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1 State of the art of the environmental behaviour and removal techniques of the  
2 endocrine disruptor 3,4-dichloroaniline

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5 **Abstract**

6 In recent years, the presence of Endocrine Disrupting Chemicals (EDCs) in wastewater  
7 discharges from agricultural and industrial sources, <sup>[1]</sup> fresh- and estuarine-waters, as well as  
8 soils, has been reported in the literature. <sup>[2]</sup> Studies of adverse changes in wildlife, linked to  
9 environmental exposure to these substances, and the suggestion that humans could also be at  
10 similar risk of adverse health effects, <sup>[3-5]</sup> have raised concern for urgent action to understand  
11 and reduce such risks. 3,4-dichloroaniline (3,4-DCA) has been recognized as an EDC, with  
12 regards to endocrine disruption data for both wildlife populations and human health. <sup>[5]</sup>  
13 3,4-DCA is present in the environment as a product of the biodegradation of phenylurea and  
14 phenylcarbamate pesticides; <sup>[6, 7]</sup> furthermore, it can be introduced from industrial and municipal  
15 wastewater that is insufficiently purified, or via accidental spills. <sup>[8-10]</sup> Increasing concentrations  
16 of 3,4-DCA in soil and water are the result of its high persistence and accumulation, as well as  
17 its low biodegradability. <sup>[11, 12]</sup> Hence, remediation techniques require in-depth study, especially  
18 when considering the low removal achieved by traditional activated sludge treatments, and the  
19 generation of carcinogenic trihalomethanes as a consequence of the chlorine oxidation methods

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24 frequently used in drinking water plants. <sup>[13]</sup> Fe<sup>0</sup>/H<sub>2</sub>O<sub>2</sub> systems, photodegradation using doped  
25 TiO<sub>2</sub>, and the use of dielectric barrier discharge reactors, seem to be the most promising  
26 techniques for the removal of 3,4-DCA from water.

27 Keywords: 3,4-DCA; water; environment; pollution; adsorption; electrochemistry

## 28 **Introduction**

29 Global annual production of 3,4-dichloroaniline (3,4-DCA) was ~42-47 kt prior to 1986 <sup>[14]</sup> and,  
30 although recent years have seen a decrease in scale, EU production was still around 13.5-  
31 15.5 kt annum<sup>-1</sup> in the period 1996-1998. <sup>[15]</sup> 3,4-DCA, a derivative of aniline, is an  
32 intermediate in the chemical synthesis of 3,4-dichlorophenylisocyanate, to make phytosanitary  
33 products, such as propanil, linuron, diuron, and neburon, <sup>[15-17]</sup> used to treat crops including rice,  
34 potatoes, beans and tobacco. <sup>[18]</sup> It is also employed in the synthesis of azo dyes for polyester  
35 fabrics <sup>[17]</sup> and pharmaceuticals. <sup>[5]</sup> Although there is no exposure risk for vulnerable groups  
36 from direct use of 3,4-DCA, indirect contact is expected via food, primarily fruit and vegetables,  
37 <sup>[5]</sup> as a result of the hydrolysis and biological degradation of phenylurea, phenylcarbamates and  
38 acylchloroanilide pesticides present in soils, <sup>[19-27]</sup> by field waters and plant enzymes. <sup>[28]</sup>  
39 Furthermore, industrial wastewater <sup>[11]</sup> may contain 3,4-DCA, mainly from microbial conversion  
40 of 3,4-dichloro-1- nitrobenzol within water treatment plants. <sup>[5, 28]</sup>

41 In this manuscript, we summarize the current knowledge concerning the introduction,  
42 movement, and fate of 3,4-DCA in the environment. We discuss the state-of-the-art remediation  
43 technologies currently in use, as well as those under development, with reference to their  
44 effectiveness for pollutant removal from soil and water systems.

## 45 **Toxicity**

46 In humans, EDCs are known to affect male and female reproductive organs, thyroid metabolism,  
47 <sup>[29-31]</sup> breast development, cardiovascular and neuro-endocrinology, <sup>[32]</sup> causing obesity and

48 some cancers, including prostate cancer. [33] Little is known about the mechanisms of action of  
49 these substances, nor their physical and chemical diversity, hence, additional research into EDCs  
50 is required, especially on the cumulative impact of EDC mixtures, which may be additive or  
51 synergistic, [32, 34] even when individual chemicals are present below the threshold of detectable  
52 effects. [35] Consequently, the current lack of knowledge regarding exposure scenarios hinders  
53 the assessment of human health risk and impact. [36]

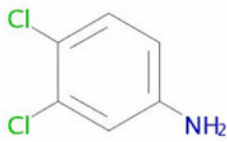
54 Chloroanilines can negatively affect soil microflora, and the presence of phenylamide herbicide  
55 degradation products has been shown to inhibit *Nitrosomonas*, hence, soil nitrification. [37] 3,4-  
56 DCA primarily acts by polar narcosis on aquatic organisms; [38, 39] fish and crustaceans are  
57 extremely sensitive with respect to water column exposure, while annelids are greatly affected  
58 by exposure to the sediment. [17] Tests have demonstrated the relatively low, acute toxicity of  
59 3,4-DCA on marine and fresh water animals, as well as unicellular algae, but there are  
60 significant chronic effects [40, 41] with consequences for marine life reproduction, [4] including  
61 changes in secondary sex characteristics; [42] while rats have shown significant hormonal effects.  
62 [3] As a consequence of these impacts, Predicted No-Effect Concentrations (PNECs) have been  
63 proposed, which are  $0.2 \mu\text{g L}^{-1}$  for freshwater and seawater bodies, and  $0.1 \text{ mg kg}^{-1}$  dry weight  
64 ( $0.04 \text{ mg kg}^{-1}$  wet weight) by mass [17] for sediments.

## 65 **Environmental behaviour and fate**

66 Chloroanilines are known to diffuse easily within the natural environment, [1, 14] and are very  
67 difficult to remediate, hence, their concentration in soils and waters is increasing due to their  
68 high persistence, accumulation, [11, 12] low biodegradation [43] and low leaching potentials. [44]  
69 By contrast, 3,4-DCA is barely measured in water bodies, [5] and it occurs in higher aqueous  
70 concentrations than the parent herbicide diuron. [45] It has been detected in European surface  
71 waters, [16, 46] and its migration is determined by transport and retention mechanisms. [47]

72 Hydrolysis of 3,4-DCA is not considered a mitigating mechanism due to aromatic stabilisation  
 73 effects, <sup>[48]</sup> and, as a result of its relatively low Henry's constant ( $K_H$ ), it is not expected to  
 74 volatilise from water columns. <sup>[17, 48]</sup> Rather, as the physical data presented in Table 1 show, 3,4-  
 75 DCA losses from natural waters occur via photochemical degradation, or adsorption on sediment  
 76 and dissolved humic materials. <sup>[49]</sup> To this end, photo-transformation is the major degradation  
 77 pathway of 3,4-DCA in environmental waters, <sup>[16]</sup> maximised at 300 nm, well within the solar  
 78 spectrum observed at sea level. <sup>[4]</sup>

79 **Table 1.** Properties of 3,4-dichloroaniline

Property	Value	Ref.
Molecular formula	$C_6H_5Cl_2N$	-
Molecular structure		<sup>[15]</sup>
Appearance	Solid at 293 K	<sup>[15]</sup>
Molecular weight	$162 \text{ g mol}^{-1}$	<sup>[15]</sup>
Molecular size	$0.35 \text{ nm}^2$	<sup>[50]</sup>
Henry's constant	$0.05 \text{ Pa m}^3 \text{ mol}^{-1}$	<sup>[15]</sup>
Solubility in water	$580 \text{ mg L}^{-1}$ at 293 K	<sup>[15]</sup>
Octanol-water partition coefficient ( $\log K_{ow}$ )	2.7 (shaken flask method)	<sup>[5, 16]</sup>
Estimated surface water half life	18 days	<sup>[15]</sup>
Measured rate of loss from outdoor water systems	$0.11 - 0.17 \text{ day}^{-1}$	<sup>[4]</sup>
	$0.06 - 0.14 \text{ day}^{-1}$	<sup>[49]</sup>
Estimated atmospheric half life	9 hours	<sup>[15]</sup>
Estimated half-life in soil and sediment	470 - 1500 days	<sup>[51]</sup>

80 It is known that soil mobility and bioavailability of pollutants, and their degradation products,  
81 depend on a combination of adsorption and desorption by soil components. <sup>[47]</sup> The binding  
82 effect of soil generally increases with time, leading to a decrease in pollutant bioavailability and  
83 toxicity, due to meteoric leaching. <sup>[52]</sup> Hence, the majority of 3,4-DCA released into the  
84 environment accumulates, over time, on the organic fraction of sediments and soils. <sup>[15]</sup> On the  
85 other hand, sorption on dissolved macromolecules and colloidal particles promotes transport in  
86 subsurface environments. <sup>[53]</sup> When chloroanilines are released into the soil with herbicides,  
87 only a small portion of the former is mineralized, consequently, many chloroanilines persist for  
88 years, <sup>[54]</sup> often immobilized by interaction with humic substances, as mentioned above. <sup>[9, 20, 55,</sup>  
89 <sup>56]</sup> Therefore, it is only a small fraction of liberated chloroanilines that undergo dimerization or  
90 polymerization, by microbial oxidases and peroxidases, forming stable azo compounds. <sup>[47, 57]</sup>  
91 Surface adsorption, due to van der Waals forces or electrostatic interactions, is often the initial  
92 phase of pollutant binding by soil, while stronger bonds may occur over time. <sup>[1]</sup> Consequently,  
93 fulvic and humic acids play a significant role in the binding of xenobiotics, such as  
94 chloroanilines, from aqueous media, via functional substituents, including hydroxyl, carboxylic  
95 acid, ketone, amino acid, saccharide and aminosaccharide groups. <sup>[58, 59]</sup> Aniline sorption to soil  
96 involves stronger interactions, starting with hydrophobic partitioning and cation exchange,  
97 before covalent bonding, due to the contribution of limited energy or availability of sorption  
98 sites, occurs. 3,4-DCA adsorbs onto sediment <sup>[49]</sup> and soil particles, building stable, most  
99 probably, covalent bonds with organic substances. <sup>[16, 17]</sup> Such initial reversible equilibrium,  
100 followed by a slower irreversible mechanism, is well described by a biphasic kinetic model. <sup>[60,</sup>  
101 <sup>61]</sup> Similar information on the sorption mechanisms of 3,4-DCA is fundamental to the  
102 development of remediation strategies. In laboratory experiments, more than 70% of radio  
103 labelled 3,4-DCA was found, as stated above, to bind to sediment and suspended matter in a  
104 water column; <sup>[62]</sup> ~80% of radioactivity was removed from the water column within 8 days, and

105 ~99% after 90 days, <sup>[63]</sup> suggesting an initially quick process, which then plateaus and requires  
106 significant time to reach its final equilibrium. As a consequence of the proposed interaction  
107 between 3,4-DCA and organic materials, the interactions between dissolved organic matter from  
108 soil, organic contaminants, and other soil components strongly affect the fate of 3,4-DCA in soil  
109 and water systems. <sup>[64-67]</sup> As a result, increasing soil organic carbon content, via organic matter  
110 amendments to a soil sample, which may also introduce dissolved organic matter, can  
111 potentially enhance sorption, and decrease leaching, of pollutants, <sup>[68, 69]</sup> including 3,4-DCA; <sup>[49]</sup>  
112 notably, similar results have been observed for organic matter amendment of inorganic soils. <sup>[8,</sup>  
113 <sup>47]</sup>

114 A study into the interaction of various humic fractions and the herbicide diuron <sup>[70]</sup> showed that  
115 the main degradation product, 3,4-DCA, was irreversibly bound on humic acids within days of  
116 formation. As a result, the risk of pollutant leaching is expected to be low for soils with high  
117 humic or fulvic acid contents. The irreversible sorption observed in these systems was described  
118 using a Freundlich isotherm model:

$$C_s = K_f C_e^n \quad (1)$$

119 where  $C_s$  is the concentration of 3,4-DCA sorbed ( $\mu\text{g g}^{-1}$ ),  $C_e$  is the equilibrium solution  
120 concentration of 3,4-DCA ( $\mu\text{g mL}^{-1}$ ) and  $K_f$  ( $\text{mL g}^{-1}$ ) expresses the soil sorption capacity. The  
121 exponent  $n$  is related to the degree of isotherm nonlinearity, and provides an indication of the  
122 favourability of the sorption process. <sup>[71]</sup>

123 The results of Freundlich analysis indicated that humic fractions have a sorptive capacity ten  
124 times that of their fulvic counterparts, due to preferential reaction of the amino groups of 3,4-  
125 DCA with the carboxyl and carbonyl groups of soil humic fractions, leading to the formation of  
126 soil bound residues, <sup>[72, 73]</sup> as confirmed by high adsorption and small desorption rates constants.  
127 <sup>[49]</sup> Hence, the sorption of 3,4-DCA in soil can be described as a physicochemical process, in

128 which a fraction of the pollutant physically binds to organic and inorganic soil components,  
129 while another fraction strongly adsorbs on the organic component. <sup>[43]</sup> Similarly, soil samples,  
130 agitated in aqueous solutions of 3,4-DCA, have shown significant pollutant removal within  
131 15 minutes of exposure and full equilibration, demonstrating up to 70% removal, after 50 hours.  
132 The authors of this previous study reported the presence of two associated processes, firstly a  
133 physical reaction, seemingly followed by chemical bond formation between 3,4-DCA and  
134 organic matter within the soil, giving biphasic kinetics with rate constants of 4.9 hour<sup>-1</sup>, for  
135 physical accumulation, and 0.03 hour<sup>-1</sup>, for chemisorption. <sup>[49]</sup> Similar kinetic performance has  
136 been observed for different agricultural soils and 3-4-DCA, <sup>[43]</sup> with sorption equilibrium  
137 reached within 48 hours regardless of initial pollutant concentration, up to 16.2 µg mL<sup>-1</sup>. Again,  
138 the data was satisfactorily described by the Freundlich equation, and the amount sorbed was  
139 highest for the sandy clay loam soil used in the study ( $K_f = 52 \text{ mL g}^{-1}$ ), as a consequence of its  
140 higher organic matter content compared to the other soils studied, and the fact that it creates a  
141 slightly acidic pH within the sorption system. By contrast the lowest sorption capacities were  
142 obtained for calcareous silty clay soil and sand.

143 As initial adsorbate concentration increases, the availability of adsorption sites decreases, as  
144 confirmed by  $n$  values lower than 1; such sorption behaviour being expressed by L-type  
145 isotherms. <sup>[74]</sup>  $K_{oc}$  values, representing the sorption constant per gram of organic carbon in the  
146 soil sample studied, show significant probability for 3,4-DCA contamination of ground-water  
147 for soils with lower sorption potentials. <sup>[44]</sup> This is due to the strong relationship exhibited  
148 between the sorption capacity and organic matter content of soil samples, and the fact there is  
149 less impact with respect to clay content or a material's cation exchange capacity. It is also  
150 noteworthy that consideration of soil organic content alone is insufficient to determine expected  
151 sorption behaviour; for example, a lower level of diuron sorption is expected on clay-rich soils,  
152 most likely as a result of a reduction in available binding sites in humic substances, due to the



153 positive interactions between humic materials and clay. <sup>[70]</sup> Soil pH may be another factor that  
154 impacts on sorption of 3,4-DCA, as demonstrated by a reduction in  $K_f$  values, by ~50%, after  
155 liming of aqueous solutions. <sup>[43]</sup> Such a trend probably results from the presence of aniline  
156 functionalities within the soils tested, which are normally protonated species under the usually  
157 acidic conditions found in such media, becoming neutral species as pH increases. <sup>[61, 75, 76]</sup>  
158 Samples of calcareous soil mixed with aqueous 3,4-DCA, and allowed to equilibrate fully <sup>[47]</sup>  
159 showed high  $K_f$  values, which indicates that adsorption is concentration dependent, <sup>[77]</sup> thereby  
160 validating the assumption that adsorption on such solid media occurs primarily via hydrophobic  
161 interactions due to the neutralisation of aniline functional groups at high soil pH. <sup>[73, 78]</sup>  
162 Additional confirmation is provided by consideration of the physical properties of 3,4-DCA;  $K_{ow}$   
163 is known to be high, <sup>[9, 79]</sup> its solubility on water is low, combined with a  $K_{oc}$  of  $338.6 \text{ L kg}^{-1}$   
164 ( $K_{oc} = K_d/[\text{organic content}] \times 100$ , where  $K_d$  is a measure of the distribution ratio of organic  
165 molecules between the sorbed phase and solution), this all suggests that 3,4-DCA has a low  
166 potential for groundwater contamination in calcareous soils with high organic matter content.

167 Dissolved organic matter has been proven to compete with organic pollutants for the sorption  
168 sites available on soil surfaces, <sup>[80, 81]</sup> as well as in the building of stable bonds between pollutant  
169 species and soil; <sup>[82]</sup> this competition enhances the apparent solubility of organic pollutants,  
170 thereby reducing sorption and increasing their mobility. <sup>[67, 83]</sup> In contrast, dissolved organic  
171 materials applied in soils may actually be adsorbed to soil surfaces, increasing sorption of  
172 hydrophobic organic compounds, <sup>[84]</sup> especially when tannic acid is added. <sup>[8]</sup> Inclusion of  
173 dissolved organic carbon extracts, derived from both a commercial peat and high-purity tannic  
174 acid, to a soil sample showed significant impact on the sorption of 3,4-DCA. <sup>[47]</sup> The  $K_{d,DOC}$   
175 coefficient, defined as  $X_{doc}/C_{doc}$  (where  $X_{doc}$  is  $\text{mg L}^{-1}$  of dissolved organic carbon and  $C_{doc}$  is  
176 the corresponding equilibrium concentration), is consistently higher than the  $K_d$  values obtained  
177 for undisturbed soil, thereby confirming the influence of dissolved organic carbon on 3,4-DCA

178 sorption. Further confirmation is provided by an increase in 3,4-DCA sorption in the presence  
179 of an environmental matrix, including inorganic ions and organic matter. <sup>[85]</sup> Sorption on  
180 sedimentary material, hosted in a sediment extract media, was higher than for pure or run-off  
181 waters, likely facilitated by previously sorbed dissolved organic content on the sediment surface,  
182 present as a result of physical interactions between the two species. <sup>[73]</sup>

### 183 **Remediation technologies**

184 Remediation technologies developed for the destruction of chloroanilines present in wastewaters  
185 can be classified as physicochemical, chemical (oxidation) or biological, and are discussed in  
186 detail below. In essence, physicochemical methods utilise either adsorption, ion exchange,  
187 electrolysis or photodegradation, chemical processes require a chemical reaction with a selected  
188 additive, while biological degradation involves the action of aerobic or anaerobic  
189 microorganisms.

### 190 ***Bioremediation***

#### 191 *Bacteria*

192 3,4-DCA is not readily biodegradable; <sup>[17]</sup> the process being particularly slow in aqueous media.  
193 Incubation of pond water, and pond water containing sewage sludge inoculum, in a darkened  
194 environment showed that, after a period of 2 weeks, 97% of 3,4-DCA was recovered from the  
195 former sample and marginally less (94%) was recovered for the sample containing sewage,  
196 indicating little biodegradation of the pollutant. <sup>[86]</sup> Similarly, no biodegradation was reported,  
197 over the same time period, for an OECD 301 C test <sup>[87]</sup> with activated sludge, <sup>[88]</sup> nor after  
198 4 weeks for an OECD 301 D test on activated sludge, and less than 5% degradation was  
199 observed after 29 days for an OECD 303 A test, <sup>[87]</sup> again using activated sludge. <sup>[17]</sup>  
200 Researchers also observed no discernible removal of 3,4-DCA from contaminated North Sea

201 water samples, <sup>[89]</sup> while only primary degradation occurred after one month using river water as  
202 an inoculum. <sup>[90]</sup>

203 Usually, xenobiotics need to be in an aqueous phase in order to allow bacterial degradation to  
204 occur. The '*bioaccessible fraction*' of a pollutant is given by the sum of its concentration in pure  
205 water, known as the '*bioavailable fraction*', plus the '*potentially available fraction*', which is  
206 the material reversibly sorbed on any material surfaces. The addition of fulvic and humic acids  
207 to inoculated soils was seen to decrease the rate of diuron degradation, reducing bioavailability  
208 but not bioaccessibility, hence, lengthening the treatment time required; so it was only after  
209 32 days that all diuron was degraded to 3,4-DCA. <sup>[70]</sup> Hence, bioaccessibility is a better  
210 indicator than bioavailability of the long-term influence of humic substances on diuron  
211 degradation. The mineralisation rate of 3,4-DCA in soils is low, and it decreases as pollutant  
212 concentration increases; <sup>[15]</sup> only 3.9-11.9% mineralisation of 1 mg kg<sup>-1</sup> radio labelled 3,4- DCA  
213 was recorded after 16 weeks within various soil types. <sup>[51]</sup> Degradation of 50% of 3,4-DCA was  
214 observed in soil slurries with indigenous soil populations, and this was only marginally  
215 influenced by the addition of buffer, mineral salts and acetate. <sup>[91]</sup> In non-acclimated sediments,  
216 dechlorination of applied 3,4-DCA started after 20 days, with anaerobic conversion to 3-  
217 chloroaniline (44%) and 4-chloroaniline (33%) within two months; these metabolites were not  
218 further degraded. <sup>[92]</sup>

219 The microbial strains *Pseudomonas acidovorans* <sup>[93]</sup> and *Pseudomonas diminuta* <sup>[94]</sup> are able to  
220 use chlorinated anilines as a sole source of carbon and energy ; the latter also being capable of  
221 growing on 3,4-DCA. <sup>[95]</sup> Addition of *Pseudomonas acidovorans* to 3,4-DCA enriched soil  
222 slurries enhanced pollutant mineralization, leading to complete elimination of chloride after  
223 10 days. <sup>[91]</sup> Up to 250 mg L<sup>-1</sup> of the pollutant and its intermediates were anaerobically degraded,  
224 in under 7 days, by a strain of *Pseudomonas fluorescens*. Without added glucose and nitrogen

225 sources, degradation was slower, with 40% of toxicant removal in the first 15 days, at an initial  
226 concentration of 75 mg L<sup>-1</sup>.<sup>[96]</sup> *Pseudomonas diminuta* was proven to dechlorinate up to  
227 50 µg mL<sup>-1</sup> of 3,4-DCA within its growth process, increasing the ratio of degradation in water  
228 samples from natural water reservoirs<sup>[97]</sup> and in fish ponds, where significant degradation of  
229 reversibly sorbed pollutant was observed within the first 12 days. It is also notable that an  
230 appreciable decrease in the irreversibly sorbed fraction occurred within the first 5 days.<sup>[98]</sup>

231 Microorganisms, from Cuban soils, were grown in two culture media, using 3,4-DCA, firstly as  
232 the sole source of carbon and secondarily as the sole source of carbon and nitrogen.<sup>[99]</sup> The  
233 pollutant was completely consumed within 3 weeks using *Pseudomonas*, *Arthrobacter*,  
234 *Aspergillus*, *Penicillium*, and *Fusarium*, isolated in the first medium, while *Bacillus*,  
235 *Arthrobacter*, *Cunninghamella*, *Trichoderma*, and *Fusarium* were isolated in the second system,  
236 demonstrating myriad bacterial growth from 3,4-DCA as a feedstock. The biodegradation  
237 pathway of 3,4-DCA, and other substituted anilines, involves conversion, by oxygenase, to the  
238 corresponding catechol, which is then metabolised via an ortho-cleavage pathway.<sup>[100]</sup> Two  
239 modes of dioxygenation have been determined, utilising degrading bacteria obtained by genetic  
240 exchange between two strains of *Pseudomonas*, and leading to the formation of 3- and 4-  
241 chlorocatechol from 3-chloroaniline. In contrast, only 4-chlorocatechol was generated from  
242 dioxygenation of 4-chloroaniline.<sup>[94]</sup> When bacterial strains of *Pseudomonas acidovorans* were  
243 used for the degradation of 3-chloroaniline and 4-chloroaniline, the rate-limiting degradation  
244 steps were found to be the first attack of the substrate, and conversion to chlorocatechols.<sup>[93]</sup>

245 Degradation of 3,4-DCA by *Pseudomonas* sp. showed that catechol 2,3-dioxygenase is integral  
246 to process efficiency;<sup>[95]</sup> activity toward 4-methylcatechol, 3-methylcatechol and 4-  
247 chlorocatechol was found to be 60, 27 and 13%, respectively, of the activity toward catechol  
248 2,3-dioxygenase. Further tests confirmed catechol 2,3-dioxygenase activity using a strain of

249 *Pseudomonas fluorescens*; the presence of 3-chloro-4-hydroxyaniline as a metabolite suggesting  
250 a pathway that includes dehalogenation and hydroxylation of the aromatic ring, followed by ring  
251 cleavage, by catechol 2,3-dioxygenase. [96]

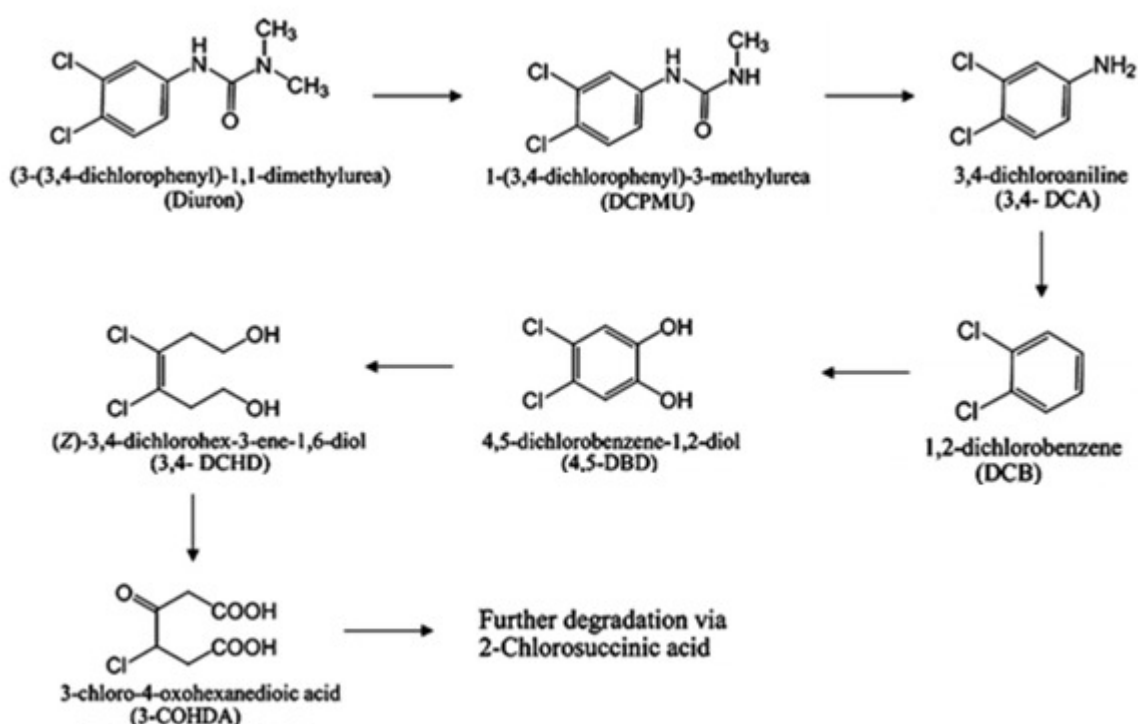
252 Recent work has shown *Micrococcus* sp. to degrade 96% of diuron within 30 hours of  
253 incubation, at a concentration of 250 ppm, and with the addition of non-ionic detergent (0.01%).

254 [101] The authors proposed a mechanism whereby a methyl group is removed, followed by a  
255 hydrolysis step, leading to the accumulation of 3,4-DCA, which undergoes conversion to 4,5-

256 dichlorobenzene-1,2-diol, and further intermediates, within 24 hours of test commencement

257 (Fig. 1). Diuron mineralization has also been confirmed by the metabolic cooperation of

258 *Arthrobacter* sp. and *Achromobacter* sp., with CO<sub>2</sub> as the only final product. [102]



259  
260 **Figure 1.** Degradation pathway of diuron by *Micrococcus* sp, confirmed by FTIR spectra and  
261 HPLC [101]

262 Strains of *Aquaspirillum itersonii*, *Aquaspirillum* sp. and *Paracoccus denitrificans* were shown  
263 to successfully use 3,4-DCA as the only source of carbon and nitrogen for growth; <sup>[103]</sup> the latter  
264 was able to metabolize the pollutant at concentrations up to 150 mg L<sup>-1</sup>, through oxidation to *o*-  
265 diphenol, intradiol cleavage of 4,5- dichloropyrocatechol, and further stages of preparatory  
266 metabolism associated with dehalogenation. A study of microorganisms isolated from Cuban  
267 soils, treated with propanide, showed a *Paracoccus denitrificans* strain to be most efficacious for  
268 3,4-DCA <sup>[50]</sup> degradation. The cleavage of the aromatic ring via the ortho- or meta-pathways,  
269 following formation of 4,5- dichloropyrocatechol, allows full decomposition. Successful  
270 adsorptive bioremediation was demonstrated with the introduction of activated carbons and  
271 bacteria to polluted soils. <sup>[104]</sup> Activated carbon acts as buffer, which keeps the pollutant  
272 concentration in the soil solution below the toxicity threshold for the bacteria, as shown by a  
273 study of three types of activated carbon saturated with 3,4-DCA and placed in a mineral medium  
274 with a *Paracoccus denitrificans* strain. <sup>[50]</sup> The pollutant was reversibly sorbed, therefore  
275 available, at a limited concentration, for the bacteria population to process. Varied degradation  
276 rates, from 2 to 10 weeks, suggest that facile desorption and more rapid decomposition are  
277 linked to a reduced micropore volume. This can be ascribed to the fact that *Paracoccus*  
278 *denitrificans* is only able to penetrate into the macroporous structure, due to size exclusion  
279 effects, thus pollutant desorption from the smaller carbon pores is necessary for the bacteria to  
280 process any 3,4-DCA sorbed therein; this bacterium seems able to accelerate desorption by  
281 acidifying the medium or via excretion of surface-active substances.

282 Biological studies have also shown microbial consortia to be successful in the removal of  
283 propanil and 3,4-DCA from repeated batch suspended cell cultures, <sup>[105]</sup> as well as in biofilm  
284 reactors for agricultural wastewater treatment. <sup>[106]</sup> In the latter case, the porous volcanic stone  
285 tezontle was used as a support for a biofilm in a continuous process able to degrade propanil and  
286 metabolic intermediates at rates of up to 24.9 mg L<sup>-1</sup> h<sup>-1</sup>, without the need for co-substrates.

287 *Pseudomonas* sp., *Acinetobacter calcoaceticus*, *Rhodococcus* sp., *Xanthomonas* sp. and *Kokuria*  
288 strains can also grow individually in 3,4-DCA, while other strains found in the biofilm, not able  
289 to degrade propanil metabolites directly, are probably involved in the metabolization of  
290 herbicide adjuvants or in the maintenance of biofilm integrity. Resultantly, the removal of  
291 chloroanilines from sewage treatment plant streams could be improved by promoting the growth  
292 of indigenous bacterial communities, and through the introduction of adapted laboratory strains.  
293 The addition of readily degradable aniline and non-toxic haloaromatics may, respectively,  
294 improve the breakdown of chloroanilines and the chlorocatechol potential. [94]

#### 295 *Uptake by fungi and cultivated plants*

296 When free chloroanilines are released as herbicide metabolites, they can be incorporated in the  
297 plant's 'insoluble' residue fraction; degradation experiments have proposed lignin as a primary  
298 binding site. [107, 108] Immersion of the bivalve *Corbicula fluminea* in cages both upstream and  
299 downstream of conventional rice fields, in the region of Camargue, [19] showed the concentration  
300 of 3,4-DCA measured downstream of the rice plantations to be approximately half that in the  
301 *Corbicula* caged upstream, suggesting a potential, partial bioaccumulation of 3,4-DCA in rice  
302 plants. Tomato plants, oat, barley and wheat, grown in nutrient solutions with 4-chloroaniline  
303 and 3,4-DCA showed that 90-95% of the chloroanilines incorporated were found in the roots,  
304 with uptake proportional to the amount of chemical applied. In contrast, distribution of the same  
305 chemicals in carrots was approximately equally divided between the roots and the upper part of  
306 the vegetables. [109] These results suggest a potential risk of chronic toxicity due to the  
307 assumption of 3,4-DCA contained in certain foods.

308 Some lignin degraders are able to metabolize chloroanilines and their lignin conjugates;  
309 experiments have shown that chloroanilines appear to be bioavailable to the white rot fungus  
310 *Phanerochaete chrysosporium* once they were mineralized as lignin. [110] More than 50% of

311 available [ring-U- 14C] -3,4-DCA was shown to be mineralized after 33 days of sample  
312 incubation and free 3,4-DCA was deemed a superior substrate for mineralization than free 4-  
313 chloroaniline. Different metabolites were formed, but chloroanilines were not detected, neither  
314 were their azo or azoxy derivatives. Hence, lignin incorporation and fungal oxidation can lead  
315 to the complete removal of 3,4-DCA from the environment; however, fungi is also known to  
316 adsorb less chloro-substituted anilines per biomass unit than bacteria, <sup>[111]</sup> and the degradation  
317 pathway of white-rot fungi could lead to the formation of toxic tetrachloroazobenzenes. <sup>[112]</sup>

### 318 *Adsorption and ligand exchange*

319 Adsorption technologies offer effective removal of many organic pollutants from aqueous  
320 media, <sup>[113]</sup> and various adsorbents have been studied for removal of chloroanilines from  
321 wastewaters. Batch adsorption experiments, conducted with an acid activated halloysite, using  
322 aqueous solutions at pH ~5, <sup>[12]</sup> gave experimental data that followed a pseudo-second order  
323 kinetic model: <sup>[114]</sup>

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e t} \quad (2)$$

324 where:  $q_t$  is the amount of chloroaniline adsorbed ( $\text{mg g}^{-1}$ ) at time  $t$  (s),  $k_2$  is the rate constant of  
325 pseudo-second order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ) and  $q_e$  is the amount of chloroaniline adsorbed at  
326 equilibrium ( $\text{mg g}^{-1}$ ). A ‘Weber–Morris’ plot of  $q_t$  versus  $t^{0.5}$  confirmed that chloroaniline  
327 removal occurred, first by fast diffusion of 3,4-DCA to the surface of the clay mineral, over the  
328 first 180 minutes, before continuing as slower interparticle diffusion. The adsorption capacity of  
329 halloysite was found to be lower for 3,4-DCA than for 3-dichloroaniline and 4-dichloroaniline.

330 Equilibrium isotherm data was effectively described by the semi-empirical Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{(K_L q_m)} + \frac{C_e}{q_m} \quad (3)$$



331 where:  $q_m$  is the monolayer adsorption capacity ( $\text{mg g}^{-1}$ ),  $q_e$  is the sorption uptake at equilibrium  
332 ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium solution concentration ( $\text{mg L}^{-1}$ ) and  $K_L$  is a coefficient related to  
333 the affinity between the adsorbent and the adsorbate ( $\text{L g}^{-1}$ ). Similar adsorption experiments  
334 have been performed with kaolinite (KGa-1) and montmorillonite (SWy-1), using standard  
335 solutions of 3,4-DCA and other chloroanilines at pH  $\sim 5$  and  $\sim 9$ , respectively; <sup>[1, 75]</sup> the specific  
336 pH conditions were chosen so as to produce neutral organic pollutant species. Kinetic  
337 evaluation indicated an initial, rapid surge in chloroaniline removal, with equilibrium achieved  
338 in under 4 days. Langmuir and Freundlich equations both adequately described the data; <sup>[75]</sup>  
339 however, the Langmuir plot showed a marginally better fit for montmorillonite, hence  
340 adsorption on this clay is likely to decrease as surface sorption sites are saturated. The  
341 chloroanilines studied would be mainly sorbed on the mineral surface of kaolinite, while the  
342 structure of montmorillonite allows swelling via sorption in the interlayer, <sup>[115]</sup> as confirmed by  
343 studying the dehydrated clay; <sup>[1]</sup> post heat-treatment, the distance between equivalent atomic  
344 planes ( $d_{001}$ ) collapsed from 11 to 9.7 Å. Further evidence was provided by X-ray spectra of the  
345 montmorillonite/3,4-DCA system. This contrast in sorption mechanism is reflected in  
346 desorption measurements, where kaolinite was shown to retain the pollutant, while  
347 montmorillonite showed a higher level of desorption when reversing the sorption process at an  
348 earlier point in the isotherm. <sup>[75]</sup>

349 While clay materials offer surface sites for adsorption, the main surface area of another well-  
350 known family of sorbents, i.e. activated carbons, is ascribed to microporous character; surface  
351 hydrophobicity determines the sorptive capacity of many organic molecules, which have  
352 molecular sizes small enough to penetrate into the micropores. Highly microporous activated  
353 carbons, obtained from coal and peat, were confirmed as better sorbents than mesoporous  
354 carbons, obtained from raw plant materials. Increased iron content and other ash elements may

355 positively influence the maximum uptake, by enhancing chemisorption of active organic  
356 compounds, such as 3,4-DCA. [50]

357 Studies of aqueous solutions of various pesticides agitated with 10 mg L<sup>-1</sup> of powdered activated  
358 carbon (surface area ~1000 m<sup>2</sup> g<sup>-1</sup>; particle size 40 μm) for 5 minutes, showed 70% removal  
359 efficiency for 3,4-DCA (initial concentration: 658 ng L<sup>-1</sup>), while complete removal was achieved  
360 via preoxidation with ozone. [103] Fitting of room temperature sorption isotherms, obtained using  
361 suspensions of activated carbon in aqueous solutions of 3,4-DCA, [50] using the Langmuir  
362 isotherm model (Equation 3), showed monolayer filling of the sorptive surface with 'L-type'  
363 isotherms, indicating strong interactions between the adsorbate and adsorbent. [116]

364 Sugar beet pulp, corncob, corncob char, perlite, vermiculite and sand have recently been studied  
365 for sorption of 3,4-DCA from aqueous solutions at pH 4.8. [85] These sorbents may be used in  
366 field conditions, so it is essential to understand their sorption behaviour in different matrices.  
367 However, liquid matrices containing cations and organic matter, except for corncob, showed no  
368 significant differences in maximum uptake of 3,4-DCA from pure water and run-off waters.  
369 The mechanism of sorption was satisfactorily described by the Freundlich isotherm model, with  
370 the highest sorption uptakes obtained at 99% removal from water for corncob char, and, 86%  
371 removal for sand. Of the sorbents studied, it is also known that vermiculite has a good  
372 resistance to mechanical abrasion. [117] Further investigations would be required to verify the  
373 adsorption capacity of low cost materials in field conditions, but it is encouraging that sorbents  
374 such as sand could present appreciable capacities capable of removing > 50% of 3,4-DCA, even  
375 from sediment extract media (Table 2).

376 **Table 2.** Surface area, pore size and adsorption data of different material tested for the removal  
377 of 3,4-DCA from water. The parameters  $q_m$  and  $b$  refer to the Langmuir model (Equation 3)

Adsorbent	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	$q_m$ (mg g <sup>-1</sup> )	$b$ (mL mg <sup>-1</sup> )	Equilibrium time (h)	Stirring method
Halloysite [12]	76.6	0.039	0.078	2.726	> 3	Rotary stirrer
Kaolinite [75]	-	-	0.311	9	> 96	Electromagnetic
Montmorillonite [75]	-	-	0.077	23	> 96	Electromagnetic
Activated carbon AG [50]	963	0.55	583	-	48	-
Activated carbon SKT [50]	1028	0.53	480	-	0.5	-
Activated carbon RS [50]	410	0.5	364	-	0.5	-

378 Within ligand exchange processes, polymeric chelating resins are able to selectively remove  
379 target contaminants; however, eluate recycle, regeneration of depleted adsorbent, and the high  
380 cost of transition metals, used as ligand complexing ions, are still significant obstacles towards  
381 commercial application of such processes in wastewater treatment. Currently, there are no  
382 studies on the application of ligand exchange processes for 3,4-DCA removal, but this would  
383 seem possible in light of the recovery of aromatic amines from water, at low concentration, as  
384 demonstrated for chelating resin-bound cobalt ions. [118] A mini-column apparatus with Co(II)-  
385 CDAE-sporopollenin resin was also tested for adsorption of chlorinated anilines, found to be  
386 described by a Langmuir model for 2-chloroaniline, 4-chloroaniline and 2,5-dichloroaniline. [6]  
387 The study showed similar values for the maximum adsorption capacity ( $q_m$ ) for binding of 2-

388 chloroanilines and 4-chloroanilines, which were consistently lower than those for 3-  
389 dichloroaniline and 2,5-dichloroaniline onto the  $\text{Co}^{2+}$  matrix, suggesting that both electrical  
390 forces and steric hindrance are involved in the sorption process. This conclusion is supported by  
391 consideration of the inductive effects of *ortho*-Cl and *para*-Cl atoms, as well as the nature of  
392 these ligands, which contain charged groups and may offer steric hindrance. Moreover, steric  
393 hindrance around the amino nitrogen weakens binding to metal ions, causing faster migration of  
394 the aforementioned pollutants. <sup>[119]</sup> The adsorption of 3-chloroaniline was better represented by  
395 a Freundlich model, possibly as a result of a more complex type of binding than the independent  
396 and univalent binding described by a Langmuir model.

#### 397 ***Chlorination, ozonisation, chemical precipitation and $\text{Fe}^0/\text{H}_2\text{O}_2$ systems***

398 A common sequence of operations adopted in many drinking water plants is that of (i)  
399 preoxidation, (ii) adsorption, and (iii) coagulation. Preoxidation of an aqueous sample with a  
400 concentration of  $658 \text{ ng L}^{-1}$  of 3,4-DCA, performed using sodium hypochlorite, demonstrated  
401 100% pollutant removal; <sup>[13]</sup> however, such treatments have an associated risk of carcinogenic  
402 trihalomethanes by-product formation. Hence, researchers have considered other oxidative  
403 species and ozonolysis of a sample, again with a concentration of  $658 \text{ ng L}^{-1}$  of 3,4-DCA,  
404 showed 85% pollutant removal; however, the subsequent coagulation and flocculation steps  
405 were found to be ineffective, while further adsorption treatment, with activated carbons, led to  
406 complete pollutant removal. <sup>[13]</sup>

407 The oxidizing potential of  $\text{Fe}^0$  towards different organic compounds is well known; <sup>[120]</sup>  $\text{Fe}^0/$   
408  $\text{H}_2\text{O}_2$  systems can be used to reduce levels of diuron, and other pesticides, in polluted  
409 environments, as well as agricultural waste.  $\text{Fe}^0$  promotes the reduction of  $\text{H}_2\text{O}_2$  to hydroxyl  
410 radicals, generating  $\text{Fe}^{2+}$ , which, in turn, also produces hydroxyl radicals via further  $\text{H}_2\text{O}_2$   
411 reduction. A  $10 \text{ mg L}^{-1}$  diuron solution, also containing  $2 \text{ mmol L}^{-1}$  of  $\text{H}_2\text{O}_2$  and  $\text{H}_3\text{PO}_4$ , was

412 flowed through a glass tube packed with 2 g of iron wool, and showed that pH strongly affected  
413 the degradation process, allowing process optimisation. At pH 2.5 more than 99.9% of the  
414 pesticide was removed after ten minutes, with only  $1 \mu\text{g L}^{-1}$  of 3,4-DCA found remaining in the  
415 effluent. [121]

#### 416 *Electrochemical and electrohydraulic methods*

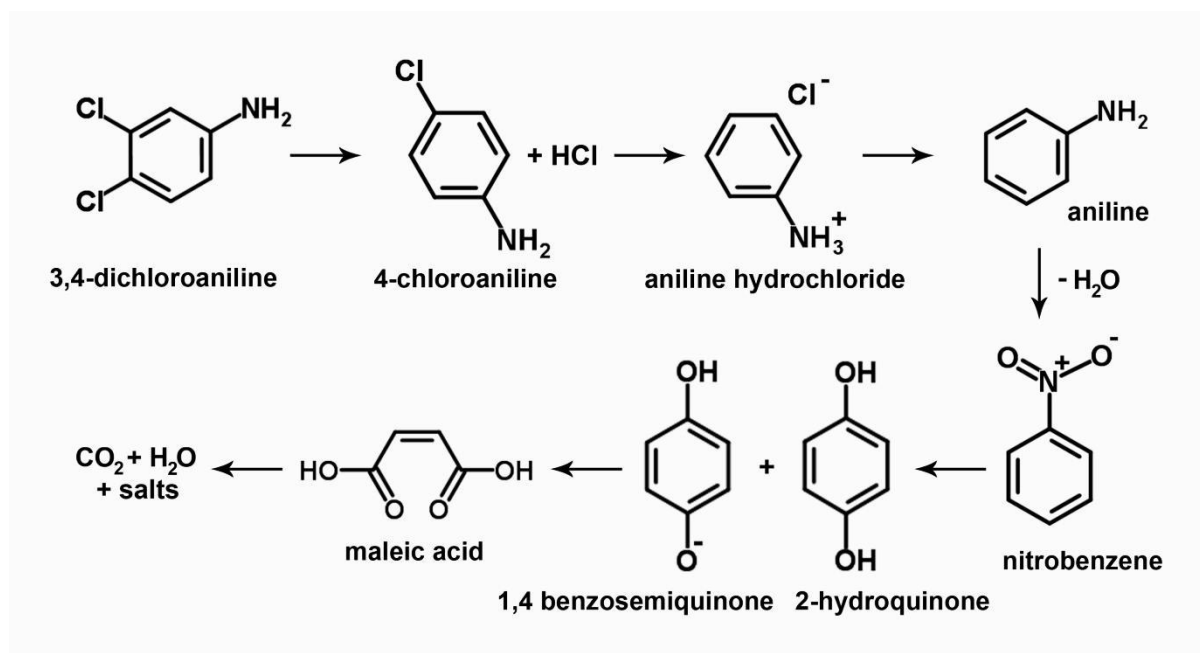
417 An electrohydraulic discharge (EHD) method for the oxidative degradation of 3,4-DCA was  
418 tested by exposing wastewaters to pulsed electrical discharges generated via submerged  
419 electrodes. [122] UV radiation is produced by a plasma channel created by EHD, thereby,  
420 generating a shockwave as it expands against the water. The degradation rate is expressed by:

$$\frac{dC}{dN} = -k_1 C_i - k_0 \quad (4)$$

421 where  $dC/dN$  is the change in concentration per discharge,  $C_i$  is the initial substrate  
422 concentration,  $k_0$  is the zero-order term (an expression of direct photolysis) and  $k_1$  is the first-  
423 order term related to oxidation in the plasma channel region.

424 As part of an Advanced Oxidation Process (AOP), photocatalysis can be employed (i) for water  
425 treatment in slurry reactors, where an additional step is required for the separation of any  
426 suspended catalysts, or (ii) into reactors, where the catalysts are immobilized on adsorbents or  
427 on membranes. Using sols of vanadium pentoxide and cerium oxide, added to a titanium  
428 dioxide sol, allowed preparation of Ti-V and Ti-Ce catalysts, respectively;  $0.1 \text{ g L}^{-1}$  of each  
429 powdered catalyst was added to agitated aqueous solutions of 3,4-DCA, irradiated in an annular  
430 reactor at  $140 \text{ mW cm}^{-2}$ , and the Ti-V catalyst gave a higher degradation than Ti-Ce, due to its  
431 band gap energy (which is more towards the visible region) and smaller particle size. The  
432 kinetic plot suggested bi-phasic kinetics, with a sharp increase in rate after 45 minutes; further

433 bench scale reactor experiments showed 85% degradation in 106 minutes <sup>[11]</sup> and Figure 2 shows  
434 the intermediate species formed.



435  
436 **Figure 2.** Intermediates formed during photo-degradation of 3,4-DCA using Ti-V (sol) catalyst,  
437 confirmed by HPLC and GC-MS analysis <sup>[11]</sup>

438 Biphasic kinetics were also observed in the photocatalytic degradation of 3,4-DCA using Ti-N  
439 and Ti-S catalysts; <sup>[28]</sup> the former showing a higher surface area, and lower particle size and  
440 band-gap energy. Higher specific surface area increases the degree of contact of the pollutant  
441 with the catalyst surface, while smaller particle size means a reduced degradation time, due to  
442 shorter distances between the charge carrier and the surface, where the reaction occurs. 3,4-  
443 DCA was fully degraded using a Ti-N catalyst in 120 minutes with optimal degradation  
444 obtained at pH = 6. At higher catalyst dosages ( $> 0.1 \text{ g L}^{-1}$ ) the reaction rate starts to decrease,  
445 due to the deactivation of molecules that collide with ground state molecules, and subsequent  
446 agglomeration of catalyst particles. Meanwhile, at 3,4-DCA concentrations  $> 10 \text{ mg L}^{-1}$ , the  
447 degradation efficiency starts to decrease, as the number of collisions between the 3,4-DCA

448 molecules increases, while there is a reduction in collisions between pollutant molecules and  
449 •OH radicals. [123]

450 Degradation of aqueous 3,4-DCA was recently performed using a dielectric barrier discharge  
451 (DBD) plasma reactor; [124] where generated ozone interacts with the pollutant directly or by the  
452 generation of hydroxyl radicals, which results in a faster rate of reaction than for molecular  
453 ozone alone. [125] The process involves the flow of a water film through the discharge zone  
454 created by two aluminium electrodes, and the degradation process is well described by pseudo-  
455 first order kinetics, with higher efficiencies reached either under acidic conditions, increasing  
456 the input power or by adding  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . The main pathways involved were deamination,  
457 hydroxylation, dechlorination, and hydroxylation and oxidation, followed by the generation of  
458 organic acids, via aromatic ring opening. Mineralization into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was only partially  
459 achieved, as confirmed by the lower rate of removal for total organic carbon than for DCA, and  
460 by degradation intermediates identified using GC-MS analysis. Solution pH decreased during  
461 DCA degradation, as observed in previous work, [124] where aqueous 3,4-DCA was degraded by  
462 a wire-cylinder DBD reactor, with an efficiency that was observed to increase when the input  
463 power was increased to 90 W, but decreased at powers above that; aqueous ozone concentration  
464 was seen to follow the same trend. It was also noted that, similar to other systems, the process  
465 was pH dependent with a lower degradation rate obtained under neutral conditions than at acidic  
466 or basic levels.

## 467 **Conclusions**

468 Myriad technologies have been developed for the degradation of pesticides; however, more  
469 attention has to be mainly focussed on the fate of metabolites. 3,4-DCA is a degradation  
470 product generally more toxic than its parent substances; if it is covalently bound to humic

471 substances within soil, the risk of groundwater contamination via leaching is low, but it also has  
472 an extremely low rate of mineralization,<sup>[70]</sup> making it a significant environmental issue.

473 Lignin incorporation and fungal oxidation are able to effect complete removal of 3,4-DCA from  
474 the environment,<sup>[110]</sup> while the use of bacteria and porous materials can be successful in  
475 bioreactors, as well as for in-situ bioremediation techniques. Bioremediation has been  
476 successfully demonstrated, introducing activated carbons and bacteria to polluted soils,<sup>[50]</sup> and  
477 the biological removal of 3,4-DCA from sewage can be enhanced by the growth of indigenous  
478 communities, and through the introduction of adapted laboratory strains;<sup>[94]</sup> however, the  
479 technical and economic feasibility of such processes also need to be considered. Further  
480 investigations are required to confirm the adsorption capacity of promising low cost materials  
481 such as activated carbons, corncob char and sand, especially within field conditions.<sup>[85]</sup> The  
482 possibility of recovering aromatic amines from low concentration water streams has been  
483 already demonstrated using chelating resin-bound cobalt ions,<sup>[118]</sup> as well as for Co(II)-CDAE-  
484 sporopollenin resin,<sup>[6]</sup> but there have been no specific studies related to the application of such  
485 technologies to 3,4-DCA removal.

486 Fe<sup>0</sup>/H<sub>2</sub>O<sub>2</sub> systems could be developed for the degradation of 3,4-DCA in agricultural soils and  
487 waste,<sup>[121]</sup> while photodegradation using doped TiO<sub>2</sub> has been successfully performed, and  
488 degradation kinetics are available for the scale up of reactors.<sup>[11]</sup> Low toxicity and cost,  
489 combined with good chemical stability and high natural abundance<sup>[126]</sup> make this catalyst  
490 potentially suitable for the environmentally friendly removal of 3,4-DCA from water. Effective  
491 degradation is also observed for the use of dielectric barrier discharge reactors, but further  
492 studies are required to reach complete mineralization of 3,4-DCA.<sup>[124]</sup>

493 Hence, there is significant scope for the application of existing technologies to the issue of 3,4-  
494 DCA removal from aqueous streams, some of which have timely potential for implementation;



495 however, there is a need for more data to be acquired to permit economic and environmental  
496 impact of these proposed systems to be fully addressed.

## 497 References

- 498 [1] Angioi, S.; Polati, S.; Roz, M.; Rinaudo, C.; Gianotti, V.; Gennaro, M.C. Sorption studies of  
499 chloroanilines on kaolinite and montmorillonite. *Environmental Pollution*. **2005**, *134*(1),  
500 35-43.
- 501 [2] Bevan, R.; Harrison, P.; Youngs, L.; Whelan, M.; Goslan, E.; Macadam, J.; Holmes, P.;  
502 Persich, T. A review of latest endocrine disrupting chemicals research implications for  
503 drinking water. 2012.
- 504 [3] Cook, J.C.; Mullin, L.S.; Frame, S.R.; Biegel, L.B. Investigation of a mechanism for leydig-  
505 cell tumorigenesis by linuron in rats. *Toxicology and Applied Pharmacology*. **1993**,  
506 *119*(2), 195-204.
- 507 [4] Crossland, N.O.; Hillaby, J.M. Fate and effects of 3,4-dichloroaniline in the laboratory and in  
508 outdoor ponds .2. Chronic toxicity to daphnia spp and other invertebrates. *Environmental*  
509 *Toxicology and Chemistry*. **1985**, *4*(4), 489-499.
- 510 [5] Groshart; Okkerman Towards the establishment of a priority list of substances for further  
511 evaluation of their role in endocrine disruption. 2000, European Commission.
- 512 [6] Ucan, M.; Ayar, A. Sorption equilibria of chlorinated anilines in aqueous solution on resin-  
513 bound cobalt ion. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*.  
514 **2002**, *207*(1-3), 41-47.
- 515 [7] Muller, L.; Fattore, E.; Benfenati, E. Determination of aromatic amines by solid-phase  
516 microextraction and gas chromatography mass spectrometry in water samples. *Journal of*  
517 *Chromatography A*. **1997**, *791*(1-2), 221-230.
- 518 [8] Flores-Céspedes, F.; Fernandez-Perez, M.; Villafranca-Sanchez, M.; Gonzalez-Pradas, E.  
519 Cosorption study of organic pollutants and dissolved organic matter in a soil.  
520 *Environmental Pollution*. **2006**, *142*(3), 449-456.
- 521 [9] Parris, G.E. Covalent binding of aromatic-amines to humates .1. Reactions with carbonyls  
522 and quinones *Environmental Science & Technology*. **1980**, *14*(9), 1099-1106.
- 523 [10] Park, J.W.; Dec, J.; Kim, J.E.; Bollag, J.M. Effect of humic constituents on the  
524 transformation of chlorinated phenols and anilines in the presence of oxidoreductive  
525 enzymes or birnessite. *Environmental Science & Technology*. **1999**, *33*(12), 2028-2034.
- 526 [11] Padmini, E.; Miranda, L.R. Nanocatalyst from sol-sol doping of TiO<sub>2</sub> with Vanadium and  
527 Cerium and its application for 3,4 Dichloroaniline degradation using visible light.  
528 *Chemical Engineering Journal*. **2013**, *232*, 249-258.
- 529 [12] Szczepanik, B.; Slomkiewicz, P.; Garnuszek, M.; Czech, K. Adsorption of chloroanilines  
530 from aqueous solutions on the modified halloysite. *Applied Clay Science*. **2014**, *101*,  
531 260-264.
- 532 [13] Ormad, M.P.; Miguel, N.; Claver, A.; Matesanz, J.M.; Ovelleiro, J.L. Pesticides removal in  
533 the process of drinking water production. *Chemosphere*. **2008**, *71*(1), 97-106.
- 534 [14] Livingston, A.G.; Willacy, A. Degradation of 3,4-dichloroaniline in synthetic and  
535 industrially produced wastewaters by mixed cultures freely suspended and immobilized  
536 in a packed-bed reactor *Applied Microbiology and Biotechnology*. **1991**, *35*(4), 551-557.
- 537 [15] Bureau, E.C. European Union Risk Assessment Report. **2006**.
- 538 [16] Gülden, M.; Turan, A.; Seibert, H. Endocrinically active chemicals and their occurrence in  
539 surface waters: research report 10204279. 1998.

- 540 [17] Sorokin, N.; Johnson, I.; Rockett, L.; Aldous, E. Proposed EQS for Water Framework  
541 Directive Annex VIII substances: 3,4- dichloroaniline. 2008.
- 542 [18] Tomlin, C. The Pesticide Manual, British Crop Protection Council, Surrey, UK (1999).  
543 1999.
- 544 [19] Roche, H.; Vollaire, Y.; Martin, E.; Rouer, C.; Coulet, E.; Grillas, P.; Banas, D. Rice fields  
545 regulate organochlorine pesticides and PCBs in lagoons of the Nature Reserve of  
546 Camargue. *Chemosphere*. **2009**, *75*(4), 526-533.
- 547 [20] Hsu, T.S.; Bartha, R. Hydrolyzable and nonhydrolyzable 3,4-dichloroaniline humus  
548 complexes and their respective rates of biodegradation *Journal of Agricultural and Food*  
549 *Chemistry*. **1976**, *24*(1), 118-122.
- 550 [21] Pothuluri, J.V.; Hinson, J.A.; Cerniglia, C.E. Propanil - toxicological characteristics,  
551 metabolism, and biodegradation potential in soil *Journal of Environmental Quality*. **1991**,  
552 *20*(2), 330-347.
- 553 [22] Cullington, J.E.; Walker, A. Rapid biodegradation of diuron and other phenylurea  
554 herbicides by a soil bacterium. *Soil Biology & Biochemistry*. **1999**, *31*(5), 677-686.
- 555 [23] Bartha, R.; Pramer, D. Pesticide transformation to aniline and azo compounds in soil  
556 *Science*. **1967**, *156*(3782), 1617-&.
- 557 [24] Di Corcia, A.; Costantino, A.; Crescenzi, C.; Samperi, R. Quantification of phenylurea  
558 herbicides and their free and humic acid-associated metabolites in natural waters. *Journal*  
559 *of Chromatography A*. **1999**, *852*(2), 465-474.
- 560 [25] Gosetti, F.; Bottaro, M.; Gianotti, V.; Mazzucco, E.; Frascarolo, P.; Zampieri, D.; Oliveri,  
561 C.; Viarengo, A.; Gennaro, M.C. Sun light degradation of 4-chloroaniline in waters and  
562 its effect on toxicity. A high performance liquid chromatography – Diode array –  
563 Tandem mass spectrometry study. *Environmental Pollution*. **2010**, *158*(2), 592-598.
- 564 [26] Loos, R.; Hanke, G.; Eisenreich, S.J. Multi-component analysis of polar water pollutants  
565 using sequential solid-phase extraction followed by LC-ESI-MS. *Journal of*  
566 *Environmental Monitoring*. **2003**, *5*(3), 384-394.
- 567 [27] Norberg, J.; Zander, A.; Jonsson, J.A. Fully automated on-line supported liquid membrane  
568 liquid chromatographic determination of aniline derivatives in environmental waters.  
569 *Chromatographia*. **1997**, *46*(9-10), 483-488.
- 570 [28] Ellappan, P.; Miranda, L.R. Two-regime kinetic study and parameter optimization of  
571 degradation of 3,4-dichloroaniline using TI-N/S catalyst under visible light. *Desalination*  
572 *and Water Treatment*. **2016**, *57*(5), 2203-2216.
- 573 [29] Vastermark, A.; Giwercman, Y.L.; Hagstromer, O.; De-Meyts, E.R.; Eberhard, J.; Stahl, O.;  
574 Cedermark, G.C.; Rastkhani, H.; Daugaard, G.; Arver, S.; Giwercman, A. Polymorphic  
575 variation in the androgen receptor gene: Association with risk of testicular germ cell  
576 cancer and metastatic disease. *European Journal of Cancer*. **2011**, *47*(3), 413-419.
- 577 [30] Swedenborg, E.; Ruegg, J.; Makela, S.; Pongratz, I. Endocrine disruptive chemicals:  
578 mechanisms of action and involvement in metabolic disorders. *Journal of Molecular*  
579 *Endocrinology*. **2009**, *43*(1-2), 1-10.
- 580 [31] Autho, Receptors mediating toxicity and their involvement in endocrine disruption, in  
581 *Molecular, Clinical and Environmental Toxicology: Volume 1: Molecular Toxicology*,  
582 A. Luch, Editor. Birkhäuser Basel: Basel, 2009; 289-323.
- 583 [32] Diamanti-Kandarakis, E.; Bourguignon, J.P.; Giudice, L.C.; Hauser, R.; Prins, G.S.; Soto,  
584 A.M.; Zoeller, R.T.; Gore, A.C. Endocrine-Disrupting Chemicals: An Endocrine Society  
585 Scientific Statement. *Endocrine Reviews*. **2009**, *30*(4), 293-342.
- 586 [33] Newbold, R.R. Impact of environmental endocrine disrupting chemicals on the  
587 development of obesity. *Hormones-International Journal of Endocrinology and*  
588 *Metabolism*. **2010**, *9*(3), 206-217.

- 589 [34] Koppe, J.G.; Bartonova, A.; Bolte, G.; Bistrup, M.L.; Busby, C.; Butter, M.; Dorfman, P.;  
590 Fucic, A.; Gee, D.; van den Hazel, P.; Howard, V.; Kohlhuber, M.; Leijds, M.; Lundqvist,  
591 C.; Moshammer, H.; Naginiene, R.; Nicolopoulou-Stamati, P.; Ronchetti, R.; Salines, G.;  
592 Schoeters, G.; ten Tusscher, G.; Wallis, M.K.; Zuurbier, M. Exposure to multiple  
593 environmental agents and their effect. *Acta Paediatrica*. **2006**, *95*, 106-113.
- 594 [35] Brian, J.V.; Harris, C.A.; Scholze, M.; Kortenkamp, A.; Booy, P.; Lamoree, M.; Pojana, G.;  
595 Jonkers, N.; Marcomini, A.; Sumpster, J.P. Evidence of estrogenic mixture effects on the  
596 reproductive performance of fish. *Environmental Science & Technology*. **2007**, *41*(1),  
597 337-344.
- 598 [36] Kortenkamp, A.; Faust, M.; Scholze, M.; Backhaus, T. Low-Level Exposure to Multiple  
599 Chemicals: Reason for Human Health Concerns? *Environmental Health Perspectives*.  
600 **2007**, *115*(Suppl 1), 106-114.
- 601 [37] Corke, C.T.; Thompson, F.R. Effects of some phenylamide herbicides and their degradation  
602 products on soil nitrification *Canadian Journal of Microbiology*. **1970**, *16*(7), 567-&.
- 603 [38] Bearden, A.P.; Schultz, T.W. Structure-activity relationships for Pimephales and  
604 Tetrahymena: A mechanism of action approach. *Environmental Toxicology and*  
605 *Chemistry*. **1997**, *16*(6), 1311-1317.
- 606 [39] Argese, E.; Bettiol, C.; Agnoli, F.; Zambon, A.; Mazzola, M.; Ghirardini, A.V. Assessment  
607 of chloroaniline toxicity by the submitochondrial particle assay. *Environmental*  
608 *Toxicology and Chemistry*. **2001**, *20*(4), 826-832.
- 609 [40] Hooftman, R.N.; Vink, G.J. The determination of toxic effects of pollutants with the marine  
610 polychaete worm ophryotrocha-diadema *Ecotoxicology and Environmental Safety*.  
611 **1980**, *4*(3), 252-262.
- 612 [41] Adema, D.M.; Vink, I.G. A comparative-study of the toxicity of 1,1,2-trichloroethane,  
613 dieldrin, pentachlorophenol and 3,4 dichloroaniline for marine and fresh-water  
614 organisms *Chemosphere*. **1981**, *10*(6), 533-554.
- 615 [42] Allner Toxikokinetik von 3,4-Dichloranilin beim dreistachligen Stichling (*Gasterosteus*  
616 *aculeatus*) unter besonderer Berücksichtigung der Fortpflanzungsphysiologie. 1997,  
617 Joannes Gutenberg Universitat.
- 618 [43] Droulia, F.E.; Kati, V.; Giannopolitis, C.N. Sorption of 3,4-dichloroaniline on four  
619 contrasting Greek agricultural soils and the effect of liming. *Journal of Environmental*  
620 *Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes*. **2011**,  
621 *46*(5), 404-410.
- 622 [44] Fava, L.; Orru, M.A.; Crobe, A.; Caracciolo, A.B.; Bottoni, P.; Funari, E. Pesticide  
623 metabolites as contaminants of groundwater resources: assessment of the leaching  
624 potential of endosulfan sulfate, 2,6-dichlorobenzoic acid, 3,4-dichloroaniline, 2,4-  
625 dichlorophenol and 4-chloro-2-methylphenol. *Microchemical Journal*. **2005**, *79*(1-2),  
626 207-211.
- 627 [45] Claver, A.; Ormad, P.; Rodriguez, L.; Ovelleiro, J.L. Study of the presence of pesticides in  
628 surface waters in the Ebro river basin (Spain). *Chemosphere*. **2006**, *64*(9), 1437-1443.
- 629 [46] Wegman, R.C.C.; De Korte, G.A.L. Aromatic amines in surface waters of The Netherlands.  
630 *Water Research*. **1981**, *15*(3), 391-394.
- 631 [47] Gonzalez-Pradas, E.; Fernandez-Perez, M.; Flores-Cespedes, F.; Villafranca-Sanchez, M.;  
632 Urena-Amate, M.D.; Socias-Viciana, M.; Garrido-Herrera, F. Effects of dissolved  
633 organic carbon on sorption of 3,4-dichloroaniline and 4-bromoaniline in a calcareous  
634 soil. *Chemosphere*. **2005**, *59*(5), 721-728.
- 635 [48] Crossland, N.O. A review of the fate and toxicity of 3,4-dichloroaniline in aquatic  
636 environments *Chemosphere*. **1990**, *21*(12), 1489-1497.
- 637 [49] Beyerlepfur, R.; Lay, J.P. Adsorption and desorption of 3,4-dichloroaniline on soil  
638 *Chemosphere*. **1990**, *21*(9), 1087-1094.

- 639 [50] Bakhaeva, L.P.; Vasilyeva, G.K.; Surovtseva, E.G.; Mukhin, V.M. Microbial degradation  
640 of 3,4-dichloroaniline sorbed by activated carbon. *Microbiology*. **2001**, *70*(3), 277-284.
- 641 [51] Süß Z. Pflanzenernähr. Bodenk. **1978**, *141*(57-66).
- 642 [52] Reid, B.J.; Jones, K.C.; Semple, K.T. Bioavailability of persistent organic pollutants in soils  
643 and sediments - a perspective on mechanisms, consequences and assessment.  
644 *Environmental Pollution*. **2000**, *108*(1), 103-112.
- 645 [53] Bengtsson, G.; Lindqvist, R.; Piwoni, M.D. Sorption of trace organics to colloidal clays,  
646 polymers, and bacteria *Soil Science Society of America Journal*. **1993**, *57*(5), 1261-  
647 1270.
- 648 [54] Freitag, D.; Scheunert, I.; Klein, W.; Korte, F. Long-term fate of 4-chloroaniline-c-14 in  
649 soil and plants under outdoor conditions - a contribution to terrestrial ecotoxicology of  
650 chemicals *Journal of Agricultural and Food Chemistry*. **1984**, *32*(2), 203-207.
- 651 [55] Li, H.; Lee, L.S.; Jafvert, C.T.; Graveel, J.G. Effect of substitution on irreversible binding  
652 and transformation of aromatic amines with soils in aqueous systems. *Environmental*  
653 *Science & Technology*. **2000**, *34*(17), 3674-3680.
- 654 [56] Li, H.; Lee, L.S. Sorption and abiotic transformation of aniline and alpha-naphthylamine by  
655 surface soils. *Environmental Science & Technology*. **1999**, *33*(11), 1864-1870.
- 656 [57] Corke, C.T.; Bunce, N.J.; Beaumont, A.L.; Merrick, R.L. Diazonium cations as  
657 intermediates in the microbial transformation of chloroanilines to chlorinated biphenyls,  
658 azo-compounds, and triazenes *Journal of Agricultural and Food Chemistry*. **1979**, *27*(3),  
659 644-646.
- 660 [58] Albers, C.N.; Banta, G.T.; Jacobsen, O.S.; Hansen, P.E. Characterization and structural  
661 modelling of humic substances in field soil displaying significant differences from  
662 previously proposed structures. *European Journal of Soil Science*. **2008**, *59*(4), 693-705.
- 663 [59] Stevenson, F.J. *Humus Chemistry: Genesis, Composition, Reactions*. Wiley & Sons: New  
664 York, 1994.
- 665 [60] Weber, E.J.; Colon, D.; Baughman, G.L. Sediment-associated reactions of aromatic amines.  
666 1. Elucidation of sorption mechanisms. *Environmental Science & Technology*. **2001**,  
667 *35*(12), 2470-2475.
- 668 [61] Weber, E.J.; Spidle, D.L.; Thorn, K.A. Covalent binding of aniline to humic substances .1.  
669 Kinetic studies. *Environmental Science & Technology*. **1996**, *30*(9), 2755-2763.
- 670 [62] Nagel, R. *Bioakkumulation und Verteilung von Umweltchemikalien in aquatischen*  
671 *Laborsystemen zur realitätsnahen Prognose der Umweltgefährlichkeit*, ed. U.F.-V.  
672 10603106/01. Berlin, 1997.
- 673 [63] Heim, K.; Schuphan, I.; Schmidt, B. Behavior of c-14 4-nitrophenol and c-14 3,4-  
674 dichloroaniline in lab sediment-water systems .1. Metabolic-fate and partitioning of  
675 radioactivity *Environmental Toxicology and Chemistry*. **1994**, *13*(6), 879-888.
- 676 [64] Dunnivant, F.M.; Jardine, P.M.; Taylor, D.L.; McCarthy, J.F. Cotransport of cadmium and  
677 hexachlorobiphenyl by dissolved organic-carbon through columns containing aquifer  
678 material *Environmental Science & Technology*. **1992**, *26*(2), 360-368.
- 679 [65] Huang, X.J.; Lee, L.S. Effects of dissolved organic matter from animal waste effluent on  
680 chlorpyrifos sorption by soils. *Journal of Environmental Quality*. **2001**, *30*(4), 1258-  
681 1265.
- 682 [66] Li, K.; Xing, B.S.; Torello, W.A. Effect of organic fertilizers derived dissolved organic  
683 matter on pesticide sorption and leaching. *Environmental Pollution*. **2005**, *134*(2), 187-  
684 194.
- 685 [67] Chiou, C.T.; Malcolm, R.L.; Brinton, T.I.; Kile, D.E. Water solubility enhancement of  
686 some organic pollutants and pesticides by dissolved humic and fulvic-acids  
687 *Environmental Science & Technology*. **1986**, *20*(5), 502-508.

- 688 [68] Guo, L.; Bicki, T.J.; Felsot, A.S.; Hinesly, T.D. Sorption and movement of alachlor in soil  
689 modified by carbon-rich wastes *Journal of Environmental Quality*. **1993**, 22(1), 186-  
690 194.
- 691 [69] Johnson, A.C.; Worrall, F.; White, C.; Walker, A.; Besien, T.J.; Williams, R.J. The  
692 potential of incorporated organic matter to reduce pesticide leaching. *Toxicological &*  
693 *Environmental Chemistry*. **1997**, 58, 47-61.
- 694 [70] Albers, C.N.; Banta, G.T.; Hansen, P.E.; Jacobsen, O.S. Effect of Different Humic  
695 Substances on the Fate of Diuron and Its Main Metabolite 3,4-Dichloroaniline in Soil.  
696 *Environmental Science & Technology*. **2008**, 42(23), 8687-8691.
- 697 [71] Freundlich, H.; Hatfield, H. *Colloid and Capillary Chemistry*. Methuen: London, 1926.
- 698 [72] Hsu, T.S.; Bartha, R. Interaction of pesticide-derived chloroaniline residues with soil  
699 organic-matter *Soil Science*. **1973**, 116(6), 444-452.
- 700 [73] Saxena, A.; Bartha, R. Microbial mineralization of humic-acid 3,4-dichloroaniline  
701 complexes *Soil Biology & Biochemistry*. **1983**, 15(1), 59-62.
- 702 [74] Giles, C.H.; Macewan, T.H.; Nakhwa, S.N.; Smith, D. Studies in adsorption .11. A system  
703 of classification of solution adsorption isotherms, and its use in diagnosis of adsorption  
704 mechanisms and in measurement of specific surface areas of solids *Journal of the*  
705 *Chemical Society*. **1960**, (OCT), 3973-3993.
- 706 [75] Polati, S.; Gosetti, F.; Gianotti, V.; Gennaro, M.C. Sorption and desorption behavior of  
707 chloroanilines and chlorophenols on montmorillonite and kaolinite. *Journal of*  
708 *Environmental Science and Health Part B-Pesticides Food Contaminants and*  
709 *Agricultural Wastes*. **2006**, 41(6), 765-779.
- 710 [76] Bouras, O.; Bollinger, J.C.; Baudu, M.; Khalaf, H. Adsorption of diuron and its degradation  
711 products from aqueous solution by surfactant-modified pillared clays. *Applied Clay*  
712 *Science*. **2007**, 37(3-4), 240-250.
- 713 [77] Autho, Adsorption-desorption phenomena, in *Interactions between Herbicides and the Soil*.  
714 Academic Press, 1980.
- 715 [78] Sheng, G.Y.; Xu, S.H.; Boyd, S.A. Mechanism(s) controlling sorption of neutral organic  
716 contaminants by surfactant-derived and natural organic matter. *Environmental Science &*  
717 *Technology*. **1996**, 30(5), 1553-1557.
- 718 [79] Gonzalez-Pradas, E.; Villafranca-Sanchez, M.; Fernandez-Perez, M.; Socias-Viciano, M.;  
719 Urena-Amate, M.D. Sorption and leaching of diuron on natural and peat-amended  
720 calcareous soil from Spain. *Water Research*. **1998**, 32(9), 2814-2820.
- 721 [80] Celis, R.; Barriuso, E.; Houot, S. Sorption and desorption of atrazine by sludge-amended  
722 soil: Dissolved organic matter effects. *Journal of Environmental Quality*. **1998**, 27(6),  
723 1348-1356.
- 724 [81] Nelson, S.D.; Farmer, W.J.; Letey, J.; Williams, C.F. Stability and mobility of napropamide  
725 complexed with dissolved organic matter in soil columns. *Journal of Environmental*  
726 *Quality*. **2000**, 29(6), 1856-1862.
- 727 [82] Lee, D.Y.; Farmer, W.J. Dissolved organic matter interaction with napropamide and four  
728 other nonionic pesticides. *Journal of Environmental Quality*. **1989**, 18, 468-474.
- 729 [83] Graber, E.R.; Gerstl, Z.; Fischer, E.; Mingelgrin, U. Enhanced transport of atrazine under  
730 irrigation with effluent (vol 59, pg 1513, 1995). *Soil Science Society of America Journal*.  
731 **1996**, 60(2), 424-424.
- 732 [84] Totsche, K.U.; Danzer, J.; KogelKnabner, I. Dissolved organic matter-enhanced retention  
733 of polycyclic aromatic hydrocarbons in soil miscible displacement experiments. *Journal*  
734 *of Environmental Quality*. **1997**, 26(4), 1090-1100.
- 735 [85] Huguenot, D.; Bois, P.; Jezequel, K.; Cornu, J.-Y.; Lebeau, T. Selection of low cost  
736 materials for the sorption of copper and herbicides as single or mixed compounds in  
737 increasing complexity matrices. *Journal of Hazardous Materials*. **2010**, 182(1-3), 18-26.

- 738 [86] Lyons, C.D.; Katz, S.E.; Bartha, R. Persistence and mutagenic potential of herbicide-  
739 derived aniline residues in pond water Bulletin of Environmental Contamination and  
740 Toxicology. **1985**, 35(5), 696-703.
- 741 [87] OECD OECD guidelines for testing of chemicals. 1992.
- 742 [88] CITI Data of existing chemicals based on the CSCL Japan. **1992**, 10-26, 32,33.
- 743 [89] Kuiper, J.; Hanstveit, A.O. Fate and effects of 3,4-dichloroaniline (dca) in marine plankton  
744 communities in experimental enclosures Ecotoxicology and Environmental Safety.  
745 **1984**, 8(1), 34-54.
- 746 [90] Bayer, A. Internal examination on the biological degradation of 2,4-, 2,5- and 3,4-  
747 dichloroaniline in samples of Rhine-water. **1992**.
- 748 [91] Brunsbach, F.R.; Reineke, W. Degradation of chloroanilines in soil slurry by specialized  
749 organisms Applied Microbiology and Biotechnology. **1993**, 40(2-3), 402-407.
- 750 [92] Struijs, J.; Rogers, J.E. Reductive dehalogenation of dichloroanilines by anaerobic  
751 microorganisms in fresh and dichlorophenol-acclimated pond sediment Applied and  
752 Environmental Microbiology. **1989**, 55(10), 2527-2531.
- 753 [93] Loidl, M.; Hinteregger, C.; Ditzelmuller, G.; Ferschl, A.; Streichsbier, F. Degradation of  
754 aniline and monochlorinated anilines by soil-born pseudomonas-acidovorans strains  
755 Archives of Microbiology. **1990**, 155(1), 56-61.
- 756 [94] Latorre, J.; Reineke, W.; Knackmuss, H.J. Microbial-metabolism of chloroanilines -  
757 enhanced evolution by natural genetic exchange Archives of Microbiology. **1984**,  
758 140(2-3), 159-165.
- 759 [95] Kim, Y.-M.; Park, K.; Kim, W.-C.; Han, W.-S.; Yu, C.-B.; Rhee, I.-K. Isolation and  
760 characterization of 3,4-dichloroaniline degrading bacteria. Korean Journal of  
761 Microbiology and Biotechnology. **2007**, 35(3), 245-249.
- 762 [96] Travkin, V.M.; Solyanikova, I.P.; Rietjens, I.; Vervoort, J.; van Berkel, W.J.H.; Golovleva,  
763 L.A. Degradation of 3,4-dichloro- and 3,4-difluoroaniline by Pseudomonas fluorescens  
764 26-K. Journal of Environmental Science and Health Part B-Pesticides Food  
765 Contaminants and Agricultural Wastes. **2003**, 38(2), 121-132.
- 766 [97] Surovtseva, E.G.; Ivoilov, V.S.; Karasevich Yu, N.; Vasil'Eva, G.K. Chlorinated anilines as  
767 a source of carbon nitrogen and energy for pseudomonas-diminuta Mikrobiologiya.  
768 **1985**, 54(6), 948-952.
- 769 [98] Sergeeva, N.R.; Sokolov, M.S.; Vasil'eva, G.K. Using bacteria to accelerate the  
770 decomposition of 3,4-dichloroaniline in fish ponds. Agrokhimiya. **1998**, 0(4), 84-90.
- 771 [99] Martinez Viera, R.; Alfonso Hernandez, M.M.; Castaneda Ruiz, R.F. Decomposition of 3 4  
772 dichloroaniline by microorganisms from two cuban soils Ciencias de la Agricultura.  
773 **1984**, (20), 117-124.
- 774 [100] Wasserfallen, A.; Zeyer, J.; Timmis, K.N. Bacterial metabolism and toxicity of  
775 halogenated anilines Experientia. **1986**, 42(1), 106-106.
- 776 [101] Sharma, P.; Chopra, A.; Cameotra, S.S.; Suri, C.R. Efficient biotransformation of  
777 herbicide diuron by bacterial strain Micrococcus sp. PS-1. Biodegradation. **2010**, 21(6),  
778 979-987.
- 779 [102] Devers-Lamrani, M.; Pesce, S.; Rouard, N.; Martin-Laurent, F. Evidence for cooperative  
780 mineralization of diuron by Arthrobacter sp. BS2 and Achromobacter sp. SP1 isolated  
781 from a mixed culture enriched from diuron exposed environments. Chemosphere. **2014**,  
782 117, 208-215.
- 783 [103] Surovtseva, E.G.; Ivoilov, V.S.; Vasileva, G.K.; Belyaev, S.S. Degradation of chlorinated  
784 anilines by certain representatives of the genera Aquaspirillum and Paracoccus.  
785 Microbiology. **1996**, 65(5), 553-559.

- 786 [104] Vasilyeva, G.K.; Bakhaeva, L.P.; Surovtseva, E.G. The Use of In Situ Soil Adsorptive  
787 Bioremediation Following an Accidental Spill of Propanide in the Krasnodar Region of  
788 Russia. *Land Contam. Reclam.* **1996**, *4*, 263-268.
- 789 [105] Carvalho, G.; Marques, R.; Lopes, A.R.; Faria, C.; Noronha, J.P.; Oehmen, A.; Nunes,  
790 O.C.; Reis, M.A.M. Biological treatment of propanil and 3,4-dichloroaniline: Kinetic and  
791 microbiological characterisation. *Water Research.* **2010**, *44*(17), 4980-4991.
- 792 [106] Emmanuel Herrera-Gonzalez, V.; Ruiz-Ordaz, N.; Galindez-Mayer, J.; Juarez-Ramirez,  
793 C.; Santoyo-Tepole, F.; Marron Montiel, E. Biodegradation of the herbicide propanil,  
794 and its 3,4-dichloroaniline by-product in a continuously operated biofilm reactor. *World  
795 Journal of Microbiology & Biotechnology.* **2013**, *29*(3), 467-474.
- 796 [107] Yih, R.Y.; McRae, D.H.; Wilson, H. *Science. Vol. 161.* Washington D.C., 1968.
- 797 [108] Still, G. *Science. Vol. 159.* Washington D.C., 1968.
- 798 [109] Fuchsichler, G.; Suss, A.; Wallnofer, P. Uptake of 4-chloro-chloraniline and 3,4-  
799 dichloroaniline by cultivated plants *Zeitschrift Fur Pflanzenkrankheiten Und  
800 Pflanzenschutz-Journal of Plant Diseases and Protection.* **1978**, *85*(5), 298-307.
- 801 [110] Arjmand, M.; Sandermann, H. Mineralization of chloroaniline lignin conjugates and of  
802 free chloroanilines by the white rot fungus *phanerochaete-chrysosporium* *Journal of  
803 Agricultural and Food Chemistry.* **1985**, *33*(6), 1055-1060.
- 804 [111] Funtikova, N.S.; Surovtseva, E.G. Adsorption of herbicides derivatives of phenyl urea and  
805 chloro substituted anilines by microorganisms *Mikrobiologiya.* **1979**, *48*(6), 1086-1092.
- 806 [112] Pieper, D.H.; Winkler, R.; Sandermann, H. Formation of a toxic dimerization product of  
807 3,4-dichloroaniline by lignin peroxidase from *phanerochaete-chrysosporium*  
808 *Angewandte Chemie-International Edition in English.* **1992**, *31*(1), 68-70.
- 809 [113] Pavlovic, I.; Barriga, C.; Hermosin, M.C.; Cornejo, J.; Ulibarri, M.A. Adsorption of acidic  
810 pesticides 2,4-D, Clopyralid and Picloram on calcined hydrotalcite. *Applied Clay  
811 Science.* **2005**, *30*(2), 125-133.
- 812 [114] Ho, Y.S.; McKay, G. The kinetics of sorption of basic dyes from aqueous solution by  
813 sphagnum moss peat. *Canadian Journal of Chemical Engineering.* **1998**, *76*(4), 822-827.
- 814 [115] Meier, L.P.; Nueesch, R.; Madsen, F.T. Organic Pillared Clays. *Journal of Colloid and  
815 Interface Science.* **2001**, *238*(1), 24-32.
- 816 [116] Bansal, R.C.; Donnet, J.-B.; Stoeckli, F. *Active Carbon.* New York, 1988.
- 817 [117] Malandrino, M.; Abollino, O.; Giacomino, A.; Aceto, M.; Mentasti, E. Adsorption of  
818 heavy metals on vermiculite: Influence of pH and organic ligands. *Journal of Colloid and  
819 Interface Science.* **2006**, *299*(2), 537-546.
- 820 [118] Chanda, M.; O'Driscoll; Rempel, G.L. *Reactive Polymers.* 1984
- 821 [119] Davankov, V.A.; Navratil, J.D.; Walton, H.F. *Ligand Exchange Chromatography.* CRC  
822 Press: US, 1988.
- 823 [120] Joo, S.H.; Feitz, A.J.; Sedlak, D.L.; Waite, T.D. Quantification of the oxidizing capacity  
824 of nanoparticulate zero-valent iron. *Environmental Science & Technology.* **2005**, *39*(5),  
825 1263-1268.
- 826 [121] Cabrera, L.C.; Caldas, S.S.; Rodrigues, S.; Bianchini, A.; Duarte, F.A.; Primel, E.G.  
827 Degradation of Herbicide Diuron in Water Employing the Fe-0/H<sub>2</sub>O<sub>2</sub> System. *Journal of  
828 the Brazilian Chemical Society.* **2010**, *21*(12), 2347-2352.
- 829 [122] Willberg, D.M.; Lang, P.S.; Hochemer, R.H.; Kratel, A.; Hoffmann, M.R. Degradation of  
830 4-chlorophenol, 3,4-dichloroaniline, and 2,4,6-trinitrotoluene in an electrohydraulic  
831 discharge reactor. *Environmental Science & Technology.* **1996**, *30*(8), 2526-2534.
- 832 [123] Lodha, S.; Vaya, D.; Ameta, R.; Punjabi, P.B. Photocatalytic degradation of Phenol Red  
833 using complexes of some transition metals and hydrogen peroxide. *Journal of the Serbian  
834 Chemical Society.* **2008**, *73*(6), 631-639.

- 835 [124] Feng, J.; Liu, R.; Chen, P.; Yuan, S.; Zhao, D.; Zhang, J.; Zheng, Z. Degradation of  
836 aqueous 3,4-dichloroaniline by a novel dielectric barrier discharge plasma reactor.  
837 Environmental Science and Pollution Research. **2015**, 22(6), 4447-4459.
- 838 [125] Haag, W.R.; Yao, C.C.D. Rate constants for reaction of hydroxyl radicals with several  
839 drinking-water contaminants Environmental Science & Technology. **1992**, 26(5), 1005-  
840 1013.
- 841 [126] Ambrus, Z.; Mogyorósi, K.; Szalai, Á.; Alapi, T.; Demeter, K.; Dombi, A.; Sipos, P. Low  
842 temperature synthesis, characterization and substrate-dependent photocatalytic activity of  
843 nanocrystalline TiO<sub>2</sub> with tailor-made rutile to anatase ratio. Applied Catalysis A:  
844 General. **2008**, 340(2), 153-161.

845

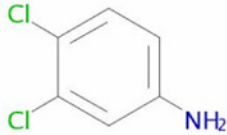
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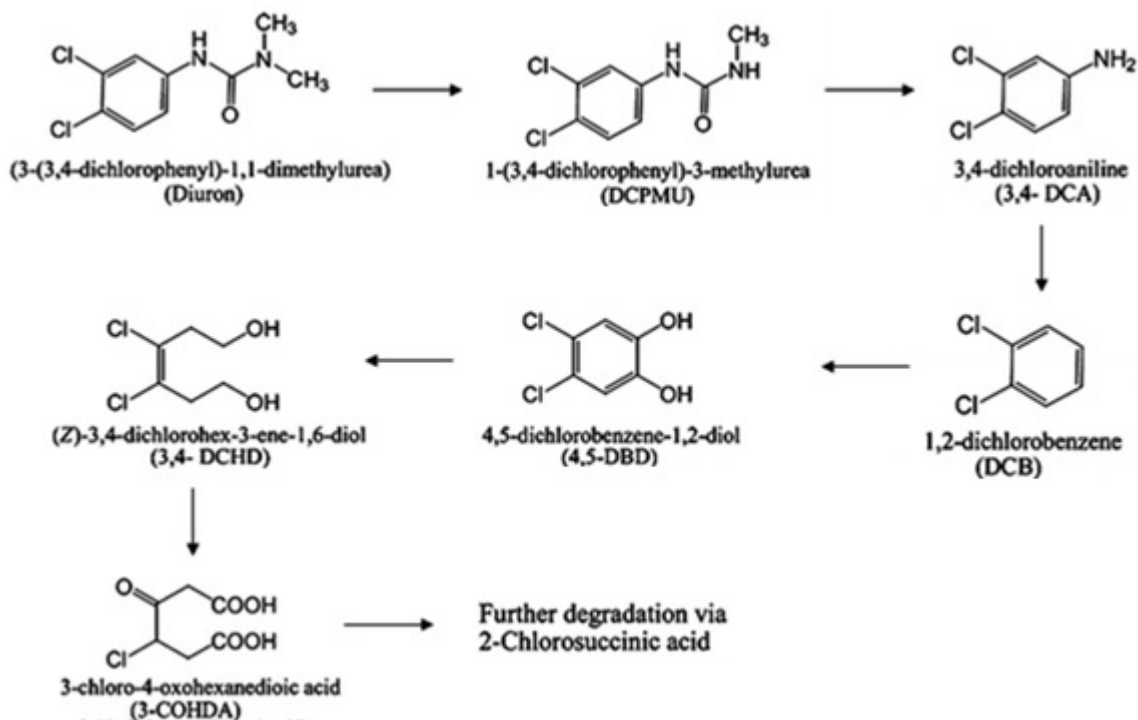
847 **Figures and Tables**

848 Figures and tables are listed below.

849 **Table 1.** Properties of 3,4-dichloroaniline

Property	Value	Ref.
Molecular formula	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> N	-
Molecular structure		[15]
Appearance	Solid at 293 K	[15]
Molecular weight	162 g mol <sup>-1</sup>	[15]
Molecular size	0.35 nm <sup>2</sup>	[50]
Henry's constant	0.05 Pa m <sup>3</sup> mol <sup>-1</sup>	[15]
Solubility in water	580 mg L <sup>-1</sup> at 293 K	[15]
Octanol-water partition coefficient (log K <sub>ow</sub> )	2.7 (shaken flask method)	[5, 16]
Estimated surface water half life	18 days	[15]
Measured rate of loss from outdoor water systems	0.11 - 0.17 day <sup>-1</sup>	[4]
	0.06 - 0.14 day <sup>-1</sup>	[49]
Estimated atmospheric half life	9 hours	[15]
Estimated half-life in soil and sediment	470 - 1500 days	[51]

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852 **Figure 1.** Degradation pathway of diuron by *Micrococcus* sp, confirmed by FTIR spectra and

853 HPLC <sup>[101]</sup>

854 **Table 2.** Surface area, pore size and adsorption data of different material tested for the removal

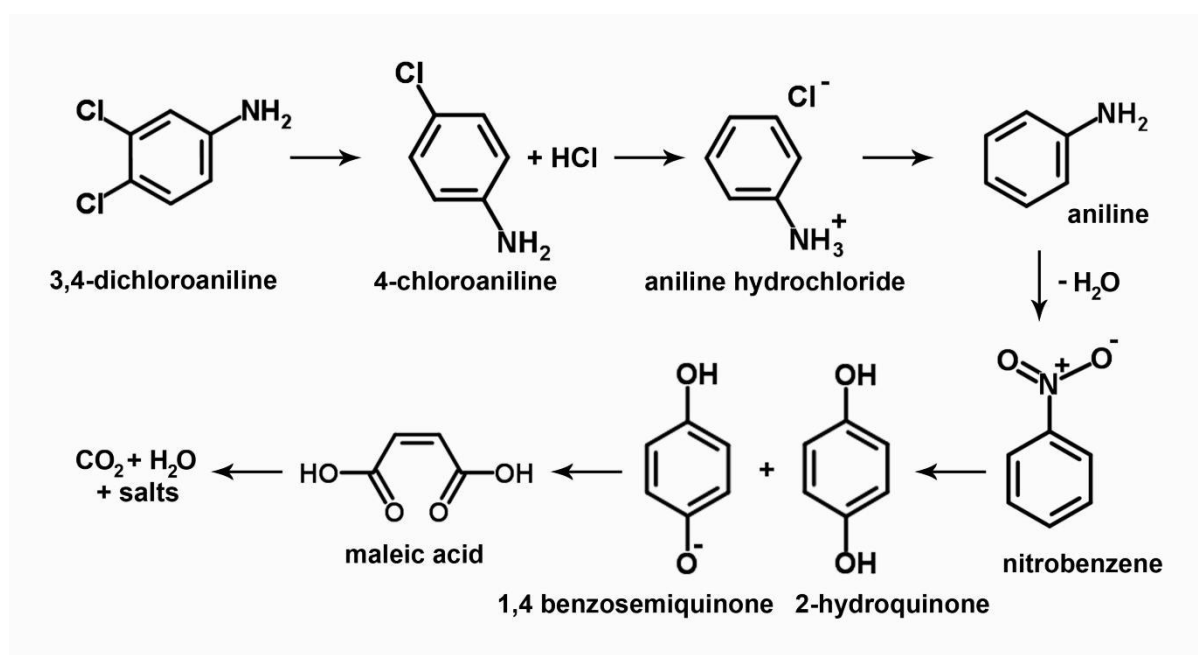
855 of 3,4-DCA from water. The parameters  $q_m$  and  $b$  refer to the Langmuir model (Equation 3)

Adsorbent	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	$q_m$ (mg g <sup>-1</sup> )	$b$ (mL mg <sup>-1</sup> )	Equilibrium time (h)	Stirring method
Halloysite <sup>[12]</sup>	76.6	0.039	0.078	2.726	> 3	Rotary stirrer
Kaolinite <sup>[75]</sup>	-	-	0.311	9	> 96	Electromagneti c
Montmorillonit e <sup>[75]</sup>	-	-	0.077	23	> 96	Electromagneti c
Activated	963	0.55	583	-	48	-

carbon AG <sup>[50]</sup>						
Activated carbon SKT <sup>[50]</sup>	1028	0.53	480	-	0.5	-
Activated carbon RS <sup>[50]</sup>	410	0.5	364	-	0.5	-

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859 **Figure 2.** Intermediates formed during photo-degradation of 3,4-DCA using Ti-V (sol) catalyst,

860 confirmed by HPLC and GC-MS analysis <sup>[11]</sup>

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