Compositional measurement of gas emissions in the Eastern Carpathians (Romania) using the Multi-GAS instrument: approach for in situ data gathering at non-volcanic areas

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Abstract

The Multi-GAS, a robust and low-cost instrument for real-time in-situ gas measurements, has previously been used mainly for compositional measurements of active volcanic plumes. Here we demonstrate novel use of a specially designed Multi-GAS instrument adapted to low temperature degassing areas. We performed compositional measurements in the Eastern Carpathians on dry and bubbling gas emissions using a sensor kit that allows measurement of CO_2, CH_4 and H_2S (three major components of low-temperature hydrothermal/volcanic manifestations). Our results demonstrate good agreement between Multi-GAS measurements and independently obtained CO_2 concentrations from gas chromatography. We also provide some novel H_2S information for some anomalous sites, which we relate to possible alteration processes of sulphide minerals. The use of Multi-GAS in such environments could open new possibilities for data collection at non-volcanic areas and exploration of mineral resources. Moreover, it can also be a useful tool in exploration surveys to select the best sampling sites for more detailed laboratory measurements.

Key words: Multi-GAS, Eastern Carpathians, CO_2-rich gas emissions, in-situ compositional measurements

1. Introduction

The study of natural processes generating CO_2, and the quantification of the carbon budget from natural reservoirs, has gained increased interest in the past decades (Archer, 2010, Werner et al., 2019). CO_2 can be generated through a variety of natural processes and phenomena, including eruptive and quiescent degassing of volcanoes (Aiuppa et al., 2007, Edmonds, 2008, Fischer, 2008, Oppenheimer et al., 2014, Fischer et al., 2019, Fischer and Aiuppa, 2020, Werner et al., 2019), degassing at convergent plate boundaries (Caracausi and Sulli, 2019), rifting (Kämpf et al., 2013,

Lee et al., 2016, Tamburello et al., 2018), degassing through metamorphic processes (Kerrick and Caldeira, 1998, Evans et al., 2008), decomposition of organic matter (Arhcher, 2010), and other, less emphasized and studied sources such as weathering processes of minerals (e.g. sulphides) and chemical reactions between minerals and fluids in the Earth's crust. The latter can also significantly contribute to the Earth's total carbon budget (Archer, 2010, Hilton and West, 2020, Zhang et al., 2020).

Mapping of degassing areas is important not only for the quantification of the natural carbon budget, but also for economic reasons, e.g., globally significant CO_2 amounts are released to the atmosphere by diffuse degassing from geothermal systems, such as: Nysiros (Greece) (Bini et al., 2019), Pantelleria (Italy) (Granieri et al., 2014) Campi Flegrei (Italy) (Brombach et al., 2001, Chiodini et al., 2001), Iceland (Fridricksson et al., 2006, Hernández et al., 2012), New Zealand (Rissmann et al., 2012, Werner and Cardellini, 2006). Soil diffuse degassing is a powerful indicator to the presence of geothermal systems and their energy potential. By mapping gas emissions in geothermal areas, we gain insights into the tectonic control of ascending geothermal fluids, the permeability of the structures, as well as the estimation of natural heat flow from the system. Such surveys are relatively low cost, provide rapid results and relevant information in the early stages of geothermal exploration. The role of such surveys may be also crucial in selecting drilling targets for geothermal energy exploitation or water resources (Chiodini et al., 2001, Fridricksson et al., 2006, Granieri et al., 2014, Voltattorni et al., 2010).

Besides geothermal exploration, the mapping of gas emissions can be a powerful tool in mineral exploration. Weathering processes of sulphide minerals, oxidation processes, chemical reactions between acid fluids and the gangue rock may produce gases like CO_2, H_2S, CH_4, SO_2, that can show anomalous concentrations at the surface, detectable by gas exploration surveys (Ball, 1990, Kesler, 1990, Reid and Rasmussen 1990, Polito et al., 2002, Muntean and Taufen., 2011, Noble et al., 2018, Plet et al., 2021, Zhang et al., 2020, Lin et al., 2021). Traditional surface geochemistry techniques, such as rock and soil geochemistry, stream sediment geochemistry, are limited for the exploration of deep-buried mineralization. For this reason, "novel pathfinders" are necessary for geochemical exploration, such as the mapping of gas emissions from the soil. Gases can move through the cover of the buried mineralization and thus provide useful information on its nature (Noble et al., 2018, Plet et al., 2021, Lin et al., 2021), structural conditions and permeability of the geological layers (Harvey and Alexander, 2011, Voltattorni et al., 2010). Even though this method seems rational, gas geochemical surveys are still experimental and show limitations in sampling and analytical methods. In addition, only a limited number of high-sensitivity, portable and low-cost analysers exist that are able to perform simultaneous measurements of different gas species on the field (Lin et al., 2021).

The most commonly used technique in gas geochemistry (especially for the geochemical study of volcanic and geothermal gas emissions) is the direct sampling of the gases in Giggenbach bottles (Giggenbach, 1975), pre-evacuated flasks, copper tubes etc. These techniques require field (sampling flasks, tubes, funnels etc.) and laboratory infrastructure that are advanced and expensive. For the acquisition of compositional gas data, the most popular and accurate laboratory methodology is gas chromatography. However, uncertainties and biases can derive from sampling difficulties and sample storage (Giggenbach, 1975, Mangani et al., 2004, Vaselli et al., 2006). The most important disadvantage of direct sampling is the low temporal resolution (delay between sampling and data availability), quantity of measurement which is often limited due to funding or the busy schedule of the laboratories (Giggenbach, 1975, Mangani et al., 2004). Additionally,

direct sampling and laboratory analyses are unable to continuously monitor a certain area, since the number of samples are limited to sample holders.

One methodology designed to specifically overcome some of the above limitations of direct sampling is the is the Multi-component Gas Analyzer System (Multi-GAS), frequently used especially in the surveillance of active volcanoes. The Multi-GAS was initially developed in the early 2000's with the purpose to create a robust and user-friendly instrument for real-time, in-situ measurement of volcanic gas plume composition (Aiuppa et al., 2005, Shinohara, 2005, Roberts et al., 2012). The instrument is easy to use, with a portable design, for use in extreme acidic volcanic environments, customizable IR detectors and electrochemical sensors and works with high power autonomy (e.g., permanent installations have used either wind turbines Ilyinskaya et al., 2015, or, more typically, solar panels and battery pack; Aiuppa et al., 2021).

The Multi-GAS has found a variety of applications in volcanology. The instrument can be used either as a portable meter or as a permanent station. Portable instruments are used for field surveys, temporal/spatial compositional mapping of the gas emissions, and vertical and horizontal plume profiling (Aiuppa et al., 2005, Allard et al., 2014). Multi-GAS instruments as permanent stations are also used for short- or long-term monitoring. In the case of short-term monitoring the instrument is used to measure fluid composition of poorly studied, remote volcanic targets (Aiuppa et al., 2015). Long-term compositional monitoring of gas emissions in active volcanic areas represents an important tool in eruption forecasting. These long-term investigations can also pave the way to determination of the CO_2 flux if combined with remote sensing units using UV spectroscopic sensors (Aiuppa et al., 2005, 2007, 2014, 2015, 2021, Shinohara et al., 2015, Moussallam et al., 2017). At dormant volcanic areas, investigations include studies on gas dynamics of volcanic and hydrothermal systems (e.g., Norris Geyser basin, Yellowstone; Lewicki et al., 2017; Campi Flegrei; Tamburello et al., 2019) and monitoring of the effect of environmental factors like wind speed, groundwater level, barometric pressure on the gas levels and compositions.

The aim of our study is to test the utility of the Multi-GAS instrument in areas of low-temperature gas emissions that are not directly related to active volcanic degassing. The use of the Multi-GAS for field surveying of gas emissions we demonstrate here opens new possibilities for prospection for gas and mineral water resources by choosing the most suitable detectors, and offers the possibility of selection of the best samples prior to detailed laboratory measurements.

For this reason, we built a specially designed Multi-GAS using a sensor kit that allows the measurement of CO_2, CH_4 and H_2S (three major components of low-temperature hydrothermal/volcanic manifestations). The selected case study area is in the Eastern Carpathians, Romania, an area with complex geology and widespread gas emissions that suggest possible gas-sourcing processes at depth. Having previous compositional information on the selected sites the comparison with the classical analytical methods was possible.

2. Geological context

The formation of the Carpathians is related to the Alpine tectonic activity and the closure of the former Tethys Ocean. After the subduction of the oceanic basins, plates that were squeezed by the movement of the Tisa-Dacia microplates, collision occurred with the Eurasian plate. As a post-collisional event, magma generation and the development of the volcanic range had started (Cloetingh et al., 2004, Seghedi et al., 2004, 2005, 2011, Schmid et al., 2020). The Călimani-Gurghiu-Harghita (CGH) is the southernmost volcanic segment, located between the Carpathian

fold and thrust belt, and the Transylvanian Basin. The CGH range is composed by the following volcanic units: Călimani, Gurghiu, North Harghita and South Harghita.

These are formed by by composite volcanoes and surrounded by volcaniclastics (Szakács and Seghedi, 1995). The basement of the South Harghita is represented by the Early Cretaceous clastic flysch sedimentary units of the Eastern Carpathians, composed by nappe-structures. The Carpathian Flysch units are built up by the alternations of sandstone, calcareous sandstone, limestone and clay/marl. The most relevant unit in our study area is the calcareous flysch of the Sinaia Formation, part of the Ceahlău nappe and the Bodoc flysch. These deposits may reach a thickness up to 2500 m (Nicolăescu, 1973, Sandulescu, 1984, Grasu et al., 1996, Matenco and Bertotti, 2000).

Volcanoes are composed by systematically overlapping edifices, volcanoes that were active concomitantly but progressively showing younger ages from north to south. From a petrological point of view they are built up by mostly andesites, andesitic lavas, basaltic andesites, dacites and shoshonites (Szakács et al., 1993, Seghedi et al., 1995, 1998, 2004). The volcaniclastic deposits up to 650 m thickness are surrounding the main edifices, extending over the flysch on the east and over the Neogene sediments of the Transylvanian Basin on west (Szakács and Seghedi, 1995).

Volcanic activity in the Neogene-Quaternary arc started around 21 Ma, in the CGH segment in the interval between 10 Ma and 32 ka. The youngest volcano is the Ciomadul volcanic dome (Moriya et al., 1996, Pécskay et al., 1995, 2006, Harangi et al., 2010, Molnár et al., 2018, 2019). The Ciomadul volcanic area is composed by small lava domes, including the Puturosul and Bálványos Hills and two explosion craters called Mohos and Saint Anna (Harangi et al., 2015, Szakács et al., 2015, Karátson et al., 2016, Molnár et al., 2018, 2019), that are hosting a peat bog and a volcanic lake.

3. The gas manifestations of the Eastern Carpathians

The surroundings of the volcanic range are characterized by intense, low temperature (*T* ~8–10 °C) gas emissions. These gas emissions appear in different manifestations, such as dry gases (mofettes) and bubbling gas, when the gas emissions interact with the local aquifers (Jánosi et al., 2011; Kis et al., 2019, 2020). The aquifers in this area are represented by CO_2-rich sparkling mineral water, with temperature up to 22.5 °C (Berszán et al., 2009; Jánosi et al., 2011; Italiano et al., 2017).

The mineral water springs are mainly exploited by the bottling industry, the area provides almost half of the bottled mineral water brands from Romania (Feru, 2012). Besides, these CO_2-rich waters are also used for balneological treatment at several locations within the Eastern Carpathians (e.g. Covasna, Borsec, Baile Tusnad). Also, factories capturing free CO_2 for industrial use existed in the past (e.g. at Baile Malnas and Baile Balvanyos). For this reason, widespread exploration and prospecting investigations occurred in the 20th Century. These exploration and prospecting activities left several unsupervised drillings and wells that are continuously emitting deep CO_2 (e.g., the investigated site ID 13). In some cases, the waters are used by the locals for drinking and spa (Pricăjan, 1972, 1985, Berszán et al., 2009).

Data on the chemical composition of gas emissions were reported for a few selected sites by Althaus et al. (2000); Vaselli et al. (2002); Frunzeti (2013); Sârbu et al., (2018) and Kis et al., (2019) (Table 1). These studies demonstrate that the emitted gases are typically CO_2-dominated (up to 99%), with minor components including N_2, CH_4 and H_2S. The minimum total CO_2 flux at

the youngest segments of the Eastern Carpathians, at Ciomadul volcano was estimated to be 8.7 × 10^3 t/year, comparable to other volcanic structures of similar age (Caracausi et al., 2015, Kis et al., 2017). In this area the carbon isotopic compositions of the emitted CO_2 ($\delta^{13}C_{CO2}$), reaches values of −4.7‰ (V-PDB) combined with helium isotopic compositions that reaches 4.48 R_a (Vaselli et al., 2002), supports the mantle origin of the gases (Althaus et al., 2000, Vaselli et al., 2002, Kis et al., 2019).

Site ID 1, the Torjai Stinky Cave, is a dry CO_2-dominated natural gas vent. The big cave itself was excavated for sulphur mining, and kept open after the site was abandoned. It is a highly studied site for gas composition (Ilosvay, 1895, Althaus et al., 2000, Vaselli et al., 2002, Frunzeti, 2013, Sârbu et al., 2018, Kis et al., 2017, 2019) and life in extreme environments (Sârbu et al., 2018). The composition of the gas vent flowing from the cave is CO_2 dominated, with other components like CH_4 and H_2S (Ilosvay, 1895, Althaus et al., 2000, Vaselli et al., 2002, Frunzeti, 2013, Sârbu et al., 2018, Kis et al., 2019). Persistence of gas emission is indicated by precipitation of the native sulphur appearing on the cave wall (Figure 2). The low temperature and dry gas flows out of the cave like a river, with a CO_2 flux of 1.92 × 10^3 t/year (Kis et al., 2017). Next to this site we find site ID 8, the Timsós or Alum Cave. This cave is special due to the native sulphur and aluminium sulphate depositions on its wall.

Site ID 2, the Băile Tușnad mofette, is also a dry gas emission, used for curative purposes by the local balneological centre of the town Băile Tușnad. A building has been built on the gas emissions and only patients of the balneological centre have access to it with medical prescription. Since it is less accessible, we could not perform more measurements at that site.

Site ID 3 and 9 are bubbling gases, site 3 is a wet mofette with a small building on it that collects the gas while site 9 is a bubbling pool. Native sulphur and orpiment were described at the vicinity of these gas manifestations. The native sulphur was also exploited (Szakáll et al., 2010).

Sites ID 4, 5, 6 and 10 are bubbling gases, small pools located at Băile Balvanyos, in the forest, representing small retreat sites especially for locals. Site ID 7 is also bubbling gas, a pool which is part of the Apor Baths region, an intensely degassing area where fluxes of 5.29 × 10^3 t/year of CO_2 were measured (Kis et al. 2017). Site ID 11 is a bubbling spring located in the contact between the sedimentary deposits of the Transylvanian Basin and the volcanoclastics of the Harghita Mts.

Site ID 12A, 12B are dry mofettes in the Harghita Mts. at the degassing area of Santimbru Băi. Here the exploitation of cinnabarite took place in the second half of the 20th Century (Szakáll et al., 2010). Site ID 13 is drilling located in the Ciuc Basin that is emitting bubbling CO_2.

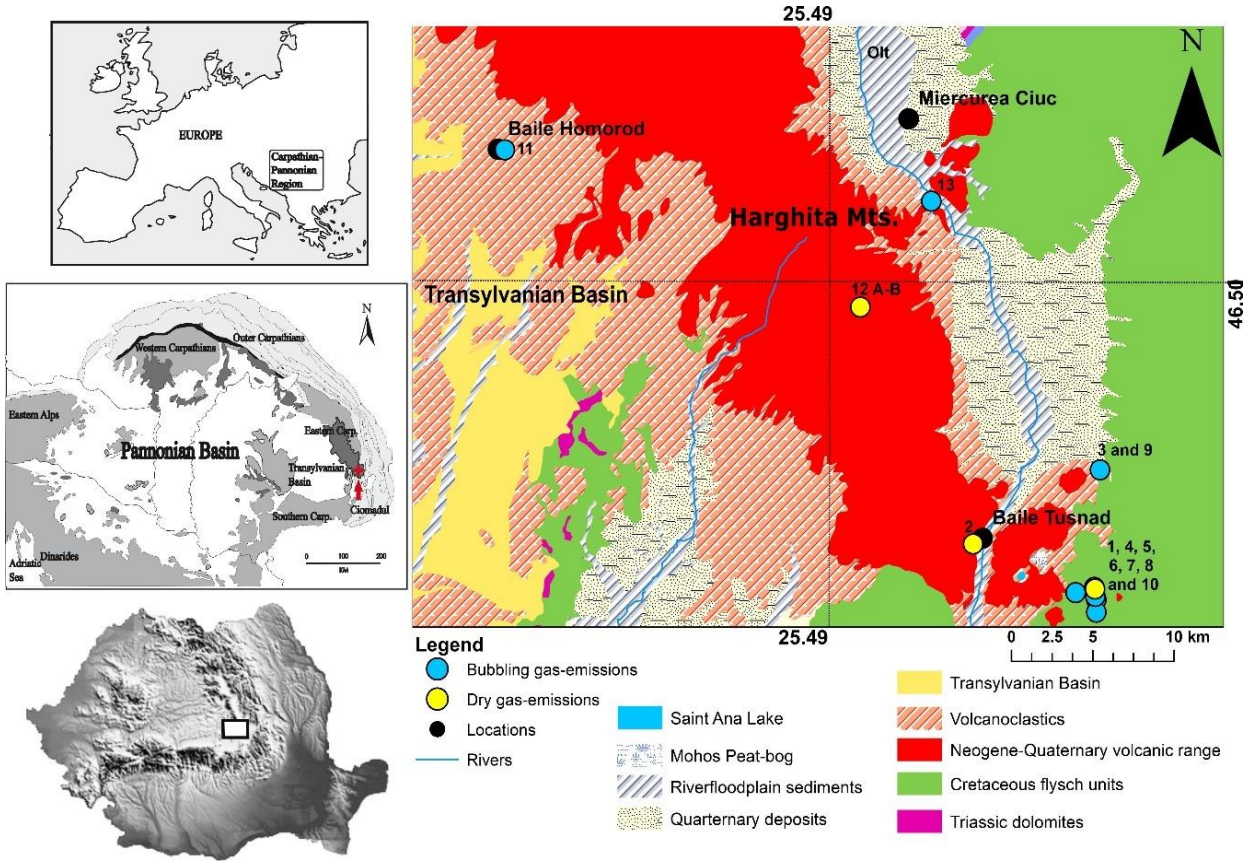

Figure 1. Geological sketch map (modified after Ianovici et al., 1968) of the investigated sites from the Eastern Carpathians, site IDs according to Table 1.

Figure 2. Pictures of selected sites: a. ID 1, Torjai Stinky Cave; b. ID 4, Gyógyvizek; c. ID 5, Csiszárfürdő Hammas pool; d. ID 6, Mikesfürdő Hammas pool; e. ID 7 Apor lányok feredeje Upper pool; f. ID 8, Timsós Cave; g ID 10 Csiszárfürdő Iker pool white; h ID 12A Sântimbru Băi mofette.

4. Materials and methods

We used a specially designed portable Multi-GAS for low-temperature, CO_2-rich gas emissions. The instrument was equipped with two specific IR spectrometers (both Gascard NG II, Edinburgh Sensors, UK) sensitive to CO_2 (0-100% range, accuracy of 2%) and CH_4 (0-5% range, accuracy of 2%), respectively, and one electrochemical sensor (T3H CiTiCeL, Gas sensor with transmitter, /City Technology Limited, UK) specific to H_2S (0-200 ppm range, resolution 0.25 ppm) concentrations. The Multi-GAS unit was calibrated at the University of Palermo by using a set of ad-hoc prepared gas mixture of known gas concentration, obtained by diluting (with air) certified gas standards of 100 vol. % CO_2, 10 vol. % CH_4, and 136 ppmv H_2S.
In the field the gas effluents from the manifestation were captured from the Multi-GAS inlet (see below, Fig.3) and pumped using a Boxer Pump, UK, S series, 12V, maximum free flow of 1.8 l/min constantly through the sensors (arranged in-series), whose output signals were logged to an internal datalogger (CR 6, Campbell Scientific) in real-time. Two filters were used to protect the internal system and detectors of the instrument from dust and water. A large sized Pall Corporation Acro 50 type 1 micrometer filter was placed in front of the inlet tube of the instrument, while the second filter (size 0.45 micrometer) was put inside the device just before the gas entrance towards the sensors for additional protection. The external large filter was regularly replaced, especially due to dust contamination, during the field surveys. The smaller size integrated filter was replaced with a new one during the annual revision and calibration procedures.

The Multi-GAS datalogger allowed full real-time control of the measurements through wi-fi connection and a palmtop computer on which the concentration curves could be followed in-situ via the Logger Link (Campbell Scientific 2017, Version 1.6.8) application (the measurements curves are shown on Figures 4 and 5, and Figures S1 to S12 from the Supplementary Material). Measurements at each site took up to several minutes, depending on flux regime of the gas. After placing the funnel on the vent (dry or bubbling gas), we started collecting the gas and continuously measure the concentrations of the CO_2, CH_4 and H_2S until the atmospheric gas was removed and the funnel was completely filled with mofettic gas. After the concentrations reached a plateau, we could read the real concentrations of the gas species. The final compositional results were calculated in Microsoft Excel (MS Office) by averaging logged data after stabile sensor reading were achieved.

We investigated two types of gas manifestations - dry gas-emissions (mofettes) and bubbling pools - in order to test the utility of the instrument in aqueous-bubbling gas environment. The Multi-GAS was used during several field surveys between autumn of 2018 and summer 2021 across the area of the Eastern Carpathians. We selected sites for which we had previous compositional data from literature (Althaus et al., 2000, Vaselli et al., 2002, Frunzeti 2013, Kis et al., 2019), that were obtained with gas chromatography and titration. We have checked the accuracy of our measurement using those data (see Table 1, Figure 2).

Gas concentrations and fluxes at low-temperature manifestations can be influenced by meteorological factors like atmospheric pressure and temperature (Airinei et al., 1975, Viveiros et al., 2008). To test the accuracy of the measurements considering these limitations, we performed measurements in different seasons.

The methodology of the measurement is briefly visualized in Figure 3. In the case of free gases, a funnel was put directly on the gas emission, to collect the gas and pump it towards the detectors. In the case of bubbling-pools we used the same funnel, which was submerged into the water to avoid direct contact with air and the gas bubbles were collected in the funnel.

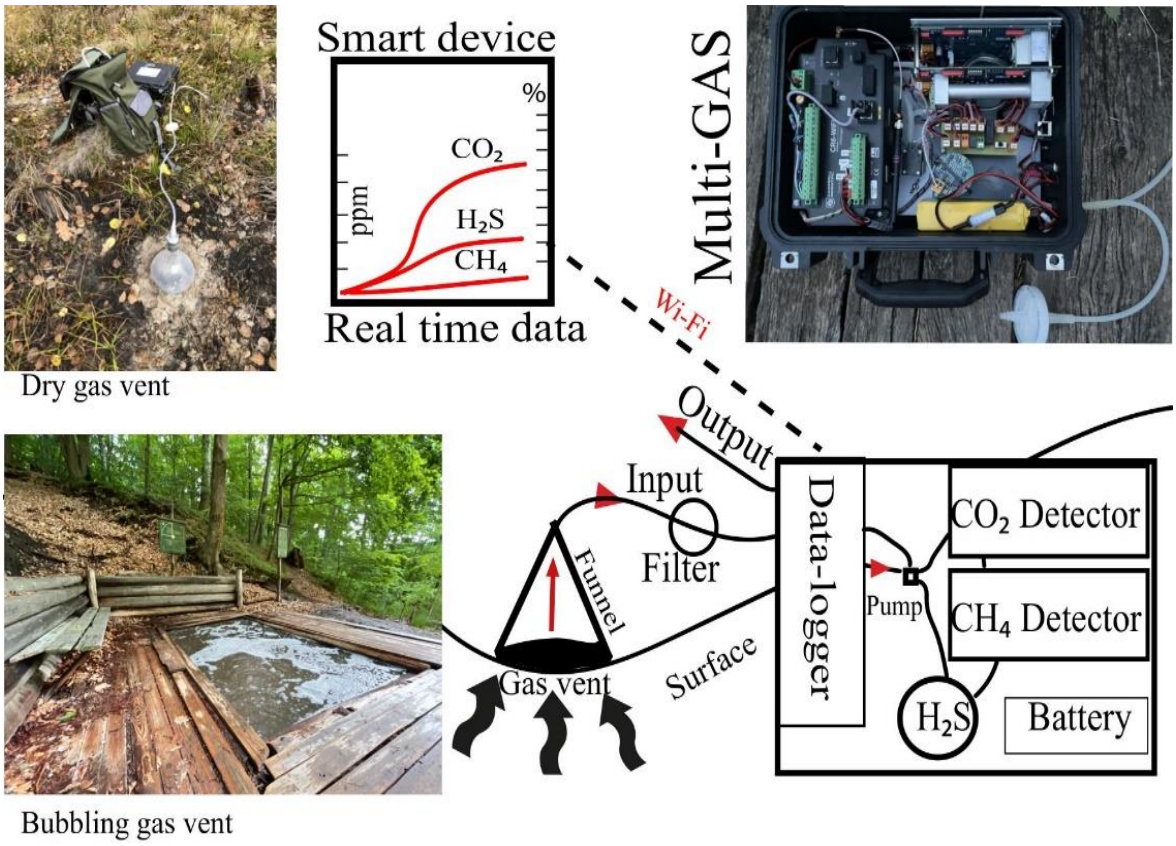

Figure 3. Sketch of the Multi-GAS measurements performed in dry gas vent and bubbling gas.

5. Results

We investigated 14 sites, containing both free gas (IDs 1, 2, 8, 12A and 12B) and bubbling gas (IDs 3, 4, 5, 6, 7, 9, 10, 11, 13). The IDs, names, and the concentrations of the different gas species measured with Multi-GAS are listed in Table 1, along with the concentrations of the same gas species from literature (Althaus et al., 2000, Vaselli et al., 2002, Frunzeti 2013, Kis et al., 2019) performed with classical analytical techniques. The CO_2, CH_4 and H_2S concentrations were measured at each site.

All the investigated gas emissions are CO_2-dominated, the concentration varied in a narrow range between 82.5 and 99%. The CH_4 varied between, 0.5 and 5.6 %. The H_2S concentrations varied between <0.1 ppm and >200 ppm. We managed to repeat seasonal measurements at several sites (ID 1, 3, 4, 5, 6, 9, 10, 12A and 13). In the case of site ID 1 four seasonal measurements were performed, in order to explore any seasonal influence on vent gas composition. The CO_2 varied between 93.4 and 97.4 %, the CH_4 2.4 and 4.2 % and the H_2S between 164.9 and >200 ppm. Detailed measurement curves for CO_2 and H_2S are illustrated in Figures 4 (for ID 1, dry gas emission) and Figure 5 (for ID 7, bubbling gas). The measurement curves illustrate the process described in Section 4. As the funnel was placed above the gas manifestation (dry gas or bubbling gas), the CO_2 concentration, which started at an atmospheric value of ~400 ppm, progressively increased depending on the gas flux at the vent, until it reached a stable value and gave the real

concentration. The same situation was observed in the case of H_2S; however, this was not always detected or it was below detection limit (e.g. ID 2-Figure S1, ID 11-Figure S9, ID 13-Figure S12). The measurement curves also gave some hints on the flux of the gas: at steeper slopes a stabilized concentration was reached more quickly, in terms of seconds, suggesting high flux (e.g. ID 1-Figure 4, ID 4-Figure S3, ID 5-Figure S4); while more gentle slopes suggested lower flux (e.g. ID 9-Figure S7, ID 10-Figure S8). During the measurements, also air contamination could be detected. This could happen if the funnel was not correctly placed on the vent of if a leak was present in the system (e.g. ID 13-Figure S12).

Further information on the measurement curves of the all the other sites can be accessed in the Supplementary Material (Figure S1 for ID 2, Figure S2, for ID 3, Figure S3 for ID 4, Figure S4 for ID 5, Figure S5 for ID 6, Figure S6 for ID 8, Figure S7 for ID 9, Figure S8 for ID 10, Figure S9 for ID 11, Figure S10 for ID 12A, Figure S11 for ID 12B, Figure S12 for ID 13.).

Table 1. Concentrations of H_2S, CH_4 and CO_2 of free and bubbling gases from selected sites of the Eastern Carpathians using the Multi-GAS measurements and data from literature. ND=not determined. *Tests in lab with calibration gases demonstrate linearity holds up to 10-20% above the "assumed" 0-5% calibration range.

ID	Site name	Location	Type	Longitude	Latitude	H_2S(ppm)	CH_4(%)	CO_2(%)	Reference	Season	Measuring Technique
1	Torjai Stinky Cave	Băile Balvanyos	Dry gas vent	25.9487	46.1198	195.2	2.4	95.2	This work	2018-Winter	M.G.
	Torjai Stinky Cave	Băile Balvanyos	Dry gas vent			200	2.5	93.3	This work	2018-Autumn	M.G.
	Torjai Stinky Cave	Băile Balvanyos	Dry gas vent			164.9	3.6	96.6	This work	2021-Spring	M.G.
	Torjai Stinky Cave	Băile Balvanyos	Dry gas vent			168	4.2	97.4	This work	2021-Summer	M.G.
	Torjai Stinky Cave	Băile Balvanyos	Dry gas vent			520	0.8	78.1	Kis et al., 2019		GC
	Torjai Stinky Cave	Băile Balvanyos	Dry gas vent			180	0.9	82.7	Kis et al., 2019		GC
	Torjai Stinky Cave (Sulfur Cave)	Băile Balvanyos	Dry gas vent			ND	ND	96.5	Sarbu et al., 2018		GC
	Torjai Stinky Cave (Puturosu)	Băile Balvanyos	Dry gas vent			ND	1.2	96.8	Frunzeti, 2013		GC
	Torjai Stinky Cave (Puturosul)	Băile Balvanyos	Dry gas vent			120	0.8	98.3	Vaselli et al., 2002		GC
	Torjai Stinky Cave	Băile Balvanyos	Dry gas vent			ND	0.8	98.2	Althaus et al., 2000		GT
	Torjai Stinky Cave (Torjai Büdös Barlang)	Băile Balvanyos	Dry gas vent			560	ND	95.5	Ilosvay L. 1895		T
2	Băile Tușnad mofetta	Băile Tușnad	Dry gas vent	25.8519	46.1422	0	1.0	90.2	This work	2018-Winter	M.G.
	Băile Tușnad mofetta	Băile Tușnad	Dry gas vent			ND	ND	98	Kis et al., 2019		GC
	Băile Tușnad mofetta	Băile Tușnad	Dry gas vent			ND	0.6	98	Kis et al., 2019		GC
	Băile Tușnad mofetta (Tusnad)	Băile Tușnad	Dry gas vent			ND	ND	95.7	Frunzeti, 2013		GC
3	Lăzărești Nyírfürdő-mofette	Lăzărești	Bubbling gas	25.952	46.183139	196.8	1.3	96.2	This work	2018-Autumn	M.G.
	Lăzărești Nyírfürdő-mofette	Lăzărești	Bubbling gas			164.9	2.2	99	This work	2019-Autumn	M.G.

	Lăzărești Nyírfürdő-mofette	Lăzărești	Bubbling gas			164.9	3.9	96.7	This work	2021-Summer	M.G.
	Lăzărești Nyírfürdő-mofette	Lăzărești	Bubbling gas			ND	ND	98	Kis et al., 2019		GC
	Lăzărești Nyírfürdő-mofette	Lăzărești	Bubbling gas			840	0.8	98	Kis et al., 2019		GC
	Lăzărești Nyírfürdő-mofette (Lăzărești Nyir)	Lăzărești	Bubbling gas			0	3.4	89.1	Vaselli et al., 2002		GC
4	Gyógyvizek	Băile Balvanyos	Bubbling gas	25.9503	46.1131	200	2.4	96.3	This work	2018-Winter	M.G.
	Gyógyvizek	Băile Balvanyos	Bubbling gas			193.9	3.5	98.7	This work	2019-Autumn	M.G.
	Gyógyvizek	Băile Balvanyos	Bubbling gas			159.3	4.6	97.1	This work	2021-Summer	M.G.
	Gyógyvizek	Băile Balvanyos	Bubbling gas			1100	1.3	97.6	Kis et al., 2019		GC
	Gyógyvizek	Băile Balvanyos	Bubbling gas			ND	0.9	78.4	Kis et al., 2019		GC
	Gyógyvizek (Izvoarele Tămăduitoare)	Băile Balvanyos	Bubbling gas			ND	1.3	97.2	Frunzeti, 2013		GC
5	Csiszárfürdő-Hammas pool	Băile Balvanyos	Bubbling gas	25.9504	46.1065	200	2.1	96.9	This work	2018-Autumn	M.G.
	Csiszárfürdő-Hammas pool	Băile Balvanyos	Bubbling gas			180.3	3.6	98.8	This work	2019-Autumn	M.G.
	Csiszárfürdő-Hammas pool	Băile Balvanyos	Bubbling gas			169.9	4.1	97.7	This work	2021-Summer	M.G.
	Csiszárfürdő-Hammas pool	Băile Balvanyos	Bubbling gas			1100	1.2	96.7	Kis et al., 2019		GC
	Csiszárfürdő-Hammas pool	Băile Balvanyos	Bubbling gas			ND	1.2	94.8	Kis et al., 2019		GC
6	Mikesfürdő-Hammas pool	Bixad	Bubbling gas	25.9339	46.1168	21.4	2.3	96.3	This work	2018-Winter	M.G.
	Mikesfürdő-Hammas pool	Bixad	Bubbling gas			15.3	5.0	94.6	This work	2021-Spring	M.G.
	Mikesfürdő-Hammas pool	Bixad	Bubbling gas			18.2	5.6*	94.9	This work	2021-Summer	M.G.
	Mikesfürdő-Hammas pool	Bixad	Bubbling gas			ND	1.0	87.7	Kis et al., 2019		GC
	Mikesfürdő-Hammas pool	Bixad	Bubbling gas			ND	1.1	94.8	Kis et al., 2019		GC
	Mikesfürdő-Hammas pool (Mikesfürdő-Hammas)	Bixad	Bubbling gas			ND	1.3	97.2	Frunzeti, 2013		GC
7	Apor lányok feredeje-Upper pool	Băile Balvanyos	Bubbling gas	25.9496	46.1150	200	2	94.8	This work	2018-Autumn	M.G.
	Apor lányok feredeje-Upper pool	Băile Balvanyos	Bubbling gas			131.6	3.4	98.7	This work	2019-Autumn	M.G.
	Apor lányok feredeje-Upper pool	Băile Balvanyos	Bubbling gas			149.6	4.9	97	This work	2021-Summer	M.G.
	Apor lányok feredeje-Upper pool (small pool)	Băile Balvanyos	Bubbling gas			ND	0.8	58.1	Kis et al., 2019		GC
	Apor lányok feredeje-Upper pool (small pool)	Băile Balvanyos	Bubbling gas			270	1.2	97.2	Kis et al., 2019		GC

	Apor lányok feredeje-Upper pool	Băile Balvanyos	Bubbling gas			ND	1.2	97.8	Althaus., et al 2000		GT
8	Timsós Cave	Băile Balvanyos	Dry gas vent	25.9493	46.1189	197.2	2.2	92.1	This work	2018-Winter	M.G.
	Timsós Cave	Băile Balvanyos	Dry gas vent				0.9	95.3	Kis et al., 2019		GC
9	Lăzărești Nyírfürdő-pool	Lăzărești	Bubbling gas	25.9518	46.1831	23.1	1.9	91.3	This work	2018-Autumn	M.G.
	Lăzărești Nyírfürdő-pool	Lăzărești	Bubbling gas			36.3	2.8	94.2	This work	2019-Spring	M.G.
	Lăzărești Nyírfürdő-pool	Lăzărești	Bubbling gas			ND	1.3	93.1	Kis et al., 2019		GC
	Lăzărești Nyírfürdő-pool	Lăzărești	Bubbling gas			ND	0.8	96.7	Kis et al., 2019		GC
10	Csiszárfürdő-Iker pool white	Băile Balvanyos	Bubbling gas	25.9504	46.1065	21.3	2.7	93.5	This work	2018-Autumn	M.G.
	Csiszárfürdő-Iker pool white	Băile Balvanyos	Bubbling gas			15.8	4.9	94.5	This work	2019-Autumn	M.G.
	Csiszárfürdő-Iker pool white	Băile Balvanyos	Bubbling gas			ND	1.7	94.7	Kis et al., 2019		GC
11	Băile Homorod-spring	Băile Homorod	Bubbling gas	25.4737	46.3503	0	0.5	84.6	This work	2019-Autumn	M.G.
	Homorod-Maria	Băile Homorod	Bubbling gas			ND	0.36	98.24	Vaselli et al., 2002		GC
12 A	Sântimbru-Băi-mofetta	Sântimbru-Băi	Dry gas vent	25.7593	46.2690	78.42	0.73	86.05	This work	2018-Autumn	M.G.
	Sântimbru-Băi-mofetta	Sântimbru-Băi	Dry gas vent			63.3	1.02	82.47	This work	2019-Autumn	M.G.
12 B	Sântimbru-Băi-mofetta	Sântimbru-Băi	Dry gas vent			2.14	0.9	94.02	This work	2018-Autumn	M.G.
	Sântimbru-Băi-mofetta	Sântimbru-Băi	Dry gas vent			ND	0.11	97.41	Vaselli et al., 2002		GC
13	Jigodin-Băi drilling	Jigodin-Băi	Bubbling gas	25.8146	46.3266	0	0.763	94.771	This work	2018-Autumn	M.G.
	Jigodin-Băi drilling	Jigodin-Băi	Bubbling gas			0	1.5	98.0794	This work	2020-Winter	M.G.
	Jigodin-Băi drilling	Jigodin-Băi	Bubbling gas			0	1.5	96.67	This work	2021-Autumn	M.G.
	Jigodin-Băi	Jigodin-Băi	Bubbling gas			ND	0.98	98.84	Vaselli et al., 2002		GC

6. Discussion

The volcanic area of the Eastern Carpathians is the largest degassing area of Romania (Airinei and Pricăjan, 1974, Vaselli et al., 2002, Kis et al., 2017, 2019). There are several thousand CO_2-rich mineral water springs in the area suggesting the interaction between upwelling deeply sourced gas and aquifers (Kis et al., 2020). The gas emissions are also present far from the volcanic areas suggesting that the circulation of these deep fluids may be influenced by the tectonic setting (Vaselli et al., 2002). Mapping and quantification of the patterns and regimes of CO_2 release in such an area can contribute to understanding Earth's non-volcanic degassing and related processes (Chiodini et at., 2010, Bräuer et al., 2016).

For this reason, in order to perform expedite explorative surveys, a device was needed that could provide in-situ, real time data acquisitions (preparatory to selection for more detailed chemical and isotopic analyses). The Multi-GAS that we used was specially designed to this aim, and its application to low-temperature gas emissions was tested in dry gas as well is in bubbling gas at different sites within the Eastern Carpathians, Romania. For the selected sites (Table 1) we had previous compositional data performed with classical analytical techniques.

The Torjai Stinky Cave (site ID 1) represents one of the most studied dry gas vents, located in the Eastern Carpathians, at the Ciomadul volcanic area. The first survey on the concentrations of different gas species at the Torjai Stinky Cave (site ID 1, Table 1, Figure 2) were conducted by Ilosvay (1895), who determined a CO_2 concentration of 95.5% using a titration technique, and estimated H_2S at 560 ppm. Later, Althaus et al., 2000, Vaselli et al., 2002, Frunzeti, 2013, Sârbu et al., 2018, Kis et al., 2019 measured similar CO_2 concentrations (ranging between 78.1 and 98.2%) using the gas chromatography technique. Regarding H_2S concentrations, Kis et al., 2019 determined 520 ppm (Table 1), very similar of that of Ilosvay (1895). H_2S sampling and measurement with classical techniques are complicated by oxidation of the gas in contact with air in the sampling flasks, so most of the H_2S is lost by the time the sample enters the laboratory. For this reason usually the best method for the sampling of H_2S is to put it into NaOH-$Cd(OH)_2$ solution and precipitate it as CdS (Vaselli et al., 2006).

Our measurements with Multi-GAS, despite the possible influences of meteorological conditions, reached similar concentrations for CO_2, in each season, with values ranging between 93.3 and 97.4%. A slight decrease in concentration and flux was observed in autumn 2018, most probably due to the previously described meteorological conditions (Table 1, Figure 4). The measurement curves shown in Figure 4 indicate that in each case the concentrations reached fully stabilized values. The obtained CO_2 concentration values with Multi-GAS, taking in consideration also the 2% accuracy of the detector, are in good agreement with those previously obtained with classical analytical techniques, such as gas chromatography (Table 1).

The CH_4 concentration varied between 2.4 and 4.2 %, or higher than obtained with other techniques, most probably due to the 2% accuracy of the detector. The measured H_2S concentrations were often approaching the 200 ppm, measurement range of the sensor, although the 240 ppm sensor saturation was not reached in any of the cases. In any case, our derived concentrations are in the same orders of magnitude of previous results found by Ilosvay (1895) and Kis et al., (2019).

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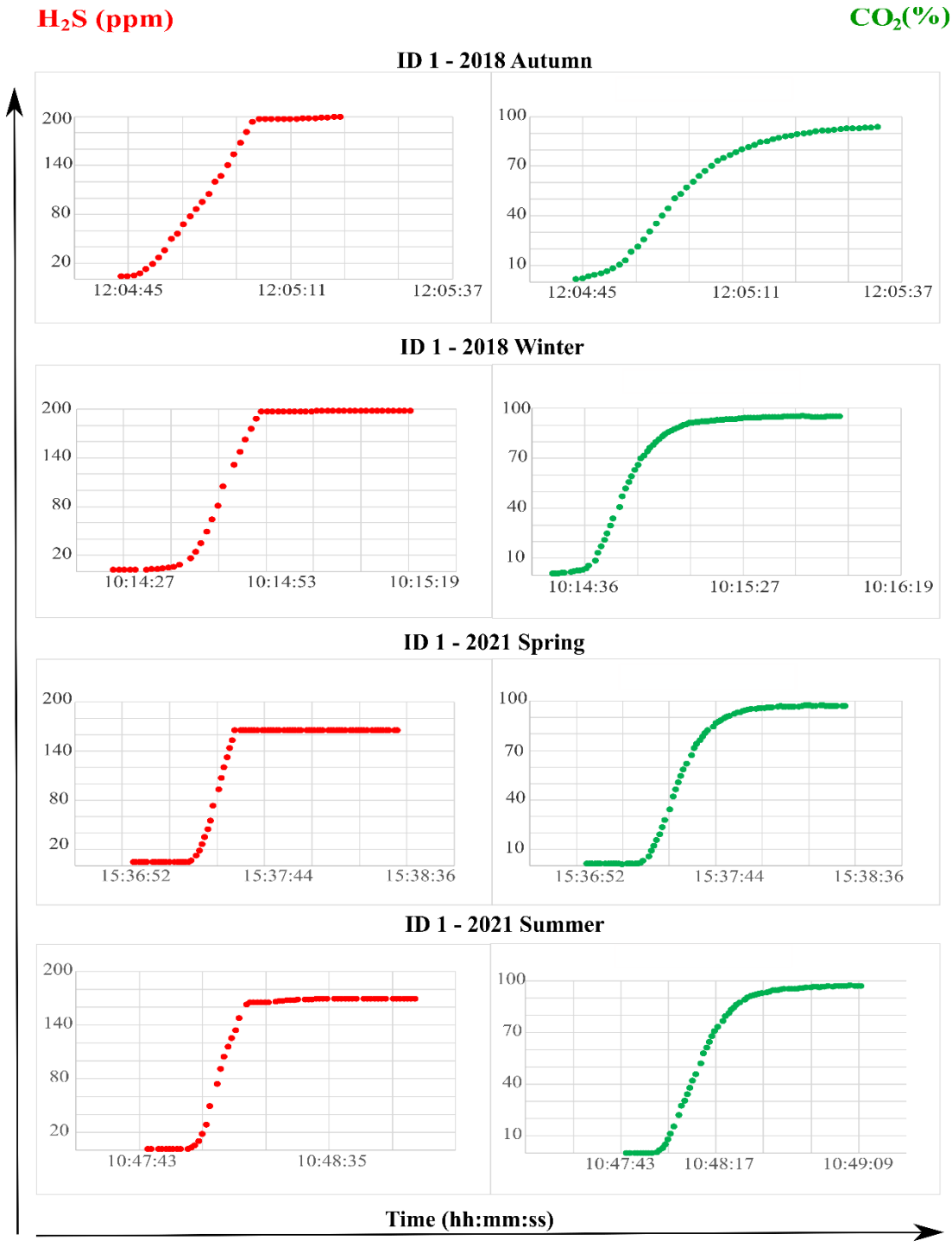

361 **Figure 4.** Seasonal measurement of H_2S and CO_2 concentrations of the free gases from Site with
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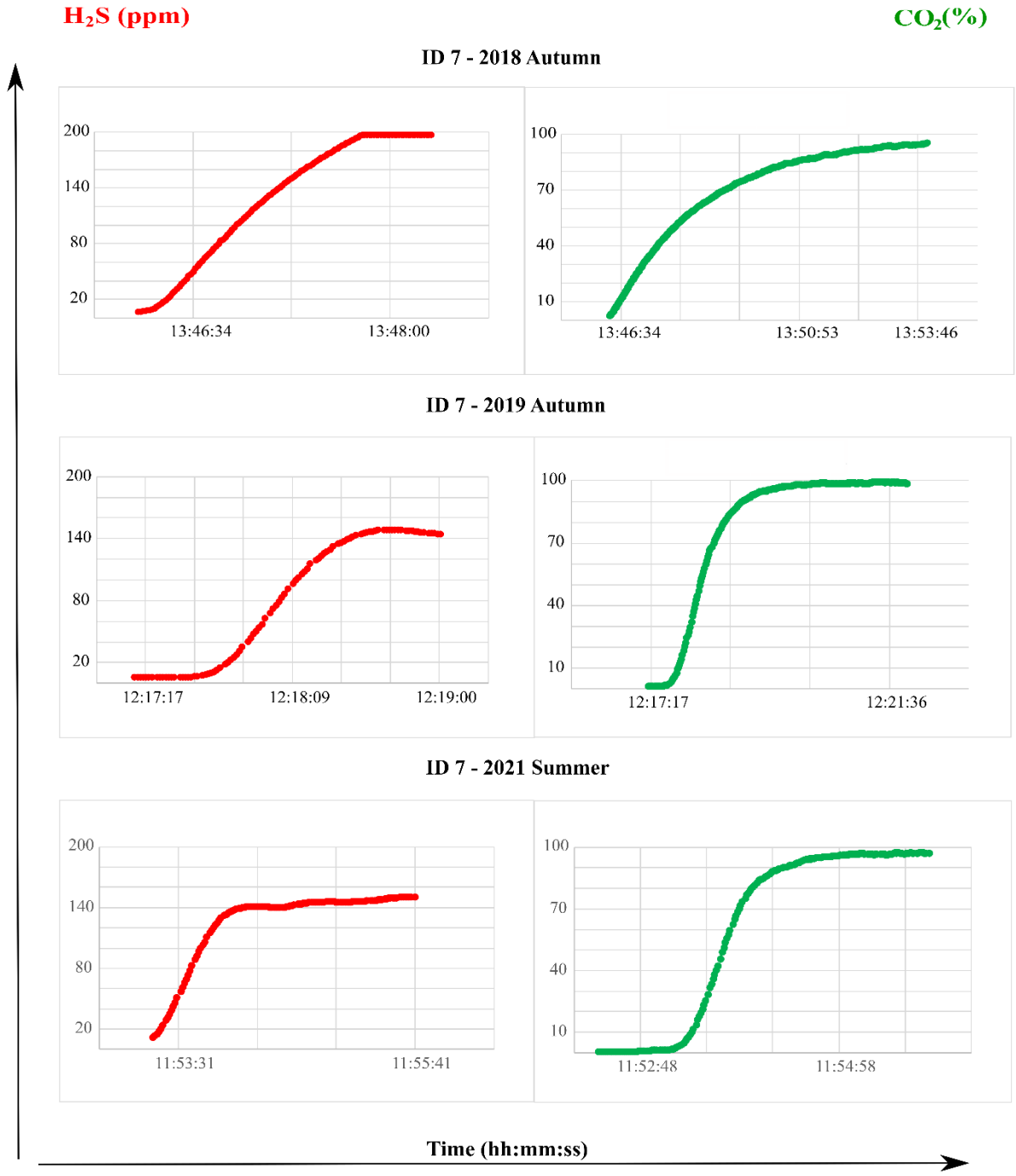

Figure 5. Seasonal measurement of H_2S and CO_2 concentrations of the bubbling gases from Site with ID no.7, the Apor Baths.

Testing the measurement of bubbling gas vents was necessary to check the influence of water on the measurements. Using Multi-GAS we were able to collect information on CO_2, CH_4 and H_2S concentrations in sites 3, 4, 5, 6, 7, 9, 10, 11, 13 (Figure 5 for site ID 7 and for the other sites the measurement curves in the Supplementary Material, Figures S2, S3, S4, S5, S7, S8, S9, S12), using the methodology described in Section 4.

At all the bubbling gas sites, the measured CO_2 concentrations are in good agreement with the results of previous studies using the classical analytical methodologies (Table 1), suggesting that the flux of the gas was high enough and the water was already overloaded with CO_2. The gas passed through the water body with high flux and without being influenced by dissolution processes.

Seasonal variations of the CO_2 flux in the case of some of these sites were previously reported by Airinei et al., 1975, but a possible seasonality of the CO_2 concentration was not explored. We did not find significant differences in terms of seasonal concentrations of the gas species. Any difference can be explained in terms of meteorological influence (Viveiros et al., 2008), that needs to be investigated more detailed in the future, or the 2% accuracy of the Gascard detector.

The CH_4 concentrations showed variations also in the literature data. For example, at site no. 3 the CH_4 concentration varied between 0.8 (Kis et al., 2019) and 3.4% (Vaselli et al., 2002), while with Multi-GAS we measured concentrations between 1.3 and 3.9% (Table 1). The high variability of the CH_4 measurements, performed both with the Multi-GAS and with gas-chromatography could be due to the low concentrations of CH_4 in general in the analysed gases, so these measurements can only give qualitative information.

As concerning the H_2S concentration, in several cases the only available data is provided by our Multi-GAS measurement. As previously explained in Section 4 the sampling and measurement of H_2S needs special care so the production of accurate data is difficult (Vaselli et al., 2006). Our measurements stabilized around 200 ppm for sites no 3, 4, 5, 7, 8 (Figure 5 from the main text and Figures S2, S3, S4 and S6 from the Supplementary Material), which was the saturation level of the H_2S sensor we have used. For these sites the H_2S concentrations were higher, as demonstrated also by the former compositional data (e.g. site ID 3, 840 ppm, at site ID 4, 1100 ppm, at site ID 5, 1100 ppm, at site ID. 7, 270 ppm was reported by Kis et al., 2019). A possible an on-site dilution of the gas sample could be a solution for the measurement of cases where the H_2S approaches the upper detection limit of the sensor.

Sulphur forms different minerals, described in the study area (Szakáll et al, 2010), it appears as a native element and precipitates on the ground as indicator for the gas went (at sites ID 1, 7, and 8). Other type of sulphur manifestations is as sulphide minerals, e.g., together with arsenic it forms orpiment (at sites ID 3 and ID 9, Figures S2 and S7 from Supplementary Material) or together with mercury it forms cinnabar (e.g., at site 12A, Figure S10, Supplementary Material) (Szakáll et al., 2010). Despite mofette 12A and 12B being both in the same locality, their H_2S concentration is different: at the 12A being with one order of magnitude higher (63.3 to 78.4 ppm) that at 12B (2.14 ppm). This can be possible due to the proximity of site 12A to the former cinnabar mining area. Intense alteration of the ore-bearing rocks and forming of secondary minerals was described by Laczkó et al., 2005, 2010 at site 12A. Heavy metal anomalies in the soil, acidic waters and springs characterized the environment of the former cinnabar mining area at Sântimbru-Băi (Laczkó et al., 2005, 2010). This anomaly is also reflected by the difference in the H_2S concentration of the two mofettes 12A and 12B (Figures S10 and S11 from Supplementary Material). Production of sulphur gases in strongly acidic and reduced environment was observed both in natural and laboratory conditions, and showed by thermodynamic models as a result of weathering of sulphide minerals (Lin et al., 2021, Plet et al., 2021). A similar scenario also can be assumed in the case of mofette12A and the rest of the sites, where the H_2S concentration reached values ~200 ppm with our Multi-GAS (IDs 1, 3, 7, 8, 9). However, the production and origin of the H_2S in the Carpathians was never clarified with detailed isotope-geochemical investigations.

The H_2S, present only at some specific cases in the CO_2-dominated gas emissions, is assumed to be both of "post-volcanic" origin and the result of the weathering-processes of sulphides (Péter and Makfalvi, 2011).

The measurements performed with the Multi-GAS instrument show good agreement with previous data gained with gas chromatography, as illustrated on the intercomparison correlation plot shown in Figure 6 for CO_2. In this plot we used the average of the seasonal values for the Multi-GAS measurements, and compared them with gas chromatography data from literature. The good agreement between gas chromatography and Multi-GAS for CO_2 is supported by the correlation coefficient of R=0.70 and the good fit to the 1:1 curve. This good correlation suggests, that although classical analytical techniques, like gas chromatography are much more precise, the Multi-GAS can be used on the field to measure concentrations of different gas species prior detailed compositional measurements in the laboratory. The Multi-GAS measurements can also help to identify anomalous spots (as suggested by the case of sites 12A and 12B) for H_2S, that can be further investigated for ore exploration. We remind that as the gas chromatography results refer to previous investigations made even years before the Multi-GAS surveys, the fact that a correlation is observed is surprising, but still in full support to the validity of the Multi-GAS approach.

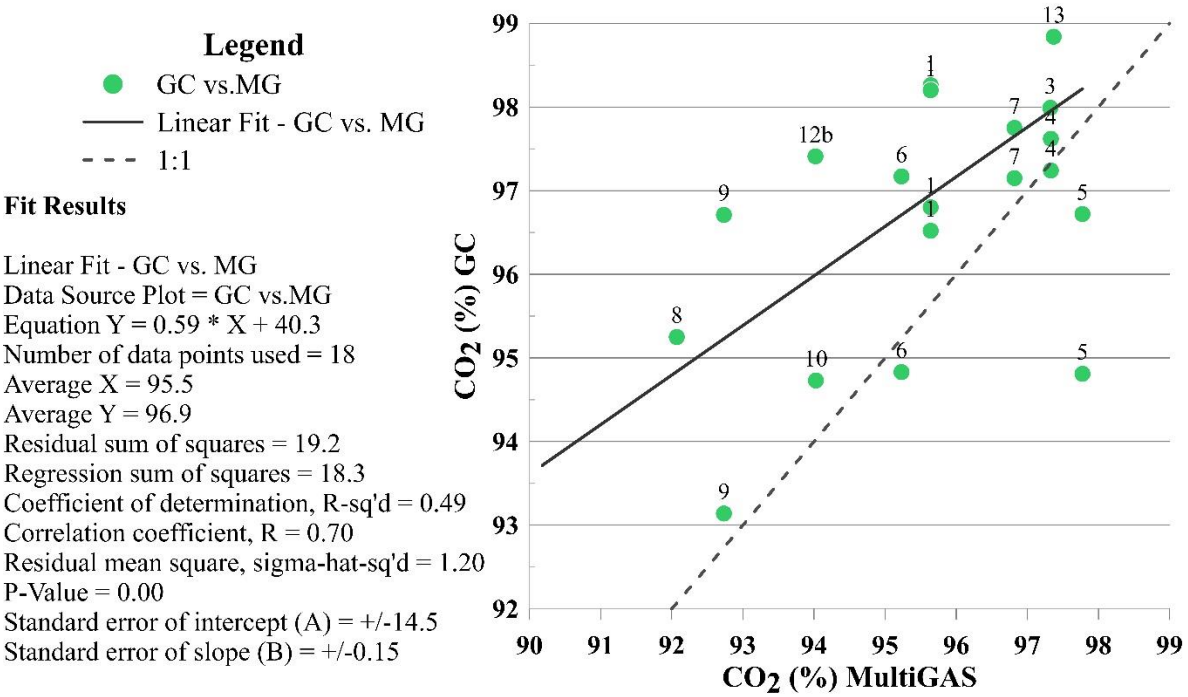

Figure 6. Intercomparison plot for CO_2 between the literature data (Althaus et al., 2000, Vaselli et al., 2002, Frunzeti 2013, Kis et al., 2019) using Gas Chromatography and the Multi-GAS data.

Conclusion

In our study we tested the utility of a specially designed Multi-GAS instrument, equipped with CO_2, CH_4 and H_2S sensors, in areas of low-temperature gas emissions, that are not directly related to active volcanic degassing. At the study area of the Eastern Carpathians some sites had previous compositional information available performed with the classical analytical techniques, which were used as comparison to our data.

Our results show that there is a good agreement between gas chromatography and the Multi-GAS measurements, with a correlation coefficient R=0.70 for CO_2. Our measurements revealed anomalies for H_2S concentration, in some cases exceeding the upper detection limit of our sensor. In this case the on-site dilution of the sample could be efficient. The H_2S anomalies can be related to geogenic sources, the alteration processes of sulphide minerals (e.g., sites 12A and 12B). The CH_4 values showed high variations both in literature data and with Multi-Gas measurements, that allows to treat the data only qualitatively.

The measurements proved that can be used as a powerful and low-cost tool in the investigations of degassing fluids in low temperature systems. The use of Multi-GAS in such environments opens new perspectives in the survey and mapping of gas emissions at low temperature areas, that can be performed prior detailed laboratory analyses.

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