Reductive Transformations of Anthropogenic Chemicals in Natural and Technical Systems

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Abstract. Reductive transformation reactions of chemical pollutants (*e.g.*, polyhalogenated hydrocarbons, aromatic azo and nitro compounds, chromium(VI) species) in the environment are important both from an ecotoxicological and from an environmental technology point of view. Using well-defined model reactors as well as more complex 'real world' systems, several groups at EAWAG are trying to unravel compound- and system-specific factors that control the reduction of a variety of anthropogenic chemicals under different conditions in the environment. The examples presented in this article include the reduction of nitroaromatic compounds under iron- and sulfate-reducing conditions, the reductive dehalogenation of chlorinated ethenes by cob(I)alamin and by a bacterium that uses such compounds as terminal electron acceptors, and the reduction of chromium(VI) by various reduced iron species. The link between microbial and abiotic (chemical) processes involved in reductive transformations of pollutants is emphasized. The major goal of this article is to illustrate the approaches taken to elucidate the mechanisms and kinetics of environmentally relevant reduction reactions of pollutants, and to discuss how the results of such studies can be used *1*) to gain insight into what is actually happening in the environment, and *2*) to develop methods for the treatment of chemical wastes or contaminated sites.

Introduction

Many industrially produced chemicals of significant toxicological and environmental concern are not easily degraded under oxic conditions. However, some of them may undergo transformations in reducing environments. Examples of such reactions are reductive dehalogenation of polyhalogenated aliphatic, olefinic, and aromatic hydrocarbons, *e.g.*, chlorinated solvents, polychlorinated biphenyls (PCBs); reduction of nitro groups in (poly)nitroaromatic compounds, *e.g.*, explosives such as 2,4,6-trinitrotoluene (TNT), pesticides such as dinitro-*o*-cresol (DNOC); reduction of aromatic azo compounds, *e.g.*, azo dyes; and reduction of chromium(VI). These types of reactions currently form an important topic in environmental chemistry, mainly for two reasons. On the one hand, it has been recognized that in anaerobic environments (*e.g.*, anaerobic sediments, soils, and aquifers), reductive transformations of anthropogenic chemicals can lead to products that may be of considerable (eco)toxicological concern. Thus, the processes involved need to be understood in order to be able to assess

the risks connected to contaminations with such reductible compounds. On the other hand, such processes are of great interest with respect to their application in the biological and chemical treatment of hazardous wastes or contaminated sites. For example, it has been proposed to reduce polynitroaromatic compounds, that are extensively found in former ammunition dump sites, to their corresponding polyamino compounds with subsequent oxidative polymerization of these reduced species [1], or to convert polyhalogenated compounds, (*e.g.*, chlorinated solvents) by reductive dehalogenation to less toxic products or to products that are more easily biodegradable. Similarly, reduction of Cr^{VI} to immobile Cr^{III} is the aim in remediation procedures for this widespread contaminant in soils, sediments, groundwaters, and surface waters. The research conducted at EAWAG that is illustrated in this paper focuses on both environmental and technological aspects, although, so far, emphasis has been mostly on improving the basic understanding of redox reactions of anthropogenic chemicals in natural systems.

Definition of the Problem and Experimental Approach

As already addressed in another paper in this issue [2], one of the major challenges in environmental chemistry is to describe quantitatively the temporal and spa-
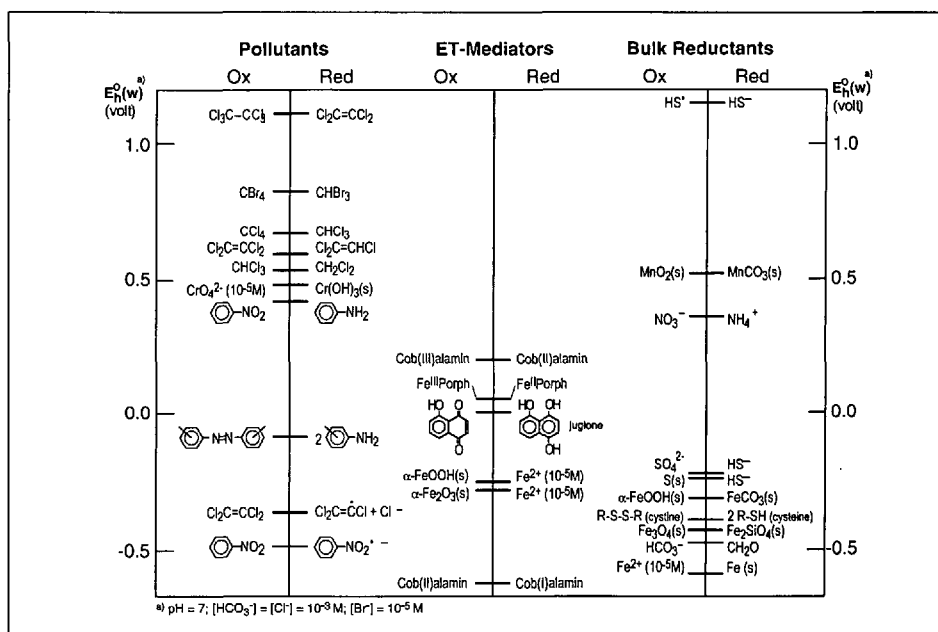
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Fig. 1. *Selection of environmentally relevant redox couples including organic pollutants such as nitroaromatic and halogenated compounds, and an inorganic pollutant, Cr^{VI}, as well as examples of electron transfer mediators and important natural bulk reductants.* The values given represent reduction potentials at pH 7 at equal (except otherwise indicated) concentrations of the redox partners but at environmental concentrations of the major anions involved: [HCO] = [Cl$^-$] = 10^{-3} M; [Br$^-$] = 10^{-5} M; porph = porphyrin.
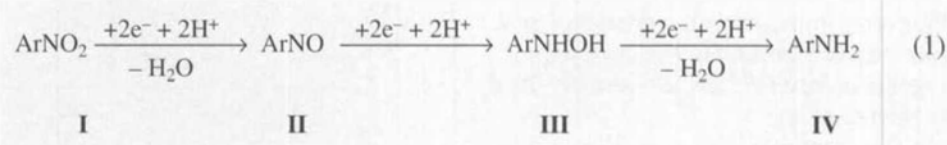
tial dynamics of the environmental factors that control abiotic as well as biological transformation processes of anthropogenic chemicals. More specifically, in the case of reductive transformations of such compounds, the identification, quantification, and an assessment of the reactivities of the relevant reductants in the system of interest are difficult. Moreover, this task is complicated by the fact that, although thermodynamically feasible, the direct reduction of many organic compounds by the prevailing bulk electron donor(s) (*e.g.*, reduced iron and sulfur species, organic material, H_2, *etc.*; see *Fig. 1*) in a given environment is very slow. In these cases, the environmental rates of both abiotic and biological processes are often controlled by so-called electron transfer mediators (*e.g.*, transition-metal complexes, quinoid-type compounds; see *Figs. 1* and *2*), *i.e.*, by species that reduce the pollutant more quickly and that are themselves re-reduced by the bulk electron donor(s). For example, the reduction of nitrobenzene by hydrogen sulfide in homogeneous aqueous solution is rather slow [3] because of the strongly endergonic nature of the first electron transfer (compare $E_h^{1'}$ values of the corresponding half reactions $HS^- \rightarrow HS^{\cdot} + e^-$ and $Ar-NO_2 + e^- \rightarrow Ar-NO_2^{\cdot-}$ in *Fig. 1*), even though the overall process (*i.e.*, reduction to the aniline) is exergonic. In the presence of a quinone such as juglone (*Fig. 1*), however, the reaction proceeds at much higher rates [3].

In a given natural system, a pollutant may react with several different reductants and the relative importance of these reductants may be strongly influenced by various environmental parameters including pH, temperature, water composition, and, most importantly, microbial activity. Depending on the compounds and reductants involved, various reaction steps – *e.g.*, desorption from unreactive solid surfaces, biological uptake, adsorption to a reactive surface, actual electron transfer, or regeneration of reductant(s) – may determine the overall reduction rate that finally controls the environmental behavior of the pollutant. Obviously, in natural systems, it is extremely difficult if not impossible to determine all important parameters independently by classical chemical methods. Therefore, the general approach is to use information gained from studies of well-defined model systems in order to evaluate the corresponding processes in more complex systems that represent the natural environment more realistically. First, relevant reductants are identified, with emphasis on electron mediators or catalytic surfaces. Second, the factors are

evaluated that control the redox kinetics and product formation of a given pollutant in order to, third, assess likely transformation pathways in the environment or design suitable remediation strategies. This is illustrated in the following by three projects that are currently in progress at EAWAG. The first example illuminates the use of nitroaromatic compounds to assess the factors that determine the 'abiotic' reduction of such soil and groundwater pollutants under iron- and sulfate-reducing conditions in the subsurface. The second example illustrates the approach taken to elucidate the reductive dechlorination of chlorinated ethenes by anaerobic microorganisms. Finally, the third example addresses important pathways that convert highly toxic chromium(VI) species to nontoxic Cr^{III} species in contaminated soils or aquifers.
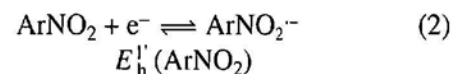
Reduction of Nitroaromatic Compounds (NACs) under Iron- and Sulfate-Reducing Conditions

As mentioned above, nitroaromatic compounds (NACs) are ubiquitous pollutants, particularly in the subsurface environment [4]. Under anoxic conditions, NACs (**I**; see *Eqn. 1*) may be reduced to the corresponding nitroso compounds (**II**), the hydroxylamines (**III**), and, ultimately, to the amines (**IV**):

$$\text{ArNO}_2 + e^- \rightleftharpoons \text{ArNO}_2^{\cdot-} \qquad (2)$$
$$E_h^{1'}(\text{ArNO}_2)$$

As illustrated in *Fig. 3*, plots of the logarithms of reduction rate data *vs.* one-electron reduction potentials, $E_h^{1'}(\text{ArNO}_2)$ (divided by 0.059 V), of a series of structurally related NACs (here ten monosubstituted nitrobenzenes) can be used to evaluate whether the actual transfer of the electron or whether other reaction steps are determining the overall reaction rate in a certain system. Thus, *e.g.*, when the reduction was mediated by juglone (*Fig. 3, a*; the structure of juglone is given in *Fig. 1*), or by natural organic matter (NOM, *Fig. 3, b*) in the presence of hydrogen sulfide as bulk electron donor in homogeneous aqueous solution, a linear correlation with a slope of 1 of the regression line was obtained. According to the *Marcus* theory [5], these findings indicate that in both systems the actual transfer of the first electron was rate-limiting and that the reaction occurred most probably by an outer-sphere mechanism. These and a number of other results (not shown) suggest that in natural systems under sulfate-reducing conditions, quinone and mercaptoquinone (formed from addition reactions of hydrogen sulfide and NOM) moieties may play an important role in the abiotic reduction of organic pollutants, particularly of compounds with high one-

$$\text{ArNO}_2 \xrightarrow[-\text{H}_2\text{O}]{+2e^- + 2\text{H}^+} \text{ArNO} \xrightarrow{+2e^- + 2\text{H}^+} \text{ArNHOH} \xrightarrow[-\text{H}_2\text{O}]{+2e^- + 2\text{H}^+} \text{ArNH}_2 \qquad (1)$$

$$\quad\quad\quad \textbf{I} \quad\quad\quad\quad\quad\quad\quad \textbf{II} \quad\quad\quad\quad\quad\quad\quad \textbf{III} \quad\quad\quad\quad\quad\quad\quad \textbf{IV}$$

where Ar stands for any unsubstituted or substituted aromatic structure.

Even though some of these reduction products (**II–IV**) may be of considerable (eco)toxicological concern as such, in this paper we do not primarily focus on NACs as pollutants but on their use as probe compounds for studying redox reactions in anaerobic environments. In general, NACs are reduced to well-defined, easily detectable products (*Eqn. 1*), allowing one to establish mass and electron balances in a given system. Furthermore, the transfer of the first electron to a given NAC is reversible and usually the rate-determining reaction step in the reduction of a given organic compound [5]. The corresponding one-electron reduction potential, $E_h^{1'}(\text{ArNO}_2)$ (see *Eqn. 2*), can be determined relatively easily and is available for a variety of NACs in aqueous solution at ambient pH [6].

electron reduction potentials such as polynitroaromatic compounds (for more details see [3][6–8]).

Fig. 3, c shows that very differently to the NOM-mediated reaction in homogeneous aqueous solution in the presence of hydrogen sulfide, the ten model NACs were transformed at almost identical, $E_h^{1'}$-independent rates in a laboratory column containing aquifer material from a river water/groundwater infiltration site [9]. In this case, zero-order kinetics were found, indicating that all reactive sites were saturated in the concentration range considered (1–100 µM NAC). It was postulated that the compounds were reduced by surface-bound iron(II) species which were generated by iron-reducing bacteria utilizing organic material as the electron source, and that the regeneration of reactive iron(II) sites rather than the actual electron transfer to the NACs was rate-

limiting. The hypothesis that iron(II) species were involved in the NAC reduction is corroborated by the data shown in *Fig. 3, d–f. Fig. 3, d* shows the typical picture obtained when relative initial pseudo-first-order rate constants of the model NACs for the reaction with ferrous iron adsorbed to iron-oxide surfaces were plotted *vs.* the one-electron reduction potentials of the compounds (for details see [10]). A very similar result was found for the reduction of the same compounds by an iron(II) porphyrin in homogeneous aqueous solution ([3]; not shown). In both cases, the relative reactivities of the compounds were proposed to be strongly dependent on the relative affinities of the compounds to the reduced iron species. This assumption was scrutinized by conducting competition experiments in columns in which the relative rates of the model NACs were determined in binary mixtures. The pertinent competition factor, Q_c, was defined as the ratio of the zero-order rate constant for a certain compound and the zero-order rate constant of 4-chloronitrobenzene when both were present. *Fig. 3, e, f* shows that, as expected, almost identical plots of the logarithms of the competition factors *vs.* the one-electron reduction potentials of the compounds were obtained for the aquifer column and for a column containing iron-oxide-coated quartz sand, a pure culture of an iron-reducing bacterium (*Geobacter metallireducens* strain GS-15) and acetate as the bulk electron donor. Furthermore, the main characteristics of these plots are very similar to *Fig. 3, d,* suggesting that indeed Fe[II] species were involved in the reaction.

The examples shown in *Fig. 3* illustrate how relative reactivities of a series of model compounds can be used to evaluate redox reactions of organic pollutants in complex environmental systems. Furthermore, these examples nicely demonstrate the importance of the coupling of biogeochemical processes and (abiotic) pollutant transformation that may occur under iron- and sulfate-reducing conditions in the environment. In fact, results very similar to the ones shown in *Fig. 3* for simple NACs were also found for polynitroaromatic compounds such as TNT and related chemicals [6], and for polyhalogenated methanes and ethanes [8][11]. Furthermore, the approach described here has been used successfully to evaluate the processes involved in reductive transformations of organic pollutants in a hazardous waste plume [12]. From an environmental engineering point of view, the ferrogenic systems investigated are of particular interest. They offer the possibility to reduce
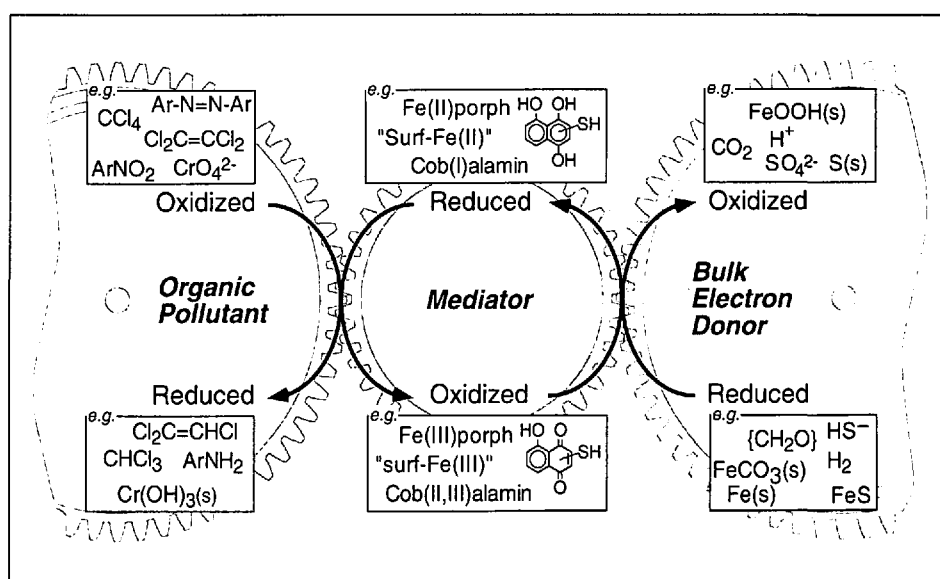

Fig. 2. *Schematic representation depicting the importance of electron transfer mediators as well as the concurrence of microbial and abiotic processes for reductive transformations of organic and inorganic pollutants*
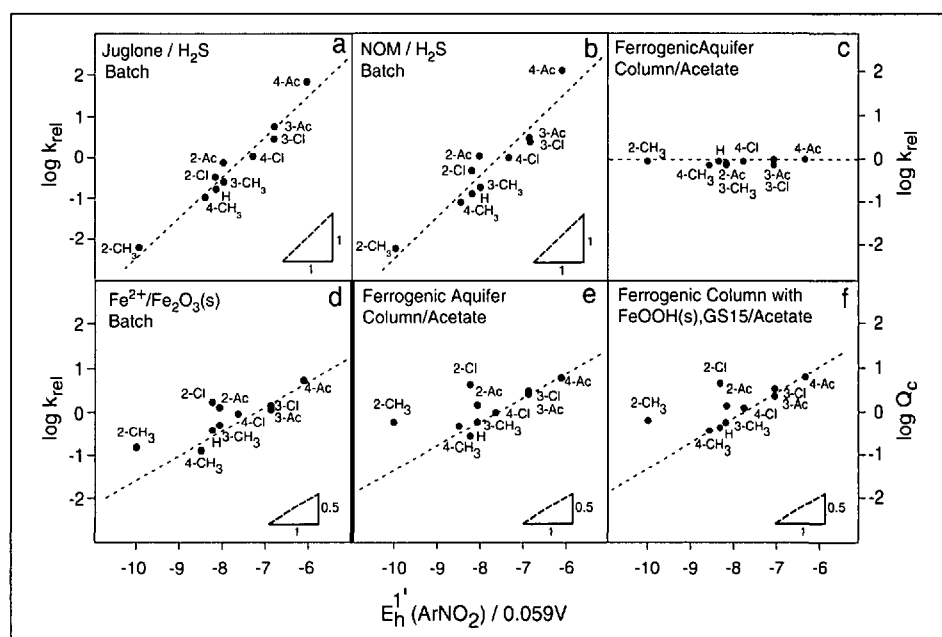

Fig. 3. *Plot of the relative* (relative to 4-chloronitrobenzene) *(a–d) reaction rate constants and competition quotients (e, f) of the ten model compounds* (nitrobenzene, 2-methyl-, 3-methyl-, 4-methyl-, 2-chloro-, 3-chloro-, 4-chloro-, 2-acetyl-, 3-acetyl-, and 4-acetylnitrobenzene) vs. *their one-electron reduction potentials* (divided by 0.059 V) *for various laboratory batch and column systems* (for details see text and cited literature)

organic pollutants with iron(II) in an abiotic reaction, thus providing an electron acceptor (namely, iron(III)) for microorganisms that, in turn, oxidize other pollutants that may serve as carbon and electron source. Further work evaluating these possibilities is presently in progress at EAWAG.

Reductive Dechlorination of Chlorinated Ethenes by Anaerobic Microorganisms

Tetrachloroethene (PCE) and trichloroethene (TCE) are among the most im-

portant soil and groundwater pollutants. Under aerobic conditions, these compounds have been found to be very persistent. However, various studies have demonstrated that under methanogenic and sulfate-reducing conditions, both compounds can be reduced microbially to dichloroethenes (DCEs, mainly *cis*-1,2-DCE), vinyl chloride (VC), ethene, and ethane (see [13] and references cited therein). Among these products, vinyl chloride is of particular environmental concern because of its high toxicity. Hence, any strategy to remove PCE or TCE from contaminated sites by processes involving reductive dehalogenations has to avoid

the accumulation of vinyl chloride. As a prerequisite, and, in general, for assessing the environmental impact of PCE and TCE, the factors that determine the reaction pathways and reaction kinetics of microbially (and possibly chemically) mediated dechlorination of chlorinated ethenes have to be understood (see, *e.g.,* [13]).

For microorganisms, reductive dehalogenations may have two different physiological meanings [14]. They can either be co-metabolic processes or novel types of anaerobic respiration. In the first case, the microorganisms do not profit from the highly exergonic reaction that they catalyze (see reduction potentials of the corresponding reactions in *Fig. 1*). Enzymes that are not designed for these reactions dehalogenate the halogenated compounds unspecifically. Dehalogenations by methanogens, acetogens, sulfate reducers, and fermentative bacteria are examples of such co-metabolic reactions. Recently, an increasing number of bacteria in pure culture have been isolated that couple the reductive dehalogenation of chlorinated ethenes to the oxidation of an electron donor in an anaerobic respiration [15]. The electron donors utilized by these bacteria are molecular hydrogen, formate, ethanol, lactate, acetate, and some other simple organic compounds. Some of the bacteria can utilize several of these electron donors, some are restricted to only one substrate.

Theoretical considerations on observed dehalogenation rates in PCE-dechlorinating systems show that co-metabolically dehalogenating bacteria are often not the organisms responsible for the dehalogenations [16]. Dehalogenation rates by methanogens and acetogens are *ca.* 10^6 times slower than dehalogenation rates by respiratory bacteria. Hence, an unrealistically high concentration of methanogens or acetogens of up to 330 g protein/l would be needed to explain the rates observed in mixed bacterial enrichment cultures or sediment columns. Therefore, at EAWAG, one bacterial strain (*Dehalobacter restrictus*) that reduces PCE and TCE in a respiratory process is presently being investigated in detail.

Dehalobacter restrictus is a bacterium that only utilizes molecular hydrogen as electron donor and, even more surprisingly, exclusively PCE and TCE as terminal electron acceptors [15]. A thorough characterization demonstrated that *D. restrictus* belongs to a yet unknown group of bacteria. A tentative model of the quite simple respiration system that builds up the proton motive force to generate ATP is depicted in *Fig. 4* [17]. The hydrogenase is
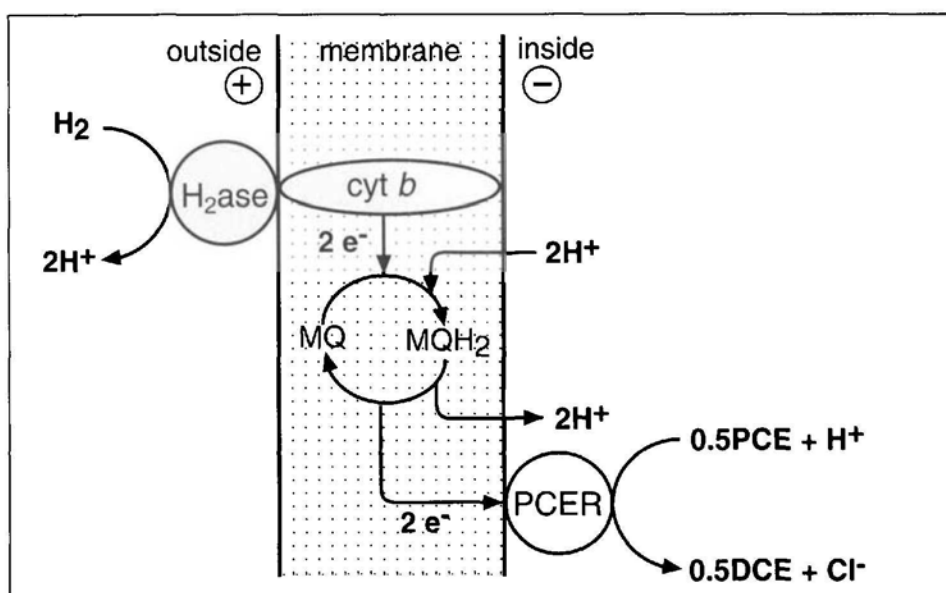

Fig. 4. *Tentative model of the respiration chain of* Dehalobacter restrictus. H₂ase = hydrogenase, cyt *b* = cytochrome *b*; MQ = oxidized menaquinone; MQH₂ = reduced menaquinone; PCER = tetrachloroethene reductase; PCE = tetrachloroethene; DCE = dichloroethene.

associated with the membrane and oxidizes molecular hydrogen at the outside of the cytoplasmic membrane. The electrons are probably transferred to a cytochrome *b* that subsequently reduces menaquinone. The electron transfer from menaquinone to the PCE reductase is not yet understood. In any case, this reaction sequence separates the charges and builds up a proton motive force which was demonstrated with oxidant pulse experiments [18]. The PCE reductase has been purified and characterized [17]. The enzyme is a membrane-bound monomer with a molecular mass of 60 kDa. Studies by optical and EPR spectroscopy showed that the PCE reductase contains two electron-transferring [4Fe-4S]$^{(2+;1+)}$ clusters with rather low redox potentials of $E'_h \approx -480$ mV and one cobalamin with E'_h(Co$^{1+/2+}$)$= -350$ mV and E'_h(Co$^{2+/3+}$) > 150 mV. The cob(II)alamin is present in the base-off configuration. It has also been demonstrated that a completely reduced enzyme sample reacted rapidly with PCE yielding base-off cob(II)alamin rather than trichlorovinyl-cob(III)alamin. This preliminary experiment indicated that also the enzyme-bound cobalamin reacted with PCE in a dissociative one-electron transfer. Further investigations including the cloning and sequencing of the PCE reductase gene and the purification and characterization of the hydrogenase and other components of respiration chain is in progress at EAWAG.

Since cobalamin has been shown to be involved in the enzymatic reduction of PCE and TCE by a variety of phylogenetically diverse anaerobic bacteria, and since it has been suggested to use cobalamin as

an electron transfer mediator in the treatment of halogenated solvent wastes, the cobalamin-mediated reduction of all chlorinated ethenes has also been investigated in homogeneous aqueous solution using titanium(III) citrate as bulk electron donor [19][20]. In this system, it was found that the highly chlorinated ethenes (PCE, TCE) reacted primarily *via* a pH-independent dissociative one-electron transfer, while the initial step for the less chlorinated ethenes (*i.e., cis-* and *trans-*DCE, 1,1-DCE, VC) was a proton-dependent addition of the cob(I)alamin to the corresponding chlorinated ethene. *Scheme 1* summarizes the postulated reaction pathways and relative second-order rate constants for the various chlorinated ethenes as well as for acetylene and ethene at pH 7, 8, and 9. From these and other data, some important conclusions can be drawn (for details see [19][20] and references cited therein). First, in the pH range between 7 and 9, *trans-* and particularly *cis-*DCE are by far the most unreactive compounds, and will, therefore, accumulate when PCE or TCE is reduced by cob(I)alamin. These findings are consistent with the results of laboratory and field studies on the microbial reduction of PCE and TCE, where *cis-*DCE is commonly found as a major metabolite. Furthermore, since the reduction of PCE and TCE does not yield any 1,1-DCE, it can be expected that no significant amounts of VC, the most toxic chlorinated ethene, should be produced. Thus, in those cases reported in the literature (see citations in [20]), in which the reduction of VC was found to be the rate-limiting step in the complete microbial dehalogenation of PCE to ethene, either

the addition of the cobalamin to the chlorinated ethene was not rate-determining in the enzymatic reaction or other cofactors such as factor F430, which can react *via* an electron transfer mechanism, may have been involved instead of superreduced cobalamin. Finally, as is also evident from *Scheme 1*, acetylene and ethene react quite rapidly with cob(I)alamin and, therefore, compete with the chlorinated ethenes. This is especially important at more positive redox potentials, because the reductive cleavage of the vinyl- and ethylcobalamin thus formed is rather slow, so that a large fraction of the cobalamin would no longer be available under such conditions, and, as a consequence, the overall rate of the reduction of the chlorinated ethene would also be slowed down dramatically.

Reductive Transformation of Cr^{VI} with Fe^{II}

In the environment, chromium occurs almost exclusively as Cr^{III} and Cr^{VI}. Released primarily as soluble chromates, Cr^{VI} is a known human carcinogen and mutagen, and it is toxic to animals, plants, and to most microorganisms. Furthermore, it is very mobile in aqueous systems. In contrast, Cr^{III} is essentially nontoxic and even essential for the glucose metabolism. It hydrolyzes to sparingly soluble Cr^{III}(hydr)oxides and adsorbs strongly to surfaces, making it generally much less mobile than Cr^{VI} [21]. (More references can be found in the few EAWAG citations referred to in this section.)

Although, from a thermodynamical point of view, Cr^{VI} should dominate in oxic environments and Cr^{III} in anoxic environments, both oxidation states are found in oxic and anoxic systems due to the slowness of Cr redox reactions. Cr^{VI}-to-Cr^{III} reduction three one-electron process in which the first reduction step is the least exergonic one, while the next two steps are strongly exergonic. Organic compounds reduce Cr^{VI} on timescales of days to years. For example, in a seasonally anoxic lake, chromium reduction lifetimes were found to be several months months [22]. More efficient natural reductants of Cr^{VI} are reduced sulfur compounds and Fe^{II}. Fe^{II}/Fe^{III} may also act as a redox mediator between organic compounds and Cr^{VI}. Once reduced, the long term stability of Cr^{III} in soils is uncertain, as Mn^{III}/Mn^{IV} (oxyhydr)oxides are potential natural oxidants [23][24].

Cr redox-reaction rates are strongly influenced by pH, organic and inorganic ligands, and by surfaces. Unfortunately,
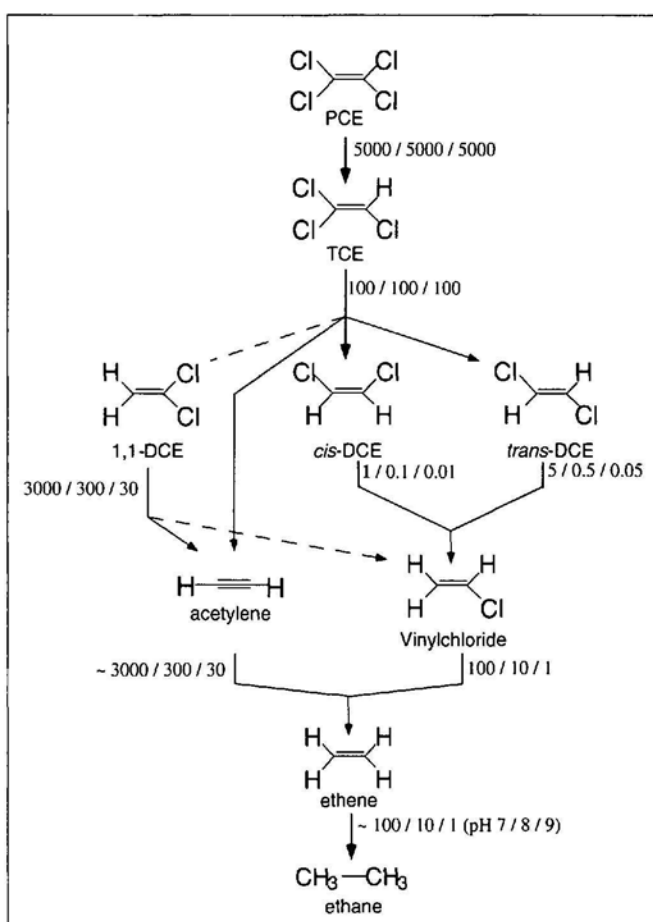
there are almost no rate data available for modelling the various possible redox reactions of chromium under environmental conditions. The objective of the work conducted at EAWAG is, therefore, to assess the pathways and the reaction rates of Cr^{VI} with Fe^{II} species, in order to get better insight into the environmental fate of chromium, and thus, to provide a basis for the optimization of remediation strategies for contaminated soils, sediments, and surface waters.

Important natural sources of Fe^{II} are Fe^{II}-bearing minerals and microbial or photochemical reduction of iron(III) species. In remediation procedures, reducing iron species are added in the form of various Fe^{II} salts, or as Fe in metallic form. A summary of relevant reactions is given in the *Table*. It has been generally assumed that Fe^{II} reduces Cr^{VI} quickly (seconds to minutes) and that mixed Cr^{III}/ Fe^{III}(oxyhyr)oxides are formed. However, in this work it was found that the reaction is rather slow at pH 4–5 and that Fe^{II}-complexing organic ligands strongly affect reduction rates and lead to dissolved Cr^{III} complexes. Thus, the reduction of Cr^{VI} to Cr^{III} does not necessarily lead to an immobilization of chromium.

Cr^{VI} reacts with Fe^{II} in a bimolecular reaction, with a pH-dependent observed rate constant k_{obs} (see insert of *Fig. 5*)

$$-d[Cr^{VI}]/dt = k_{obs}(pH) \cdot [Cr^{VI}] \cdot [Fe^{II}] \quad (1)$$

Above pH 4, the overall reaction can be expressed by three parallel reactions with pH-independent rate constants:

$$-d[Cr^{VI}]/dt = [Cr^{VI}] \cdot \{ k_1[Fe^{II}] + k_2[FeOH^+] + k_3[Fe(OH)_2^0] \} \quad (2)$$

with $k_1 = 0.34 \pm 0.47$ M^{-1}s^{-1}, $k_2 = (1.41 \pm 0.28) \cdot 10^5$ M^{-1}s^{-1}, $k_3 = (2.84 \pm 0.90) \cdot 10^9$ M^{-1}s^{-1} (for more details see [25]). Also with lower Fe^{II} and Cr^{VI} concentrations, the same rate law was found [26], supporting a scheme in which the first of the three consecutive reduction steps is rate-determining. An earlier suggestion that the reduction of Cr^{V} to Cr^{IV} (coordination change from tetrahedral to octahedral) is rate-limiting, is inconsistent with the rate law observed in this study.

The high rate constants for the reactions of Fe^{II}-hydroxo complexes with Cr^{VI} correlate with the strongly decreasing reduction potentials of iron mono- and dihydroxy complexes, suggesting a linear free-energy relationship as shown in *Fig. 5*.

An acceleration of the reaction was observed in the presence of organic ligands. For example, the thermal reaction of Cr^{VI} with Fe^{II} at pH 5 was described by [27]:

Scheme 1. *Overview of the Reaction Pathways and Relative Second-Order Rate Constants at pH7, 8 and 9 for the Reduction of All Chlorinated Ethenes by Cob(I)alamin in Homogeneous aqueous solution* (from [20])

$$-d[Cr^{VI}]/dt = (1.2 \pm 0.3) \cdot$$
$$10^7 \, M^{-2}s^{-1} \cdot [Cr^{VI}] \cdot [Fe^{II}] \cdot [Ox] \qquad (3)$$

Experiments with various ligands with known Fe^{II} and Fe^{III} complex formation constants and kinetic modeling revealed a more general rate law:

$$-d[Cr^{VI}]/dt = k_L \, (pH) \cdot$$
$$[Fe^{II}L] \cdot [Cr^{VI}] \qquad (4)$$

where L was oxalate, tartrate, salicylate, or NTA. These are naturally occurring ligands and/or models for functional groups in fulvic and humic acids. An extract from a DOC-rich soil showed a similar acceleration of Cr^{VI} reduction. There was no detectable buildup of Cr^V and Cr^{IV} inter-

mediates, indicating that the first reduction step was rate-determining. In a plot of log$k$ vs. the reduction potential of the corresponding Fe^{III}/Fe^{II} redox couples, the various Fe^{II} complexes at pH 5 fall on the same line as the Fe^{II}-hydroxo species. Such linear free-energy relationships as shown in *Fig. 5* are very important tools for the prediction of rates in complex systems.

Fe^{II}/Fe^{III} can act as a mediator in the reaction of organic compounds with Cr^{VI}, not only in thermal but also in photochemical reactions. For example, diurnal variations of Cr^{VI} concentrations in an estuary [28] have been interpreted as Cr^{VI} reduction by photochemically formed Fe^{II}. Many surface waters contain a variety of low-

molecular-weight organic acids and fulvic and humic acids which complex Fe^{III} and engage in photochemistry resulting in the formation of Fe^{II} and other reactive reaction products [29]. At EAWAG, photochemical Cr^{VI} reduction has been investigated with two naturally occurring ligands, oxalate and citrate [27]. Light absorption in the near ultraviolet region into ligand-to-metal charge-transfer bands of Fe^{III} oxalate and Fe^{III} citrate leads to the formation of Fe^{II} and organic radicals, e.g., CO_2^- as shown in *Scheme 2*. In aerated solutions, organic radicals are typically oxidized by O_2, whereby the superoxide (O_2^-) formed leads to Fe^{II}/Fe^{III} cycling with formation of H_2O_2 (not shown) and smaller steady-state concentrations of $O_2^-/HO_2^\cdot$ and $OH^\cdot$. These reactive oxygen species might be important reductants for Cr^{VI} or for Cr^V and Cr^{IV} intermediates. In model systems containing 5–200 µM Cr^{VI}, Cr^{VI} reduction quantum yields (relative to light absorption by Fe^{III}-oxalate) of up to 0.53 were observed with polychromatic light (300–500 nm). The reaction products in oxalate- or citrate-containing solutions were dissolved Cr^{III} oxalate and citrate complexes. Given the high quantum yields, it seems likely that photochemical reduction of Cr^{VI} in contaminated wetlands and in atmospheric water is important and that a variety of Cr^{III} complexes are formed in this process.

An important issue in remediation procedures is the speciation of the Cr^{III} which is formed during the reduction process. Addition of dissolved Fe^{II} to a solution of Cr^{VI} between pH 4–7, in the absence of organic ligands, leads to a fine, X-ray-amorphous precipitate. In heterogeneous systems, crystalline surfaces of iron-(oxy)-hydroxide particles seem to catalyze the reaction and might lead to more crystalline, mixed Cr^{III}/Fe^{III} phases. Such heterogeneous systems are currently investigated with various methods (*Table*). In the presence of organic ligands, the products were dissolved Cr^{III} complexes. With a knowledge of the relative reaction rates, the distribution of products in remediation procedures can be estimated and possibly steered into a desirable direction. While extraction of soluble Cr^{III} might be preferable in some situations, formation of insoluble, stable phases might be the goal in others.

Table. *Solution and Surface Reactions of Fe^{II} and Cr^{VI} Species, Ranges of Bimolecular Reaction Rate Constants (k), and* in situ *Analytical Methods Employed in Our Studies.* The vertical arrows indicate hydrolysis and finally precipitation of Fe^{III} and Cr^{III} species at higher pH.

| Phase	Species involved in redox reactions		k [$M^{-1}s^{-1}$]	Analytical Method
	Reactants	Products		
Liquid:	$Fe^{II}L^{2-y}+L^{-y} + Cr^{VI}$	$\rightarrow$ $Cr^{III}L^{3-y} + Fe^{III}L^{3-y}$	0–10^9	UV-VIS
Initially	$Fe^{2+} + Cr^{VI}$	$\rightarrow$ $Cr^{3+} + Fe^{3+}$	0–1	with multi-
dissolved	$FeOH^+ + Cr^{VI}$	$\rightarrow$ $CrOH^{2+} + FeOH^{2+}$ $\downarrow$	10^5	component
species	$Fe(OH)_2^0 + Cr^{VI}$	$\rightarrow$ $Cr(OH)_2^+ + Fe(OH)_2^+$ $\downarrow$	10^9	fitting
$Cr^{VI} =$				
$HCrO_4^-/CrO_4^{2-}$				
Solid:	$\equiv MeO-Fe^+ + Cr^{VI}$			ATR-FTIR
Surface species	$Fe^{2+} + \equiv Me-CrO_4^-$	$\rightarrow$ Cr^{III}/Fe^{III}-solid phases		AFM, XRD
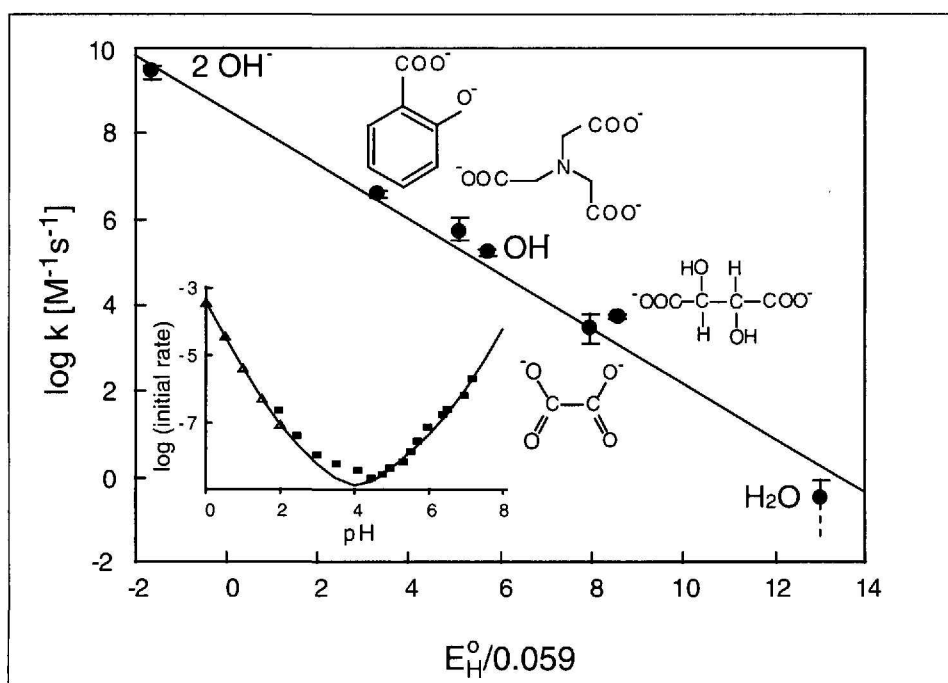
Fig. 5. *Relationship between the reduction potentials of $Fe^{II}L/Fe^{III}L$ redox couples and the bimolecular rate constants for the reaction with Cr^{VI}.* This linear free energy relationship (LFER) is useful for an estimation of rate constants in similar systems. Insert: pH dependence of initial reduction rates of 20 µM Cr^{VI} with 60 µM uncomplexed Fe^{II}, a consequence of the increasing contributions of $FeOH^+$ and $Fe(OH)_2$ at higher pH, and the acceleration by H^+ at lower pH values.

Concluding Remarks

Redox and hydrolysis reactions are among the most important transformation processes which organic and inorganic

pollutants can undergo under environmentally relevant conditions in aquatic environments. Many pollutants are thermodynamically unstable under environmental conditions, but the processes by which these chemicals are transformed into environmentally benign compounds are kinetically controlled.

The three examples presented were aimed primarily at illustrating the approaches taken at EAWAG to unravel the basic factors, i.e., the compound- and system-specific parameters that control abiotic and microbially mediated reductions of anthropogenic chemicals in natural systems. In particular, the importance of electron transfer mediators for controlling the reduction of pollutants in natural environments was emphasized. These mediators break otherwise slow processes up into two (or more) kinetically favored reactions.

As has been illustrated in this article, only a thorough elucidation of the factors that govern the mechanisms and kinetics of reduction reactions of anthropogenic chemicals in well-defined model systems will ultimately allow one to understand, and possibly to quantify such processes in more complex environments. The results of the three studies show that, depending on the conditions prevailing in a given natural system (i.e., the nature and reactivities of the reductants present), absolute and/or relative reduction rates of a given chemical and/or a series of chemicals may vary by orders of magnitude. Thus, in contrast to, e.g., hydrolysis reactions, a priori prediction of absolute rates for reductive transformations of anthropogenic chemicals in the environment is, in general, virtually impossible. Nevertheless, comparison of results from studies in model systems with those obtained from field investigations can provide important clues about the controlling factors in the environment and, possibly, about how such processes can be influenced (e.g., for the remediation of contaminated sites). Furthermore, by using appropriate probe compounds, it should be possible to calibrate, much like it is done in the assessment of transient photooxidants (see [30]), the reactivity of a given system in order to be able to predict absolute rates of transformation of other, similar types of compounds. Finally, from an environmental technology point of view, the results of these studies offer interesting perspectives with respect to the treatment of hazardous wastes and/or contaminated sites.
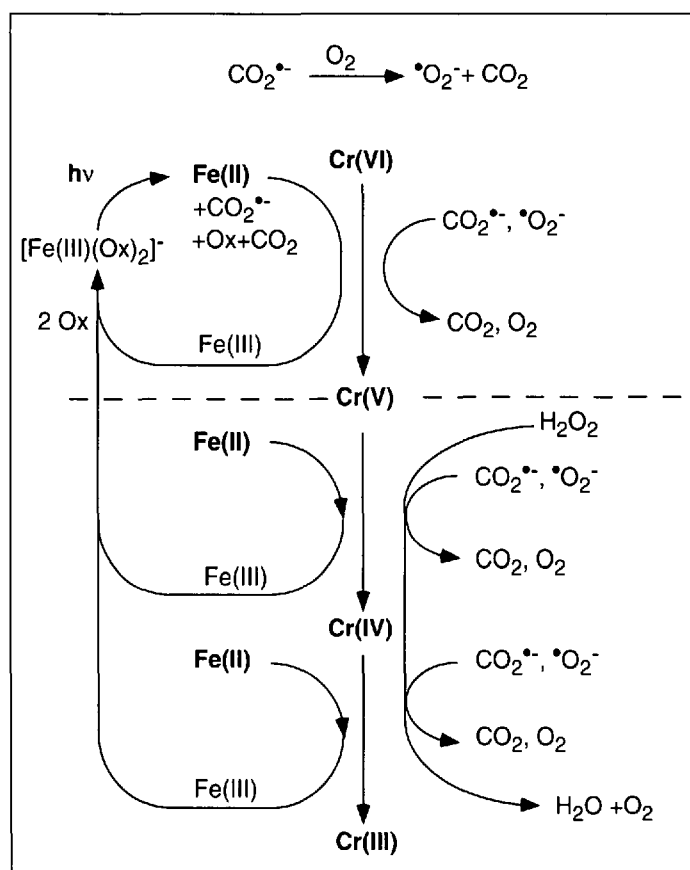
Scheme 2. *Proposed Scheme for the Photochemical Reduction of* Cr^{VI}. Ox = oxalate.

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