Comments on "**1,1,2,2-Tetrachloroethane Reactions with OH⁻, Cr(II), Granular Iron, and a Copper-Iron Bimetal: Insights from Product Formation and Associated Carbon Isotope Fractionation**." By Elsner et al. 2007 (*Environ. Sci. Technol.* **41**, 4111).

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The paper by Elsner et al. (2007) is a justified attempt to contribute to the elucidation of the mechanism of reductive dehalogenation of organohalides in real-world permeable reactive barriers (field Fe^0–H_2O systems or field Fe^0 PRBs) by means of a very well-established scientific tool (carbon isotope fractionation). For this purpose, the authors used well-mixed batch experiments that are unfortunately known not to be representative for real-world conditions. Therefore, using column experiments rather than batch systems would have closely simulated field conditions (Henderson and Demond 2007). Moreover, it is yet to be proven that abiotic contaminant reduction in laboratory batch experiments and in the field occurs with the same mechanism, since the hydrodynamic regimes in both systems are largely different.

The hydrodynamic regime in a field Fe^0 PRB is governed by the natural hydraulic gradient of the contaminated groundwater. Under these conditions the Fe^0 surface is covered with an oxide-film at an earlier time scale of the barrier life before the occurrence of quantitative contaminant inflow (Scott et al. 2005). Various types of reducible contaminants (Henderson and Demond 2007), electrochemically non-reducible contaminants like zinc (Ludwig and Jekel 2007), and biological agents like viruses (You et al. 2006) are successfully removed from aqueous solutions in Fe^0–H_2O systems. Therefore, the premise that some classes of inorganic and organic contaminants are mostly removed by reductive processes through electrons from Fe^0 materials (direct reduction) should have been carefully demonstrated. This

has not been the case as the premise is of pure thermodynamic origin and is based on the low redox potential of the couple Fe^{II}/Fe^0 (Matheson and Tratneyk 1994, Powell et al. 1995). The efficiency of various other reductants ($Fe^{II}_{(aq)}$, $Fe^{II}_{(s)}$, H/H_2) at reducing contaminants in the presence of oxide surfaces (largely present in Fe^0–H_2O systems) has been demonstrated (~~Matheson and Tratnyek 1994,~~ White and Paterson 1996). Because these secondary redox couples are partly thermodynamically more powerful at reducing contaminants than the couple Fe^{II}/Fe^0, there is no reason why direct reduction should be a priori considered as the major mechanism path of abiotic contaminant reduction as observed in column studies and in field Fe^0 PRBs. In field Fe^0 PRBs microbially mediated processes may play an important role in reducing contaminant.

From the huge available literature on iron corrosion it is known that under environmental pH conditions, the Fe^0 surface is always covered by an oxide-film (Cohen 1959, Schmuki 2002, Stratmann and Müller 1994, Wilson 1923). Thus, investigations regarding the processes of contaminant removal in Fe^0–H_2O systems should be performed under conditions favouring the formation of oxide-films on Fe^0 materials. In particular mixing operations should be justified as they have been proven disturbing for the processes of oxide generation and transformation (Büchler et al. 1998, Tomashov and Vershinina 1970). In the reactive wall literature mixing operations (shaking, stirring) are generally considered as an important tool to facilitate the transport of contaminant to the Fe^0 surface, and therefore, speed up the reduction kinetics (Agrawal and Tratnyek 1996). This was also the intention of Elsner et al. (2007) as their systems were "sufficiently mixed at all times to ensure rapid solid/water mass transfer". However, mixing operations enhance Fe^0 oxidation and hinder or delay the formation of oxide-film on Fe^0 or in its vicinity. Therefore, mixing intensities above natural turbulences should be avoided. Even though Elsner et al. (2007) have not specified their mixing intensity, high mixing intensities are used in referenced works. For example, Cwiertny and Roberts (2005) used mixing intensities varying from 20 to 250 rpm. While using such mixing

intensities it is possible that reductive conditions are generated and/or maintained, that will not occur in field Fe^0 PRBs. Therefore, it is possible that contaminant reduction under the experimental conditions of Elsner et al. (2007) are not representative for field conditions. This remark is a strong criticism of the majority of works dealing with the investigation of processes in Fe^0–H_2O systems, in particular for mechanistic investigations.

Before using well-established scientific tools to investigate reductive processes in Fe^0–H_2O systems one should make sure that: (i) reduction occurs, and (ii) the experimental conditions mimic field conditions as closely as possible. Therefore, Elsner et al. (2007) could have made isotopic investigations for parallel experiments under different mixing regimes (including non-disturbed systems).

Another ~~work~~ recent work has used isotope fractionation to investigate the mechanism of uranium removal in Fe^0–H_2O systems (Rademacher et al. 2006) and reported different conclusions than the original work (no U(VI) reduction) of Gu et al. (1998). The reports of Gu et al. (1998) were mostly based on the results of fluorescence spectroscopic studies. This contradiction should have been discussed by Elsner et al. (2007) as the work of Rademacher et al. (2006) was published in the same journal four months before their manuscript submission. These two examples (organohalides and uranium) show that something is wrong in the conception of experiments to investigate processes in Fe^0–H_2O systems. Diversities in the large array of contaminants and in the reactivity of used Fe^0 materials (Miehr et al. 2004, Noubactep et al. 2005) are certainly among the reasons for these observations, but should not explain why two well-established scientific methods (fluorescence spectroscopic and isotope fractionation) deliver different results for the same contaminant.

In conclusion, the work of Elsner et al. (2007) certainly reiterates the importance of isotope fractionation for the elucidation of reaction mechanisms. However, because used hydrodynamic regimes were not pertinent to environmental conditions, it is difficult to see how these results can enable a better prediction of the formation of harmful versus benign

organohalide reaction products. A unified procedure for the investigation of processes in Fe^0–H_2O systems is needed.

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