ENVIRONMENTAL REDUCTION REACTIONS

Reducing environments abound in nature: subsurface waters and soils, aquatic sediments, sewage sludge, waterlogged peat soils, hypolimnia of stratified lakes, oxygen free sediments of eutrophic rivers. Some common naturally occurring reductants (and mediators) are biologically derived molecules (e.g., iron porphyrins, quinoid compounds) that are no longer associated with living organisms and we will call redox reactions with these compounds, *abiotic*.

Recognition of Redox Reactions

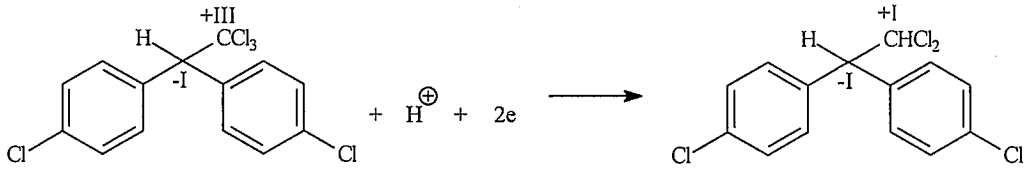
We can recognize a reduction half-reaction from any one of the following:

- gain of electrons,
- increase in hydrogen or decrease in oxygen,
- decrease in oxidation state

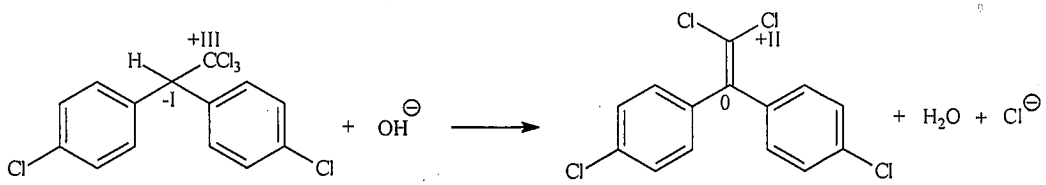
For redox reactions of large organic molecules, we use the net change in oxidation state(s) of the atoms (commonly C, N or S) involved in the reaction. For each atom in an organic molecule the oxidation state may be computed by adding a value of;

- +1 for each bond with a more electronegative atom or for each positive charge
- −1 for each bond with a less electronegative atom or for each negative charge
- 0 for each bond with an identical atom

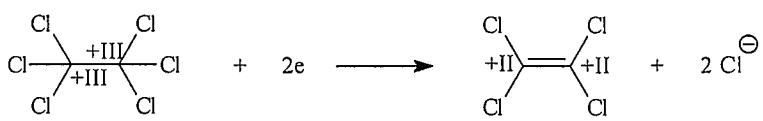
For example, the transformation of DDT to DDD involves a net change in oxidation state of the carbon atom at which the reaction occurs of +III to +I, whereas the oxidation states of all the other atoms remain the same. Hence conversion of DDT to DDD requires a total of two electrons to be transferred from an electron donor to DDT, i.e., a reduction. Since a hydrogen atom is gained and a chlorine atom is lost, we can write the half-reaction as;



This type of reaction is termed a reductive dechlorination. Note all the rules for balancing half-reactions apply, they must be balanced for atoms and charge. The elimination of DDT to DDE is not a redox reaction, as the change in oxidation state of one of the carbon atoms (+III to +II) is compensated by the change in oxidation state of the adjacent carbon atom (–I to 0). Hence dehydrochlorination requires no net electron transfer from or to the compound.



In the transformation of hexachloroethane (HCE) to tetrachloroethylene (a.k.a. perchloroethylene, PCE), the oxidation states of both carbon atoms decrease by –1, so two electrons are transferred from an unspecified electron donor to HCE and we can write the half-reaction as;



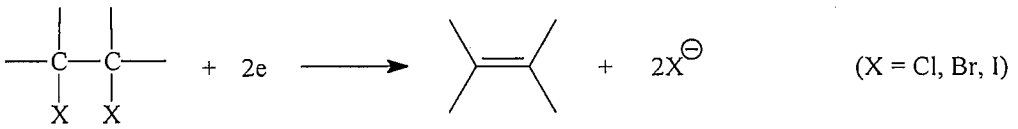
Reductive transformations known to occur in natural reducing environments

Carbon

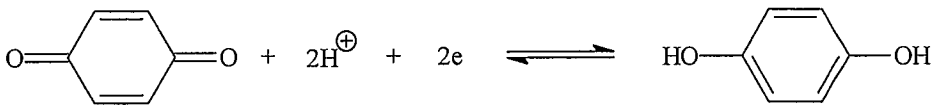
1. hydrogenolysis

$$R\text{–}X + H^+ + 2e \rightarrow R\text{–}H + X^- \qquad (X = Cl, Br, I)$$

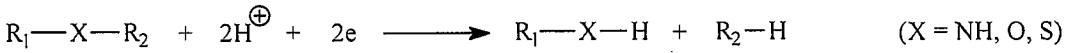
2. vicinal dehalogenation



3. quinone reduction



4. reductive dealkylation



Nitrogen

5. nitroaromatic reduction

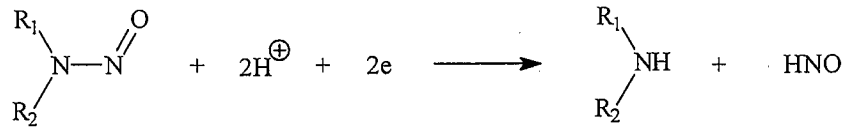
$$Ar\text{–}NO_2 + 6\,H^+ + 6e \rightarrow Ar\text{–}NH_2 + 2\,H_2O$$

6. aromatic azo reduction

$$Ar\text{–}N{=}N\text{–}Ar + 2\,H^+ + 2e \rightarrow Ar\text{–}NH\text{–}NH\text{–}Ar$$

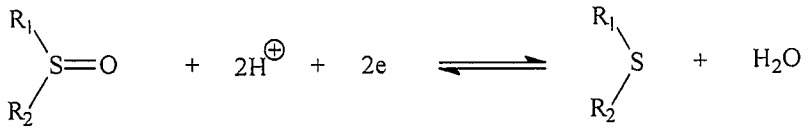
$$Ar\text{–}NH\text{–}NH\text{–}Ar + 2\,H^+ + 2e \rightarrow 2\,Ar\text{–}NH_2$$

7. N-nitrosoamine reduction

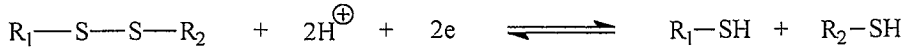


Sulfur

8. sulfoxide reduction



9. disulfide reduction



Redox Processes That Determine Redox Conditions In The Environment

From the data in the table above (Standard Reduction Potentials At 25°C Of Some Redox Couples That Are Important In Natural Redox Processes), we can get a general idea about the maximum free energy that microorganisms may gain from catalyzing redox reactions. On earth, the maintenance of life resulting directly or indirectly from a steady input of solar energy is the main cause for nonequilibrium redox conditions. In the process of photosynthesis, organic compounds exhibiting reduced states of carbon, nitrogen and sulfur are synthesized, and at the same time oxidized species including molecular oxygen, O_2 (oxic photosynthesis) or oxidized sulfur species (anoxic photosynthesis) are produced. Using glucose as a model organic compound, we can express oxic photosynthesis by combining equations (1) and (13) from the above table. Since we are looking at the overall process, it is convenient to write the reaction with a stoichiometry corresponding to the transfer of one electron (remembering that $E°_H$ and $E°_H(w)$ are independent of the number of electrons transferred). Equation (13):

	$E°_H(w)$ (v)	$\Delta G°_H(w)/n$ (kJ.mol^{-1})
$\frac{1}{4}\,CO_2 + H^+ + e \;—\; \frac{1}{24}\,C_6H_{12}O_6$(glucose) $+ \frac{1}{4}\,H_2O$	−0.43	+41.0

We take the reversed form of equation (1) and changing the sign:

$\frac{1}{2}\,H_2O \;—\; \frac{1}{4}\,O_2(g) + H^+ + e$	−0.81	+78.3
$\frac{1}{4}\,CO_2 + \frac{1}{4}\,H_2O \;—\; \frac{1}{24}\,C_6H_{12}O_6 + \frac{1}{4}\,O_2(g)$	−1.24	+119.3

Thus, under standard environmental conditions (pH 7), on a "per electron basis", an organism utilizes 119.3 kJ.mol^{-1} of the suns energy to photosynthesize glucose from CO_2 and H_2O.

The chemical energy stored in reduced chemical species (including organic pollutants) can now be utilized by organisms that are capable of catalyzing energy yielding redox reactions. For example, we can see from the table above, that in the oxidation of glucose (reversed Reaction 13), oxygen is the most favorable oxidant (i.e., electron acceptor) from an energetic point of view, at least, if O_2 is reduced all the way to H_2O (which is commonly the case in biologically mediated processes):

	$E°_H(w)$ (v)	$\Delta G°_H(w)/n$ (kJ.mol^{-1})
$\frac{1}{4}\,O_2(g) + H^+ + e \;—\; \frac{1}{2}\,H_2O$	+0.81	−78.3

The $\Delta G°_H(w)/n$ value for the reaction of glucose with O_2 (reversed reaction 13 with reaction 1) is:

$\frac{1}{24}\,C_6H_{12}O_6 + \frac{1}{4}\,O_2(g) \;—\; \frac{1}{4}\,CO_2 + \frac{1}{4}\,H_2O$	+1.24	−119.3

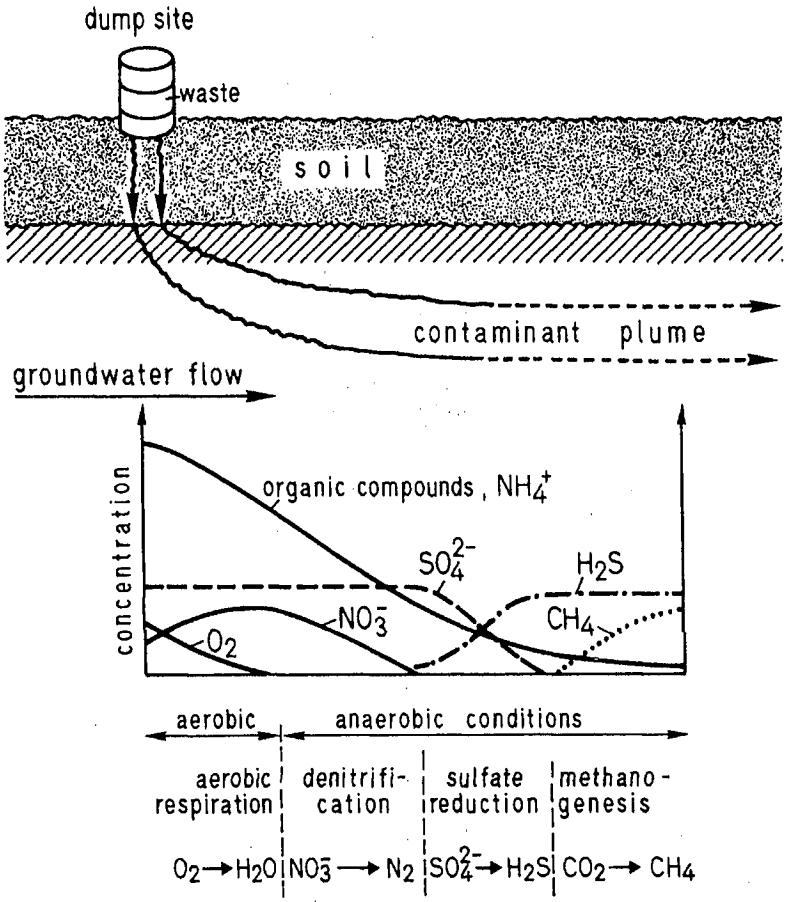
and the organism obtains −119.3 kJ.mol^{-1} of energy on a "per electron basis".

The next "best" electron acceptors would be nitrate, NO_3^- (if converted to N_2), then $MnO_2(s)$, and so on going down the list in the table above.

$\frac{1}{5}\,NO_3^- + \frac{6}{5}\,H^+ + e \;—\; \frac{1}{10}\,N_2(g) + \frac{3}{5}\,H_2O$	+0.74	−71.4
$\frac{1}{2}\,MnO_2(s)\;\; \frac{1}{2}\,HCO_3^-(10^{-3}M) + \frac{3}{2}\,H^+ + e \;—\; \frac{1}{2}\,MnCO_3(s) + H_2O$	+0.52	−50.2

For the reaction of these oxidants with glucose, the organisms would obtain −112.4 and −91.2 kJ.mol^{-1} respectively on a "per electron basis". Interestingly, the chemical reaction sequence given in the table above (that is based on standard free energy considerations) is, in essence, paralleled by a spatial and/or temporal succession of different microorganisms in the environment. In other words, in a given (micro)environment, those organisms will be dominant that are capable of utilizing the "strongest"

oxidants available (i.e., the electron acceptor with the most positive reduction potential). These microorganisms then in turn determine the redox conditions in that (micro)environment. The figure below illustrates the dynamics of some redox species along the flow path of a contaminant plume in the ground. For simplicity, we assume a situation where we have constant input of reduced (e.g., organic compounds) and oxidized species (e.g., O_2, NO_3^-, SO_4^{2-}). Natural or synthetic organic compounds (the major electron donors) are degraded over the whole length of the plume. As long as there is molecular oxygen present, *aerobic (oxic) respiration* takes place, which involves the oxidation of organic compounds by oxygen, O_2. Once the oxygen is consumed, *denitrification* is observed until the nitrate is no longer present. In the region where denitrification occurs, one often observes the reductive dissolution of oxidized manganese phases (e.g., MnO_2(s), MnOOH(s)). Under these conditions iron is still present in oxidized forms (e.g., FeOOH(s)). Then, a marked decrease in redox potential occurs when the only electron acceptors left in significant abundance, are those that exhibit low reduction potentials (see table above). This redox sequence has led to a somewhat different terminology in that one speaks of the *oxic* (aerobic), *suboxic* (denitrification, manganese reduction), and *anoxic* conditions (low redox potential). Processes involving electron acceptors (oxidants) exhibiting a low redox potential include, in sequence: *iron reduction*, *sulfate respiration* (or sulfate reduction), and *fermentation* including *methogenesis*. The temporal and/or spatial succession of redox processes as illustrated in the diagram below for the groundwater environment is also observed for other environments in which access to oxygen and other electron acceptors is limited, for example, in sediments of lakes, rivers, and the oceans.



The table below gives $E°_H(w)$ values for some organic half-reactions involving organic pollutants.

Examples of standard reduction potentials at 25°C and pH 7 of some organic redox couples

Half-Reaction	$E°_H$ (w) (volts)
hexachloroethane + 2e → tetrachloroethene + 2 Cl^-	+1.13
carbontetrachloride + H^+ + 2e → chloroform + Cl^-	+0.67
chloroform + H^+ + 2e → dichloromethane + Cl^-	+0.56
carbontetrabromide + H^+ + 2e → tribromomethane + Br^-	+0.83
tribromomethane + H^+ + 2e → dibromomethane + Br^-	+0.61
nitrobenzene + 6 H^+ + 6e → aniline + 2 H_2O	+0.42
dimethylsulfoxide + 2 H^+ + 2e → dimethylsulfide + H_2O	+0.16
dimethylsulfone + 2 H^+ + 2e → dimethylsulfoxide + H_2O	−0.24
cystine (RSSR) + 2 H^+ + 2e → 2 cysteine (RSH)	−0.39

Environmental Standard Conditions are taken as: $[H^+] = 10^{-7}$ M, $[Cl^-] = 10^{-3}$ M, $[Br^-] = 10^{-5}$ M

These values are calculated from $\Delta G°_f$ values of the reactants and products and should be used as rough estimates. $\Delta G°_f$ values are normally given for the gaseous species and/or for the pure organic phase (i.e., liquid or solid). Since we are interested in aqueous-phase free energy of formation values, we need to add the free energy contribution for transferring the compound from the gaseous or pure liquid (solid) phase to the aqueous phase. This is given by:

$$\Delta G°_{gl\text{-}a} = \Delta G°_f(aq) - \Delta G°_f(g) = RT\ln K_H$$

where K_H is the Henry's Law constant.

For example, we wish to calculate $E°_H(w)$ for the reaction:

$$C_2Cl_6(aq) + 2e \text{ — } C_2Cl_4(aq) + 2\ Cl^-(aq)$$

In the literature we find; $\Delta G°_f[C_2Cl_4(g)]$ +20.5 kJ.mol^{-1}, $\Delta G°_f[C_2Cl_6(g)]$ −54.9 kJ.mol^{-1}, $\Delta G°_f[Cl^-(aq)]$ −131.3 kJ.mol^{-1}, and K_H $[C_2Cl_6]$ 3.9 atm.L.mol^{-1}, K_H $[C_2Cl_4]$ 27.5 atm.L.mol^{-1} at 25°C.

Since $$\Delta G°_f(aq) = \Delta G°_f(g) + RT\ln K_H$$

we calculate $\Delta G°_f[C_2Cl_4(aq)]$ to be +28.7 kJ.mol^{-1}, and $\Delta G°_f[C_2Cl_6(aq)]$ to be −51.5 kJ.mol^{-1}.

Now
$$\Delta G°_H = 2\,\Delta G°_f[Cl^-(aq)] + \Delta G°_f[C_2Cl_4(aq)] - \Delta G°_f[C_2Cl_6(aq)]$$
$$= (-262.6\text{ kJ}) + (28.7\text{ kJ}) - (-51.5\text{ kJ})$$
$$= -182.4\text{ kJ.mol}^{-1}$$
$$E°_H = -\Delta G°_H / nF = +0.95\text{ v}$$
$$E°_H(w) = E°_H - \frac{0.05916}{n}\log\left(\frac{[C_2Cl_6]}{[C_2Cl_4]\cdot[Cl^-]^2}\right)$$
$$E°_H(w) = 0.95 - \frac{0.05916}{2}\log\left(\frac{1M}{1M\cdot[10^{-3}M]^2}\right) = +1.13v$$

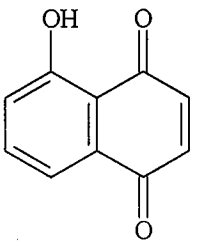
Kinetics of REDOX Reactions

Rates of disappearance of some halogenated ethanes in an anaerobic sediment-water slurry

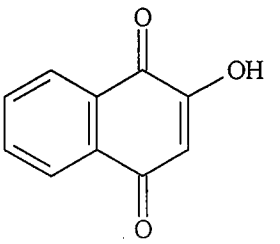
Compound Name	Structure	k_{obs} (s^{-1})	$t_{½}$ (h)	Sediment-Water Distribution Coeficient K_d ($L.kg^{-1}$)	Percent Sorbed
1,2-dichloroethane	CH_2Cl-CH_2Cl	$<<2 \times 10^{-7}$	>>950	1.3	9
1,2-dibromoethane	CH_2Br-CH_2Br	3.5×10^{-6}	55	2.0	13
1,2-diiodoethane	CH_2I-CH_2I	4.8×10^{-4}	0.4	3.5	21
1,1,2,2-tetrachloroethane	$CHCl_2$-$CHCl_2$	1.2×10^{-6}	160	3.4	20
hexachloroethane	CCl_3-CCl_3	3.2×10^{-4}	0.6	29	69

Structures of molecules that behave as electron mediators.

Quinones

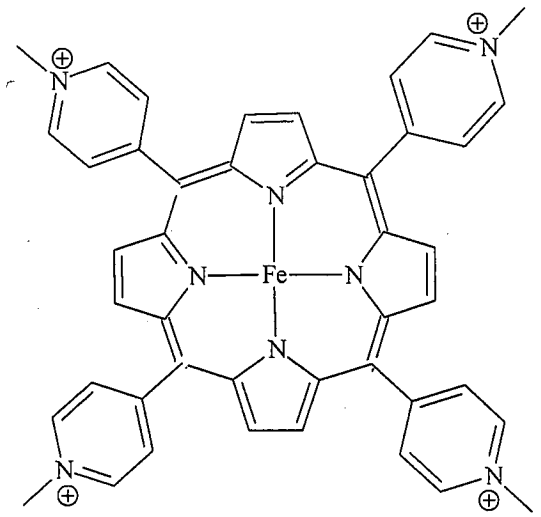


juglone

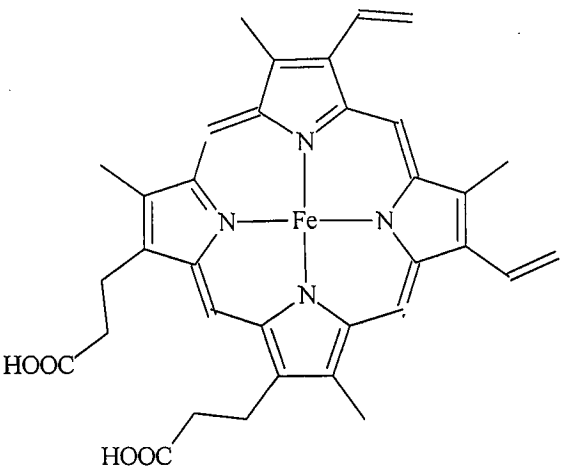


lawsone

Iron Porphyrins



meso-tetrakis(N-methylpyridyl)iron porphin



hematin

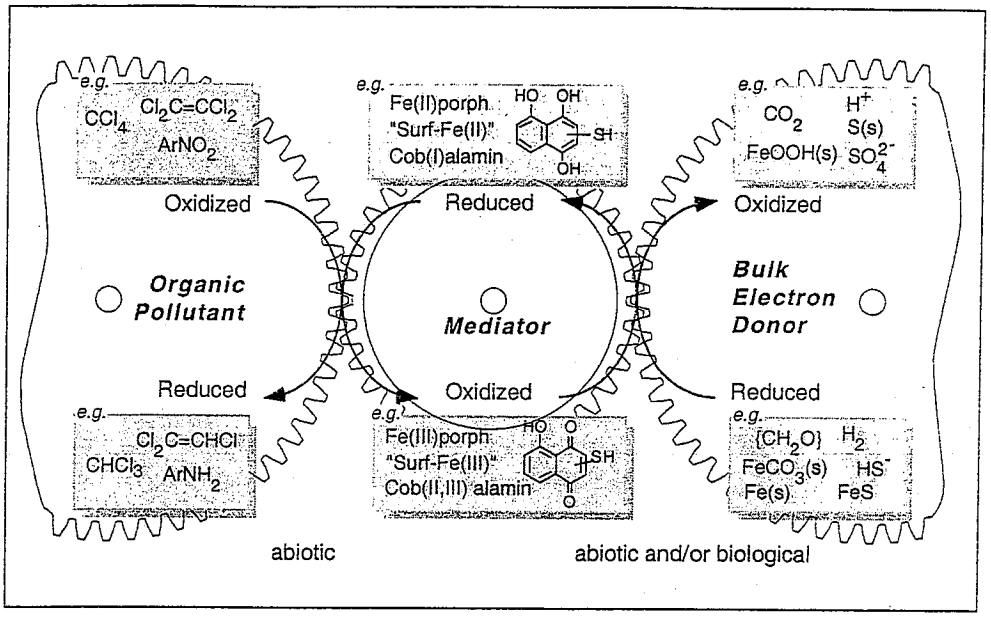


Figure 14.1 Schematic representation depicting the importance of electron transfer mediators as well as the concurrence of microbial and abiotic processes for reductive transformations of organic pollutants. Adapted from Schwarzenbach et al. (1997).

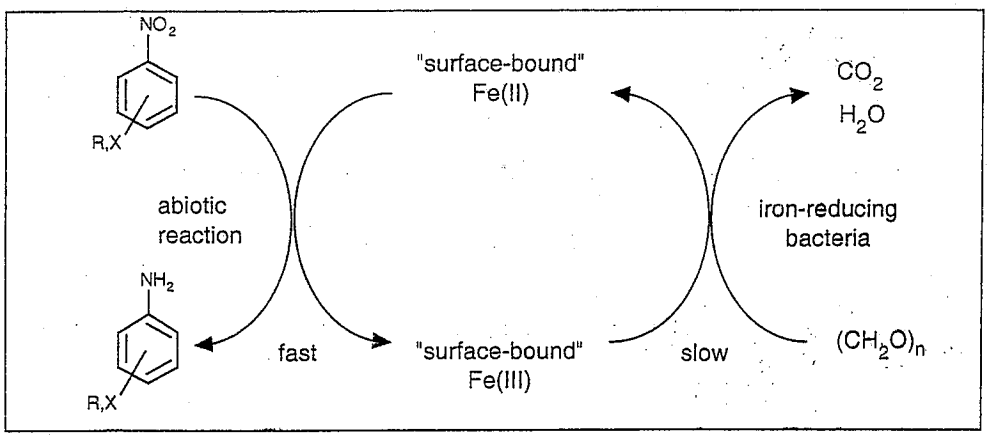
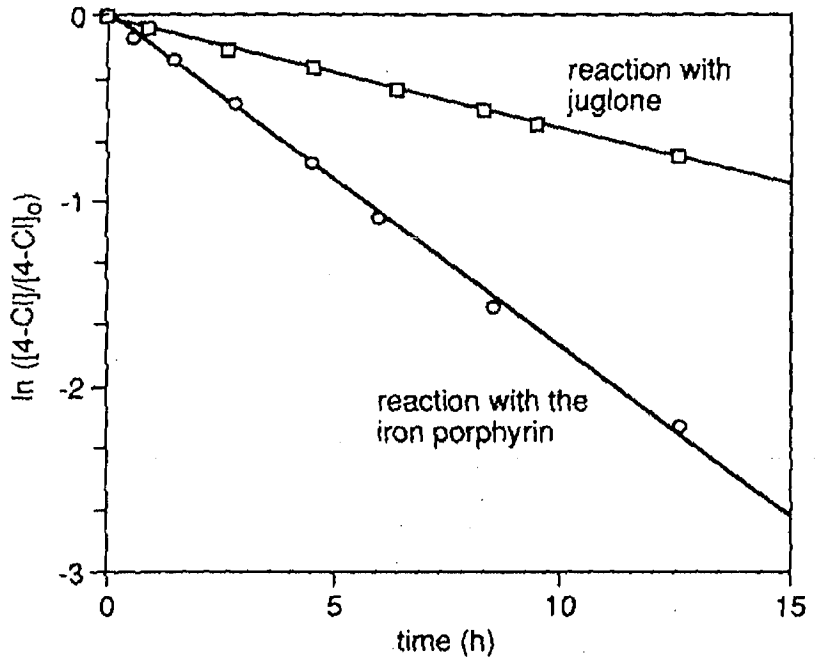
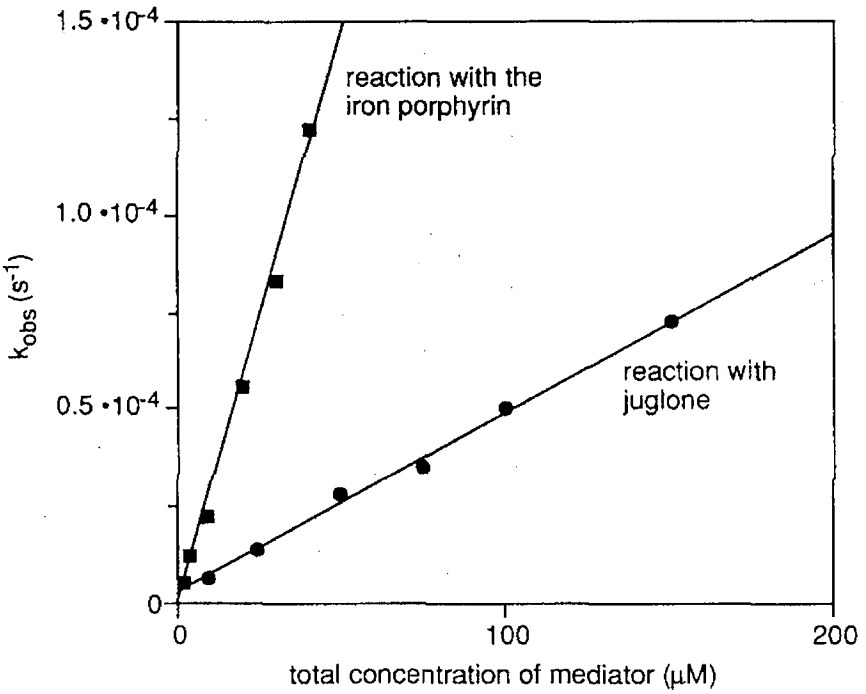


Figure 14.13 General reaction scheme proposed by Heijman et al. (1995) for the reduction of NACs in aquifer columns under ferrogenic conditions.

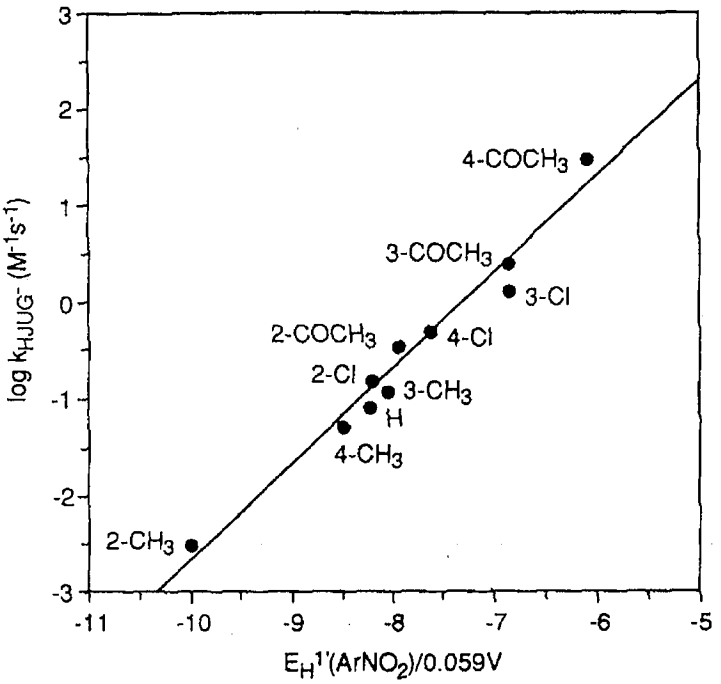
Plot of ln([4-chloronitrobenzene]$_t$ / [4-chloronitrobenzene]$_o$) versus time showing the rate of disappearance of 4-chloronitrobenzene (4-Cl) at 25°C in the two model systems. The conditions were: juglone (50μM, pH 7.08); iron porphyrin (20μM, pH 7.03); initial concentration of 4-Cl: 100μM.



Reduction of 4-chloronitrobenzene (4-Cl) in the two model systems. Observed pseudo-first-order rate constant at 25°C versus total electron mediator concentration. The conditions were: juglone (pH 7.18); iron porphyrin (pH 7.03); initial concentration of 4-Cl: 100μM.

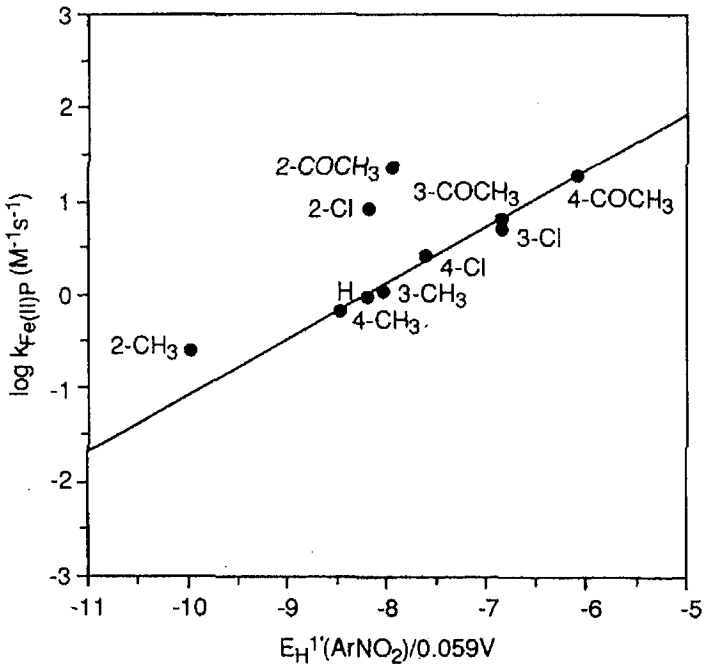


Plot of log k_{HJUG^-} versus $E_H^{1'}$ **(ArNO$_2$)**/0.059 v for the substituted nitrobenzenes listed in the table above.



The linear regression analysis yields: log k_{HJUG^-} = $E_H^{1'}$ 1.0**(ArNO$_2$)**/0.059 v + 7.21 (R^2 = 0.99)

Plot of log $k_{Fe(II)P}$ versus $E_H^{1'}$ **(ArNO$_2$)**/0.059 v for the substituted nitrobenzenes listed in the table above.



The linear regression analysis yields for the meta- and para-substituted compounds:
log $k_{Fe(II)P}$ = $E_H^{1'}$ 0.60**(ArNO$_2$)**/0.059 v + 4.95 (R^2 = 0.99)

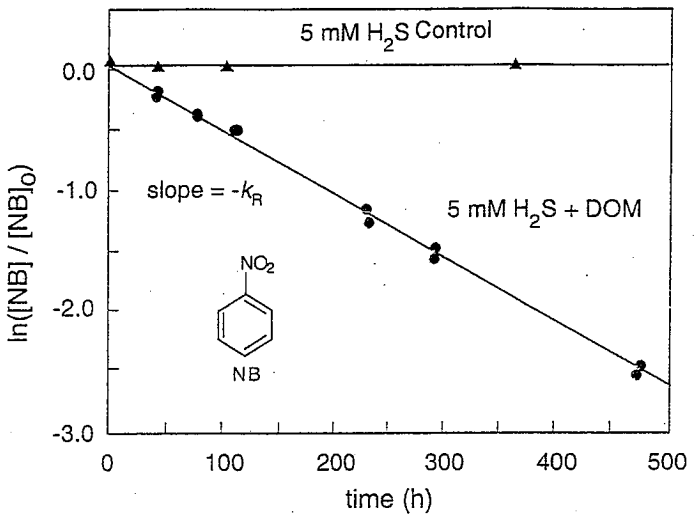


Figure 14.7 Reduction of nitrobenzene (NB) in 5 mM aqueous hydrogen sulfide solution in the absence (▲) and presence (●) of DOM (Hyde County, 66 mg DOC/L) at pH 7.2 and 25°C: Plot of ln ($[NB]/[NB]_0$) versus time. $[NB]_0$ and [NB] are the concentrations at time zero and *t*, respectively. Adapted from Dunnivant et al. (1992).

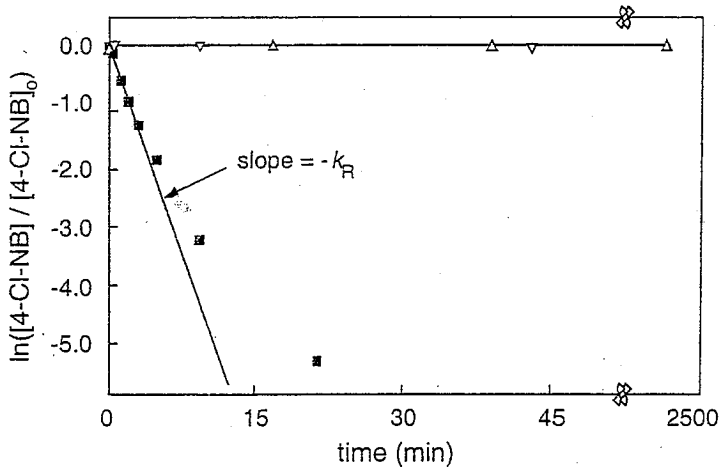


Figure 14.12 Reduction of 4-chloronitrobenzene (4-Cl-NB) in aqueous solution in the presence of 17 m^2 L^{-1} magnetite and an initial concentration of 2.3 mM Fe(II) at pH 7 and 25°C: plot of ln ($[4\text{-Cl-NB}]/[4\text{-Cl-NB}]_0$) versus time (■). $[4\text{-Cl-NB}]_0$ and [4-Cl-NB] are the concentrations at time zero and *t*, respectively. Adapted from Klausen et al. (1995). Note that experimental points deviate from pseudo-first-order behavior for long observation times. 4-Cl-NB was not reduced in suspensions of magnetite without Fe(II) (▽), or solutions of Fe(II) without magnetite (△).