## Comments on "Degradation of 1,2,3-Trichloropropane (TCP): Hydrolysis, elimination,

## and reduction by iron and zinc"

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Sarathy et al. (1) recently reported their results on the aqueous degradation of 1,2,3-Trichloropropane (TCP) by  $Fe^0$  and  $Zn^0$ . Their work is a justified attempt to support ongoing risk assessments of emerging contaminants in a perspective to identify methods for their efficient mitigation (2–5). There is a general trend to test the applicability of various technologies for the removal of emerging contaminants from water (4, 5). However, despite gaps in knowledge of the nature of metabolites, the state-of-the-art knowledge on the mechanism of contaminant removal by metallic iron (Fe<sup>0</sup>) suggests that filtration on Fe<sup>0</sup> beds will be efficient at removing emerging contaminants and their metabolites. In fact, filtration on Fe<sup>0</sup> beds has been proven efficient for the quantitative removal of various contaminants (6-9). Accordingly, regardless on the actual removal mechanism (hydrolysis, elimination, and reduction), a well-designed Fe<sup>0</sup> filter will successfully remove TCP and its metabolites from the aqueous phase as discussed below.

There are three fundamental mechanisms of solute removal in porous media during fluid flow: (i) straining (size exclusion), (ii) adsorption (or/and deposition), and (iii) hydrodynamic bridging (10). The characteristic feature of  $Fe^0$  filters is the chemical reactivity of iron (oxidative oxidative dissolution). Therefore, beside adsorption and deposition contaminants can be chemically transformed (oxidized or reduced if applicable). Iron oxidative dissolution is volumetric expansive in nature (11). Accordingly, the initial pore volume of a  $Fe^0$  bed/filter is progressively occupied by voluminous hydrated ferrous/ferric oxides (HFO) which are further transformed to amorphous and crystalline oxides upon dehydration. Any crystalline oxide is at least 2.1 times larger in volume than Fe<sup>0</sup> in the lattice structure (11). Pore filling by in-situ generated iron oxides is responsible for (i) porosity and permeability loss, and (ii) increased size exclusion capability. On the other hand, intermediate HFO are good adsorbents which trap contaminants in their structure during crystallization (co-precipitation). Moreover, continuously generated HFO can be regarded as instantaneous spider-like webs trapping contaminants in the porous media (12). In other words so far progressive HFO generation is warranted all contaminants will be removed in a well-designed Fe<sup>0</sup> beds. Available tools to sustain Fe<sup>0</sup> reactivity include bimetallics, nano-sized materials, porous Fe<sup>0</sup>-composites.

The discussion above has not accounted for the nature of the contaminant (size, solubility, reactivity towards  $Fe^{0}$ ). Solely the properties of corroding  $Fe^{0}$  and precipitating oxides (at pH > 4.5) are considered. Accordingly, in  $Fe^{0}$  filters working at pH > 4.5, contaminants are basically removed by adsorption, co-precipitation, and size exclusion. Accordingly, understanding the impact of individual contaminants on (i) long-term  $Fe^{0}$  reactivity and (ii) system permeability is more important than understanding the actual removal mechanism. Given the huge number of emerging contaminants (2-5), it is not likely that the removal mechanism of individual contaminants will be investigated on a case-by-case basis.

In conclusion, this discussion belittles the relevance of TCP removal mechanism (hydrolysis, elimination or reduction) for field  $Fe^0$  reactive walls. The test of  $Zn^0$  is intrinsically questioned. It is shown that contaminants are removed by  $Fe^0$  independently from their intrinsic characteristics. This is a strong criticism to dozens of works aiming at discussing the toxicity of intermediates and metabolites of some contaminants or contaminant groups in  $Fe^0$  beds. A strong argument supporting this assertion is the efficiency of SONO arsenic filters (7). In SONO filters, porous  $Fe^0$ -based composites primarily designated to remove arsenic from well waters in Bangladesh and Nepal have been shown efficient in the removal of up to 24 other species including bacteria and viruses (7, 9). Because  $Fe^0$  are also used for wastewater treatment in batch systems, the study of Sarathy et al. (1) yet provides useful

understanding of the substantial challenges confronted in studying the removal potential of Fe<sup>0</sup>-based systems.

## References

- Sarathy, V.; Salter, A.J.; Nurmi, J.T.; Johnson, G.O.; Johnson, R.L.; Tratnyek, P.G. Degradation of 1,2,3-Trichloropropane (TCP): Hydrolysis, elimination, and reduction by iron and zinc. *Environ. Sci. Technol.* **2010**, 44, 787–793.
- (2) Petrovic, M.; Gonzalez, S.; Barcelo, D. Analysis and removal of emerging contaminants in wastewater and drinking water. *TrAC Trends Anal. Chem.* **2003**, 22, 685–696.
- (3) Ternes, T.A.; Stüber, J.; Herrmann, N.; McDowell, D.; Ried, A.; Kampmann, M.; Teiser,
  B. Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Res.* 2003 37, 1976–1982.
- (4) Heberer, T.; Massmann, G.; Fanck, B.; Taute, T.; Dünnbier, U. Behaviour and redox sensitivity of antimicrobial residues during bank filtration. *Chemosphere* 2008, 73, 451–460.
- (5) Ghauch, A.; Assi, H.A.; Tuqan, A. Investigating the mechanism of clofibric acid removal in Fe<sup>0</sup>/H<sub>2</sub>O systems, J. Hazard. Mater. (2009), doi:10.1016/j.jhazmat.2009.10.125.
- (6) Henderson, A.D.; Demond, A.H. Long-term performance of zero-valent iron permeable reactive barriers: a critical review. *Environ. Eng. Sci.* **2007**, 24, 401–423.
- (7) Hussam, A.; Munir, A.K.M. A simple and effective arsenic filter based on composite iron matrix: Development and deployment studies for groundwater of Bangladesh. J. *Environ. Sci. Health A* 2007, 42, 1869–1878.
- (8) Johnson, R.L.; Thoms, R.B.; Johnson, R.O'B.; Krug, T. Field evidence for flow reduction through a zero-valent iron permeable reactive barrier. *Ground Water Monit. Remed.* 2008, 28, 47–55.
- (9) Tuladhar, S.; Smith, L.S. SONO filter: An excellent technology for save water in Nepal. SOPHEN 2009, 7, 18–24.

- (10) Ramachandran, V.; Fogler, H.S. Multilayer Deposition of Stable Colloidal Particles during Flow within Cylindrical Pores *Langmuir* **1998**, 14, 4435–4444.
- (11) Caré, S.; Nguyen, Q.T.; L'Hostis, V.; Berthaud, Y. Mechanical properties of the rust layer induced by impressed current method in reinforced mortar. *Cement Concrete Res.* 2008, 38, 1079–1091.
- (12) Noubactep, C. The suitability of metallic iron for environmental remediation. Environ.Progr. (2009) doi 10.1002/ep.10406.