INSTITUT EGID BORDEAUX 3
Environnement Géo-Ingénierie et Développement
UNIVERSITÉ MICHEL DE MONTAIGNE - BORDEAUX 3

To
Environemental Science and
Technology
editing services

Dear editor,

You will find below supporting information for the paper : « Validation of reactive model assumptions with isotope data : application to the Dover case ».

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Yours faithfully

Prof. O. Atteia

« PHREEQC test file for degradation of chlorinated solvents with isotopic calculation »

```
SOLUTION_MASTER_SPECIES  #  on fait que de la dégradation des chlorés
      Pc  Pc  0  1  167
      Pch Pch 0  1  168  # Pc avec un 13C
      Tce  Tce  0  1  131.5
      Tceh Tceh 0  1  132.5
      Dce  Dce  0  1  97
      Dceh  Dceh  0  1  98
      Vc   Vc  0  1  62.5
      Vch   Vch  0  1  63.5
      Et  Et  0 1 28
      Eth Eth  0  1 29
SOLUTION_SPECIES
Pc = Pc; log_k 0.0
Pch = Pch; log_k 0.0
Tce = Tce; log_k 0.0
Tceh = Tceh; log_k 0.0
Dce=Dce; log_k 0.0
Dceh=Dceh; log_k 0.0
Vc=Vc; log_k 0.0
Vch=Vch; log_k 0.0
Et=Et; log_k 0.0
Eth=Eth; log_k 0.0
END
SOLUTION 1-100 # cellules départ
      units mmol/L
      pH    7.0
      temp  25
      Na 1
      Cl 0.5 charge
END
SOLUTION 0  # solution entrante
      units mmol/L
      pH    7.0
      temp  25
      Pc  2; Pch 0.0218;#Tce 1e-8;Dce 1e-8;Vc 1e-8;Et 1e-8   #-30 °/.. de 13C Pc
      K    1
      Cl  0.5 charge
END
RATES
PCE
        -start
150  moles=0
170  Per=TOT("Pc")
200  if Per<=1e-9 then goto 600
400  moles = TIME*Per*parm(1)/3600
500  if moles>Per then moles=Per
600  SAVE moles
        -end
PCEh
        -start
150  moles=0
170  Perh=TOT("Pch")
200  if Perh<=1e-9 then goto 600
400  moles = TIME*Perh*parm(1)/3600
500  if moles>Perh then moles=Perh
600  SAVE moles
        -end
TCE
```

```
        -start
150  moles=0
170  Tri=TOT("Tce")
200  if Tri<=1e-7 then goto 600
400  moles = TIME*Tri*parm(1)/3600
500  if moles>Tri then moles=Tri
600  SAVE moles
        -end
TCEh
        -start
150  moles=0
170  Tri=TOT("Tceh")
200  if Tri<=1e-7 then goto 600
400  moles = TIME*Tri*parm(1)/3600
500  if moles>Tri then moles=Tri
600  SAVE moles
        -end
DCE
        -start
150  moles=0
170  Di=TOT("Dce")
200  if Di<=1e-7 then goto 600
400  moles = TIME*Di*parm(1)/3600
500  if moles>Di then moles=Di
600  SAVE moles
        -end
DCEh
        -start
150  moles=0
170  Di=TOT("Dceh")
200  if Di<=1e-9 then goto 600
400  moles = TIME*Di*parm(1)/3600
500  if moles>Di then moles=Di
600  SAVE moles
        -end
VC
        -start
150  moles=0
170  V=TOT("Vc")
200  if V<=1e-7 then goto 600
400  moles = TIME*V*parm(1)/3600
500  if moles>V then moles=V
600  SAVE moles
        -end
VCh
        -start
150  moles=0
170  V=TOT("Vch")
200  if V<=1e-9 then goto 600
400  moles = TIME*V*parm(1)/3600
500  if moles>V then moles=V
600  SAVE moles
        -end
KINETICS 1-40
PCE
      -formula Pc -1 Tce 1; -parms 1.5      # en h-1 mais an -1 ds reel (il
merde)
PCEh
      -formula Pch -1 Tceh 1; -parms 1.497      # alpha=.998 (ne pas mettre
.6*.95!!
TCE
      -formula Tce -1 Dce 1; -parms 1.2
TCEh
      -formula Tceh -1 Dceh 1; -parms 1.194     # alpha=
```

```
DCE
      -formula Dce -1 Vc 1 ; -parms 0.85
DCEh
      -formula Dceh -1 Vch 1 ; -parms 0.8398
VC
      -formula Vc -1 Et 1 ; -parms 0.4
VCh
      -formula Vch -1 Eth 1 ; -parms 0.392
PRINT
      -reset  false
      #-warnings 5
TRANSPORT
 -cells 45;  -length 50
 -shifts 40; -timest 900  # tstep: 1/4 "an" vp 200 m/an
 -disp 5;    -punch_frequency 40
USER_GRAPH
 -head x Pc Tce Dce Vc Eth 13Pc 13Tce 13Dce 13Vc 13Et
 -axis_titles "Distance, m" "mmol/l"  "d13C"
 -axis_scale x_axis 0 2200
 -axis_scale y_axis 0 2e-3
 -axis_scale sy_axis 0.008 .012 .0005
 -start
  2 if step_no = 0 then goto 50
  20 graph_x dist
  30 graph_y Tot("Pc"),Tot("Tce"),Tot("Dce"),Tot("Vc"),Tot("Et")
  40 graph_sy Tot("Pch")/Tot("Pc") Tot("Tceh")/Tot("Tce") \
      Tot("Dceh")/Tot("Dce") Tot("Vch")/Tot("Vc") Tot("Eth")/Tot("Et")
  50 end
 -end
END
```

Comparison of MIKSS and RT3D

In order to verify the MIKSS model and to show that the major differences between the models come from the size of the reducing zone, we made a simulation with RT3D using the same constants as the one of MIKSS model (Figure SI.1). One can see that the plumes of all chlorinated solvents are quite similar to ones obtained by MIKSS (see figure 2 in text for comparison) with a slightly higher lateral dispersion, although the imposed values are the same. For δ^{13}TCE the results are similar to MIKSS, with a slightly different spatial distribution (see figure 3 in text for comparison) : RT3D gives higher transverse dispersion (as shown above) and MIKSS gives longer plumes for δ^{13}TCE. As said in the text, this may come from the fact that MIKSS does not mix core and fringe water after the reaction are done. Therefore, for this point RT3D longitudinal extension seem to be more reliable.

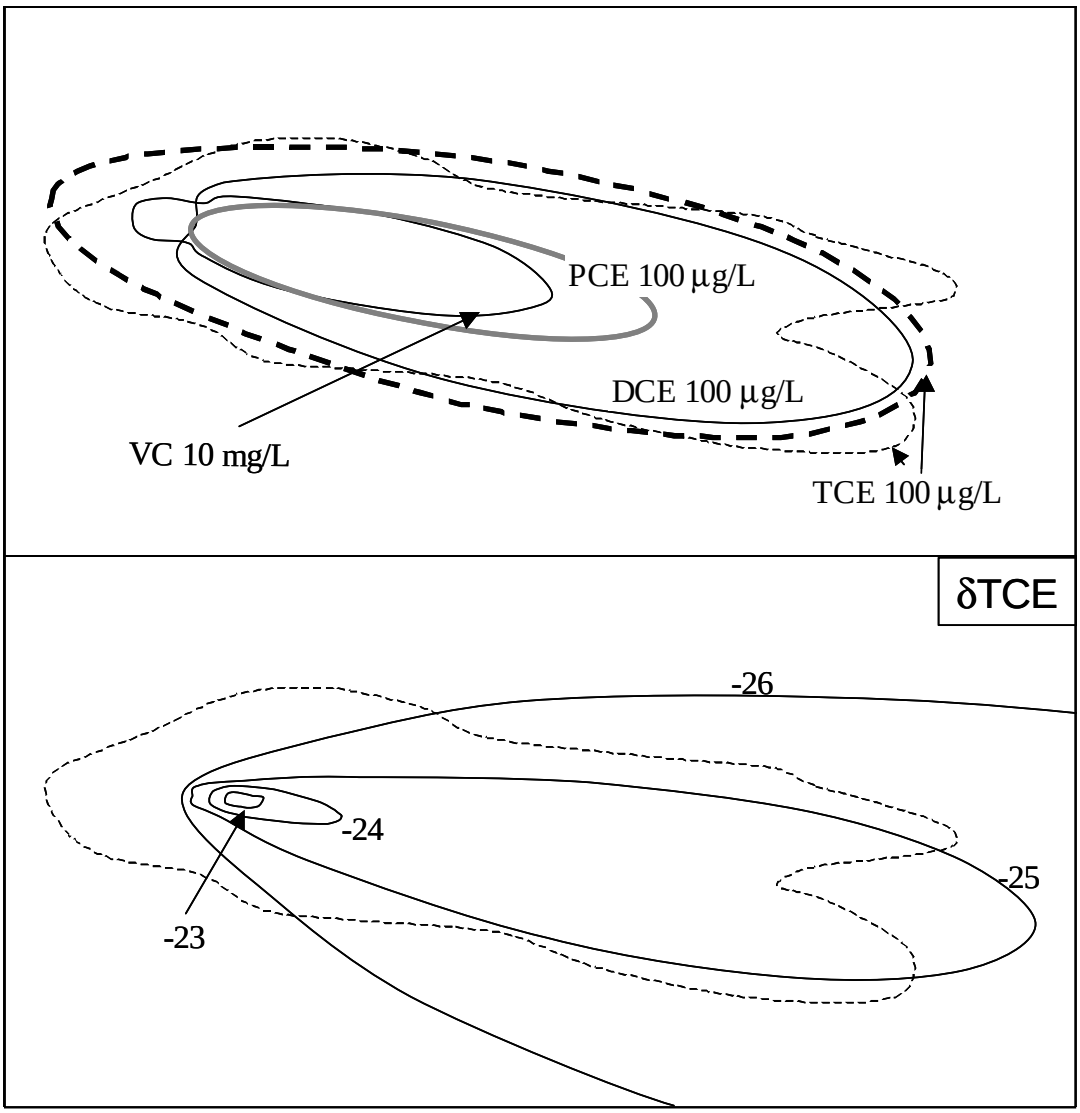

Figure SI.1 : simulations of the plume and δ^{13}TCE values with RT3D but using reactive zones as given by MIKSS and kinetic constants from MIKSS model.

Sensitivity study

At first we studied the role of changing the ε enrichment factors values within a range of values found in literature (see main text for references). Data are shown for the RT3D model for four cases, values of ε are given in the table SI.1 below.

Table SI.1 : values of ε $^{o}/_{oo}$ used for sensitivity study for the "RT3D" model

	Case 1	Case 2	Case 3	Case 4
PCE	-5	-5,6	-1,8	-4,5
TCE	-12	-15,2	-6,6	-8
cDCE	-20	-21,9	-14,1	-19
CV	-23	-31,1	-21,1	-25

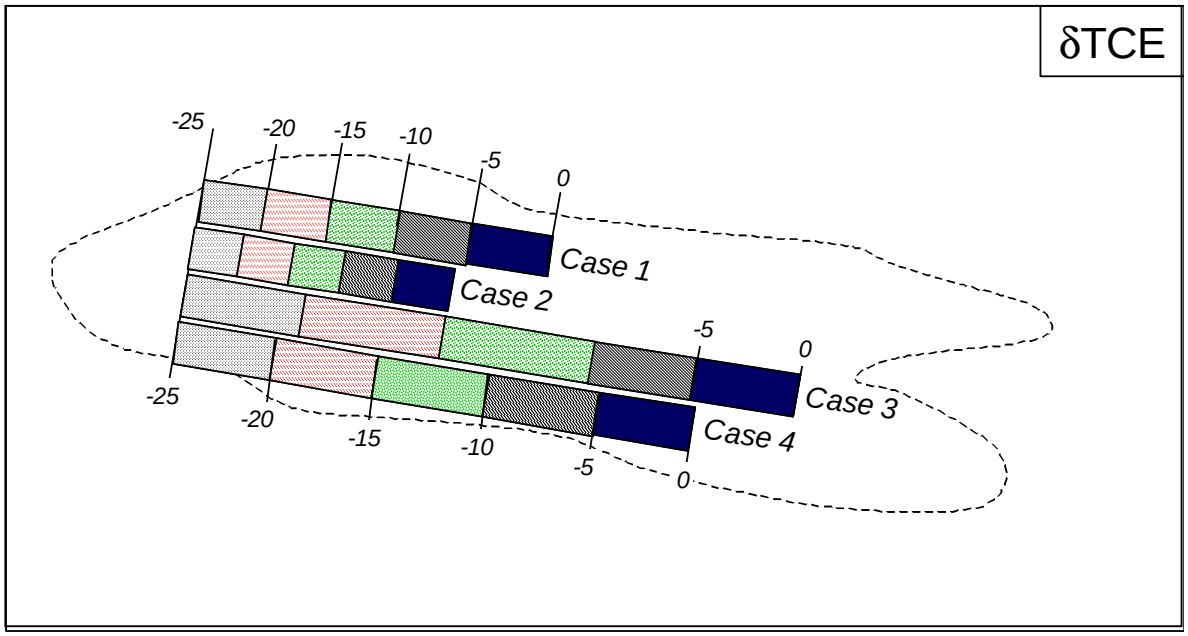

Figure SI.2 : values of δTCE for the "RT3D" model for the 4 sensitivity cases given in table SI.1, in order to be on the same figure, only a part of the plume is shown but the values are equal in the lateral direction for all simulations.

We also made a sensitivity study on the values of the kinetic constants. This was done with MIKSS with three values of kinetic constants given in table SI.2. The case 1 is the reference case used along the text, case 2 is one with faster degradation (constants approx. multiplied by two), and case 3 for slower degradation (constants approx. divided by two). The plumes are quite similar and differences can be seen only in the plume axis, the difference is higher for 1mg/L contour line than for lower values. The δ^{13}TCE spatial distribution are quite similar, except that the reached values are slightly different. In the thin central region where δ^{13}TCE increases, the values vary between –23 to –14 $^{o}/_{oo}$. However the spatial distribution of δ^{13}TCE does not change much. This enhances the fact the

the spatial distribution of isotope enrichment are directly linked to the region where reaction occurs.

Table SI.2. values of first order constants imposed on the reducing area (where H2 is produced) for sensitivity testing

k (y^{-1})	case 1	case 2	case 3
kPCE	0.15	0.25	0.05
kTCE	0.25	0.4	0.1

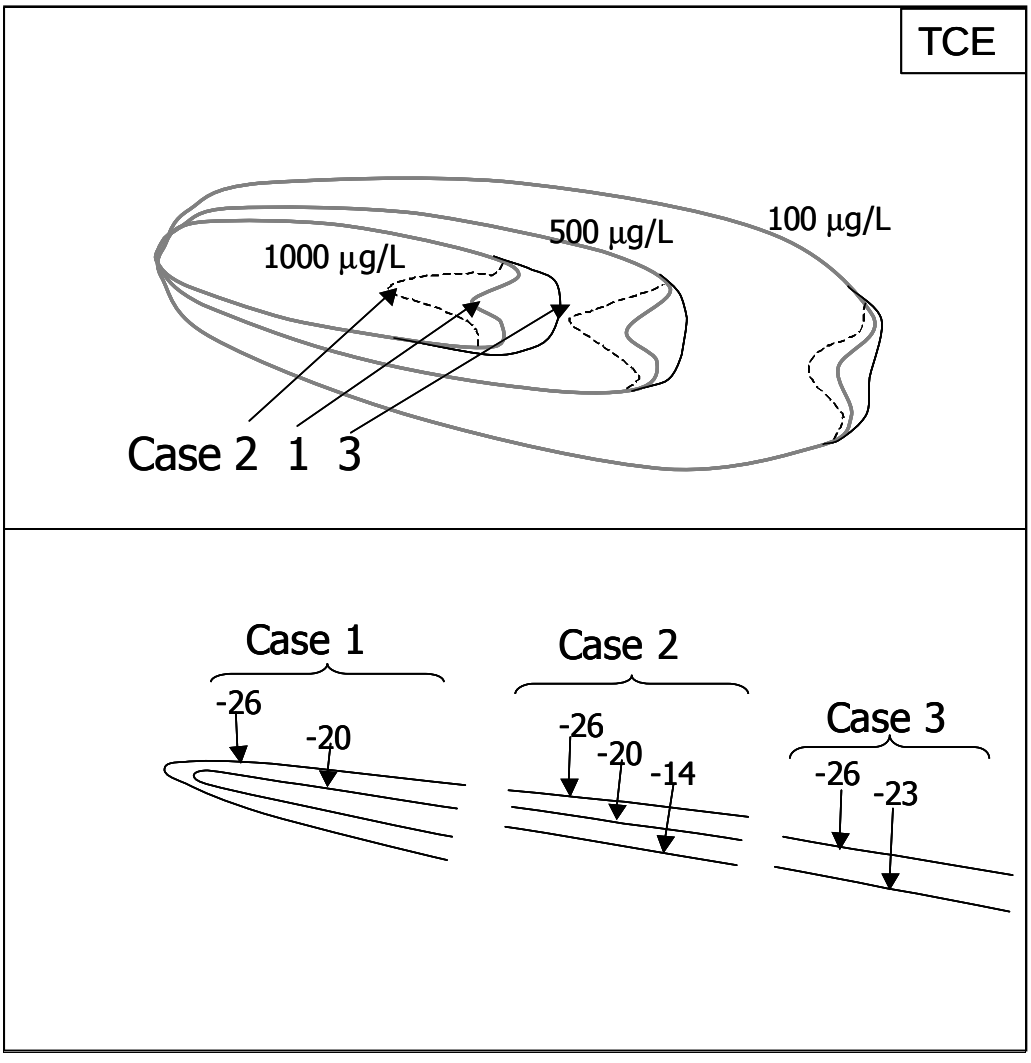

Figure SI.3. Senstivity of TCE concentration and δ^{13}TCE contours for the three cases described in table SI.2. Please note that for δ^{13}TCE only a part of the contours are given for no overlapping. However the lines have exactly the same shape so they can be continued visually.