Alteration of natural $^{37}$Ar activity concentration in the subsurface by gas transport and water infiltration

Sophie Guillon, Yunwei Sun, Roland Purtschert, Lauren Raghoo, Eric Pili, Charles R. Carrigan

Abstract

High $^{37}$Ar activity concentration in soil gas is proposed as a key evidence for the detection of underground nuclear explosion by the Comprehensive Nuclear Test-Ban Treaty. However, such a detection is challenged by the natural background of $^{37}$Ar in the subsurface, mainly due to Ca activation by cosmic rays. A better understanding and improved capability to predict $^{37}$Ar activity concentration in the subsurface and its spatial and temporal variability is thus required. A numerical model integrating $^{37}$Ar production and transport in the subsurface is developed, including variable soil water content and water infiltration at the surface. A parameterized equation for $^{37}$Ar production in the first 15 m below the surface is studied, taking into account the major production reactions and the moderation effect of soil water content. Using sensitivity analysis and uncertainty quantification, a realistic and comprehensive probability distribution of natural $^{37}$Ar activity concentrations in soil gas is proposed, including the effects of water infiltration. Site location and soil composition are identified as the parameters allowing for a most effective reduction of the possible range of $^{37}$Ar activity concentrations. The influence of soil water content on $^{37}$Ar production is shown to be negligible to first order, while $^{37}$Ar activity concentration in soil gas and its temporal variability appear to be strongly influenced by transient water infiltration events. These results will be used as a basis for practical CTBTO concepts of operation during an OSI.

Keywords: $^{37}$Ar, CTBTO, gas transport, numerical model, water saturation, uncertainty
1. Introduction

Radioactive noble gases are part of the verification regime of the Comprehensive Nuclear Test Ban Treaty (CTBT), for detecting, localizing and identifying clandestine nuclear explosions. Underground nuclear explosions produce radioactive noble gases, especially radioxenon isotopes and $^{37}$Ar, that migrate through the subsurface and are released into the atmosphere. The detection of an anomalously elevated activity of radioxenon or radioargon in the subsurface during an On-Site Inspection (OSI) will be key evidence for a nuclear explosion.

$^{37}$Ar is a radioactive noble gas with a half-life of 35.04 days, which is naturally produced in rocks and soils from Ca activation by cosmic ray neutrons. Because of its half-life, longer than those of radioxenon isotopes, $^{37}$Ar is a very promising tool for OSIs, especially when it is conducted several weeks after a detected explosion. However, a key issue is that the natural background of $^{37}$Ar in the first 10 m below the surface can be of the same magnitude as the anomaly expected from an underground nuclear explosion (Carrigan et al., 1996).

Previous works gave ranges for natural $^{37}$Ar background and natural variability, based on numerical modeling of $^{37}$Ar production (Johnson et al., 2015; Wilson et al., 2015) and transport in soil (Carrigan and Sun, 2014; Riedmann and Purtschert, 2011). The $^{37}$Ar production term has thus been well defined in various types of rocks and soil (Johnson et al., 2015; Wilson et al., 2015). However, the role of transport on $^{37}$Ar activity concentrations and distribution in the subsurface remains poorly studied while possibly largely variable. In addition to production, emanation and transport have to be considered in order to get relevant information on $^{37}$Ar for OSI.

An approach of sensitivity analysis and uncertainty quantification was adopted by Jordan et al. (2014) for radioxenon transport in the subsurface, and Carrigan and Sun (2014) for $^{37}$Ar production and transport. In spite of the effort, a complete discussion of physical processes and parameters controlling $^{37}$Ar activity concentrations and distribution in the subsurface was still lacking.

As water is a strong neutron moderator (Dunai et al., 2014; Phillips et al., 2001), Johnson et al. (2015) demonstrated a reduction of $^{37}$Ar production in a saturated soil. Carrigan and Sun (2014) considered steady-state soil water content in their models, and its contribution to $^{37}$Ar dynamics through the solubility of gas in the pore water and the reduction in porosity and perme-
ability. However, to our knowledge, an integrated study of the alteration of not only production but also transport of $^{37}$Ar by water was lacking.

Understanding and being able to predict the natural distribution and dynamics of $^{37}$Ar in the subsurface is crucial for OSI, requiring a model integrating production and transport, and including the role of water. This work thus presents a detailed and comprehensive numerical model of $^{37}$Ar baseline that combines $^{37}$Ar production and transport in the subsurface.

After a presentation of the numerical tools used in this study, a parameterization of $^{37}$Ar production in the subsurface is built, taking into account the moderating effect of water. Numerical simulations of $^{37}$Ar production and transport in homogeneous and heterogeneous partially saturated soils are then performed. Realistic probability distribution of natural $^{37}$Ar activity concentrations to be expected in soil gas are determined, and allow to identify the parameters that control most of the variability of $^{37}$Ar activity concentration.

2. Material and methods

2.1. Numerical methods

2.1.1. Two-phase flow and transport in porous media

The NUFT code (Non-isothermal Unsaturated-saturated Flow and Transport), developed at Lawrence Livermore National Laboratory, is a highly flexible computer software package for modeling multiphase, multi-component mass flow and reactive transport in unsaturated and saturated porous media (Hao et al., 2011; Nitao, 1998). It has already been used for modeling migration of $^{37}$Ar and other gases in the subsurface zone in the framework of underground nuclear explosion detection (Carrigan et al., 1996; Carrigan and Sun, 2014; Sun and Carrigan, 2014).

The NUFT code is based on integrated finite volumes. Two-dimensional cartesian meshes are used in single porosity models. The equations required for modeling two-phase flow and transport are implemented in the NUFT code (Sun et al., 2010). Constitutive equations are required for the dependence of the relative permeabilities as well as the capillary pressure as a function of soil water saturation. The equations developed by van Genuchten-Mualem (van Genuchten, 1980) are used for capillary pressure and water-relative permeability, while gas-relative permeability is calculated following Brooks-Corey model (Brooks and Corey, 1966).
$^{37}$Ar production is implemented as a source term in each cell, expressed in kg s$^{-1}$ for consistency with the code units. $^{37}$Ar decay, with a half-life of 35.04 days, is directly implemented in the code.

Argon is a volatile noble gas with very low solubility. Liquid-gas partitioning is implemented in the NUFT code, with the dependence on total gas pressure and temperature (Sun and Carrigan, 2014). The value of partitioning coefficient for argon in standard temperature and pressure conditions is $1.77 \times 10^{-3}$ mol kg$^{-1}$ atm$^{-1}$ (corresponding to $3.34 \times 10^{-5}$ in mole fraction ratio as used in the NUFT code).

2.1.2. Sensitivity analysis and uncertainty quantification

Sensitivity analyses are becoming increasingly important in evaluating the validity of numerical models, quantifying the "sensitivity of one or more model responses to different factors such as model parameters and forcings" (Razavi and Gupta, 2015). For modeling $^{37}$Ar production and transport, sensitivity analysis is needed to identify the factors and processes that are the most influential, as well as to identify the main sources of uncertainty on the model outputs, namely $^{37}$Ar activity in the subsurface.

Local sensitivity, defined by partial derivatives of the model output around one point in the parameter space, gives a limited view of the sensitivity. Here the total sensitivity coefficients are calculated following Sobol’s method (Sobol’, 2001), to give a more global view of the response surface and to take into account both the main effect and interactions between parameters.

This global sensitivity approach, integrating across the entire parameter space, can differ from our intuitive understanding of sensitivity (Razavi and Gupta, 2015). Scatter plots of model outputs as a function of a single input parameter are also used to get a qualitative but more intuitive view of the sensitivity of the parameters.

A set of input parameters are to be sampled in a high dimensional parameter space, which is allowed by Latin hypercube sampling (McKay et al., 1979), or Monte Carlo sampling.

These statistical sampling and sensitivity analyses are performed using PSUADE (Problem Solving Environment for Uncertainty Analysis and Design Exploration) (Jordan et al., 2014; Sun and Carrigan, 2014; Tong, 2005).

Besides sensitivity analysis, uncertainty quantification is also crucial in $^{37}$Ar models, especially as they aim at providing detection thresholds and sampling guidelines for OSIs. In order to quantify the range of possible $^{37}$Ar
activities that can be expected in the subsurface, a range of values was chosen for each input parameter.

For parameters, like permeability, porosity or chemical composition, that are known to have a central tendency, a normal probability density function was then chosen when sampling the sets of parameters. The average values for the probability density functions were based on the literature for generic sandy soil, or on site characterization. For other parameters, like tortuosity or the van Genuchten capillary-pressure parameters, that do not have defined central tendency, and can be assumed to vary randomly between sites, a uniform probability density function was chosen. The min-max limits were then chosen based on the previous study of Carrigan and Sun (2014).

2.2. $^{37}\text{Ar}$ production in the subsurface and water content

$^{37}\text{Ar}$ production in the subsurface is often approximated by the sole production from neutron activation of calcium $^{40}\text{Ca}(n,\alpha)^{37}\text{Ar}$ (Johnson et al., 2015; Riedmann and Purtschert, 2011). Here we also include production from spallation of potassium $^{39}\text{K}(n,p+2n)^{37}\text{Ar}$, which contributes about 10% of the $^{37}\text{Ar}$ production (Fabryka-Martin, 1988).

In the first 10 to 15 m below the surface, the flux of fast cosmic ray neutrons is dominant, but is rapidly attenuated and moderated with depth in the subsurface. $^{37}\text{Ar}$ production by muon induced fast neutrons is one order of magnitude lower than by cosmic ray neutrons, and is therefore neglected here (Riedmann and Purtschert, 2011). Thermal neutrons are produced by in situ radioactive decay of uranium and thorium, and become dominant below 10 m.

Detailed calculations of $^{37}\text{Ar}$ production in rocks have already been performed elsewhere (Johnson et al., 2015; Wilson et al., 2015). Here we propose a simplified parameterized equation to represent the main processes of $^{37}\text{Ar}$ production in the subsurface, incorporating the effects of water. The sensitivity of this production term to the various parameters can thus easily be quantified.

2.2.1. Cosmic ray fast neutrons

$^{37}\text{Ar}$ production from cosmic ray neutrons is modified from Riedmann and Purtschert (2011), by explicitly adding K spallation as well as the influence of water. The cross-section of the $^{37}\text{Ar}$ spallation reaction on K is 38% of that on Ca (Fabryka-Martin, 1988). Since Ca concentrations in soils are typically
one order of magnitude higher than for K. Ca concentration is by far the
dominant factor for the variability of $^{37}$Ar production.

A scaling factor $X_{sc}$ for the neutron flux at the surface is introduced to
represent the variability of $^{37}$Ar production due to latitude, altitude, but
also to the presence of snow cover. A layer of snow of 0.5 to 2 m thickness
causes an attenuation of 0.9 to 0.5 to the neutron flux at the surface (Dunai
et al., 2014). The range of possible latitudes for a site leads to a scaling
factor from 0.55 to 1, while a range of 1 to 10 corresponds to altitudes from
sea level to 2000 m (Riedmann and Purtschert, 2011). Scaling effects due to
topographic shielding as well as temporal variations of cosmic ray intensity
are not considered here.

Water in the pore space of the soil column increases the bulk density,
which reduces the attenuation length and thus $^{37}$Ar production at depth
(Phillips et al., 2001). $^{37}$Ar production by fast neutrons $R_{fast}$ (in kg·cm$^{-3}$·s$^{-1}$)
is then described by the following equation:

$$R_{fast}(z) = ([Ca] + 0.38[K]) \cdot X_{sc} \cdot \Psi_f(0) \cdot \exp \left\{ \frac{-z}{\Lambda_f} \right\} \left\{ (1 - \phi) \rho_g + \phi S_w \rho_w \right\}$$

(1)

where [Ca] is soil calcium concentration (in mg·kg$^{-1}$), $X_{sc}$ is scaling factor for
surface neutron flux, $\Psi_f(0)$ is the surface production normalized to location
and Ca content (in atom·cm$^{-3}$·yr$^{-1}$·mg$^{-1}$·kg), $z$ is depth below the surface (in
cm), $\phi$ is soil porosity, $\rho_g$ (resp $\rho_w$) is soil grain density (resp water density)
in g·cm$^{-3}$, $S_w$ is soil water content, and $\Lambda_f$ is attenuation length for fast
neutrons in soils or rocks (in g·cm$^{-2}$). The values of the parameters are given
in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi_f(0)$</td>
<td>atom·cm$^{-3}$·yr$^{-1}$·mg$^{-1}$·kg</td>
<td>1.41×10$^{-5}$</td>
</tr>
<tr>
<td>$\Lambda_f$</td>
<td>g·cm$^{-2}$</td>
<td>200</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>g·cm$^{-3}$</td>
<td>2.65</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>g·cm$^{-3}$</td>
<td>1.0</td>
</tr>
<tr>
<td>$\Psi_{radio}$</td>
<td>atom·cm$^{-3}$·yr$^{-1}$·mg$^{-2}$·kg$^2$</td>
<td>4.58×10$^{-6}$</td>
</tr>
</tbody>
</table>

2.2.2. Radiogenic thermal neutrons

$^{37}$Ar production from radiogenic thermal neutrons produced by uranium
and thorium decay is also taken into account. This in situ contribution
becomes predominant below 10 to 15 m, where the cosmic ray induced pro-
duction has decreased.

The probability to reach thermal energies increases with increasing water
content (Phillips et al., 2001). However since flux and reaction cross-sections
for fast neutrons dominate for $^{37}$Ar production in the shallow alluvium, the
effect of water for low energy neutrons was neglected here.

A simplified equation for $^{37}$Ar production from radiogenic neutrons is
taken, based on Lehmann et al. (1993):

$$R_{\text{radio}}(z) = [Ca] \cdot [U] \cdot \Psi_{\text{radio}}^*$$  (2)

where $[U]$ is soil uranium concentration (in mg·kg$^{-1}$), and $\Psi_{\text{radio}}^*$ is the radiogenic production normalized to rock composition (in atom·cm$^{-3}$·yr$^{-1}$·mg$^{-2}$·kg$^2$). The value of $\Psi_{\text{radio}}^*$ is given in Table 1. In Equation 2, the thorium contribu-
tion is lumped in the production $\Psi_{\text{radio}}^*$, as a constant U/Th ratio was
assumed in soils.

2.2.3. Emanation in the pore space

Emanation is defined as the ratio of the amount of $^{37}$Ar atoms released
in the pore space to the total amount of $^{37}$Ar atoms produced in the grains.
The recoil length of $^{37}$Ar in grains is only 0.38 µm (Onstott et al., 1995), and
therefore only $^{37}$Ar atoms produced from Ca or K atoms located closer than
this distance to a grain boundary can be released in the pore space. Some of
these $^{37}$Ar atoms will however be trapped into the opposite grain. Data from
groundwater studies (Lehmann and Purtschert, 1997; Pearson et al., 1991)
indicate $^{37}$Ar emanation in the range 2 to 7%.

A water film increases emanation since recoiling atoms are more likely
stopped within the pore space instead of in the opposite grain. This effect
has been investigated for radon by numerical models and experimental data
(Adler and Perrier, 2009; Barillon et al., 2005). A similar approach was used
for $^{37}$Ar here:

$$E = E_{\max} \cdot \left[1 - \exp \left(-\frac{S_w}{S_s}\right)\right]$$  (3)

where $E$ is argon emanation, $E_{\max}$ is the maximum argon emanation at full
water saturation, $S_s$ is saturation threshold below which emanation decreases
rapidly.

While emanation gives the amount of $^{37}$Ar atoms released in the pore
space, liquid-gas partitioning according to the Henry’s law solubility coeffi-
cient then determines the amount of $^{37}$Ar available for transport in the gas phase.

### 2.2.4. Sensitivity analysis of $^{37}$Ar production

A sensitivity analysis was conducted to rank the parameters involved in $^{37}$Ar production. The parameterized production equation is obtained by combining Equations 1 and 2, with a total of 6 input parameters. These parameters are listed in Table 2, along with the ranges of variability that were chosen.

A total of 5000 sets of parameters were sampled using PSUADE and Latin hypercube. The corresponding depth dependent production terms were calculated. PSUADE was again used to determine the total Sobol sensitivity coefficients of $^{37}$Ar production, that are presented in Table 2.

### Table 2: Sensitivity analysis of $^{37}$Ar production: range of values of the controlling parameters, and total Sobol sensitivity. Probability density functions are uniform for all parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Min</th>
<th>Max</th>
<th>Sens.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z$</td>
<td>m</td>
<td>0</td>
<td>20</td>
<td>0.86</td>
</tr>
<tr>
<td>Ca</td>
<td>mg·kg$^{-1}$</td>
<td>$10^2$</td>
<td>$3.2 \times 10^5$</td>
<td>0.79</td>
</tr>
<tr>
<td>$X_{sc}$</td>
<td>-</td>
<td>0.27</td>
<td>10</td>
<td>0.23</td>
</tr>
<tr>
<td>$E_{max}$</td>
<td>-</td>
<td>0.02</td>
<td>0.07</td>
<td>0.13</td>
</tr>
<tr>
<td>$S_w$</td>
<td>-</td>
<td>0</td>
<td>1</td>
<td>0.04</td>
</tr>
<tr>
<td>$\phi$</td>
<td>-</td>
<td>0.2</td>
<td>0.5</td>
<td>0.01</td>
</tr>
<tr>
<td>U</td>
<td>mg·kg$^{-1}$</td>
<td>0.29</td>
<td>11</td>
<td>0.009</td>
</tr>
<tr>
<td>K</td>
<td>mg·kg$^{-1}$</td>
<td>50</td>
<td>$6.3 \times 10^4$</td>
<td>0.002</td>
</tr>
<tr>
<td>$S_s$</td>
<td>-</td>
<td>0.05</td>
<td>0.2</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

### 2.3. Coupling $^{37}$Ar production and transport in unsaturated soil

$^{37}$Ar transport in partially saturated porous soil is investigated using the NUFT code. Three cases were considered to investigate processes of increasing complexity. In each case, a large number of simulations were conducted to identify the controlling factors and quantify the range of uncertainty. In all models, a mesh was used, of 100 m, 1 m and 16 m dimensions in X, Y and Z directions respectively, with cells of $1 \times 1 \times 0.1$ m$^3$.

In all models, the boundary condition at the bottom of the mesh, representing the water table, was fixed at full water saturation, constant pressure
and $^{37}$Ar activity concentration in water at equilibrium with average activity concentration in soil air. At the surface, the boundary condition consisted in barometric pressure fluctuations, constant or variable water infiltration and 1 mBq·m$^{-3}$ of $^{37}$Ar. Atmospheric pressure time series used in the model come from the Belp site in Switzerland, at 980 m above sea level (MeteoSwiss, 2014). The duration of the simulations was 1 year, with a maximum time step of 1 hour.

2.3.1. Homogeneous sandy soil

The first case is spatially homogeneous, and corresponds to a sandy soil. A constant infiltration is applied at the surface. A factor ranging between 0 and 2 is applied to atmospheric pressure time series to scale its amplitude, and quantify the sensitivity of $^{37}$Ar activity concentration in soil gas to barometric pumping.

An initialization run of the model allows to determine the steady-state water saturation profile, controlled by infiltration rate at the surface and soil water retention parameters. This water saturation depth profile is then used to calculate $^{37}$Ar production and emanation, according to Equations 1, 2 and 3. This $^{37}$Ar source term is then incorporated in the model, and a run with constant atmospheric pressure allows calculating the equilibrium diffusion profile for $^{37}$Ar. This profile is used as initial conditions for the final run, including $^{37}$Ar production and surface boundary conditions.

Table 3 lists the 10 uncertain input parameters considered in this case, along with their ranges of variability. The average Ca and U contents for soils were taken from Shacklette and Boerngen (1984). Hydraulic parameters were defined as typical values for a sandy soil, similar to the values taken for $^{37}$Ar models in Carrigan and Sun (2014). For this first case, large uncertainties were assumed for the input parameters, to represent a site where almost no specific information is available.

Using the Monte Carlo method, 1000 sets of parameters were sampled and the corresponding models were run. The output variables extracted out of the models are the $^{37}$Ar activity concentration in soil gas at 1 m depth, the depth of the maximum activity concentration, and the range of variability of $^{37}$Ar activity concentration at 1 m depth. For each output variable, the total Sobol sensitivity coefficients were calculated for all parameters, and are summarized in Table 3. For each depth, the probability density function of $^{37}$Ar activity concentrations in soil gas was calculated from the models outputs at that depth. Figure 1a presents these probability density functions.
versus depth. Scatter plots of the output variables as a function of the most
influencing parameters are in Figure 2.

Table 3: Sensitivity analysis in the homogeneous sandy soil case: uncertain parameters, ranges of values and total Sobol sensitivity for \(^{37}\)Ar activity concentration in soil gas and range of variability at 1 m, as well as depth of \(^{37}\)Ar peak. Input ranges are given either by interval for uniform distribution (U), and mean and standard deviation for normal
distribution (N).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PDF</th>
<th>(^{37})Ar</th>
<th>(\Delta^{37})Ar</th>
<th>Peak depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Phi)</td>
<td>N</td>
<td>0.35 ± 20%</td>
<td>0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>\text{log}(k)</td>
<td>N</td>
<td>-11.5 ± 10%</td>
<td>0.35</td>
<td>0.58</td>
</tr>
<tr>
<td>Ca (mg·kg(^{-1}))</td>
<td>N</td>
<td>4.38 ± 20%</td>
<td>0.21</td>
<td>0.09</td>
</tr>
<tr>
<td>U (mg·kg(^{-1}))</td>
<td>N</td>
<td>2.7 ± 40%</td>
<td>0.21</td>
<td>0.02</td>
</tr>
<tr>
<td>(m)</td>
<td>U</td>
<td>[0.5236 ; 0.7920]</td>
<td>(\leq 10^{-3})</td>
<td>0.003</td>
</tr>
<tr>
<td>\text{log}(\alpha)</td>
<td>U</td>
<td>[-4.6938 ; -3.8069]</td>
<td>0.21</td>
<td>0.07</td>
</tr>
<tr>
<td>(\tau)</td>
<td>U</td>
<td>[0.2 ; 0.7]</td>
<td>0.002</td>
<td>0.03</td>
</tr>
<tr>
<td>Infiltr. (mm/yr)</td>
<td>U</td>
<td>[0 ; 700]</td>
<td>0.83</td>
<td>0.96</td>
</tr>
<tr>
<td>(X_{sc})</td>
<td>U</td>
<td>[0.27 ; 10]</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>Pressure scaling</td>
<td>N</td>
<td>1 ± 20%</td>
<td>0.03</td>
<td>0.04</td>
</tr>
</tbody>
</table>

2.3.2. Heterogeneous sand and clay soil

The second case deals with the effect of spatial heterogeneity on \(^{37}\)Ar activity concentration in soil gas. As will be explained in Section 3, the modulation of \(^{37}\)Ar production by soil water content was found to be negligible in the production and transport model, and is not considered in this second case. The model is here based on the one proposed by Carrigan and Sun (2014) with horizontal lenses of clay embedded in sand. While these authors considered only a single gas phase, the effect of water infiltration was included here.

Random 2D maps of clay lenses in sand were first defined following a Gaussian distribution, based on horizontal \(a_x\) and vertical \(a_z\) correlation lengths, and a fraction of sand material. Permeability, porosity retention parameters as well as Ca content are defined separately for sand and clay. The numerical scheme is defined as in the first case, with constant infiltration, atmospheric pressure fluctuations and \(^{37}\)Ar production.

In this case, the number of uncertain parameters amounts to 16, as listed in Table 4. A total of 1000 simulations were run with various sets of param-
eters. The output variables of interest are defined as for the homogeneous sand case. Total Sobol sensitivity coefficients are summarized in Table 4. Figure 3 presents the average $^{37}$Ar activity concentration in soil gas and soil water saturation for one of the model realizations.

Table 4: Sensitivity analysis in the heterogeneous sand and clay soil case: uncertain parameters, ranges of values and total Sobol sensitivity for $^{37}$Ar activity concentration in soil gas and range of variability at 1 m, as well as depth of $^{37}$Ar peak. Probability density functions are uniform for all parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PDF</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Sand fraction</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td>Correlation length $a_x$</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Correlation length $a_z$</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>$\Phi$ (Sand)</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>$\Phi$ (Clay)</td>
<td>0.33</td>
<td>0.60</td>
</tr>
<tr>
<td>$k$ (m$^2$) (Sand)</td>
<td>$10^{-12}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$k$ (m$^2$) (Clay)</td>
<td>$10^{-17}$</td>
<td>$10^{-13}$</td>
</tr>
<tr>
<td>$m$ (Sand)</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>$m$ (Clay)</td>
<td>0.06</td>
<td>0.3</td>
</tr>
<tr>
<td>$\alpha$ (Pa$^{-1}$) (Sand)</td>
<td>$10^{-4.7}$</td>
<td>$10^{-3.9}$</td>
</tr>
<tr>
<td>$\alpha$ (Pa$^{-1}$) (Clay)</td>
<td>$10^{-5.5}$</td>
<td>$10^{-4.1}$</td>
</tr>
<tr>
<td>Ca (mg·kg$^{-1}$) (Sand)</td>
<td>$10^3$</td>
<td>$10^{5.5}$</td>
</tr>
<tr>
<td>Ca (mg·kg$^{-1}$) (Clay)</td>
<td>$10^4$</td>
<td>$10^{5.7}$</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Infiltration (mm/yr)</td>
<td>0</td>
<td>800</td>
</tr>
<tr>
<td>Pressure scaling</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

2.3.3. Site specific case with transient rain infiltration

The last case corresponds to the Belp site (Switzerland) for which some knowledge on transport properties (permeability, porosity) and chemical composition (Ca, U) of the sandy-loamy soil, as well as meteorological forcings (pressure, rain) is available. The values of the parameters that have been measured at this site are used as average values for the input normal distributions (cf. Table 5), with a standard deviation of 10% (and 5% for permeability), smaller than in the first less constrained case. For input parameters without specific knowledge, the same range and uniform distribution as for the general sandy soil case are kept.
The time series of atmospheric pressure fluctuations corresponds to the site area, and are considered as a forcing without uncertainty. Similarly, a realistic time series for water infiltration at the surface can be obtained for this specific site, and used instead of the constant infiltration in the previous cases. Water infiltration is calculated from a simple water budget, based on rain data (MeteoSwiss, 2014), the evapo-transpiration calculated using the Penman-Monteith equation (Allen et al., 1988) and soil storage capacity. The resulting infiltration pattern, with an annual infiltration of 810 mm/year, is not taken as uncertain input here, thus neglecting the intrinsic errors of the evapotranspiration and water budget calculations.

The 8 uncertain parameters and their defined ranges are listed in Table 5. A total of 1000 sets of parameters were sampled using Monte Carlo method and following these distributions. As in the second case, the modulation of $^{37}$Ar production by soil water content was not considered in the model. The numerical scheme is the same as for the two other cases. Similar to the first case, probability density of $^{37}$Ar activity concentrations in soil gas is presented in Figure 1b, and scatter plots of the output variables as a function of the most influencing parameters are in Figure 2.

Table 5: Sensitivity analysis in the specific sandy soil case with transient infiltration: uncertain parameters, ranges of values and total Sobol sensitivity for $^{37}$Ar activity concentration in soil gas and range of variability at 1 m, as well as depth of $^{37}$Ar peak. Input ranges are given either by interval for uniform distribution (U), and mean and standard deviation for normal distribution (N).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PDF</th>
<th>$^{37}$Ar Sensitivity</th>
<th>$\Delta^{37}$Ar</th>
<th>Peak depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi$</td>
<td>N</td>
<td>0.40 ± 10%</td>
<td>0.64</td>
<td>0.43</td>
</tr>
<tr>
<td>log($k$)</td>
<td>N</td>
<td>-12.3 ± 5%</td>
<td>0.007</td>
<td>0.58</td>
</tr>
<tr>
<td>Ca (mg·kg$^{-1}$)</td>
<td>N</td>
<td>3800 ± 10%</td>
<td>0.06</td>
<td>0</td>
</tr>
<tr>
<td>U (mg·kg$^{-1}$)</td>
<td>N</td>
<td>2.3 ± 10%</td>
<td>0.45</td>
<td>0.44</td>
</tr>
<tr>
<td>$m$</td>
<td>U</td>
<td>[0.5236 ; 0.7920]</td>
<td>0.002</td>
<td>0.43</td>
</tr>
<tr>
<td>log($\alpha$)</td>
<td>U</td>
<td>[-4.6938 ; -3.8069]</td>
<td>0.02</td>
<td>0.31</td>
</tr>
<tr>
<td>$\tau$</td>
<td>U</td>
<td>[0.2 ; 0.7]</td>
<td>1.07</td>
<td>0.45</td>
</tr>
<tr>
<td>$X_{sc}$</td>
<td>U</td>
<td>[0.27 ; 10]</td>
<td>0.03</td>
<td>0.21</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Production and emanation of $^{37}$Ar

Production in various rock types has been thoroughly studied with codes like MCNP (Johnson et al., 2015; Wilson et al., 2015). The parameterized equation that is used here, built on these works, allows a systematic investigation of parameter sensitivity.

The parameters controlling $^{37}$Ar activity concentration in soils are ranked in Table 2 from the most to the least influential. In a global perspective, the variability from one site to the other is mainly controlled by the Ca concentration of the rock matrix. The geographical location of the site, altitude, latitude but also presence of snow cover at the surface, scales the surface neutron flux and production and is the third most important parameter.

At a given site, the largest variability of $^{37}$Ar activity concentration in the subsurface arises from exponential decrease of cosmic ray neutron flux with depth. The influence of the K content was found to be negligible, and a constant K content was assumed in all the coupled production and transport simulations.

The main influence of the soil water content on $^{37}$Ar production is a faster moderation of high energy neutrons with depth, leading to a shorter attenuation length. In combination with a reduced gas porosity and permeability at high soil water content, this shifts the $^{37}$Ar activity concentration peak towards shallower depths. At greater depth, soil water affects the $^{37}$Ar activity concentrations mainly in relation to emanation and water/gas partitioning. However, as will be discussed below, water is of second order importance for its effects on $^{37}$Ar production in contrast to its effects on gas transport.

3.2. Processes controlling $^{37}$Ar activity concentration in the subsurface

Global sensitivity coefficients for the intensity and variability of $^{37}$Ar activity concentration in soil gas as well as depth of the maximum activity concentration are presented in Tables 3, 4 and 5 for the general sandy soil, heterogeneous sand-clay and Belp site cases respectively. Drawing a clear picture out of the sensitivity coefficients appears quite challenging, especially when the number of parameters is large, as in the second case (Table 4). It must also be kept in mind that these sensitivity coefficients depend on the chosen ranges for the input parameters. Sensitivity coefficients were thus combined with scatter plots (Figure 2) to identify the most important parameters in the homogeneous cases.
The global shape of $^{37}$Ar profile in the subsurface shows a maximum value at shallow depth, between 2 to 5 m (Figures 1a and b), as already known from the literature (Carrigan and Sun, 2014; Riedmann and Purtschert, 2011). This shape results from the combination of the exponentially decreasing production (Equation 1) and diffusion towards the atmosphere where the $^{37}$Ar activity concentration is on average $1 \text{ mBq m}^{-3}$ (Loosli et al., 1970) much smaller than in the subsurface.

Consistently with this diffusive transport, the depth of $^{37}$Ar peak is mainly controlled by soil tortuosity and porosity (Figures 2e and f). When porosity or tortuosity are large, the depth range for diffusive exchange with the atmosphere becomes larger and thus the peak becomes deeper.

The average value of $^{37}$Ar activity concentration in the shallow subsurface is found to be controlled by Ca content and by neutron scaling (Figure 2a), in agreement with findings obtained by Riedmann and Purtschert (2011). At a specific site with better constraints on Ca content, the neutron scaling factor becomes the main controlling parameter, which is one of the easiest
Figure 2: Scatter plots in the homogeneous sandy soil (grey) and Belp site (red) cases. For each stochastic model, $^{37}\text{Ar}$ activity concentration in soil gas (a-b) and range of variability (c-d) at 1 m, as well as depth of $^{37}\text{Ar}$ peak (e-f) are plotted as a function of input parameters. For other input parameters, the scatter plots do not show any correlation.

factors to be estimated since it depends mainly on the (known) geographical location and altitude. Besides this production effect, higher $^{37}\text{Ar}$ activity concentrations in soil gas at 1 m depth are also obtained at low permeability and low tortuosity, which is explained by the reduced ventilation and diffusion into the atmosphere.

As opposed to what was discussed for $^{37}\text{Ar}$ production, soil water content and water infiltration play a major role in $^{37}\text{Ar}$ transport dynamics through several processes. High $^{37}\text{Ar}$ activities are obtained for soils with high water saturation, either because of a large infiltration rate or because of the water retention properties of the soil. This can be explained by two processes: on the one hand, the exchange rate between the soil and the atmosphere, through diffusion or barometric pumping, is reduced when the soil is wet, leading to a build-up of $^{37}\text{Ar}$ at depth. On the other hand, gas-available pore space is reduced in wet soils and the low solubility of $^{37}\text{Ar}$ leads to its concentration in the gas phase. This enrichment by liquid-gas partitioning effect was mainly observed at high water content, especially in clay lenses in the heterogeneous model, or in the capillary fringe. However this effect might not be relevant for large volume soil gas samples since the gas originates preferentially from the more permeable and thus less saturated soil.
compartments.

The temporal variability of $^{37}$Ar activity concentration in the subsurface was only induced by atmospheric pressure fluctuations in the first case, while in the third case, transient rain events were also included. In both cases, permeability is the main control on temporal variability, but with contrasting effects (Figure 2c).

Under steady-state water saturation conditions (first case), a higher permeability facilitates transport, e.g. due to barometric pumping. In the transient water saturation scenario (third case), this effect is masked by the restriction of soil transport properties and the increased gas-water partitioning, which both lead to a higher $^{37}$Ar variability with lower permeability. A small effect of the $\alpha$ parameter is also obtained (Figure 2d), and confirms this role of water saturation.

In the heterogeneous case, the same processes are at play, but the typical shape of $^{37}$Ar depth profile is lost because of the spatial variability between sand and clay. The high water saturation in clay layers is systematically associated with high $^{37}$Ar activities (Figure 3), which is explained by the aforementioned partitioning effect.

Figure 3: $^{37}$Ar activity concentration in soil gas (a) and water saturation (b) maps, in the case of a heterogeneous model with clay (high water saturation) and sand patches.
3.3. Uncertainty on average $^{37}$Ar depth profile

The global uncertainty on $^{37}$Ar activity concentration in soil gas versus depth is represented for the homogeneous sandy soil case in Figure 1a, and for the Belp site with transient infiltration in Figure 1b.

In the general and poorly constrained case, there is a very large uncertainty of 3 orders of magnitude on $^{37}$Ar activity concentration at depth (Figure 1a), from less than 1 mBq·m$^{-3}$ (below detection limit), to several Bq·m$^{-3}$. The range of variability becomes even larger when heterogeneity is considered (data not shown). This uncertainty reduces to one order of magnitude in the more constrained Belp case (Figure 1b). An uncertainty limited to one order of magnitude or less was also obtained in previous works (Carrigan and Sun, 2014; Riedmann and Purtschert, 2011), that considered relatively narrow ranges of parameters, especially for soil Ca content. Including water content and infiltration in the models thus does not increase too much the uncertainty on the average $^{37}$Ar activity concentration in the subsurface. This uncertainty mainly results if the location of the site and chemical composition of the soil are poorly known.

3.4. Temporal variability from barometric pumping and water infiltration

While the uncertainty on the average $^{37}$Ar depth profile is mainly due to production, the temporal variability of $^{37}$Ar activity concentration at a specific point is driven by transport processes, and especially by water infiltration.

To our knowledge, this study is the first detailed investigation of the temporal dynamics of $^{37}$Ar in the subsurface. A large temporal variability is obtained in the simulations (Figure 2c and d). The temporal dynamics are rapidly attenuated in the first meters below the surface, pressure or infiltration perturbations being dampened in geological media. The variability solely due to barometric pumping is 10 to 40% of the average activity concentration at 1 m, and decreases to 3 to 15% at 5 m depth. When transient rain events are considered, the range of variability increases in the range 20 to 100% at 1 m (Figure 2c), and 10 to 60% at 5 m depth.

Figure 4 illustrates the dynamics of $^{37}$Ar activity concentration in soil gas at 1 and 5 m depth for one arbitrarily chosen set of parameters, along with the surface forcings, namely infiltration and atmospheric pressure fluctuations. Water infiltration events clearly lead to a greater $^{37}$Ar variability compared to barometric pumping. In Figure 4, peaks of $^{37}$Ar activity concentration in the subsurface are obtained following the periods of large infiltration. The
Figure 4: $^{37}$Ar temporal variability. Boundary conditions at the surface (a): atmospheric pressure fluctuations (grey) and transient water infiltration (blue). Modeled evolution of $^{37}$Ar dynamics at 1 m (solid black line) and 5 m (solid red line) in the subsurface (b). The dashed lines correspond to the same model but with a constant infiltration of 810 mm/yr, the average value of the time series in (a).

The processes coupling water infiltration events and increased $^{37}$Ar activity concentration in the subsurface have already been discussed above. These results regarding $^{37}$Ar temporal dynamics in the subsurface have been obtained for given barometric pressure and water infiltration time series. The sensitivity to these forcings will have to be investigated in the future, as was done for radioxenon migration and barometric pressure by Jordan et al. (2014). However, the general conclusions can easily be adapted to any site, with its hydrogeological and meteorological conditions. In dry locations, barometric pumping will become the main process driving $^{37}$Ar temporal
variations, but the range of variability is not expected to be of more than a few percent.

4. Conclusions

The main contributions of this work are first to propose a realistic and comprehensive probability distribution of natural $^{37}$Ar activity concentrations to be expected in soil gas, including the effects of water infiltration, and second to identify site location and soil composition as the parameters allowing for a most effective reduction of the possible range of $^{37}$Ar activity concentrations. This will be the basis for practical CTBTO concepts of operation, and these parameters will have to be constrained during an On-Site-Inspection. The conceptual and numerical models developed in this work could be further used for the interpretation of $^{37}$Ar time series in the subsurface, as are currently acquired at the Belp site.

The influence of soil water content on $^{37}$Ar production is demonstrated to be negligible to first order, but transient water infiltration events control $^{37}$Ar activity concentration and its temporal variability in the subsurface, especially by reducing diffusive exchange with the atmosphere.

The probability distributions of natural $^{37}$Ar activity concentrations obtained in this study enable us to draw some recommendations for soil gas sampling and interpretation of the measured $^{37}$Ar activity concentrations in soil gas during an OSI. A depth between 2 to 5 m should be ensured when sampling soil gas, to limit dilution by atmospheric air, reduce the temporal variability and thus increase the sensitivity to anomalies.

The definition of the threshold for anomalous $^{37}$Ar activity concentration in soil gas has to be done carefully, and would require a measurement of the local $^{37}$Ar background and variability. Based on this study, it appears "very unlikely" that values of $^{37}$Ar activity concentration in soil gas above 1 Bq·m$^{-3}$ are natural, and this value is proposed as a robust and conservative threshold. Ongoing and future work will allow investigating the probability densities for the $^{37}$Ar activity profiles following an underground nuclear explosion, and finally be able to define the likelihood that an $^{37}$Ar elevated signature is of nuclear origin or not. In any case, interpretation of $^{37}$Ar activity concentration in soil gas has to be very careful, considering the large uncertainty and the limited number of data that would be available.
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