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

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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 radon isotopes and ^{37}Ar , that migrate through the subsurface and are released into the atmosphere. The detection of an anomalously elevated activity of radon 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 radon 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 radon 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).

³⁷Ar production is implemented as a source term in each cell, expressed in $\text{kg}\cdot\text{s}^{-1}$ for consistency with the code units. ³⁷Ar 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 $1.77\times 10^{-3} \text{ mol kg}^{-1} \text{ atm}^{-1}$ (corresponding to 3.34×10^{-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 ³⁷Ar 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 ³⁷Ar 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 parametric 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 ³⁷Ar models, especially as they aim at providing detection thresholds and sampling guidelines for OSIs. In order to quantify the range of possible ³⁷Ar

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}Ar production in the subsurface and water content

^{37}Ar production in the subsurface is often approximated by the sole production from neutron activation of calcium $^{40}\text{Ca}(\text{n},\alpha)^{37}\text{Ar}$ (Johnson et al., 2015; Riedmann and Purtschert, 2011). Here we also include production from spallation of potassium $^{39}\text{K}(\text{n},\text{p}+2\text{n})^{37}\text{Ar}$, which contributes about 10% of the ^{37}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}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}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}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}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}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 $\text{kg}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$) is then described by the following equation:

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

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

Table 1: Parameters used for ^{37}Ar production following Equations (1) and (2)

Parameter	Unit	Value
$\Psi_f^*(0)$	$\text{atom}\cdot\text{cm}^{-3}\cdot\text{yr}^{-1}\cdot\text{mg}^{-1}\cdot\text{kg}$	1.41×10^{-3}
Λ_f	$\text{g}\cdot\text{cm}^{-2}$	200
ρ_g	$\text{g}\cdot\text{cm}^{-3}$	2.65
ρ_w	$\text{g}\cdot\text{cm}^{-3}$	1.0
Ψ_{radio}^*	$\text{atom}\cdot\text{cm}^{-3}\cdot\text{yr}^{-1}\cdot\text{mg}^{-2}\cdot\text{kg}^2$	4.58×10^{-6}

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

169 becomes predominant below 10 to 15 m, where the cosmic ray induced pro-
 170 duction has decreased.

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

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

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

177 where $[U]$ is soil uranium concentration (in $\text{mg}\cdot\text{kg}^{-1}$), and Ψ_{radio}^* is the radio-
 178 genic production normalized to rock composition (in $\text{atom}\cdot\text{cm}^{-3}\cdot\text{yr}^{-1}\cdot\text{mg}^{-2}\cdot\text{kg}^2$).
 179 The value of Ψ_{radio}^* is given in Table 1. In Equation 2, the thorium contri-
 180 bution is lumped in the production Ψ_{radio}^* , as a constant U/Th ratio was
 181 assumed in soils.

182 2.2.3. Emanation in the pore space

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

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

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

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

199 While emanation gives the amount of ^{37}Ar atoms released in the pore
 200 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.

Parameter	Unit	Min	Max	Sens.
z	m	0	20	0.86
Ca	$\text{mg}\cdot\text{kg}^{-1}$	10^2	3.2×10^5	0.79
X_{sc}	-	0.27	10	0.23
E_{max}	-	0.02	0.07	0.13
S_w	-	0	1	0.04
ϕ	-	0.2	0.5	0.01
U	$\text{mg}\cdot\text{kg}^{-1}$	0.29	11	0.009
K	$\text{mg}\cdot\text{kg}^{-1}$	50	6.3×10^4	0.002
S_s	-	0.05	0.2	0.0005

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 $1\times 1\times 0.1\text{ m}^3$.

In all models, the boundary condition at the bottom of the mesh, representing the water table, was fixed at full water saturation, constant pressure

222 and ^{37}Ar activity concentration in water at equilibrium with average activity
223 concentration in soil air. At the surface, the boundary condition consisted in
224 barometric pressure fluctuations, constant or variable water infiltration and 1
225 $\text{mBq}\cdot\text{m}_{\text{air}}^{-3}$ of ^{37}Ar . Atmospheric pressure time series used in the model come
226 from the Belp site in Switzerland, at 980 m above sea level (MeteoSwiss,
227 2014). The duration of the simulations was 1 year, with a maximum time
228 step of 1 hour.

229 2.3.1. Homogeneous sandy soil

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

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

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

250 Using the Monte Carlo method, 1000 sets of parameters were sampled
251 and the corresponding models were run. The output variables extracted out
252 of the models are the ^{37}Ar activity concentration in soil gas at 1 m depth, the
253 depth of the maximum activity concentration, and the range of variability
254 of ^{37}Ar activity concentration at 1 m depth. For each output variable, the
255 total Sobol sensitivity coefficients were calculated for all parameters, and are
256 summarized in Table 3. For each depth, the probability density function
257 of ^{37}Ar activity concentrations in soil gas was calculated from the models
258 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).

Parameter	PDF		Sensitivity		
			^{37}Ar	$\Delta^{37}\text{Ar}$	Peak depth
Φ	N	$0.35 \pm 20\%$	0.20	0.09	0.59
$\log(k)$	N	$-11.5 \pm 10\%$	0.35	0.58	0.02
Ca ($\text{mg}\cdot\text{kg}^{-1}$)	N	$4.38 \pm 20\%$	0.21	0.09	0.34
U ($\text{mg}\cdot\text{kg}^{-1}$)	N	$2.7 \pm 40\%$	0.21	0.02	0.002
m	U	[0.5236 ; 0.7920]	$\leq 10^{-3}$	0.003	0.002
$\log(\alpha)$	U	[-4.6938 ; -3.8069]	0.21	0.07	0.86
τ	U	[0.2 ; 0.7]	0.002	0.03	0.002
Infiltr. (mm/yr)	U	[0 ; 700]	0.83	0.96	0.11
X_{sc}	U	[0.27 ; 10]	0.006	0.006	0.68
Pressure scaling	N	$1 \pm 20\%$	0.03	0.04	0.004

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.

Parameter	PDF		Sensitivity		
	Min	Max	^{37}Ar	$\Delta^{37}\text{Ar}$	Peak depth
Sand fraction	0.35	0.65	10^{-2}	$\leq 10^{-2}$	$\leq 10^{-2}$
Correlation length a_x	10	50	$\leq 10^{-2}$	$\leq 10^{-2}$	0.03
Correlation length a_z	0.2	2	$\leq 10^{-2}$	$\leq 10^{-2}$	0.17
Φ (Sand)	0.25	0.50	0.02	$\leq 10^{-2}$	$\leq 10^{-2}$
Φ (Clay)	0.33	0.60	$\leq 10^{-2}$	$\leq 10^{-2}$	0
k (m^2) (Sand)	10^{-12}	10^{-9}	0.04	0.01	$\leq 10^{-2}$
k (m^2) (Clay)	10^{-17}	10^{-13}	$\leq 10^{-2}$	$\leq 10^{-2}$	0.39
m (Sand)	0.5	0.8	$\leq 10^{-2}$	$\leq 10^{-2}$	0.26
m (Clay)	0.06	0.3	1.05	1.00	0.05
α (Pa^{-1})(Sand)	$10^{-4.7}$	$10^{-3.9}$	0.31	0.13	0.30
α (Pa^{-1})(Clay)	$10^{-5.5}$	$10^{-4.1}$	0.45	0.33	0.08
Ca ($\text{mg}\cdot\text{kg}^{-1}$) (Sand)	10^3	$10^{5.5}$	0.26	0.41	0.06
Ca ($\text{mg}\cdot\text{kg}^{-1}$) (Clay)	10^4	$10^{5.7}$	0.48	0.63	0.01
Tortuosity	0.2	0.7	$\leq 10^{-2}$	0.01	0.36
Infiltration (mm/yr)	0	800	$\leq 10^{-2}$	$\leq 10^{-2}$	0.12
Pressure scaling	0	2	$\leq 10^{-2}$	$\leq 10^{-2}$	$\leq 10^{-2}$

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.

292 The time series of atmospheric pressure fluctuations corresponds to the
 293 site area, and are considered as a forcing without uncertainty. Similarly, a
 294 realistic time series for water infiltration at the surface can be obtained for
 295 this specific site, and used instead of the constant infiltration in the previous
 296 cases. Water infiltration is calculated from a simple water budget, based on
 297 rain data (MeteoSwiss, 2014), the evapo-transpiration calculated using the
 298 Penman-Monteith equation (Allen et al., 1988) and soil storage capacity. The
 299 resulting infiltration pattern, with an annual infiltration of 810 mm/year, is
 300 not taken as uncertain input here, thus neglecting the intrinsic errors of the
 301 evapotranspiration and water budget calculations.

302 The 8 uncertain parameters and their defined ranges are listed in Table 5.
 303 A total of 1000 sets of parameters were sampled using Monte Carlo method
 304 and following these distributions. As in the second case, the modulation
 305 of ^{37}Ar production by soil water content was not considered in the model.
 306 The numerical scheme is the same as for the two other cases. Similar to
 307 the first case, probability density of ^{37}Ar activity concentrations in soil gas is
 308 presented in Figure 1b, and scatter plots of the output variables as a function
 309 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).

Parameter	PDF		Sensitivity		
			^{37}Ar	$\Delta^{37}\text{Ar}$	Peak depth
Φ	N	$0.40 \pm 10\%$	0.64	0.43	0.01
$\log(k)$	N	$-12.3 \pm 5\%$	0.007	0.58	0.71
Ca ($\text{mg}\cdot\text{kg}^{-1}$)	N	$3800 \pm 10\%$	0.06	0	0.006
U ($\text{mg}\cdot\text{kg}^{-1}$)	N	$2.3 \pm 10\%$	0.45	0.44	0.03
m	U	[0.5236 ; 0.7920]	0.002	0.43	0.75
$\log(\alpha)$	U	[-4.6938 ; -3.8069]	0.02	0.31	0.02
τ	U	[0.2 ; 0.7]	1.07	0.45	0.23
X_{sc}	U	[0.27 ; 10]	0.03	0.21	0.06

310 3. Results and discussion

311 3.1. Production and emanation of ^{37}Ar

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

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

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

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

335 3.2. Processes controlling ^{37}Ar activity concentration in the subsurface

336 Global sensitivity coefficients for the intensity and variability of ^{37}Ar ac-
337 tivity concentration in soil gas as well as depth of the maximum activity
338 concentration are presented in Tables 3, 4 and 5 for the general sandy soil,
339 heterogeneous sand-clay and Belp site cases respectively. Drawing a clear
340 picture out of the sensitivity coefficients appears quite challenging, espe-
341 cially when the number of parameters is large, as in the second case (Table
342 4). It must also be kept in mind that these sensitivity coefficients depends
343 on the chosen ranges for the input parameters. Sensitivity coefficients were
344 thus combined with scatter plots (Figure 2) to identify the most important
345 parameters in the homogeneous cases.

Figure 1: Probability density of ^{37}Ar activity concentration in soil gas as a function of depth for the stochastic models of homogeneous sandy soil (a) and of Belp site (b).

346 The global shape of ^{37}Ar profile in the subsurface shows a maximum value
 347 at shallow depth, between 2 to 5 m (Figures 1a and b), as already known from
 348 the literature (Carrigan and Sun, 2014; Riedmann and Purtschert, 2011).
 349 This shape results from the combination of the exponentially decreasing pro-
 350 duction (Equation 1) and diffusion towards the atmosphere where the ^{37}Ar
 351 activity concentration is on average $1 \text{ mBq}\cdot\text{m}_{air}^{-3}$ (Loosli et al., 1970) much
 352 smaller than in the subsurface.

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

357 The average value of ^{37}Ar activity concentration in the shallow subsurface
 358 is found to be controlled by Ca content and by neutron scaling (Figure 2a),
 359 in agreement with findings obtained by Riedmann and Purtschert (2011).
 360 At a specific site with better constraints on Ca content, the neutron scaling
 361 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}Ar activity concentration in soil gas (a-b) and range of variability (c-d) at 1 m, as well as depth of ^{37}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}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}Ar production, soil water content and water infiltration play a major role in ^{37}Ar transport dynamics through several processes. High ^{37}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}Ar at depth. On the other hand, gas-available pore space is reduced in wet soils and the low solubility of ^{37}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

381 compartments.

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

387 Under steady-state water saturation conditions (first case), a higher per-
388 meability facilitates transport, e.g. due to barometric pumping. In the tran-
389 sient water saturation scenario (third case), this effect is masked by the
390 restriction of soil transport properties and the increased gas-water partition-
391 ing, which both lead to a higher ^{37}Ar variability with lower permeability. A
392 small effect of the α parameter is also obtained (Figure 2d), and confirms
393 this role of water saturation.

394 In the heterogeneous case, the same processes are at play, but the typical
395 shape of ^{37}Ar depth profile is lost because of the spatial variability between
396 sand and clay. The high water saturation in clay layers is systematically
397 associated with high ^{37}Ar activities (Figure 3), which is explained by the
398 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.

399 *3.3. Uncertainty on average ^{37}Ar depth profile*

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

403 In the general and poorly constrained case, there is a very large un-
404 certainty of 3 orders of magnitude on ^{37}Ar activity concentration at depth
405 (Figure 1a), from less than $1\text{ mBq}\cdot\text{m}^{-3}$ (below detection limit), to several
406 $\text{Bq}\cdot\text{m}^{-3}$. The range of variability becomes even larger when heterogeneity
407 is considered (data not shown). This uncertainty reduces to one order of
408 magnitude in the more constrained Belp case (Figure 1b). An uncertainty
409 limited to one order of magnitude or less was also obtained in previous works
410 (Carrigan and Sun, 2014; Riedmann and Purtschert, 2011), that considered
411 relatively narrow ranges of parameters, especially for soil Ca content. In-
412 cluding water content and infiltration in the models thus does not increase
413 too much the uncertainty on the average ^{37}Ar activity concentration in the
414 subsurface. This uncertainty mainly results if the location of the site and
415 chemical composition of the soil are poorly known.

416 *3.4. Temporal variability from barometric pumping and water infiltration*

417 While the uncertainty on the average ^{37}Ar depth profile is mainly due
418 to production, the temporal variability of ^{37}Ar activity concentration at a
419 specific point is driven by transport processes, and especially by water infil-
420 tration.

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

430 Figure 4 illustrates the dynamics of ^{37}Ar activity concentration in soil gas
431 at 1 and 5 m depth for one arbitrarily chosen set of parameters, along with the
432 surface forcings, namely infiltration and atmospheric pressure fluctuations.
433 Water infiltration events clearly lead to a greater ^{37}Ar variability compared
434 to barometric pumping. In Figure 4, peaks of ^{37}Ar activity concentration in
435 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).

436 amplitude of such peaks could be slightly enhanced by the decreasing baro-
 437 metric pressure that often accompanies rain events.

438 The processes coupling water infiltration events and increased ^{37}Ar activ-
 439 ity concentration in the subsurface have already been discussed above.

440 These results regarding ^{37}Ar temporal dynamics in the subsurface have
 441 been obtained for given barometric pressure and water infiltration time series.
 442 The sensitivity to these forcings will have to be investigated in the future, as
 443 was done for radionon migration and barometric pressure by Jordan et al.
 444 (2014). However, the general conclusions can easily be adapted to any site,
 445 with its hydrogeological and meteorological conditions. In dry locations,
 446 barometric pumping will become the main process driving ^{37}Ar temporal

447 variations, but the range of variability is not expected to be of more than a
448 few percent.

449 4. Conclusions

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

460 The influence of soil water content on ^{37}Ar production is demonstrated
461 to be negligible to first order, but transient water infiltration events control
462 ^{37}Ar activity concentration and its temporal variability in the subsurface,
463 especially by reducing diffusive exchange with the atmosphere.

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

470 The definition of the threshold for anomalous ^{37}Ar activity concentration
471 in soil gas has to be done carefully, and would require a measurement of
472 the local ^{37}Ar background and variability. Based on this study, it appears
473 "very unlikely" that values of ^{37}Ar activity concentration in soil gas above 1
474 $\text{Bq}\cdot\text{m}^{-3}$ are natural, and this value is proposed as a robust and conservative
475 threshold. Ongoing and future work will allow investigating the probabil-
476 ity densities for the ^{37}Ar activity profiles following an underground nuclear
477 explosion, and finally be able to define the likelihood that an ^{37}Ar elevated
478 signature is of nuclear origin or not. In any case, interpretation of ^{37}Ar ac-
479 tivity concentration in soil gas has to be very careful, considering the large
480 uncertainty and the limited number of data that would be available.

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