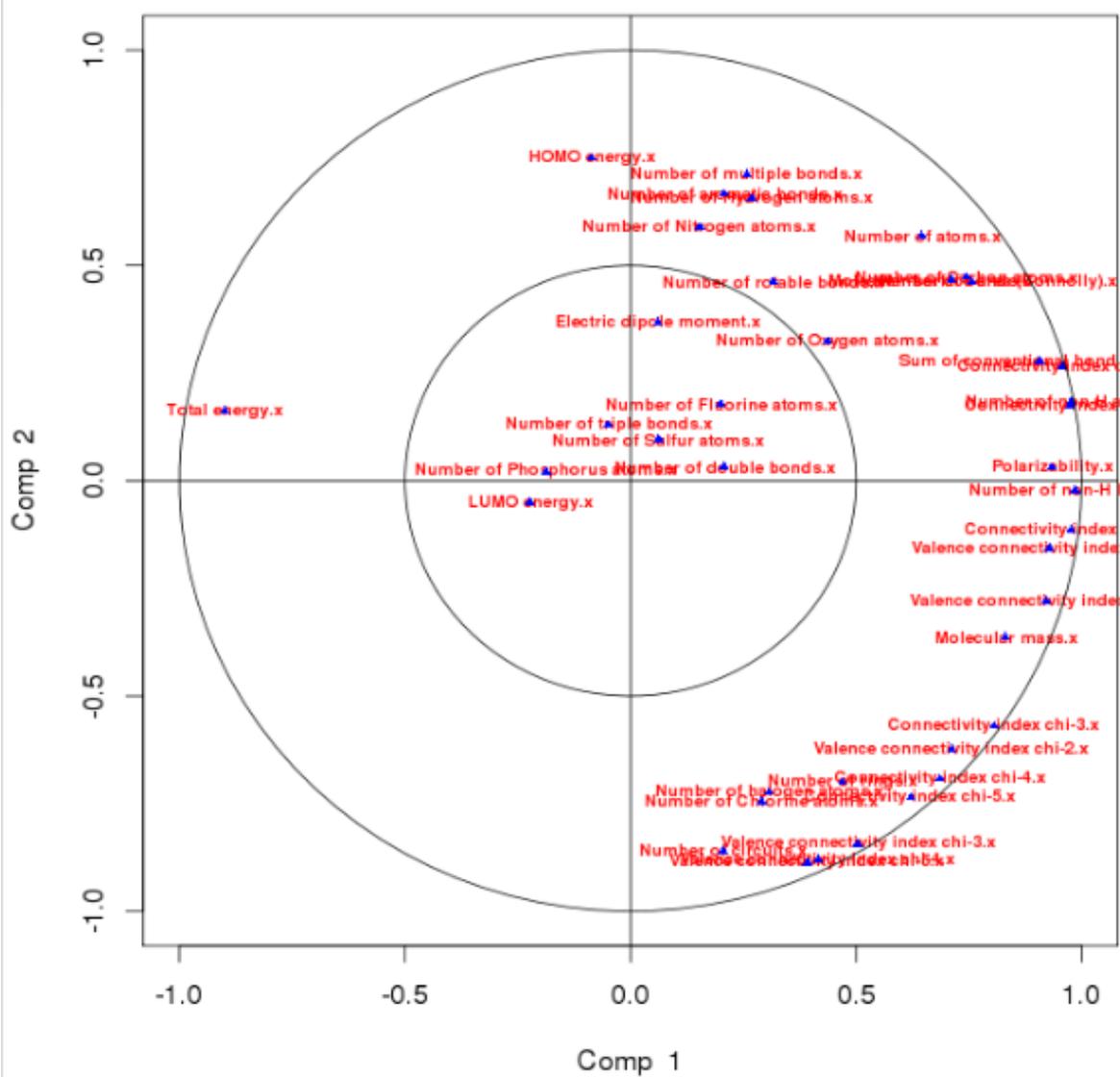


Fig. 4

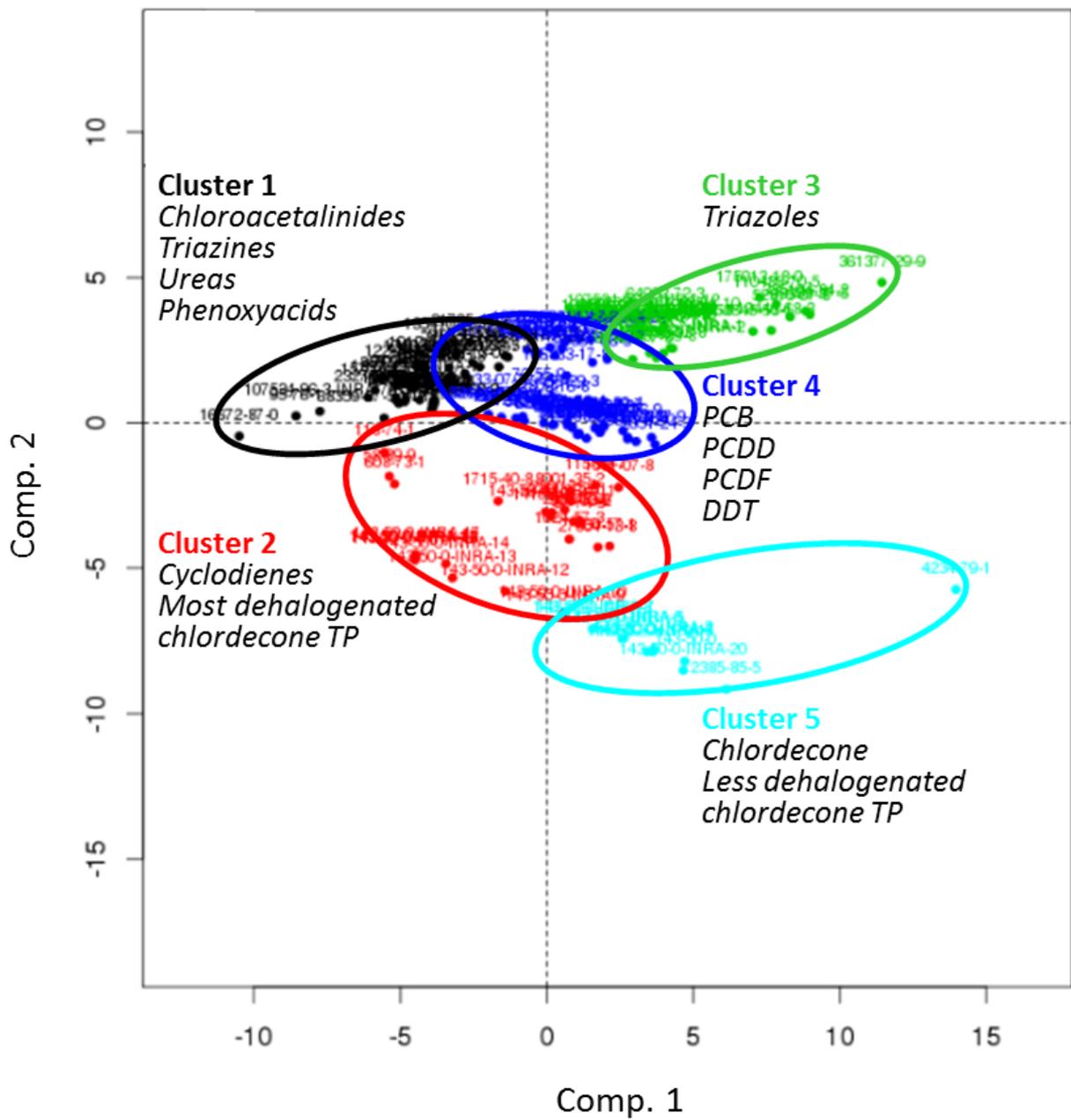


Fig. 5

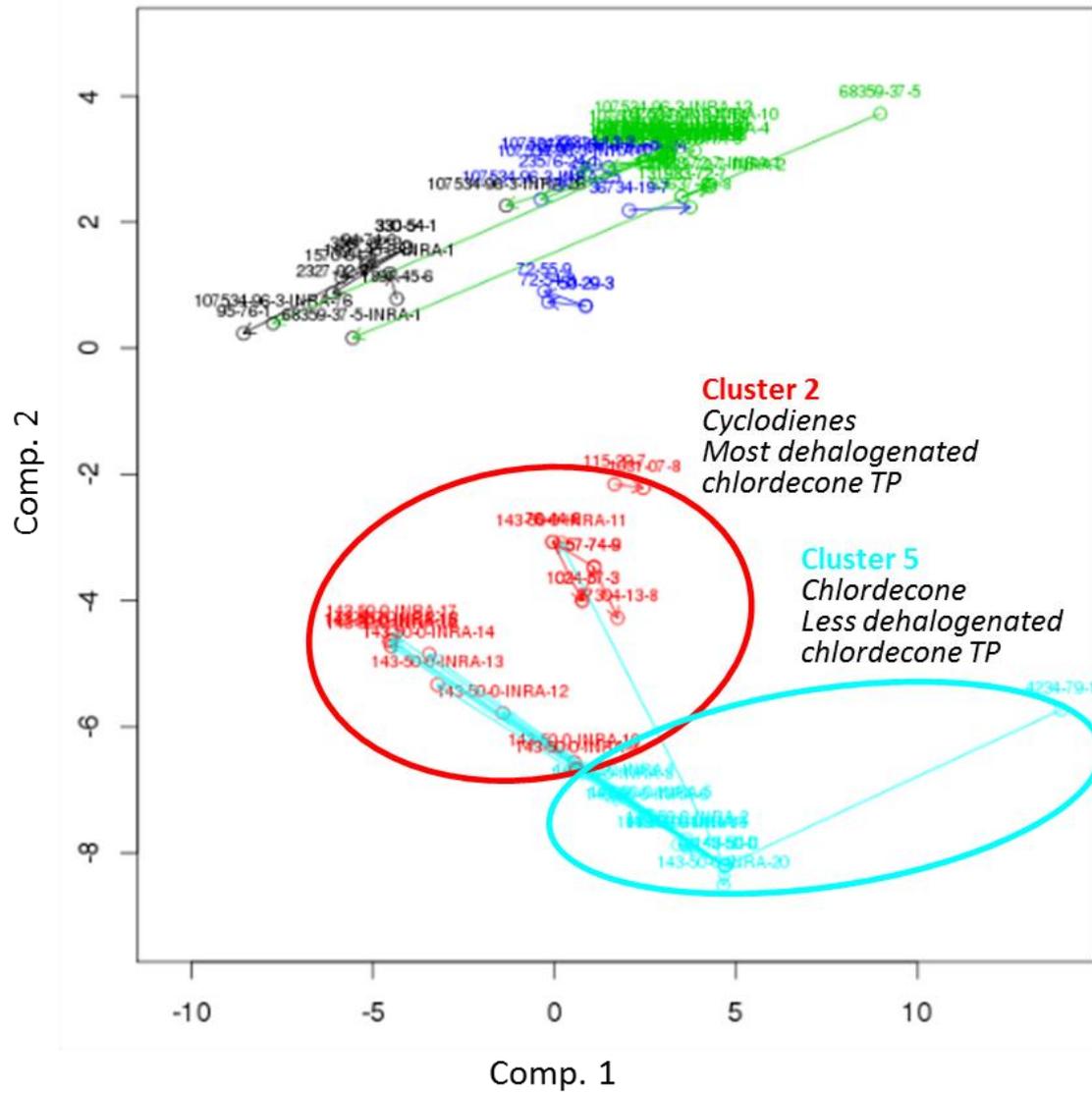


Fig. 6