

1 **Comments on “Reductive dechlorination of organochlorine pesticides in soils from an**
2 **abandoned manufacturing facility by zero-valent iron” by Cong et al. [Sci. Tot. Environ.**
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8 Recently, Cong et al. (2010) published a comprehensive study on the characterization of
9 reductive properties of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethane
10 (DDTs) using powdered metallic iron (Fe^0). Quantum chemical descriptors characterizing
11 different molecular structures and physicochemical properties of the seven tested
12 organochlorine pesticides (4 HCHs and 3 DDTs) were computed to discuss the major
13 influential factors over their reductive dechlorination rates. A model was reported to be
14 established, which correlates the reductive dechlorination properties of pollutants with their
15 structural descriptors. As major result, the reductive dechlorination rate of tested
16 organochlorine pesticides appears to be mainly limited by the rate of dissolution in the
17 aqueous phase. It is evident that this conclusion is not specific to reduction by Fe^0 but rather a
18 simple solubility issue.

19 The work of Cong et al. (2010) is a justified attempt to correlate the intrinsic properties of
20 individual contaminants to their chemical reactivity in a aqueous systems. Accordingly, the
21 authors are to be commended for having listed up to twenty two (22) structural and
22 thermodynamic parameters which may influence the chemical reactivity of individual
23 contaminants. Table 1 gives three structural [molecular weight (Mw) and average molecular
24 polarizability (Polar), Van der waals volume of molecule (V)] and one thermodynamic
25 parameters [formation free energy ($\Delta_f G^0$)] representative for discussing the reactivity. For
26 instance, if Mw is the most determinant parameter for the reactivity then two classes of

27 reactivity (1 and 2) should have been observed. However Cong et al. (2010) reported seven 7
 28 reactivity's classes as each tested pollutant's reactivity was significantly different from that
 29 from others. Table 1 shows that from the three other selected parameters each exhibit a
 30 different reactivity order for the pollutants. This order of reactivity was different from the one
 31 reported by Cong et al. (2010). The exception of V and $\Delta_f G^0$ which yield the same order of
 32 reactivity should be noticed. This identity is not surprising as V is a thermodynamic constant
 33 used for the calculation of $\Delta_f G^0$. A closed look on Tab. 1 reveals that HCHs (1, 2, 3, 4) are
 34 more reactive than DDTs (5, 6, 7) for all selected parameters. But for the comparison based on
 35 the soil contaminant concentrations ($[X]$ in $\mu\text{mol/kg}$), this order is perturbed. Suggesting that
 36 relevant aspects were not purposefully considered in the experimental design.

37

38 **Table 1:** Selected structural and thermodynamic parameters of organochlorine pesticides
 39 tested by Cong et al. (2010) and related relative order of reactivity.

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Pollutant	[X]	Polar	V	$\Delta_f G^0$	Relative reactivity					
	($\mu\text{mol/kg}$)	(a.u.)	(cm^3/mol)	(kJ/mol)	present	[X]	Mw	Polar	V	$\Delta_f G^0$
γ-HCH	3.7	118.9	177.015	133.562	1	2	1	2	4	4
δ-HCH	27.3	117.6	139.522	137.806	2	5	1	1	1	1
β-HCH	92.8	121.6	170.585	132.205	3	6	1	4	3	3
α-HCH	23.9	119.6	139.661	130.04	4	5	1	3	2	2
o,p'-DDT	3.8	191.6	247.826	311.879	5	3	2	5	7	7
p,p'-DDT	4.4	195.4	242.140	309.503	6	1	2	7	6	6
p,p'-DDE	1.9	193.3	200.024	307.898	7	4	2	6	5	5

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42 First, the tested HCHs (4) and DDTs (3) were not added as chemicals into the aqueous phase
43 but were characterized from their leaching extent (and subsequent removal by Fe^0) from
44 contaminated soils from a former pesticide manufacturing facility. However, the leachability
45 of individual contaminants depends on their affinity to soil materials. This explains why some
46 HCHs are more sensitive to water leaching than DDTs (Tab. 1).

47 Second, given the difference in molecular weight of tested pollutants (287.860 and 315.938
48 a.m.u) the extent of contaminant removal should have been expressed in molar unit.

49 Third, Cong et al. (2010) have randomly interchanged “contaminant removal” and
50 “contaminant reductive transformation” by Fe^0 . Aqueous Fe^0 is rigorously a system in which
51 the surface of iron (bare Fe^0) is permanently covered with a layer of iron oxides (Statmann
52 and Müller, 1994; Noubactep, 2007; Noubactep, 2008). Accordingly the rate of contaminant
53 removal is necessarily a function of contaminant affinity to iron oxides. This suggests that
54 beside the properties of tested organochlorine pesticides, the properties of the adsorbing
55 phases should have been considered as well.

56 In conclusion, the experimental results of Cong et al. (2010) could be differently presented.
57 The fact that Cong and his colleagues attributed contaminant removal to reductive
58 dechlorination demonstrates the extent to which researchers have been driven deep into
59 confusion by the concept considering Fe^0 as a reducing agent. However, before introducing
60 this proven inconsistent concept, no survey of available data on the $\text{Fe}^0/\text{H}_2\text{O}$ system and the
61 link of the data for all possible hypotheses and the consequences for contaminant removal was
62 achieved (Noubactep 2007, Noubactep 2008).

63 **References**

64 Cong X, Xue N, Wang S, Li K, Li F. Reductive dechlorination of organochlorine pesticides in
65 soils from an abandoned manufacturing facility by zero-valent iron. *Sci. Tot. Environ.*, 2010,
66 doi:10.1016/j.scitotenv.2010.04.035.

- 67 Noubactep C. Processes of contaminant removal in “Fe⁰-H₂O” systems revisited. The
68 importance of co-precipitation. *Open Environ. J.* 2007;1, 9–13.
- 69 Noubactep C. A critical review on the mechanism of contaminant removal in Fe⁰-H₂O
70 systems. *Environ. Technol.* 2008; 29: 909–20.
- 71 Stratmann M, Müller J. The mechanism of the oxygen reduction on rust-covered metal
72 substrates. *Corros. Sci.* 1994; 36:327–59.