

a) Title

Assessing health impacts of CO₂ leakage from a geological storage site into buildings: role of attenuation in the unsaturated zone and building foundation

b) Authors

L. de Lary¹, A. Loschetter¹, O. Bouc¹, J. Rohmer¹, C.M. Oldenburg²

c) Affiliation

¹ BRGM, 3 av. C. Guillemin BP36009, F-45060 Orléans Cedex 2, France.

²Earth Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

Corresponding author:

E-mail address: l.delarydelatour@brgm.fr (L. de Lary)

Tel.: (+33) 2 38 64 46 24; fax: (+33) 2 38 64 36 89

d) Abstract

Geological storage of the greenhouse gas CO₂ has the potential to be a widespread and effective option to mitigate climate change. As any industrial activity, CO₂ storage may lead to adverse impact on human health and the environment in the case of unexpected leakage from the reservoir. These potential impacts should be considered in a risk assessment process.

We present an approach to assess the impacts on human health in case of CO₂ leakage emerging in the unsaturated zone under a building. We first focus on the migration of the CO₂ in the unsaturated zone and the foundation through numerical simulation with sensitivity analysis. Our results show that the intrusion of CO₂ into a building is substantially attenuated by the unsaturated zone and the foundation and may lead only under very specific conditions (very low ventilated parts of buildings, high flow rate and/or building situated very close to a leaking pathway) to hazardous CO₂ indoor concentrations.

We have then integrated the former results in a global toolbox that provides an efficient and easy-to-use tool for decision support, which enables to assess the impacts on human health of CO₂ leakage from the reservoir to a building.

e) Keywords

Geological storage, Leakage, CO₂, Health, Unsaturated zone, Indoor exposure.

f) Main Text

1 Introduction

Carbon dioxide capture and storage (CCS) is now widely acknowledged as one of the promising mitigation options for reducing atmospheric greenhouse gas emissions. It provides a way to avoid releasing CO₂ in the atmosphere by capturing CO₂ from industrial facilities, transporting it to a storage site and injecting it into a suitable underground geological formation, typically at depth greater than 800 m. The purpose of geological storage is permanent containment of CO₂ (IPPC, 2005).

As any industrial activity, geological storage may lead to potential risks on human health and environment. To be viable, a CO₂ storage project must be environmentally safe and socially sustainable, thus, it must be demonstrated that no significant leak will occur (West et al., 2005). The European Directive 2009/31/EC which establishes a legal framework for the

deployment of the geological storage of CO₂, underlines the fact that “a geological formation shall only be selected as a storage site, [] if no significant environmental or health risks exist” (European Commission, 2009). To ensure this goal, the Directive requires the consideration of numerous criteria for the characterization and assessment of the storage complex. In particular, a risk assessment that considers the effects of leakage on environment and human health must be carried out. A risk analysis should take into account the consequences (*i.e.* the impacts) and the probabilities of occurrence (*i.e.* the likelihood) of unexpected events.

Among the unexpected events, the migration from the reservoir formation to the surface by a preferential permeable pathway (*e.g.* a faulted zone or an improperly abandoned well) has been determined to be one of the most critical risk scenarios because the flow rate may be high in such situations (Lewicki et al., 2007; Oldenburg et al., 2009). To date, most research has focused on the assessment of the CO₂ flow rate that could migrate away from the reservoir (*e.g.* Nordbotten et al., 2009; Pruess, 2011a) rather than on the impacts of such a flow (Price and Oldenburg, 2009). However, the effects of CO₂ depend much more on the level of exposure (defined as a quantity of substance put in contact with the body barriers) than on the total quantity of CO₂ released (Hepple, 2005).

The objective of the present paper is twofold: 1) quantify the impacts on humans of CO₂ leakage from a geological storage site into a building in a more realistic way than what has been done so far and, 2) make the results usable within an integrated risk assessment framework. It is worth mentioning that we focus on impacts and not on risks, since we do not quantify the probability of occurrence (which is likely to be very site-specific).

In the first part of this paper, we investigate the potential health effects of CO₂ (section 2). Then, current approaches to characterize hazardous components migration in the unsaturated zone (*i.e.*, the zone between the ground level and the water table) and intrusion into a building are reviewed in different contexts and in the CCS domain (section 3). After identifying limits of current available approaches, we propose a conceptual model to assess CO₂ indoor concentration and associated hazards resulting from a leakage due to a transmissive faulted zone which emerges at some meters depth under a building (section 4). We first investigate the migration of CO₂ in the unsaturated zone and the foundation through numerical simulation with sensitivity analysis (section 5). In section 6, we discuss these results more specifically regarding the relevance of the considered leakage scenario (likelihood and magnitude) and the assumptions of the modeling procedure. On this basis, we finally show how these results could be integrated in a global, efficient and easy-to-use tool to support decision-making of stakeholders and authorities reviewing risk assessment procedures for CO₂ storage projects.

2 Potential health effects of CO₂

Carbon dioxide is a naturally occurring gas which exists in ambient air in low proportion (about 0.038 % in volume or 380 ppm). It is harmless and even essential to life at low concentration, but it can become hazardous or even lethal at high concentration. Furthermore, carbon dioxide is a color-free gas that cannot be detected by taste or smell below concentration of 10 to 20 % (NIOSH, 1976).

The effects of CO₂ on healthy humans are quite well known. Exposure to CO₂ can be hazardous by two mechanisms: (1) because it reduces the oxygen content of ambient air and thus can lead to asphyxia; (2) because of its own direct toxicity. From Hepple (2005), direct toxicity of high levels of CO₂ occurs before the effects of oxygen lack.

Carbon dioxide behaves as a threshold substance. This means that the effects of its inhalation are entirely defined by a concentration and duration of exposure. From 1 to 3 % CO₂ leads to a decrease of blood pH and a stimulation of respiration. Above 3 %, the

breathing rate increases exponentially, hearing loss or visual disturbance may occur. When CO₂ concentration exceeds 5 %, symptoms are more severe and unconsciousness can occur after one to several minutes at concentrations reaching 10-15 %. At level reaching 30 % of CO₂ death occurs within a few minutes.

In France, public authorities have prescribed CO₂ acute toxicity thresholds to be used for industrial hazard studies (Table 1). The “15 minutes Short-Term Exposure Limit Level” of 3 % and the “Immediately Dangerous to Life and Health level” of 4 % are used in the United States (Hepple, 2005). Robinson (2010) considers a cautious “action level” (*i.e.* level above which measures should be taken) of 0.5 % in building.

Table 1 - Thresholds for CO₂ acute toxicity in France used for hazard studies (Ministry of Ecology, 2007).

Thresholds	Corresponding CO ₂ level (% vol.)
Irreversible effects	5%
First lethal effects	10%
Significant lethal effects	20%

On natural sites where strong degassing of deep-origin CO₂ occurs, it has been noted that the CO₂ level in soil could be very high (up to 95 % or even more), while in the atmosphere at an elevation of 1 or 2 meters above ground level the CO₂ content is often only twice to thrice the usual concentration (Carapezza et al., 2003; Farrar et al., 1999). Thus, CO₂ is able to dilute rapidly in the atmosphere in open terrain with adequate ventilation. However, because CO₂ is 50 % denser than air (in normal temperature and pressure conditions), it tends to migrate downwards and accumulate in depressions or in confined space potentially creating much higher concentrations (Chow et al., 2009; Benson and Cook, 2005; Bogen et al., 2006). At natural strong degassing sites, human fatalities due to CO₂ have been recorded under particular situations (Carapezza et al., 2003; Holloway et al., 2007; Rogie et al., 2001). Annunziatellis et al. (2003) have shown that a danger may exist for exposure in the basement of houses situated near localized sites where strong natural degassing occurs under specific geological conditions. Human fatalities due to CO₂ have also been recorded in other situations such as work in poorly ventilated space (Louis et al., 1999).

3 Review of current approaches to assess indoor exposure to hazardous compounds.

3.1 Analogies with other domains

In order to investigate the issue of CO₂ intrusion into buildings, we took interest in the literature related to other hazardous compounds for which more data are currently available. Some similarities between CO₂ and volatile organic compounds (VOC) have been established, especially regarding the transport in the unsaturated zone (*e.g.* Zhang et al., 2004). The main difference comes from the consequences on environment and human health, the VOCs being potentially harmful at low concentrations. For these compounds, risk assessment methodologies and remediation measures have been available for more than 20 years (EPA, 1997; Khan et al., 2004). Two main entry mechanisms from underlying soil to indoor air are identified: diffusion or advection through the structural elements or through openings in the structural elements. Diffusion is the result of a concentration gradient between the underlying soil and the indoor air. Advection is due to a difference of pressure between the soil and the interior of the building. Pressure differentials may be caused by numerous mechanisms such as thermal differences, wind, barometric pressure changes or

building ventilation (Patterson and Davis, 2009). Field study by Patterson and Davis (2009) show that the molecular diffusion of VOC vapors through the concrete of a slab-on-grade is the dominant intrusion pathway under normal meteorological conditions. However, when the interior of the building is under artificially reduced pressure, their results suggest that the advective vapors intrusion through gaps or cracks in the slab becomes dominant. The authors underline that these results are highly dependent on site specific conditions.

Numerous analytical or numerical models have been developed to quantitatively assess the intrusion of radon¹ or other contaminants into buildings (e.g. Améon et al., 2006; Andersen, 2001; Johnson and Ettinger, 1991). However, these models are not directly applicable in the case of CO₂ leakage because they use as input data a concentration of contaminant in soil; whereas current approaches for CO₂ calculate a mass flow rate through a flow transport model from the reservoir to a shallow aquifer formation or to the surface (e.g. Chang et al., 2009; Pruess, 2008).

Analogies may also be found with CO₂ pollution cases: 1) in case of natural degassing of deep origin CO₂; 2) in buildings situated near reclaimed or abandoned coal mines (Robinson, 2010). However, only few investigations have been made about the characteristics and mechanisms of CO₂ intrusion in this context.

3.2 Critical review in the CCS domain

Two main approaches have been suggested to assess the exposure to CO₂:

1. In case of unexpected migration of CO₂ from reservoir into the atmosphere, numerical dispersion calculations have been suggested in order to assess the exposure level of vulnerable entities in open areas. Simulations of plume dispersion have been performed for point sources of CO₂ such as wells (e.g. Aines et al., 2009; Bogen et al., 2006; Chow et al., 2009) and for more dispersed source zones (Oldenburg and Unger, 2004). Several difficulties have been underlined by these studies, especially about taking into consideration the risks of CO₂ accumulation in low-lying areas, the characteristics of the CO₂ source, and the extent of the reservoir footprint.
2. In order to quantitatively evaluate the impact on human health at the Weyburn site, Stenhouse et al. (2009) proposed a conceptual model of exposure to CO₂ into a dwelling resulting from a leakage through an abandoned well. This model converts a flow of CO₂ into an indoor concentration in a very simple way and with few input data (leakage flow rate, volume of dwelling, building ventilation rate) in comparison to the numerical dispersion approach. The calculation of the indoor CO₂ level into the dwelling is based on a mass balance at steady-state conditions. However, this model is overly conservative because it assumes that the CO₂ migrates from the wellhead to the dwelling without any attenuation or resistance during the transport via the upper soil layers or the foundation of the building. It is equivalent to the unlikely situation where a permeable pathway directly emerges inside the building. Furthermore, simulations by Oldenburg and Unger (2003) showed that the unsaturated zone has a potential, although limited, to attenuate a CO₂ leakage due to different processes such as solubility trapping, gas ponding due to CO₂ density, or dilution in soil gas. A model considering the transport of CO₂ leaking from a wellhead to a building was suggested by Duguid and Celia (2006). It assumes that the only mechanism responsible for the transport of CO₂ in the unsaturated zone is diffusion. However, simulations carried out by Oldenburg et al. (2010) have shown that both advection and diffusion control CO₂ transport in the unsaturated zone. Thus the model

¹ Radon is a naturally occurring gas which is present everywhere at the Earth crust. Contrary to CO₂ radon may lead to adverse impact at very low concentration. Very extensive literature is available about the entry mechanisms of this gas into buildings.

suggested by Duguid and Celia (2006) is likely to underestimate the CO₂ intrusion into buildings.

In the present paper, we chose to focus on the second type of approach to assess the exposure in an enclosed (low ventilated) space, CO₂ being more likely to be harmful in such a situation (Oldenburg et al., 2009).

4 Methods

4.1 Proposed general conceptual model

The general conceptual model is presented in Figure 1. We suppose that, due to an insufficient site characterization during site selection or an unexpected behavior of the storage complex, the CO₂ is able to migrate upward and to reach the surface by a leakage pathway. We consider that the leakage pathway is a permeable faulted zone situated under an inhabited area. In sedimentary basins, such as the Paris Basin which could be possible candidate for deep saline aquifers storage (Grataloup et al., 2009), the parent rock is covered by a layer of regolith and soil. Thus, we consider that the leakage pathway does not emerge directly in the house but at some meters below the soil surface. In a zone having an old history of hydrocarbon exploration and exploitation, the leakage pathway may also be an improperly abandoned or an orphan well which has not been mapped during site characterization (Oldenburg et al., 2009). The migration from the reservoir towards the surface could be much more complicated than suggested in Figure 1, because of various phenomena such as secondary accumulation or migration in permeable formations situated on the leakage pathway (Chang et al., 2009; Nordbotten et al., 2005; Pruess, 2008). Furthermore, under the soil layer, the parent rocks are often highly fractured, and thus the migration near the surface is probably more complex than suggested.

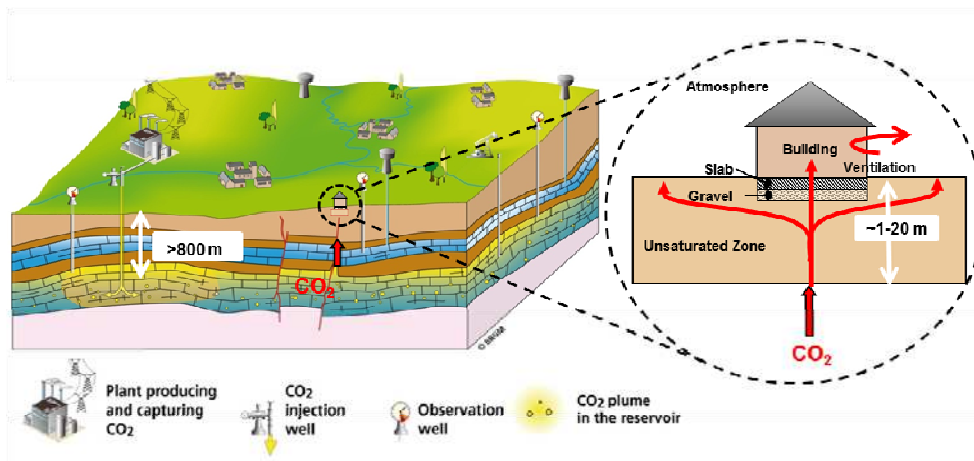


Figure 1 - Conceptual model for CO₂ migration from a reservoir and point-source CO₂ leak in the unsaturated zone under a building.

We focus on what happens when the leaking flow reaches the top bound of a transmissive faulted zone situated some meters under a building. To reach the indoor air of the building, the CO₂ has to migrate in the unsaturated zone and through the foundation. During this migration, several attenuation processes may occur. We propose to study these mechanisms and the associated consequences on human health with the conceptual model presented in the circle of Figure 1. The CO₂ source in the unsaturated zone is situated at some meters depth under a building. The building is a slab-on-grade house whose foundation is composed

of a layer of gravel and a layer of concrete. This sort of building is more vulnerable to geological gas intrusion than buildings with crawl-space. The interior of the building is modeled as a global volume with a known ventilation rate. This volume can be considered either as a basement or as a ground-level story, depending on the kind of construction. Note that the CO₂ entry in the unsaturated zone is conceptualized as a point source which is located directly beneath the center of the building: we chose this geometrical hypothesis in order to be in a conservative configuration regarding the CO₂ intrusion. To perform this study, two specific models were successively used: 1) a model of migration of CO₂ in the unsaturated zone that assesses the intrusion rate into the building; 2) a model of exposure which converts the intrusion rate into the building into a volume concentration.

4.2 Model for CO₂ migration and intrusion into the building

We used a numerical simulation approach to simulate the migration of CO₂ through the unsaturated zone and the building foundation considering a large range of configurations.

Simulations were carried out using the multiphase and multi-component simulator TOUGH2 (Pruess et al., 1999) combined with the research module EOS7CA (Oldenburg et al., 2010), which is designed for near-surface applications where the pseudo component air is present (Oldenburg and Unger, 2003).

We used an axisymmetric model for the unsaturated zone and the building foundation, with the symmetry axis in the vertical direction Z passing through the center of the building and the leakage source (Figure 2). The leakage source is at the bottom of the unsaturated zone. Numerical dispersion due to the grid size was found negligible for the simulated time period.

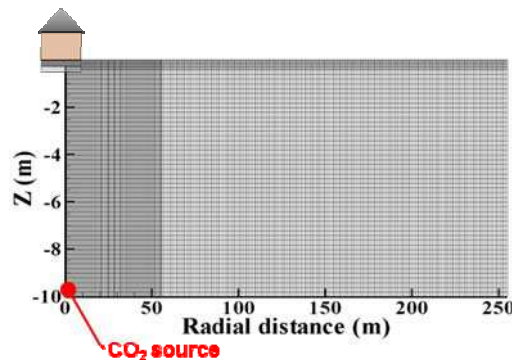


Figure 2 - Mesh used for the base-case simulation. Here with a 10 m thick unsaturated zone.

A constant atmospheric pressure of 10^5 Pa is kept at the top of the system. The lateral model boundary is located at 250 m from the leakage source to ensure that the CO₂ plume is not affected by this boundary, which is held at constant gas-static pressure corresponding to the initial soil moisture-air gravity and capillary equilibrium. In a conservative approach, a no flow condition is used at the bottom of the model in order to force the CO₂ plume to migrate upwards. This hypothesis may be representative of reality if the underlying stratum is made of a parent rock or an impervious layer. The initial state of modeling corresponds to a steady state capillarity-gravity equilibrium obtained through a preliminary modeling.

The other hypotheses of the model are the following:

- The unsaturated zone is composed of homogeneous and isotropic material with no fractures or preferential pathways.
- Temperature is assumed to be constant throughout the model and equals 15 °C.

- The leakage source is situated at the bottom of the unsaturated zone on a 1 m² surface disk with a view to model a point source. We consider that the CO₂ arrives in the unsaturated zone in gaseous state.

4.3 Model for CO₂ exposure in the building

CO₂ entering the building accumulates depending on the ventilation rate of the building. We evaluate the indoor concentration with a simple analytical model based on a mass balance for CO₂ which is extensively used in the area of pollutant intrusion in buildings (e.g. Loureiro et Abriola, 1990; UNSCEAR, 1988). Assuming an instantaneous and homogeneous mixing of CO₂ in the building, the CO₂ indoor air level may be expressed as (Eq.1):

$$\rho_{CO_2} \times V \times \frac{dC_{in}}{dt} = Q - (C_{in} - C_{out}) \times V \times \rho_{CO_2} \times \lambda \quad (1)$$

Where C_{in} is the CO₂ level in indoor air (% vol.), C_{out} is the CO₂ level in outdoor air (% vol.), λ is the ventilation rate (s⁻¹), V is the volume of the building (m³), ρ_{CO_2} is the density of CO₂ (g/m³), Q is the intrusion rate of CO₂ into the building (g/s).

Solving this equation at steady state provides the order of magnitude for the indoor CO₂ concentration (Eq. 2):

$$C_{in}(t = \infty) = C_{out} + \frac{Q}{V \times \rho_{CO_2} \times \lambda} \quad (2)$$

In a real condition, the ventilation rate could be subject to important variations within a few hours (UNSCEAR, 1988) due to human activities (opening or closing windows) or meteorological conditions (wind, temperature change, pressure change). Furthermore, the ventilation rate could be contrasted within buildings and within rooms in the same building. The following values (Table 2) are used in this paper (Patterson and Davis, 2009; Stenhouse et al., 2009; UNSCEAR, 1988).

Table 2 – Range of building ventilation rates used in our model.

Ventilation rate (h ⁻¹)	
Basement	0.13
Building (Low)	0.5
Building (Average)	1
Building (High)	2

4.4 Base case scenario

The hypothetical reference building is assumed to be circular with a floor surface area of 100 m² and a volume of 250 m³. These correspond to standard values for a building (Andersen, 2001; UNSCEAR, 1988). The thickness of the slab is 0.20 m. Under the slab there is a 0.20 m highly permeable layer of gravel. The building and the unsaturated zone properties in the base case are shown in Table 3. The relative permeability and the capillarity functions are set to different values depending on the considered material (soil; gravel; concrete). The parameters of the van Genuchten (1980) model for the concrete slab are from Monlouis-Bonnaire et al. (2004). The parameters for van Genuchten relation for the gravel layer are set to arbitrary values in order to attribute a lower liquid saturation to the gravel. The diffusion coefficient of CO₂ in the gaseous phase is set to 1.5x10⁻⁵ m²s⁻¹ (Oldenburg and Unger, 2003). Intrinsic permeability and porosity for both the slab and the gravel layer are based on Andersen (2001) and correspond to a standard house. The liquid saturation is set

to 0.30 for the unsaturated zone in the base case. For the unsaturated zone, the parameters correspond to fine sand.

Table 3 - Properties of the unsaturated zone and the building foundation in the base case setting.

Material	Thickness (m)	Permeability (m ²)	Porosity (%)	Capillary pressure, relative permeability
Concrete slab	0.2	10 ⁻¹⁵	20 %	Van Genuchten; Slr=0.25; Sgr=0.01; $\alpha=10^{-7}$; m=0.5
Gravel layer	0.2	5x10 ⁻⁹	40 %	Van Genuchten; Slr=0.1; Sgr=0.01; $\alpha=10^{-3}$; m=0.4
Unsaturated zone	10	10 ⁻¹²	30 %	Van Genuchten; Slr=0.15; Sgr=0.01; $\alpha=10^{-4}$; m=0.2

A literature review shows that depending on the situation and the modality of CO₂ uprising from the reservoir, the flow rate which reaches the surface following a leakage from the reservoir could be subject to substantial variations. Simulations of leakage through a faulted zone situated near a hypothetical reservoir performed by Pruess (2011a and 2011b) and accounting for self-enhancing and self-limiting effects showed that an order of magnitude for the CO₂ outflow at ground level could be 1 g/s/m². Pruess (2008) used a 1.6 g/s flow rate to study the role of secondary accumulation during CO₂ migration by a fault. Chang et al. (2009) modeled the upward CO₂ migration from fault and attenuation by surrounding permeable layers and found that the flux rate reaching the top of the leakage pathway could range from nearly zero to 70 g/s/m² depending on the situation. A well leakage model used by Oldenburg et al. (2009) for a hypothetical geologic CO₂ storage project leads to a leakage flux rate from 5.10⁻⁴ to about 5 g/s/m² depending of the permeability of the pathway. However, the maximum leakage flow rate from well with open casing from reservoir to the land surface could be much higher (Aines et al., 2009). On natural sites where deep geological CO₂ is degassing, fluxes measured at ground level can vary from background values (usually less than 1.10⁻⁴ to 3.10⁻⁴ g/s/m²) to more than 1 g/s/m² near the vent core (Beaubien et al., 2008; Carrapezza et al., 2003; Farrar et al. 1999).

In the base case setting we chose a leakage rate in the unsaturated zone of 1 g/s (which corresponds to a 10⁻⁵ /year fractional leakage rate from a 3 million tons reservoir). However we performed a sensitivity analysis to take into account very contrasted situations.

5 Results

5.1 Base case

The simulations show that the concentration of CO₂ in the considered building reaches, after 3 months, a steady value which depends on the ventilation rate (Figure 3). The intrusion rate of CO₂ into the building is about 0.17 g/s in the base case. Comparison with the total leakage rate in the unsaturated zone (1 g/s) shows that only a small proportion of the leaking CO₂ enters the building due to attenuation mechanisms that are discussed below. Hazardous levels from Table 1 are not reached in the base case whatever the ventilation rate. Not considering those attenuation mechanisms leads to an indoor concentration above the French irreversible effect threshold of 5 % for the lowest ventilation rate.

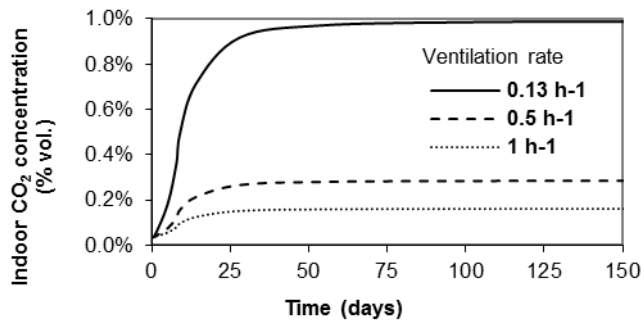


Figure 3 – Concentration in the building as a function of time in the base case for different ventilation rates.

5.2 Sensitivity analysis

The CO₂ footprint of storage reservoirs will generally be very large (order of magnitude in the hundreds of km²), and the properties of the unsaturated zone and of buildings in such a wide area are expected to significantly vary. An unforeseen leakage by a fault or an abandoned well may eventually occur anywhere in the footprint of the storage reservoir and thus may occur in very different situations. To be confident that a wide range of situations (including the most deleterious) has been considered, we performed a sensitivity analysis considering a large range of parameters.

From the base case configuration, we performed a single-factor sensitivity analysis based on the OAT technique, which consists in varying one factor at a time to show the influence of this factor (Campolongo et al., 2000). The ventilation rate was set to the lowest value (0.13 h⁻¹) (except for the sensitivity analysis on the ventilation rate). The leakage rate value was kept below 20 g/s in order to avoid excessive pressure build-up in the unsaturated zone. The investigated range of permeability for the unsaturated zone corresponds to soil textures varying from gravel to silt. Very wide ranges of permeability and porosity were chosen to model different slab properties. Results are presented on the “Tornado-type” diagram in Figure 4.

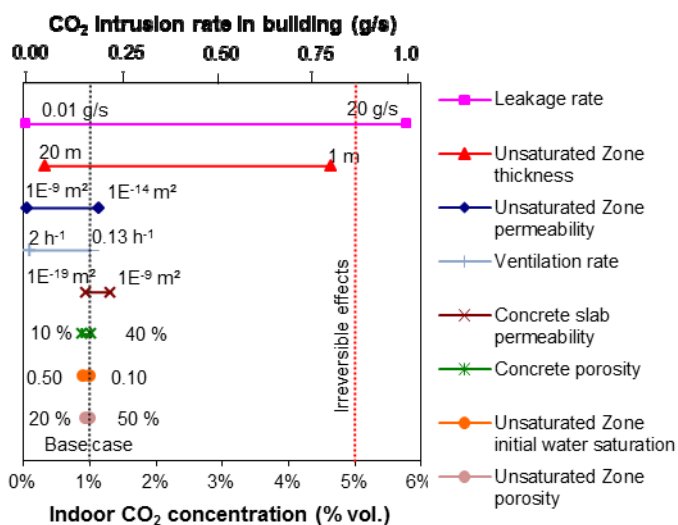


Figure 4 – Results of the sensitivity analysis. The values on the figure are the values of the considered parameters for which the extrema are reached. Note that the scale for the intrusion rate is not applicable for the sensitivity analysis on ventilation rate because in this

particular case the intrusion rate is the same whatever the situation. The French threshold for irreversible effect due to acute toxicity (5% CO₂) is indicated in the figure.

Two main results can be drawn from this sensitivity analysis:

- For the range of parameters used in this sensitivity analysis, the CO₂ indoor concentration varies from nearly zero to about 6 %, which is above the French value for first irreversible effects of 5 %. The Immediately Dangerous to Life or Health level of 4 % is exceeded only for the situations with a low unsaturated zone thickness or a very high flow rate. For all other situations, acute toxicity thresholds are not reached. Therefore, intrusion of leaking CO₂ in low ventilated parts of buildings (basement) may lead, only under very specific conditions, to hazardous situations.
- The most influential parameters on the indoor concentration are ranked based on the width of the variation in the following order: 1) the leakage flow rate; 2) the thickness of the unsaturated zone; 3) the permeability of the unsaturated zone; 4) the building ventilation rate. It is worth noting that we found only a limited number of crucial parameters.

5.3 Dominant CO₂ transport mechanisms

In our simulations, the transport of CO₂ in the liquid phase of the unsaturated zone is negligible compared to the transport in the gaseous phase. The leakage provokes a pressure build-up in the unsaturated zone ranging in the base case (Figure 5a) from a hundred of Pa at one meter depth under the building to about 4×10^3 Pa at the leakage source zone. With a low permeability ($k=10^{-14}$ m²) unsaturated zone (Figure 5b), the pressure build-up is about 4×10^3 Pa whatever the depth under the building. Such variations of pressure are very significant compared to other variations of pressure (due to barometric pumping, thermal effects etc. – cf. discussion in section 6.1) which are known to have strong effects on the intrusion of geological gases. With a high permeability unsaturated zone ($k=10^{-9}$ m²), the pressure buildup reaches only a few Pa close to the leakage source zone (not shown). In this situation, the intrusion in the building is very weak and the resulting indoor concentration is only 700 ppm or 0.07 % (Figure 4) due to a very limited advective migration. In the base case the transport is mainly advective near the source of CO₂ where the pressure build-up is the most significant whereas it is essentially diffusive near the soil surface due to a strong concentration gradient and low pressure gradient (Figure 6). These findings are in agreement with the simulations performed on the CO₂ release test at the Montana site (Oldenburg et al., 2010).

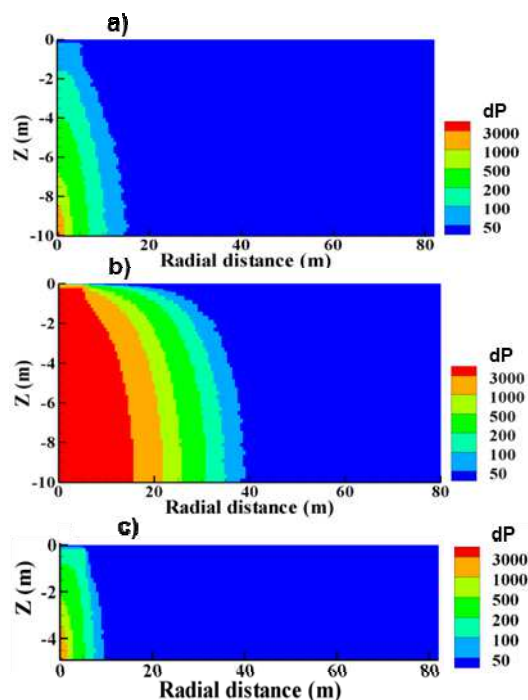


Figure 5 – Pressure increase in the model when a nearly steady state is reached (a) in the base case, (b) with a 10^{-14} m² (silt) and 10 m thick unsaturated zone (c) with a 10^{-12} m² and 5 m thick unsaturated zone; dP is the pressure variation in Pa.

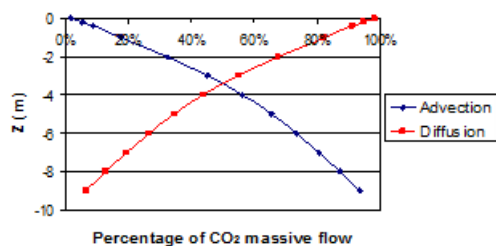


Figure 6 – Advection vs diffusion of the CO₂ as a function of depth at the center of the model in the base case.

5.4 Attenuation processes of the leakage rate

In the base case, the flow intruding into the building is significantly attenuated compared to the flow penetrating the unsaturated zone: only about 17 % of the leaking flow (1 g/s) enters the building. We suggest two main mechanisms to explain this attenuation: 1) the horizontal spreading effect of the CO₂ plume in the unsaturated zone, which enables the CO₂ to bypass the foundation of the building; and 2) the barrier effect of the foundation of the building. The horizontal spreading of a CO₂ plume in the unsaturated zone is a phenomenon that has already been underlined by Oldenburg and Unger (2003). The barrier effect of foundation has been largely studied in the field of pollutant intrusion into buildings because it can have a strong influence on the component intrusion rate (e.g. Patterson and Davis, 2009). We assessed the barrier effect of the foundation through numerical simulations with hypothetical buildings without foundation: it seems to be limited and leads to a less substantial attenuation than the spreading effect. Thus, properties of the foundation are not among the most influential parameters controlling the intrusion of CO₂ (Figure 4).

The spreading effect explains the results of Figure 7: the higher the total flow rate, the larger the plume, and the lower the percentage of the total flow entering the building due to by-passing. Thus, the indoor exposure increases much slower than the leakage rate (Figure 7).

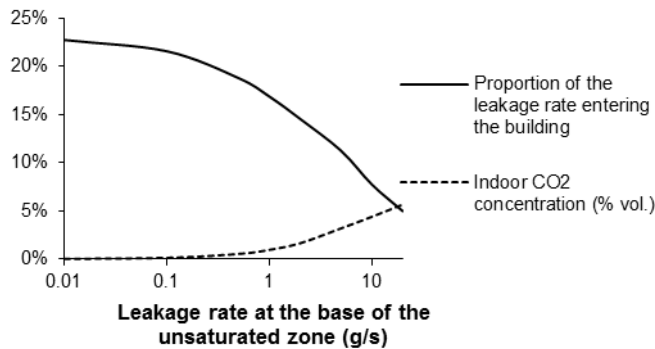


Figure 7 – Influence of the leakage flow rate in the unsaturated zone on the percentage of CO₂ entering the building and on the indoor CO₂ concentration.

5.5 Influence of the unsaturated zone properties on CO₂ migration

The permeability of the unsaturated zone also appears to control the intrusion rate. The shape of the plume with contrasted permeability values for the unsaturated zone (assumed homogeneous and isotropic) is shown in Figures 8a, 8b and 8d. In a highly permeable soil, the vertical transport of the plume is limited and the horizontal transport is dominant. Therefore a significant proportion of the flow rate passes around the building and the resulting indoor concentration is low.

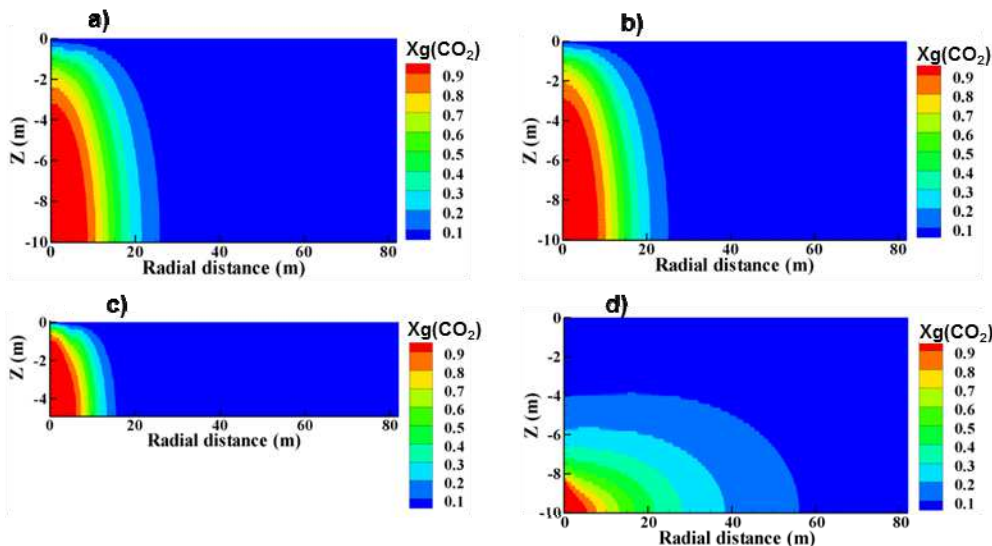


Figure 8 – Plume of CO₂ in the model when a nearly steady state is reached (a) in the base case, (b) with a 10^{-14} m² (silt) and 10 m thick unsaturated zone, (c) with a 10^{-12} m² and 5 m thick unsaturated zone, (d) for a 10^{-9} m² permeability and 10 m thick unsaturated zone. Xg(CO₂) is the mass fraction of CO₂ in the gas phase.

Figure 4 shows that the indoor concentration increases from 0.3 % to nearly 5 % when the thickness of the unsaturated zone varies from 20 to 1 meter. Again, this difference is due to

the spreading of the plume in the unsaturated zone: it becomes less important as its thickness decreases. (cf. Figure 8c).

6 Discussion and perspectives

6.1 Discussion concerning the model

The choice of our model aims at obtaining a compromise between high consequences / very low probability cases (e.g. orphan leaking well directly emerging in the building as considered by Stenhouse et al. (2009)) and moderate consequences / higher probability (e.g. leakage at hundreds of meters to kilometers from habitations). Thus, this model is less conservative in terms of risk assessment than the one proposed by Stenhouse et al. (2009), however, we consider that this model is still conservative for several reasons.

- The position of the building right above the leakage pathway is the most conservative and does not seem very realistic. Additional simulations should be carried out varying the relative position of the leakage pathway and the building; however the model, assumed axisymmetric so far, should be adapted to that purpose.
- The building considered is a slab-on-grade building, which tends to reinforce the entry of geological gases. Groves-Kirkby et al. (2008) show that other situations such as the ventilated sub-slab configuration significantly reduce the intrusion of geological gases into buildings. Furthermore, in modern slab-on-grade foundation, a polyethylene film prevents the intrusion of gases.
- In our model the pressure in the building is held constantly equal to atmospheric pressure. However, indoor pressure is often a few Pa lower (Andersen, 2001; Johnson and Ettinger, 1991) because of the wind effect and of the “stack effect” due to temperature differences between indoor and outdoor air (Améon et al., 2006). This difference of pressure may lead to an advective gas flow from the soil to the building. However, from Andersen (2001) and Loureiro and Abriola (1990) while the permeability of the soil under the foundation is lower than about 10^{-11} m², the main mechanism of intrusion remains diffusion, so neglecting in our model indoor depressurization and cracks in foundation may, only for the highest permeability soils, lead to underestimating the proportion of CO₂ intrusion into the building.
- From simulation results (Oldenburg and Unger, 2003) and on-field experiments (Robinson, 2010), barometric pumping (due to cyclic natural variations of barometric pressure) may cause local maxima both in the CO₂ flux released from the soil and in the resulting exposure concentration in the atmosphere or in buildings. As barometric pumping is not included in our model, the calculated concentration in the building remains constant after a near steady state is reached, whereas in real situation it should fluctuate with time. Thus, indoor CO₂ exposure could be higher than calculated for short periods of time during rapid drops in barometric pressure. However, Oldenburg and Unger (2003) found that barometric pumping should have negligible effect on the time-average flow of CO₂ which migrates out of the ground.
- We performed some additional simulations to show the influence of permeability anisotropy in the vertical direction to take into account hypothetical soil layering. When the anisotropy factor between radial and vertical permeabilities varies from 1:1 (base case) to 1000:1 the percentage of CO₂ flow entering the building decreases from 17 % to 4 % because of the spreading of the plume in the unsaturated zone.
- Other attenuation processes such as dissolution in a saturated zone or dissolution into the downward infiltrating meteoric water (Oldenburg and Unger, 2003) have not been modeled in our conceptual model. In a real situation, such attenuation processes would decrease even more the percentage of CO₂ entering the building and the resulting indoor concentration. However, if rainfall is intense enough, the compression of soil gases by the wetting front may, by contrast, increase temporarily

the CO₂ intrusion and the indoor concentration (Guo et al., 2008; Robinson et al., 2010).

Moreover, our model is not meant to predict real consequences of a leakage at a CO₂ storage site: the intent is to use it as a first approach to conservatively evaluate what could be the consequences in the case of a leak. As part of an iterative risk management process, risk assessment is used to design appropriate mitigation and monitoring measures. If a leakage pathway is suspected, additional characterization should be performed to properly understand the potential for a leak; the operations should be designed so as to reduce as far as possible the risk of leakage, including programming corrective measures to remediate any detected leak; and a monitoring plan should be implemented to detect any leak before it leads to adverse consequences. We emphasize that a site would not be selected for CO₂ storage if the risk of leakage were found significant. Therefore the consequences computed in our work should not happen; our model is simply one of the tools to be used in this process of assessing the risk related to CO₂ leakage in order to manage it.

Further work is necessary to improve and complete our approach, especially:

- The probability to encounter the modeled scenario leading to hazardous exposure should be assessed. Anyway, in a carefully selected storage site this probability is expected to be very low, as it implies the conjunction of several unlikely circumstances regarding CO₂ leakage and the presence of an inhabited building: (i) the plume has to reach a preferential pathway (faulted zone or abandoned well), (ii) the CO₂ has to migrate along this pathway from depth to the surface in sufficient quantities, (iii) a building has to be built at the top of this conductive pathway (iiii) somebody has to be exposed under specific conditions.
- In the proposed approach, we relied on a One-At-a-Time approach for the sensitivity analysis. The future direction of the present work is to estimate quantitatively the importance of each parameter accounting for the possible interactions and correlations between them with more sophisticated tools for a global sensitivity analysis (e.g. Saltelli et al., 2008).
- Our modeling approach would benefit from validation by comparison to fields experiments (e.g. monitoring an instrumented building submitted to a CO₂ artificial flow).

6.2 Further developments towards a decision-making tool

The scenario considered above involves different physical phenomena which correspond to different spatial zones:

- Firstly, migration in the saturated zone through a fault or a well (not investigated in this paper);
- Secondly, migration in the unsaturated zone and the foundation of the building;
- Thirdly, accumulation in the building.

In order to use the results presented in this paper in a risk assessment workflow, there is necessity to integrate them in a global tool that compiles various information and knowledge. The need for different process models for the different zones means that it is not possible to carry out a single global simulation from reservoir to ground surface. Therefore we suggest an adequate modular approach (cf. Figure 9) composed of:

- Module 1: CO₂ leakage from the reservoir and migration in the saturated zone through a fault or a well,
- Module 2: CO₂ migration in the unsaturated zone and the foundation of the building,
- Module 3: CO₂ accumulation and exposure in the building,
- Module 4: Exposure to impurities.

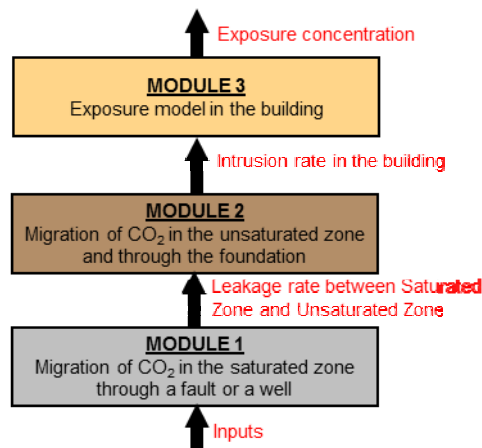


Figure 9 – Proposed segmentation in modules

6.2.1 Justification of the segmentation

The segmentation in “saturated zone”, “unsaturated zone” and “building” may appear obvious given the fact that specific models exist for these different parts. However the relevance of such segmentation with relevant inputs and outputs had to be validated, especially for module 1 and module 2.

Most models concerning the migration of CO₂ plumes in the saturated zone deliver a leakage rate. However, the few meters of soil and the building foundation may behave as a “stopper” and decrease the total leakage rate. This would make the previous segmentation non-relevant, since there would be a feedback from module 2 on module 1.

We carried out an extensive survey based on an analogy between Darcy’s law and Ohm’s law (e.g. Endo et al., 2009) in order to compute a “resistance parameter”. This analytical approach was compared against numerical results and was found to be correct. Using this approach enabled to compare the order of magnitude for resistance in the saturated zone and in the unsaturated zone. Sensitivity analyses were carried out and gave evidence that the resistance due to the unsaturated zone is less, or even greatly less than the resistance in the saturated zone. In a conservative approach, it is then concluded that module 1 and module 2 can indeed be tackled separately and linked together through the leakage rate (output of module 1 and input of module 2).

6.2.2 Module 1: Migration of CO₂ from a geological reservoir through a fault or a well

The development of this module is not the aim of this paper. In order to elaborate a first complete and functional version of the toolbox, we implemented a very simple analytical model based on Darcy’s law. A literature review shows a number of models for the migration of CO₂ in the saturated zone that could be used in order to further develop this first module, in particular: Pruess (2005, 2010), Pruess and Garcia (2002), Chang et al. (2009), Silin et al. (2009), Hayek et al. (2009), Nordbotten et al. (2005).

6.2.3 Module 2: Migration of CO₂ in the unsaturated zone and through the foundation

This module aims at obtaining the intrusion rate in the building given a point source leakage rate a few meters deep below the building, as described above. The results of the sensitivity analysis may be used in order to obtain an accurate value for a known situation. We suggest that a 60% attenuation of the CO₂ flow rate entering the unsaturated zone constitutes a conservative value for assessing a large area containing a high variety of settings.

6.2.4 Module 3: Exposure in the building

The goal of this module is to convert the intrusion rate in the building into indoor air concentration. We use the analytical model presented above (cf. 4.3). More complex models developed taking into account the indoor circulation between rooms and floors may alternatively be used to develop this module. To broaden the field of application of the tool, it may also be interesting to develop a surface module corresponding to free atmosphere based on atmospheric surface-layer advection and dispersion (cf. Oldenburg and Unger, 2004; Chow et al., 2009; Bogen et al., 2006).

6.2.5 Module 4: Integration of a realistic CO₂ stream (CO₂ and gaseous impurities)

Leakage from a geological reservoir is likely to be mostly composed of CO₂. However, the injected CO₂ may contain other components, which we call impurities. Some substances may also be mobilized during the ascent of CO₂.

As shown in Table 4, exposure limits for some gaseous impurities are far lower than for CO₂.

Table 4: Thresholds considered as references for irreversible effects for different gases based on a 30 minutes exposure in France (Baulig et al., 2004; Tissot and Pichard, 2000, 2004a, 2004b)

Component	CO ₂	H ₂ S	NO ₂	NO	SO ₂
Thresholds	5,00 %	0,010 %	0,005 %	0,010 %	0,010 %

Consequently, regarding health effects, CO₂ may not be the most critical component. Table 5 illustrates that a CO₂ flux from precombustion capture (upper value from IPCC, 2005) may contain 165 times less H₂S than CO₂; since the effect threshold is 500 times greater for CO₂ than H₂S, in a dilution calculation the most penalizing substance would be H₂S.

Table 5: Comparison of ratios concerning maximum exposure concentration and possible composition of injected gas for CO₂ and H₂S

	CO ₂	H ₂ S
Threshold (cf. Table 4)	5%	0.01%
Possible composition of injected gas corresponding to precombustion technology (IPPC, 2005)	99%	0.6%

Studies concerning impurities injected with CO₂ and their possible evolution, or concerning impurities mobilized during the ascent of CO₂ have been carried out (e.g. Jacquemet et al. 2009) but no comprehensive model is currently available.

To take into account these impurities in our tool, we propose an independent module, while making strong hypotheses. We suppose that the leaking flow entering into the building has the same composition than the injected CO₂. This neglects the possible chemical reactions or mobilizations during CO₂ migration in the reservoir and then through upper layers. We also assume that impurities behave as passive gases: due to their low concentrations, their transport is governed by the CO₂ movement.

Based on these hypotheses we calculate a dilution rate for CO₂:

$$\text{Dilution Rate} = \frac{\text{Concentration of CO}_2 \text{ in the injected flow}}{\text{Concentration of CO}_2 \text{ in the building}}$$

This dilution rate is then used to obtain the concentration of each gaseous impurity:

$$\text{Concentration in the building} = \frac{\text{Concentration in the injected flow}}{\text{Dilution Rate}}$$

This approach completes our model and enables to obtain orders of magnitude, even though it should be improved in the future and gain more integration with other modules.

6.2.6 Presentation of the global toolbox

The aggregation of these 4 modules into a global toolbox provides an efficient, quick and easy-to-use tool for decision support, which can be used to assess the impact to human health of a leak from a CO₂ storage site, with respect to threshold concentrations. In the current development of the toolbox, shown in Figure 10 with values corresponding to a hypothetical site, the user interacts through an interface implemented in a simple calculation sheet by filling yellow cells concerning the parameters of the leakage pathway and the reservoir (Module 1), the attenuation in the unsaturated zone (Module 2), the building characteristics (Module 3), the composition of the injected gas (Module 4). Then, the conclusions of the impact analysis are immediately generated. In the example Figure 10, effects on health are possible for H₂S, because the injected gas contains significant proportion of this highly toxic gas.

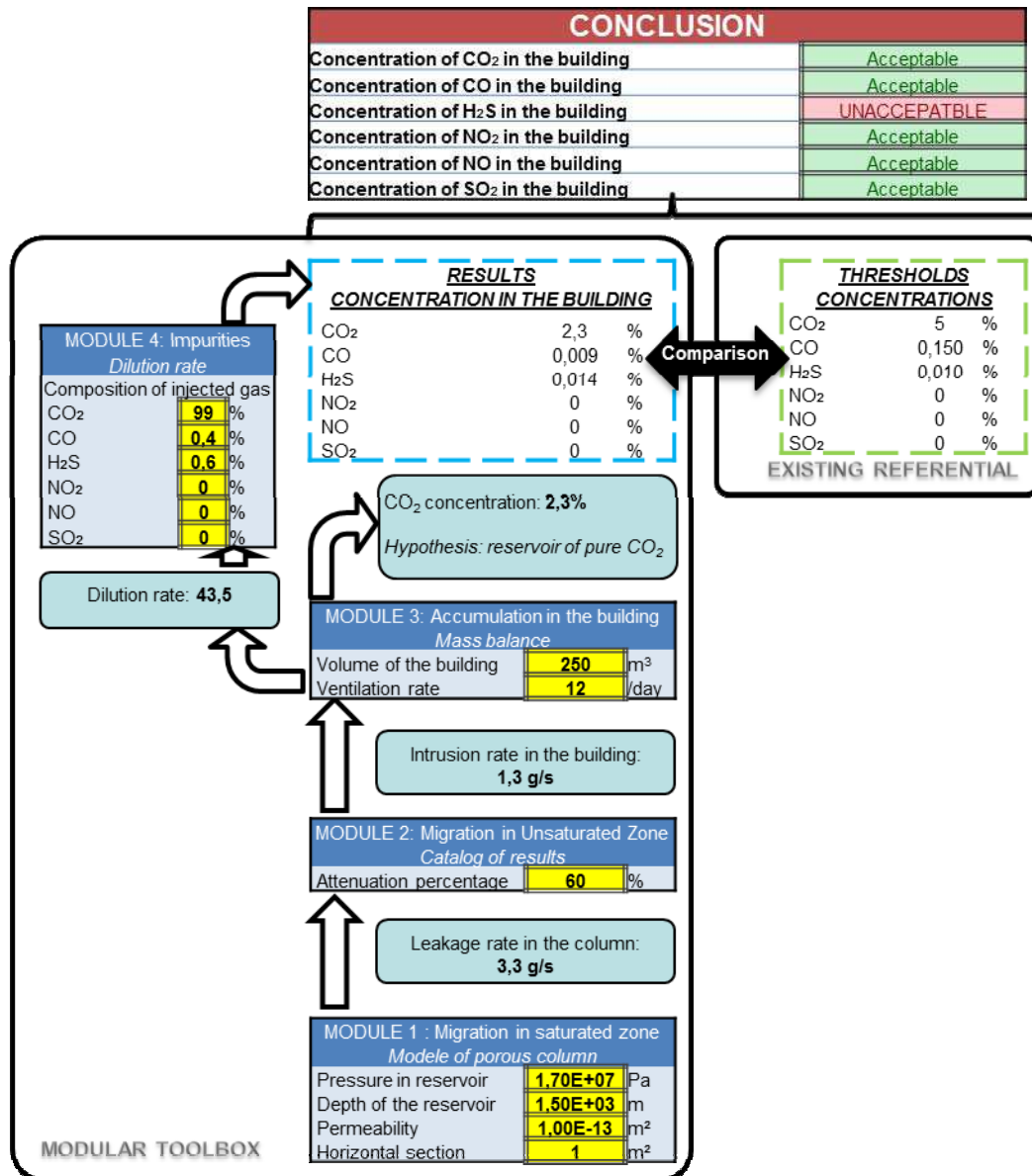


Figure 10 - Overview of the global toolbox. Input values must be entered in yellow cells. Figures in rounded frames indicate intermediary results (output of the module below, input of the module above).

7 Conclusion

We set up a conceptual model to assess indoor exposure to CO₂ resulting from a leakage from a faulted zone or an abandoned well, which is located beneath a building at some meters depth. The aim of this approach is to assess the health consequences on humans in case of leakage. The probability to be exposed to hazardous concentrations is not assessed, but it is expected to be very low in a carefully characterized, assessed and monitored site.

We performed a sensitivity analysis regarding the migration of CO₂ in the unsaturated zone in order to understand the possible attenuating roles of the unsaturated zone and the foundation. For the ranges of parameters investigated, the indoor CO₂ concentration varies from no effect level to hazardous concentrations. A main finding of this study is that hazardous concentrations are reached in a building only under specific conditions: very low indoor ventilation rate, high flow rate and/or building situated very close to a leaking fault or well. The most influential parameters controlling the indoor CO₂ concentration are the leakage flow rate, the thickness of the unsaturated zone, its permeability, and the building ventilation rate.

The CO₂ leakage flow is attenuated mainly due to the horizontal spreading of the plume in the unsaturated zone with a complementary but weaker attenuation due to the barrier effect of the building foundation. The transport of CO₂ is mainly advective close to the leakage source and diffusive close to the surface.

The main benefit of this model is to assess in a more realistic way than previously suggested approaches the exposure in a building following a CO₂ leakage. A site-specific approximation of the indoor exposure could be easily deduced from the most influential parameters. In the general case, a 60% attenuation of the CO₂ flow rate entering the unsaturated zone is considered a conservative value. Nevertheless, further improvements are necessary especially regarding the control of building-related processes on CO₂ intrusion.

We have integrated these results in a global toolbox, so as to be able to assess the consequences on human of a leakage from the reservoir to the surface. The problem has been segmented in three modules corresponding to the different spatial zones: the saturated zone, the unsaturated zone, the building. Their association delivers the CO₂ content in the indoor air. A fourth module roughly estimates the concentrations of impurities, based on a dilution model. The global toolbox provides an efficient, quick and easy-to-use tool for decision support, which can be used to assess the impact to human health of a leak from a CO₂ storage site.

It is worth mentioning that this toolbox deals with impacts and not with risks: if it were to be employed to assess risk, the impacts should be multiplied by the probability of the event. Benefit could be taken from this computing time efficient tool in a risk assessment process were numerous simulations would be necessary to take into account ranges of uncertainty.

Moreover, such a global tool would be useful for decision-makers in a preliminary risk analysis and would emphasize the most critical points that would require more detailed studies. It could for instance be valuable to help authorities and stakeholders auditing risk assessment studies (Bouc et al., 2009 ; Oldenburg et al., 2009).

g) Acknowledgement

We thank Dr. James Dooley and the other editors for their helpful comments and suggestions.

h) Appendix

i) References

Aines, R.D., Leach, M.J., Weisgraber, T.H., Simpson, M.D., Friedmann, S.J., Bruton, C.J., 2009. Quantifying the potential exposure hazard due to energetic releases of CO₂ from a failed sequestration well. *Energy Procedia* 1, 2421-2429.

Améon, R., Diez, O., Dupuis, M., Lions, J., Marie, L., Tymen, G., 2006. Experimental and theoretical study of radon levels in a house. 2nd European IRPA Congress on Radiation Protection 15-19 May 2006.

Andersen, C.E., 2001. Numerical modelling of radon-222 entry into houses: an outline of techniques and results. *The science of the total environment* 272, 33-42.

Annunziatellis, A., Ciotoli, G., Lombardi, S., Nolasco, F., 2003. Short- and long-term gas hazard: the release of toxic gases in the Alban Hills volcanic area (central Italy). *Journal of Geochemical Exploration* 77 (2003) 93–108

Baulig, A., Delrue, N., Pichard, A., 2004. Seuils de Toxicité aiguë – Dioxyde de soufre (SO₂). Rapport INERIS-DRC-04-47021-ETSC-STi-04DR146 pour le Ministère de l'Écologie et du Développement Durable et le Ministère de la Santé, de la Famille et des Personnes Handicapées, 46 p. *In French*

Beaubien, S.E., Ciotoli, G., Coombs, P., Dictor, M.C., Krüger, M., Lombardi, S., Pearce, J.M., West, J.M., 2008. The impact of a naturally-occurring CO₂ gas vent on the shallow ecosystem and soil chemistry of a Mediterranean pasture (Latera, Italy). *Int. J. Greenhouse Gas Control* 2 (3), 373-387.

Benson, S., Cook, P., 2005. Underground geological storage, in IPCC Special Report on Carbon Dioxide Capture and Storage, Prepared by Working Group III of the IPCC. Cambridge University Press, New York. pp. 195-276.

Bogen, K., Burton, E.A., Friedmann, S.J., Gouveia, F., 2006. Source terms for CO₂ risk modeling and GIS/simulation based tools for risk characterization. In: Eighth International Conference on Greenhouse Gas Control Technologies (GHGT-8), Trondheim, Norway, 19-22 June 2006.

Bouc, O., Audigane, P., Bellenfant, G., Fabriol, H., Gastine, M., Rohmer, J., Seyedi, D., 2009. Determining safety criteria for CO₂ geological storage. *Energy Procedia* 1 (2009) 2439–2446

Campolongo, F., Kleijnen, J., Andres, T., 2000. Screening methods, in Sensitivity Analysis. Saltelli. A., Chan. K., Scott. M. (eds), John Wiley and Sons Publishers, pp.65-89.

Carapezza, M. L., Badalamenti, B., Cavarra, L., et al., 2003. Gas hazard assessment in a densely inhabited area of Colli Albani Volcano (Cava dei Selci, Roma). *Journal of Volcanology and Geothermal Research*, 123(1–2), 81–94.

Chang, K.W., Minkoff, S.E., Bryant, S.L. 2009. Simplified Model for CO₂ Leakage and its Attenuation due to Geological Structures, *Energy Procedia* 1 (2009) 3453-3460.

Chow, F.K., Granvold, P.W., Oldenburg, C.M., 2009. Modeling the effects of topography and wind on atmospheric dispersion of CO₂ surface leakage at geologic carbon sequestration sites. *Energy Procedia* 1 1, 1925-1932, Proceedings of GHGT-9.

Duguid, A., Celia, M., 2006. Geologic CO₂ sequestration in abandoned oil and gas fields and human health risk assessment. Fifth annual conference on carbon capture and sequestration. DOE/NETL May 8-11, 2006.

Endo, Y., Ngan, C., Nandiyanto, A., Iskandar, F., Okuyama, K., 2009. Analysis of fluid permeation through a particle-packed layer using an electric resistance network as an analogy. *Powder Technology*, Volume 191, Issues 1-2, 4 April 2009, Pages 39-46

EPA, 1997. Analysis of Selected Enhancements for Soil Vapor Extraction. EPA-542, R97-007, Office of Solid Waste and Emergency Response.

European Commission, 2009. Directive 2009/31/EC of the European Parliament and of the Council of 23 April 2009 on the geological storage of carbon dioxide and amending Council Directive 85/337/EC, European Parliament and Council Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC, 2008/1/EC and Regulation (EC) No 1013/2006.

Farrar, C.D., Neil, J.M., Howle, J.F., 1999. Magmatic carbon dioxide emissions at Mammoth Mountain, California. U.S. Geological Survey, Water-Resources Investigations Report 98-4217, 34 p.

Grataloup, S., Bonijoly, D., Brosse E., Dreux, R., Garcia, D., Hasanov, V., Lescanne, M., Renoux, P., Thoraval, A. 2009. A site selection methodology for CO₂ underground storage in deep saline aquifers: case of the Paris Basin. *Energy Procedia* 1 (2009) 2929–2936.

Groves-Kirkby, C.J., Denman, A.R., Phillips, P.S., Tornberg, R., Woolridge, A.C., Crockett. R.G.M., 2008. Domestic radon remediation of U.K. dwellings by sub-slab depressurisation: evidence for baseline contribution from constructional materials. *Environment International* 34 (2008) 428-436.

Guo, H., Jiao, J.J., Weeks, E.P., 2008. Rain-induced subsurface airflow and Lisse effect. *Water Resour. Res.*, 44, W07409, doi:10.1029/2007WR006294.

Hayek, M., Mouche, E., Mügler, C., 2009. Modeling vertical stratification of CO₂ injected into a deep layered aquifer. *Advances in Water Resources* 32, 450–462.

Hepple, R.P., 2005. Human Health and Ecological Risks of Carbon Dioxide. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project*, Vol. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, Benson S.M., Oldenburg C., Hoverstein M., Imbus S. (eds). Elsevier Publishing: Oxford; 1143–1172.

Holloway, S., Pearce, J.M., Hards, V.L., Ohsumi, T., Gale, J., 2007. Natural emissions of CO₂ from the geosphere and their bearing on the geological storage of carbon dioxide. *Energy* 32 (2007) 1194-1201.

IPPC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 p.

Jacquemet, N., Le Gallo, Y., Estublier, A., Lachet, V., Von Dalwigk, I., Yan, J., Azaroual, M., Audigane, P., 2009. CO₂ streams containing associated components – a review of the thermodynamic and geochemical properties and assessment of some reactive transport codes. *Energy Procedia* 1 (2009) 3739-3746

Johnson, P.C., Ettinger, R.A., 1991. Heuristic model for predicting the intrusion rate of contaminant vapors into buildings. *Environ. Sci. Technol.* 1991, 25, 1445-1552.

Khan, F., Husain, T., Hejazi, R., 2004. An overview and analysis of site remediation technologies. *Journal of Environmental Management* 71 (2004) 95–122.

Lewicki, J.L., Birkholzer, J., Tsang, C-F., 2007. Natural and industrial analogues for leakage of CO₂ from storage reservoirs: identification of features, events, and processes and lessons learned. *Environ. Geology*, v. 52, p. 457-467.

Louis, F., Guez, F., Le Bacle., C. 1999. Intoxication par inhalation de dioxyde de carbone. Documents pour le médecin du travail N°79, troisième trimestre 1999. INRS. *In french*.

Loureiro, C.O., Abriola, L. M., 1990. Three-dimensional simulation of radon transport into house basements under constant negative pressure. *Environ. Sci. Technol.* 1990, 2, 1338-1348.

Ministry of Ecology, 2007. Note du 16/11/07 du Ministère chargé de l'Ecologie relative à la concentration à prendre en compte pour l'O₂, le CO₂, le N₂ et les gaz inertes. Available at : http://www.ineris.fr/aida/?q=consult_doc/navigation/2.250.190.28.8.3965/4/2.250.190.28.6.9476. *In French*

Monlouis-Bonnaire, J.P., Verdier, J., Perrin, B., 2004. Prediction of the relative permeability to gas flow of cement-based materials. *Cement and Concrete Research* 34 737-744.

NIOSH (National Institute of Occupational Safety and Health), 1976. Criteria for a Recommended Standard: Occupational Exposure to Carbon Dioxide. NIOSH Publication No. 76-194.

Nordbotten, J. M., Celia, M. A., Bachu, S., Dahle., H.K., 2005. Semianalytical solution for CO₂ leakage through an abandoned well. *Environ. Sci. Technol.* 39 (2), 602–611.

Nordbotten, J.M., Kavetski, D., Celia, M.A., Bachu, S., 2009. Model for CO₂ leakage including multiple geological layers and multiple leaky wells. *Environ. Sci. Technol.* 43 (3) (2009), pp. 743–749.

Oldenburg, C.M., Unger, A., 2003. On leakage and seepage from Geologic Carbon Sequestration Sites: Unsaturated zone attenuation. *Unsaturated Zone Journal* 2:287-296 (2003).

Oldenburg, C.M., Unger, A.J.A., 2004. Coupled Vadose Zone and Atmospheric Surface-Layer Transport of Carbon Dioxide from Geologic Carbon Sequestration Sites. *Vadose Zone Journal* 3, pp.848–857.

Oldenburg, C.M., Bryant, S.L., Nicot, J-P., 2009. Certification framework based on effective trapping for geologic carbon sequestration. *International Journal of Greenhouse Gas Control* 3 (2009) 444–457.

- Oldenburg, C.M., Lewicki, J.L., Dobeck, L., Spangler, L., 2010. Modeling Gas Transport in the Shallow Subsurface during the ZERT CO₂ release test. *Trans Porous Med* (2010) 82:77-92 DOI 10.1007/s11242-009-9361-x.
- Patterson, B. M., Davis, G. B., 2009. Quantification of Vapor Intrusion Pathways into a Slab-on-Ground Building under Varying Environmental Conditions. *Environ. Sci. Technol.*, 2009, 43 (3), 650–656.
- Price, P., Oldenburg, C., 2009. The consequences of failure should be considered in siting geologic carbon sequestration projects. *Int. J. of Greenhouse Gas Control* 3 (5) 658-663
- Pruess, K., Oldenburg, C., Moridis, G., 1999. TOUGH2 user's guide. Version 2.0. Report LBNL-43134. Lawrence Berkeley National Laboratory, Berkeley, CA.
- Pruess, K., Garcia, J., 2002. Multiphase flow dynamics during CO₂ injection into saline aquifers, *Environ Geol* 42:282–295.
- Pruess, K., 2005. Numerical Simulation of CO₂ Leakage from a Geologic Disposal Reservoir, Including Transitions from Super- to Sub-Critical Conditions, and Boiling of Liquid CO₂, *Soc. Pet. Eng. J.*, pp. 237 – 248.
- Pruess, K., 2008. Leakage of CO₂ from geologic storage: Role of secondary accumulation at shallow depth. *International Journal of Greenhouse Gas Control* 2 (2008) 37 – 46.
- Pruess, K., 2010. Modeling CO₂ leakage scenarios, including transitions between super and sub-critical conditions and phase change between liquid and gaseous CO₂. *Energy Procedia*
- Pruess, K., 2011a. Modeling CO₂ leakage scenarios, including transitions between super- and sub-critical conditions, and phase change between liquid and gaseous CO₂. *Energy Procedia* 4 (2011) 3754–3761.
- Pruess, K., 2011b. Integrated modeling of CO₂ storage and leakage scenarios including transitions between super- and subcritical conditions, and phase change between liquid and gaseous CO₂. *Greenhouse Gas Sci Technol.* 1:237–247 (2011).
- Robinson, B.A., 2010. Occurrence and attempted mitigation of carbon dioxide in a home constructed on reclaimed coal-mine spoil, Pike County, Indiana: U.S. Geological Survey Scientific Investigations Report 2010–5157, 21 p.
- Rogie J.D., Kerrick D.M., Sorey M.L. *et al.* 2001. Dynamics of carbon dioxide emission at Mammoth Mountain, California. *Earth and Planetary Science Letters*, 188, 535–541.
- Saltelli, A., Ratto, M., Andres, T., Campolongo, F., Cariboni, J., Gatelli, D., Saisana, M., Tarantola, S., 2008. *Global Sensitivity Analysis: The Primer*. Wiley, Chichester, UK 304 pp.
- Silin, D., Patzek, T.M., Benson, S.M., 2009. A Model of Buoyancy-Driven Two-Phase Countercurrent Fluid Flow. *Transp Porous Med*, 76:449–469 DOI 10.1007/s11242-008-9257-1
- Stenhouse, M., Arthur, R., Zhou, W., 2009. Assessing environmental impacts from geological CO₂ storage. *Energy Procedia* 1 (2009) 1895-1902.
- Tissot, S., Pichard, A., 2000. Seuils de Toxicité aiguë - Hydrogène sulfuré (H₂S). Rapport INERIS-DRC-00-25425-ETSC-STi-00DR294 pour le Ministère de l'Écologie et du

Développement Durable et le Ministère de la Santé, de la Famille et des Personnes Handicapées, 39 p. *In French*

Tissot, S., Pichard, A., 2004a. Seuils de Toxicité aiguë – Dioxyde d'azote (NO₂). Rapport INERIS-DRC-03-47021-ETSC-STi-03DR164 pour le Ministère de l'Écologie et du Développement Durable et le Ministère de la Santé, de la Famille et des Personnes Handicapées, 49 p. *In French*

Tissot, S., Pichard, A., 2004b. Seuils de Toxicité aiguë – Monoxyde d'azote (NO). Rapport INERIS-DRC-03-47021-ETSC-STi-03DR163 pour le Ministère de l'Écologie et du Développement Durable et le Ministère de la Santé, de la Famille et des Personnes Handicapées, 18 p. *In French*

UNSCEAR, 1988. Sources, Effects and Risks of Ionizing Radiation. Report of United Nations Scientific Committee on the Effects of Atomic Radiation. Annex A. UNSCEAR, New York, USA, 127 p.

Van Genuchten, M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Sci. Soc.*, 44, 892-898, 1980.

West, J.M., Pearce, J.P., Bentham, M., 2005. Issue Profile: Environmental Issues and the Geological Storage of CO₂. *European Environment* 2005; 15; 250–259.

Zhang, Y., Oldenburg, C., Benson, S., 2004. Unsaturated Zone Remediation of Carbon Dioxide Leakage from Geologic Carbon Dioxide Sequestration Sites. *Unsaturated Zone Journal*, pp 858-866.