Liquid chromatography–high-resolution mass spectrometry for identifying aqueous chlordecone hydrate dechlorinated transformation products formed by reaction with zero-valent iron

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Chlordecone (CLD) is a persistent toxic chlorinated pesticide which contaminates different ecosystems in French West Indies. A soil remediation process including zero-valent iron (ZVI) has produced promising results but failed to completely degrade CLD, and the analytical procedures used yielded little information on the transformation products. To fill these gaps, dechlorination of aqueous CLD by micrometric particles of ZVI has been investigated. Aliquots of water with 25\% (v/v) of acetone spiked with 100 ppm CLD were taken at different times during a 30-day ZVI treatment and directly analysed by ultra-high-performance liquid chromatography in negative electrospray ionisation mode. CLD has been totally transformed after 14 days into 14 dechlorinated degradation products, including 9 isomeric compounds. The maximum chloride concentrations appearing in the medium represent 44\% of that which would result from total dechlorination of CLD. The CLD transformation products identified by accurate mass measurements on an ultra-high-resolution Q-TOF mass spectrometer (Q-TOF-MS) were \(\text{C}_{10}\text{H}_{3}\text{Cl}_{9}\text{O}_{2}\), \(\text{C}_{10}\text{H}_{4}\text{Cl}_{8}\text{O}_{2}\), \(\text{C}_{10}\text{H}_{5}\text{Cl}_{7}\text{O}_{2}\), \(\text{C}_{10}\text{H}_{6}\text{Cl}_{6}\text{O}_{2}\) and \(\text{C}_{10}\text{H}_{7}\text{Cl}_{5}\text{O}_{2}\). The results show the interest of LC-Q-TOF-MS for identifying transformation products of organic contaminants, and the effectiveness of micrometric ZVI particles to totally transform CLD into less chlorinated products.

**Keywords:** chlordecone; Kepone; reductive dechlorination; zero-valent iron; remediation; ultra-high-resolution Q-TOF mass spectrometer

1. Introduction

Chlordecone (CLD), also known as Kepone\textsuperscript{®} (\(\text{C}_{10}\text{Cl}_{10}\text{O}\); CAS name: 1,1a,3,3a,4,5,5a,5b,6-decachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalen-2-one), is a toxic organochlorine insecticide which has been widely used against the banana weevil in the French West Indies (FWI) between 1972 and 1993 [1]. The arable land area at high risk of Kepone\textsuperscript{®} contamination in the FWI often covers the recharge areas of ground and surface water abstraction wells [1,2]. CLD still pollutes waters and soils and may have a half-life in soils of several decades or centuries [1], generating contamination of freshwater fauna, seafood and plant products [3,4]. Statutory limitations on human consumption were issued for vegetables in 2003, and bans on consumption and commercialisation of fish and sea food have recently been issued [5]. Furthermore, recent studies showed that exposure to CLD can increase risks of prostate cancer [6] and have a negative impact on the cognitive, visual and motor development of infants [7–9].
It is clear that the bioaccumulation of CLD, together with its poor biodegradability, makes this compound of special concern for ecological, economical and health considerations. Several ongoing research projects address various aspects of the fate of CLD at different scales, including possible means of remediation [10–13].

CLD is a stable tan to white, crystalline, odourless solid which decomposes over 350°C. It is soluble in acetone, lower aliphatic alcohols and somewhat soluble in benzene, toluene and hexane. Its aqueous solubility is 1.75–2.37 ppm for the most common environmental pH (4–8) and increases progressively under more alkaline conditions up to 176 ppm for a pH of 10.9 [14]. Its affinity for organic matter (17500 L/kg [15] and log $K_{oc}$ between 3.38 and 3.41 [16] corresponding to 2000–2500 L/kg) and partition ratio between octanol and water (log $K_{ow} = 4.6–5.6$) are high. Infrared and nuclear magnetic resonance (NMR) analysis in solution indicated that CLD exists in benzene as a mixture of ketone form ($C_{10}Cl_{10}O$, Figure 1a) and gem-diol form ($C_{10}H_{2}Cl_{10}O_{2}$; CLD hydrate, Figure 1b), as the gem-diol form in acetonitrile and as the hemiketal form ($C_{11}H_{4}Cl_{10}O_{2}$, Figure 1c) in methanol [17]. By contrast, no such data are available on the CLD form in aqueous solution, even though this matrix is of utmost importance for environmental issues. The persistence of CLD in the environment can be explained by its poor biodegradability [18,19] due to its chemical structure and high steric hindrance.

Very few data are available on the transformation products of CLD. US patent 4,144,152 used UV radiation, with and without added hydrogen, over a range of pH values [20]. With UV radiation and added hydrogen in alkaline aqueous or methanol solution, and based on the chlorine mass balance, the study indicated that 6–8 chlorine atoms were removed from CLD [20]. However, no identification of transformation products has been performed in this study. According to Reimers et al. in a general review about the treatment of toxic substances, the formation of mono-, di-, tri-, tetra- and penta-hydro CLD derivatives was apparently observed during the UV+H$_2$ process, but the original source of this information and the corresponding detailed information seem to be unavailable in the literature [21]. In another study, two photoproducts of CLD were determined by NMR spectroscopy to be chlordecone-5b-hydro (CAS nomenclature: 1,1a,3,3a,4,5,5a,5b-nonachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalen-2-one) and 5b,6-dihydrochlordecone (CAS: 1,1a,3,3a,4,5,5a-octachlorooctahydro-1,3,4-metheno-2 H-cyclobuta[cd]pentalen-2-one) [22]. Microbial transformation of CLD by Pseudomonas aeruginosa strain K03 in aerobic enrichment culture showed the formation of products identified by gas chromatography coupled with mass spectrometry using authentic standards as being a monohydrochlordecone and a dihydrochlordecone identical to the photoproducts described above [23]. Schrauzer and Katz showed that CLD could be degraded in vitro under reducing conditions with stoichiometric and catalytic reaction of vitamin B$_{12}$, forming less chlorinated metabolites, from –1 to –7 Cl; the authors do not however give any indication as to how they determined the structures of these compounds [24].

Such laboratory studies, the conditions they require and the processes they involve did not lead to possible applications to remediation in field situations. By contrast, in situ chemical reduction (ISCR), which aims at promoting both chemical reduction and biodegradation through cycles of oxic-anoxic phases [25], is an established process for the remediation of soils and groundwater contaminated by chlorinated herbicides and pesticides (e.g. Dieldrin and toxaphene) [26]. Daramend®, the key component of ISCR for soils, combines solid controlled-released carbon and micro-scale zero-valent iron (ZVI). After 6 months of ISCR treatment with Daramend® in laboratory conditions, the concentration of CLD in historically impacted FWI soils decreased by 20% in andosol and 70% in ferralsol and nitisol [13,27]. These soils correspond to the three main types of volcanic soils on which banana were grown in the FWI. This promising study however provides only limited information on the nature of the
transformation products, nor does it quantify the respective role of the organic constituent of Daramend, on the one hand, and ZVI, on the other hand.

ZVI has been found to be a suitable and cost-effective donor of electrons for the in situ remediation of groundwater and soil contaminated with chlorinated organic compounds such as trichloroethylene and tetrachloroethylene [28], trichloroethane [29] and 1,1,1-trichloro-2,2-

Figure 1. Structures and carbon numbering according to CAS nomenclature of (a) chlordecone, (b) chlordecone hydrate, (c) chlordecone as the hemiketal form, (d) chlordecol, (e) hydro-5b-chlordecone-hydrate, (f) hydro-5a-chlordecone-hydrate, (g) hydro-5-chlordecone-hydrate and (h) hydro-3-chlordecone-hydrate.
bis\((p\text{-chlorophenyl})\text{ethane} [30]. The possible effect of ZVI on a chlorinated organic compound with cage structure such as CLD has however never been studied.

The goal of the present work was therefore to study the reductive transformation of CLD by ZVI, with a special focus on the characterisation of the transformation products by high-resolution mass spectrometry coupled with ultrahigh-performance liquid chromatography. Identification of CLD degradation products is a challenging issue since only two metabolites, chlordecol (Figure 1d) and chlordecone-5b-hydro (Figure 1e), are presently available as analytical standards. Furthermore, the only two published studies that analysed the CLD transformation products used gas chromatography coupled with mass spectrometry with chemical [17] and electron ionisations [17,24], a technique that is not the most appropriate for characterisation of unknown CLD transformation products. Indeed, the electronic ionisation can lead to a lot of fragments and the absence of molecular ions, and the chemical ionisation needs optimisation with appropriate reagent gases. By contrast, liquid chromatography coupled to mass spectrometry (LC-MS) is the most suitable technique for analytes with a wide range of polarities, as can be expected for CLD dechlorinated transformation products. LC-MS has however been used only to study the CLD in spiked bananas, at that time with moving belt-interface and chemical ionisation using methane and ammonia as reagent gases [31], and recently using electrospray ionisation in standard solutions [32] and surface and wastewaters [33]. Moreover, when the identification of transformation products is a major objective, as in our study, high-resolution mass spectrometry (HRMS) such as an ultra-high-resolution quadrupole-time-of-flight mass spectrometer (UHR-Q-TOF-MS) is the most adequate technique as it enables accurate mass measurements and separation of isobaric interferences. The present work therefore combines liquid chromatography with the high-resolution mass spectrometry for the study of CLD and its transformation products.

2. Experimental

2.1 Reagents

Certified CLD hydrate solid with a purity (% area of all chromatographic peaks) of 99.9% (ref. 49046) was purchased from Supelco (Bellefonte, PA, USA), and chlordecone-5b-hydro solution at 10 ng/µL in cyclohexane with a purity of 98% (ref. LA11220200CY) from Dr. Ehrenstorfer GmbH (Augsburg, Germany). According to the CAS nomenclature rule, chlordecone-5b-hydro should be named chlordecone-6-hydro because position 6 = 5b, but since it is commercialised and known as chlordecone-5b-hydro, this name has been used here to avoid confusion. Chlordecol with a purity of 98% (CAS number: 1034–41-9) was purchased from Alpha Chimica (Châtenay-Malabry, France). ZVI was provided by Lovink Technocast BV (Terborg, The Netherlands), particles (dry sieving) between 250 and 400 µm represent 40% of the total mass, 160–250 µm particles represent 12% and 50–160 µm particles constitute 48%. HPLC-grade acetonitrile and acetone were purchased from Carlo-Erba (Val-de-Reuil, France). Ultrapure water was obtained by purifying water in an Elgastat UHQ II filtration system (Elga, Antony, France) (its chloride concentration was lower than the limit of quantification, 0.5 mg/L). Chloride standard solution (1000 mg/L) (ref. 19897) was purchased from Merck (Darmstadt, Germany).

2.2 Batch experiments

A 10000 mg/L stock solution of CLD hydrate was prepared in acetonitrile and stored at 4°C. A 100 mg/L of CLD hydrate solution was prepared by injecting the appropriate volume of stock
solution into a mixture of 1.120 L of deoxygenated (purging with \( \text{N}_2 \) 99.9%) ultrapure water and 0.380 L of acetone to maximise the solubilisation of CLD. The final solutions (25% acetone, v/v) were manually agitated for 5 min. Batch experiments were conducted using 40 mL vials with Teflon-lined septum caps that were filled with 30 mL of the spiked aqueous solution (10 mL headspace was \( \text{N}_2 \) gas). Also, 0.2 g of ZVI was added to each vial. The vials were continually shaken using an end-over-end shaker Reax 2 (Heidolph, Schwalbach, Germany) at 40 rpm at room temperature (27 ± 3°C) in the dark in a glove box under \( \text{N}_2 \) atmosphere. Control vials were prepared exactly the same way, except for ZVI that was not added.

Triplicate vials with and without ZVI were randomly selected and were taken after 4 h, 2, 7, 14, 21 and 30 days when 3 mL aliquots from each vial were taken for analysis of CLD and transformation products by liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS), and analysis of chloride by ion chromatography (IC). The oxidation-reduction potential (ORP) was measured in the remaining 27 mL of each vial in the glove box under \( \text{N}_2 \) atmosphere using InLab\textsuperscript{®} Redox Combined electrode (Pt/Ag/AgCl, 3 M KCl) (Mettler Toledo, Schwerzenbach, Switzerland). The ORP reading was taken after 30 min of equilibration, when the variation over two successive minutes was less than 0.5 mV. The redox potential values given in the paper will be expressed in mV versus the standard hydrogen electrode. The direct ORP readings were converted to the standard hydrogen electrode potential by adding the measured ORP value of the standard buffer solution (220 mV) to the direct ORP readings.

2.3 **Instrumentation conditions**

2.3.1 **Chloride analysis**

Chloride concentrations in aqueous solution were measured using a Dionex ICS-3000 system (Dionex-ThermoScientific, Sunnyvale, CA) with an AS autosampler and eluant generator (KOH cartridge, 058900). Chloride ions were separated with an IonPac AS15 anion-exchange column (250 × 4 mm i.d., Dionex) coupled with an IonPac AG15 (50 × 4 mm i.d.) guard column. The column was thermostated at 35°C. The eluent was isocratic 20 mM KOH. The flow rate was 1.2 mL/min, and the injection volume was 100 µL. The limit of quantification was 0.5 mg/L.

2.3.2 **CLD and degradation products analysis**

Analysis were performed using an UltiMate 3000 RS LC system equipped with a binary pump, an autosampler and a thermostated column compartment (Dionex, Germering, Germany). The column was an Acquity UPLC BEH C18 (1.7 µm, 100 × 2.1 mm) (Waters, Manchester, UK) fitted with a C18 SecurityGuard Ultra (2.1 mm) guard filter (Phenomenex, Le Pecq, France). The mobile phase consisted of water (solvent A) and acetonitrile (solvent B). The composition was 10% B for 3 min, followed by a linear gradient reaching 100% B at 30 min, returning to initial conditions in 1 min and re-equilibrating for 3 min. The column was thermostated at 40°C. The flow rate was set to 350 µL/min. The injection volume was 1 µL. MS experiments were carried out on a maXiS UHR-Q-TOF mass spectrometer (Bruker, Bremen, Germany) (resolution was 25,000) in negative electrospray ionisation mode. Capillary voltage was set to 4.5 kV. The flows of nebulising and drying gas (nitrogen) were respectively set at 1.2 bar and 12 L/min, and drying gas was heated at 200°C. Mass spectra were recorded at 1 Hz in the range of 50 to 1700 m/z. Calibration was performed using ESI-TOF tuning mix (Agilent, Palo Alto, CA, USA) and lock masses at m/z 666.0199 and 1265.9816 were used for calibration corrections.
Chemical formulae were generated using accurate mass measurements and the Smart Formula™ algorithm from DataAnalysis 4.0 software (Bruker). The algorithm calculates all possible formulae according to criteria fixed by the user, in our case mass tolerance \( \leq 4 \) ppm; even electron configuration; authorised atoms were C, H, O and Cl; number of chlorine atoms was adjusted according to isotopic profile, and a minimum of four carbon atoms was set.

3. Results and discussion

3.1 Evolution over time of CLD hydrate and chloride concentrations

The CLD hydrate concentration in the vials with ZVI decreased to 62\% of that in the control after 2 days and was lower than our limit of detection (20 ppb) after 14 days, indicating complete transformation of CLD hydrate (Figure 2). In the control vials without ZVI, no decrease in CLD hydrate concentration was observed, which indicates that the CLD hydrate removal in the presence of ZVI is not due to sorption on the glass walls of the vials or their Teflon septa.

Chloride in the controls remained below 1 mg/L. The evolution over time of chloride concentrations in the vials with ZVI is the inverse of that observed for CLD hydrate up to day 14 when all CLD hydrate has been transformed. In the vials with ZVI, chloride reached 4.6 \( \pm \) 0.9 mg/L (which represents 7\% of the chloride concentration that would result from total dechlorination of the CLD hydrate added at the start of the experiment – Cl\(_T\)) already after 2 days, showing the most rapid increase during the first 2–7 days (from 7\% to 27\% of Cl\(_T\)), and reached after 30 days (end of the experiment) a maximum value of 30.3 \( \pm \) 0.4 mg/L (Figure 2), which represents 44\% of Cl\(_T\). Now, a mass balance of 44\% chloride formed may reflect an infinite number of combinations between levels of dechlorination (from 1 to 10 Cl removed), on the one hand, and the percentage of CLD hydrate with any of these 10 levels of dechlorination,
on the other hand. Whatever the actual combination (which could not be determined with the data available here), 44% is a very significant dechlorination, all the more so for a compound known to be highly persistent \(^{1,34}\). The analysis of CLD hydrate transformation products, presented below, will yield complementary information on the levels of dechlorination actually reached.

### 3.2 Analysis of CLD and its transformation products by LC-Q-TOF-MS

The spectrum of CLD hydrate analytical grade standard revealed the presence of an ion at \(m/z\) 502.6856 (Figure 3) corresponding to \([\text{C}_{10}\text{HCl}_{10}\text{O}_{2}]^-\). Our studies by \(^{13}\text{C}\) NMR (supplementary material) and X-ray diffraction (data not shown) indicated that the molecule observed in our conditions is a CLD hydrate under the form of a gem-diol (Figure 1b), which confirmed that the ion observed at \(m/z\) 502.6856 corresponds to \([\text{M-H}]^-\).

Identification of degradation products was performed in aliquots taken after each of the reaction times, 4 h, 2, 7, 14, 21 and 30 days. Previous studies identified chlordecone-5b-hydro as a degradation product of CLD by photodegradation \(^{22}\), microbial transformation \(^{23}\) and vitamin B\(_{12}\) \(^{24}\). We formulated the hypothesis that CLD hydrate was degraded into a monohydrochlordecone-hydrate with gem-diol form \(\text{C}_{10}\text{H}_3\text{Cl}_9\text{O}_2\) whose isotopic distribution of the deprotonated ion \([\text{C}_{10}\text{H}_2\text{Cl}_9\text{O}_2]^-\) and corresponding intensities in brackets are the following: \(m/z\) 468.7257 (27); \(m/z\) 470.7228 (78); \(m/z\) 472.7198 (100); \(m/z\) 474.7169 (75); \(m/z\) 476.7139 (36) and \(m/z\) 478.7109 (12). Proceeding with extracted ion chromatogram at \(m/z\) 468.7257 ± 0.005, we highlighted two chromatographic peaks (Figure 4) at RT = 16.5 min (peak 12) and 17.4 min (peak 14) corresponding to two isomeric compounds with \(\text{C}_{10}\text{H}_3\text{Cl}_9\text{O}_2\) formula. We confirmed by comparison with the standard substance that the compound at RT = 17.4 min (peak 14) corresponds to chlordecone-5b-hydro-hydrate (Figure 1e).

The second isomeric compound at RT = 16.5 min (peak 12) could not be identified since no standard is available; the detailed characterisation of the two isomers required therefore MS/MS experiments. The MS/MS spectra obtained at collision energies of 20, 25 and 30 eV were very similar for the two isomeric compounds, with fragments at \(m/z\) 352 corresponding to \([\text{C}_9\text{Cl}_7]^-\).

![Figure 3](image_url) (a) TOF mass spectrum for the standard solution of CLD hydrate at 100 ppm in water/acetone (80/20) (v/v) with (b) observed and (c) theoretical isotope distributions of the \([\text{M-H}]^-\).
m/z 388 corresponding to [C₉HCl₈]⁻, m/z 416 corresponding to [C₁₀HCl₉O]⁻ and m/z 432 corresponding to [C₁₀HCl₉O₂]⁻. By contrast, the ion at m/z 450 corresponding to [C₁₀Cl₉O]⁻ by loss of H₂O is only present in chlordecone-5b-hydro-hydrate (Figure 5). The loss of H₂O has not been observed with the LC-MS as a fragment of CLD hydrate [32], which indicates that the ion m/z 450 is characteristic of the presence of hydrogen in the molecule. The fact that the ion m/z 450 is observed only for chlordecone-5b-hydro-hydrate may be due to the proximity of hydrogen (in position 5b) with the gem-diol function. The absence of the ion m/z 450 for the compound at RT = 16.5 min (peak 12) suggests that the hydrogen is not as close to the gem-diol function as it is in chlordecone-5b-hydro-hydrate. This being said, there remains however several possible structures for the compound of peak 12 as dechlorination can occur on the position 5, 5a, 4, 1a and 3 (CAS nomenclature). Since the positions 5a and 4, on the one hand, and the positions 1a and 3, on the other hand, are identical by rotation on the C2–C5 axis, and applying the CAS rules giving the name of a substance according to the hydrogen-carrying carbon with the highest number, compound 12 at RT = 16.5 min can only be, using CAS nomenclature, hydro-5a-chlordecone-hydrate (Figure 1f), or hydro-5-chlordecone-hydrate (Figure 1g) or hydro-3-chlordecone-hydrate (Figure 1h). The hydro-3-chlordecone-hydrate is the less probable structure of monohydrochlordecone-hydrate (peak 12) at RT = 16.5 min since the hydrogen in position 3 in the vicinity of the gem-diol favours the loss of H₂O. Thus, we can deduce the hypothesis that the monohydrochlordecone-hydrate (peak 12) at RT = 16.5 min is the hydro-5a-chlordecone-hydrate (Figure 1f) or the hydro-5-chlordecone-hydrate (Figure 1g).

Table 1 summarises the final mass measurements, errors and empirical formulae of the transformation products detected in the vials with ZVI (no transformation product was detected at any sampling time in the undiluted samples of the control vials) at 14 days (sole sampling time when all 14 compounds are present, and first sampling time when the CLD hydrate has

Figure 4. Extracted ion chromatograms (EIC) of an aliquot sample taken from (a) a control vial without ZVI at day 30 diluted 10 times; (b) a ZVI treated vial at day 14; (c) a ZVI treated vial at day 30. The peak numbers given in increasing order of retention time are used throughout the text.
Figure 5. (1) TOF mass spectrum of the degradation product of CLD hydrate taken at retention time of 16.5 min (peak 12); (2) TOF-MS/MS spectra of m/z 468 at 25 eV of (a) compound 12 at RT = 16.6 min and (b) hydro-5b-chlordecone at 17.6 min.

Table 1. Retention time, measured m/z, formula of deprotonated ion, calculated m/z and accuracy (ppm) of the 14 degradation products observed in an aqueous aliquot after 14 days of degradation of CLD hydrate (peak 15; peak 14 = chlordecone-5b-hydro-hydrate) by zero-valent iron.

| Peak | Retention time (min) | Measured m/z | [M-H]$^-$ formula | Calculated m/z | Accuracy [ppm] |
|------|----------------------|--------------|--------------------|----------------|----------------|
| 1    | 11.1                 | 332.8827     | C$_{10}$H$_6$Cl$_5$O$_2$ | 332.8816       | 0.35           |
| 2    | 12.3                 | 366.8426     | C$_{10}$H$_5$Cl$_6$O$_2$ | 366.8426       | -0.75          |
| 3    | 12.9                 | 366.8424     | C$_{10}$H$_5$Cl$_6$O$_2$ | 366.8426       | -2.72          |
| 4    | 13.7                 | 366.8418     | C$_{10}$H$_5$Cl$_6$O$_2$ | 366.8426       | -2.72          |
| 5    | 14.1                 | 400.8024     | C$_{10}$H$_4$Cl$_7$O$_2$ | 400.8036       | 0.18           |
| 6    | 14.4                 | 400.8026     | C$_{10}$H$_4$Cl$_7$O$_2$ | 400.8036       | 2.60           |
| 7    | 14.7                 | 434.7635     | C$_{10}$H$_3$Cl$_8$O$_2$ | 434.7647       | -0.9           |
| 8    | 15.0                 | 400.8027     | C$_{10}$H$_3$Cl$_8$O$_2$ | 400.8036       | 1.37           |
| 9    | 15.4                 | 434.7636     | C$_{10}$H$_3$Cl$_8$O$_2$ | 434.7647       | -0.74          |
| 10   | 15.6                 | 434.7640     | C$_{10}$H$_3$Cl$_8$O$_2$ | 434.7647       | -0.81          |
| 11   | 15.8                 | 434.7640     | C$_{10}$H$_3$Cl$_8$O$_2$ | 434.7647       | -0.07          |
| 12   | 16.5                 | 468.7257     | C$_{10}$H$_2$Cl$_9$O$_2$ | 468.7257       | -0.89          |
| 13   | 16.4                 | 434.7639     | C$_{10}$H$_2$Cl$_9$O$_2$ | 434.7647       | -1.41          |
| 14   | 17.4                 | 468.7249     | C$_{10}$H$_2$Cl$_9$O$_2$ | 468.7257       | 0.43           |
| 15   | 18.6                 | 502.6854     | C$_{10}$HCl$_{10}$O$_2$ | 502.6867       | -2.9           |
been totally transformed by the ZVI). The 14 products consist of 2 isomers corresponding to \( \text{C}_{10}\text{H}_3\text{Cl}_9\text{O}_2 \) formula, 5 to \( \text{C}_{10}\text{H}_4\text{Cl}_8\text{O}_2 \), 3 to \( \text{C}_{10}\text{H}_5\text{Cl}_7\text{O}_2 \) and \( \text{C}_{10}\text{H}_6\text{Cl}_6\text{O}_2 \) and 1 to \( \text{C}_{10}\text{H}_7\text{Cl}_5\text{O}_2 \).

Chlordecol (Figure 1d), which results from reduction of the CLD to chlordecone alcohol, has been identified as the only end product of CLD metabolism in man and some mammals [35,36]. Chlordecol and alcohol dechlorinated transformation products have been detected by reductive reaction of the CLD with vitamin B\(_{12}\)'s [24]. In our conditions, no chlordecol or any alcohol dechlorinated product of CLD hydrate has been detected (data not shown), even though the analytical conditions used enable quantification of chlordecol down to 0.5 mg/L. This result is consistent with Gibbs-free enthalpies that indicate that reductive dechlorination of CLD is energetically more favourable than its reduction to chlordecol [37]. Together with the fact that all the transformation products identified are dechlorinated compounds, the absence of chlordecol formation strongly suggests that the transformation of the CLD hydrate by ZVI was driven only by reductive dehalogenation.

Based on the exact masses of dechlorinated transformation products, extracted ion chromatograms were plotted after 14 days of reaction, the first sampling time when CLD hydrate had been totally transformed, and at the end of the experiment, 30 days. The chromatograms (Figure 4) showed the formation of the same seven major (peak intensity >10,000) degradation products whatever the reaction time with ZVI: RT = 11.1 min (peak 1), RT = 12.3 min (peak 2), RT = 14.1 min (peak 5), RT = 14.7 min (peak 7), RT = 15.4 min (peak 9), 15.6 min (peak 10) and RT = 16.5 min (peak 12). All these compounds are probably more polar than CLD hydrate (peak 15) since their retention times are shorter than that of CLD hydrate (RT = 18.6 min).

The evolution over time of the peak areas of these degradation products is illustrated in Figure 6. The CLD hydrate degradation due to ZVI results mainly in the monohydrochlordecone-hydrate (5a- or 5-, see above) at RT = 16.5 min (peak 12), which is formed already after 4 h, reaches a maximum peak area at 7 days, then decreases slowly until day 30 when the peak

![Figure 6. Evolution over time of the peak areas of the major degradation products of the CLD hydrate formed through reaction with ZVI (numbers in brackets correspond to the chromatogram peaks shown in Figure 4); error bars correspond to SD (n = 3; except at 21 and 30 days when n = 2).](image)
area represents 55% of its maximum value. The isomer chlordecone-5b-hydro-hydrate at RT = 17.4 min (peak 14) is the compound appearing after 2 days with the second highest peak area. As for the compound of peak 12, it reaches a maximum peak area at 7 days (corresponding to a concentration of 3.44 ± 0.26 mg/L, i.e. 3–4% of the initial CLD hydrate concentration, taking into account the molar conversion), but, contrary to peak 12, had vanished completely at day 21. Such evolutions over time suggest that these compounds are intermediates in the process of CLD hydrate degradation by ZVI, leading to compounds of higher level of dechlorination through replacement of several chlorine atoms by hydrogen ones.

The di-, tri-, tetra- and pentahydrochlordecone hydrates appear after 2 days, the highest peak areas, by far, being observed during all the experiment for the dihydrochlordecone hydrates (peaks 7 and 10) and the trihydrochlordecone hydrate (peak 5). At the end of the experiment (30 days), peak areas of the dihydrochlordecone hydrate peak 7 and the trihydrochlordecone hydrate peak 5 are 9–10 times higher than the peak areas of the tetra- (peak 2) and pentahydrochlordecone hydrate (peak 1). This suggests that the transformation products are formed in amounts inversely correlated to the degree of dechlorination. However, for the same degree of dechlorination, the dihydrochlordecone hydrate peak 9 area is 5–10 times lower than that of the two other dihydrochlordecone hydrate peaks 7 and 10. Therefore, in addition to the level of dechlorination, the position where the chlorines are removed has also a great influence on the peak area of the compounds formed.

No decrease in peak area over the 30 days of reaction was observed for the di-, tri-, tetra- and pentahydrochlordecone hydrate, although reducing conditions (−222 ± 41 mV; n = 16) were maintained all along the experiment. This may be due to the fact that these molecules are true end products or that their further transformation requires a longer duration of treatment.

In line with the (eco)toxicity issues commonly raised with the formation of degradates from organic contaminants, it is worth noting that the data available in the literature suggest that chlordecone-5b-hydro-hydrate and 5b,6-dihydrochlordecone formed by photodegradation are less toxic than CLD [38,39]. This may not stand for the chlordecone-5a or 5-hydro-hydrate, peak 12, and the dihydrochlordecones formed by treatment with ZVI, but gives however a positive sign in relation with the possible side effects of the treatment.

4. Conclusion

The data presented here are the first to show a complete transformation of CLD hydrate in aqueous solution, through reaction with micrometric particles of ZVI. Knowing how severe the environmental and socioeconomic impacts of CLD contamination in the FWI are, this result is of significant importance. LC-HRMS, thanks to the determination of accurate mass measurements, allowed the detection of 14 dechlorinated degradation products including isomeric compounds. The monohydrochlordecones formed already within 2 days are intermediate products, leading the way for the formation of di-, tri-, tetra- and pentahydrochlordecone, strongly suggesting a sequential reaction. More research on the structures and dechlorination positions of the transformation products will help to better understand the degradation pathways. The work to be conducted for that purpose could also be used to yield analytical standards of the main transformation products in order to enable their quantification and to study their toxicity.

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Supplemental data
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