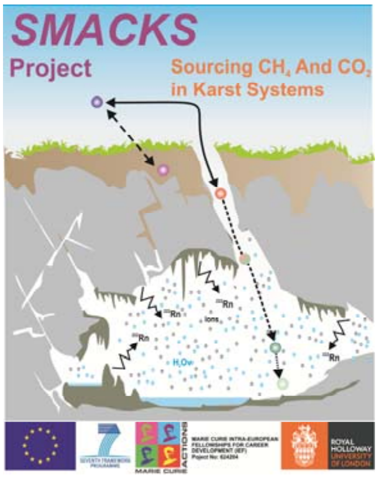
1. PUBLISHABLE SUMMARY

1.1. Summary description of the project objectives:

The increasing concentration of greenhouse gases (GHGs) in the atmosphere and its relationship to the Earth's climate has received increasing scientific attention in the recent years. One of the biggest current challenges is the identification and characterization of all possible sources, reservoirs and sinks of GHGs, in order to more accurately calculate the carbon greenhouse gas budget. In consideration of these facts, the subterranean atmospheres are key locations to be considered regarding the balance of atmospheric carbon. Between 15% and 25% of the continental surface is capable of harboring underground air masses (mainly linked to karstified outcrops of carbonates) that are periodically renewed by interaction with the atmospheric boundary layer and directly influence their physicochemical properties. However, the pathways and mechanisms that control the fluxes of carbon in various gaseous forms (CO_2 or CH_4) among atmosphere, soil and subsurface reservoirs have not been thoroughly characterised to date.



This IEF Marie Curie project "SMACKS" aims to study the dynamics of the main GHGs: CO_2 and CH_4 in natural underground environments of karst terrains and the identification and quantification of their role in the terrestrial ecosystems C-budget. The main goal of this project is to define and characterize the biotic and abiotic processes that regulate the production, consumption and storage of these GHGs in near-surface underground environments and assess their interaction with the external atmosphere. The derived results of this project will contribute to the identification, characterization and quantification of biogeochemical agents and mechanisms responsible for consumption and emissions of GHGs in the shallow vadose zone in diverse geologic, geographic and climatic locations.

1.2. Description of the work performed since the beginning of the project:

The research project has been mainly based on the combination of continuous multi-parameter monitoring of the cave-soil-atmosphere system at selected sites (main climatic data and gas composition) with geochemical tracing using the stable carbon isotopic ($d^{13}C$) of both CO_2 and CH_4. The main research activities performed since the beginning of the project have been grouped on the following work packages:

<u>WP-1: Fieldwork</u>

The main field sites were: Garma cave (Cantabria, Spain), Ojo Guareña cave (Burgos, Spain), Castañar cave (Cáceres, Spain), Rolande and Pech Merle caves (France) and Pooles cavern (UK). These caves have hosted the greater part of the research tasks of the project because the scientist in charge and the Marie Curie fellow (and his collaborators) have maintained some comprehensive monitoring and sampling networks in place during the project for air analysis of soil and subsurface and the real time monitoring described in the original research proposal. These field sites cover a wide latitudinal transect across Europe and complete a full suite of monitoring scenarios in terms of prevailing climate, geomorphologic and karst features.

Two types of field surveys will be implemented throughout the project;

1) Spot sampling, maintenance of monitoring equipments and data download: Field surveys of 1-2 days-long for spot sampling of the atmosphere, soil and cave air for isotope analysis, in conjunction with the maintenance and data download of environmental control equipments and the calibration of sensors. Predefined networks of sampling points were spatially distributed from the entrance to the innermost accessible areas of the cavities. The exterior and soil air were also sampled at fixed locations throughout the day, and, preferably, during maximum (midday) and minimum photosynthetic activity (early morning). Air samples have been analysed in two

laboratories: GHG lab of the Department of Earth Sciences at RHUL (Royal Holloway, University of London) and the Department of Geology at the National Museum of Natural Sciences - MNCN (CSIC- Spanish Research Council) for determining CO_2 and CH_4 concentrations and the isotopic $d^{13}C$ signal for both gases using wavelength scanned cavity ring-down spectroscopy (CRDS-WS) and continuous flow-mass spectrometry.

2) Real-time CRDS monitoring: In order to achieve an assessment of the complete daily cycles of the GHG mixing ratios in shallow cave and its gas exchange pattern under extreme and opposite weather conditions, continuous and in situ monitoring of air and isotope analysis based on wavelength scanned cavity ring-down spectroscopy (CRDS-WS) for 2-3 days period was centred on two peak summer and peak winter periods. This task has comprised a continuous monitoring of cave climate and geochemical tracing using the stable carbon isotopic ($d^{13}C$) of both CO_2 and CH_4 in cave air, soil air and the exterior. The selected field site for this real-time monitoring has been the Castañar cave (Cáceres, Spain) that offer suitable facilities (external building and secure power supply) to carry out a comprehensive real-time logging using a field-deployable CRDS analyser for several days or longer periods.

During the reporting period it has been conducted 28 field campaigns considering all the main studied sites and distributed as follows: 7 (Garma and Ojo Guareña caves), 4 Castañar and Pooles cave), 3 (Pech Merle and Rolande caves).The periodicity of the air sampling and the cave monitoring works in the main field sites have been bimonthly (mainly in La Garma and Ojo Guareña caves) or seasonal (others).

WP-2: Training-through-research activities.

This work package has been mainly focused on analysing the samples collected in the field to quantify the concentrations and isotope signal of trace gases in the subsurface, soil air and background atmosphere and the subsequent data processing and analysis of results. The equipment and facilities, which belong to the Greenhouse Gas Laboratory at RHUL, have provided this project with the excellent option for training and performing high accuracy analyses of gas abundances and isotopic compositions. CO_2 and CH_4 mole fractions of the air samples in Tedlar bags were measured independently in the laboratory with a Picarro G1301 CRDS analyser with an average precision of ±0.5 ppb. The carbon isotopic ratio ($d^{13}C$) was measured in triplicate to high precision (±0.05‰) by continuous flow gas chromatography isotope ratio mass spectrometry (CF GC-IRMS).

WP-3: Data processing and modelling geochemical database

This work package has comprised the data gathering, including the updating of data from previous monitoring programs and the data interpretation and modelling of the geochemical processes. These work tasks have been performed each time at a couple of field surveys and training-through-research tasks were achieved. At some field sites, the data gathering and processing has been periodically in collaboration with the research groups responsible for the active monitoring programs in each site: Pooles cavern (Prof. I. Fairchild and Prof. J. Gunn, School of Geography, Earth and Environmental Sciences at University of Birmingham), Perch Merle cave (Dr. F. Bourges – GEconseil, France), and the researchers from MNCN-CSIC (Dr. S. Sanchez-Moral and Dra. S. Cuezva) in the case of the Spanish caves.

The $d^{13}C$ variations of both gases (CO_2 and CH_4) in soil and cave air provide considerable insight into the nature of gas exchange between the atmospheric, soil and underground air gas reservoirs. In this sense, some of the preliminary data assessments after the fieldwork campaign have comprised the Keeling plot analysis of each GHG and the modelling of the carbon isotope fractionation of both gases during its consumption, accumulation, mobilization (e.g., bacterial oxidation of CH_4 or diffusion of soil-derived CO_2) or the mixture of gases with distinguishable origins or resulting from different consumption or production processes. Modelling has also implied that the combination of results should be used in order to establish the cause-effect pattern of GHG turnover rates at the subsurface. For instance, the comparison of CO_2 and CH_4 has enabled the assessment of the influence of the exterior atmosphere and soil on the gas contents of cave air, that is, the degree of isolation of the subsurface environment. Finally, in cases with a long data base (e.g., subterranean karst system of Ojo Guareña) a mass balance of air advection was performed to estimate the total CO_2 flux from the cave to the external atmosphere under different meteorological conditions, as well as some first attempts to infer an up-scaled model of GHG variations in dynamically ventilated caves.

1.3. Description of the main results achieved so far:

During this first period of the project, a valuable acquired knowledge and data base it has been compiled sourcing GHGs in different karst systems across Europe. To date, the results of the ongoing monitoring programs and the air analyses have greatly improved the understanding of the current cause-effect pattern between climatic factors and the exchange of CO_2 and CH_4 from the atmosphere and soil to the subsurface. These results have provided evidence that the subterranean atmosphere of karst systems may play a key role in regulating greenhouse gases in the atmosphere.

In general, these results confirm that the vadose zone of karst ecosystems may act as a significant reservoir of CO_2-gas on an annual scale. A pooled analysis of the data compiled during the project has allowed us to assess the processes by which the atmospheric air that is inhaled into dynamically ventilated caves can return to the lower troposphere as CO_2-rich cave air. With respect to methane, the results provided by the project have demonstrated that the sub-atmospheric CH_4 concentrations in underground air imply that caves are functioning as CH_4 sinks. The CH_4 consumption rate in underground air varies depending on the CH_4 input ratio from the atmosphere, which is determined by the intensity of cave air ventilation represented by the CO_2 levels, among other trace gases (e.g., radon). The increase in the residence time of atmospheric-derived air in the subterranean environment provokes a more effective CH_4 consumption, depleting CH_4 concentrations almost to zero throughout an annual cycle. Thus, the complete database regarding the gas composition compiled during the project has also allowed the assessment of the influence of the exterior atmosphere and soil on the gas contents of cave air. This influence represents the degree of isolation of the subsurface environment in function of the inverse relationship between the two GHGs along a subsurface-soil-atmosphere profile. Most isolated caves with the lowest ventilation rates (or the deepest remote cave locations) present a steady state with practically null CH_4 levels and higher CO_2 concentrations, thus suggesting a complete removal of CH_4 from the underground air.

The results from modelling the carbon isotope fractionation and CH_4 abundances show that the methane dynamics of subterranean environments on karst is consistent with atmospheric methane consumption. These results are also consistent in some cave locations or certain periods over an annual cycle, with minor biogenic methane sources that are highly diluted with cave air with sub-atmospheric CH_4 concentrations (Figure 1, for an example corresponding to La Garma cave – see the attached document).

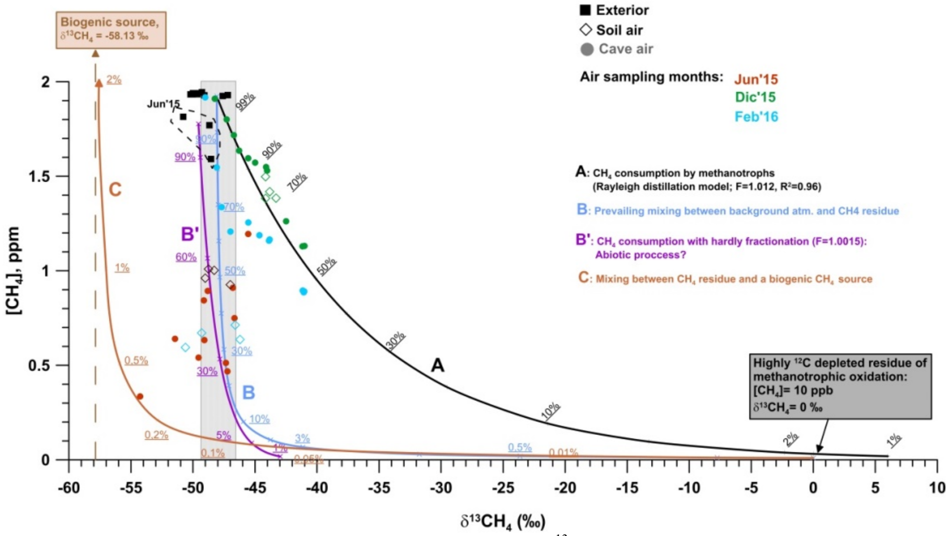


Figure 1. Relationships between methane concentration and d[13]C in the background atmosphere, cave and soil air for samples collected in La Garma cave (Cantabria, Spain).

To date, the abovementioned results derived from the SMACKS project have turned into two main scientific publications, in which the Fellow is the first and corresponding author (oversaw all fieldwork, designed the research and edited the manuscript) of these publications;

1. Fernandez-Cortes, A. et al. 2015. Subterranean atmospheres may act as daily methane sinks. *Nature Communications* 6 - 7003, pp. 1 - 11.

This article presents remarkable results regarding methane (CH_4) sources and sinks and their evolution over time. Through seasonal geochemical tracing of air in the atmosphere, soil and underground at diverse geographic and climatic locations, carried out under the SMACKS Project, we revealed that near-surface cavities in the uppermost vadose zone are actively removing atmospheric CH_4. Our results also indicate that subterranean atmospheres may be acting as sinks for atmospheric CH_4 on a daily scale. Furthermore, the results derived from our continuous monitoring of underground air confirm that a complete CH_4 depletion occurs in underground air under near vapour-saturation conditions, as it is enriched in radon and ions (Figure 2; example corresponding to Ojo Guareña cave – see the attached document). It is noteworthy to mention some quality indexes of this publication: Journal Impact Index 11.470 (in accordance to 2014 edition of Journal Citation Report© - Thomson Reuters) and belonging to the first quartile Q1 in the category "Multidisciplinary Sciences" (position 3 of 57 total journals in the category).

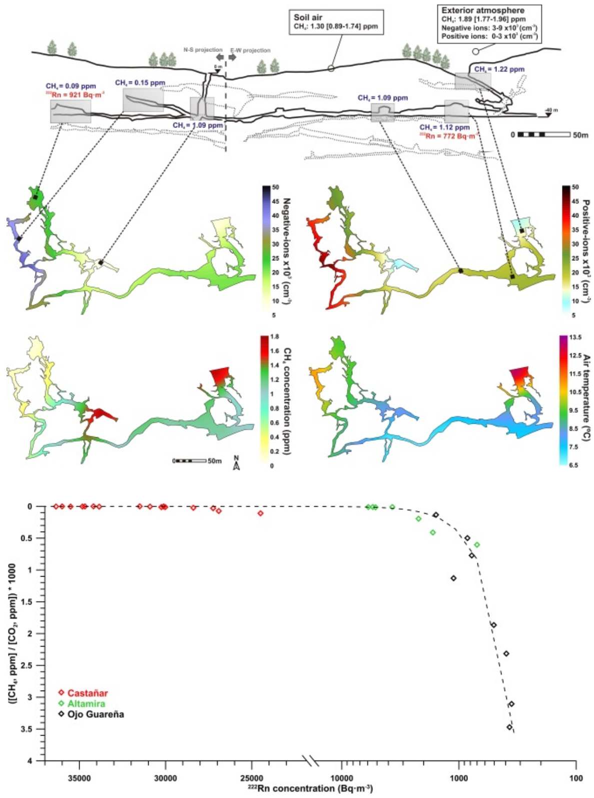


Figure 2: Spatial variation of air ion concentration, temperature and CH_4 concentration and variations in the ratio of the concentrations of both greenhouse gases (CO_2 and CH_4) in underground air in relation to radon activity. The data are from a dynamically ventilated cave (Ojo Guareña cave, Spain).

2. Fernandez-Cortes, A. et al. 2015. Changes in the storage and sink of carbon dioxide in subsurface atmospheres controlled by climate-driven processes: the case of the Ojo Guareña karst system. *Environmental Earth Sciences*. 74, pp. 7715 - 7730.

This scientific publication comprises the main results of a comprehensive environmental monitoring program conducted in one of the longest cave systems in Europe (Ojo Guareña karst system, Spain) as a part of the field work performed under the SMACKS project. In this study, an assessment of the spatiotemporal changes in carbon dioxide gas (CO_2) in the cave–soil–atmosphere profile was conducted. The key climate-driven processes involved in gas exchange, primarily gas diffusion and cave ventilation due to advective forces, were characterized by continuous logging systems. The seasonal and daily pattern of CO_2 concentrations and its carbon isotopic signal were modelled in order to calculate the CO_2 balance after ventilation pulses (Figure 3 – see the attached document). Additionally, there was a first attempt to up-scale on a global scale and on different time scales, the CO2-rich underground air that can return to the lower troposphere from dynamically ventilated caves.

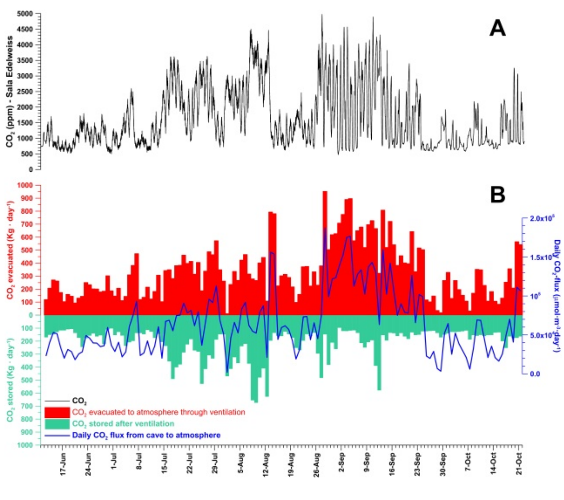


Figure 3. A: Daily variations in carbon concentrations in underground air of the Ojo Guareña cave (Spain) and B: Balance between CO2 outgassing and storage underground after each daily pulse of ventilation (CO2 flux expresses as mmol day-1 per cubic meter of air).

The Marie Curie Fellow has also been involved in collaborations with some scientists from other research centers (Cambridge University, University of Alicante and University of Almeria) with ongoing projects with a similar topic to the SMACKS project, which has allowed publishing three other scientific articles related to GHG dynamics in underground environments and cave climates. These publications in journals indexed in the Journal Citation Reports (JCR) (*Environmental Earth Sciences, Journal of Hydrology and Journal of Environmental Radioactivity*) relating to foreground and the research topic of the project are described in the final report, including works presented in International conferences, two other manuscripts submitted to journals indexed in JCR (currently under consideration).

1.4. Expected final results and their potential impact and use

The records and findings obtained in the SMACKS project and the expected final results have a direct application and a significant short-term impact on the monitoring and control of greenhouse gases and understanding the carbon balance in terrestrial ecosystems. In particular, this project is contributing with new data and an understanding of the variations of gas composition of underground air at a small scale in detailed field studies of a diverse set of shallow atmospheres of the vadose zone. The vadose zone is a terrestrial ecosystem whose operation is still largely unknown in terms of the exchange, storage or sinks of the main greenhouse gases.

The Smacks project is providing a detailed knowledge of the processes underlying gases emissions or storage in subterranean environments with direct connections with the lower troposphere. This is vital for understanding, attributing and managing sinks and sources related to this type of terrestrial ecosystem. Such understanding leads to improvements in flux estimates, allowing inventories with greater sensitivity to management and climate, and advances the upscaling modelling of feedbacks between climate, GHGs and carbon exchange in the vadose zone. Along these lines, the Intergovernmental Panel on Climate Change (IPCC) highlights the need to identify and quantify sinks and sources of atmospheric GHGs to enable management for sink optimization. The results and database of the project could also be useful for any policy maker, who requires information on GHG emissions at field-scale and inferring estimates of emissions and sinks at large scales.

The multi-disciplinary nature of the SMACKS project will also result in future benefits to the European Research Area, by bringing together different research fields on the study of gas exchange within the atmosphere-soil-subsurface system, including microclimatic, gas monitoring and the control of abiotic and biotic processes involved. In this context, tackling climate change and the need for more knowledge regarding the geological storage (or release) capacity of natural ecosystems is one of the six societal challenges in the European Horizon 2020. In particular, the SMACKS project falls within Action SC5-16-2014: Making Earth Observation and Monitoring Data usable for ecosystem modelling and services, included in the Horizon 2020 Societal Challenge: Climate action, environment, resource efficiency and raw materials.

The removal of unburned hydrocarbons from exhaust, such as CH_4, is a main issue to solve in energy production systems. To date, the catalytic oxidation of CH_4 is the most common method for removing this GHG, where it is need to reach a high temperature (>350°C). From this technical point of view, the SMACKS project is providing a valuable database concerning the agents and mechanisms of oxidation of methane at low temperatures under natural conditions, and in particular, in subterranean environments. These results will contribute to the knowledge base and improved knowledge regarding the oxidation of CH_4 in the subsurface atmosphere under characteristic temperature and pressure conditions of the troposphere near sea level. In the medium and long term, these findings could lead to development of new and cost-effective technological alternatives for atmospheric CH_4 elimination in underground environments as a mitigation strategy for emissions of this gas.