Reduction Processes

Another process which involves electron transfer (except in the opposite direction as AOP) is reductive dechlorination. An example is the reduction of halogenated hydrocarbons.

Reductive dehalogenation with zero valent iron:

$$RX + H^+ + 2e^- \rightarrow RH + X^-$$

$$Fe^o \rightarrow Fe^{2+} + 2e^-$$

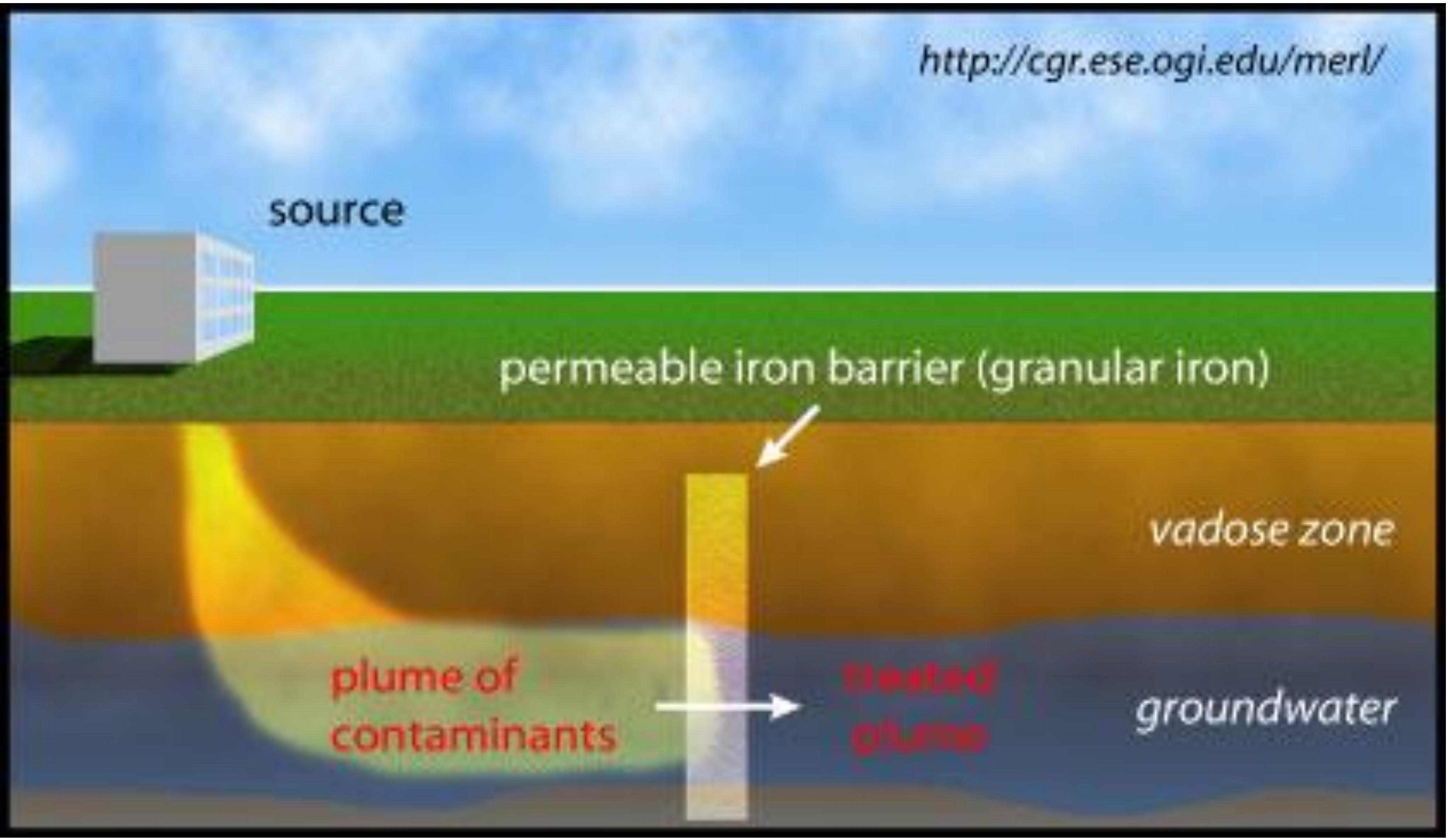
$$RX + H^+ + Fe^o \rightarrow Fe^{2+} + RH + X^-$$

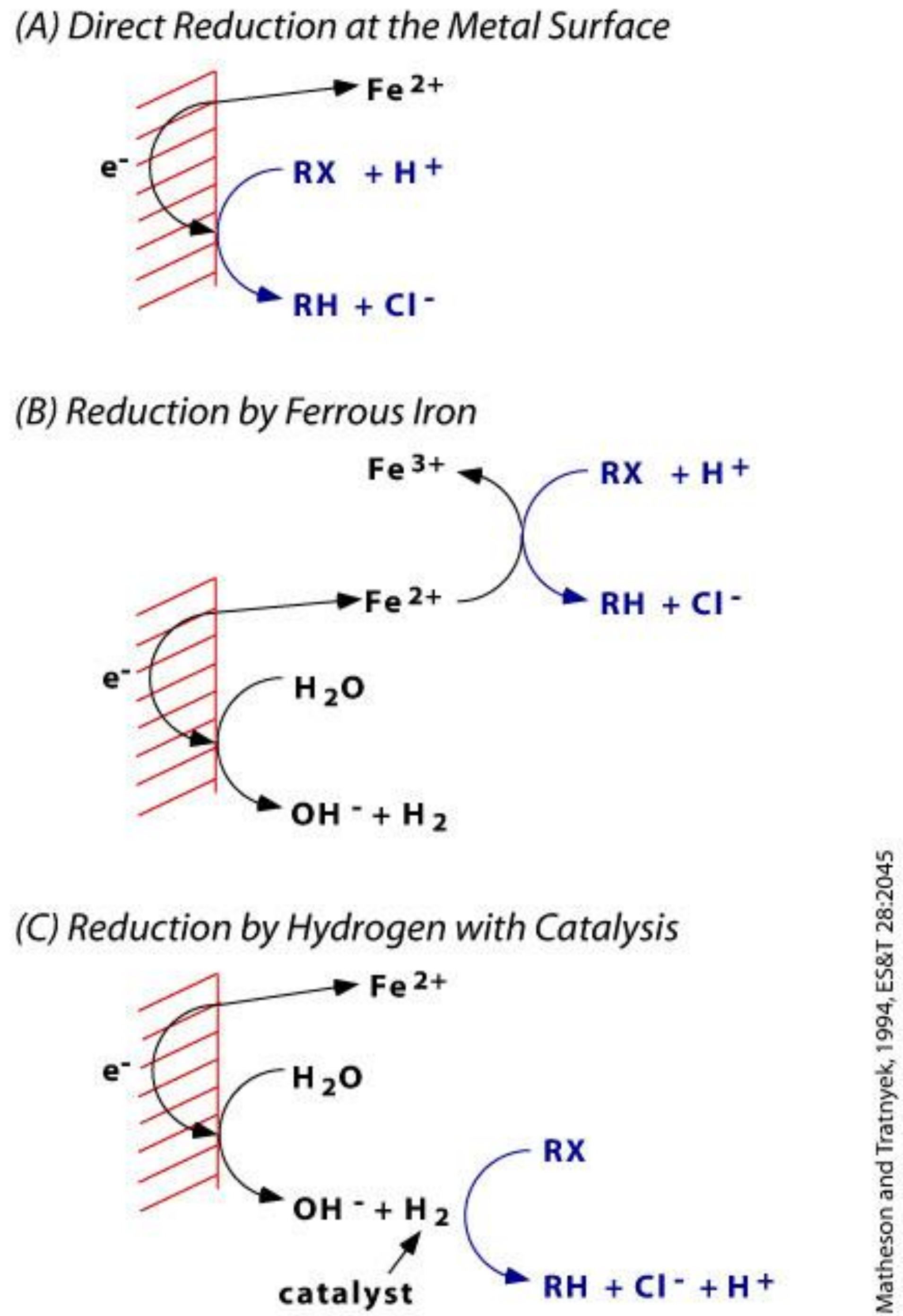
Hydrogen gas is usually inert but in the presence of Pd, Ni, Pt and possibly Fe^o hydrodehalogenation is possible.

$$H_2 + RX \xrightarrow{\Delta M} RH + H^+ + X^-$$

It is also possible that Fe^o can react with H^+ to form H_2.

$$Fe^o + 2H^+ \rightarrow Fe^{2+} + H_2$$


http://cgr.ese.ogi.edu/merl/
source
permeable iron barrier (granular iron)
vadose zone
plume of
contaminants
groundwater


(A) Direct Reduction at the Metal Surface
Fe 2+
e-
RX + H +
RH + Cl -
(B) Reduction by Ferrous Iron
Fe 3+
RX + H +
Fe 2+
RH + Cl -
e-
H 2O
OH - + H 2
(C) Reduction by Hydrogen with Catalysis
Fe 2+
e-
H 2O
RX
OH - + H 2
catalyst
RH + Cl - + H +
Matheson and Tratnyek, 1994, ES&T 28:2045

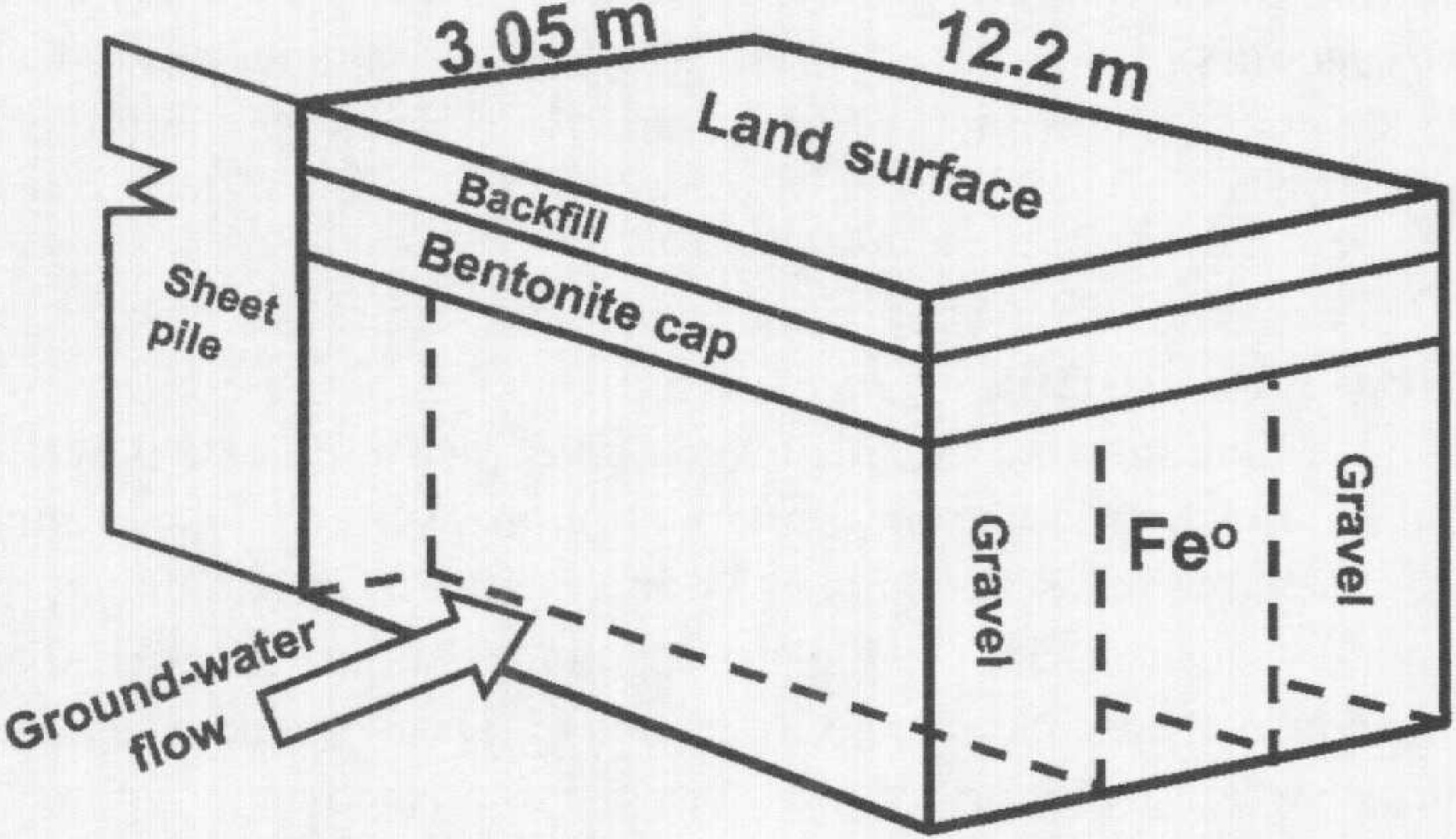


Figure 4. Schematic of a treatment gate in the permeable reactive barrier.

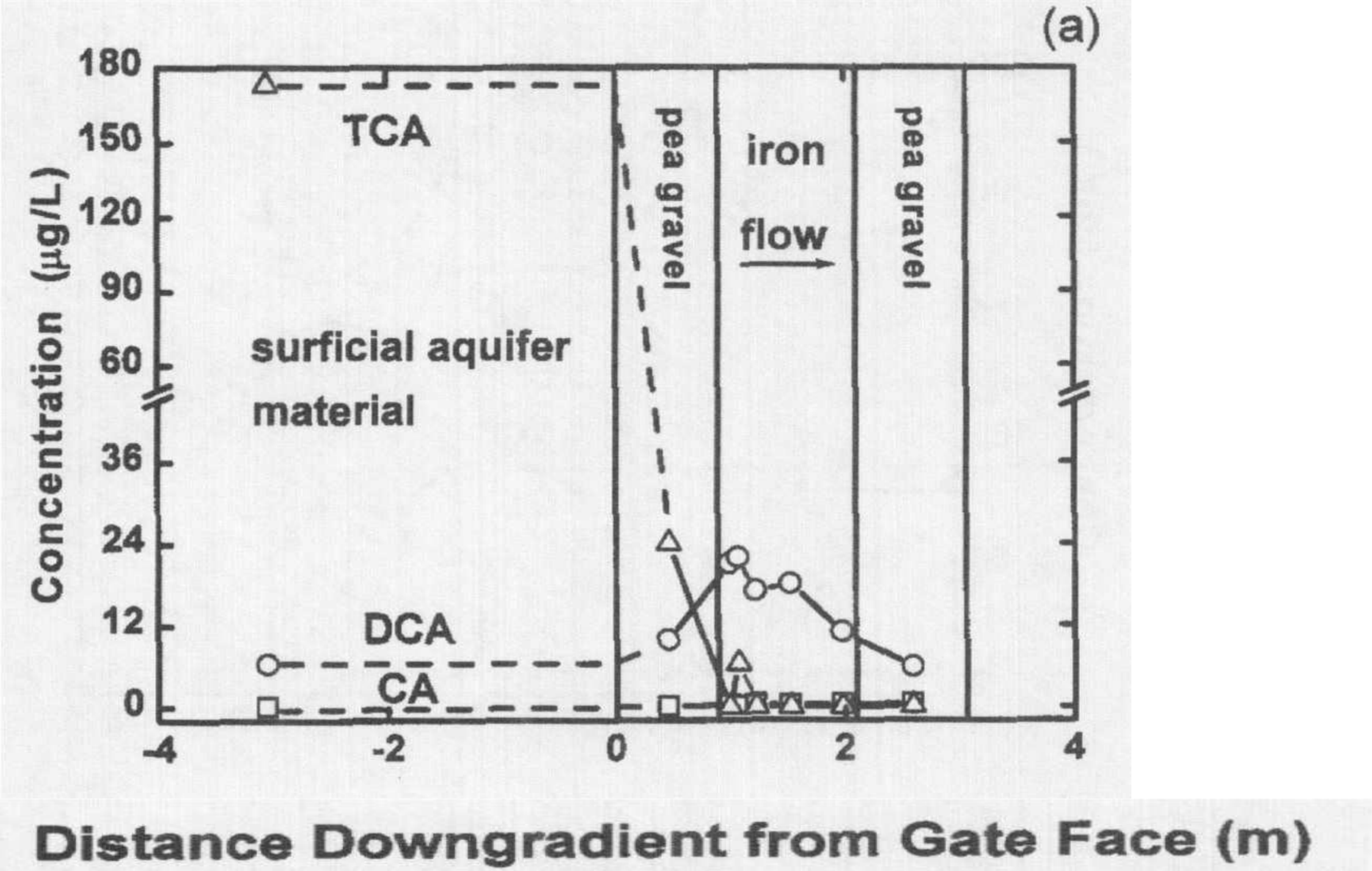
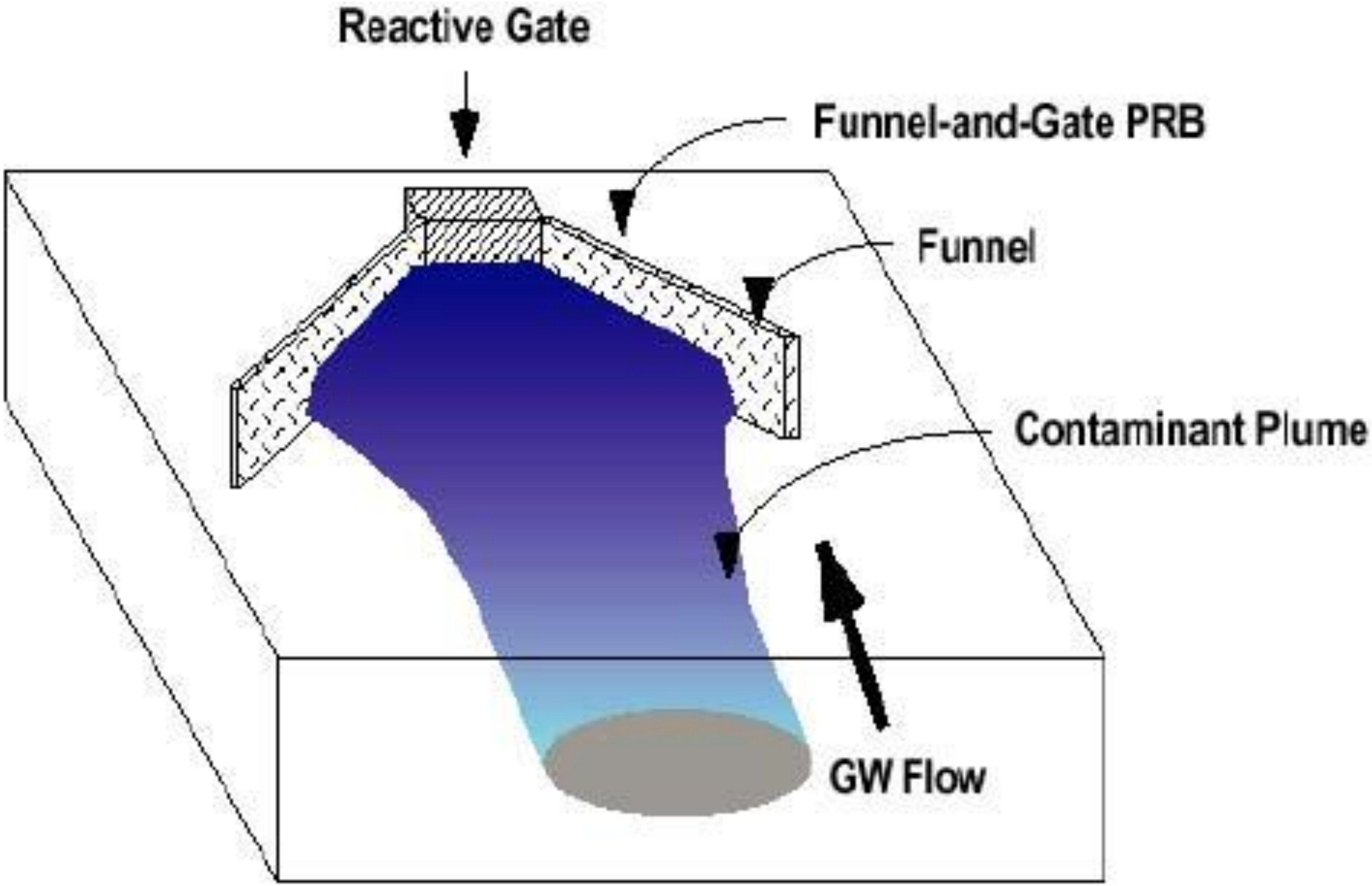


Figure 10. Concentrations of (a) TCA, DCA, and CA (chloroethane) and (b) organic carbon as CAHs and as C_1 and C_2 hydrocarbons in water from piezometers in gate 2. Dashed lines infer that the concentrations in water entering the upgradient gravel equal the concentrations in water 3 m upgradient from the gate face. The decrease in concentrations in the upgradient gravel indicates that Fe^o was not completely excluded from this zone during construction.


Reactive Gate
Funnel-and-Gate PRB
Funnel
Contaminant Plume
GW Flow

Other chemical species can be reduced by the iron.

For example nitrate can be reduced to nitrogen gas:

$$10Fe^{0} + 6NO_3^{-} + 3H_2O \rightarrow Fe_2O_3 + 6OH^{-} + 3N_2$$

Potential long term problem:

As the dehalogenation process proceeds pH will rise as H^+ is used. This could result in precipitation of $CaCO_3$ or $FeCO_3$ which will ultimately reduce porosity of the permeable barrier.

Typical Design Results:

First order decay rate approx.

0.03 per hour (half life = 20 hours)

With a Fe^{o} barrier of 1.2 m thickness and a flow rate through the barrier equal to 0.4 m/day get approx. 90% reduction in RX.