

Comparative study of geophysical and soil–gas investigations at the Hartoušov (Czech Republic) natural CO₂ degassing site

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Abstract Our study at this natural analog site contributes to the evaluation of methods within a hierarchical monitoring concept suited for the control of CO₂ degassing. It supports the development of an effective monitoring concept for geological CO₂ storage sites—carbon capture and storage as one of the pillars of the European climate change efforts. This study presents results of comprehensive investigations along a 500-m long profile within the Hartoušov (Czech Republic) natural CO₂ degassing site and gives structural information about the subsurface and interaction processes in relation to parameters measured. Measurements of CO₂ concentrations and investigation of the subsurface using electrical resistivity tomography and self-potential methods provide information about subsurface properties. For their successful application it is necessary to take seasonal variations (e.g., soil moisture,

temperature, meteorological conditions) into consideration due to their influence on these parameters. Locations of high CO₂ concentration in shallow depths are related to positive self-potential anomalies, low soil moistures and high resistivity distributions, as well as high $\delta^{13}\text{C}$ values and increased radon concentrations. CO₂ ascends from deep geological sources via preferential pathways and accumulates in coarser sediments. Repetition of measurements (which includes the effects of seasonal variations) revealed similar trends and allows us to identify a clear, prominent zone of anomalous values. Coarser unconsolidated sedimentary layers are beneficial for the accumulation of CO₂ gas. The distribution of such shallow geological structures needs to be considered as a significant environmental risk potential whenever sudden degassing of large gas volumes occurs.

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Introduction

The potential leakage of hazardous volumes of carbon dioxide (CO₂) from subsurface reservoirs caused by either geogenic sources or man-made subsurface CO₂ storages (see e.g., IEA 2006; Cooper et al. 2009) has consequences on the environment (Holloway et al. 2007). Potential risks have to be assessed to mitigate hazardous situations such as e.g., the high CO₂ gas emissions of Lake Nyos (Cameroon) (Kling et al. 1987), the death of several people and animals in Italy caused by elevated CO₂ fluxes (Beaubien et al. 2003) or the high CO₂ flux that occurred because of a well failure in a natural CO₂ reservoir in Sheep Mountain (USA)

(Lynch et al. 1985). Therefore, detection and monitoring of CO₂ migrations (seepage and leakage) due to preferential pathways (e.g., fractures, porous unconsolidated sediments) in the subsurface are crucial. Adequate methods are required to identify and appraise leaks, to be able to impede any detrimental effects on the environment and mitigate ecological consequences (Holloway et al. 2007; Lamert et al. 2012). However, even if trapping of CO₂ within reservoir rocks takes place and barrier mechanisms are present, the risk of leakage nonetheless still exists (Lewicki et al. 2007). Anomalous CO₂ occurrences located in the shallow subsurface, at surface level and in the atmosphere imply the presence of preferential zones which encourage the migration and accumulation of large gas volumes of CO₂ from deep sources. An effective monitoring program has to be developed and should be comprised of the general detection of emissions and their precise localization and quantification, using appropriate combined methods adapted to the specific field conditions present (Benson 2006).

These previously mentioned factors are especially important in terms of the implementation and monitoring of geological CO₂ storages as part of carbon dioxide capture and storage (CCS) technology. The responsibilities to monitor leakages and migrations of CO₂ at CCS sites are regulated by the EU directive (“CCS-RL”, 2009/31/EG) (European parliament and the council 2009) and e.g., legalized by the framework of the German Act on the demonstration and use of the technology for the capture, transport and permanent storage of CO₂ (KSpG) (Federal German Government 2012).

Nevertheless, some uncertainties (e.g., energy efficiency of the capture facilities, long-term stability of storage sites) and a generally negative public perception impede the establishment of CCS technology (Blohm et al. 2006; Fischeidick et al. 2007). Therefore, a monitoring strategy combining appropriate methods is required to obtain information about potential migration pathways, leakages and the CO₂ distribution in the shallow subsurface in time. Development of such a strategy may lead to more widespread public acceptance of CCS storage applications (Gal et al. 2014; Lewicki et al. 2010; Schütze et al. 2012; Spangler et al. 2010; Wielopolski and Mitra 2010).

Within the MONACO project (monitoring approach for geological CO₂ storage sites using a hierarchical observation concept) (funded by the German Priority Program GEOTECHNOLOGIEN, started in September 2011), a hierarchical concept is being developed and validated to detect and assess areas that are either particularly susceptible to CO₂ seepages from storage formations into shallow subsurface zones or susceptible to leakages into the atmosphere. Various methods such as atmospheric gas and soil–gas analytics as well as geophysics are complementarily combined within an integrative hierarchical structure

of characteristic scales (Sauer et al. 2013b; Schütze et al. 2013).

Here, combinations of soil–gas investigations (e.g., CO₂ concentration measurements, determination of isotopic composition) were used to identify and to observe gas permeable migration zones in shallow sediments. Geophysical methods (e.g., electrical resistivity tomography (ERT), self-potential (SP)) are applied to characterize the heterogeneous subsurface conditions. Using non-invasive geophysical techniques, insights into the sediments and their structural settings are provided. Furthermore, electrical properties (resistivity, natural electrical field distribution) are strongly related to the occurrence of fluids and their migration. Hence, in particular, the geoelectrical methods can contribute information about preferential migration pathways (e.g., Flechsig et al. 2008; Pettinelli et al. 2010; Schütze et al. 2012, 2013). Such methodical combinations using geophysical surveys and gas measurements are successfully applied in volcanic and hydrothermal areas (e.g., Byrdina et al. 2009; Finizola et al. 2010; Lewicki et al. 2003; Revil et al. 2011).

The methods are combined in the hierarchical concept and validated at natural CO₂ degassing sites, or so-called natural analogs, which provide excellent opportunities to evaluate the methods used for the detection and monitoring of CO₂ migration and leakages (Arts et al. 2009; Gal et al. 2012; Sauer et al. 2013a).

Combinations of geophysical (ERT, SP) and soil–gas (CO₂ and radon concentration, $\delta^{13}\text{C}_{\text{CO}_2}$ values) investigations as well as determinations of relevant soil–physics parameters (soil moisture and soil temperature) were performed at the Hartoušov natural CO₂ degassing site. The study aims analyzing and jointly interpreting significant phenomena i.e., anomalous gas occurrences and presence of permeable structures, and to define the diffuse degassing zone in the field. Repeated measurements (SP, CO₂ concentration, soil temperature and moisture) were performed under various weather conditions which allowed us to evaluate the influence of soil properties and to what extent meteorological and environmental conditions affected our measured parameters. Furthermore, our study aims to highlight the importance of subsurface investigation as monitoring concept to assess potential risks and to emphasize the significance as a tool for evaluating the appropriateness of our methods. Thus, repeated measurements act as a quality control for the applied methods.

Hartoušov natural CO₂ degassing site

The Hartoušov mofette field is a natural degassing site that constitutes a suitable natural laboratory to investigate CO₂ degassing processes along preferential pathways, due to its

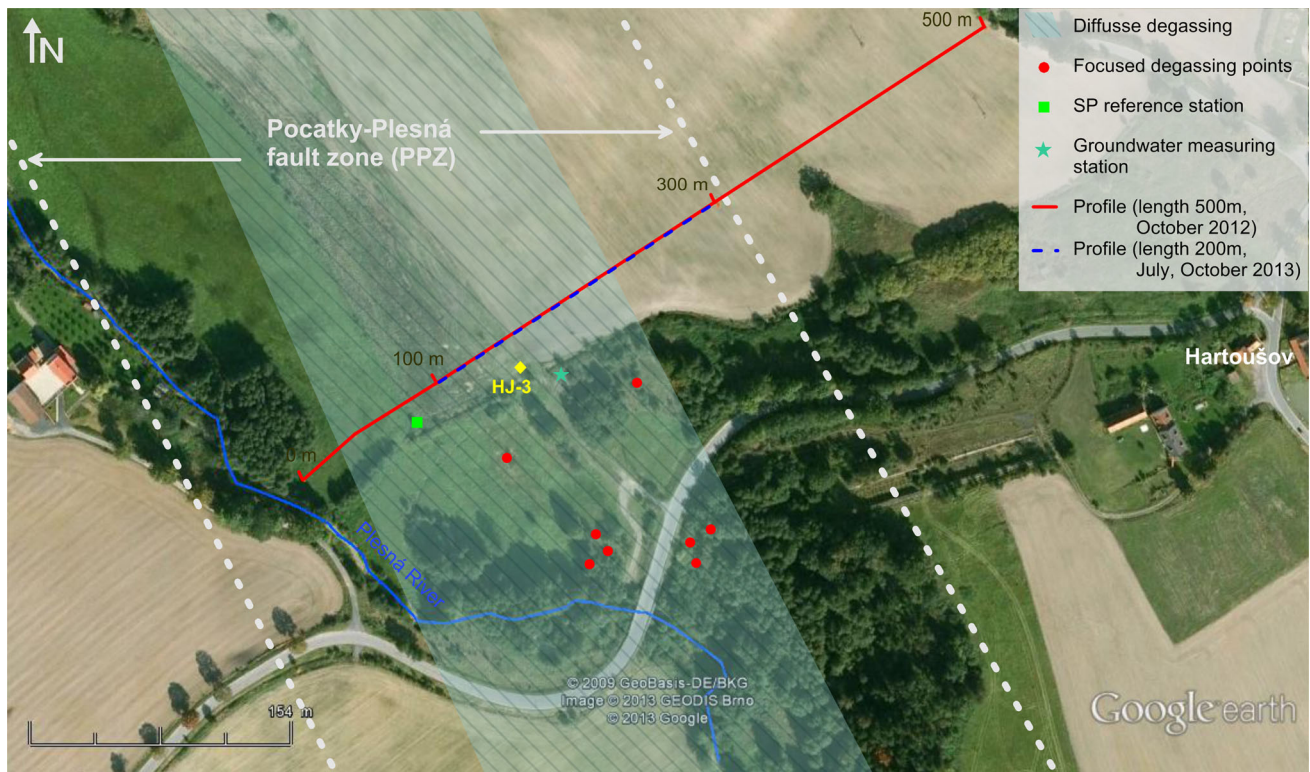


Fig. 1 The generalized map of the Hartoušov investigation area shows the zone of diffuse degassing and locations of focused CO₂ releases. The site is contained within the Počatky-Plesná fault zone. The mofettes of Hartoušov are situated at a NNW striking segment of this sinistral N–S trending wrench fault (according to Bankwitz et al.

2003). The investigation profile traverses the area from the WSW to the ENE and crosses the PPZ. The location of the borehole HJ-3 (Czech Geological Survey 1992, www.geofond.cz), the self-potential (SP) reference station and the groundwater measuring station is highlighted

diffuse and focused degassing structure. This enables us to validate methods included in the hierarchical monitoring concept.

The site is situated in the Cheb Basin (NW Bohemia, Czech Republic). This neogene small intra-continental basin is located in the West of the ENE trending Eger/OHře Rift, a part of the European Cenozoic rift system (Mal'kovský 1987; Ziegler 1992). Its crystalline basement consists of granitoids and crystalline schists (Fiala and Vejnar 2004). In the Cheb basin a lot of CO₂ degassing locations are known. Investigation of the isotope ratios (³He/⁴He, δ¹³C_{CO2}) confirmed the origin of CO₂ from a magmatic reservoir in the upper mantle (e.g., Weinlich et al. 1999; Bräuer et al. 2004, 2011).

In the Eastern part of the basin along the N–S striking Počatky-Plesná fault zone (PPZ), areas of high CO₂ emanation, so-called mofettes (e.g., Hartoušov and Bublák mofette fields), occur (Bankwitz et al. 2003; Kämpf et al. 2013). The Plesná River partly adopts the PPZ and borders the Hartoušov investigation area to the West and Southwest (Fig. 1).

The basin is filled with lacustrine and fluvial sediments. A basic description of the lithostratigraphic layers can be

derived from the 13.8-m deep borehole HJ-3 (see Fig. 1; Data from the Czech Geological Survey 1992, www.geofond.cz). The basal Miocene clayey sediments are located at a depth of 9 m below the surface level. They are overlain by 8 m thick late Pliocene and Pleistocene fluvial sand and gravel layers with varying clay contents. Holocene loamy and clayey mixed sediments form the upper layer, to a maximum depth of 1 m (Flechsigt et al. 2008; Schütze et al. 2012; Špičáková et al. 2000). Upward gas migration through tectonic faults and release into the atmosphere is influenced by various environmental conditions of the near-surface (groundwater level, sediment composition) which results in a diffuse or focused degassing in the investigation area. This diffuse degassing can also be identified in the field by vegetation anomalies (Flechsigt et al. 2008; Sassmannshausen 2010).

Data acquisition and methods

This study investigates a profile of length 500 m which traverses the Hartoušov site in a WSW to ENE direction. The profile crosses a NNW striking segment of the

prominent Počátky-Plesná fault zone. Data acquisition at the natural CO₂ degassing site was carried out in October 2012 and repeated in July and October 2013 using a combination of soil–gas measurements and geophysical applications. The determination of sampling points along the profile was performed using a handheld GPS (accuracy of ±5 m), defined significant points and a surveyor's tape to define the sampling distances. Hence, our repeated investigation during each campaign cannot guarantee identical locations of measurements and possibly evolve small-scale local variations. Firstly, gas measurements were performed to generally characterize the soil CO₂ concentrations along the profile. Subsequently, geophysical investigations were undertaken to obtain information about the subsurface characteristics (e.g., geological structures, sediment properties) and responsible permeable pathways liable for CO₂ presence. Soil physics determinations were undertaken to identify several seasonal variations in the soil. Furthermore, meteorological conditions were considered and will be included in our interpretation. Thus, specified meteorological effects, i.e., air pressure, precipitation or the distinctive ground water level during and prior to the campaign can be controlling factors. In October 2012 and July 2013, a groundwater level of 2.6 m was observed and in October 2013 a level of 3.1 m below ground level was measured.

Gas measurements (CO₂, ²²²Rn, δ¹³C_{CO2})

CO₂ concentration

In October 2012, the CO₂ concentration was measured with a sampling distance of 5 m along the profile. A representative section of 200 m length was repeatedly measured during July 2013 and October 2013 with the same spacing. A mobile gas analyzer (ANSYCO GA94) was used that measures CO₂ in an effective range of 0–100 % with appropriate accuracies of ±0.5 to ±3 % according to measuring ranges. The device operates based on the principle of infrared absorption to efficiently determine the carbon dioxide (CO₂), oxygen (O₂) or methane (CH₄) concentrations. The soil–gas was sampled at a depth of 0.4–0.8 m, similar to Kämpf et al. (2013). There were several sampling points where deeper measurements were impeded or not possible with our equipment due to coarse gravel ground, non-permeable clay layers (which prevented the extraction of gas samples) or perched water presence due to tiny intermediate clay layers in the vadose zone. Hence, the sampling was carried out for all points in shallow depths to allow them to be compared. However, biogenic and atmospheric influences on the concentrations cannot be completely excluded. However, the results of Rennert et al. (2011) show the significance of soil–gas

samples also taken from shallow depths between 0.4 and 0.6 m. However, the CO₂ concentration here is controlled by several parameters such as the geological supply, the soil conditions or properties of the sediments (see Finizola et al. 2002; Flechard et al. 2007 or Vodnik et al. 2009).

Radon measurements

Radon measurements were performed primarily to verify the assumption of coexistent elevated CO₂ and ²²²Rn concentrations e.g., due to upward gas migrations through faults (see Beaubien et al. 2003; Weinlich et al. 2006; Michel-le pierres et al. 2010). The radon (²²²Rn) measurements were only undertaken in July 2013 using the RTM 1688-2 active measuring device (SARAD, Germany) and the radon fast mode.

At identified points of higher CO₂ concentration, the radon concentration was investigated (in depths of up to 0.6 m). Measurement in greater depths (>0.6 m) was restricted due to the presence of perched water caused by higher clay content layers—which unfortunately limits the comparability of the data and does not guarantee the safety of the instrument. Six sampling points along the profile (100, 120, 160, 175, 200 and 280 m) were defined. Sampling was repeated several times at each point and measurement took approx. 30 min until the radon concentration leveled out at a maximum value or decreased again. In only one instance did sampling require almost a full hour to perform.

Isotope measurement

The measurement of the δ¹³C values aimed to characterize the origin of the soil CO₂ along the Hartoušov profile (see Fig. 1, blue dashed highlighted profile). The soil CO₂ was studied along the 200 m segment of the profile in July 2013. In order to determine both the soil CO₂ concentration and the δ¹³C values of the CO₂, the CO₂ concentration was initially measured in a 0.5-m deep borehole using a mobile IR gas analyzer (ANSYCO GA94). Then a capillary tube reaching down to a depth of 0.5 m was inserted into the borehole. The borehole was then plugged and an evacuated glass vessel (~350 ml volume) with Kontes valves was connected to the capillary tube. After waiting for approx. 30 min, the gas was sampled. In the lab, the filled glass vessel was connected to vacuum equipment. CO₂ and water were separated from the non-condensable gas by a two-step cryogenic separation at liquid nitrogen temperature. CO₂ was separated from water using a mixture of dry ice and alcohol at −78 °C. The CO₂ was filled into small glass containers. The δ¹³C values were analyzed using a Delta V isotope mass spectrometer with dual inlets and related to PDB (δ¹³C standard error <0.05 ‰). The total error for

isotope measurement and sample handling/procedure was ± 0.2 ‰, when sampling was repeated 1 h later.

Geoelectrical observations (SP, ERT)

The self-potential (SP) method is an efficient applicable method to investigate contamination sites, to indicate groundwater flows or to map structures (faults and degassing structures) at volcanoes (Jardani et al. 2007; Zlotnicki and Nishida 2003). Subsurface processes, such as oxidation–reduction reactions at ore bodies or chemical gradients in water-saturated zones (electrochemical potential), movements of ionic fluids through porous media (electrokinetic potentials) and temperature gradients (thermoelectric potential) can act as sources of electrical fields measurable at ground surface level.

Obviously, it is very difficult to separate the various simultaneous sources of SP signals in the measured data, which are induced by a combination of electrokinetic (=streaming), electrochemical or thermoelectric coupling effects. The self-potential signals caused by streaming potentials can provide information about transported fluids during water infiltration or strong upward evaporation in permeable geological structures (Corwin and Hoover 1979; Revil et al. 1999a). Hence, the SP can indicate zones which are either more or less permeable (Byrdina et al. 2009; Flechsig et al. 2008; Zlotnicki and Nishida 2003). In the context of ascending CO₂, streaming potentials could be possible parameters that feature CO₂ migrations or could at least be indicators of gas transport in the soil (Revil et al. 1999b). However, the identification of influencing subsurface properties (e.g., porosity, gas or water saturations, conductivity) on the SP signal is not possible using this method alone, other diverse investigation methods (e.g., ERT) must be applied (Flechsig et al. 2008; Jardani et al. 2007).

In October 2012, self-potentials were quantified using two non-polarizing Cu/CuSO₄ electrodes along the 500 m profile at 5 m measuring intervals while CO₂ concentration was simultaneously determined. In July 2013 and October 2013, SP measurements were repeated at the representative 200 m section of the profile. A voltmeter (37XR Digital Multimeter, Meterman Test Tools) with a high internal impedance of 10 M Ω and a resolution of 0.1 mV was used to investigate the electric potential difference between the survey and reference electrodes. The contact resistance between the reference station and the survey electrode was inspected at each point to eliminate coupling problems with the ground and for the estimation of soil moisture conditions. At the reference station, a third permanent electrode was installed to consider diurnal variations of SP. The variations recorded during a single day were in an acceptable range of approx. ± 2 mV.

Electrical resistivity tomography (ERT) is a non-invasive technique that is applied for several engineering and environmental problems. This method provides information about the subsurface electrical resistivity pattern using injections of electrical currents and by measuring electric voltages. The spatial resistivity values depend on the geology and sediment properties, soil composition, water saturation and the electrolyte concentration (Knödel et al. 2007; Reynolds 1997).

In October 2012, data acquisition was performed using a GMS150 multi-electrode device (GeoSys, Leipzig). The investigation of the 498 m long profile was undertaken by designating five sub-profiles—each with 75 electrodes and an electrode spacing of 2 m. The Wenner-alpha configuration was applied due to its good signal-to-noise ratio for larger offsets and good vertical resolution (Dahlin and Zhou 2004). The Wenner-alpha configuration was applied using a four-point alignment with a distance factor between the electrodes ranging from $n = 1$ to 16 to realize variable depth investigations. The measured resistivity along the profile reveals values of 3–1,400 Ω m with a measuring error of approx. 3 %. The inversion processing of 3,549 data values was performed using the Res2DInv inversion program (Loke and Barker 1996a, b, Geotomo, Malaysia). The final resistivity model represents the characteristics of the subsurface up to a calculated maximum investigation depth of 18 m below ground level. An inversion error (RMS) of 5.2 % for the final iteration was achieved, thereby reflecting the quality of the calculated model.

Soil physics

The soil temperature and soil moisture were determined as assumed potential influencing factors on the geophysical and soil–gas parameters. The soil temperature was measured in the upper soil zone (depth of 0.1 m) simultaneously as SP values were recorded in October 2012 and July/October 2013. A PT100 insertion thermometer was used. The soil moisture, simultaneously determined as the soil temperature and SP, was measured in a depth of approx. 0.1 m using the TRIME-HD instrument (Eijkelkamp Agrisearch Equipment). This instrument operates according to the time domain reflectometry (TDR) to determine the water content.

Results and discussion

Results of the measurements at the Hartoušov mofette field in October 2012 (Fig. 2) provide an insight into the subsurface characteristics of the investigation area. Information about the shallow structures of the traversing PPZ beneath the earth's surface and the diffuse degassing are

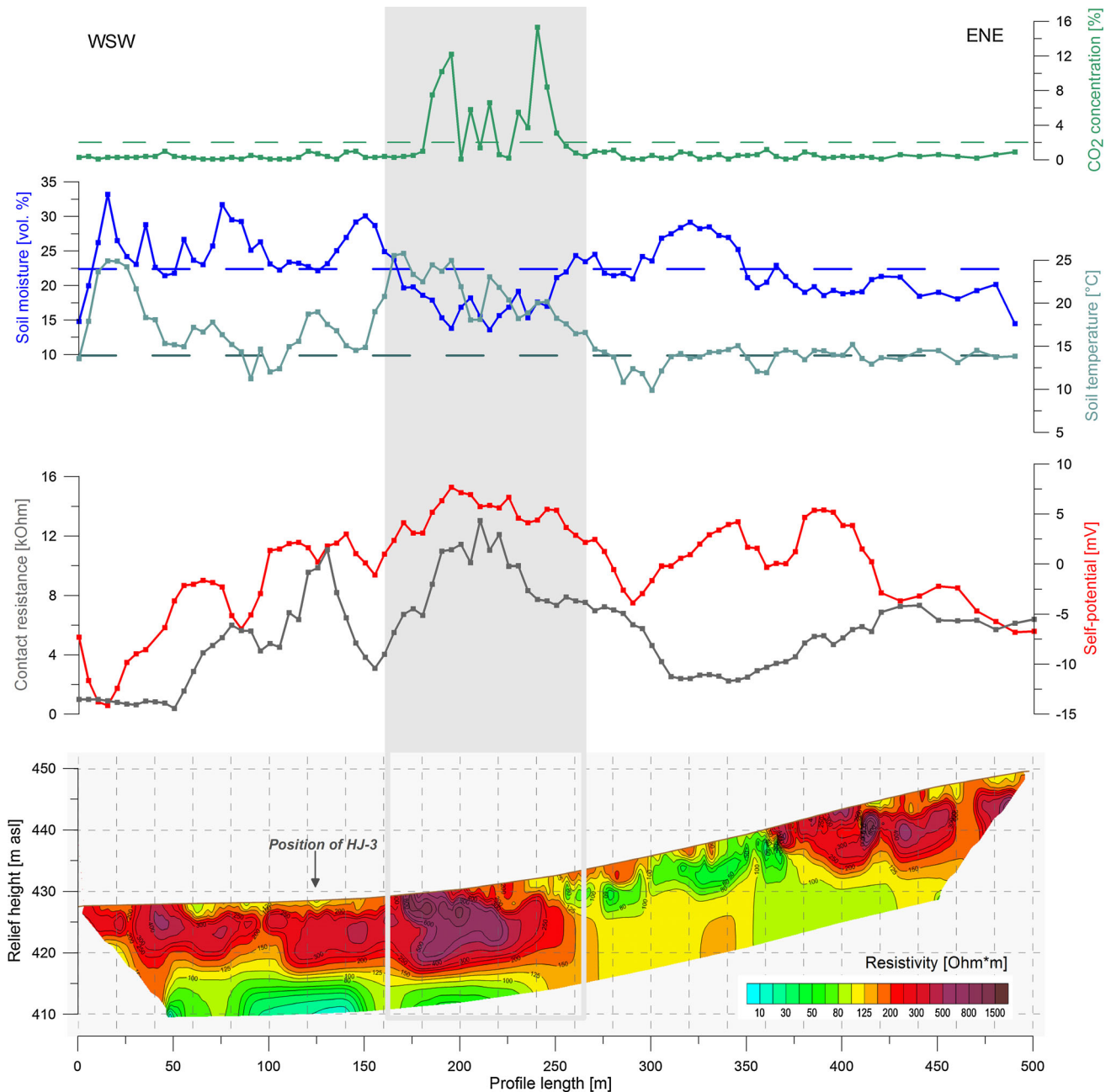


Fig. 2 The diagram represents observed values of CO₂ concentration, soil temperature and moisture, self-potential and contact resistance measured in October 2012 along the profile. The soil temperature values are trend corrected and applied to the average value of the soil temperature along the profile. Apart from the CO₂ concentration, the presented values are moving averaged values (averaged over 3 values) to smooth the curves. In the soil moisture

and soil temperature diagram, the averaged values along the profile are displayed (*dashed lines*). The lower model represents the resistivity distributions up to a depth of 18 m along the profile. The mentioned HJ-3 borehole reflecting the sediment characteristics up to the depth of 13.8 m is roughly located at approx. 10 m distance. The zone of distinctive values is highlighted in *gray*

identifiable. Focused repetition measurements carried out in July and October 2013 on an appropriate representative part of the profile showed similar trends, irrespective of whether or not temporal dynamics of the parameters were registered.

The CO₂ concentration measured in October 2012 varied along the profile from 0.1 to 15.3 %. A prominent zone of high concentrations (approx. 170–270 m) (see Fig. 2) is observable. Nevertheless, this highlighted region shows strong variations up to 12 % CO₂ concentration within a

5–10 m distance and indicates diffuse degassing. During the field measurements, small-scale sediment variations at the surface were obvious which may be responsible for small-scale variations of the CO₂ concentrations.

The other parts of the profile have no prominent features. Starting in the WSW and ending in ENE, CO₂ concentration values mostly not higher than 2 % are detected and signify no prominent anomalies (Schütze et al. 2012).

The soil moisture and temperature of the shallow sub-surface show distinctive variations along the profile and prominent patterns, especially in the highlighted zone between 170 and 270 m. Here, soil temperatures (trend corrected) reach values between 15.2 and 24.9 °C and minimum soil moisture values between 10 and 15 vol. % occur (see Fig. 2). In the ENE direction, the values fluctuate around the average value of 13.9 °C. As the soil moisture fluctuates in the WSW direction, the soil temperature also varies strongly. Such strong temperature changes over short distances are also reported for this region by Tank et al. (2005). The soil moisture, however, shows nearly completely opposite trends. Highest moisture values occur in the WSW direction and decrease almost completely below the average value (22.4 vol. %) in the ENE direction. Due to the high variations of our values (soil moisture, soil temperature, SP, contact resistance), a moving average window to smooth the curves was applied.

The results of the complementary self-potential measurements show distinctive trends, with positive as well as negative anomalies occurring. Rather negative self-potential signals occur in the WSW direction and at the end of the profile in the ENE direction. In the zone of high CO₂ concentrations between 170 and 270 m, positive self-potentials occur and maximum values up to 10.1 mV at 190 m were detected. The step to -4.4 mV between 275 and 300 m is also prominent.

Additional parameter contact resistance, which acts as a factor for ground coupling, provides indications of the soil properties—especially soil moisture. Evidently the contact resistance shows approximately opposite values to the soil moisture results, starting with low values in moist zones close to the Plesná River and reaching maximum resistance values in the highlighted zone, where the soil moisture attains its lowest values along the profile.

In the lower part of Fig. 2, the resistivity distribution reflects the sediment variations in the investigation area. The upper zone of the resistivity model up to a depth of 1 m represents low resistive sediments of values <150 Ωm and conforms to the Holocene deposits of clayey and loamy mixed sediments (according to stratigraphic information derived from borehole HJ-3). However, this layer is discontinuous in the field and exists mainly in the WSW direction from 60 to 160 m and in the ENE region from

410 to 498 m. An underlying layer of sand and gravel sediments is widely present along the profile and corresponds with the high resistivity (>150 Ωm) up to depths of approx. 9 m. In the absence of the Holocene layer, the coarser sediments are present at surface level as obviously between 160 and 230 m. The downward following Miocene layer of clayey sediments and clay stone corresponds with the decreasing resistivity from depths >9 m. A prominent area of low resistivity between 250 and 375 m (<125 Ωm) separates the zones of higher resistivity. This part does not correspond with the layered sediment pattern. Here, the resistivity values suggest the presence of a rather fine-grained filling. Consistently high CO₂ concentration anomalies are recognizable and denote the existence of porous zones—in this case, coarser unconsolidated sediments which offer migration paths and act as a reservoir for the ascending CO₂ from deeper sources (Lamert et al. 2012; Sauer et al. 2013a; Schütze et al. 2012). The coincidence of the coarse-grained sediments with lower clay content and the presence of gas phase in pore spaces provide evidence of the higher resistivity values, as stated by Byrdina et al. (2009) or Lamert et al. (2012). Therefore, the unconsolidated sediments and their porosity are the crucial conditions for the accumulation of CO₂ gas and its release into the atmosphere. Fine-grained, conductive sediments at the near-surface would impede CO₂ release (Schütze et al. 2012).

The repeated measurements from July and October 2013 show similar results with regard to the location of higher CO₂ concentrations (see Fig. 3). The zone of increased CO₂ concentration between 170 and 270 m remained present. However, the amplitudes of the gas anomalies in soil were much higher in July and October 2013. In July, concentrations of up to 92 % at 175 m were observed. Similar values were achieved in the results for October 2013, reaching concentrations of up to 70.3 % at 175 m. Furthermore, some small isolated anomalies e.g., at 265 m of 18.9 % are particularly visible in October 2013. We have to take into account that also small deviations in sampling locations and depths could be responsible for varying values over time and cannot be neglected in interpretation. Furthermore, the agricultural land use and varying soil moisture levels affecting the degassing and sampling scenarios have to be considered. The groundwater level has an impact on measured CO₂ in shallow depths; e.g., the groundwater level in October 2012 was higher (2.6 m) than during other campaigns and lower CO₂ concentrations were measured. In general, the greater the water volume, the more CO₂ is dissolved and, in turn, the less CO₂ reaches the unsaturated zone. The identification of such challenges in monitoring applications is important and required for the observation of CCS sites.

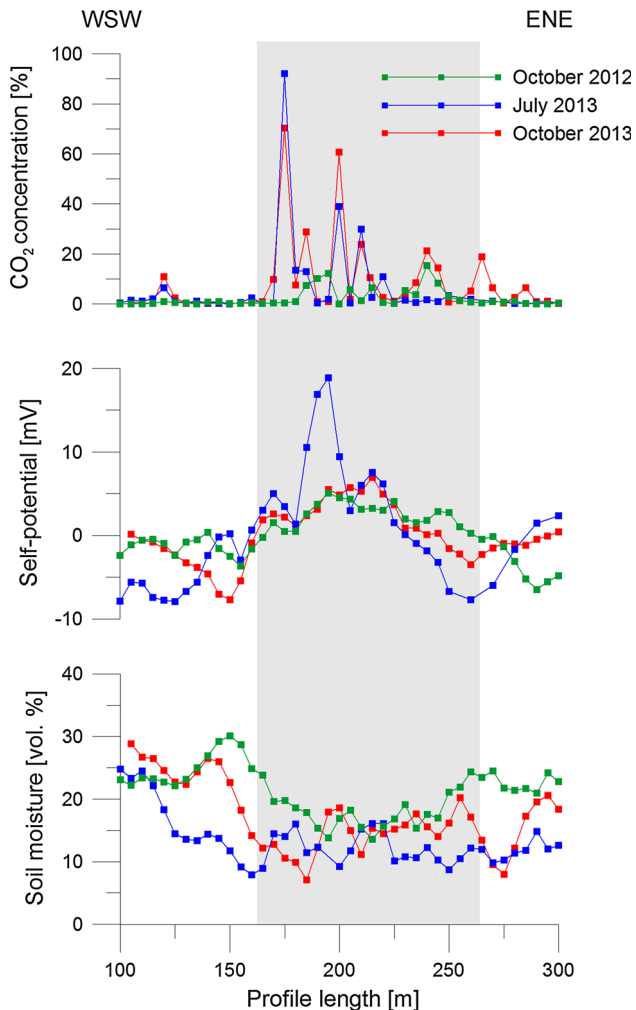


Fig. 3 These diagrams compare the CO₂ concentrations, self-potentials, and soil moisture values from October 2012, July 2013 and October 2013 between 100 and 300 m along the profile. The area highlighted in *gray* points to highest CO₂ concentrations, positive SP anomalies and lowest soil moistures here. The self-potential values are processed values. From the self-potential value at each point, the average of all values was subtracted to generate an equal level for all campaigns what was not given due to specified seasonal drifts. The presented values (SP, soil moisture) are moving average values (averaged over 3 values)

The self-potential signals show a similar trend over time, irrespective of whether the value levels were different or not. In Fig. 3, to guarantee comparability, the self-potential values were adjusted to obtain an equal level during each campaign. The highlighted zone again reveals positive anomalies. Generally negative values occur in ENE and WSW direction. Extreme changes within short distances along the profile and e.g., the peak at 195 m in July 2013 are distinctive. Between 250 and 275 m, a relevant negative anomaly occurs exactly where the resistivity changes to lower values. The soil moisture represents a similar trend during each campaign, with lowest values occurring between 170 and 270 m in the coarse sediments.

In October 2013 the moisture was lower (average along the profile 17.7 vol. %) than in October 2012 (21.3 vol. %) and the lowest value was achieved in July 2013 (13.7 vol. %).

Obviously, the subsurface along the profile exhibits prominent zones of beneficial properties for high CO₂ concentrations. The pattern of higher resistivity and its appropriate sediment characteristics (according to borehole HJ-3, Czech Geological Survey 1992) seem to correlate with increased accumulation of CO₂, with the lower soil moisture and correspond with positive self-potential anomalies over time.

Controlling factors for the temporal dynamic of the CO₂ concentration in soil may be varying soil moisture and meteorological conditions (Flechar et al. 2007; Jassal et al. 2005; Sauer et al. 2013a) as well as the variable geological supply (Kämpf et al. 2013).

High water content in unconsolidated sediments impedes gas migration in the pores (Sauer et al. 2013a). Therefore, higher soil moisture values observed in October 2012 cause a lowering of the CO₂ gas diffusivity due to water-filled intergranular spaces in shallow depths (Ball et al. 1999; Jassal et al. 2005). E.g., fine-grained sediments such as clay particularly retain the moisture and in turn reduce CO₂ release into the atmosphere due to high impermeability (Sauer et al. 2013a). However, a higher accumulation of CO₂ in the subsurface can be initiated, assuming that these sediments act as impermeable layer against release (Finizola et al. 2002; Schütze et al. 2012). The meteorological conditions control the soil moisture and accordingly the CO₂ concentration. For instance, the dry conditions in July 2013 caused the evolution of more pore space in the sediments compared to other months and encourage greater CO₂ dispersion in shallow depths (Jassal et al. 2005; Schütze et al. 2012). However, the soil moisture is determined by the appropriate sediment and soil properties e.g., by the water retention effect i.e., what is reduced in coarse sediments (Saxton and Rawls 2006; Hillel 2006) as can be seen in the prominent zone. The changes in CO₂ concentration can be caused by deep-seated processes and/or changes in near-surface conditions. Accordingly, blocked paths in shallow depths can affect onward CO₂ migration to other permeable zones or blocked paths can be opened over time, whereby an increased accumulation is initiated at other positions (Holloway et al. 2007). We observed this phenomenon in our measurements from July 2013.

The self-potential signals specify significant features such as transport processes in appropriate sediment compositions and structures. Higher SP values and higher resistive sediments correspond along the profile. Byrdina et al. (2009) describe self-potential and resistivity results which are assumed to be related to preferential pathways for fluids. Revil et al. (1999b) explain that SP values

increase with grain size and gas saturation, as we observed in the field. The positive anomalies in the field are potentially driven by an upward gas flow associated with transport of a water phase within the permeable zones, which has also been observed by Byrdina et al. (2009), Revil et al. (1999b) and Sauer et al. (2013a).

However, the negative self-potentials that occur in the WSW of the profile may be related exclusively to water infiltration and drainage processes (Jardani et al. 2007). In zones with high CO₂ presence, the water infiltration is most likely superimposed by upward fluid transport (Sauer et al. 2013a). The SP trend is relatively similar during each campaign, differing only due to seasonal meteorological and subsurface conditions (rain, water infiltration, barometric pressure, groundwater flow). This trend simultaneously reveals that the evolving electrical potentials along the profile are driven by sediment porosities and resistivity (Jardani et al. 2007; Revil et al. 1999b). Hence, the SP signals indicate the hydraulic properties of the subsurface. However, the interpretation of distinctive SP signals is not simple due to various sources of electrical potentials in the subsurface—for instance, presence of clay and the previously mentioned dissolution effect or the groundwater flow (Maineult et al. 2006; Schütze et al. 2013; Zlotnicki and Nishida 2003). The generation of self-potentials is a complex process and e.g., Byrdina et al. (2009) showed several self-potential pattern related to fluid active fault zones. The positive SP anomaly indicates the fault zone location (100–450 m) caused by upward fluid migration. However, infiltration of meteoric water causes negative anomalies which superimpose themselves onto the SP signal. This is why we assume a downward flow of water at 250–375 m profile length.

The qualitative explanation of gas migration processes using self-potential measurements is not yet possible. SP along with ERT can help provide insights about preferential pathways which are responsible for seepage and leakage of CO₂.

Figure 4 summarizes the main information and points to processes that take place in the Hartoušov CO₂ degassing area. The subsurface along the profile is characterized by layered sediments of the Miocene, Pleistocene and Holocene age. The transecting fine-grained zone reflects the escarpment of the traversing Počátky-Plesná fault zone (PPZ). The escarpment of the PPZ steeply dips in the western direction and morphologically forms a slope in the Hartoušov area, as was clearly seen in the field (Bankwitz et al. 2003). We assume that this scarp is smoothed and filled with fine-grained material due to gradual erosion and deposition processes.

CO₂ degassing in the area relates to the existing faults, whereby migration pathways for seepage into shallow subsurface zones are given. The deep-reaching fault zones

are responsible for the ascent of CO₂ from the upper mantle into shallow permeable zones (Kämpf et al. 2013).

Evidence of CO₂ migration from deep sources was on the one hand provided by the isotopic composition of soil-gas and otherwise by the coexistence of upward migrating geogenic gases (e.g., ²²²Rn) along preferential paths. The ²²²Rn concentration was analyzed to check the assumption of coexistent elevated CO₂ and ²²²Rn concentrations in the shallow subsurface. Curve B in Fig. 4 represents the radon concentration and suggests high radon values (max. 16,220 Bq/m³) coincide with high CO₂ concentrations (max. 92 %) (curve A) e.g., at 175 m profile length.

The amount of radon in the soil is controlled by the migration intensity of a carrier gas because radon itself has a low intrinsic mobility. In this case, the CO₂ acts as a carrier gas for radon (²²²Rn) (Etiopie and Martinelli 2002; Gal and Gadhia 2011; Yang et al. 2003). The high concentration e.g., at 175 m reflects the strong CO₂ migration at higher velocities from deep sources whereby the short-lived radon (half-life $T_{1/2} = 3.8$ days) is simultaneously carried upwards within permeable structures and causes significant anomalies at ground level (Beaubien et al. 2003; Weinlich et al. 2006, 2013). Etiopie and Martinelli (2002) discuss the relation of U-rich soil and bedrock as granitic zones and high Rn concentration. In the Cheb basin the primary radioactive decay is on the one hand related to the basement rocks of granitoids and crystalline schists but otherwise, it is likely that it originates from near-surface sediments. The resulting radon concentrations are relatively moderate due to low radioactive sediments at the Cheb basin or the large distance between the basement rocks through to the thick sediment layers (maximum sedimentary fill of 280 m according to Peterek et al. (2011)) and the effect of its relatively short-lived characteristics.

The measured values correspond with the radon risk classification of the Czech Republic (Hartoušov, 10–40 kBq/m³) provided by the Czech Geological Survey (www.geology.cz).

The deep source of CO₂ is confirmed by the isotope signature of the soil-gas. The δ¹³C values (curve C, Fig. 4) vary along the profile from −23.5 to −0.6 ‰. The δ¹³C signature of the magmatic CO₂ escaping in the Cheb basin was determined to be approx. −2 ‰ based on characterization of the free gas at wet mofettes with high gas flows close to the diffuse degassing structure (Bräuer et al. 2004).

Detailed time series studies at degassing locations along the PPZ showed that the magmatic signature may be modified by fractionation processes due to CO₂–water interaction. The degree of this affect depends on the gas/water ratio, pH value and conductivity. At small gas flows δ¹³C values > −2 ‰ were observed (Bräuer et al., 2011). The first δ¹³C values of soil-gas from the Hartoušov

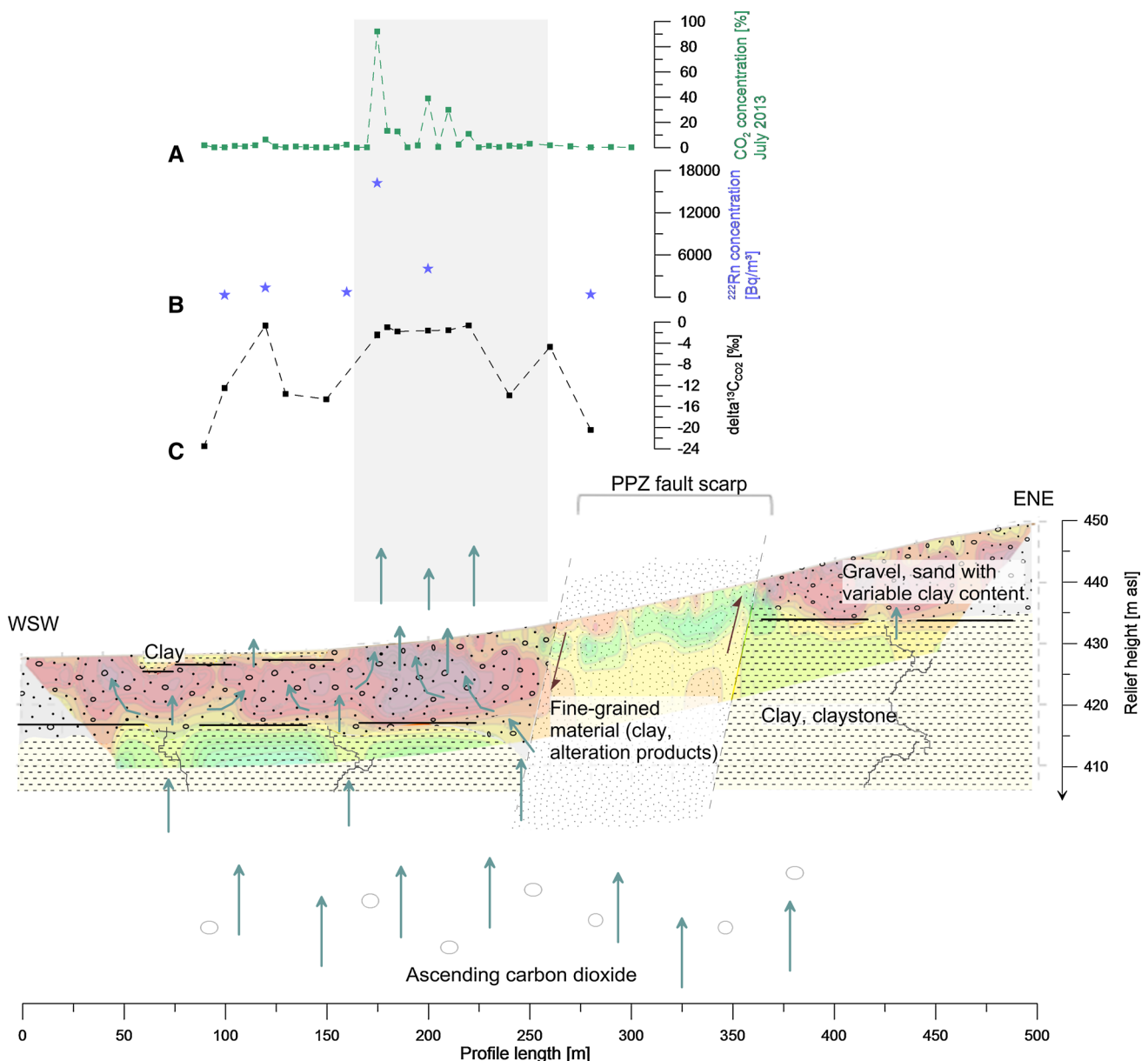


Fig. 4 A model of the subsurface along the profile traversing the Hartoušov diffuse degassing area is presented. Distinctive pattern of diverse sediments and the PPZ escarpment is visible. The sediment classification was defined according to the lithostratigraphic layers of the HJ-3 borehole and the resistivity distribution (Fig. 2). The escarpment zone is filled by fine-grained sediments and intersects the layered subsurface. The CO₂ ascends due to the existing fault systems and follows permeable zones before being released into the atmosphere. The fault scarp is filled with fine-grained sediments which restrict gas migration. We assume in the vicinity of secondary permeable structures, small channels allow the upward gas migration

through clay/claystone into the gravel/sand layer. Clearly, the sediment composition has a great impact on gas migration and leakage. If clay dominates in the upper subsurface zone, the gas accumulates beneath and lower CO₂ concentration occurs due to the sealing mechanism. The accessory curves of the CO₂ (a) and ²²²Rn (b) concentration as well as the δ¹³C signatures (c) of July 2013 represent the ongoing processes in the subsurface and the origin of the upwardly traveling gas. Simultaneously occurring high CO₂ and radon concentrations evidence the origin of the gas from deeper sources. This is confirmed by δ¹³C signatures

predominantly mantle-derived origin of the gas. Kämpf et al. (2013) describe a substructure of the PPZ where high CO₂ fluxes correlate with isotope signatures (δ¹³C; ³He/⁴He) as found at gas-rich wet mofettes. Our profile crosses this structure and shows similar recorded CO₂ concentrations and δ¹³C values. Simultaneously

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determined CO₂ fluxes can improve the interpretation of measured δ¹³C values. Due to high CO₂ fluxes, the admixture of the biogenic-produced CO₂ as well the effects of isotope fractionation due to CO₂/water interaction can be neglected (Kämpf et al. 2013). Sampling sites with lower CO₂ concentrations show decreased δ¹³C values and indicate the predominantly admixture of biogenic-produced soil CO₂ (Bekele et al. 2007; Parks et al. 2013). The CO₂ flux along the profile was not measured and should be envisaged during further campaigns. At this site, e.g., Flechsig et al. (2008) and Sauer et al. (2013a) found a correlation between logarithmic CO₂ concentrations and logarithmic CO₂ fluxes for elevated CO₂ concentration values (>3 %). Chiodini et al. (2008) stated that lower CO₂ concentrations reflect the biogenic effects in soil which coincides with low δ¹³C values.

As previously stated, the gas follows preferential structures such as fractures or faults, migrating and accumulating in inter-granular pore spaces of coarse-grained sediments from where it can leak into the atmosphere. Accordingly, a model presented by Sauer et al. (2013a) depicts high CO₂ concentrations above existing faults and decreasing concentrations with distance from the permeable zone as it is observed along the profile.

Furthermore, the resistivity contrasts in the area simultaneously suggest changes in permeability, mainly due to variations in clay and water content (Schütze et al. 2013). Therefore, higher porosity sediments are preferential for CO₂ emission, resulting in more dispersed gas leakage, as we observed in the field (Schütze et al. 2012). In contrast, fine-grained sediments lead to an accumulation of CO₂ in below existing porous sediments where, due to the constructive pressure of the ascending CO₂, small channels can evolve and a more focused degassing occurs (Flechsig et al. 2008; Sauer et al. 2013a). These fine-grained sediments (such as clay) in shallow depths along the profile (between 50 and 150 m) act as retaining layer due to decreased permeability, especially in conditions of high moisture, and cause the little or no CO₂ seepage to surface level.

Concluding remarks

- This study highlights the importance of detecting preferential degassing pathways. Porous zones can act as reservoirs for quantities of gas volumes and therefore can be constituted as a potential risk. In particular, accumulation under pressure within a sealed secondary reservoir poses the danger of a sudden degassing into the atmosphere. The opening and change of paths due to internal or external influences can affect the migration of CO₂ and potentially cause dangerous leakages at other positions. A fortiori, it is important to precisely

analyze the subsurface, especially in areas of geological CO₂ storages and to monitor the location with a combination of methods adapted to the circumstances present at the storage site, so as to minimize any potentially catastrophic effects on the environment.

- The combined geoelectrical and soil–gas measurements provide various specific information about the subsurface and revealed that coarse unconsolidated sediments and permeable structures offer migration and accumulation options for ascending CO₂ from deep sources and prospective ways for release into the atmosphere.
- In the Hartoušov mofette field, locations of high CO₂ concentration in shallow depths are related to positive self-potential anomalies, low soil moistures and high resistivity distributions, as well as high δ¹³C values and increased radon concentrations. The CO₂ rises through the deep-reaching fault system into shallow depths and accumulates preferentially in coarse sediments. From here, it can leak into the atmosphere, depending on the conditions of the upper layers. Our repeated measurements showed that a dynamic of the CO₂ concentration in shallow layers and a variation of self-potentials exist. Hence, it is assumed that conditions of the soil, external influences and the geological supply of CO₂ have an impact on these parameters. Simultaneously, the SP trend along the profile provides an indication of preferential migration pathways. Therefore, permeable structures and unconsolidated sediments can have a large impact (i.e., causing hazardous accumulations and leakages) and must be detected and closely monitored.
- Our results showed significant indicators for repeated measurements to characterize subsurface conditions and to observe changes in the field to appraise potential risks. Furthermore, our periodic repetitions showed the necessity of a long-term monitoring including the continuous observation.
- These long-term measurements can help to evaluate the influence of certain parameters on each other and provide conclusions about dependences on distinctive properties (e.g., resistivity, soil moisture, barometric pressure). The complementary combination of various methods is crucial and help us to detect, locate and quantify potential emissions. Evaluation of the applied methods at a natural analog such as the Hartoušov site offers the opportunity to develop monitoring technology and to obtain further information concerning the fundamental parameters required which are necessary to develop an integrated hierarchic investigative concept.
- In future it is important to perform further long-term measurements at the Hartoušov site, especially under different seasonal conditions, so as to improve the evaluation of the methods used.

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