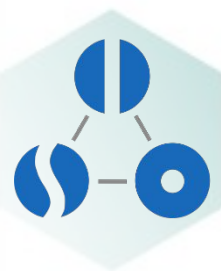




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# **SOURCE ALLOCATION AND DEGRADATION EVALUATION OF HCHS WITHIN A CONTAMINATED AQUIFER USING COMPOUND-SPECIFIC STABLE CARBON ISOTOPE ANALYSIS (CSIA)**

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# How to assess HCH-contaminated sites



Who was this and how many?

Is degradation taking place?

Can degradation be stimulated?



Compound-specific Stable Isotope Analysis (CSIA)



# What are isotopes ?

Number of Neutrons

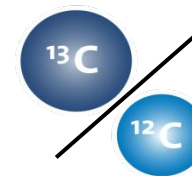
p	1	2	3	4	5	6	7	8
	H	He	Li	Be	B	C	N	O
n	Number of Protons							
0	<sup>1</sup> H							
1	<sup>2</sup> D	<sup>3</sup> He						
2	<sup>3</sup> T	<sup>4</sup> He	<sup>5</sup> Li	<sup>6</sup> Be		<sup>8</sup> C		
3		<sup>5</sup> He	<sup>6</sup> Li	<sup>7</sup> Be	<sup>8</sup> B	<sup>9</sup> C		
4		<sup>6</sup> He	<sup>7</sup> Li	<sup>8</sup> Be	<sup>9</sup> B	<sup>10</sup> C	<sup>11</sup> N	
5			<sup>8</sup> Li	<sup>9</sup> Be	<sup>10</sup> B	<sup>11</sup> C	<sup>12</sup> N	<sup>13</sup> O
6		<sup>8</sup> He	<sup>9</sup> Li	<sup>10</sup> Be	<sup>11</sup> B	<sup>12</sup> C	<sup>13</sup> N	<sup>14</sup> O
7				<sup>11</sup> Be	<sup>12</sup> B	<sup>13</sup> C	<sup>14</sup> N	<sup>15</sup> O
8			<sup>11</sup> Li	<sup>12</sup> Be	<sup>13</sup> B	<sup>14</sup> C	<sup>15</sup> N	<sup>16</sup> O
9					<sup>14</sup> B	<sup>15</sup> C	<sup>16</sup> N	<sup>17</sup> O
10				<sup>14</sup> Be	<sup>15</sup> B	<sup>16</sup> C	<sup>17</sup> N	<sup>18</sup> O
11						<sup>17</sup> C	<sup>18</sup> N	<sup>19</sup> O
12					<sup>17</sup> B	<sup>18</sup> C	<sup>19</sup> N	<sup>20</sup> O
13						<sup>19</sup> C	<sup>20</sup> N	<sup>21</sup> O
14							<sup>21</sup> N	<sup>22</sup> O
15								<sup>23</sup> O
16								<sup>24</sup> O

- stable isotopes
- radioactive isotope
- synthetic

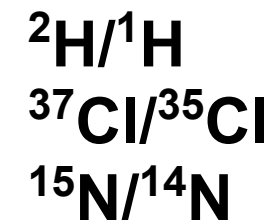
...atoms of an element with the same number of protons but **different numbers of neutrons**

**For example Carbon:**

$$\begin{aligned}
 {}^{13}\text{C} &= 0.96\% \text{ to } 1.16\% \\
 {}^{12}\text{C} &= 98.84\% \text{ to } 99.04\%
 \end{aligned}$$



**Isotope ratio**



measured via isotope ratio mass spectrometry (IRMS)

$$\delta^{13}\text{C} [\text{‰}] = \left( \frac{\frac{{}^{13}\text{C}}{{}^{12}\text{C}}_{\text{sample}}}{{}^{13}\text{C}}{{}^{12}\text{C}}_{\text{standard}}} - 1 \right)$$



# Why do I need to analyze them



Isotope signature of the  
primary compound

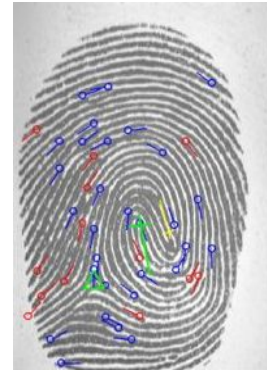
$$\delta^{13}\text{C} = -26 \text{ ‰ VPDB}$$

$$\delta^{37}\text{Cl} = +4 \text{ ‰ SMOC}$$

$$\delta^2\text{H} = -50 \text{ ‰ SMOW}$$

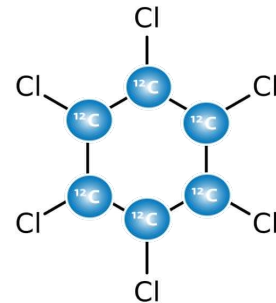
$$\delta^{18}\text{O} = +2 \text{ ‰ SMOW}$$

$$\delta^{15}\text{N} = +7 \text{ ‰ AIR}$$



## FINGERPRINT – Source Identification

$^{12}\text{C}$ -HCH

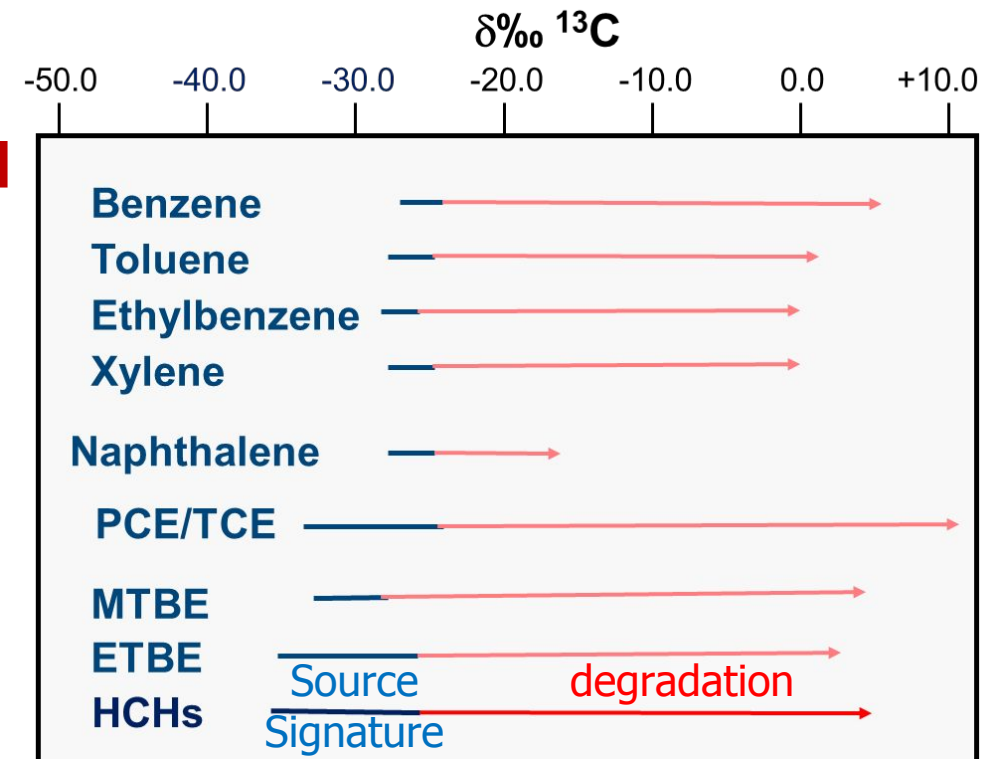
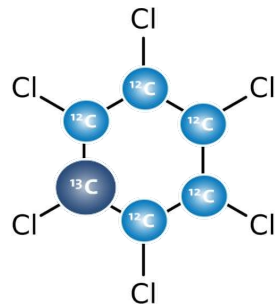


## DEGRADATION

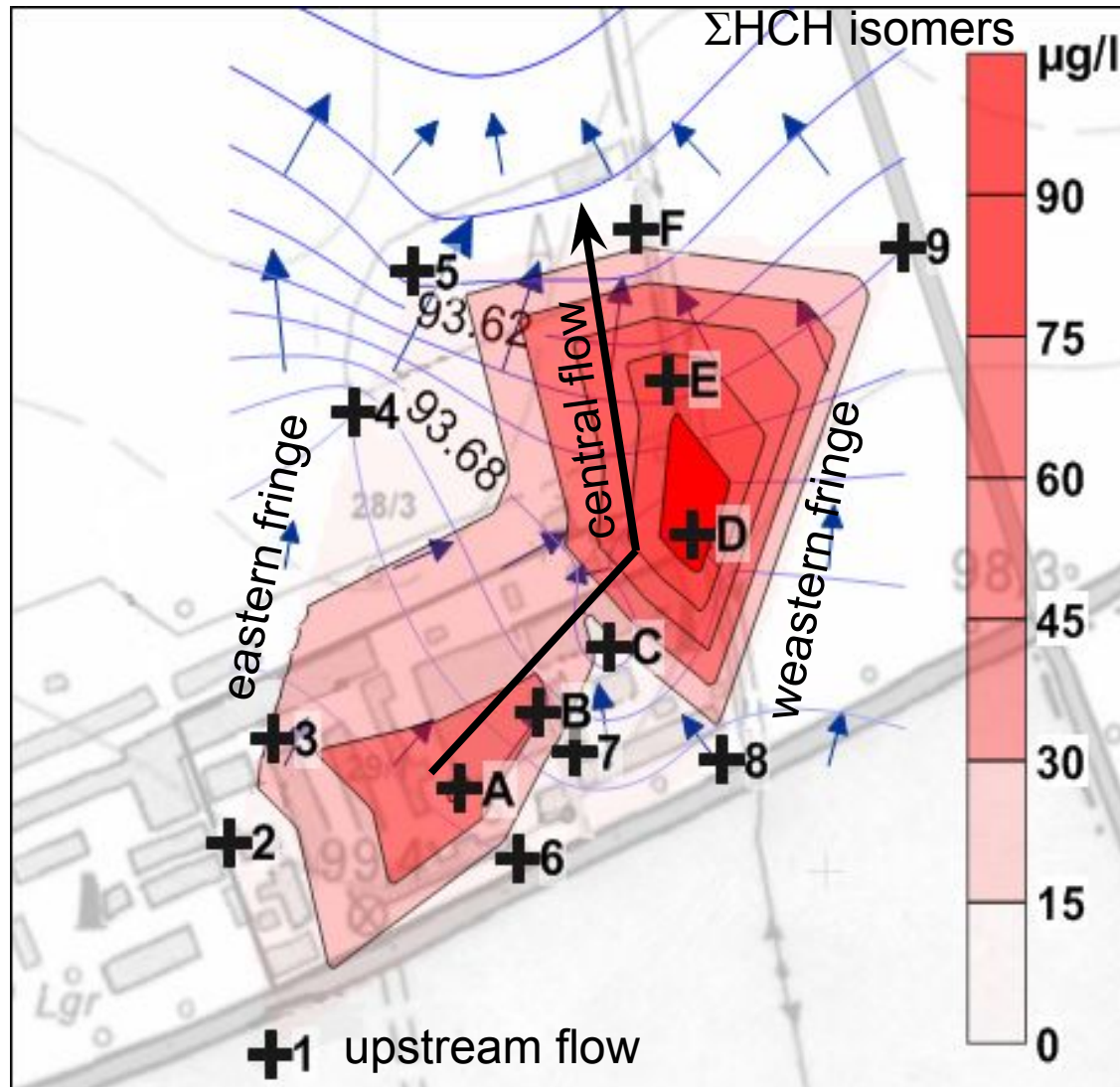


Pollutant molecules with **heavy isotopes** ( $^{13}\text{C}$ )  
are **degraded more slowly**.

$^{13}\text{C}$ -HCH

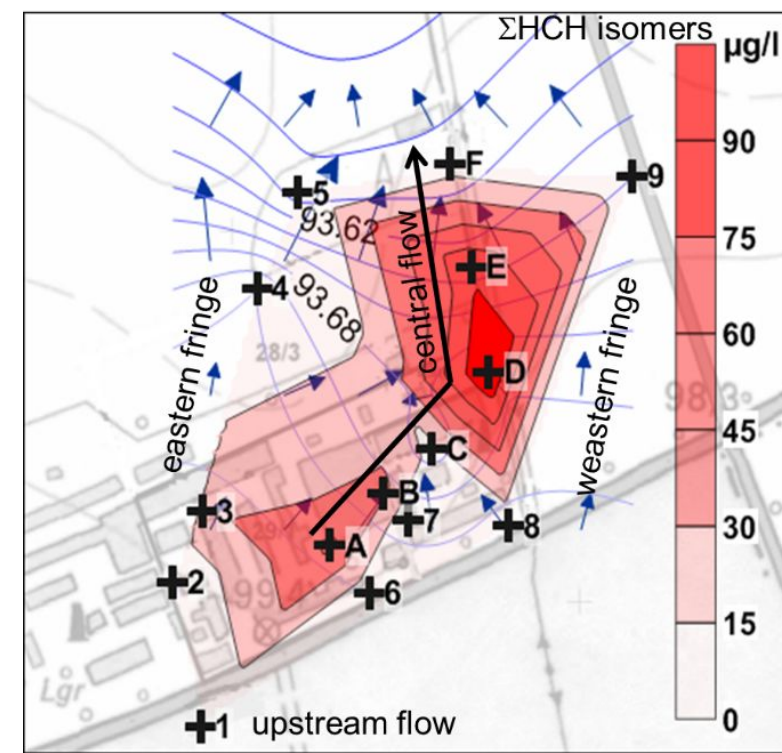
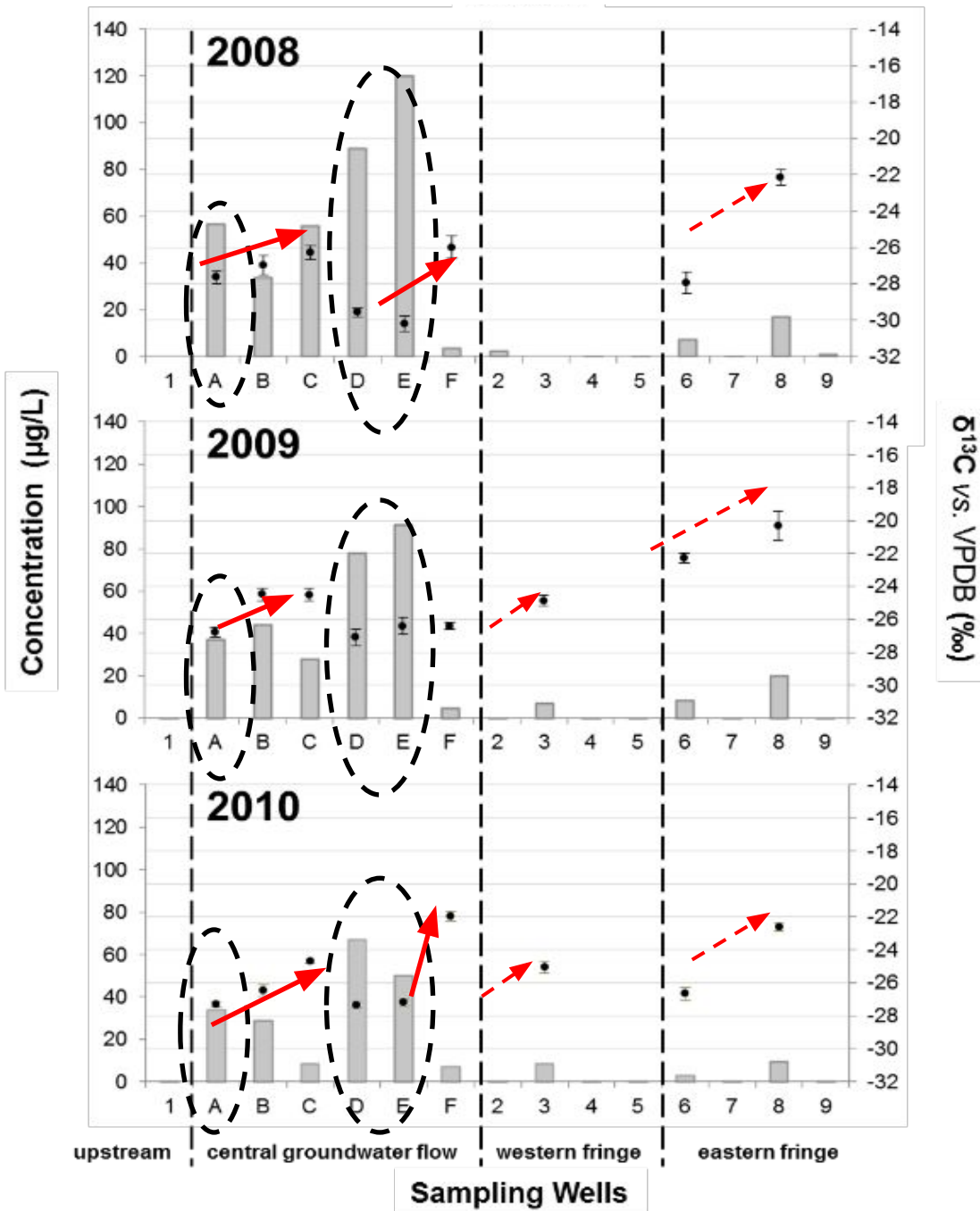


# Field site: HCH-contaminated aquifer



1. Can source zones of HCHs be confirmed by CSIA?
2. Does *in situ* degradation of HCHs take place and to which extend?



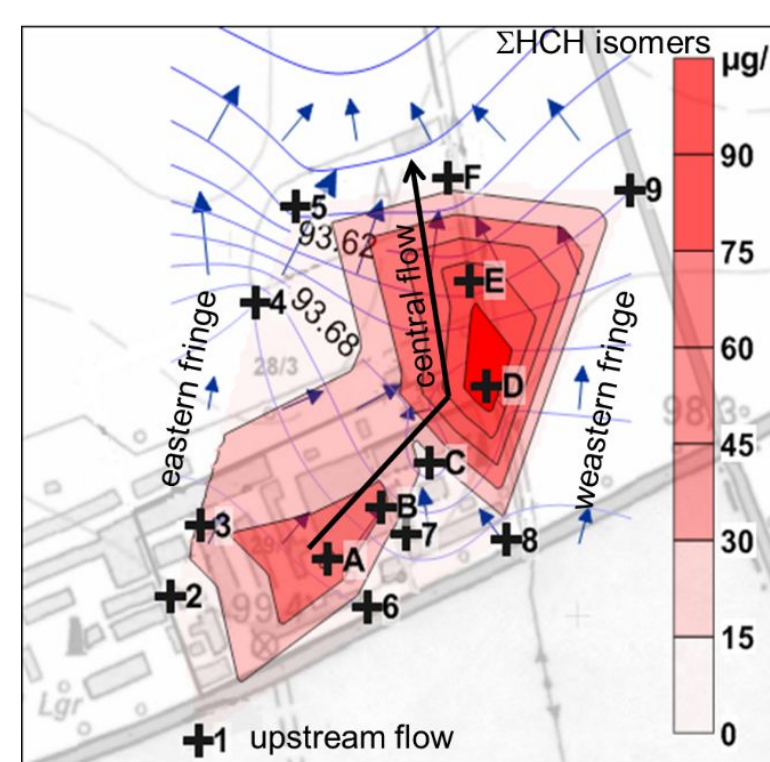
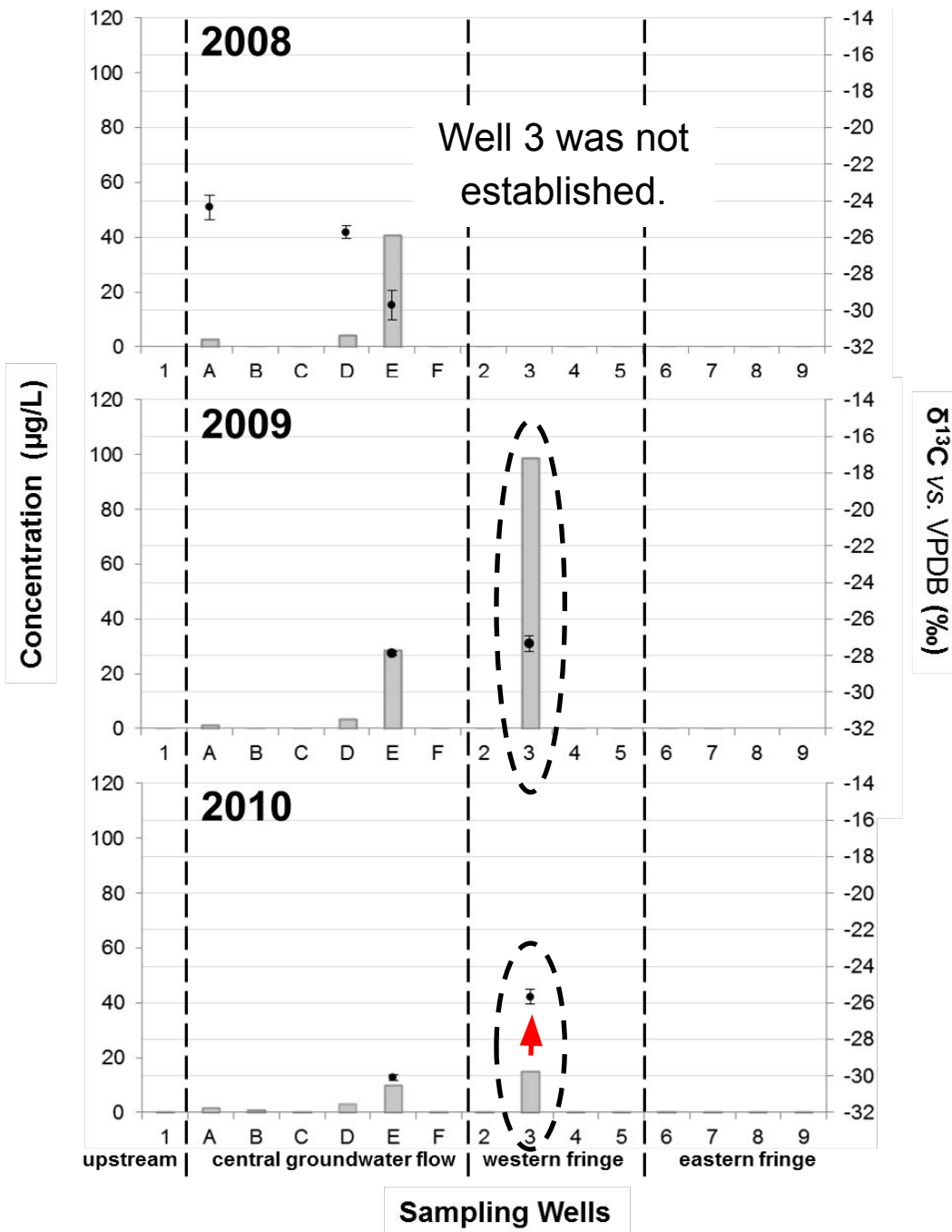


**Source**

Former production facilities at well A

Former HCH-dump at wells D/E

**Degradation**



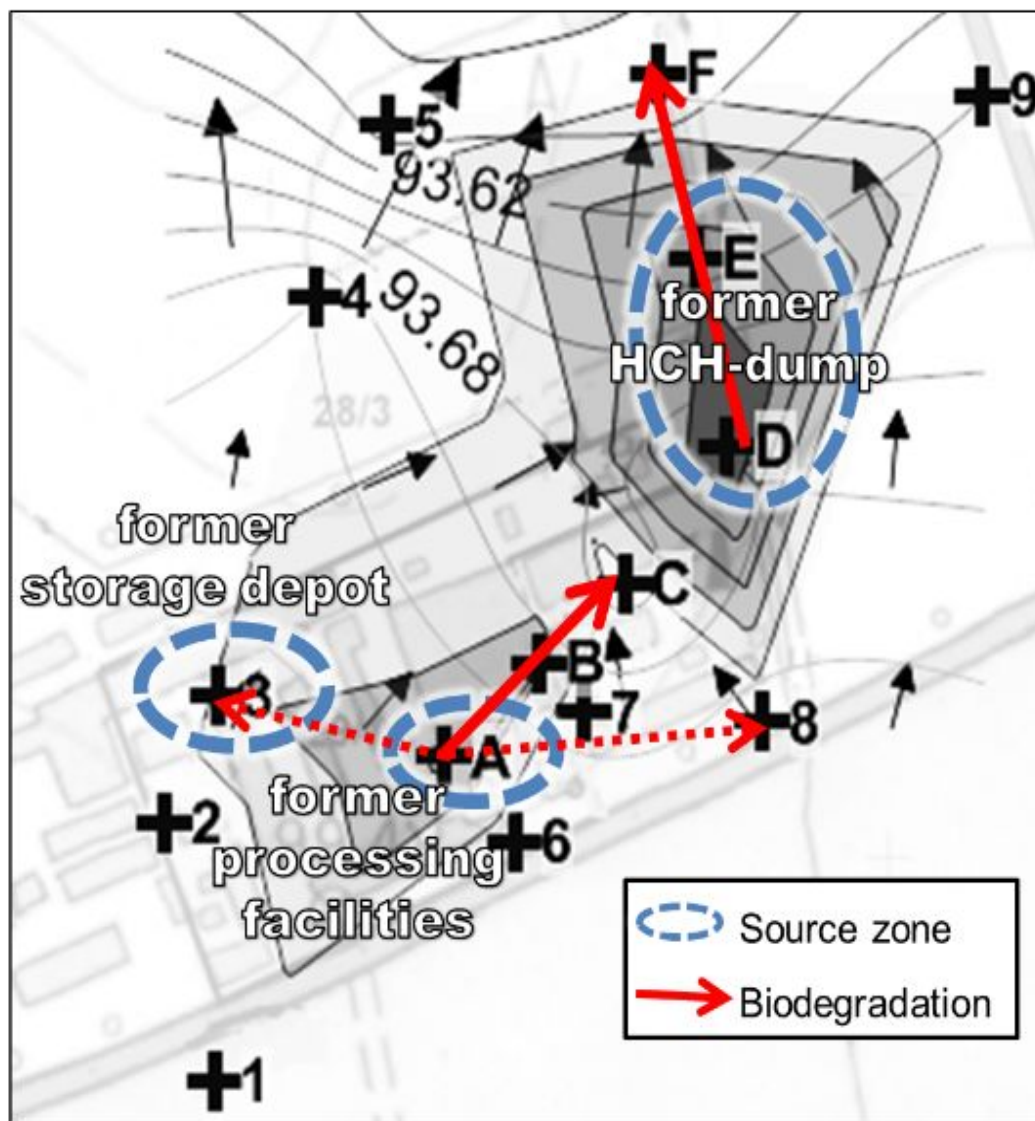
(Source)

Former storage  
depot

Degradation

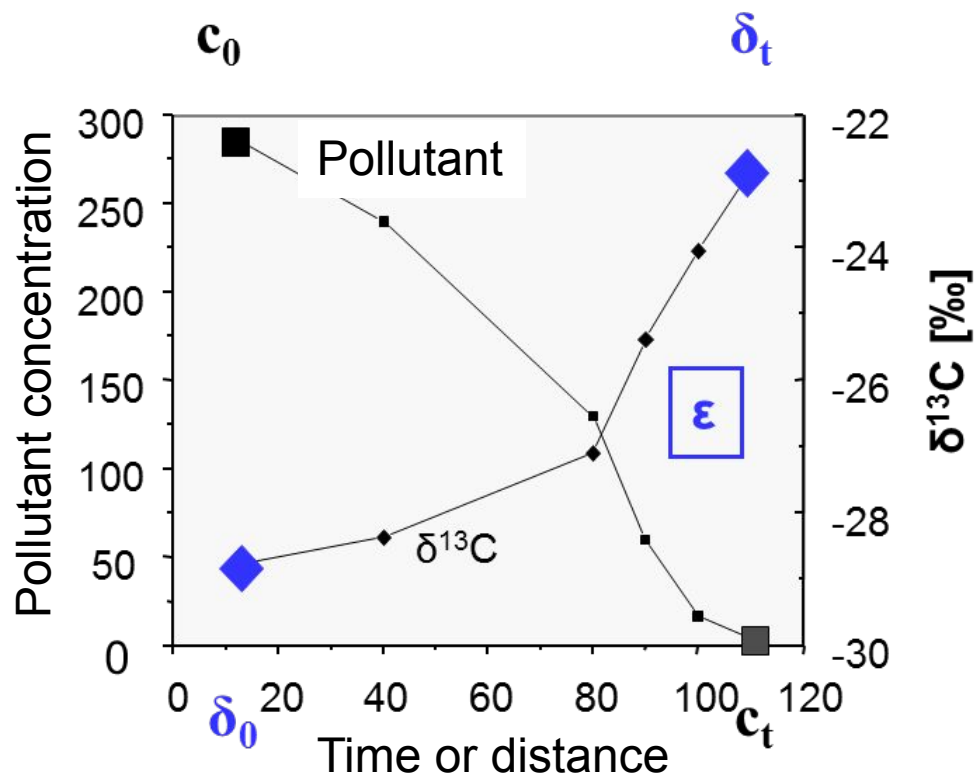


# Improved conceptual site model due to CSIA





# Quantification of pollutant biodegradation



Laboratory  
experiment

Field data

Rayleigh equation

$$\lambda = -\frac{1000}{\epsilon \times t} \ln \left( \frac{\delta_t + 1000}{\delta_0 + 1000} \right)$$

1. Order degradation rate constant

Distance-related

Time-related

	$\lambda_s$ [1/m]	$\lambda_t$ [1/d]
$\delta$ -HCH:	$19 \times 10^{-3}$	$6 \times 10^{-3}$
$\alpha$ -HCH:	$10 \times 10^{-3}$	$3 \times 10^{-3}$
$\beta$ -HCH:	$37 \times 10^{-3}$	$11 \times 10^{-3}$



# Conclusions

- CSIA confirmed different source zones at the investigated field site
- CSIA provided evidence of HCH degradation in the investigated aquifer
- CSIA allowed quantification of HCH degradation for expected flow paths



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### **Environmental Monitoring Tools**

Compound-specific stable isotope analysis (CSIA)  
*In situ* Microcosms (BACTRAP®)  
Laboratory Microcosms / Treatability Studies  
PLFA Analysis  
Molecular Genetic Analysis (qPCR)  
GC-MS Analysis (GC-Fingerprints)  
Metabolite Analysis  
Enantiomer Analysis (Pesticides!)

### **Evaluating drinking water resources**

(e.g., Tritium,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ , FCKW/SF<sub>6</sub>,  $^3\text{He}$ ,  $^{85}\text{Kr}$ ,  $^{14}\text{C}$ )

### **Investigating renewable and fossil energies**

(e.g., Evaluating microbial processes in hydrogen underground storage)