The use of alkaline hydrolysis as a novel strategy for chloroform remediation: the feasibility of using construction wastes and evaluation of carbon isotopic fractionation

Clara Torrentó†*, Carme Audí-Miró†, Geneviève Bordeleau‡, Massimo Marchesi†§, Mònica Rosell†, Neus Otero† and Albert Soler†

†Grup de Mineralogia Aplicada i Medi Ambient, Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona (UB), Martí Franquès s/n, 08028. Barcelona, Spain. clara.torrento@ub.edu, carmeaudi@ub.edu, monica.rosell@ub.edu, notero@ub.edu, albertsolergil@ub.edu

‡National Scientific Research Institute (INRS-ETE), 490 de la Couronne, G1K 9A9 Quebec, QC, Canada. hazufelle@yahoo.ca

§Department of Earth & Environmental Sciences, University of Waterloo, 200 University Ave. W, N2L 3G1 Waterloo, Ontario, Canada. m2marchesi@uwaterloo.ca

Corresponding Author:

*Clara Torrentó Phone: +34 93 403 37 73; Fax: +34 93 402 13 40, e-mail: clara.torrento@ub.edu

1 **Abstract**

2 Laboratory and field-scale pilot experiments were performed to evaluate the feasibility of

3 chloroform degradation by alkaline hydrolysis and the potential of $\delta^{13}C$ values to assess this

4 induced reaction process at contaminated sites. In batch experiments, alkaline conditions were

5 induced by adding crushed concrete (pH 12.33±0.07), a filtered concrete solution (pH

6 12.27±0.04), a filtered cement solution (pH 12.66±0.02) and a pH 12 buffer solution (pH

7 11.92±0.11). The resulting chloroform degradation after 28 days was 94, 96, 99 and 72%,

8 respectively. The experimental data were described using a pseudo-first-order kinetic model,

9 resulting in pseudo-first-order rate constant values of 0.10, 0.12, 0.20 and 0.05 d^{-1}, respectively.

10 Furthermore, the significant chloroform carbon isotopic fractionation associated with alkaline

11 hydrolysis of chloroform (-53±3‰) and its independence from pH in the admittedly limited

12 tested pH range imply a great potential for the use of $\delta^{13}C$ values for in situ monitoring of the

13 efficacy of remediation approaches based on alkaline hydrolysis. The carbon isotopic

14 fractionation obtained at the lab scale allowed the calculation of the percentage of chloroform

15 degradation in field-scale pilot experiments where alkaline conditions were induced in two

16 recharge water interception trenches filled with concrete-based construction wastes. A maximum

17 of approximately 30-40% of chloroform degradation was achieved during the two studied

18 recharge periods. Although further research is required, the treatment of chloroform in

19 groundwater through the use of concrete-based construction wastes is proposed. This strategy

20 would also imply the recycling of construction and demolition wastes for use in value-added

21 applications to increase economic and environmental benefits.

22

23 **Keywords:** alkaline hydrolysis, remediation, chlorinated methanes, isotopic fractionation.

1. Introduction

Halogenated volatile organic compounds are some of the most prevalent contaminants in groundwater.[1] Chloroform (CF) is one of the highest ranked halogenated volatile organic compounds on the Agency for Toxic Substances and Disease Registry (ATSDR) priority list of hazardous substances. This list compiles the compounds found at sites on the National Priorities List (NPL) in the United States that pose the most significant potential threat to human health.[2] In Europe, an environmental quality standard of 2.5 µg/L for CF has been established in the framework of water policy (Directive 2008/105/EC).
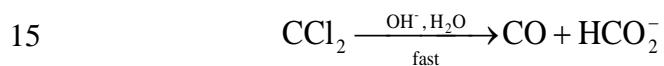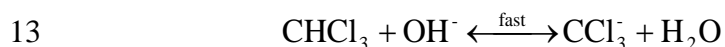
CF aerobic and anaerobic microbial cometabolic processes have been described.[4] However, apart from recent reports describing CF as a terminal electron acceptor during growth of *Dehalobacter*-containing cultures[5,6], CF cometabolic degradation is restricted by several environmental factors (inhibition by the presence of growth substrates such as other chlorinated compounds, toxicity of derived metabolites, etc.).[4] Bioremediation of CF by biostimulation and/or bioaugmentation strategies has been suggested.[3,7] Nevertheless, to our knowledge, in situ bioremediation of these compounds has not been reported to date. Furthermore, although removal of many halogenated hydrocarbons from groundwater can be achieved by in situ chemical oxidation (ISCO), CF is poorly reactive with common oxidants, such as permanganate, iron-activated persulfate, ozone, hydrogen peroxide or Fenton's Reagent.[8] New remediation strategies, that are efficient for this recalcitrant compound, should therefore be developed. Alkaline hydrolysis has been proposed as a remediation technology for other types of contaminants, such as explosives[9-13], organophosphorous insecticides[14], tert-butyl formate[15], and 1,2,3-trichloropropane[16]. To our knowledge the Bondgaard et al.[17] study is the only pilot-scale experiment for in situ alkaline hydrolysis-based groundwater remediation implemented in a

1   contaminated site until now. However, alkaline hydrolysis has received little attention so far with

2   respect to chlorinated methanes. In general terms, hydrolysis is a reaction in which an organic

3   molecule reacts with a water molecule (or hydroxide ion) and one part of the organic molecule

4   (i.e., the leaving group) is split off from the molecule.[18] In the halogenated hydrocarbons, the

5   leaving group is a halide ion, and hydrolysis of these compounds includes both nucleophilic

6   substitution and elimination reaction mechanisms. The competition between elimination and

7   nucleophilic substitution reactions depends on the structure of the substrate, the nature of the

8   base and stereoelectronic factors. Because strong nucleophiles favor elimination over

9   nucleophilic substitution, alkaline hydrolysis reactions (i.e., reaction with OH^-) of

10   polyhalogenated aliphatic compounds are expected to be dominated by elimination reactions,

11   whereas neutral hydrolysis (i.e., reaction with H_2O) is expected to occur primary by nucleophilic

12   substitution reactions.[19] The pH at which the changeover from the dominance of neutral reactions

13   to the dominance of alkaline reactions occurs, I_{NB}, is different for each compound, being 6.5 in

14   the case of CF.[18]

15   Hydrolysis of chlorinated compounds has been well demonstrated in the literature.[20-24]

16   However, reaction rates are often quite slow within the range of normal groundwater

17   temperatures and pH values. For this reason, reported rates of hydrolysis reactions involving

18   chlorinated solvents are typically the result of extrapolation from experiments performed at

19   higher temperatures. Neutral hydrolysis of CF is very slow, with reported neutral first-order rate

20   constants (K_N) at 25 ºC and pH 7 ranging from 6.2×10^{-8} (extrapolated from Fells and Moelwyn-

21   Hughes[25]) to 2.8×10^{-7} day^{-1},[22] which would translate into half-lives of approximately 30700 and

22   6900 years, respectively. Because OH^- cannot compete successfully with water in substitution

23   reactions with simple halogenated hydrocarbons at typical ambient conditions, the neutral

1   hydrolysis reaction may be described by a first-order law, regardless of whether the reaction

2   occurs by an SN_1 or SN_2 substitution mechanism or a mixture of both. Neutral hydrolysis of CF

3   is therefore first-order with respect to the concentration of CF and is independent of pH.[22]

4   Regarding the alkaline hydrolysis of CF in an aqueous solution, experimental and theoretical

5   approaches suggested that it proceeds through an $E1_{CB}$ mechanism and that the SN_2 mechanism

6   is unlikely to play a major role.[20,26] The $E1_{CB}$ mechanism is a type of elimination reaction,

7   which, in general terms, consists of a first step where a C-H bond is broken by deprotonation

8   with a base, followed by a second step where the leaving group is expelled. In the case of CF, the

9     $E1_{CB}$ mechanism features the rapid, reversible, base-catalyzed deprotonation of the molecule

10   with the formation of trichloromethyl carbanion (CCl_3^-), followed by the rate-determining

11   unimolecular loss of a chloride ion to produce the reactive intermediate carbon dichloride, which

12   is then rapidly transformed into the final products, carbon monoxide and formate ion.

13
$$CHCl_3 + OH^- \xleftarrow{\text{fast}} CCl_3^- + H_2O$$

14
$$CCl_3^- \xrightarrow{\text{slow}} CCl_2 + Cl^-$$

15
$$CCl_2 \xrightarrow[\text{fast}]{OH^-, H_2O} CO + HCO_2^-$$

16   The rate of the reaction has been suggested to be first order with respect to both OH^- and CF

17   concentrations.[20,25] Following this assumption and using the neutral and alkaline rate constants

18   (k_N and k_B, respectively) of the hydrolysis of CF at 25 ºC reported by Jeffers et al.[22] ($k_N = 2.8 \times 10^{-7}$

19   d^{-1}; $k_B = 7.5$ $M^{-1}d^{-1}$) and extrapolated from Fells and Moelwyn-Hughes[25] ($k_N = 6.2 \times 10^{-8}$ d^{-1};

20     $k_B = 5.7$ $M^{-1}d^{-1}$), pseudo-first-order rate constant ($k'_{obs} = k_N + k_B$ C_{OH^-}) values of 0.075 and 0.057

21   day^{-1}, respectively, can be calculated at constant pH 12 (Table 1). This yields half-lives of

22   approximately 9-12 days, which implies an attractive potential use of CF remediation strategies

23   based on alkaline hydrolysis. All the literature cited above determined the kinetics of CF

1   hydrolysis in homogeneous solutions. In contrast, the effects of heterogeneity on the hydrolysis

2   rates have received little attention so far.[27] Amonette et al.[27] studied the effect of various mineral

3   phases (montmorillonite, kaolinite, albite and muscovite) on the hydrolysis rates of CF. The

4   authors observed a significant effect of the type of solid on the CF hydrolysis rates at 50 ºC,

5   which was attributed to the different pH values maintained by the solid phases in contact with the

6   aqueous phase.

7   In the present study, we propose that concrete might be used to maintain alkaline conditions

8   and thus to induce alkaline hydrolysis of CF. Concrete is an artificial conglomerate stone made

9   essentially of Portland cement, aggregates, water and supplementary cementitious materials.

10   Portland cement is made by heating finely ground limestone and finely divided clay at high

11   temperatures. Concrete has high pH buffering capacity due to the lime content of the cement. For

12   these reasons, recycled concrete has been used as a reactive material for neutralizing acidic

13   groundwater.[28-30] Furthermore, cement-based stabilization/solidification (s/s) treatments have

14   been proven to immobilize chlorinated solvents from contaminated soils and groundwater.[31-33]

15   These s/s treatments have been used in combination with abiotic reductive dechlorination

16   treatments with additions of Fe(II), in which ferrous iron and cement are used as an electron

17   donor and a catalyst, respectively. The feasibility of the use of concrete to induce alkaline

18   hydrolysis and/or sorption of CF at contaminated sites merits evaluation.

19   To assess the efficiency of remediation strategies at contaminated sites, the interpretation of

20   concentration data alone is often insufficient; therefore, isotopic data are required. For example,

21   the presence of a contaminant downgradient of a permeable reactive barrier (PRB) may result

22   from incomplete degradation within the PRB, from bypassing under or around the PRB or from

23   contaminants already present before the installation of the PRB. To distinguish these origins,

compound specific isotope analysis (CSIA) can be used. The fundamentals of this approach imply that biological and chemical degradation reactions, which involve the cleavage of chemical bonds, usually cause isotopic fractionation. The result is generally an enrichment in heavy isotopes in the remaining substrate because light isotopomers (e.g., ^{12}C, ^{1}H and ^{35}Cl) typically react faster than heavy isotopomers (e.g., ^{13}C, ^{2}H and ^{37}Cl).[34] In contrast, non-destructive abiotic natural processes, such as dispersion, sorption or volatilization, generally do not cause significant isotopic fractionation.[35-39] Therefore, significant changes in isotope ratios over time and space can be used to monitor the success of remediation strategies at contaminated sites.[30] Quantification of the extent of contaminant transformation based on stable isotopes requires the experimental determination of the isotopic fractionation associated with the reaction under consideration.

In this study, laboratory batch experiments and field-scale pilot experiments were performed. The batch experiments were carried out to investigate the capacity of concrete to induce alkaline hydrolysis of CF. Additionally, the field-scale pilot experiments were performed to evaluate the feasibility of inducing alkaline hydrolysis of CF in the recharge water of a highly polluted fractured bedrock aquifer by implementing two interception trenches filled with construction wastes (recycled concrete aggregates). The main objectives of this study were i) to evaluate, through the batch experiments, CF consumption under alkaline conditions (pH 12.0-12.7) induced by a solution with crushed concrete, a filtered concrete solution, a filtered cement solution and a pH buffer solution; ii) to use carbon isotopic tools to determine whether fractionation occurs in both batch and field experiments in order to discriminate if a reduction in concentration is produced due to degradation or to non-transformation processes; and iii) to determine if the magnitude of the lab-obtained carbon isotopic fractionation is high enough to

1   assess and quantify the induced alkaline hydrolysis of CF, first, at the pilot field experiment and,

2   later, at contaminated field sites. Because tetrachloromethane (CT), commonly found together

3   with CF, is considered a recalcitrant compound listed on the ATSDR priority list as well,

4   additional laboratory batch experiments and field-scale pilot experiments were also conducted to

5   assess the behavior of CT under induced alkaline conditions. Concentration and isotope results

6   and a discussion about CT are found in the Supporting Information (SI).

7

8   **2. Materials and methods**

9   **2.1. Laboratory-scale experiments**

10 Batch experiments were performed to assess the induced alkaline hydrolysis of CF and to

11 determine the magnitude of carbon isotopic fractionation associated with this process. The

12 materials and solutions used in the experiments are detailed in the SI. Alkaline conditions were

13 induced by adding concrete particles (achieving a pH value of 12.37 ± 0.03) or by using the three

14 different alkaline solutions described in the SI. The experiments with the filtered concrete

15 solution and with the concrete particles were performed to distinguish the effects of degradation

16 versus sorption. Glass vials (26 mL) were used as reaction vessels for the filtered concrete,

17 filtered cement, chemical buffer and control experiments. These vials were filled with the

18 corresponding alkaline solutions or, in the case of the control experiments, with distilled water

19 (pH 5.5 ± 0.2). For the experiments with concrete particles, 39-mL glass vials were filled with 20

20 g of crushed concrete and approximately 30 mL of distilled water. In all vials, the reaction was

21 started by adding an appropriate volume of the contaminant stock solution described in the SI to

22 provide an initial CF concentration of 30 mg L^{-1}. The vials were completely filled without any

23 headspace to avoid partitioning of chlorinated compounds between the aqueous and gas phases

1   and were closed with PTFE-lined caps. Furthermore, the vials were covered with aluminum foil

2   to avoid photochemical effects. Duplicates (labeled A and B) were performed and all the

3   experiments were conducted at a room temperature of 23 ± 2 °C. The experiments were started at

4   different times to achieve reaction times varying from 0 to 28 d. After 28 d from the earliest

5   prepared vials, all the vials were sacrificed at the same time, ensuring that from the stop of the

6   reactions until the analyses, which would be on the same day for all the reactors, all the samples

7   underwent the same storage conditions. Appropriate volumes of the pH 6 buffer solution were

8   added to the vials to neutralize the solution to pH 6 and quench the alkaline hydrolysis reaction

9   (i.e., 2.1 mL for the 26-mL vials). Preliminary experiments proved that no catalyst effect was

10 induced by the added quenching solution (data not shown). In the experiments with concrete

11 particles, the particles were discarded and the solution was filtered with a 0.45-µm syringe nylon

12 filter (Uptidisc 25 mm, Interchim, France) before neutralization. Samples were held at 4 ºC in

13 darkness until analysis (within one week).

14

15 **2.2. Field-scale pilot experiments**

16 Two field-scale pilot interception trenches were installed in the unsaturated zone of a

17 contaminated fractured bedrock aquifer to induce alkaline hydrolysis of CF in the contaminated

18 recharge water accumulated in the trenches before the water reaches the aquifer. The aquifer is

19 unconfined fractured bedrock, consisting mainly of an Eocene blue-gray limestone bed, which

20 forms a low-permeability matrix with conductive fractures and fissures.[40] The aquifer is mainly

21 contaminated by chlorinated ethenes, ethanes, methanes and chlorobenzenes, together with traces

22 of BTEX and pesticides. An underground wastewater tank and a disposal pit located outside of

23 the factory building were identified as the main contaminant release sources. High volatile

1   organic compounds concentrations were detected in the subsurface in the areas located around

2   the main pollution sources (SI Fig. S1). The main measures implemented for the mitigation of

3   the contamination, performed in July 2006, were the removal of approximately 2000 t of

4   contaminated soil in the vicinity of the pollution source areas and the installation of the two

5   interception trenches in the unsaturated zone where contaminated soil had been removed (pit

6   trench and tank trench). The pit trench is 14 m long, 6 m wide and 6.5 m deep, whereas the tank

7   trench is 28 m long, 6 m wide and 6.5 m deep (SI Fig. S2). The trenches were filled with 40-70

8   mm-sized recycled concrete-based aggregates from a construction and demolition waste

9   recycling plant. These aggregates had a density of approximately 1.10 t m^{-3}. Finally, at 50 cm

10   below the ground surface, a geotextile sheet was placed, which was covered by a layer of

11   compacted clays. Three and five monitoring wells were installed along the pit and tank trenches,

12   respectively (SI Fig. S2). Rainwater lixiviates contaminants retained in the unsaturated zone and

13   infiltrates to the trenches, where CF alkaline hydrolysis can be induced. Trench water discharges

14   to the unsaturated zone towards the SSE, following the main water flow direction until reaching

15   a fracture connected to the underlying carbonate aquifer (SI Fig. S3). The trenches discharge

16   until a minimum level, and the water accumulated in both trenches is occasionally removed for

17   its management.

18   Sampling of the water accumulated in the trenches through one of the monitoring wells of each

19   trench was performed monthly from June 2010 until April 2013. This periodical sampling started

20   15 days after the trenches were emptied. The collected data are divided into two different

21   periods, henceforth called the first (9 months, from June 12th 2010 to February 23rd 2011) and the

22   second (26 months, March 21st 2011 to April 29th 2013) recharge periods, following water

23   removals on May 26th 2010 and February 23rd 2011, respectively. Physicochemical parameters

1   (pH, temperature, conductivity, Eh and dissolved oxygen) were measured in situ using a flow-

2   through cell (Eijkelkamp, Netherlands) to avoid contact with the atmosphere. Additional details

3   are provided in the SI. Water samples for concentration measurements and isotopic analyses of

4   chlorinated volatile organic compounds were collected in 125-mL amber glass bottles,

5   completely filled and closed with PTFE-lined caps. Samples were held at 4 ºC in darkness until

6   analysis. The water level in the trenches and groundwater level in two wells downgradient from

7   both trenches were continuously recorded using Cera- and Mini-Divers® (Schlumberger Water

8   Service, Postbus, Netherlands), respectively.

9

10 **2.3. Analytical methods**

11 Chlorinated compound concentrations were determined by headspace (HS) analysis using a

12 FOCUS Gas Chromatograph coupled with a DSQ II Mass Spectrometer (Thermo Fisher

13 Scientific, Waltham, MA, USA). Concentrations in the batch experiments were corrected for the

14 dilution induced by the addition of the quenching solution. Carbon isotope analyses of

15 chlorinated compounds were performed using a Thermo Finnigan Trace GC Ultra instrument

16 coupled via a GC-Isolink interface to a Delta V Advantage isotope ratio mass spectrometer

17 (Thermo Scientific GmbH, Bremen, Germany). Additional details are provided in the SI.

18   Aliquots of samples were preserved in nitric acid to measure concentrations of cations by

19 inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled

20 plasma mass spectrometry (ICP-MS). Dissolved chloride concentration was measured in

21 duplicate by titration with a $AgNO_3$ 0.0125 N solution using a 702 SM Titrino automatic titrator.

22 The error based on replicate measurements was 5%. Solution pH was measured with a calibrated

1   WTW pH Meter at room temperature (23 ± 2 °C). The pH error was 0.02 pH units. Alkalinity (as

2   HCO_3^-) was analyzed by automatic titration using unfiltered samples.

3

4   **3. Results**

5   **3.1. Laboratory experiments**

6   Consumption of CF was observed over time in all the experiments, except in the controls, in

7   which concentrations remained unchanged up to 28 d (Fig. 1A) and chloride formation was not

8   detected (data not shown). The results of the control experiments rule out possible losses of CF

9   as a result of processes not induced by alkaline conditions. Under alkaline conditions,

10   contaminant degradation ranged from 72% (buffer experiments) to 99% (filtered cement

11   experiments) after 28 d (Fig. 1A). In each treatment, the pH remained constant over the duration

12   of the experiments (12.33 ± 0.07 in the concrete experiments, 12.27 ± 0.04 in the filtered concrete

13   experiments, 12.66 ± 0.02 in the filtered cement experiments and 11.92 ± 0.11 in the buffer

14   experiments). The hydrolysis of CF under alkaline conditions followed pseudo-first-order

15   kinetics, as evidenced by the linear correlation relationship in $\ln(C/C_0)$ vs. time graphs (SI Fig.

16   S4). Least-squares regression analysis showed $R^2 > 0.95$ (Table 1). The rate of CF degradation

17   generally increased as the pH of the alkaline solutions increased, with pseudo-first-order rate

18   constant values, k'_{obs}, ranging from 0.047 to 0.201 d^{-1}. For all tested alkaline pH values, the half-

19   life was less than 15 d (Table 1). The obtained second-order rate constant was 4.6 ± 2.4 (95%

20   confidence interval) M^{-1} d^{-1} (see SI for calculation details and Fig. S5). The order of the reaction

21   was obtained as the slope of the same logarithm plot, and was 1.1 ± 0.5. Hydroxide concentrations

22   were not directly measured but were estimated from pH values and ionic strength data using the

23   code PHREEQC and the thermodynamic database MINTEQ.v4.[41]

1   The initial concrete and cement solutions contained 2.1 and 15.8 mg L^{-1} of chloride,

2   respectively. The chloride concentration related to CF dechlorination at each sampling time was

3   determined by subtracting the background concentrations (measured in the initial concrete and

4   cement solutions) from the measured dissolved chloride concentrations in the samples. The total

5   molar mass balance of chlorine (chloride released + chlorine in the remaining CF) at each

6   sampling time ranged from 81 to 127%, 91 to 105% and 92 to 112% of the initial chlorine mass

7   throughout the experiments with concrete particles, filtered concrete solution, and filtered

8   cement solution, respectively (SI Fig. S6). In addition to chloride, the experiments with concrete

9   particles released Ca, K, S, Sr, Ba, Li, Al and Zn into solution, with concentrations after 28 d of

10   approximately 240, 80, 6.0, 1.5, 1.0, 0.15, 0.1 and 0.05 mg L^{-1}, respectively (SI Table S1). Other

11   measured cations (Cd, As, Cu, Ni, Pb, Cr, Hg, Fe and Mg) were below detection limits.

12   All of the CF experiments, except the control experiments, show a considerable enrichment in

13   ^{13}C in the remaining CF over the course of the experiments (Fig. 1B). Carbon isotopic

14   fractionations (ε_C) were evaluated by a linear regression of the data following the Rayleigh

15   equation (more details are shown in the SI). The resulting plots can be found in the SI (Fig. S7),

16   and the experimental results are summarized in Table 2. Good fits (i.e., $R^2 > 0.96$) were obtained

17   for all regressions. Carbon isotopic fractionation ranged from -49±7‰ to -56±10‰ for all

18   experiments. The 95% confidence intervals of all ε_C values overlap. Consequently, an average ε_C

19   value combining all data was determined to be -53±3‰ ($R^2 = 0.98$). The apparent kinetic carbon

20   isotope effect (AKIE) obtained was 1.056 ±0.003 (see SI for calculation details).

21

22

23

3.2. Field-scale experiments

The pH values of the water sampled from the two trenches remained constant (11.6±0.3) throughout the 35-month sampling period. These results confirm the high buffering capacity of the recycled construction wastes. It should be noted that groundwater collected in all the aquifer monitoring wells shown in Fig. S2 (SI), including the two wells located a few meters downgradient from the trenches, had neutral pH values, showing that alkaline conditions are restricted to the trenches. The results of additional lab experiments evaluating the interaction between alkaline water and the carbonate aquifer confirmed the high buffering capacity of the aquifer and the restriction of the alkaline conditions to the trenches (see SI for details). Table S1 (SI) shows the concentrations of cations in water collected on May 2008 from both trenches. The temperatures of the water collected from both trenches during the sampled period ranged between 14 and 17 ℃ (with mean values of 15.6±1.0 ℃ and 15.3±1.1 ℃ for both trenches) according to seasonality, whereas the groundwater remained constant at a similar mean value of 15.4±0.2 ℃ during the same studied period.

During the study period, the water table elevation in the trenches ranged from approximately 431 to 434 meters above sea level (masl) (SI Fig. S9). Water table fluctuations occurred in response to rainfall. A lag period of approximately 5-7 and 20-30 days was observed between the precipitation events and the water level increases in the tank and pit trenches, respectively. The rapid recharge of the trenches can be seen after February 23rd 2011, when water of both trenches was removed for its management. Trench discharge after the high-intensity precipitation events proceeds according to Maillet's law. Under the four discharge conditions observed from May 2011 to March 2013 (Fig. S9), the recession curves were used to calculate the average discharge flow rates for both trenches. The obtained average discharge flow rates were 0.18±0.03 m^3d^{-1}

1   and 0.23 ± 0.06 m^{3}d^{-1} for the pit and tank trenches, respectively. The mean residence time of

2   water in the trenches was calculated as the ratio of the effective trench volume to the average

3   discharge flow rate. The obtained mean residence time was 513 ± 86 d and 730 ± 190 d for the pit

4   and tank trenches, respectively. At the end of each of the four observed discharge cycles,

5   discharge becomes zero and trench water remains at the minimum level (Fig. S9). It should be

6   noted that the first discharge cycle, with a duration of 90 days (see the period from June to

7   October 2011 in Fig. S9), is the only period without significant precipitation events and therefore

8   corresponds to the maximum period without water entering the trenches.

9   In both trenches, significant variations in the CF concentration were observed over time (Fig.

10   2). These fluctuations could be attributed not only to CF degradation but also to dilution effects

11   due to the entry of rainwater after short-duration high-intensity precipitation events, to the

12   leaching of contaminants retained in the unsaturated zone by rainwater after long-duration low-

13   intensity precipitation events, to sorption and/or desorption processes of the contaminants on the

14   mineral micropores, etc. Substantial enrichments in ^{13}C of CF over time occurred in both

15   trenches (Fig. 2), demonstrating CF transformation. In the two recharge periods, there was a

16   general tendency of CF δ^{13}C values to increase in both trenches, with isotopic shifts of up to 20

17   and 28‰. Despite this general trend, certain CF δ^{13}C variability was observed due to the entry of

18   non-degraded contaminant leaching from the subsoil after any precipitation event. Using the

19   isotopic fractionation obtained from laboratory experiments (ε_C=-53$\pm$3‰), the extent of CF

20   degradation in the trenches (D) was estimated assuming that the alkaline hydrolysis induced by

21   construction wastes was the only degradation fractionation process and fitted to the following

22   expression derived from the Rayleigh distillation equation:

$$D(\%) = \left[1 - \left(\frac{\delta^{13}C_t + 1000}{\delta^{13}C_0 + 1000} \right)^{\frac{1000}{\varepsilon_c}} \right] \times 100 \qquad (1)$$

where $\delta^{13}C_t$ and $\delta^{13}C_0$ are the current and initial isotopic compositions (‰) of CF, respectively. The δ^{13}C-CF values measured in both trenches at the start of the study period (-23.0±0.1‰ and -29.5±0.2‰), which correspond to the lightest values measured, were used as the initial isotopic compositions of CF for the tank and pit trenches, respectively. This assumes that these isotopic compositions represent the contaminant that has been subjected to the least degradation before reaching the trenches. The calculated percentage of CF degradation in both trenches is shown in Fig. 3. The observed δ^{13}C enrichments in the tank trench translate to maximum estimated extents of degradation of 34±5% and 39±9% for the first and the second recharge periods, respectively. In the pit trench, the two enrichment periods translate to maximum estimated extents of degradation of 32±5% and 40±3%. The highest degrees of CF degradation occurred at the end of each observed discharge cycle, when discharge becomes zero and trench water was at the minimum level (Fig. 3 and Fig. S9).

The evolution over time of the concentration and carbon isotopic composition of the other major chlorinated volatile organic compounds present in the trench water (CT, perchloroethylene and trichloroethylene) is shown in the SI.

4. Discussion

The laboratory experiments show that concrete particles immersed in water induced alkaline hydrolysis of CF, with 95% consumption after 28 d (Fig. 1). Degradation of CF was also observed in the other three alkaline treatments (chemical buffer, filtered cement and filtered concrete solutions), with half-lives below 15 days (Table 1). Aside from CF, no other chlorinated

1   volatile compounds were detected by GC-MS in scan mode. This result supports the E1$_{CB}$

2   degradation mechanism of CF reported by Hine[16], for which the final stable products were

3   carbon monoxide (CO), formate (HCO$_2^-$), and chloride (Cl$^-$). Furthermore, excellent chlorine

4   balances were achieved in the filtered experiments, indicating that CF was degraded without

5   accumulation of chlorinated intermediates (SI Fig. S6). Nevertheless, no special attempts were

6   made to identify other potential products of CF degradation. In the experiments with concrete

7   particles, dissimilar chlorine balances were achieved in the two duplicates (set A and set B),

8   reflecting the variability in chloride leaching due to the heterogeneity of the concrete particles.

9   This heterogeneity could also be responsible for the poorer linear correlation between the CF

10   concentration data and time and for the slightly lower degradation rate observed in the

11   experiment with concrete particles compared to the filtered concrete experiment (Table 1 and SI

12   Fig. S4). Further research on the solid phase is required to confirm this assumption. The pseudo-

13   first-order rate constants and half-lives obtained in this study of the hydrolysis of CF at room

14   temperature are comparable to those calculated from the published values of Jeffers et al.[22] and

15   Fells and Moelwyn-Hughes[25] for pH values of 12 and 13 and a temperature range between 20

16   and 25 ℃ (Table 1).

17   The lab-scale mean carbon isotopic fractionation associated with alkaline hydrolysis of CF was

18   -53±3‰ (Table 2). To our knowledge, carbon isotopic fractionations associated with any abiotic

19   CF degradation process have not been determined to date. The AKIE obtained at the lab-scale

20   experiments (1.056 ±0.003) is consistent with the theoretical maximum carbon primary KIE for

21   the C-Cl bond breakage (Streitwieser semiclassical upper limit of 1.057, Huskey[42]). The good

22   correspondence between the theoretical KIE and the measured AKIE is consistent with an E1$_{CB}$

23   mechanism for CF alkaline hydrolysis where the C-Cl bond breakage is the rate determining step

1 and, moreover, indicates that this type of abiotic reaction is not influenced by rate-limiting

2 factors or masking effects due to mass transfer processes.

3 It is worth noting that microbial reductive dechlorination of CF by a *Dehalobacter*-containing

4 culture resulted in a ε_C of -27.5±0.9‰[43], which represents the only documented CF ε_C value until

5 now. Therefore, the difference between the carbon fractionation associated with CF abiotic

6 alkaline hydrolysis and that associated with CF anaerobic respiration might potentially be used to

7 distinguish abiotic from biotic degradation processes at contaminated sites.

8 The large carbon isotopic fractionation observed in the experiments implies a great potential

9 for the use of $\delta^{13}C$ values for in situ monitoring of the degree of degradation of CF by alkaline

10 hydrolysis. Even minor extents of degradation will result in significant carbon isotope shifts that

11 can easily be detected by CSIA. For example, considering a carbon fractionation of -53±3‰, a

12 5% degradation will involve a change in $\delta^{13}C$ values of +2.7±0.1‰, which is significantly larger

13 than the analytical uncertainty of ±0.5‰.

14 The real concrete-based construction wastes used in the field-scale experiments maintained a

15 constant pH of 11.6±0.3 in pore water during the entire study period (35 months), confirming the

16 longevity of concrete-based aggregates for inducing alkaline conditions. The results of the long-

17 term field-scale pilot interception trenches, with significant ^{13}C enrichments, confirmed the

18 capability of concrete-based construction wastes to induce alkaline hydrolysis of CF. Although

19 the pH achieved by the used construction wastes in the field-scale experiments was slightly

20 lower than the pH range studied in the lab-scale experiments, the independence observed

21 between pH (from 12.0 to 12.7) and ε_C should allow us to estimate the extent of induced alkaline

22 hydrolysis of CF in the field-scale experiments through the laboratory-obtained ε_C (-53±3‰).

23 However, further experiments at lower pH values should be done to ensure this assumption. A

1   maximum CF degradation percentage between 32 and 40% was achieved in both trenches during

2   the two studied periods (Fig. 3). The efficiency in CF degradation depends on the precipitation

3   regime. Any precipitation event could result in the entry of non-degraded contaminant leaching

4   from the subsoil that would dilute the degradation effect. The alkaline conditions induced by the

5   recycled concrete-based construction wastes were restricted to the trenches and did not

6   negatively affect the natural attenuation processes of chlorinated compounds in the aquifer below

7   the trenches[40]. Actually, a concentration reduction of CF might be a key strategy for

8   bioremediation purposes[44] because CF is a potent inhibitor of several microbial processes, such

9   as methanogenesis or reductive dechlorination of chlorinated ethenes, the other major group of

10   pollutants at the site.[45] Moreover, temperature has a substantial effect on the abiotic degradation

11   rates of chlorinated compounds. The half-lives recalculated from published kinetic data at a

12   typical groundwater temperature of 10 ºC are approximately 15 times higher than those for 25 ºC

13   (Table 1). At lower groundwater temperatures, for example 5 ºC, alkaline hydrolysis of CF at pH

14   12 would yield a half-life of approximately 500 days (Table 1). Therefore, temperature must be

15   accounted for to predict the effectiveness of remediation strategies based on alkaline hydrolysis

16   in the field. In the present field-scale experiments, the temperature remained approximately 15ºC

17   in both trenches, which was very similar to the underlying groundwater. The half-life calculated

18   from the published values of Fells and Moelwyn-Hughes[25] for pH 11.6 and 15 ºC was 179 days,

19   which is a promising result for the potential full implementation of this remediation approach at

20   the site. For the mean calculated residence time of water in the trenches (513±86 and 730±190

21   d), a maximum theoretical percentage of degradation of approximately 90% would be achieved if

22   there was no entry of new non-degraded contaminant leaching from the unsaturated zone by

23   rainwater. Taking into account the maximum period without water entry into the trenches, and

1   thus non-degraded contaminant entry (90 days, from June to October 2011, Fig. S9), a maximum

2   theoretical percentage of CF degradation of 30% can be estimated for both trenches, which is in

3   agreement with the isotopic results. Therefore, the actual efficiency of the treatment depends on

4   the precipitation regime and can easily be estimated by monitoring the CF isotopic composition.

5   Taking this into account, improvements in the design of the interception trenches can be

6   proposed to increase the residence time in the system, such as the enlargement of the dimensions

7   of the trenches or increasing the pH by choosing different concrete-based materials. The pH of

8   leaching solutions of recycled concrete aggregates depends on the degree of carbonation. A study

9   from Engelsen et al.[46] on the alkaline capacity of several recycled concrete aggregates, including

10   waste construction materials, found not only similar pH ranges as the ones observed in this study

11   but also that a higher pH of 12.6 was reached with concrete material recycled from a highway

12   pavement constructed in the beginning of 1980's. This material would result in a CF half-life of

13   18 days, which would translate into a maximum extent of degradation of 97% in the trenches

14   during periods without the entrance of non-degraded contaminant. Monitoring of the isotopic

15   composition would be required to estimate the actual efficiency of the treatment.

16   Overall, these results indicate that alkaline hydrolysis induced by concrete-based construction

17   wastes seems to represent a potential alternative remediation strategy for CF-contaminated

18   recharge water before the water reaches fractured aquifers. Furthermore, it is proposed that

19   construction wastes could be implemented as a permeable reactive barrier (PRB) system to

20   degrade CF by alkaline hydrolysis in combination with ISCO, which would be able to remove

21   the rest of the accompanying pollutants (usually perchloroethylene, trichloroethylene and cis-

22   1,2-dichloroethylene). Thus, the combination of the two methods, neither of which alone could

23   achieve the degradation of all the compounds, might achieve an efficient decontamination of the

1   groundwater. The usefulness of carbon isotope analyses to evaluate the effectiveness of these

2   types of remediation approaches is also verified in this study. Recycling and reusing construction

3   wastes would furthermore result in environmental and economic benefits.

4

5   **Supporting Information**. Experimental details, the approach for the quantification of isotopic

6   fractionation and the kinetics of alkaline hydrolysis, the field-scale pilot experiment layout with

7   compound concentrations and piezometric information, a schematic representation of the

8   proposed hydrogeological performance of the trenches, the ln(C/C0) vs. time plot for the lab-

9   scale experiments, the correlation between the OH^- concentrations and pseudo-first-order rate

10   constants of the lab experiments, the chlorine mass balance in selected lab experiments, plots for

11   the calculation of εC during CF degradation by alkaline hydrolysis for selected lab experiments,

12   additional lab experiments of alkaline water and carbonated aquifer interaction, the evolution of

13   the water table elevation over time in the field-scale experiments, a discussion of cation release,

14   the evolution of the concentration and carbon isotopic composition of other chlorinated volatile

15   organic compounds over time in the field-scale experiments and a discussion of CT behavior.

16   This information is available free of charge via the Internet at http://pubs.acs.org/.

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1   **Figure captions**

2   **Figure 1.** Changes in the concentration (A) and $\delta^{13}C$ values (B) of CF over time in the alkaline

3   hydrolysis laboratory experiments: unfiltered concrete experiments (black circles), filtered

4   concrete experiments (gray circles), filtered cement experiments (squares), buffer experiments

5   (triangles) and control experiments (diamonds). The error bars show the standard deviation for

6   duplicate experiments.

7

8   **Figure 2.** Variation over time of CF concentration (gray diamonds) and carbon isotope ratios

9   ($\delta^{13}C$-CF, black circles) in the (A) tank trench and (B) pit trench during the studied period. The

10   error bars show the standard deviation for replicate measurements of the concentration and

11   isotopic data. Dashed lines indicate the day when the trenches were completely emptied for the

12   management of the contaminated water.

13

14   **Figure 3.** Estimation of the extent of chloroform degradation by alkaline hydrolysis induced by

15   construction wastes in the (A) tank trench and the (B) pit trench using Equation 1. The

16   uncertainty in the percentage of degradation was calculated by error propagation of the known

17   total errors for $\delta^{13}C$-CF measurements (the standard deviation of duplicated measurements) and

18   ε_C estimation ($\pm3\permil$). Dashed lines indicate the day when the trenches were completely emptied

19   for the management of the contaminated water.

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1 **Table captions**

2 **Table 1.** Summary of the kinetics of CF degradation by hydrolysis under alkaline conditions.

3 Pseudo-first-order rate constant (k'_{obs}) errors are given as the standard deviation (sd) calculated

4 on the regression of the pseudo first-order kinetic model. Half-life ($t_{1/2}$) uncertainties were

5 calculated by propagation of the first-order rate constant errors. Pseudo-first-order rate constants

6 and half-lives calculated from the published data of Jeffers et al.[22] and Fells and Moelwyn-

7 Hughes[25] for pH values of 12 and 13 and for temperatures (T) of 5, 10, 20 and 25 ºC are also

8 shown. The empirical temperature dependence relationships reported by Fells and Moelwyn-

9 Hughes[25] (SI Equations 12 and 13) were used to extrapolate rate constants to the selected

10 temperatures.

11

12 **Table 2.** Carbon isotopic fractionation (ε_C) and 95% confidence interval (95% CI) of the

13 regression lines for hydrolysis of CF under the alkaline conditions reported for the experiments,

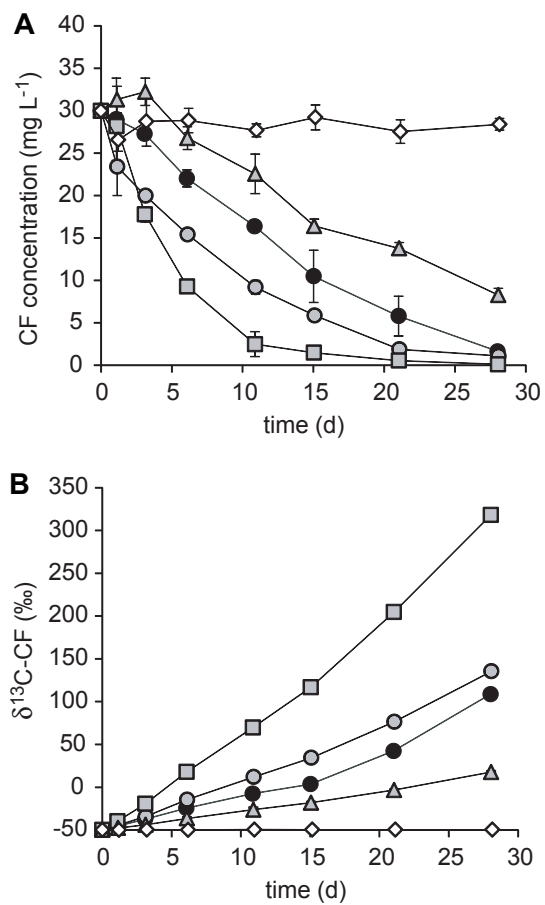14 as well as total combined data.

Figure 1

Figure 1. Changes in the concentration (A) and δ¹³C values (B) of CF over time in the alkaline hydrolysis laboratory experiments: unfiltered concrete experiments (black circles), filtered concrete experiments (gray circles), filtered cement experiments (squares), buffer experiments (triangles) and control experiments (diamonds). The error bars show the standard deviation for duplicate experiments.
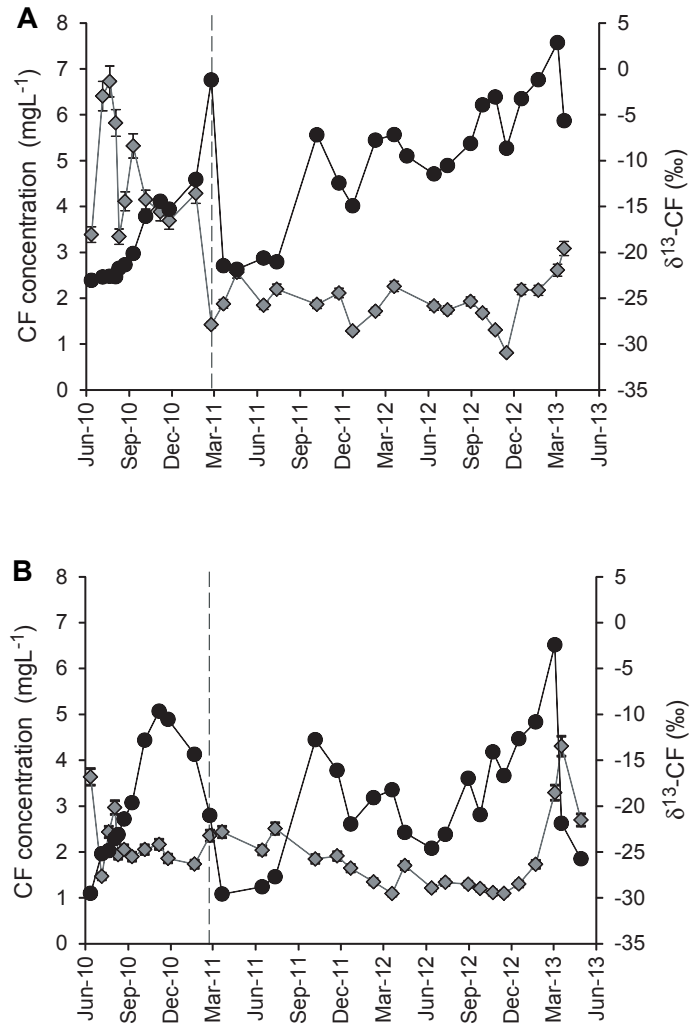
Figure 2

Figure 2. Variation over time of CF concentration (gray diamonds) and carbon isotope ratios (δ^{13}C-CF, black circles) in the (A) tank trench and (B) pit trench during the studied period. The error bars show the standard deviation for replicate measurements of the concentration and isotopic data. Dashed lines indicate the day when the trenches were completely emptied for the management of the contaminated water.
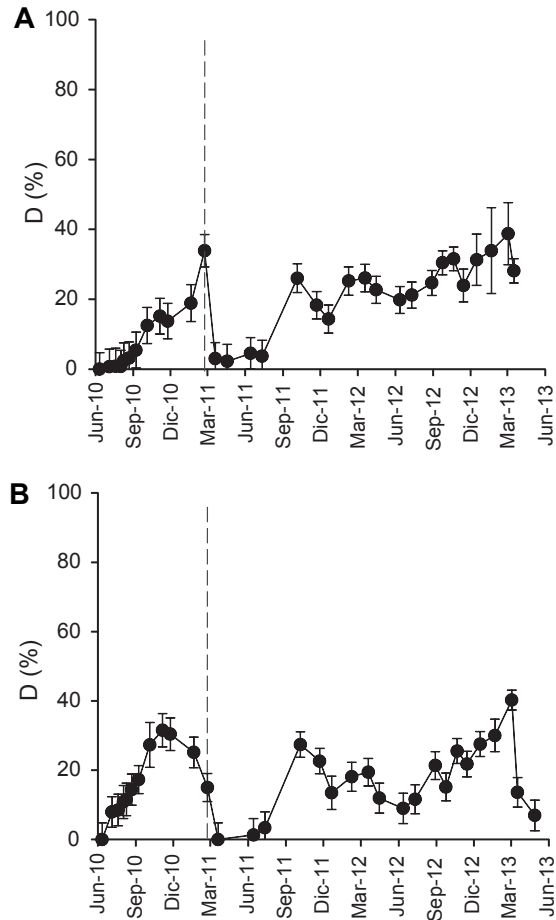
Figure 3

Figure 3. Estimation of the extent of chloroform degradation by alkaline hydrolysis induced by construction wastes in the (A) tank trench and the (B) pit trench using Equation 1. The uncertainty in the percentage of degradation was calculated by error propagation of the known total errors for δ^{13}C-CF measurements (the standard deviation of duplicated measurements) and ε_C estimation (±3‰). Dashed lines indicate the day when the trenches were completely emptied for the management of the contaminated water.

Table 1. Summary of the kinetics of CF degradation by hydrolysis under alkaline conditions. Pseudo-first-order rate constant (k'$_{obs}$) errors are given as the standard deviation (sd) calculated on the regression of the pseudo-first-order kinetic model. Half-life (t$_{1/2}$) uncertainties were calculated by propagation of the first-order rate constant errors. Pseudo-first-order rate constants and half-lives calculated from the published data of Jeffers et al.[22] and Fells and Moelwyn-Hughes[25] for pH values of 12 and 13 and for temperatures (T) of 5, 10, 20 and 25 ºC are also shown. The empirical temperature dependence relationships reported by Fells and Moelwyn-Hughes[25] (SI Equations 12 and 13) were used to extrapolate rate constants to the selected temperatures.

Observed pseudo-first-order rate constants and half-lives for CF degradation by hydrolysis at the experiments					
experiments	pH	T (ºC)	k'$_{obs}$ (d^{-1}) ± sd	R^2	t$_{1/2}$ (d) ± sd
Filtered cement	12.7	23±2	0.20±0.01	0.994	3.4±0.1
Filtered concrete	12.4	23±2	0.12±0.01	0.987	5.8±0.3
Unfiltered concrete	12.4	23±2	0.10±0.01	0.950	7.1±0.7
pH 12 buffer	12.0	23±2	0.05±0.00	0.967	14.7±1.3

Kinetic parameters of CF hydrolysis calculated from published data for selected pH and temperature conditions				
reference	pH	T (ºC)	k'$_{obs}$ (d^{-1})	t$_{1/2}$ (d)
Modified from Jeffers et al.[22]	12.0	25	0.08	9.2
	13.0	25	0.75	0.9
Modified from Fells and Moelwyn-Hughes[25]	12.0	25	0.06	12.2
	12.0	20	0.02	28.8
	12.0	10	0.004	186.2
	12.0	5	0.001	513.8
	13.0	25	0.57	1.2
	13.0	20	0.24	2.9
	13.0	10	0.04	18.6
	13.0	5	0.01	51.4

Table 2. Carbon isotope fractionation (εC) and 95% confidence interval (95% CI) of the regression lines for hydrolysis of CF under the alkaline conditions reported for the experiments, as well as total combined data.

experiments	ε_C (‰) ± 95% CI	n	R^2
Filtered cement	-56±10	8	0.968
Filtered concrete	-53±5	11	0.985
Unfiltered concrete	-51±4	16	0.983
pH 12 buffer	-49±7	11	0.964
Total combined data	-53±3	46	0.977

n : number of analyzed data points