Natural soil attenuation of organic compounds associated with coal seam gas extraction

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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acknowledgments</td>
<td>8</td>
</tr>
<tr>
<td>Executive summary</td>
<td>9</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>10</td>
</tr>
<tr>
<td>2 Modelling process</td>
<td>12</td>
</tr>
<tr>
<td>2.1 Conceptual model</td>
<td>12</td>
</tr>
<tr>
<td>2.1.1 Soil – shallow groundwater pathway</td>
<td>12</td>
</tr>
<tr>
<td>2.1.2 Soil hydrological model</td>
<td>14</td>
</tr>
<tr>
<td>2.1.3 Soil geochemical model</td>
<td>15</td>
</tr>
<tr>
<td>2.2 Numerical model for multi-component reactive transport modelling in saturated/unsaturated media</td>
<td>17</td>
</tr>
<tr>
<td>2.2.1 HYDRUS-1D</td>
<td>17</td>
</tr>
<tr>
<td>2.3 Model implementation</td>
<td>18</td>
</tr>
<tr>
<td>2.3.1 Soil hydrological characteristics</td>
<td>18</td>
</tr>
<tr>
<td>2.3.2 Soil geochemical Model</td>
<td>20</td>
</tr>
<tr>
<td>3 Natural attenuation parameters for typical organic compounds</td>
<td>24</td>
</tr>
<tr>
<td>3.1 Organic compounds considered in this assessment</td>
<td>24</td>
</tr>
<tr>
<td>3.2 Degradation in soil</td>
<td>26</td>
</tr>
<tr>
<td>3.2.1 Phenolic compounds</td>
<td>26</td>
</tr>
<tr>
<td>3.2.2 Polycyclic aromatic hydrocarbons</td>
<td>29</td>
</tr>
<tr>
<td>3.2.3 Hydraulic fracturing additives</td>
<td>30</td>
</tr>
<tr>
<td>3.2.4 Summary of chemical parameters of organic compounds</td>
<td>31</td>
</tr>
<tr>
<td>4 Detailed description of the simulation cases</td>
<td>37</td>
</tr>
<tr>
<td>4.1 Sensitivity analysis</td>
<td>37</td>
</tr>
<tr>
<td>4.2 Phenolic compounds</td>
<td>39</td>
</tr>
<tr>
<td>4.2.1 Phenol</td>
<td>39</td>
</tr>
<tr>
<td>4.2.2 2-methylphenol</td>
<td>40</td>
</tr>
<tr>
<td>4.3 Polycyclic aromatic hydrocarbons</td>
<td>41</td>
</tr>
<tr>
<td>4.3.1 Naphthalene</td>
<td>41</td>
</tr>
<tr>
<td>4.4 Hydraulic fracturing additives</td>
<td>42</td>
</tr>
<tr>
<td>4.4.1 2-butoxyethanol</td>
<td>42</td>
</tr>
<tr>
<td>4.4.2 Bronopol</td>
<td>42</td>
</tr>
<tr>
<td>4.4.3 Limonene</td>
<td>43</td>
</tr>
<tr>
<td>4.4.4 Dilution attenuation factors</td>
<td>44</td>
</tr>
<tr>
<td>5 Conclusions</td>
<td>45</td>
</tr>
</tbody>
</table>
Appendix 1 New HYDRUS-1D module: Dependency of $K_d$ and $\mu$ on soil organic carbon
Figures

Figure 1.1 Estimated volumes of produced water in Queensland (Source: DNRM, 2012) ........................................10

Figure 2.1 Phases of development and operation of a coal seam gas project with typical activities. Duration of each phase is indicative (length of arrows is not to scale). .................................................................12

Figure 2.2 Schematic description of the sources and pathways of contamination during the CSG extraction depressurisation phase ..............................................................................................................14

Figure 2.2 Finite element grid with soil layers (left) and location of four observation nodes (right) ..........19

Figure 2.3 Calculated soil water content at five observation depths. Depths 2-20 cm belong to soil layer 1, depth 50 cm belongs to soil layer 2 ........................................................................................................20

Figure 2.4 Soil organic carbon versus soil depth and modelled organic carbon depth-dependency (data from Ringrose-Voase et al., 2003).................................................................22

Figure 2.5 Principle of modelling the depth-dependency of organic carbon in HYDRUS-1D. Left: original organic carbon data; right: depth-reduction factor. ..................................................22

Figure 2.6 Example demonstrating organic carbon profile (a), the derived depth-reduction factor (b), the depth-reduction factor applied to the distribution coefficient for three chemicals involved in first-order transformation reactions (c) and the first-order degradation constant for the same three chemicals (d) ...........................................................................23

Figure 3.1 Reported degradation pathway for phenol. Rectangle indicates compounds included in the current assessments (Omokoko et al. 2008)..........................................................................................................................27

Figure 3.2 Summary of reported metabolic degradation pathway for o-cresol (Ahammad et al., 2001). Based on work by Dagley and Patel (1957); Nakagawa and Takeda (1962); Bayly et al. (1966); Ribbons (1966); Bayly and Wigmore (1973); Hughes et al. (1984). Rectangle indicates compounds included in the current assessments .............................................................................................................................................28

Figure 3.3 Proposed pathway for 3-methylcatechol degradation by the Rhodococcus bacteria (strain ZWL3NT) (Tian et al., 2013). ..................................................................................................................29

Figure 3.4 Potential degradation pathway of toluene by the Burkholderia fungorum FLU100 strain (Dobslaw and Engesser, 2015) ................................................................................................................29

Figure 3.5 Proposed catabolic pathway for naphthalene by soil bacteria (Denome et al., 1993; Kiyohara et al., 1994; Goyal and Zylastra, 1997). Rectangle indicates compounds included in the current assessments ................................................................................................................................................30

Figure 4.1 Effect of distribution coefficient Kd on chemical breakthrough curves at the depths of 2 and 5 cm (left) and 10 and 20 cm (right). Biodegradation is not considered (decay constant = 0). Source concentration = 1000 mg/L ..................................................................................................................................................37

Figure 4.2 Effect of distribution coefficient Kd on chemical breakthrough curves at the depths of 2 and 5 cm (left) and 10 and 20 cm (right). Biodegradation is accounted for: decay constant µ = 0.001 day⁻¹ (left) and 0.01 day⁻¹ (right). Source concentration = 1000 mg/L.................................................................................................................................................................................38

Figure 4.3 Breakthrough curves of phenol (red), catechol (blue) and HMSA (green) in a shallow soil profile accounting for sorption (Kd) and biodegradation (µ); (a) maximum Kd and µ, (b) mean Kd and µ, (c) minimum Kd and µ. A hypothetical source concentration C0 of 1 mg/L is used................................................................................................................................................39

Figure 4.4 Breakthrough curves of 2-methylphenol (o-cresol) (red) and 3-methylcatechol (blue) in a shallow soil profile accounting for sorption (Kd) and biodegradation (µ); (a) maximum Kd and µ, (b) mean Kd and µ, (c) minimum Kd and µ. A hypothetical source concentration C0 of 1 mg/L is used. ..........................................................................................................................40

Figure 4.5 Breakthrough curves of naphthalene (red) and DHDHN (cis-1,2-dihydroxy 1,2dihydronaphthalene) (blue) in a shallow soil profile accounting for sorption (Kd) and biodegradation (µ); (a) maximum Kd and µ, (b) mean Kd and µ, (c) minimum Kd and µ. A hypothetical source concentration C0 of 1 mg/L is used. ..................................................................................................................41
Figure 4.6 Breakthrough curves of 2-butoxyethanol in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used.

Figure 4.7 Breakthrough curves of bronopol (red) and formaldehyde (blue) in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used.

Figure 4.8 Breakthrough curves of limone in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used.

Figure 4.9 Dilution attenuation factors as function of attenuation parameters {$u$, $K_d$}. A = phenol, B = catechol, C = HMSA; D = 2-methylphenol, E = 3-methylcatechol; F = naphthalene, G = DHDHN; H = 2-butoxyethanol; I = bronopol, J = formaldehyde; K = limonene.
Tables

Table 2.1 Defined variable boundary conditions ................................................................. 18
Table 2.2 Mean van Genuchten soil hydraulic properties for Vertosols (average across the Cox’s Creak Catchment area, NSW) (source: Bennett, 2012) ........................................................................................................... 19
Table 3.1 Chemical identification information on CSG-related chemicals.............................. 24
Table 3.2 Summary of the chemical parameters of organic compounds reviewed in this study, .......... 33
Table 3.3 Sorption (Kd), half-life (t_{1/2}) and degradation parameters (\mu) used as input for HYDRUS-1D simulations ............................................................................................................................................................................. 36
Table 3.4 Approximate retardation factors R calculated for a water content of 0.305 (cm^3 cm^{-3}) and bulk density of 1.32 g/cm^3 (representative for the layer 1 during the leak period) ................................................................. 36
Table 4.1 Dilution attenuation factors for mean, minimum and maximum attenuation (2 cm depth)......... 44
Acknowledgments

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Executive summary

Coal Seam Gas production generates large volumes of produced water that may contain compounds originating from the use of hydraulic fracturing fluids. Produced water also contains elevated concentrations of naturally occurring inorganic and organic compounds, and usually has a high salinity. Leaking of produced water from storage ponds may occur as a result of flooding or containment failure. A review of Australian coal seam gas literature has identified several contamination pathways from surface spills through soil and shallow groundwater to several potential receptors such as rivers, water bores, wetlands, stygofauna, etc.

In this report, the fate of hydraulic fracturing chemicals and naturally occurring organic chemicals in soil as a result of unintentional release from storage ponds has been evaluated, and exposure pathways and relevant hydro-biogeochemical processes along such pathways reviewed. A collation of physico-chemical properties of organic contaminants served as input to a set of generic simulations of transport and attenuation in variously saturated soil profiles. Attenuation was simulated by means of a coupled equilibrium partitioning - first-order biodegradation model. The coupled processes of unsaturated flow, transport and attenuation in soil of selected contaminants that are associated with hydraulic fracturing fluids or that occur naturally in coal seams have then been modelled.

Naturally occurring organic compounds considered in this study include phenolic compounds and polycyclic aromatic compounds. Chemical additives of hydraulic fracturing fluids studied include a biocide, a surfactant and a solvent. Biodegradation pathways of these organics were reviewed and those relevant for soils were considered in the assessment. By considering a sequence of organics consecutively undergoing degradation and transformation, coupled with sorption onto soil organic carbon, the natural attenuation of organic compounds in soil was calculated.

Organic carbon is one of the most important soil properties influencing sorption and transformation of organic compounds. To account for this key soil property and its depth-dependency in soil, a new module was developed for HYDRUS-1D which automatically distributes organic carbon with depth, given observed organic carbon in the top soil and background organic carbon at the bottom of the soil profile. On the basis of detailed organic carbon data from the Liverpool Plains (NSW), this depth-dependency of organic carbon was implemented in the model, and the sorption \((K_{OC} \times \text{fraction of organic carbon})\) and degradation parameters (first-order degradation rate calculated from the chemical’s half-life) were adjusted accordingly.

Results showed that for all chemicals considered in the assessment, the combined effect of strong sorption and fast biodegradation resulted in complete degradation of all chemicals, including their transformation products, in the top 5 to 10 cm of the soil profile. These results are true for a broad range of sorption and degradation parameter values. This indicates that the risk of bioaccumulation in soil and leaching to groundwater is very small for the scenarios considered in this study. The methodology developed here can be easily extended to a more systematic analysis of leaching risks of a broad range of organic compounds introduced in soil.
1 Introduction

Extraction of coal seam gas requires de-pressurisation of the coal seam layers by removing large amounts of groundwater through pumping. Reducing the hydrostatic pressure on the methane gas in the pores allows gas to be released and flow towards the production wells. Coal layers generally have relatively low permeability (i.e. ability to transmit fluids, including gas), particularly at greater depths. In the least permeable coal measures, coal seam gas operations require the use of hydraulic fracturing as a means to increase connectivity between naturally occurring fractures in coal beds, and thus enhance the flow of hydrocarbons and other fluids towards the well. In Australia, coal measures in the Bowen Basin (Queensland) have much lower permeability than, for example, the Surat Basin (Queensland) and are therefore likely to require higher levels of hydraulic fracturing.

The forecasts of coal seam gas water production will vary over time and geographically (DNRM, 2012). For example, Figure 1.1 shows estimates of expected volumes of produced water per development area and the whole-of-industry forecast in Queensland. Much of the variation is due to different assumptions about the size and rate of coal seam gas industry development over the 50-year time frame that is generally assumed for forecasting water production (DNRM, 2012). By 2050, most coal seam gas areas will have reached the end of their production stage. During approximately 30 years, water production will be most significant and presents a period during which risks of contamination of soil, groundwater and surface water with produced water are the highest.

![Figure 1.1 Estimated volumes of produced water in Queensland (Source: DNRM, 2012)](image)

The produced water continuously emerges from the well and is usually stored temporarily in surface ponds; for some of the coal seam gas wells, hydraulic fracturing will have been applied to enhance gas recovery (Vidic et al., 2013; Ward et al., 2015). Produced water has a high load of dissolved solutes (Batley et al.,...
2012; Ward et al., 2015), a high alkalinity (Ward et al., 2015) and contains organic and inorganic chemicals (Batley et al., 2012).

The aim of this study is to simulate the transport and transformation of organic compounds present in coal seam gas-produced water infiltrating into soil. Such produced water may infiltrate into soil as a result of spills following extreme rain events causing flooding of storage ponds containing produced water (DERM, 2011). Infiltration may also occur due to leaks from the same storage ponds in case the liner is breached (NSW Government, 2013). Finally, large-scale diffusive leakage across the liners of storage ponds at very low flow rates may also cause produced water to infiltrate soil (Rowe, 2012; Rowe and Hosney, 2010).

Our simulations involve coupled water flow and solute transport, sorption/desorption of organic compounds on soil organic carbon, and degradation and transformation of such compounds which themselves are subject to transport and transformation. Both naturally occurring chemicals in coal-seam water (geogenics) and hydraulic-fracturing organics are considered in the assessment.
2 Modelling process

2.1 Conceptual model

2.1.1 SOIL – SHALLOW GROUNDWATER PATHWAY

The lifetime of an individual coal seam gas well or an entire coal seam gas well field can be divided into different phases (Figure 2.1). Each phase has a number of typical activities with a relatively well-defined duration and set of risks. Importantly, these risks are not equally distributed across time and space.

![Figure 2.1 Phases of development and operation of a coal seam gas project with typical activities. Duration of each phase is indicative (length of arrows is not to scale).](image)

The phases of development and operation of a coal seam gas well field are as follows:

1. Baseline or pre-development phase: starts when the site is being established and includes activities such as site identification, site access and preparation, baseline monitoring prior to production well construction. This may take between two to five years.

2. Drilling and completion phase: includes activities such as well construction starting with a bare site, building a pad and pond, setting up the rig, drilling, installing casing and piping, and cementing. This is followed by pump installation, completion of the surface gathering system, and connecting the well to the gathering system. The duration of the phase is normally from two to seven weeks per coal seam gas well.

3. Pressurisation or hydraulic fracturing fluid injection phase: starts with the first injection of hydraulic fracturing fluid into the coal formation and terminates when the last fluid is injected. There may be a number of injection events in the life-time of the site. The duration of the injection phase is from hours to days. It should be noted that the majority of production wells in Queensland and New South Wales have not required hydraulic fracturing because the permeability is sufficiently high for gas to flow due to natural fractures. Companies are preferentially targeting these areas initially. Coal seams in the Bowen Basin (Queensland) have a much lower permeability than the Surat Basin (Queensland), and as a result, hydraulic fracturing will likely have greater application in the Bowen Basin than in the Surat.

4. Depressurisation phase: starts soon after hydraulic fracturing phase ends, and covers both flowback and production, including the extraction of gas and water from the coal seam until gas and water extraction ends. In a coal seam gas well, water flow rates are initially high with low gas flow rates but as the coal seam formation is progressively depressurised, gas flow rates continue to rise to a peak rate.
(months or years after dewatering started) and water flow rates decline. There may be a number of depressurisation events intermittent with injection phases. The total duration of the depressurisation phase may be up to 20 or 30 years.

5. Return to equilibrium or post-operational phase: starts at the end of the depressurisation phase and finishes when groundwater pressures have been restored to their pre-operational levels. It includes activities such as decommissioning, plugging, rehabilitation, and monitoring. This is done progressively as wells are depleted, plugged, and abandoned. The cessation of water extraction via a coal seam gas well does not necessarily result in an overall restoration of the original groundwater pressures. It will depend, among other things, on how fast groundwater can flow towards the zones that experienced depressurisation. In other words, although the depressurisation phase has ended because water extraction has stopped, it may still take a very long time to restore all groundwater pressures to the pre-operational conditions. Duration of the post-operational phase can be easily in excess of 100 years, and might in some circumstances take a thousand years or longer to reach a new equilibrium (CH2MHill, 2013).

There are several possibilities for the contamination of surface- and groundwater during the lifetime of a hydraulic fracturing operation site. This can happen by via an accidental spill of the fracturing fluid prior to the injection, a failure in the well casing, a leakage in a transport line or a spill from a storage pond (NYSDEC, 2011; Royal Society and Royal Academy of Engineering, 2012; DERM, 2013; NSW Government, 2013). This study is based on the hypothetical scenario that a spill from a storage pond of produced water occurs over several years during the CSG depressurisation phase. It implicates a surface source of contamination, which subsequently migrates through the upper soil. The extent of the contaminated area will vary, depending on the chemical, volumetric and temporary characteristics of the spill, the soil geochemical characteristics and the soil hydrological characteristics. The pathways can include a primary surface runoff, infiltration through the upper soil layers with a possible reach of a shallow groundwater table, lateral transport within the aquifer or an accelerated downward flux through natural cracks and faults. Accordingly, possible receptors are groundwater, the surrounding ecosystem including wetlands, springs, surface water and flora and fauna, and possibly existing water supply bores for domestic use (Figure 2.2).
In this study the focus is on the vertical reactive transport through the upper soil. For soils on a slope lateral transport may be important, especially when a textural contrast exists between soil horizons. Analysis of two-dimensional flow is typically addressed by means of two-dimensional saturated/unsaturated simulation codes such as HYDRUS (2D/3D) (Šimůnek et al., 2006, 2008).

### 2.1.2 SOIL HYDROLOGICAL MODEL

Simulation of variably saturated flow in soil requires a mathematical relationship between: (i) the soil water content ($\Theta$) and the soil pressure head ($h$), and, (ii) either the water content or the pressure and the unsaturated hydraulic conductivity $K(\Theta)$ and $K(h)$, respectively. The most commonly used mathematical expression for the soil water retention curve, $\Theta(h)$, is the van Genuchten equation (van Genuchten, 1980) since it permits a relatively flexible and accurate description of $\Theta(h)$ for many soils using only a limited number of parameters. The van Genuchten soil moisture retention characteristic is defined as:

$$\Theta(h) = \Theta_r + \frac{\Theta_s - \Theta_r}{\left(1 + \alpha h |^{n} \right)^{m}} \quad \text{Equation 1}$$

where $\Theta_r$ is the residual water content (cm$^3$/cm$^3$), $\Theta_s$ is the saturated water content (cm$^3$/cm$^3$), and $\alpha$ (1/m), $n$ and $m = 1 - 1/n$ are unitless curve shape parameters specifically for the van Genuchten equation.

The second important soil hydraulic property is the unsaturated hydraulic conductivity function, $K(h)$. The hydraulic conductivity characterises the ability of a soil to transmit water, and as such is inversely related to the resistance to water flow. The hydraulic conductivity depends on many factors, including the pore-size distribution of the porous medium, and the tortuosity, shape, roughness, and degree of interconnectedness of pores. The hydraulic conductivity decreases considerably as the soil becomes unsaturated and less pore space is filled with water. The unsaturated hydraulic conductivity function gives
the dependency of the hydraulic conductivity on the water content, \(K(\Theta)\), or pressure head, \(K(h)\). The conceptual model that views the soil as a bundle of capillaries of different radii may be used to evaluate the hydraulic conductivity function. By adding the conductivity of all capillaries that are filled with water at a particular water content or pressure head, one obtains the hydraulic conductivity of the complete set of capillaries, and consequently of the soil itself.

Similarly, as for the soil water retention curve, analytical models are often used also for the unsaturated hydraulic conductivity function, \(K(h)\). The van Genuchten (1980) retention function is coupled mostly with the model of Mualem (1976) to give

\[
K(h) = K_s S_e^m \left[1 - \left(1 - S_e^{1/m}\right)^m \right]^2
\]

Equation 2

where

\[
m = 1 - \frac{1}{n}, \quad n > 1
\]

\(K_s\) is saturated hydraulic conductivity, \(S_e = (\Theta - \Theta_r)/(\Theta_s - \Theta_r)\) is the effective saturation, and \(m\) and \(n\) are as defined previously. The pore-connectivity parameter \(l\) was estimated by Mualem (1976) to be about 0.5 as an average for many soils.

### 2.1.3 SOIL GEOCHEMICAL MODEL

Migration of chemicals in soil is primarily by advection\(^1\) and dispersion (ignoring gaseous transport). By mathematically solving the solute transport or advection-dispersion equation (ADE when advection is used, or CDE when convection is used), predictions of solute concentrations at different depths and times can be obtained (Mallants et al., 2011).

For transport of inert, non-adsorbing contaminants during variably-saturated water flow the ADE is as follows (Toride et al., 1995):

\[
\frac{\partial \Theta c}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial c}{\partial z} \right) - \frac{\partial q c}{\partial z}
\]

Equation 3

where \(c\) is solute concentration in the water phase (mg/L), \(t\) is time (s), \(D\) is hydrodynamic dispersion (total dispersion, which is the sum of molecular diffusion and mechanical dispersion) (m\(^2\)/s), \(z\) is soil depth (m), and \(v\) is pore-water velocity (m/s).

In the unsaturated zone, advective transport usually becomes an important component of the overall transport, hence the two-component dispersion coefficient \((D)\) (m\(^2\)/s) has to be used. Molecular diffusion \((D_m)\) (m\(^2\)/s) is one component of the hydrodynamic dispersion, but unless water flow is extremely slow, molecular diffusion is of secondary importance\(^2\) in the migration of elements in soils and permeable aquifer sediments. The second component of hydrodynamic dispersion is mechanical dispersion, \(\alpha \times v\), as shown in the following equation:

\[
D = D_p + \alpha \times v
\]

Equation 4

where \(D\) is hydrodynamic dispersion, or simply dispersion, \(\alpha\) is dispersivity\(^3\) (m), and \(v\) is pore-water velocity (m/s). Water content \(\Theta\) is needed to obtain pore-water velocities \(v\) from water fluxes \((q)\) following:

---

1 Sometimes referred to as convection
2 Mechanical dispersion in most subsurface transport problems dominates molecular diffusion in the liquid phase, except when the fluid velocity becomes relatively small or is negligible. Diffusion-dominated transport occurs in low permeability media, such as clays and rock matrices.
3 Longitudinal dispersivity \((\alpha_l)\) is a term used to indicate dispersion along the main direction of flow.
\( \nu = \frac{q}{\theta} \)  

Equation 5

Diffusion or molecular diffusion is transport of solutes from an area of higher concentration to an area of lower concentration. It occurs as long as such a concentration gradient exists, even if the water is not flowing. Mechanical dispersion is a transport process due to heterogeneous distribution of water flow velocities within and between different soil pores (Mallants et al., 2011). The result is that some solutes will be ahead of the solute front, whereas others will lag behind, leading to solute mixing and generally a bell-shaped distribution of velocities and thus of arrival times, typical of a breakthrough curve. The processes of molecular diffusion and mechanical dispersion are incorporated into one parameter, the hydrodynamic dispersivity coefficient \( D \). Phenomenologically, dispersion has two effects: it increases the passage time of a complete solute pulse and it decreases the maximum concentration. In the case of a toxic contaminant for example, it leads to a longer exposure time but also to a lower maximum concentration.

Dispersivity is a transport parameter that is often obtained experimentally by fitting measured breakthrough curves with analytical solutions of the advection-dispersion equation (Mallants, 2014; Seuntjens et al., 2001). In this study a dispersivity = 0.1 m was taken, or one tenth of the total travel distance (i.e. 1 m) from top to bottom of the soil profile.

When chemicals interact with the soil solid phases (organic carbon, clay, iron oxides), sorption has to be accounted for in the solute transport equation. The sorption process is usually described by means of the retardation factor \( R \), defined as:

\[ R = 1 + \frac{\rho_s K_d}{\theta} = 1 + \frac{(1-n) \rho_s K_d}{\theta} \]

Equation 6

where \( \rho_s \) is solid density (g/cm\(^3\) of solids), and \( K_d \) is the distribution coefficient for instantaneous, linear and reversible sorption (L/kg). The latter parameter depends on the type of porous medium and on the element. It describes the capacity of a solid to remove a dissolved chemical from the liquid phase to the solid phase. If sorption is fast compared to the flow velocity, the element will reach some equilibrium condition between liquid and solid phase. This is called equilibrium sorption. The Freundlich equation is the simplest approach to quantify the behaviour of retention of reactive solutes with the soil matrix. It has been widely used to describe solute retention by soils and aquifer sediments (Helfferich, 1962; Sposito, 1984; among others). The Freundlich equation is expressed as:

\[ C_{ads} = K_d C_{liq}^b \]

Equation 7

where \( C_{ads} \) is the concentration of solute retained by the soil in mg/g of dry soil, \( C_{liq} \) is the solute concentration in solution in mg/ml, \( K_d \) is the soil-water distribution coefficient, also referred to as distribution coefficient, in ml/g, and the parameter \( b \) is dimensionless and typically has a value of \( b < 1 \). For \( b = 1 \), the (nonlinear) Freundlich equation reduces to a linear sorption equation.

In case chemicals are consecutively undergoing biodegradation and transformation, the rate of transformation is often described as a first-order process. Especially biodegradation kinetics (the time-dependent substrate removal and metabolism) in soil have conveniently been described by means of relatively simple mathematical models including first-order kinetics (Scow and Johnson, 1997). In this case a biodegradation constant \( \mu \) (days\(^{-1}\)) is calculated according to:

\[ \mu = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \]

Equation 8

where \( t_{1/2} \) is the chemical half-life (days). In case several chemicals are involved in a sequential first-order decay or degradation chain (\( C_i, i = 1, n \)):

\[ C_1 \rightarrow C_2 \rightarrow \ldots \rightarrow C_n \]

Equation 9

a set of coupled differential equations governing advection-dispersion, linear-equilibrium transport of a sequence of solutes consecutively undergoing biodegradation and transformation will be invoked. For two
elements, $C_1$ and $C_2$, the coupled advection-dispersion equilibrium partitioning – first-order biodegradation equation becomes (van Genuchten, 1985):

$$\frac{\partial R_1 \theta C_1}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C_1}{\partial x} \right) - \frac{\partial q C_1}{\partial x} - \mu_1 R_1 C_1$$  \hspace{1cm} \text{Equation 10}$$

$$\frac{\partial R_2 \theta C_2}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C_2}{\partial x} \right) - \frac{\partial q C_2}{\partial x} - \mu_2 R_2 C_2 + \mu_1 R_1 C_1$$  \hspace{1cm} \text{Equation 11}$$

where $R_1$ and $R_2$ are retardation factors for chemical $C_1$ and $C_2$, respectively and $\mu_1$ and $\mu_2$ are first-order biodegradation constants for chemical $C_1$ and $C_2$, respectively.

### 2.2 Numerical model for multi-component reactive transport modelling in saturated/unsaturated media

#### 2.2.1 HYDRUS-1D

HYDRUS-1D (Šimunek et al., 2008) is a public domain computer software package (www.hydrus2d.com) that simulates the one-dimensional movement of water, heat, and multiple solutes in variably saturated media. The program uses finite elements to numerically solve the Richards equation for saturated-unsaturated water flow and Fickian-based advection-dispersion equations for both heat and solute transport. The flow equation includes a sink term to account for water uptake by plant roots as a function of both water and salinity stress. The heat transport equation considers conduction as well as advection with flowing water. The solute transport equations account for advective-dispersive transport in the liquid phase, and diffusion in the gaseous phase. The transport equations also include provisions for non-linear and/or non-equilibrium reactions between the solid and liquid phases, linear equilibrium reactions between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions: one which is independent of other solutes, and one which provides the coupling between solutes involved in the sequential first-order decay reactions.

The program may be used to analyse water and solute movement in unsaturated, partially saturated, or fully saturated media. The flow region itself may consist of non-uniform (layered) soils. The unsaturated soil hydraulic properties (the constitutive relationships) are described using van Genuchten (1980) or Brooks and Corey (1964) type analytical functions, or modified van Genuchten type functions that produce a better description of the hydraulic properties near saturation. HYDRUS-1D incorporates hysteresis by assuming that drying scanning curves are scaled from the main drying curve, and wetting scanning curves from the main wetting curve. Root growth is simulated by means of a logistic growth function. Water and salinity stress response functions can also be considered.

HYDRUS-1D has capabilities to simulate the transport of viruses, colloids, and bacteria (Schijven and Šimunek, 2002; Bradford et al., 2003). HYDRUS-1D uses a Microsoft Windows based Graphics User Interface (GUI) to manage the input data required to run the program, as well as for nodal discretisation and editing, parameter allocation, problem execution, and visualization of results. All spatially distributed parameters, such as those for various soil horizons, the root water uptake distribution, and the initial conditions for water, heat and solute movement, are specified in a graphical environment. The program offers graphs of the distributions of the pressure head, water content, water and solute fluxes, root water uptake, temperature and solute concentrations in the soil profile at pre-selected times. Also included is a small catalogue of unsaturated soil hydraulic properties (Carsel and Parish, 1988), as well as pedotransfer functions based on neural networks (Schaap et al., 2001).
2.3 Model implementation

2.3.1 SOIL HYDROLOGICAL CHARACTERISTICS

Simulation of coupled variably-saturated water flow and solute transport requires flow boundary conditions and soil hydraulic properties. Boundary conditions implemented in this study are summarised in Table 2.1. The top boundary is simplified by assuming net infiltration only, thereby simplifying processes of evapotranspiration, runoff, and soil water redistribution into a single process of recharge (i.e. the next result of all those processes). This means that the imposed water flux is continuous across the entire soil profile, and the water flux at the bottom of the profile equals that at the top. The following features were simulated with HYDRUS-1D:

- Time series of soil water content, matric head, and solute concentrations (organic compounds)
- Depth profiles of soil water content, matric head, and solute concentrations (organic compounds) at prescribed time intervals
- Time series of water fluxes at the bottom (drainage) of the soil profile, as well as solute fluxes (these will be shown to be effectively zero for all compounds considered).

<table>
<thead>
<tr>
<th>Time (years)</th>
<th>Recharge flux (mm/year)</th>
<th>Boundary solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20 warming up</td>
<td>40</td>
<td>Rainwater</td>
</tr>
<tr>
<td>20-50 leakage period</td>
<td>35</td>
<td>Produced water</td>
</tr>
<tr>
<td>50-60 post-leakage</td>
<td>40</td>
<td>Rainwater</td>
</tr>
</tbody>
</table>

While generally low, leakage (the combination of advective and diffusive migration of fluids) from a composite liner (geomembrane (GM) combined with either a compacted clay liner or a geosynthetic clay liner) cannot be avoided and is mainly due to the fact that a GM installed as part of liner system generally will likely have some holes (2.5 to 5 holes per hectare being most commonly assumed, Rowe et al. 2004; Rowe and Hosney, 2010; Rowe, 2012). Holes may form as a result of (i) manufacturing defects, (ii) handling of the GM rolls, (iii) on-site placement and seaming, (iv) cleaning of residue from a water holding pond, and (v) stress cracking as the GM ages (Rowe, 2012). Leakage from a single GM with 2.5 holes per hectare (leakage head or water depth of 5 m typical of a water holding pond) was calculated to be 1,000 lphd\(^4\) (1.2×10\(^{-9}\) m/s) and 4,000 lphd (4.6×10\(^{-9}\) m/s) for 0.5 and 1 mm radius holes, respectively (Rowe, 2012).

In Australia design requirements for storage basins are stipulated by the QLD Department of Environment and Resource Management “Manual for Assessing Hazard Categories and Hydraulic Performance of Dams” (DERM, 2012) and the NSW Dam Safety Committee (DSC) requirements (NSW Government, 1978). Further relevant guidance regarding liner design may be obtained from DITR (2007) for tailings management; a compacted clay liner would normally be expected to achieve a saturated hydraulic conductivity of less than 10\(^{-8}\) m/s.

The 35 mm/y (~10\(^{-9}\) m/s) leak rate chosen here is assumed to be typical for a design with a single geomembrane liner, or a compacted clay liner if sufficiently thick. While lower leak rates may be obtained with geosynthetic clay liners and composite liners, the purpose of selecting 35 mm/y was to impose an upper bound estimate for the water flux and assess the natural attenuation capacity of soil under such circumstances.

\(^4\) lphd = liters per hectare per day
The soil profile is assumed 1-m deep, with three soil layers: 0-0.3 m, 0.3-0.7 m, and from 0.7-1.0 m. The van Genuchten soil hydraulic properties were taken from Bennet (2012). These soil hydraulic properties were calculated on the basis of the pedotransfer functions of Minasny and McBratney (2002) using soil data points within the Cox’s Creek catchment, NSW. For three soil horizons particle size distribution and the bulk density from the SALIS (New South Wales Soil And Land Information System) dataset were used as predictor variables in the pedotransfer functions. From a total of six soil types identified from a soil survey (Tenosols, Dermosols, Vertosols, Chromosols, Sodosols, Kandosols), Vertosols were most prominent with 84 out of 143 soil profiles (59%). Mean Vertosol hydraulic properties were therefore selected here for the simulations (Table 2.2).

Table 2.2 Mean van Genuchten soil hydraulic properties for Vertosols (average across the Cox’s Creek Catchment area, NSW) (source: Bennett, 2012)

<table>
<thead>
<tr>
<th>Soil layer</th>
<th>Θr (cm³/cm³)</th>
<th>Θs (cm³/cm³)</th>
<th>α (1/m)</th>
<th>n (-)</th>
<th>Ks (m/day)</th>
<th>l (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (0-0.3 m)</td>
<td>0.059</td>
<td>0.515</td>
<td>8.3</td>
<td></td>
<td>1.217</td>
<td>6.04</td>
</tr>
<tr>
<td>2 (0.3-0.7 m)</td>
<td>0.066</td>
<td>0.538</td>
<td>7.4</td>
<td></td>
<td>1.190</td>
<td>4.51</td>
</tr>
<tr>
<td>3 (0.7-1.0 m)</td>
<td>0.070</td>
<td>0.515</td>
<td>7.9</td>
<td></td>
<td>1.150</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Bulk density for the three soil layers is 1.32, 1.42 and 1.45 g/cm³ for layers 1, 2 and 3, respectively. The 1-m numerical domain was discretised in 100 finite elements, each 0.01 m long. The numerical grid, the three soil layers and four observations nodes for detailed output are shown in Figure 2.3. Note that this grid had to be refined for the simulations with the chemical limonene to achieve an acceptable mass balance; a smaller discretisation at the soil surface was implemented based on a nodal density value of 0.1 applied to the top model node.
Total simulation time ranged from 5 to 125 sec on Personal Computer with an Intel Core i5-2540M CPU and 2.6 GHz. Simulated water content (Figure 2.4) time series show typical patterns linked to the warming-up period, the leakage period with a lower recharge rate, and again a higher recharge for the third period. At the deeper depth of 50 cm, the water content is higher (0.35 cm³/cm³) due to the different hydraulic properties in this soil layer (Table 2.2). At all other depths water content is about 0.305 cm³/cm³ during the leakage period.

![Figure 2.4 Calculated soil water content at five observation depths. Depths 2-20 cm belong to soil layer 1, depth 50 cm belongs to soil layer 2](image)

### 2.3.2 SOIL GEOCHEMICAL MODEL

The two most important parameters determining chemical attenuation in soil are the soil-water partition coefficient $K_d$ and the first-order degradation constant $\mu$. For nonpolar organic chemicals, $K_d$ is strongly related to the organic carbon in soil (Scow and Johnson, 1997); the same is true for the degradation constant $\mu$. Generally, the higher the organic carbon content, the higher is $K_d$. Dry mineral surfaces are also known to adsorb organic compounds. Upon wetting, however, water generally causes organic compounds to desorb from mineral sorption sites; the small remaining fraction of mineral sorption is generally much smaller than the sorption by organic matter (Chiou, 1990).

Several studies have investigated the effect of sorption on biodegradation rates. When chemicals become partitioned between adsorbed and dissolved phase, either the dissolved phase only or both the dissolved and sorbed phase may be metabolized. In case rapid exchange occurs between dissolved and equilibrium sorbed chemical, all material in the labile pool may be available to microbes (Hamaker and Goring, 1976). If a constant equilibrium is maintained between a dissolved substrate available to microorganisms and its sorbed, unavailable form, sorption should affect biodegradation kinetics only by lowering the amount of substrate metabolised in each time step. This assumes biodegradation rates are independent from chemical concentration. Scow and Johnson (1997) argue that when sorption/desorption kinetics are very fast compared to microbial kinetics, kinetics resembling liquid culture biodegradation rates will likely occur.

Some studies showed that only the dissolved phase was metabolised and that both attached and suspended organisms were responsible for degradation (Ogram et al., 1985). Different microbial strains have been shown different abilities in metabolising sorbed and dissolved chemicals: some can utilise the
sorbed compound, whereas others can only metabolise the dissolved compound, as was the case for naphthalene (Guerin and Boyd, 1992, 1993).

In HYDRUS-1D, biodegradation can be applied to either the dissolved phase, the adsorbed phase, or both phases. If applied to both phases, different degradation rates can be applied to dissolved and adsorbed phases. Because degradation rates are generally only available for the dissolved phase, often derived from solution cultures or batch tests, identical values are commonly applied to both phases. We here assume that both adsorbed and dissolved chemicals are metabolised, and their biodegradation rate is identical.

Microbial biomass (fungi and bacteria) is affected by soil moisture and carbon content (Cookson et al., 2008; Araújo et al., 2009). The variation of carbon content with soil depth is therefore a useful indicator of microbial biomass variation, and thus of the biodegradation rate (Anderson, 1984). Combining this with the previous model assumption that sorption does not affect the ability for biotransformation, delivers a model where both sorption and biodegradation are linked to the organic carbon content (see further in Section 2.3.2.2).

In soil, organic carbon is generally highest in the top layers and decreases with depth. This implies that if $K_d$ and $\mu$ are determined by organic carbon content, these values will decrease with increasing soil depth. For this study to have some local relevance for Australian soils, soil data from the Liverpool Plains (NSW) was reviewed and soil organic carbon data extracted and summarised as function of soil depth.

### 2.3.2.1 Organic carbon versus depth

Detailed soil data from the Integrated Catchment Management Project (Ringrose-Voase et al., 2003) were evaluated and soil organic carbon data extracted for three soil types: Vertosols, Chromosols, and Sodosols. The Vertosols comprise a combination of Grey, Black, Aquic, and Red Vertosols. Organic carbon data as a function of soil depth are shown in Figure 2.5. As expected, the highest carbon content occurs in the top 10 cm with a geometric mean value of 2.17%, then decreases somewhat exponentially with depth until it reaches a minimum background value of approximately 0.14% at the depth of 150 cm. From then onwards, it remains more or less constant with depth. While an exponential model best describes the depth-dependency of organic carbon (Kookana et al., 1995), a linear approximation was derived for use in HYDRUS-1D. The average value of 2.17% or 0.0217 g/g will be used to derive $K_d$ values from $K_{oc}$ values and $f_{OC}$, where $f_{OC} = 0.0217$ g/g (see section 3.2.4).
2.3.2.2 Depth reduction of the retardation and biodegradation constants.

A new module was developed in HYDRUS-1D to automatically update $K_d$ and degradation constant $\mu$ as the organic carbon decreases with depth, following the scheme suggested by Kookana et al. (2005). The retardation and degradation constants are reduced by a depth-dependent function, which has a constant value (1) in the top of the soil profile (above $aDepth$), then decreasing linearly down to a depth of $bDepth$. Below this depth the reduction function has the value of $cValue$ (Figure 2.6). $cValue$ is calculated as the ratio of organic carbon at $bdepth$ to organic carbon at $aDepth$ (i.e. the mean value between soil surface and $aDepth$). In the example of Figure 2.5, the mean organic carbon % from surface to $aDepth$ is 0.65, and the carbon content at $cValue$ is 0.12. As result, $cValue = 0.12/0.65 = 0.185$.

![Figure 2.6 Principle of modelling the depth-dependency of organic carbon in HYDRUS-1D. Left: original organic carbon data; right: depth-reduction factor.](image)

The parameters of this function are read from the input file Depth_Red.in, which looks as follows:
and which needs to be placed into the project folder. When this file does not exist, or the logical variable lDepthRed is equal to false, the depth reduction is not considered. Note that the z-coordinate of the surface is equal to zero, and the axis is positive upward (the depths are thus in negative values).

The new executable (h1d_calc.exe) has to be either placed into the HYDRUS-1D installation folder and then it can be run directly from GUI, or can be run outside of the GUI. Then one has to place next to the exe file a new file Level_01.dir, which contains the path to where the project is located:

Figure 2.7 illustrates: (i) the initial organic carbon data versus depth and the derivation of the parameters aDepth, bDepth, cValue, (ii) the depth-reduction factor as calculated in HYDRUS-1D, (iii) the depth-dependency of Kd, and (iv) the depth-dependency of the degradation constant as implemented in HYDRUS-1D. Note the curved lines in Figure 2.7c and d are due to the logarithmic X-axis.

Figure 2.7 Example demonstrating organic carbon profile (a), the derived depth-reduction factor (b), the depth-reduction factor applied to the distribution coefficient for three chemicals involved in first-order transformation reactions (c) and the first-order degradation constant for the same three chemicals (d).

When the principle of depth-reduction factor is applied to the organic carbon data from the Liverpool Plains (see section 2.3.2.1), the following parameters are derived: aDepth = -0.1, bDepth = -150, cValue = 0.136/2.17 = 0.063. These values have been included in the Depth_Red.in file when running HYDRUS-1D.
3 Natural attenuation parameters for typical organic compounds

3.1 Organic compounds considered in this assessment

The assessment considers two broad categories of chemicals: (i) chemicals that naturally occur in coal seam pore-waters and that could end up in flowback and/or produced water, albeit at low concentrations, and (ii) chemicals associated with hydraulic fracturing additives such as surfactants, solvents and biocides. The first category of chemicals tested here includes the phenolic compounds phenol and 2-methylphenol, and the polycyclic aromatic hydrocarbon (PAH) naphthalene. The second category tested here includes the hydraulic fracturing additives 2-butoxyethanol, limonene and bronopol (Table 3.1). Where data on transformation products were readily available, these have been included in Table 3.1.

Table 3.1 Chemical identification information on CSG-related chemicals.

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS No.</th>
<th>Chemical Structure</th>
<th>Chemical formula</th>
<th>IUPAC name</th>
<th>Parent compound (P)/ transformation products (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>108-95-2</td>
<td><img src="image" alt="Phenol Structure" /></td>
<td>C₆H₆O</td>
<td>Phenol</td>
<td>P</td>
</tr>
<tr>
<td>1,2-Catechol (1,2-dihydroxybenzene)</td>
<td>120-80-9</td>
<td><img src="image" alt="1,2-Catechol Structure" /></td>
<td>C₆H₆O₂</td>
<td>Benzene-1,2-diol</td>
<td>D1</td>
</tr>
<tr>
<td>HMSA 2-hydroxymuconic acid-6-semialdehyde</td>
<td>3270-98-2</td>
<td><img src="image" alt="HMSA Structure" /></td>
<td>C₆H₆O₄</td>
<td>(3E,5E)-6-hydroxy-2-oxohexa-3,5-dienoic acid</td>
<td>D2</td>
</tr>
<tr>
<td>2-methylphenol</td>
<td>95-48-7</td>
<td><img src="image" alt="2-Methylphenol Structure" /></td>
<td>C₇H₈O</td>
<td>Other name: o-cresol</td>
<td>P</td>
</tr>
<tr>
<td>3-methylcatechol</td>
<td>488-17-5</td>
<td><img src="image" alt="3-Methylcatechol Structure" /></td>
<td>C₇H₈O₂</td>
<td>3-Methylbenzene-1,2-diol</td>
<td>D</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>91-20-3</td>
<td><img src="image" alt="Naphthalene Structure" /></td>
<td>C₁₀H₈</td>
<td>Bicyclo[4.4.0]deca-1,3,5,7,9-pentene</td>
<td>P</td>
</tr>
<tr>
<td>cis-1,2-dihydroxy-1,2-dihyronaphthalene</td>
<td>51268-88-3</td>
<td><img src="image" alt="cis-1,2-Dihydroxy-1,2-Dihyronaphthalene Structure" /></td>
<td>C₁₀H₁₀O₂</td>
<td>[1R,2S]-1,2-dihyronaphthalene-1,2-diol</td>
<td>D</td>
</tr>
<tr>
<td>2-butoxyethanol</td>
<td>111-76-2</td>
<td><img src="image" alt="2-Butoxyethanol Structure" /></td>
<td>C₆H₁₄O₂</td>
<td>2-Butoxyethanol Other name: ethylene glycol monobutyl ether</td>
<td>/</td>
</tr>
</tbody>
</table>
### Phenolic Compounds

Phenolic compounds such as phenol and 2-methylphenol have been observed in both low-rank and bituminous coals (Siskin and Aczel, 1983) and these are likely to be derived from cleavage of aromatic compounds as well as transformation of plant cell walls under high pressure and temperature during coal formation. In the US phenolic compounds such as dimethylphenol have been detected in coal seam gas produced water in concentrations up to 5.89 mg/L (Orem et al., 2007). Phenol was detected at a level of 0.3 µg/L in Australian coal seam gas water holding ponds of the Walloon production area (Stearman et al., 2014). Specific drinking water guidelines for phenols currently do not exist (Orem et al., 2007; NHMRC, 2011; WHO, 2011). Therefore, the effect of chronic, long-term exposure to phenolic compounds is not well established. For the protection of aquatic life in freshwater ecosystems a threshold of 4.0 µg/L was recommend by the Canadian Council of Ministers of the Environment (CCME, 1999). For aquatic ecosystem protection (95% protection level) the Australia & New Zealand water quality guideline for phenol is 320 µg/L (ANZECC & ARMCANZ, 2000).

PAHs such as naphthalene belong to the naturally occurring compounds also known as geogenic compounds. Owing to their low water solubility (de Maagd et al., 1998), PAH contamination of water is generally considered to be of lesser concern. Nevertheless, they are of significance due to the known hazards, such as carcinogenicity, that they can present for human and environmental health (EC, 2003). For aquatic ecosystem protection (95% protection level) the Australia & New Zealand water quality guideline for naphthalene is 16 µg/L (ANZECC & ARMCANZ, 2000). Analysis of coal seam gas produced waters from the Powder River Basin (WY, USA) indicated PAHs were the most commonly observed group of organic compounds; total PAH concentrations ranged up to 23 µg/L (Orem et al., 2007). In a more recent study total PAH concentrations in coal seam gas produced water from the US were shown to exceed 50 -100 µg/L (Orem et al. 2014). Based on 47 sampled wells of the Walloon coal seam gas production area, Stearman et al. (2014) reported only seven wells with detectable levels of PAHs, including naphthalene and phenanthrene. The maximum naphthalene and phenanthrene concentrations from a single well were 0.046 µg/L and 0.02 µg/L, respectively. Of all detected PAHs, naphthalene was detected at the highest concentration. Naphthalene was detected at a level of 0.06 µg/L in Australian coal seam gas water holding ponds of the Walloon production area (Stearman et al., 2014).

2-butoxyethanol or 2BE is a surfactant used as pre-flush hydraulic fracturing additive and acid additive. Large quantities have been used in the US and Canada (US Congress Report, 2011; Wylde and O’Neil, 2011). It is also one of the hydraulic fracturing chemicals used in Australian coal seam gas operations (APPEA, 2014). The role of the pre-flush additive is to preferentially wet the formation to allow for better propagation of the fracture through the production zone and post-fracture production of the load water, and ultimately, hydrocarbons (Wylde and O’Neil, 2011). Despite being readily degradable, 2BE is also known to bioaccumulate and is generally toxic (Harris et al., 1998). 2BE was declared a Priority Existing Chemical under Australia’s National Industrial Chemicals Notification and Assessment Scheme. The assessment of 2BE demonstrated it is highly mobile in soil and water and has been detected in groundwaters underlying municipal landfills and hazardous waste sites in the US.

Bronopol is a biocide used in hydraulic fracturing wells in the US (US Congress Report, 2011; Kahrilas et al., 2014) and Australia (QGC, 2012). It is toxic to marine invertebrates such as oysters; the observed LC50 is 1.6

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS Number</th>
<th>Structure</th>
<th>Molecular Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limonene</td>
<td>138-86-3</td>
<td><img src="image" alt="Limonene Structure" /></td>
<td>C_{10}H_{16}</td>
<td>1-Methyl-4-(1-methylene)-cyclohexene</td>
</tr>
<tr>
<td>Bronopol</td>
<td>52-51-7</td>
<td><img src="image" alt="Bronopol Structure" /></td>
<td>CH_3BrNO_4</td>
<td>2-bromo-2-nitropropane-1,3-diol</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
<td><img src="image" alt="Formaldehyde Structure" /></td>
<td>CH_2O</td>
<td>Methanal</td>
</tr>
</tbody>
</table>

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mg/L for *Daphnia magna* (Sigma-Aldrich, 2014) and 0.77 mg/L for the Eastern Oyster (US EPA, 1995). Substantial spills into surface waters or streams may therefore have noticeable ecotoxicological effects on aquatic species. Bronopol was shown to produce tris(2-hydroxymethyl-2-nitropropane-1,3-diol) (US EPA, 1995). Bronopol has been reported to hydrolyze within 3 h at 60 °C and pH 8, producing formaldehyde, nitrosamines, and other molecules (Swenberg et al., 1980; Dunnett and Telling, 1984; Challis and Yousef, 1990; Loeppky, 1994; US EPA, 1995). Although, the parent compound (bronopol) is rather short-lived in the environment, its degradation products are still toxic and more persistent (Douglass et al., 1978; Swenberg et al., 1980).

Limonene is a chemical additive of water and guar based hydraulic fracturing fluid systems; its use has been reported for the US (US Congress Report, 2011) and Australia (Santos, 2013). Limonene is a terpene hydrocarbon and is increasingly being used as a solvent for cleaning purposes. Terpenes such as limonene are replacements for xylene- and toluene-based solvents. They are derived from plant products, including orange peels and pine sap. Compared with aromatic solvents, terpenes have good solvency, and are biodegradable, less toxic, and less flammable.

### 3.2 Degradation in soil

Biodegradation involves biochemical reactions within the soil sub-surface through which a parent compound is changed or transformed to organic or inorganic end products or via a series of intermediates. It is an important mechanism for the removal of organic compounds in soil (Loehr, 1989). Aerobic biotic degradation rates (half-life) and pathways for organic compounds in soils are influenced by many factors including; their initial concentration at the time of release to the environment, the toxicity of a given compound and its daughter compounds, the physical and chemical properties of the compound in question and the physical, chemical and biological properties of the soil (Scow and Johnson, 1997). In the sections below, we briefly present and summarise the previously reported degradation pathways and aerobic biotic degradation half-lives where available, for some of the organic compounds reviewed in this assessment. Aerobic rather than anaerobic degradation rates are considered appropriate in the current assessment involving shallow and well-aerated soil.

Biodegradation studies and the parameters derived for modelling (e.g., biodegradation rate) often involve tests in solution culture and batch systems, with experimental conditions often different from those in soil. Two important questions arise: (i) whether biodegradation rates measured in solution culture are appropriate to soil, and (ii) whether parameters measured in batch systems can be extrapolated to dynamic flow systems such as real soil. The few comparative studies reported to date suggest differences in kinetic parameters are mainly due to indirect effects (differences in solution chemistry between solution cultures and solutions with soil or sediments present) rather than direct effects of sorbing surfaces on microorganisms (Scow and Johnson, 1997). When batch-derived biodegradation parameters are applied to coupled flow and transport systems, mass-transfer limitations may occur which might require correction of the batch-derived parameters (Scow and Johnson, 1997). To address these uncertainties around biodegradation parameters, introduced when solution cultures and batch systems are the primary source of degradation tests, we here define a range of parameter values rather than using single values and subsequently run the simulations multiple times (i.e. for minimum, mean, and maximum parameter values).

#### 3.2.1 PHENOLIC COMPOUNDS

**Phenol (parent compound)**

The degradation pathway of phenol is illustrated in Figure 3.1. Once phenol is released to the soil environment, it has been found to initially degrade to catechol and then 2-hydroxymuconic acid-6-semialdehyde (HMSA) (Omokoko et al., 2008). Subsequent further degradation by hydrolysis can result in the formation of compounds such as pyruvate and acetdehyde. Degradation studies of phenol in soil conducted by Scott et al. (1983) and Shiu et al. (1994) have provided important insights into the range in
half-life for phenol (hours to days) and the importance of either the initial concentration in soil or the pH of the soil. Further degradation products such as pyruvate are important chemical compounds in biochemistry; pyruvate is the output of the metabolism of glucose. Because of their inherently low toxicity, the transformation products pyruvate and acetaldehyde are not considered in the current assessments. Only the first three compounds of the phenol degradation pathway (phenol, catechol and HMSA) are considered in the coupled transport-sorption-degradation calculations.

**Figure 3.1 Reported degradation pathway for phenol. Rectangle indicates compounds included in the current assessments (Omokoko et al. 2008)**

**Catechol (daughter compound)**

Catechol is the first degradation product of phenol (Figure 3.1). Depending on the degradation pathway, similar compounds are formed as is the case for phenol including, HMSA, pyruvate and acetaldehyde (Zeyuallah et al., 2009). Soil-based studies on the aerobic biotic degradation half-life of catechol by Martin et al. (1979) and Scott et al. (1983) have highlighted that its half-life is far greater (weeks to months) than that of phenol. The stability of catechol in soil is influenced by its rapid polymerisation into new phenolic polymers, incorporation into existing phenolic polymers by enzymes in the soil or by phenolases or autoxidation (Martin et al., 1979). Similarly for phenol, the study by Stott et al. (1983) highlighted the influence of the initial concentration of catechol in soil, the soil pH and the type of soil on the range in degradation rate found.

**2-Hydroxymuconic acid-6-semialdehyde (HMSA) (daughter compound)**

The second transformation product of phenol, 2-hydroxymuconic acid-6-semialdehyde (HMSA; C₆H₇O₄), has found to be readily degradable in soil, with 95% of the initial concentration of HMSA degraded within 6 days in the Zahn-Wellens test (Luck, 1993). A biodegradation study on a similar compound (sorbic acid, C₆H₇O₃) conducted by the Chemicals Inspection and Testing Institute (1992) also found 83% biodegradation after 2 weeks using an activated sludge seed, and an initial chemical concentration of 100 mg/L. Primary aerobic biotic degradation rates for HMSA were also estimated in this assessment to be in the order of hours to days, using the US EPA (2015b) BIOWIN biodegradability of organic chemicals software. Primary biodegradation is the transformation of a parent compound to an initial metabolite. HMSA is further transformed into simple molecules, including pyruvate, citrate and acetaldehyde, used in the tricarboxyl acid cycle through which microbes derive energy.

**2-Methylphenol (o-cresol) (parent compound)**

Ahamad et al. (2001) summarised literature reported metabolic pathways for o-cresol degradation by *Pseudomonas* in soil (see Figure 3.2). O-cresol initially degrades to 3-methylcatechol and subsequently degrades to form 2-hydroxy-6 keohepta-2,4 dieonate, followed by 2-ketopent-4-eonate and 4-hydroxy-2-ketopentanoate. Degradation studies of o-cresol in agricultural soils Loehr (1989) determined half-lives
ranging between 1.6 to 5.1 days. Similar to the other phenolic compounds discussed here, reported degradation rates appear to have been influenced by their initial concentration in soil, the pH of the soil and factors including cation exchange capacity (CEC) and organic carbon content of the test soils.

3-Methylcatechol (daughter compound)

The first degradation product of o-cresol, 3-methylcatechol, degrades to form compounds such as 2-hydroxy-6 ketohepta-2,4 dieionate. A degradation study using a pure bacterial culture by Tian et al. (2013) highlights the ability of the Rhodococcus sp. bacteria strain ZWL3NT to degrade 3-nitrotoluene (3NT) to 3-methylcatechol (Figure 3.3); further degradation produces compounds as found in the degradation pathway for o-cresol (Figure 3.2). Owing to the inherently low toxicity of 2-hydroxy-6 ketohepta-2,4
dieonate and subsequent transformation products, only o-cresol and 3-methylcatechol are included in the current calculations.

Furthermore, a study by Dobslaw and Engesser (2015) using pure cultures demonstrated the ability of *Burkholderia fungorum*, a species of proteobacteria, to degrade toluene. The potential degradation pathway proposed by Dobslaw and Engesser (2015) in Figure 3.4 has similarities to the one proposed by Tian et al. (2013) (Figure 3.3). Aerobic biodegradation rates for 3-methylcatechol were estimated in this assessment to be in the order of days, using the BIOWIN software (US EPA, 2015b).

**Figure 3.3** Proposed pathway for 3-methylcatechol degradation by the *Rhodococcus* bacteria (strain ZWL3NT) (Tian et al., 2013).

**Figure 3.4** Potential degradation pathway of toluene by the *Burkholderia fungorum* FLU100 strain (Dobslaw and Engesser, 2015)

### 3.2.2 POLYAROMATIC HYDROCARBONS

**Naphthalene (parent compound)**

Naphthalene has been the subject of numerous degradation studies where bacteria in soil have degraded naphthalene to compounds such as naphthalene diol, salicylic acid, and catechol. Some pure culture studies have shown bacteria utilise naphthalene as a source of carbon (Treccani et al., 1954), whilst others have emphasised the ability of fungi to oxidise naphthalene (Cerniglia, 1984). Oxidation pathways for culture conditions published in Cerniglia (1984) include five metabolites of naphthalene along the degradation pathway: cis-1,2-dihydroxy-1,2-dihydronaphthalene, 1,2-dihydroxynaphthalene, cis-o-hydroxybenzalpyruvic acid, salicylic acid, and catechol (Figure 3.5). Biodegradation has been shown to remove naphthalene from soil, with an estimated half-life of more than 80 days (Howard, 1989).

Naphthalene is very toxic to aquatic organisms, with PNEC values of 2.4 microgram/L (EC, 2003). As far as
human health is concerned, combined exposure may result in haemolytic anaemia, inhalation toxicity and carcinogenicity (EC, 2003).

![Diagram of catabolic pathway for naphthalene]

**Figure 3.5** Proposed catabolic pathway for naphthalene by soil bacteria (Denome et al., 1993; Kiyohara et al., 1994; Goyal and Zylastra, 1997). Rectangle indicates compounds included in the current assessments

### 3.2.3 HYDRAULIC FRACTURING ADDITIVES

**2-Butoxyethanol (parent compound)**

Degradation studies of 2-butoxyethanol have received little attention in the literature and therefore a paucity of data exists. A review of the toxicological profile for 2-butoxyethanol by ATSDR (1998) did not identify any studies that report degradation products or known pathways. Hydrolysis of 2-butoxyethanol is unlikely, as it contains both alcohol and ether functional groups, which are generally resistant to hydrolysis.
(Harris, 1990). Aerobic biodegradation studies of 2-butoxyethanol using sewage for inocula and mineralisation (of the compound to carbon dioxide and water) as a measure of biodegradation indicated, 5% mineralisation in 5 days (Dow, 1993), 57-74% in 10 days (Dow, 1993; Price et al., 1974), and 72-88% in 20 days (Dow, 1993; Price et al., 1974). Waggy et al. (1994) determined the biodegradation of 2-butoxyethanol to be 47% in 5 days, 70% in 15 days and 75% in 28 days, using a closed bottle test with settled sewage as a microbial inoculum. The aerobic biodegradation half-life of 2-butoxyethanol in surface water has been estimated by Howard et al. (1991) to range between 7-28 days. An aerobic biodegradation half-life was also estimated as part of this assessment to be ~416 hours using BIOWIN (US EPA, 2015b).

Limonene (parent compound)

Similar to 2-butoxyethanol, limonene does not have functional groups for hydrolysis, its cyclohexene ring and ethylene group are known to be resistant to hydrolysis and it therefore is an unlikely process in terrestrial or aquatic environments (US EPA, 1994). Biotic degradation of limonene by some species of microorganisms has been reported. For example, Penicillium digitatum, Corynespora cassicola and Diplodia gossypina (Abraham et al., 1985), and a soil strain of Pseudomonas sp. (PL strain) (Dhavalikar & Bhattacharayya, 1966; Shulka & Bhattacharayya, 1968). MITI (1992) demonstrated that limonene was readily biodegradable with 41–98% degradation by biochemical oxygen demand in 14 days; testing was under aerobic conditions in a standard test specified by the OECD (OECD, 1981).

Bronopol (parent compound)

Bronopol can be stable to hydrolysis under normal/ambient conditions, but susceptible to hydrolysis when exposed to elevated temperatures and alkaline conditions (US EPA, 1995). Degradation pathways for bronopol vary depending on the environmental conditions and medium. Bronopol has been found to degrade to formaldehyde, 2-hydroxymethyl-2-nitropropane-1,3-diol (tris) and 2-bromo-2-nitroethanol in a review summarised by the United States Environmental Protection Agency (US EPA, 1995). Other degradation products consist of bromo-nitroethane, bromo-ethanol, and bromo-nitroethanol (Wang et al., 2002). In ambient laboratory conditions, the half-life for bronopol due to hydrolysis was determined to be approximately 18 years at pH 4, about 1.5 years at pH 6 and about 2 months at pH 8. At an elevated temperature of 60°C and a pH of 4 and 8, half-lives were found to be much shorter, 4 days and 3 hours, respectively (US EPA, 1995). For the purpose of this study, it was assumed that bronopol will degrade to formaldehyde.

Formaldehyde (daughter compound)

There are limited data available on the degradation pathway for formaldehyde in soil and sediment. A number of studies however, have reported that formaldehyde is readily degraded by soil bacteria such that accumulation in soil does not occur (US EPA, 1985; IPCS, 1989). Similarly, the reported degradation rates in a handful of studies have all cited Howard et al. (1991), who estimated a soil half-life of 24–168 h, based on estimated aqueous aerobic biodegradation half-lives.

3.2.4 SUMMARY OF CHEMICAL PARAMETERS OF ORGANIC COMPOUNDS

For each of the organic compounds considered in the current assessment, several chemical parameters relevant to the calculation of their transformation in soil were compiled from a literature review. Two sets of parameters were considered: (i) parameters required for simulation of attenuation and transport processes in soil (degradation pathway; sorption-related parameters such as Kow, Koc, Koii, and half-lives), and (ii) additional parameters that provide auxiliary information not directly used in the simulations (solubility, Henry constant, toxicity).
Table 3.2 summarizes the two sets of parameters; the data is organised for four groups of chemicals (naturally occurring phenolic compounds and PAHs, and chemical additives in hydraulic fracturing fluids), and, within each group, the parent compound is listed first followed by one or more transformation compounds (daughter compounds).

In deriving sorption values $K_d$, the following procedure was used:

1. Preference was given to using soil-based $K_d$ values if available; this was found to be the exception.
2. Calculated $K_d$ as $K_d = f_{OC} \times K_{OC}$, where $K_{OC}$ is the soil organic carbon partition coefficient, $f_{OC}$ is the fraction of organic carbon in the top soil equal to 0.0217 g/g (see section 2.1.3); this is the most frequent method applied here.
3. If $K_{OC}$ is not available, then $K_{OC}$ is estimated from $K_{OW}$ using EPI (Estimation Program Interface) models (US EPA, 2011).

The data from Table 3.2 were used to derive parameter ranges for the purpose of simulations with HYDRUS-1D. Minimum, mean, and maximum values for $K_d$ and half-life ($t_{1/2}$) were obtained (Table 3.3). Because HYDRUS-1D uses first-order degradation constant values ($\mu$) rather than half-life, $\mu$ was calculated for each $t_{1/2}$ value using $\mu = \ln 2 / t_{1/2} = 0.693 / t_{1/2}$. Identical values for mean, minimum and maximum indicate only a single value was available from the review.
Table 3.2 Summary of the chemical parameters of organic compounds reviewed in this study.

<table>
<thead>
<tr>
<th>Compound group</th>
<th>Parent Compound</th>
<th>Aqueous Solubility at 25 °C (mg/L)</th>
<th>Octanol-Water Partition Coefficient (Log $K_{ow}$)</th>
<th>Henry’s law constant ($K_{hn}$) (atm.m$^3$/mol)</th>
<th>Primary degradation pathway</th>
<th>Soil Organic Carbon-Water Partitioning Coefficient ($K_{oc}$) (L/kg)</th>
<th>Partition coefficient ($K_d$) (L/kg)</th>
<th>Aerobic biotic degradation (half-life)</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic compounds</td>
<td>Phenol</td>
<td>82,800$^*$</td>
<td>1.46$^*$, [1]</td>
<td>3.31E-7$^*$</td>
<td>Hydrolytic route (aerobic): catechol =&gt; 2-hydroxymuconic acid-6-semialdehyde =&gt; 2-oxopent-4-dienoate =&gt; pyruvate</td>
<td>16$^{[20]}$ (soil) 39 – 91$^{[6]}$ (soil) 2900-3100$^{[7]}$ (sediment)</td>
<td>0.35-1.9$^*$ (soil) 2.7 – 3.5$^{[6]}$ h (soil) 98 – 552$^{[21]}$ h (soil)</td>
<td>Mutagen class 3</td>
<td></td>
</tr>
<tr>
<td>Catechol (1,2-dihydroxybenzene)</td>
<td>461,000$^*$</td>
<td>0.88 – 0.9$^{[1]}$</td>
<td>1.2E-9$^*$</td>
<td>3.3E5$^*$ – 414,800</td>
<td>118$^{[22]}$ (soil) 2.6$^{[8]}$ (soil) 2.5$^{[23]}$ (kaolinites)</td>
<td>183 – 365 days$^{[24]}$ (soil)</td>
<td>0.0045$^*$ Hours to days$^{[30]}$</td>
<td>42-d NOEC for Eisenia fetida = 500 mg/kg dw (growth) and 2000 mg/kg dw (mortality)</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxymuconic acid-6-semialdehyde</td>
<td>3.3E5$^*$ – 414,800</td>
<td>-0.44 – 0.36$^{[30]}$</td>
<td>2.62E-10$^*$</td>
<td>0.207$^{[23]}$</td>
<td>Microbial degradation route: 3-methylcatechol =&gt; 2-hydroxy-6 keoheta-2,4 dioneate =&gt; 2-ketopent-4-eionate =&gt; 4-hydroxy-2-ketopentanoate</td>
<td>21.9$^{[23]}$ (soil) 47$^{[8]}$ (soil) 1.0$^{[8]}$ (soil)</td>
<td>1.6 – 5.1$^{[25]}$ days (soil) 7$^{[36]}$ days (soil)</td>
<td>Possible human carcinogen</td>
<td></td>
</tr>
<tr>
<td>2-Methylphenol (o-cresol)</td>
<td>25,900$^*$</td>
<td>1.95 – 2.17$^{[26]}$</td>
<td>1.2E-6$^*$</td>
<td>6.4E-11$^*$</td>
<td>136$^{[9]}$</td>
<td>2.9$^{[9]}$ Days to weeks$^{[30]}$</td>
<td>Low toxicity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methylcatechol</td>
<td>16,480$^*$ – 27,910</td>
<td>1.58$^*$, [$^{[20]}$]</td>
<td>6.4E-11$^*$</td>
<td>0.35-1.9$^*$</td>
<td>Microbial degradation route: =&gt; cis-1,2-dihydroxy-1,2-</td>
<td>870.9$^{[28]}$ (soil) 200 – 1470$^{[27]}$ 1500$^{[6]}$</td>
<td>87.37$^<em>$ (soil) 18.9$^</em>$ 4.3 –</td>
<td>Very toxic to aquatic organisms; Combined exposure</td>
<td></td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbon</td>
<td>Naphthalene</td>
<td>31$^*$</td>
<td>3.29$^{[1]}$</td>
<td>4.4E-4$^*$</td>
<td>Microbial degradation route: =&gt; cis-1,2-dihydroxy-1,2-</td>
<td>870.9$^{[28]}$ (soil) 200 – 1470$^{[27]}$ 1500$^{[6]}$</td>
<td>87.37$^<em>$ (soil) 18.9$^</em>$ 4.3 –</td>
<td>Very toxic to aquatic organisms; Combined exposure</td>
<td></td>
</tr>
<tr>
<td>Chemical additives in hydraulic fracturing</td>
<td>2-Butoxyethanol</td>
<td>Sweet orange oil (limonene)</td>
<td>Bronopol (2-bromo-2-nitropropane-1,3-diol)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>cis-1,2-Dihydroxy-1,2-dihydronaphthalene</strong></td>
<td>8,121</td>
<td>7.57</td>
<td>2E5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.07&lt;sup&gt;[20]&lt;/sup&gt;</td>
<td>4.57&lt;sup&gt;[35]&lt;/sup&gt;</td>
<td>0.032&lt;sup&gt;[5]&lt;/sup&gt;</td>
<td>0.64&lt;sup&gt;[29]&lt;/sup&gt;</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.82E-9</td>
<td>0.032&lt;sup&gt;[5]&lt;/sup&gt;</td>
<td>1.3E-11&lt;sup&gt;[29]&lt;/sup&gt;</td>
<td>1.3E-11&lt;sup&gt;[29]&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>dihydronaphthalene =&gt; 1,2-dihydroxy-naphthalene, cis-o-hydroxybenzal-pyruvic acid =&gt; salicylic acid =&gt; catechol</td>
<td>1288&lt;sup&gt;[10]&lt;/sup&gt;</td>
<td>Products formed from the hydroxyl radical reaction with limonene are 4-acetyl-1-methylcyclohexene&lt;sup&gt;[32,33,34]&lt;/sup&gt;, ketoaldehyde&lt;sup&gt;[32,34]&lt;/sup&gt;, formaldehyde, 3-oxobutanal, glyoxal, and a C10 dicarbonyl&lt;sup&gt;[33]&lt;/sup&gt;</td>
<td>Formaldehyde, nitrosamines; tris (2-hydroxymethyl-2-nitropropane-1,3-diol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5&lt;sup&gt;[9]&lt;/sup&gt;</td>
<td>8&lt;sup&gt;[*,[1], [11]&lt;/sup&gt;</td>
<td>1324&lt;sup&gt;[12]&lt;/sup&gt;</td>
<td>0.93&lt;sup&gt;[29]&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.097&lt;sup&gt;[*,[9]&lt;/sup&gt;</td>
<td>6.9&lt;sup&gt;[*,[2]&lt;/sup&gt;</td>
<td>1306&lt;sup&gt;[13]&lt;/sup&gt;</td>
<td>0.02&lt;sup&gt;[*,[29]&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Days&lt;sup&gt;[30]&lt;/sup&gt;</td>
<td>1.5&lt;sup&gt;[*,[1], [11]&lt;/sup&gt;</td>
<td>1259&lt;sup&gt;[8]&lt;/sup&gt;</td>
<td>60 days (pH 8) – 2 years (pH 6)&lt;sup&gt;[29]&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Not bio-accumulative or persistent</td>
<td>416 hr&lt;sup&gt;[30]&lt;/sup&gt; (soil)</td>
<td>28.7&lt;sup&gt;[*,[12&lt;/sup&gt;</td>
<td>Low mammalian toxicity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Human health: haemolytic anaemia, inhalation toxicity and carcinogenicity</td>
<td>7 – 28 days&lt;sup&gt;[16]&lt;/sup&gt; (soil)</td>
<td>28.8&lt;sup&gt;[*,[13&lt;/sup&gt;</td>
<td>In the aquatic environment, limonene exhibits high acute toxicity to fish and Daphnia (toxnet)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| **Formaldehyde**  
(formalin; methanal; Methylene oxide; formol; Oxomethane) | 4E5* [5] | 0.35 [3] | 2.2E-2 – 3.4E-2 [18] | Formic acid and carbon monoxide. In water or soil, formic acid is expected to rapidly biodegrade. | 3.6 [14] | 0.08# [14] | 24 – 168 hours [16]  
(soil) | Unlikely to cause adverse effects on terrestrial or aquatic organisms; probably carcinogenic to humans (inhalation) [31] |

* Listed in EPI (Estimation Program Interface) Suite™ models (US EPA 2011; EPI Suite. Ver. 4.1. Jan, 2011. Available from, as of Sept 23, 2011: http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm); $K_{oc}$ calculated from $K_{ow}$; # calculated as $K_d = f_{oc} \times K_{oc}$ with $f_{oc} = 0.0217$ g/g;  
\# toxnet http:://toxnet.nlm.nig.gov; HHE = human health effect; EE: environmental effect; AAT = acute aquatic toxicity (Stoiber et al. 2015)

Table 3.3 Sorption ($K_d$), half-life ($t_{1/2}$) and degradation parameters ($\mu$) used as input for HYDRUS-1D simulations

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>$K_d$ (L/kg)</th>
<th>Half-life $t_{1/2}$ (days)</th>
<th>Decay constant $\mu$ (days$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>Phenol</td>
<td>1.38</td>
<td>0.35</td>
<td>1.9</td>
</tr>
<tr>
<td>Catechol</td>
<td>13.8</td>
<td>2.6</td>
<td>25</td>
</tr>
<tr>
<td>MHSA</td>
<td>0.0045</td>
<td>0.0045</td>
<td>0.0045</td>
</tr>
<tr>
<td>2-Methylphenol</td>
<td>0.74</td>
<td>0.47</td>
<td>1</td>
</tr>
<tr>
<td>3-Methylcatechol</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>33.83</td>
<td>4.3</td>
<td>87.37</td>
</tr>
<tr>
<td>cis-1,2-Dihydroxy 1,2 dihydronaphthalene</td>
<td>0.097</td>
<td>0.097</td>
<td>0.097</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>1.4</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Limonene</td>
<td>42.05</td>
<td>22.35</td>
<td>103.7</td>
</tr>
<tr>
<td>Bronopol</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Based on Equation 6, the retardation factor $R$ was calculated for the top layer assuming a water content of 0.305 (cm$^3$ cm$^{-3}$) and bulk density of 1.32 g/cm$^3$. Mean retardation factors range from 1 to 1605, while maximum $R$ values are as high as 3957 (Table 3.4).

Table 3.4 Approximate retardation factors $R$ calculated for a water content of 0.305 (cm$^3$ cm$^{-3}$) and bulk density of 1.32 g/cm$^3$ (representative for the layer 1 during the leak period)

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>$R$ (L/kg)</th>
<th>min</th>
<th>max</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>Phenol</td>
<td>54</td>
<td>14</td>
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<tr>
<td>Catechol</td>
<td>527</td>
<td>100</td>
<td>955</td>
</tr>
<tr>
<td>MHSA</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>2-Methylphenol</td>
<td>29</td>
<td>19</td>
<td>39</td>
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<tr>
<td>3-Methylcatechol</td>
<td>112</td>
<td>112</td>
<td>112</td>
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<tr>
<td>Naphthalene</td>
<td>1292</td>
<td>165</td>
<td>3334</td>
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<tr>
<td>cis-1,2-Dihydroxy 1,2 dihydronaphthalene</td>
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<td>5</td>
<td>5</td>
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<tr>
<td>2-Butoxyethanol</td>
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<tr>
<td>Limonene</td>
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<td>854</td>
<td>3957</td>
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<td>Bronopol</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
4 Detailed description of the simulation cases

Sensitivity analyses are undertaken in Section 4.1 to illustrate the combined effect of sorption and biodegradation on chemical concentration in soil following release from a surface source. These initial calculations use hypothetical compounds with assumed parameter values.

Migration of specific compounds in soil is discussed in Sections 4.2, 4.3, and 4.4. Literature-based values for sorption and biodegradation are used, while a hypothetical unit source concentration of 1 mg/L is assumed. Because of the latter assumption, results are generic and will be used to derive dilution attenuation factors. Concentrations for other source concentrations can be readily obtained from those dilution attenuation factors.

4.1 Sensitivity analysis

Prior to the discussion of attenuation behaviour of particular CSG-related chemicals, sensitivity analyses were undertaken to illustrate the combined effect of sorption and biodegradation on chemical concentration in soil following release from a surface source. The first set of calculations assumed chemicals migrate through soil according to the advection-dispersion process; sorption onto the organic carbon in soil was accounted for, while biodegradation was not considered. Three values for the distribution coefficient $K_d$ were considered: 5, 10 and 20 L/kg. The hypothetical chemical source consisted of a release at the soil surface of 1000 mg/L during a period of 30 years. The water flux into the soil had three characteristic periods: a warming up period of 20 years with a water flux of 40 mm/year, followed by a 30-year period during which the chemical source existed considering a water flux of 35 mm/year, followed by a 110-year period to allow for complete solute breakthrough with a water flux of 40 mm/year. Chemical breakthrough curves were calculated at the depths of 2, 5, 10, and 20 cm depth.

![Image](image-url)

Figure 4.1 Effect of distribution coefficient $K_d$ on chemical breakthrough curves at the depths of 2 and 5 cm (left) and 10 and 20 cm (right). Biodegradation is not considered (decay constant = 0). Source concentration = 1000 mg/L.
The calculated breakthrough curves show that with increasing $K_d$ the maximum chemical concentrations decrease; at the depths of 2 and 5 cm the time at which the maximum concentrations occur are more or less independent from $K_d$, while at the deeper depths of 10 and 20 cm the time of maximum concentrations is retarded as $K_d$ increases (Figure 4.1). At a depth of 2 cm, the maximum concentrations have a ratio of 1.7/1.4/1 for a ratio of $K_d$s of 5/10/20. At a depth of 20 cm, the ratio of maximum concentrations is 3.5/1.9/1. This increase in this ratio is the combined effect of sorption and dispersion.

The next set of calculations incorporated both the effect of sorption and biodegradation. Biodegradation was simulated as a first-order degradation process, which means the concentration decreases following an exponential decay function $C = C_0 \exp(-\mu t)$, where $C_0$ is the concentration at time (t) = 0 and $\mu$ is the decay constant. The same $K_d$ values as above were used, together with decay constants $\mu$ of 0.001 and 0.01 day$^{-1}$. The first decay constant corresponds to a half-life $t_{1/2} = \ln(2)/\mu = 693$ days while the second one to a half-life of 69.3 days.

The calculated breakthrough curves now show much lower concentrations owing to the loss of chemical from the soil due to degradation (Figure 4.2). The larger the decay constant (or the shorter the chemical half-life) the smaller the maximum concentrations become. For a decay constant of 0.01 day$^{-1}$ the maximum concentrations at the 5 cm depth are 2, 0.2 and 0.007 for a $K_d$ of 5, 10 and 20 L/kg, respectively. Compared to the source concentration $C_0$ of 1000 mg/L, these maximum concentrations $C$ represent a dilution attenuation factor ($C_0/C$) of 500, 5000 and 140,000, respectively.

**Figure 4.2 Effect of distribution coefficient $K_d$ on chemical breakthrough curves at the depths of 2 and 5 cm (left) and 10 and 20 cm (right). Biodegradation is accounted for: decay constant $\mu = 0.001$ day$^{-1}$ (left) and 0.01 day$^{-1}$ (right). Source concentration = 1000 mg/L**
4.2 Phenolic compounds

4.2.1 PHENOL

Calculated breakthrough curves using HYDRUS-1D for phenol and its daughter compounds catechol and HMSA are shown in Figure 4.3 using the minimum, mean, and maximum values for sorption ($K_d$) and biodegradation ($\mu$) from Table 3.3. Concentrations are shown only at depths of 2 and 5 cm; at deeper soil depths concentrations become insignificant.

Using mean parameter values for $K_d$ and $\mu$ shows that phenol concentrations are lower than those of its two daughter compounds by more than an order of magnitude (at the 2 cm depth) (Figure 4.3b). This behaviour is due to the much longer half-life of catechol (274 days) compared to that of phenol (6.84 days), despite the higher $K_d$ for catechol (13.8) compared to phenol (1.38). HMSA, on the other hand, has a much shorter half-life (2 days) compared to its parent catechol. It therefore follows closely the concentration of its parent, but is still lower in concentration due to short half-life. At 5 cm depth, phenol concentrations have become less than 0.0001 mg/L (not visible on the graph) because of the combined effect of sorption and degradation. Catechol and HMSA concentrations have also decreased, but especially the longer half-life of catechol keeps concentrations of both compounds between 0.001 and 0.01 mg/L.

When minimum values for $K_d$ and $\mu$ are used (i.e. resulting in the lowest degree of attenuation), concentrations of phenol and catechol are higher than when mean parameters are used. The exception is for HMSA with lower concentrations for minimum than for mean parameters. This is due to the much higher half-life of its parent, catechol (365 days compared to 274), which will generate, per unit of time, much less of the daughter compound HMSA.

For maximum values of $K_d$ and $\mu$ (i.e. resulting in the highest degree of attenuation), phenol concentrations have dropped below 0.0001 mg/L (very short half-life of 0.11 days) whereas catechol concentrations are only slightly smaller than for mean parameters given relatively similar half-lives. HMSA is now larger than catechol due the considerably larger sorption value for catechol.

Figure 4.3 Breakthrough curves of phenol (red), catechol (blue) and HMSA (green) in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used.
4.2.2 2-METHYLPHENOL

Breakthrough curves for 2-methylphenol and its daughter 3-methylcatechol at two soil depths again demonstrate the considerable reduction in chemical concentration due to the combined effect of sorption and biodegradation (Figure 4.4). Using mean parameter values (i.e. resulting in a mean degree of attenuation) produces concentrations for both 2-methylphenol and 3-methylcatechol between 0.01 and 0.001 mg/L at 2 cm depth. The combination of very similar half-lives (4.57 and 7) and a slightly higher $K_d$ for 3-methylcatechol (2.9 compared to 0.74) produces nearly identical concentrations. Once the chemicals have reached the depth of 5 cm, their concentrations have further decreased to less than 0.0001 mg/L.

Minimum parameter values for $K_d$ and $\mu$ result in the overall highest concentrations (Figure 4.4c) for both chemicals. 2-methylphenol has a maximum concentration around 0.01 mg/L, whereas maximum concentrations for its daughter compound are between 0.01 and 0.001 mg/L. At the depth of 5 cm, concentrations are between 0.001 and 0.0001 mg/L.

A maximum degree of attenuation produces 2-methylphenol concentrations less than $10^{-5}$ mg/L (at 2 cm depth), whereas 3-methylcatechol has maximum concentrations around 0.001 mg/L (Figure 4.4a). The higher concentrations for the daughter compound are the result of the longer half-life (7 days) compared to 1.6 days for 2-methylphenol. At 5 cm depth 2-methylphenol has obtained negligible concentrations (< $10^{-7}$ mg/L).

Figure 4.4 Breakthrough curves of 2-methylphenol (o-cresol) (red) and 3-methylcatechol (blue) in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used.
4.3 Polycyclic aromatic hydrocarbons

4.3.1 NAPHTHALENE

Breakthrough curves at 2 cm depth for mean parameters show naphthalene concentrations between 0.001 and 0.0001 mg/L, while its daughter compound has nearly 100 times higher maximum concentration (Figure 4.5b). The much lower sorption for DHDHN ($K_d = 0.097 \text{ L/kg}$) compared to naphthalene ($K_d = 33.8 \text{ L/kg}$) explains its higher concentration. At 5 cm depth naphthalene concentrations have decreased to nearly $10^{-7}$ mg/L, while the daughter compound remains at $10^{-4}$ mg/L.

Using minimum attenuation parameters (note that mean, minimum and maximum half-lives for the respective compounds are identical) results in naphthalene concentrations between 0.1 and 0.01 mg/L, and slightly lower DHDHN concentrations (Figure 4.5c). Because sorption values for both compounds are more similar now ($K_d = 0.097$ for DHDHN and 4.3 for naphthalene) compared to the mean values, the larger half-life for naphthalene (80 days) compared to DHDHN (2 days) results in higher concentrations for the former.

With maximum $K_d$ values the naphthalene concentrations are around $10^{-6}$ mg/L, the overall lowest results across the three parameter values (Figure 4.5a). The much higher DHDHN concentrations are due to the much lower $K_d$ for DHDHN ($K_d = 0.097$) compared to naphthalene ($K_d = 87.4$). At 5 cm depth naphthalene has degraded to values below $10^{-8}$ mg/L.

![Breakthrough curves of naphthalene (red) and DHDHN (cis-1,2-dihydroxy 1,2dihydronapthalene) (blue) in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used.](image-url)
4.4 Hydraulic fracturing additives

4.4.1 2-BUTOXYETHANOL

Maximum concentrations for 2-butoxyethanol at 2 cm depth were approximately 0.0002, 0.002, and 0.02 mg/L for maximum, mean, and minimum attenuation, respectively (Figure 4.6). These results are uniquely due to differences in half-lives, as the sorption parameters are virtually identical ($K_d = 1.3, 1.4, \text{ and } 1.5$). At 5 cm depth maximum concentrations are less than $10^{-6}$ mg/L for maximum attenuation, $10^{-5}$ mg/L for mean and $10^{-3}$ mg/L for minimum attenuation.

![Figure 4.6 Breakthrough curves of 2-butoxyethanol in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used](image)

4.4.2 BRONOPOL

Bronopol sorption and degradation parameters are identical for mean, minimum and maximum attenuation conditions. As a result, all predicted bronopol concentrations are identical for the three conditions (Figure 4.7). The degradation product formaldehyde has concentrations that display the typical effect of increasing half-lives when comparing Figure 4.7a, Figure 4.7b, and Figure 4.7c. Because of the somewhat lesser degradation of bronopol (half-life = 60 days) combined with a very low sorption ($K_d = 0.02$ L/kg), concentrations are shown at 5, 10 and 20 cm depth. At the 5 cm depth, concentrations are approximately 0.2 mg/L; at 20 cm depth maximum bronopol concentrations have dropped to 0.02 mg/L. Formaldehyde concentrations at 5 cm depth range from 0.003 to 0.02 mg/L.
4.4.3 **LIMONENE**

Limonene concentrations at 2 cm depth were very low for all parameter combinations considered, i.e. from less than $10^{-4}$ mg/L for the minimum attenuation parameters to less than $10^{-11}$ mg/L for the maximum attenuation parameters (Figure 4.8). Only for the minimum attenuation parameters was the concentration larger than zero at the 5 cm depth, i.e. between $10^{-9}$ and $10^{-10}$ mg/L.

With mean parameter values $K_d = 42$ L/kg and half-life = 10.4 days, limonene is very strongly sorbed onto the soil organic carbon while biodegradation is very fast. For instance, after about 70 days, the equivalent of 7 half-lives, the concentration at any depth will have decreased by a factor 100 due to biodegradation. The risk for bioaccumulation of limonene in soil environments is therefore very small.

Figure 4.8 Breakthrough curves of limonene in a shallow soil profile accounting for sorption ($K_d$) and biodegradation ($\mu$); (a) maximum $K_d$ and $\mu$, (b) mean $K_d$ and $\mu$, (c) minimum $K_d$ and $\mu$. A hypothetical source concentration $C_0$ of 1 mg/L is used.
4.4.4 DILUTION ATTENUATION FACTORS

Dilution attenuation factors are calculated as \( \frac{C_0}{C_{\text{max}}} \), where \( C_0 \) is source concentration (1 mg/L) and \( C_{\text{max}} \) is the maximum calculated concentration. Based on maximum concentrations at the 2 cm depth, dilution attenuation factors for mean, minimum and maximum concentrations range from 4 for bronopol to \( 5.5 \times 10^7 \) for limonene (Table 4.1).

Table 4.1 Dilution attenuation factors for mean, minimum and maximum attenuation (2 cm depth).

<table>
<thead>
<tr>
<th>Chemical compounds</th>
<th>Dilution attenuation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
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<tr>
<td>Phenol</td>
<td>42</td>
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<tr>
<td>Catechol</td>
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<tr>
<td>MHSA</td>
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<td>2-Methylphenol</td>
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<td>3-Methylcatechol</td>
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<td>Naphthalene</td>
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<tr>
<td>cis-1,2-Dihydroxy</td>
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<tr>
<td>1,2-dihydronaphthalene</td>
<td></td>
</tr>
<tr>
<td>2-butoxyethanol</td>
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<tr>
<td>Limonene</td>
<td>5.5 \times 10^7</td>
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<tr>
<td>I = bronopol</td>
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<tr>
<td>Formaldehyde</td>
<td>65</td>
</tr>
</tbody>
</table>

The dilution attenuation factors are expressed as function of the combined attenuation factors \( K_d \) and \( \mu \), calculated as \( \frac{(\exp(-\mu))}{K_d} \). This parameter is generally positively correlated with the dilution attenuation factor (Figure 4.9). This means that for most compounds strong sorption (high \( K_d \)) is combined with a short half-life (small \( t_{1/2} \) or large \( \mu \)), and low sorption with large half-life.

Figure 4.9 Dilution attenuation factors as function of attenuation parameters \( \{u, K_d\} \). A = phenol, B = catechol, C = HMSA; D = 2-methylphenol, E = 3-methylcatechol; F = naphthalene, G = DHDHN; H = 2-butoxyethanol; I = bronopol, J = formaldehyde; K = limonene.
5 Conclusions

Hydraulic fracturing chemicals and naturally occurring organic compounds may occur in soil as a result of unintentional release of coal seam gas produced water from storage ponds owing to flooding and leaks. Naturally occurring organic compounds considered in this study include phenolic compounds (phenol and 2-methylphenol) and polycyclic aromatic compounds (naphthalene). Chemical additives of hydraulic fracturing fluids included a biocide (bronopol), a surfactant (2-butoxyethanol) and a solvent (limonene). A literature review resulted in a range of distribution coefficient ($K_d$) and biodegradation constant ($\mu$) values, from which mean, minimum and maximum values were determined for use in simulations of natural soil attenuation. For the majority of the organic compounds involved in the review, direct measurements of soil $K_d$ were not available. For those cases, $K_d$ was derived from $K_{OC}$ when available, and the fraction of soil organic carbon. In only a few cases $K_{OC}$ had to be derived from $K_{OW}$ using $K_{OC}$-$K_{OW}$ relationships from the literature.

Calculation of natural soil attenuation of the organic compounds involved implementation of biodegradation pathways, i.e. a sequence of organics consecutively undergoing biodegradation and transformation, coupled with sorption onto soil organic carbon. These coupled processes were numerically simulated using the HYDRUS-1D simulator for a scenario where produced water leaks from a storage pond into soil during a 30-year period, corresponding to the assumed duration of gas and water production. Incorporating transformation products in the simulations is important because some of the transformation products have a higher ecotoxicity than their parent compounds; such is the case for catechol which is the transformation product of phenol.

Organic carbon is one of the most important soil properties influencing sorption and transformation of organic compounds. To account for the measured soil organic carbon depth-dependency in soil and its effect on sorption and biodegradation, a new module was developed for HYDRUS-1D which automatically distributes organic carbon with depth. On the basis of detailed organic carbon data from the Liverpool Plains (NSW), this depth-dependency of organic carbon was implemented in the model, and the sorption and degradation parameters were updated accordingly. Three representative soil types of the Liverpool Plains were considered for analysis of the organic carbon data: Vertosols, Chromosols and Sodosols.

Results showed that for all chemicals considered in the assessment, the combined effect of strong sorption and fast biodegradation resulted in nearly complete degradation of all chemicals in the top 5 to 10 cm of the soil profile. These results are true for a broad range of sorption and degradation parameter values. This indicates that the risk of bioaccumulation in soil and leaching to groundwater is very small for the conditions of this study, i.e. a small infiltration flux approximately equal to the long-term recharge rate of several tens of mm per year. The methodology developed here can be easily extended to a more systematic analysis of leaching risks of a broad range of organic compounds introduced in soil. Further work should include testing the attenuation behaviour under different flow conditions, including higher infiltration rates typical of saturated or near-saturated soils in case of flooding, preferential flow typical of cracking Vertosol soils, and the effect of the high-pH produced water on sorption and transformation of organics. To further reduce uncertainty around predicted attenuation of some of the more toxic compounds, soil-specific sorption and biodegradation laboratory experiments are recommended.
References


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Appendix 1 New HYDRUS-1D module: Dependency of $K_d$ and $\mu$ on soil organic carbon

******************************************************************************

subroutine ReadDR(cDataPath)
character cFileName*260,cDataPath*260
logical lDepthRed,lOpen
common /depth_reduction/ lDepthRed,aDepth,bDepth,cValue

iLengthPath = Len_Trim(cDataPath)
cFileName = cDataPath(1:iLengthPath)//'\Depth_Red.in'

open(37,file=cFileName, status='old',err=998)
inquire(unit=37,opened=lOpen)
if(lOpen) then
  read(37,*,err=998)
  read(37,*,err=998) lDepthRed,aDepth,bDepth,cValue
  write(*,321) lDepthRed,aDepth,bDepth,cValue
  ! 'cValue','=',f7.3)
end if
return
998 continue
lDepthRed=.false.
return
end

******************************************************************************

function rX(z)
logical lDepthRed
common /depth_reduction/ lDepthRed,aDepth,bDepth,cValue
rX=1.
if(.not.lDepthRed) return
if(z.gt.aDepth) then
  rX=1.
else if(z.lt.bDepth) then
  rX=cValue
else
  rX=cValue+(1.-cValue)/(aDepth-bDepth)*(z-bDepth)
end if
return
end

******************************************************************************
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