



Invited review

Cave aerosols: distribution and contribution to speleothem geochemistry

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ABSTRACT

There is developing interest in cave aerosols due to the increasing awareness of their impacts on the cave environment and speleothem; this paper provides the first attempt to synthesize the issues. Processes of cave aerosol introduction, transport, deposition, distribution and incorporation are explored, and reviewed from existing literature. Key issues of specific aerosol processes of distribution and production as well as cave location and morphology effects are highlighted through the presentation of preliminary monitoring data. This study identifies the strong relationship between cave ventilation, cave aerosols and their consequent spatial distribution.

The contribution of cave aerosol deposition to speleothem geochemistry is modelled and evaluated using a mass balance framework. As an example, speleothem trace element data from Obir Cave (Austria) are compared with aerosol inputs to evaluate their significance. The mass balance study demonstrates that generally, under normal continuous growth and environmental conditions aerosol deposition will be of only minor importance. However, it highlights specific scenarios in which aerosol contributions will be significant: speleothem hiatuses (or slow growth), high aerosol deposition, and secondary microbiological feedback.

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1. Introduction

A new sector of interest is developing within cave science regarding the influence of aerosols on the cave environment and the potential palaeoenvironmental record which may be preserved within cave precipitates as a result of aerosol incorporation.

The potential degradation of the cave environment resulting from cave aerosol deposition and associated mitigation practices are growing issues among cave management organisations especially for show caves. Degradation can occur from external pollutants or from visitor disturbances to the natural cave environment.

The effects of anthropogenic dust on caves may be subtle, but threaten the long-term preservation of cave environments.

Soiling of the cave environment has occurred as a result of coal industry pollutants (Christoforou et al., 1994; Salmon et al., 1994, 1995) and airborne dust from regional dust storms (Christoforou et al., 1994). Black deposits causing degradation in other caves have been attributed to deposits from vehicle exhaust (Jeong et al., 2003; Chang et al., 2008) and biomass burning emissions (Chang et al., 2008). Michie (1999) partially attributed the slow degradation of cave aesthetic values to cave visitors transporting, releasing and causing re-suspension of aerosols within the cave. In caves where candlelight or carbide lamps tours are operated (e.g. Ohms, 2003) the introduction of aerosols as a result of combustion will likely result in the degradation of cave surfaces in addition those stated by Michie (1999). In some cases aerosol

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issues are remediated through improved cave conservation practices. For instance, Altamira Cave (Spain) was closed to visitors due to anthropogenic fine particle resuspension from cave floor sediments, provoking microparticle detachment (releasing bacterial and fungal spores), among other factors. Installation of a thermally insulated access door reduced the entry of airborne particles, the condensation rate in the entrance area, and the metabolic activity of the main visible microbial colonies (Saiz-Jimenez et al., 2011).

Aerosols are generally defined as the suspension of fine solid or liquid particles within a gaseous medium (often being the Earth's atmosphere). Aerosols become suspended into the Earth's atmosphere via many processes, both natural (e.g. volcanic eruptions, windblown sands, forest fires) and anthropogenic (e.g. biomass burning, vehicle emissions, constructions); examples of emissions to the external atmosphere are displayed in Fig. 1. Aerosols can be grouped and identified based on a range of properties, both physical (e.g. colour, morphology, size) and chemical (e.g. inorganic, organic, isotopic).

Atmospheric aerosols enter cave networks due to external transportation processes, travel within caves as a result of cave ventilation, and are either deposited, or transported with cave air and eventually removed from the cave system. The removal of aerosols from air occurs as a result of either wet or dry deposition. Dry deposition is the process by which atmospheric trace constituents are transferred by air motions to the surface of the Earth (Wesely and Hicks, 2000). The main processes by which dry deposition occurs are outlined below (Petroff et al., 2008):

- Brownian diffusion – The random movement and collision of particles can cause deposition; this process affects very fine particles typically smaller than 0.1 μm .
- Interception – Particles entrained in a stream flow are retained by an obstacle when their path passes within one particle radius of the object.

- Impaction – An aerosol with significant inertia transported by the flow towards an obstacle cannot follow the flow deviation in the vicinity of the obstacle causing particle collision with the obstacle and remaining on the surface.
- Sedimentation – particle fall-out due to gravitation.

Wet deposition is the removal of material from the atmosphere by hydrometeors as a result of condensation and precipitation. Wet deposition can also be referred to as precipitation scavenging, rainout (typically used for in-cloud processes), and washout (typically used for below-cloud processes) (Loosmore and Cederwall, 2004).

The dry depositional efficiency is expressed as a deposition velocity, v_d , where

$$v_d = F/C$$

where F is the particle flux to the surface, and C the airborne concentration at a reference height. Because deposition involves several mechanisms, as outlined above, v_d is a complex function of particle size, with the highest values for very small (<0.1 μm diameter) and large (>1 μm) particles. In the range 0.1–1 μm where much of the mass of atmospheric aerosol resides, values of v_d are very small. For very large particles, typically >10 μm diameter, v_d becomes almost equal to the gravitational settling velocity, but for smaller particles (<10 μm) it is substantially greater (Seinfeld and Pandis, 1998).

Aerosols, once suspended into the atmosphere through emission processes, will be carried with parcels of air and mixed with other aerosol types which may have properties characteristic of their emission and geographical source. Hence it may be possible to determine palaeoenvironmental conditions through the incorporation of aerosols within speleothem. Sr isotope studies have demonstrated the ability to utilise aerosols to identify the geological source region of terrestrial dust by comparing to the Sr isotopic ratio

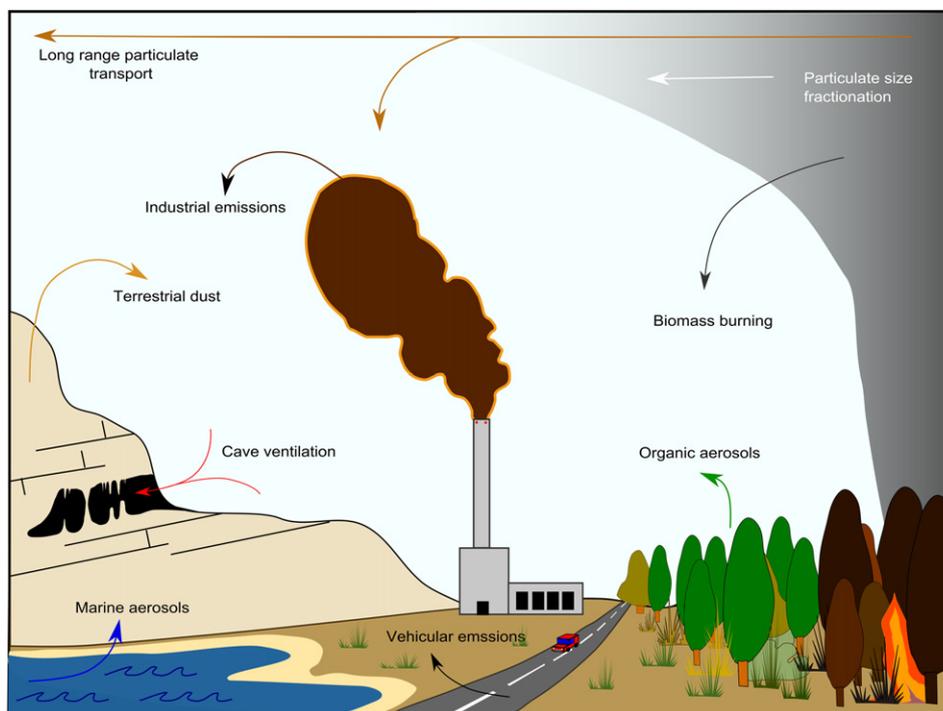


Fig. 1. Illustration of tropospheric aerosols which are likely to be emitted in large enough quantities to be incorporated and detectable within speleothems. Aerosols produced within the cave environment also have the potential to become incorporated in detectable quantities.

of dust surface deposits (Li et al., 2005; Yang et al., 2009; Masson et al., 2010), of waters (Jin et al., 2011) and in speleothem (Goede et al., 1998; Verheyden et al., 2000; Frumkin and Stein, 2004; Zhou et al., 2009) although the mode of transmission of the chemical signal is normally proposed to be via dripwater. Fire events and source regions have been successfully identified through constraining region-specific vegetation burning events in ice and sediments (Laird and Campbell, 2000; Wang et al., 2005; Zhou et al., 2007; Kehrwald et al., 2010a; 2010b; Wang et al., 2010) using a range of organic proxies (reviewed in Simoneit, 2002). Different types of vegetation have known associated organic components which are released during burning events; the region of burning and therefore the direction of transport can then be deciphered. Similar fire-proxy work may be applicable to speleothems.

For modern studies, air mass travel paths can be tracked and modelled. Atmospheric transport and dispersion modelling using HYSPLIT and other programs allows air mass trajectory estimation of past air movements, or projections to produce forecast trajectories (<http://ready.arl.noaa.gov/HYSPLIT.php>). These simulations are based on recorded or predicted meteorological conditions for past and future modelling respectively. Air mass trajectories provide an insight into the likely long-range aerosol source locations and thus aid in the identification of aerosol emission processes.

The presence of cave aerosols is controlled by a combination of internal aerosol production and the incorporation of transported externally sourced aerosols. Cave ventilation and morphology will strongly influence how aerosols are transported and deposited within the cave environment. The quantity and effect of cave aerosols on speleothem geochemistry has rarely been explicitly considered so far. By investigating and gaining an improved understanding of how aerosols are transported, distributed, deposited and ultimately incorporated into forming speleothem we will potentially be able to identify aerosol signatures within the speleothem palaeoenvironmental record. This paper provides the first attempt to synthesise the issues concerning cave aerosols, with particular focus on the situations in which aerosols will provide a significant contribution to speleothem chemistry. Specific processes affecting the transport and deposition of cave aerosols will be highlighted through the presentation of monitoring data at several sites. We demonstrate that although aerosols are expected to be of minor influence during normal speleothem growth, they can provide a major contribution to bulk chemistry at hiatuses.

The review will be structured as follows: previous aerosol investigations, associated methods and the methods (sampling, extraction and analytical) utilised for monitoring work presented in this paper will be discussed. Next, aerosol sources, processes, distribution and deposition mechanisms are explored. In the results section, specific aerosol processes will be highlighted with preliminary data from cave monitoring. Finally, aerosol contributions to speleothem geochemistry will be evaluated through the comparison of known deposition fluxes to dripwater and speleothem geochemistry in Obir cave, Austria, a site where distinct aerosol contributions to speleothem chemistry have been proposed (Fairchild et al., 2010).

2. Methods

A plethora of aerosol properties can be analysed to investigate specific processes. Some of the key properties and associated processes are summarised in Table 1.

An extensive range of methods exist for the sampling, monitoring and analysis of cave aerosols, each specific to the information required and depending on the application. Due to the logistics of working in the cave environment cave aerosol investigations will often require passive or self-powered portable equipment for aerosol sampling and in-situ analysis.

Table 1

Aerosol properties and the processes which can be explored as a result of their investigation.

Cave aerosol property	Reason for investigation
Suspended concentration	Aerosol transport and distribution
Deposition flux	Aerosol distribution (especially to speleothem surface)
Inorganic chemistry	Source identification, potential chemical addition to speleothem, transport.
Organic chemistry and/or associated microorganisms	Source identification (especially processes associated with biomass burning), transport, airborne bacteria and fungi identification
Aerosol size	Transport, distribution
Aerosol morphology	Transport, source identification (lesser extent than chemistry)

2.1. Sampling

2.1.1. Dry deposition sampling

There is no generally accepted method to directly measure or estimate dry deposition (Chu et al., 2008). However, it has been established that a smooth horizontal surrogate surface provides a lower bound estimate of the dry deposition flux onto a horizontal surface (Sehmel and Hodgson, 1978; Holsen and Noll, 1992). Dry deposition is determined through the capture of aerosol deposition to a known surface area. Surrogate surface sampling does not require power and designs can be portable, making this method highly suitable for cave monitoring studies.

There is a range of apparatus currently being used for surrogate surface sampling. The most basic and generally used being a smooth horizontal plate surface to collect deposition. Smooth surfaces provide an interface which can be cleaned making it ideal for elemental chemistry analysis: polyvinyl chloride (Lim et al., 2006; Chu et al., 2008; Zhang et al., 2011) and glass slides (Salmon et al., 1995) have been used.

The positioning of surrogate surfaces within the cave network appears to be relatively robust in its sensitivity and exposure of the surrogate surface relatively unimportant: Michie (1997) found that even when sheltered by a covered surface (28 mm above) dust deposition is only reduced by 50%. In the external environment, retention has been shown to be influenced by atmospheric precipitation (Lyman et al., 2007). Therefore, in the cave environment care should be taken about the placement of surrogate surfaces in relation to active drip sites.

Petri dishes (see supplementary material section S.3 Figure S.1) provide a convenient means as the collection surface can be readily capped and then sealed with Parafilm™ reducing the potential of contamination during transportation once cleaned, and after sampling. Specific preparation and extraction procedures are required for the collection and analysis of the different aerosol species. In this study Polytetrafluoroethylene (PTFE) filters were used as a surrogate surface collection medium in samples where the inorganic aerosol component was to be analysed. PTFE filters provide reduced blank levels in comparison to other filter media available, and provide a rough collection surface. Further details on surrogate surface types and sampling methods can be found in the supplementary material section S.1.2.

2.1.2. Suspended aerosol sampling

Where access to cave networks and time is available, active sampling provides an alternative to surrogate surfaces. Active sampling is conducted by pumping a known volume of air through a filter medium. The use of active sampling is advantageous over surrogate surfaces due to its ability to produce quantitative aerosol concentration levels at higher temporal resolution. Total atmospheric aerosol concentrations or specific aerosol species

concentrations can be determined. This method is versatile since post-capture, aerosols can be weighed, observed and analysed dependent on the investigation type.

Increased pumping rates provide better aerosol collection and shorter durations offer improved temporal resolution, but generally pumped samples are run for 24–48 h at 1 to 30 L min⁻¹ in the cave environment (Sanchez-Moral et al., 1999; Alfödy et al., 2000; 2001; Yang et al., 2006; Faimon et al., 2006) as well as in confined situations (Nava et al., 2010) and often in the external environment too (e.g. Allen et al., 2001; Harrison et al., 2003). For this study pumps were run at 3 L min⁻¹ for 24 h duration. A dual pump setup (see supplementary material section S.3, Figure S.2) was chosen for simultaneous sampling onto two filter media for the collection of both inorganic and organic aerosols.

Suspended aerosol particle counters offer essentially instantaneous aerosol concentration values. Particle counters measure directly providing high resolution temporal data. A range of portable battery-powered particle counters exist which can be used for temporal monitoring of aerosol concentrations in cave systems and are suitable for detailed spatial monitoring. This has been successful both in the cave environment (Michie, 1999; Sanchez-Moral et al., 1999; Kertész et al., 2000; 2002; Iskra et al., 2010) and in the external atmosphere (Allen et al., 2001; Jones and Harrison, 2005). Particle sizes reflect how aerosols become entrained and transported in the atmosphere; they are therefore a useful tool for the investigation of aerosol transport within the cave environment. Fig. 2 displays the size ranges for the aerosols types used in this investigation.

A TSI SidePak AM510 particle counter for 0.1–10 µm diameter particles was used in this investigation to determine suspended aerosol particle mass. Additionally, a TSI Aerotrak™ Model 9306 airborne particle counter was specifically used in the aerosol monitoring carried out at Altamira Cave (Spain). This device has a 0.1 CFM (2.83 L/min) flow rate and counts up to bin sizes from 0.3 to 25 µm, logging up to 6 particle sizes simultaneously.

Filter preparation in this study was the same for both pumped and surrogate surface sampling. PTFE filters and glass Petri dishes were cleaned for a minimum of 24 h in 2% HNO₃ then triple-rinsed with DDIW. The surrogate surface equipment was prepared in a clean laboratory environment to minimise blank values.

2.2. Extraction and analysis

Protocols for material extraction from filters and chemical analysis of deposited aerosols vary greatly, and are dependent on elements under investigation and sampling methods, but all techniques are constructed with the intention of reduced sample contamination throughout the procedure. Extraction methods will only be summarised and the methods chosen for this investigation justified. Detailed methods of extraction and analysis are presented in the supplementary material, section S.1.

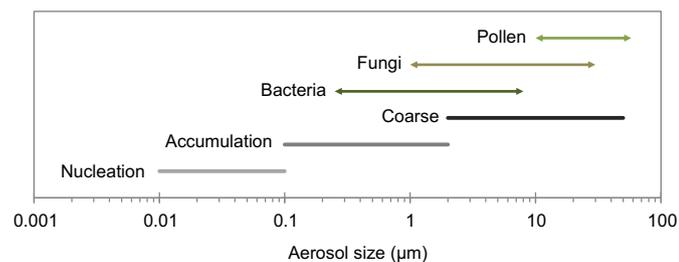


Fig. 2. Aerosol size distributions, both inorganic (Seinfeld and Pandis, 1998) and organic (Jones and Harrison, 2004) compared with size classes of Whitby and Cantrell (1975).

2.2.1. Inorganic

One of the most established and widely used methods (Janssen et al., 1997; Harrison et al., 2003) of air sample extraction from a filter medium is the reverse aqua regia digestion method developed in Harper et al. (1983). Various method combinations exist, but the majority involve ultrasonication and acid extraction with nitric acid (or DDIW for ionic species) as key components (Allen et al., 2001; Lim et al., 2006; Chu et al., 2008; Wai et al., 2010). More intensive digestion can also be used with a combination of HNO₃, HF and HClO₄ (e.g. Chang et al. 2008). In order to replicate a similar extraction to speleothem analysis a 2% HNO₃ and 120 min ultrasonication with heat was the chosen extraction method for this investigation. DDIW and 120 min ultrasonication was used for major ion species extraction (since 98% of sulphate, nitrate, and ammonium can be extracted with 120 min of ultrasonication (Chu et al., 2008)).

Inorganic aerosol chemistry in this investigation was obtained through ICP-AES analysis at Royal Holloway University of London. A suite of elements were analysed, total deposition in this paper refers to a total deposition of elements: Al, Fe, Mg, Na, K, Ti, P, Mn, Ba, Ni, Sr, V and Zn. Elements that demonstrate key processes will be displayed, as well as elements of importance to speleothems such as Mg and Sr.

2.2.2. Carbon

Carbon deposits have been established as a significant contributor to cave degradation and therefore the identification of carbon and its types are of increasing importance. Optical and thermal analytical techniques are most frequently used to measure carbon in atmospheric investigations (Ghedini et al., 2000). Studies often aim to investigate carbon types, total carbon (Nava et al., 2010) and differentiate between elemental and organic carbon (Jones and Harrison, 2005). Carbon isotopic composition offers an insight into the carbon mass fraction allowing for improved source identification. Characterization of radiocarbon as well as ¹³C/¹²C has been utilised by Chang et al. (2008) to distinguish cave carbon deposits and emission sources.

2.2.3. Organic – bioaerosols

Atmospheric organic aerosol investigations typically involve the emission products of combustion for human health and environment studies. Emission products can be utilised as a tracer for aerosol transportation in suitable case locations, and organic aerosols in speleothem have the potential to be used as a proxy for emission events. PAHs (Polycyclic aromatic hydrocarbons) are widely investigated as a proxy for hydrocarbon combustion and emission. PAHs have been extracted from soils, sediments and speleothem samples, but extraction methods are refined dependent on the species under investigation. Perrette et al. (2008) used dichloromethane in both Soxhlet and ultrasonication extraction for the extraction of organic species from stalagmites and sediments. PAH analysis is often carried out by Gas chromatography–mass spectrometry (GC–MS) and High performance liquid chromatography (HPLC) techniques.

Microbial air sampling was conducted in this investigation to quantify the level of airborne bacteria and fungal spores in the aerosol monitoring survey carried out at Altamira Cave (Spain). A Duo SAS 360 sampler (International PBI, Milan, Italy) containing Petri dishes with Dichloran Rose Bengal Agar was used for the sampling of fungi. For bacteria, the medium Tryptone-Soya Agar (TSA) was used. Duplicate samples of 100 L in air volume were selected as the most appropriate method for easy counting in this cave. Some specific applications of these aerobiological techniques in subterranean environments, including this cave, are described by Fernandez-Cortes et al. (2011) and Porca et al. (2011). Further details can be found in the supplementary material section S.3.

3. Cave aerosol processes

In this section, aerosol transport, distribution and deposition mechanisms will be highlighted with preliminary data from cave monitoring. Cave locations were chosen to isolate and investigate specific aerosol emitting processes. Data from a range of cave sites throughout Europe will be used to demonstrate the relationship between aerosol deposition flux rates and speleothem growth rates.

3.1. Cave aerosol sources

3.1.1. Externally sourced cave aerosols

Source areas and long-range transport of external aerosols can be determined to a degree through the utilisation of air mass trajectories since a body of air will incorporate aerosols released into the atmosphere which will then be transported as the air mass moves. Aerosols are then incorporated into the cave atmosphere through specific transport processes which are explored in Section 3.2.1.

3.1.2. Internally produced cave aerosols

In addition to the transport of aerosols from external sources there is the possibility for the addition of suspended aerosols to the cave atmosphere from internal sources. In some cases the contribution of aerosols from within the cave network will be orders of magnitude greater than that of externally sourced and transported aerosols.

3.1.2.1. Anthropogenic (cave visitor) production. Degradation of the cave environment as a result of aerosol deposits from human or animal visitors is known (Cigna, 1983, 1989, 1993). Particulate matter can be present as an existing aerosol deposit and therefore the visitor disruption simply results in the re-suspension of particulates from an aerosol source or suspension of particulates from subaqueous deposition within the cave. Cave visitors can also act as a carrier of externally sourced aerosol and release them inside the cave (e.g. lint, mud on shoes).

Measurements have shown a constant rate of deposition of airborne particulate material from show cave visitors of approximately one microgram per person per second (Michie, 1999). Bartenev and Veselova (1987) carried out measurements of dust sedimentation from aerosols in the Cupp-Coutunn Cave System (Turkmenistan) noting that the rate of sedimentation raises more than 10 times within 20 m surrounding the main tourist passages, indicating the significant aerosol production from cave visitors.

3.1.2.2. Hydrological production. Aerosols can be generated from water drops falling from a cave ceiling or generated by rapids and waterfalls in cave streams (Maltsev, 1997). Turbulent water can produce aerosols by a similar mechanism to that which occurs in the production of sea spray, with gas scavenging resulting in bubbles which rise to the surface and burst producing hydro-aerosols. ‘Splash’ aerosols can also be produced as falling drip-water impacting on cave surfaces resulting in small enough liquid aerosols to be transported in suspension. Aerosol deposition to water bodies causes suspension of liquid aerosols in the form of film and jet drops (Bridgman, 1994).

3.1.2.3. Bedrock production. Klimchouk (1994) and Klimchouk et al. (1995) proposed that cave aerosols can be generated as a result of radioactivity in the cave environment. It was proposed that alpha decay dislodges bedrock to form aerosols. This was further investigated by Pashenko and Dublyansky (1997) who suggested that the process of alpha decay dislodging bedrock is

a physically plausible but not essential role in the production of cave aerosols, since bedrock particles are produced during normal erosional processes of cave ceiling (Pashchenko and Sabelfeld, 1992) and walls. Cave wall aerosol generation can be augmented through host-rock alteration and corrosion as a consequence of condensation weathering processes. During further weathering the surface becomes increasingly fragile, from which fine carbonate particles can be derived (Zupan Hajna, 2003). Condensation weathering will be controlled by cave humidity and condensation processes as described in Section 3.2.2.4.

3.2. Distribution

The mechanisms of aerosol removal will be specific to each cave system, will vary within a cave, and may vary seasonally as the cave environment changes. Cave aerosol distribution processes will be explored in this section.

3.2.1. Aerosol transport

In order to be incorporated into a speleothem once the aerosols reach the troposphere region surrounding the cave entrance they must be transmitted into the cave air which occurs via two main routes; direct transport into the cave through air exchange (Pashchenko et al., 1993) and dust carried in by visitors (Michie, 1999; Jeong et al., 2003) and animals.

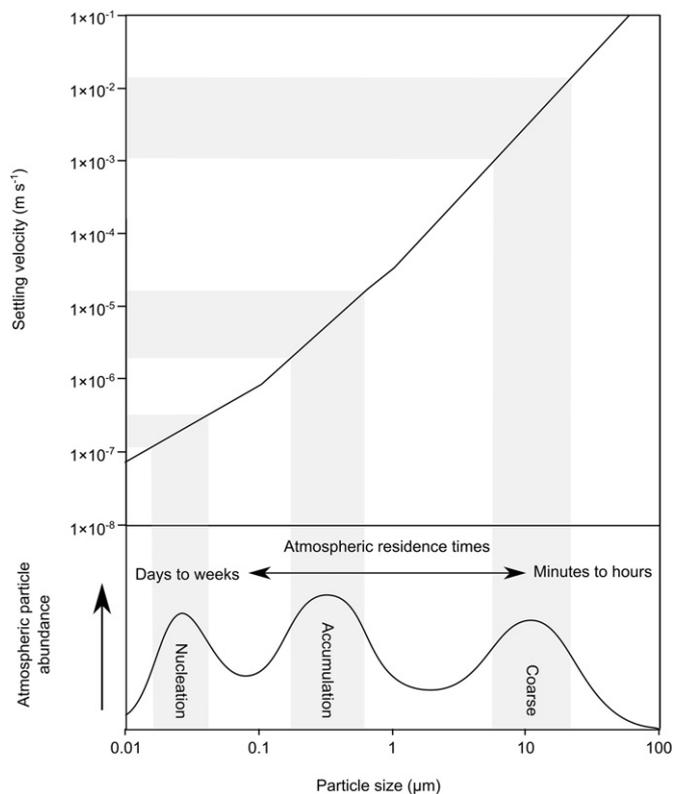


Fig. 3. Relationship between particle size and settling velocities. Relative atmospheric abundance of aerosols by particle size (Whitby and Cantrell, 1975) and particle size settling velocities (Kulkarni et al., 2011). Three dominant aerosol size groups (modes) present in the atmosphere: coarse (D1), accumulation (D2) and nucleation (D3) (Whitby and Cantrell, 1975). Each particle size mode is removed from the atmosphere at its associated deposition velocity. The aerosol contribution to speleothem chemistry will occur as a result of the total deposition to the speleothem surface from all aerosol types and sizes. Therefore the range and distribution of aerosol particle sizes must be considered when investigating chemistry.

Cave ventilation occurs as a result of several phenomena: cave breathing, wind-induced flow, chimney circulation or stack effect, convection and water-induced flow (Fairchild and Baker, 2012) and sometimes with short-term local turbulence as a result of anthropogenic influences (Fernandez-Cortes et al., 2009). The vigour of the air circulation affects the removal of internally generated gases such as carbon dioxide, radon (and its particulate daughters) and the introduction of aerosols (Fairchild and Baker, 2012). Christoferou et al. (1996a) determined that cave ventilation and its air flow patterns act as the primary mode of transport for pollutant particles into caves from the outdoors. However, the relative influence of cave visitors and natural cave ventilation will be dependent on the cave under investigation and the relative influence of its visitor footfall numbers and ventilation strength on aerosol production. Aerosols in the cave environment can essentially be thought of as a smaller version of the Earth's atmospheric system. The cave suspended aerosol load is a product of externally introduced aerosols which are analogous to long-range transported aerosols and internally produced aerosols resembling locally sourced aerosols.

3.2.1.1. Transport source identification. Pollen is perhaps the most intensively studied single cave aerosol type due to its significance in speleothem palaeoenvironmental archives as a recorder of terrestrial vegetation. A range of studies exploring the distribution of pollen through caves has been presented in the literature. A comprehensive review of literature regarding their mode of transport and distribution can be found in Caseldine et al. (2008).

Coles et al. (1989) proposed three transport mechanisms for pollen: airborne, waterborne and insect-borne. Similarly Lauritzen et al. (1990) emphasized percolating water, floodwaters that submerge speleothems, or airborne transport by cave

draughts as predominant mechanisms. They noted the importance of understanding transport mechanisms for interpreting pollen assemblages in speleothems. Although a method is yet to be established for the source discrimination of pollen, the airborne pollen influx into caves and modern surface pollen deposition has been reported to be similar in several investigations (Burney and Burney, 1993; McGarry and Caseldine, 2004). It is critical for internal cave aerosol composition to be representative of external aerosols for palaeoenvironmental studies. It may be assumed that the behaviour of pollen can be extrapolated to other aerosols of similar size which are controlled by the same transportation processes.

Source separation can be achieved through cave monitoring of aerosol deposition and using aerosol chemistry as a tool for identification. Where aerosol deposits are of contrasting composition to that of speleothem growth chemistry it may be possible to identify periods of significant aerosol deposition. The significance and ability to recognise aerosols in speleothem is discussed later in Section 5.

3.2.2. Aerosol deposition

3.2.2.1. Gravitational sedimentation. Gravitational sedimentation as a result of reduced air flow rates is thought to be the main mechanism behind aerosol deposition of coarse aerosols in cave networks. Michie (1997) determined the main processes which control the deposition of particles within the cave network: Brownian diffusion and collision for the smaller particles, and gravitation for the larger particles. It should be noted that gravitational sedimentation processes will not be of importance for stalactite samples which consequently may receive significantly lower aerosol fluxes than stalagmite surfaces.

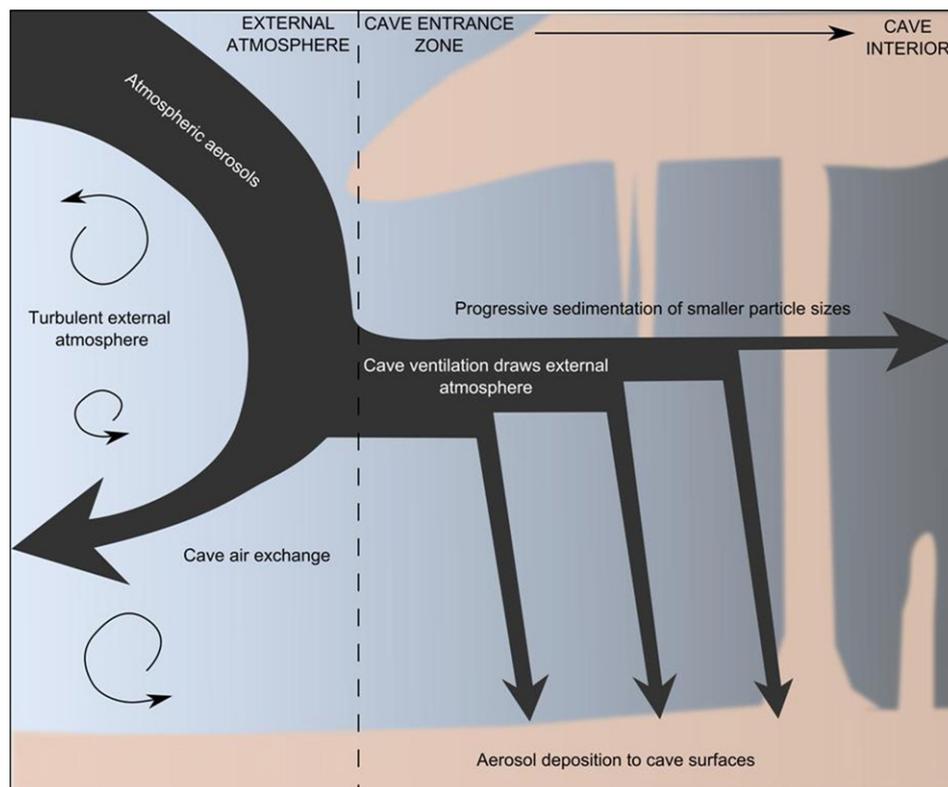


Fig. 4. Schematic of introduction and gravitational sedimentation of cave aerosols within the cave environment. A body of atmospheric air (of average composition) with air velocity greater than or equal to 0.1 m s^{-1} will have a suspended load (L_s) produced from a combination of groups D1, D2 and D3, therefore $L_s = \sum(D1, D2, D3)$. Taking the simplified example of a horizontal cave with a singular entrance in which air exchange becomes progressively less influential with distance from the entrance (A), air velocity (V) will decrease with distance from the entrance to the back of the cave (A'). At A' L_s will be equal to $\sum(D1, D2, D3)$, as the air progresses towards A' and loses velocity, particle modes D1, D2 and D3 will be progressively depleted by deposition.

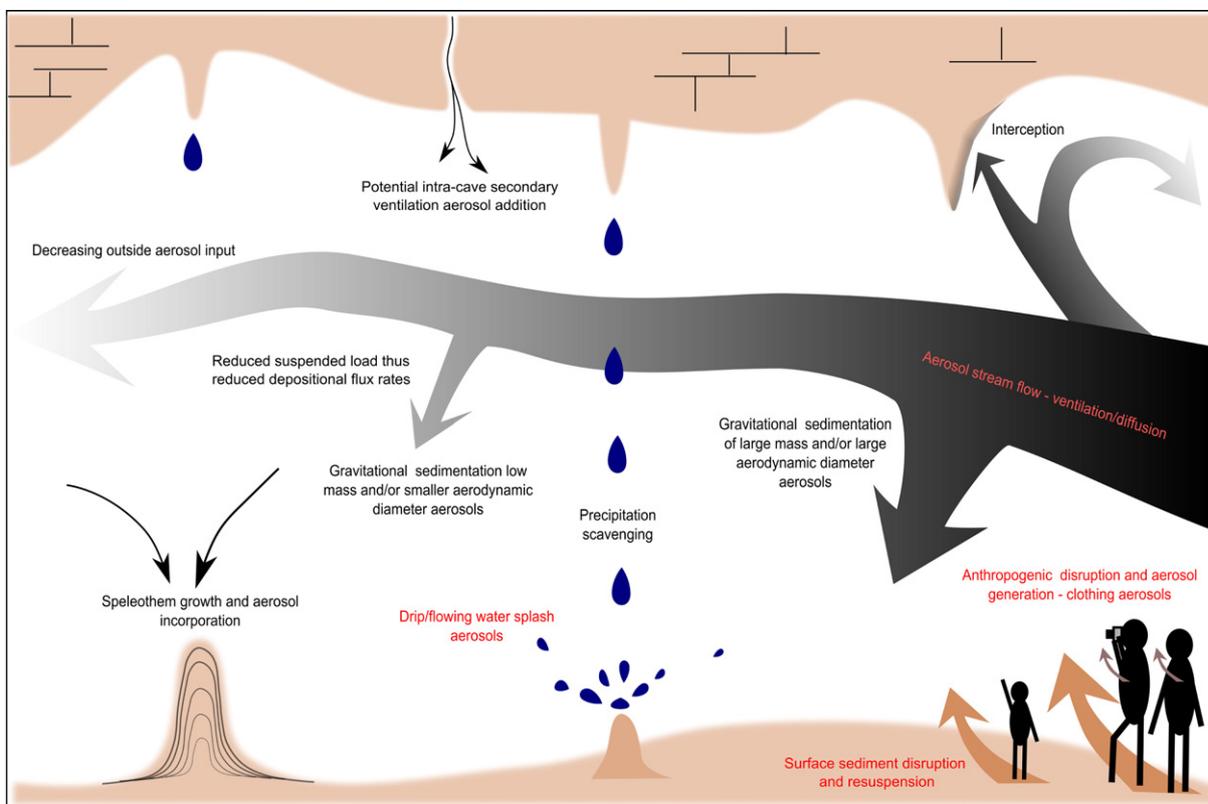


Fig. 5. An illustration summary of cave processes: aerosol creation (red), and aerosol removal processes (black).

Pollen grains which are known to be aerally transported are detected close to the entrance of cave systems (McGarry & Caseldine, 2004; Caseldine et al., 2008) with a reduction towards the cave interior (Burney and Burney, 1993; Coles and Gilbertson, 1994; Navarro et al., 2001). This distribution is expected since pollen as a coarse aerosol requires relatively high energy levels for particle transportation above that which can be sustained by cave ventilation flow (as displayed in Fig. 3).

The pattern of distribution presented by various investigations into pollen, although generally representative, can only be assumed if there is a single known cave entrance. It is also necessary to know that cave air flow rates are high enough to transport coarse aerosols whilst meeting threshold terminal velocity speeds to allow for total gravitational sedimentation of suspended aerosol particulates within the cave. Fig. 3 displays the relationship between particle size, deposition and air flow rates. Each cave should be monitored (as with other environmental variables) on a case study basis to ensure that an accurate understanding of cave aerosol transportation dynamics has been gained before interpretations are made. It is necessary to understand air flow rates and the factors controlling air flow in order to fully understand aerosol deposition (Christoforou et al., 1996b).

Air flow rates in cave locations will vary greatly and are generally too low for the transportation of coarser aerosols (cf. settling velocities shown in Fig. 3). However it is known in some instances that flow rates are sufficient for the transportation of even very coarse particulates. Flow velocities of 0.5 m s^{-1} have been reached during winter ventilation in the interior of Obir cave (Fairchild et al., 2010) and exceptionally high velocities ($> 10 \text{ m s}^{-1}$) are known to be reached in some cave sites (Conn, 1966). During periods of higher ventilation speeds larger suspended aerosol loads and large particles may be transported and deposited within the cave increasing the potential for aerosol contributions to speleothem geochemistry.

An aerosol deposition gradient was noted by Christoforou et al. (1994) with a loss in deposition rates over the entrance region, from $13.4 \mu\text{g m}^{-2} \text{ s}^{-1}$ outdoors to $5.2 \mu\text{g m}^{-2} \text{ s}^{-1}$ inside (over 1 year of monitoring). This indicates either low external aerosol transportation into the cave or significant suspended aerosol loss over the entrance zone. This progressive loss in suspended load is displayed schematically in Fig. 4. The flux of aerosols throughout the cave will be a product of the air velocity (driven by ventilation strength), cave cross-section A to A', and cave morphology. Cave ventilation is known to be highly variable displaying strong diurnal and seasonal variations; consequently aerosol transport may display temporal variations. Cave cross-section and morphology

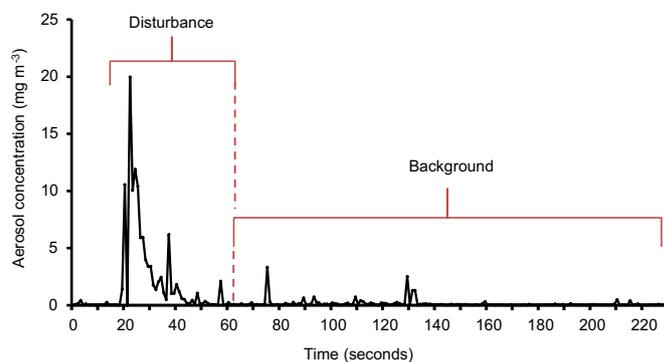


Fig. 6. Short term anthropogenic cave aerosol production in Gough's cave, Cheddar Gorge Show Cave, UK. Suspended aerosols monitored as a cave visitor passes by with TSI instruments SidePak AM510. The effect of the disturbance clearly dominates the background levels of aerosols. However, the impact of the disturbance on suspended aerosol loads is short-lived and is dependent on the cave situation and cave surface dusts.

will also be highly variable depending on the cave under investigation, altering the distribution of deposition of the particle modes (discussed later in Section 3.2.2.2).

3.2.2.2. Cave morphology effects on deposition processes. Cave morphology has been postulated as a control on the distribution of pollen in cave sediments (Burney and Burney, 1993; Navarro et al., 2001). Cave morphology will strongly influence the transportation and deposition of aerosols throughout the cave network. Surface irregularity will result in turbulence within the air column causing increased particle collisions with the walls and consequently greater deposition. Cave morphology will also control ventilation-forced air flow rates and therefore gravitational sedimentation distribution. As a result increased gravitational aerosol depositional flux may be observed in open chambers, with interception and impaction (Section 3.2.2.3) processes being dominant in high flow constriction areas of a cave system. Changes in cave profile (floor elevation) may also induce gravitational processes. A package of cave air that reaches a rise in elevation may stagnate enough to fall below threshold deposition velocities, resulting in zones of increased deposition.

Interception of the streamline by irregularities will also result in impaction onto cave surfaces (as described in Section 3.2.2.3). Aerosols of greater inertia will be removed from the cave ventilation air flow stream. Therefore the ‘windward’ side of cave features (i.e. stalagmites) will have a greater aerosol impaction flux to the surface.

3.2.2.3. Interception and impaction. Interception and impaction are both the result an obstacle interrupting the air flow; in the cave environment this is likely to be speleothem formations. In addition to increased interception/impaction processes, the wet

surfaces of actively growing speleothems may retain more particles than dry cave surfaces as a consequence of hydraulic retention processes. As a result speleothem surfaces will potentially have higher depositional flux and aerosol retention rates than other surrounding cave surfaces. This proposed pattern of distribution was noted by Chang et al. (2008) who observed concentrated aerosol deposition to speleothem surfaces throughout Gosu, Ondal, and Sungryu caves in South Korea of 0.1 to several millimetres in thickness.

3.2.2.4. Wet deposition. Wet deposition can occur as a result of three main processes. Wet deposition can occur as dripwater falls through the cave atmosphere. However this contribution is likely to be negligible.

Badino (2004) considered the processes that could potentially result in the formation of clouds in caves. A key factor in cloud formation is the presence of aerosols which act as nucleation points for vapour condensation. The presence of a stable aerosol forming haze in a cave atmosphere is direct evidence of a supersaturation of moist air (water vapour pressure is above equilibrium), and it leads to thermal imbalances between the aerosols and the air (i.e. clouds are usually found near the cave ceiling and in the highest galleries because a humid air parcel is less dense than the drier air parcel). Aerosols may facilitate the formation of clouds through providing a surface for atmospheric condensate aerosol formation from high humidity cave air.

Condensation from atmospheric humidity can have an important speleogenetic role (Dublyansky and Dublyansky, 2000; Dreybrodt et al., 2005). Condensates from cave air will scavenge and deposit aerosol through wet deposition and in specific scenarios may influence speleothem geochemistry. In addition to influencing already precipitating speleothems, aerosols can

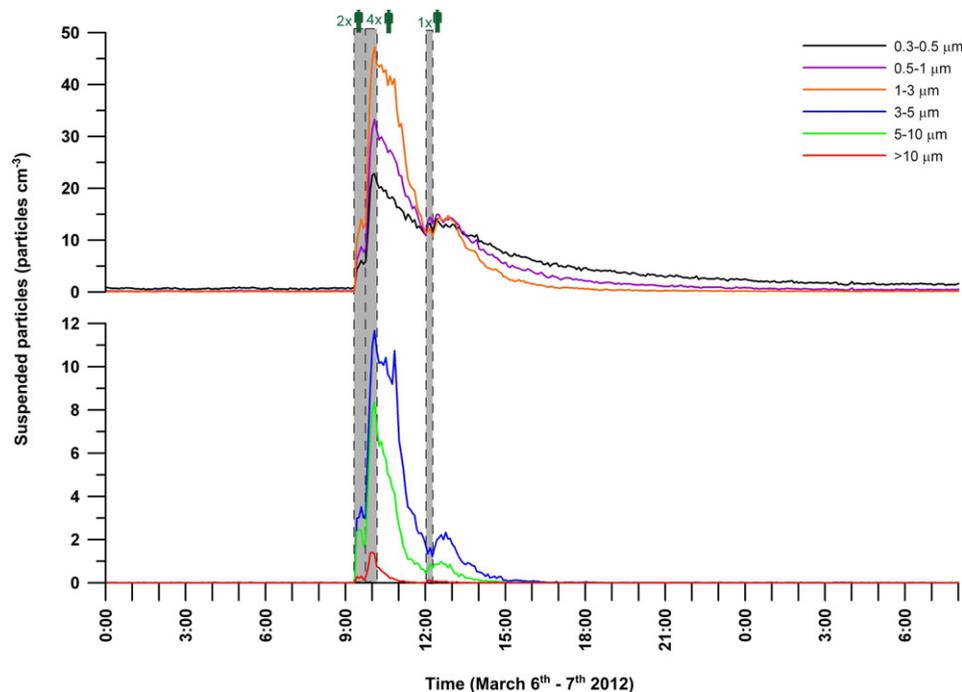


Fig. 7. Example of aerosol contributions and particle resuspension from ground sediments by short visits to Altamira Cave, Spain (1–4 people during less than 30 min) during maintenance operations of microclimatic monitoring equipments. The size distribution of particles was monitored every 5 min during a day cycle (6th March, 2012) by using an airborne particle counter (TSI Aerotrak™ Model 9306). The coarsest particles (>10 μm) were only detected once the visitors went into cave, provoking the microparticle detachment from soil and their own clothes. Levels of airborne particles rose to more than a thousand times the previous background levels (as in Goughs Cave). Particle detachment affected particles of 0.5–3 μm in size more than the finest particles of 0.3–0.5 μm diameter. Coarsest particles (>10 μm) were removed from suspension 3 h after the visit and particles ranging from 3 to 10 μm in size took approximately 9 h for removal. The finest particles (<3 μm) remained suspended for longer periods (roughly up to 24 h).

produce a mineral deposit when it reaches a cave wall, or directly from the vapour state (in the same mechanism of sublimation of ice from water vapour) (Cigna and Hill, 1997).

An illustration providing a summary of aerosol processes is displayed in Fig. 5.

4. Results

Through cave monitoring, results from this investigation will be displayed to demonstrate some of the key issues discussed above.

4.1. Internally sourced aerosols

4.1.1. Anthropogenic disruption

Internal production of aerosols in some cave locations is likely to be dominated by anthropogenic processes. The magnitude of potential aerosol production relative to show cave background levels is displayed in Fig. 6.

Fig. 6 displays an example of short term aerosol impacts from a single disruption event by one cave visitor. The data presented in Fig. 7 displays a greater duration of cave atmosphere aerosol impact by longer, multiple visitor disturbances.

Monitoring work demonstrates the range of impacts and duration of anthropogenic aerosol production events. Such observations

are critically important for evaluating risk to cave environments from visitor disruption.

4.1.2. Hydrological aerosol production

The production of water aerosols may prove a significant source to the total aerosol budget for specific regions in some cave locations. The impact of hydrologically produced aerosol will only be of notable levels in caves with significant waters flows, which may be seasonally controlled. Fig. 8 displays an example of hydraulic internal aerosol production.

The peak in suspended aerosol concentrations at the Abyss/Waterfall locations which has been attributed to the internal cave production of liquid aerosols, forming as a result of turbulent water from a flowing stream (Smith et al., 2013). The production of aerosols in this specific location is localised but substantial and has the potential to notably alter the geochemistry of proximal speleothem formations.

4.2. Cave ventilation and aerosol distribution

Cave air CO₂ is used as an indicator of cave ventilation, as the concentration of CO₂ in a cave passage is a function both of production and ventilation processes (Fairchild and Baker, 2012) with increased CO₂ concentrations being indicative of reduced air-

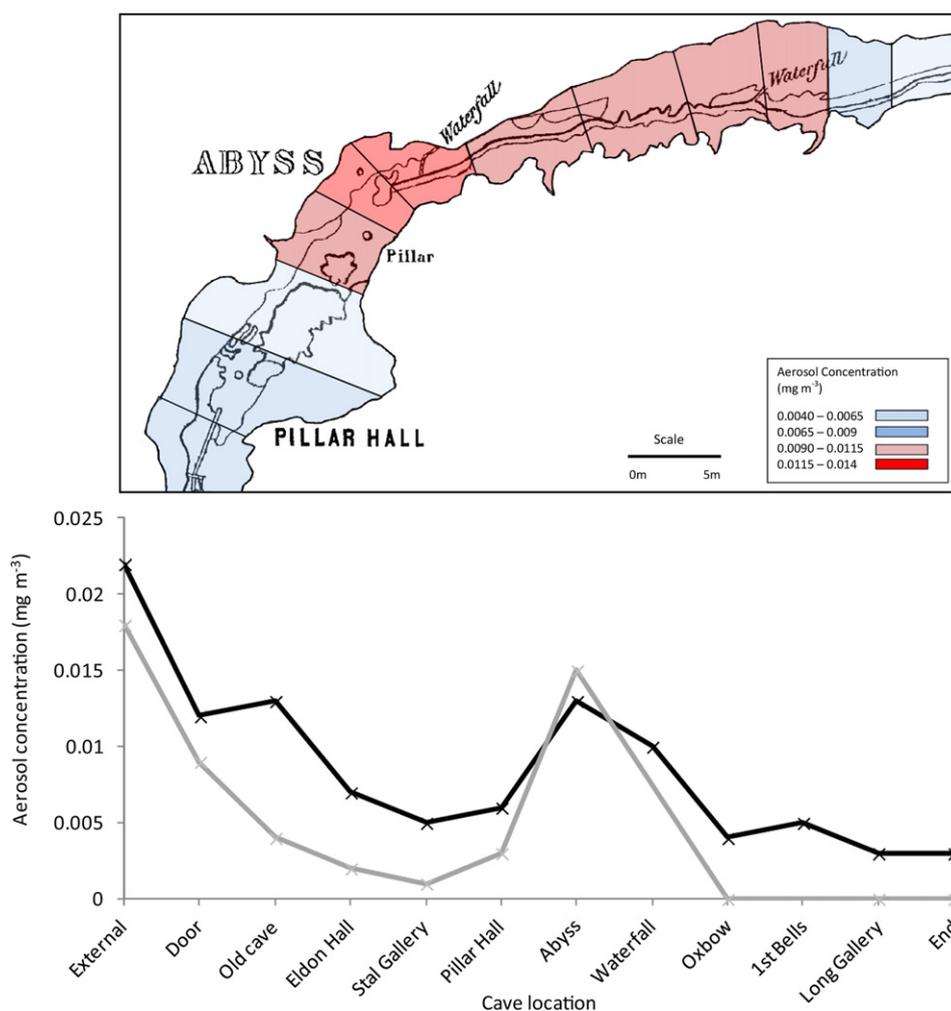


Fig. 8. Spatial distribution of suspended aerosols from Ingleborough show cave, UK. External site to ‘End’ is a distance of approximately 500 m, the ‘End’ location marks the end of the show cave not the entire system which continues for >1 km further. Data collection using TSI AM510 optical aerosol counter during winter (black) on the 28th Feb 2011 and summer sampling (grey) on the 14th July 2009. The insert displays waterfall zone aerosol concentrations (Smith et al., 2013). Hydro-aerosol production remains an apparent feature in both summer and winter monitoring.

exchange with the low CO₂ concentration of external atmospheric air. Fig. 10 displays data from spot monitoring of Goughs Cave, Cheddar Gorge (UK) (sampling locations shown in Fig. 9).

Monitoring shows CO₂ rises towards the cave interior which can be interpreted as reducing air exchange and therefore reduced air velocity. Suspended aerosol concentrations demonstrate the opposite of CO₂, decreasing towards the cave interior. Temperature demonstrates a similar trend to aerosols. However, cave interior temperatures reached closer to the cave entrance (before location 2) and are then remain relatively constant throughout the cave.

The zone of significant change for CO₂ and suspended aerosol concentrations occurs between locations 3 and 5. The increase in CO₂ and associated reduction in suspended aerosol concentration indicates reduced air exchange. Reduced air exchange will be associated with lower air flow rates allowing for increased settling deposition processes. This is confirmed by an increased aerosol deposition flux being observed between locations 3–5 as shown in Fig. 11. A rise in cave floor elevation can be observed in Fig. 9 (in section) between location 2 and 3. This may account for the reduction in air exchange, as discussed in Section 3.2.2.2, increased elevation may result in the stagnation of air flow rates resulting in increased aerosol deposition.

The correlation of suspended aerosols, aerosol deposition flux and CO₂ demonstrates the relationship between deposition processes and cave ventilation. Cave ventilation has been confirmed as the one of the key processes controlling cave aerosol introduction, transport and deposition.

4.3. Entrance zone deposition

In addition to gravitational sedimentation there is also the potential for hygroscopic effects due to the high humidity compared to the external atmospheric humidity. Dry aerosols entering the cave environment may absorb water, increase in size, and fall out of the air stream flow. An example of substantial suspended load loss (and therefore deposition) occurring within the entrance zone is displayed in Fig. 13 presenting aerosol deposition monitoring data from Altamira Cave, Spain.

A detailed survey of suspended aerosol, airborne microorganisms and microclimatic monitoring was carried out at Altamira Cave (Spain), a World Heritage UNESCO site, world famous for a collection of Palaeolithic rock paintings and engravings that are mainly located in Polychromes Hall (Fig. 12). The preservation of these paintings is as a result of the cave being characterized by low rates of water infiltration, precipitation of mineral deposits and exchange with the external atmosphere; and the maintenance of very stable microenvironmental conditions because of limited air flow in the chamber. However, the opening to the public during previous decades provoked air warming and turbulence caused by visitors, resulting in increased air exchange between Polychromes Hall and areas closest to the entrance, where there are microbial colonization on walls and ceilings (Cuezva et al., 2009). The corrective measures implemented in recent years (since it last closed in 2002) have reduced the exchange between the cave atmosphere and exterior, decreasing the entry of airborne particles,

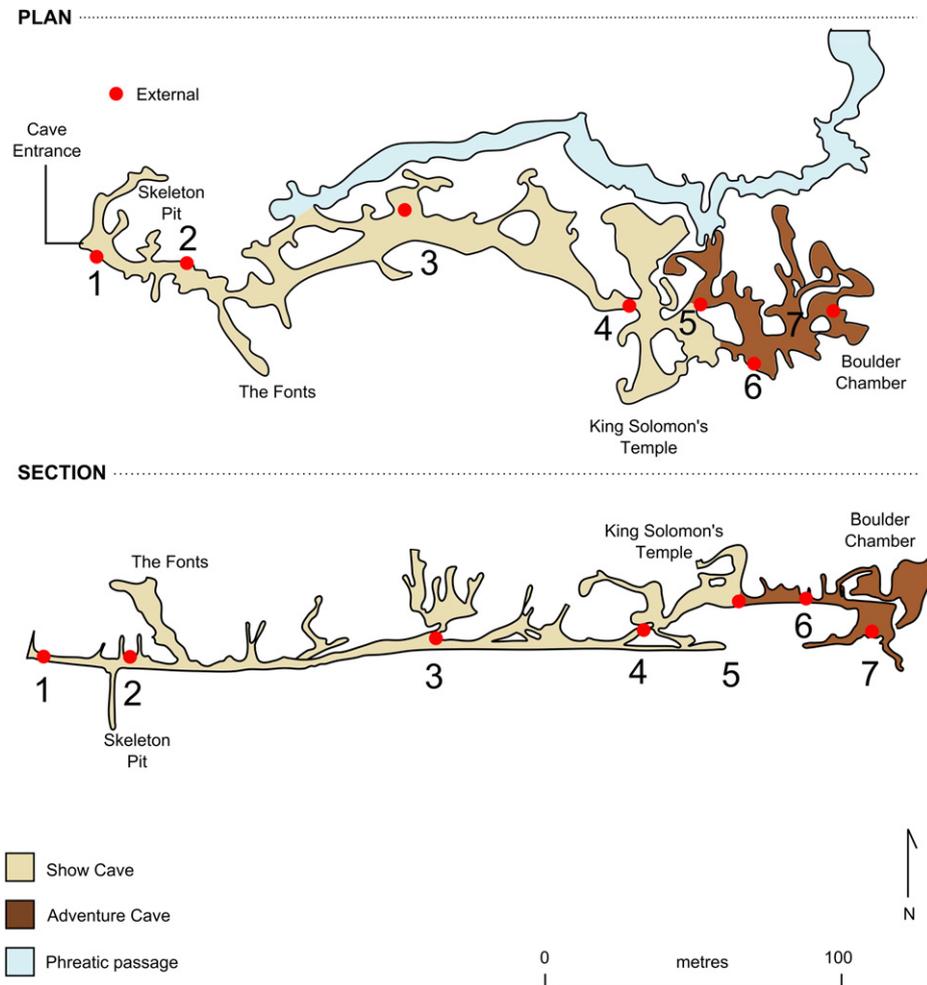


Fig. 9. Map of Goughs Cave, Cheddar Gorge with aerosol sampling locations. After Farrant (2010), based on survey data by Stanton (1953).

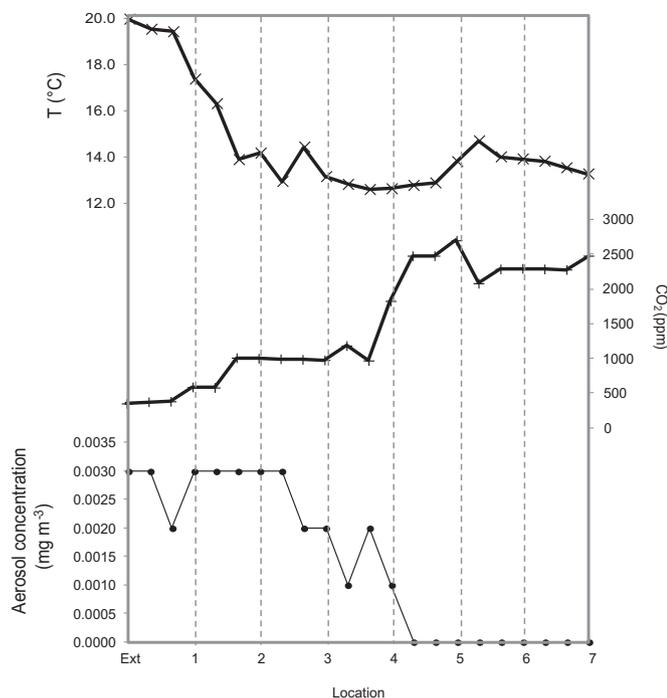


Fig. 10. Cave air CO₂ and suspended aerosol concentrations from spot monitoring throughout the Gough's Cave network on 19th and 20th July 2011. CO₂ recorded with a Sperián PHD6 instrument. Aerosol concentrations measured with TSI SidePak AM510 optical counter (data presented are counting duration minima during the 5 min sampling duration, in order to best achieve background levels). Five minute averages of temperature are displayed, measured with a Tinytag temperature logger. Samples were spread over ~275 m from the cave entrance to deepest interior.

the condensation rate in the entrance area, and the metabolic activity of the main visible microbial colonies (Saiz-Jimenez et al., 2011).

The transportation of aerosols throughout Altamira cave will also be hampered by the effect of a double-access door equipped with a thermal insulation system that reduces the entry of airborne particles (Saiz-Jimenez et al., 2011; Garcia-Anton et al., 2012).

The same relationship between suspended aerosols, CO₂ and temperature as observed in Gough's Cave (Fig. 10) is apparent in Altamira Cave as shown in Fig. 14. The loss in suspended aerosols

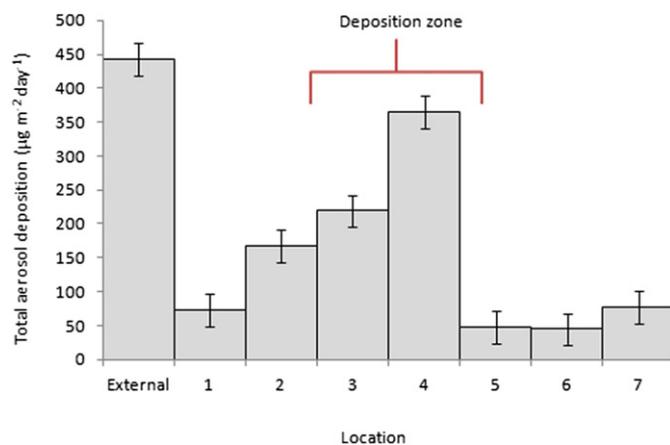


Fig. 11. Goughs Cave, Cheddar Gorge: the spatial distribution of depositional flux rates based on one month of surrogate surface monitoring over July. Total elemental deposition displayed as described in Section 2.2.1. Samples collected on the 20th of July. Limit of detection (3σ) displayed with error bars.

from optical particle counting methods confirms the results displayed in Fig. 13 from pumped sampling and ICP-AES analysis. Smaller particles of less than 1 μm demonstrate the strongest relationship with CO₂ and the highest variance (Fig. 15). This is consistent with the idea of entrance zone coarse aerosol deposition and the concept of progressive gravitational sedimentation throughout caves.

4.4. Progressive gravitational sedimentation

Under a simplified cave model where gravitational sedimentation is the key process of aerosol deposition, progressive deposition will be observed. Fig. 17 displays a pattern of aerosol distribution that may represent progressive gravitational deposition in St Michaels Cave, Gibraltar (Mattey et al., 2008, 2010).

Often the relationship between cave ventilation and aerosol processes will be significantly influenced by cave morphology, with caves often having an intricate morphology associated with an extensive network of interconnecting fissures resulting in a complex distribution of aerosol deposition. Additional processes to gravitational sedimentation may overprint any trends, making deciphering such processes difficult.

4.5. Cave morphology and aerosol deposition

An example of the control of cave morphology on aerosol deposition rates has been observed at Obir cave, Austria. Surrogate surfaces were deployed in two locations (shown in Fig. 18) within the cave to determine the deposition rates close to the position of speleothems previously studied by Fairchild et al. (2010). One sample was situated at in Säulenhalle (S), an open chamber with active speleothem formation and a terminal pool (Silbersee) and the other at Düse (D), a nearby constricted passage with sensible air flow.

Fig. 19 displays a comparison of depositional flux rates at locations S and D, with location S recording greater levels of total aerosol deposition flux. This can be accounted for simply by gravitational processes. Aerosols remain in suspension as they travel through the constriction due to the higher flow rates, upon entering the larger Säulenhalle chamber where air flow velocities are reduced. Increased deposition will likely occur near Silbersee pool regardless of the suspended load and ventilation direction simply as a result of the proposed morphologically controlled reduction in ventilation air flow rates.

With knowledge of the potential processes affecting aerosol deposition fluxes to speleothem surfaces it is possible to evaluate the contribution of aerosol deposition to speleothem geochemistry.

5. Aerosol contributions to speleothem geochemistry

The mode of transport and deposition is expected to have a relationship with the chemistry of aerosol being deposited. For instance, in the case of gravitational sedimentation, the larger and denser particulates will be removed from suspension first and will often be associated with specific sources and chemical composition. In a study by Faimon et al. (2006) aerosol compositions were determined to be highly variable with space and time but were broadly composed of Si, Ca, Al and Fe with fine particles formed of S, P, K and Cl. This relationship was not observed with the preliminary spatial deposition monitoring pattern and the chemical composition of aerosol deposition in Obir cave. The lack of a relationship between location and chemistry is likely due to the range of processes effecting the transport and deposition of aerosols, combined with the changing environmental conditions inside the cave and externally.

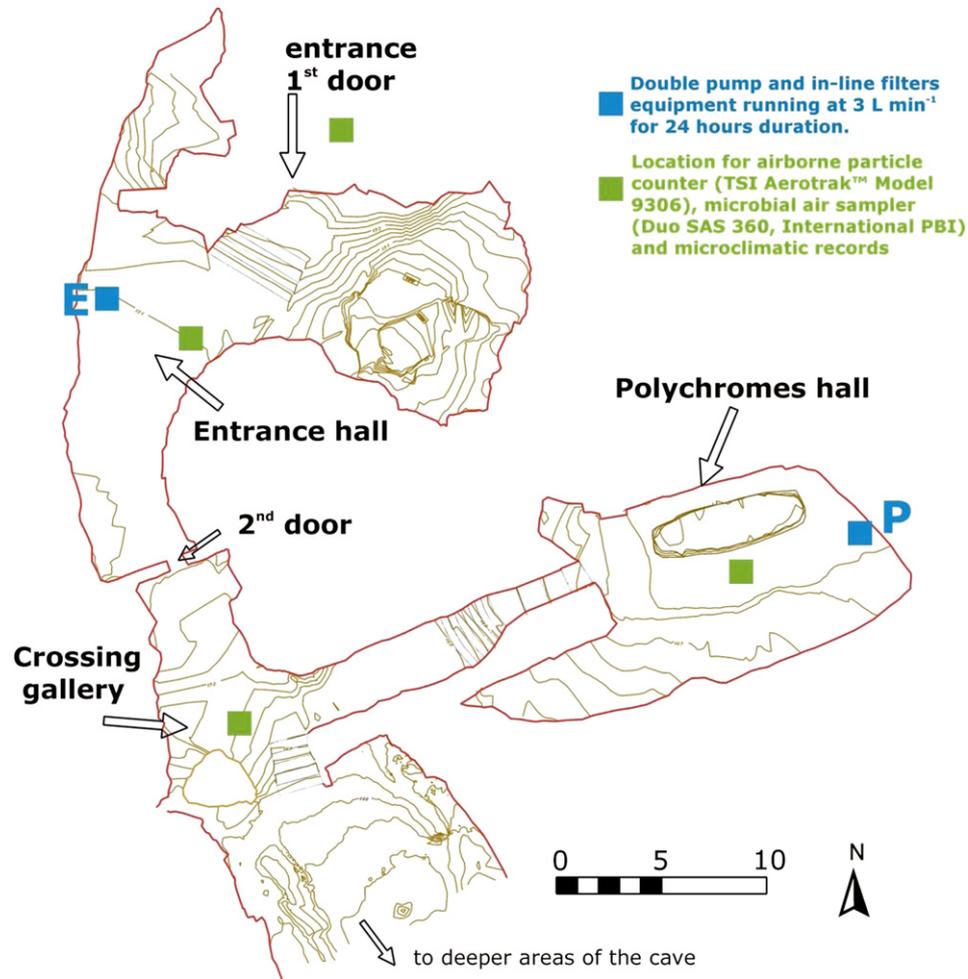


Fig. 12. Locations at Altamira Cave during the aerosols survey utilising a double pump and in-line filter equipment, running at 3 L min^{-1} for 24 h duration, airborne particle counter (TSI Aerotrak™ Model 9306), microbial air sampler (Duo SAS 360, International PBI) and microclimatic records.

The comparison of aerosol deposition data from Obir cave demonstrates that elemental deposition flux rates differ between elements and some display trends unlike the overall total depositional flux rate distribution. Internally produced aerosols would be expected to be observed at greater concentrations in the cave interior in comparison to the entrance region, but no clear distinction was identifiable.

Based on monitoring data at Obir, it is possible to calculate the aerosol addition to speleothem geochemistry. The following calculations are based on deposition per 1 mm^2 of speleothem surface over a period of one year, assuming constant growth (as shown in Fig. 20).

In order to determine the impact of aerosol deposition upon speleothem composition the rate of deposition and the calcite supply must be known. The potential (maximum) aerosol concentration in calcite (P) is a function of aerosol depositional flux and speleothem growth rate and is related to aerosol deposition and speleothem growth as follows:

$$P = F / (R \times \rho)$$

where P = Potential aerosol concentration in calcite ($\mu\text{g g}^{-1}$)

$$F = \text{aerosol depositional flux } (\mu\text{g mm}^{-2} \text{ year}^{-1})$$

$$R = \text{speleothem growth rate } (\text{mm year}^{-1})$$

$$\rho = 0.00271 = \text{calcite density } (\text{g mm}^{-3})$$

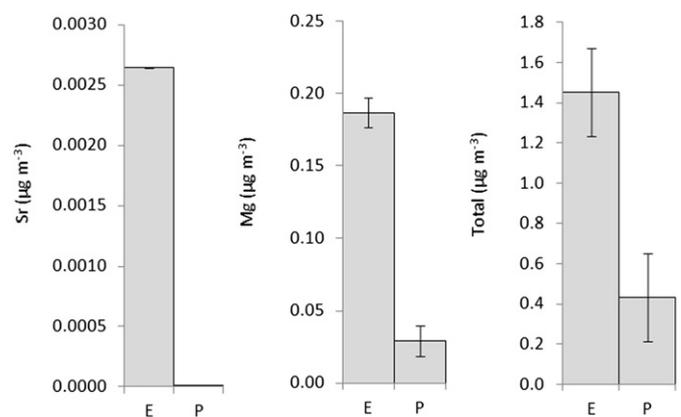


Fig. 13. Comparison of suspended aerosol concentrations from the cave entrance zone and Polychromes hall, Altamira Cave within the cave interior. Pumped collection of suspended aerosols at 3 L min^{-1} over 24 h. Limit of detection (3σ) are displayed for each element with error bars. A significant reduction in suspended aerosol concentrations from the entrance zone (E) to the Polychromes Hall (P) within the cave interior can be observed. This is consistent with the patterns of distribution observed in previous studies involving the transportation of coarse aerosols. However, Location P is a side chamber which may experience reduced ventilation and the lower detected aerosol concentrations can also be attributed to the chamber's location relative to active ventilation stream flow (a bidirectional flux between cave entrance and deeper areas).

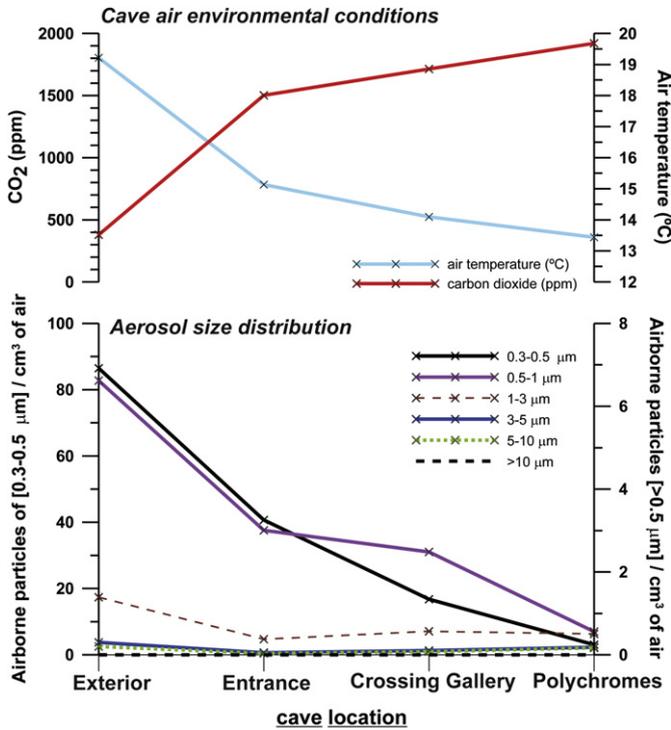


Fig. 14. Aerosol size distribution: Suspended particle counts of particle size ranges 0.3–0.5 μm (secondary axis), 0.5–1, 1–3, 3–5, 5–10 and >10 μm. Cave air environmental conditions: CO₂ (ppm) and temperature (°C). Data displayed is averaged from four cave visits on the same day 7:18–7:57am, 9:29–10:05 am, 11:49 am–12:17 pm and 2:57–3:27 pm. During this time monitoring was only exposed to the influence of the operator.

The relationship between speleothem calcite concentration and aerosol deposition flux as a function of growth rate is displayed graphically in Fig. 21.

By adding known deposition flux rates into the equation the potential aerosol contribution in calcite can be calculated. Here, data from Obir cave monitoring (Fairchild et al., 2010) are presented to demonstrate the maximum possible extent of aerosol contribution to speleothem chemistry. An approximation of aerosol contributions to calcite trace element concentrations is shown in Fig. 22 based on maximum aerosol deposition flux rates.

Aerosol contributions can be expressed as a percentage of the speleothem concentration of individual elements:

$$A(\text{aerosol contribution, \%}) = (P/C) \times 100$$

where:

C = elemental calcite concentration

The maximum theoretical contribution of aerosols to speleothem chemistry has been shown to vary significantly between different elements as shown in Table 2. Values range from 0.002% to 71.8% dependent on the element and speleothem under investigation. Fairchild et al. 2006 introduced three different types of control on trace element incorporation efficiencies: 1) Crystal dominated, where crystallographic factors control variability. 2) Temperature, where incorporation efficiencies are temperature dependent such as for Mg. 3) Fluid-dominated pattern where changes in elemental composition of the fluid trace element source drives comparable variations in calcite. Fluid dominated situations are typical when large variations of trace element composition occur over time and this is the case here.

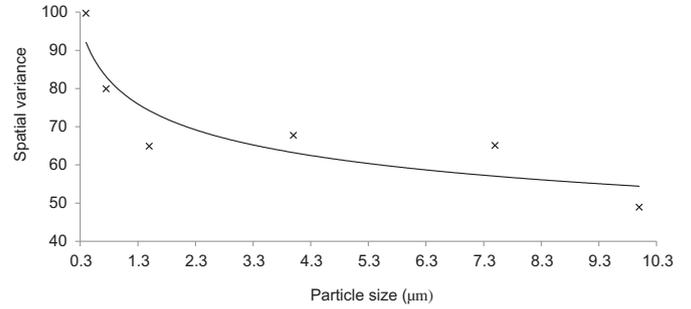


Fig. 15. Relationship between spatial variance of aerosols and particle size. Spatial variance = [STDEV(aerosol counts)/aerosol counts] × 100.

The comparison of drip water supply and aerosol flux supply to modern calcite concentrations (Table 3) has shown that at current drip water flow rates the drip water chemistry supply is orders of magnitude greater than that offered by aerosol flux. Limiting drip rates demonstrate that for all elements compared a >99.9% reduction in flow rates is required to reduce the drip water supply to quantities equal to the aerosol supply.

The data and calculations presented here so far are based on several assumptions. The first is that the surrogate surface aerosol deposition provides a suitable replication of the type of aerosol flux that would occur to the speleothem surface. Secondly and likely to be of greater impact is that the above calculations are based on complete incorporation (i.e. 100% efficiency). There are however several processes that will occur that would result in less than total incorporation of aerosol deposition within growing speleothem.

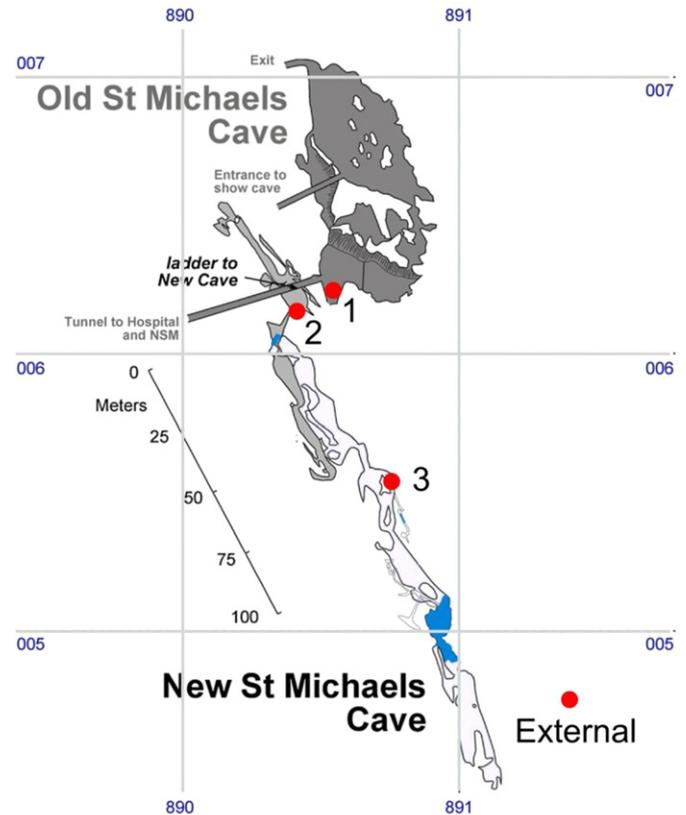


Fig. 16. Lower New St Michaels Cave network map with cave aerosol sampling locations (after Matthey et al., 2008).

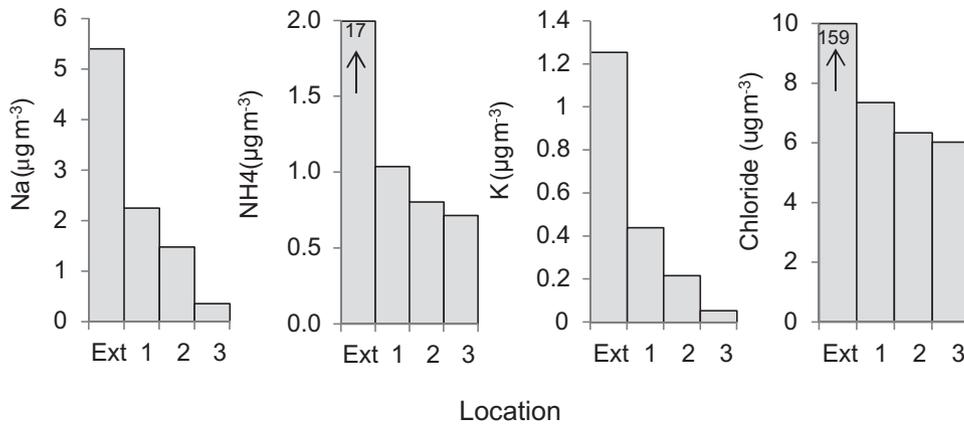


Fig. 17. Examples of potential evidence for progressive gravitational sedimentation. Suspended aerosol distribution in St Michaels Cave, Gibraltar. Samples spread over approximately 100 m distance from the cave entrance (Ext = Exterior) to interior.

5.1. Potential aerosol calcite contribution – incorporation

The aerosol contribution to speleothem geochemistry (P) is in practice a maximum since aerosol preservation will be highly dependent on drip water flow rates and the mechanism of deposition. Aerosols deposited to the surface of an actively growing speleothem may be washed away by drip water flowing over the speleothem surface. Conversely, deposition to the surface of a dry speleothem (during a speleothem growth hiatus) could result in the formation of a deposit predominantly composed of aerosol deposits and the incorporation mechanisms

of trace elements within the solid deposit may differ from that operative during partitioning into calcite during normal growth. Any aerosol deposits during a hiatus period would be affected by the possible drip water removal processes upon resumption of drip water flow over the speleothem surface. However, if binding of aerosol deposits occur to produce a consolidated horizon of calcareous or non-calcareous composition it would be resistant to drip water flow. Since calcite concentration will be a function of growth rates, it is during hiatus events where aerosol deposition will have the greatest influence on speleothem chemistry.

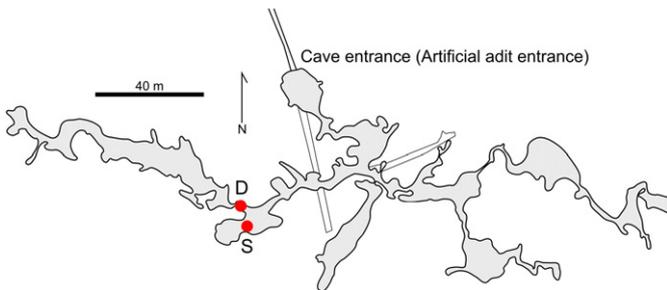


Fig. 18. Obir Cave map and surrogate surface locations (after Spötl et al., 2005).

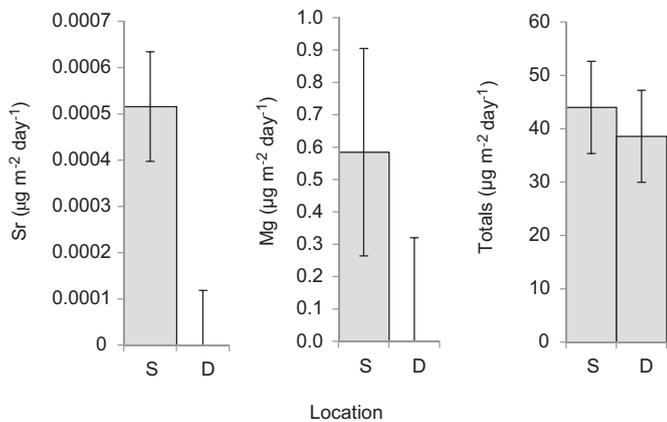


Fig. 19. Depositional flux rates at two locations: near Silbersee pool (S) and at Düse (D). Results from surrogate surface monitoring from 15th April to 11th July 2012 in Obir Cave, Austria. Error bars display elemental limit of detection (3σ) as errors.

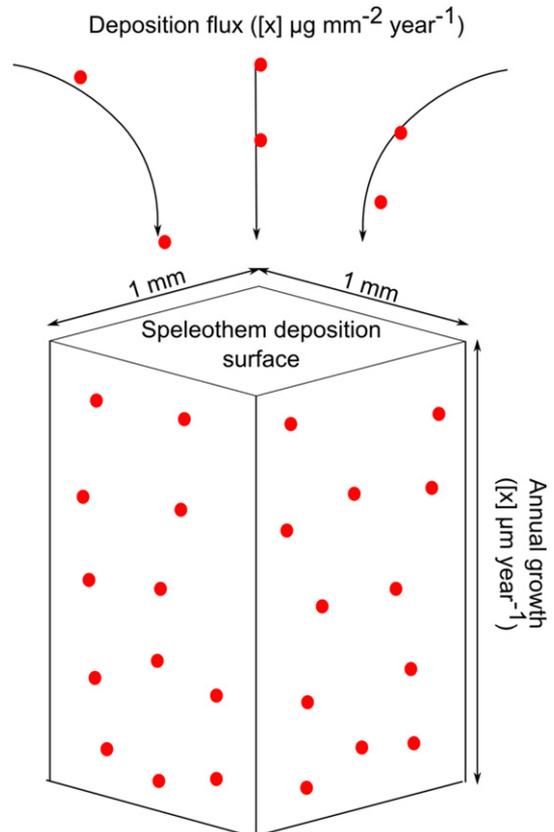


Fig. 20. Calculation variables: deposition flux and growth rate. Calculations are based on 1 mm² calcite surface area for one year of speleothem growth.

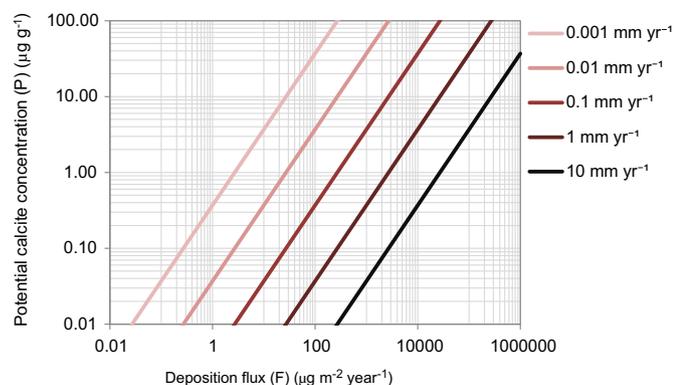


Fig. 21. Relationship between aerosol deposition flux (F) of a trace species and its potential concentration in calcite (P) as a function of varying growth rates from 0.001 mm yr^{-1} to 10 mm yr^{-1} .

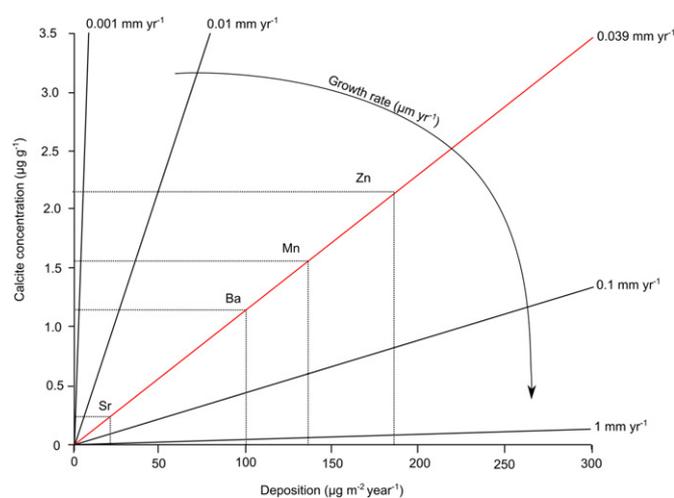


Fig. 22. The relationship between aerosol deposition flux (F), growth rate (R) and potential concentration in calcite (P) for speleothem OBI12 with a recorded growth rate of 0.039 mm yr^{-1} . Maximum Sr, Ba, Mn and Zn deposition flux rates are plotted to give their corresponding potential concentration in calcite contribution values based on this annual growth rate.

5.1.1. Incorporation type

Deposited aerosols remaining on the surface retain the potential to become incorporated into the speleothem. However, this process will not be 100% efficient in capturing the entire aerosol signature. Solutes will be coprecipitated, providing an addition to drip water chemistry. Particulates are likely to become incorporated through intercrystalline capture.

In evaporative scenarios with low to zero drip rates it may be possible for liquid aerosols to create a defined horizon through precipitation. Aerosols which become incorporated into the crystal lattice will be subjected to incorporation factors dependent on the chemistry and type of aerosol deposited. Notably, a number of trace elements are preferentially incorporated in the solid phase as a result of adsorption and complexing processes described in

Table 3

Comparison of drip water (at 287 L year^{-1} flow rate) and aerosol flux contributions to speleothem geochemistry. Limiting drip rates are those at which drip water chemistry supply is equal to that of aerosol flux. Drip water oversupply (%) = $1/[\text{mg of element per year calcite growth}/\text{mg of drip water supply per year} \times 100] \times 100$. Aerosol flux oversupply (%) = $1/[\text{mg of element per year calcite growth}/\text{mg of aerosol flux to speleothem surface per year} \times 100] \times 100$.

Element	Oversupply (%)		Limiting drip rate (L yr^{-1})
	Drip water	Aerosol flux	
Zn	18	0.00014	0.0022
Mg	9583	0.00073	0.000022
P	99	0.012	0.036

Fairchild and Baker (2012, chapter 8). Here we modelled potential contributions from aerosols assuming 100% efficiency of incorporation into the solid phase. Whereas ions are removed from dripwater at quite low efficiencies (and this is specifically the case as Obir cave, Fairchild et al., 2010), at minimal drip rates, solid phase accretion processes will tend to be less discriminatory between elements. Aerosol preservation will therefore be a function of: drip water flow rates, speleothem growth rates (also a function of flow rates), aerosol deposition type (wet or dry deposition) and aerosol type.

5.2. Cave aerosol, aerobiology and microbial communities

Microbial material is known to be distributed throughout cave networks (Jurado et al., 2009, 2010; Cuezva et al., 2009; Bastain and Alabouvette, 2009, Bastian et al., 2009a, 2009b, 2010). The distribution of microorganisms may be influenced by transportation as aerosols. In addition to, or as a separate process, microbiological activity throughout caves is known to occur as a consequence of anthropogenic transportation and is often an issue for cave management practices. Aerosols of fungi (Wang et al., 2011) and bacteria (Wang et al., 2010; Martin-Sanchez et al., 2011) have been shown to be distributed throughout cave networks with visitors having a significant influence of the type and concentration of the biological aerosols. Visitors carry spores, seeds and bacteria on clothing and deposit them within the cave network. In addition to providing an introduction mechanism visitors result in increased disturbance and aerosol production.

Regarding the contribution of aerosol deposition to speleothem, microbiological processes may provide an additional feedback. Aerosol deposition contributions to speleothem surfaces may not be sufficient to influence speleothem chemistry directly to a significant degree. However, the presence of deposits may facilitate and sustain microbial communities which subsequently, through bio-accumulative processes, result in inorganic concentration horizons of notable levels. Some bacteria are known to be capable of concentrating metals from their environment (Dorn and Oberlander, 1981) and have been known to increase the rate of manganese oxidation by up to five orders of magnitude (Tebo et al., 1997). Microorganisms may contribute to the formation of manganese and iron oxide-rich deposits (Northup et al., 2003). In addition to metals cave biota have been also shown to accumulate and precipitate calcium phosphate in significant quantities (Jones, 2009). In the particular case study of Altamira Cave, the

Table 2

Values of maximum theoretical aerosol contributions (A, %) to concentrations of individual elements for samples taken across the growth range of the Obir speleothems, based on depositional flux at location S. Uncertainties are one standard deviation. Extended statistical results of OBI12 and OBI84 for location S are displayed in the supplementary material S.4, Table S.1.

	Mg	P	Mn	Zn	Sr	Ba
OBI12	1.1 ± 0.31	14 ± 5.4	72 ± 34	0.0068 ± 0.0027	0.45 ± 0.11	0.20 ± 0.043
OBI84	0.43 ± 0.34	5.0 ± 4.0	30 ± 32	0.0024 ± 0.0015	0.13 ± 0.18	0.079 ± 0.066

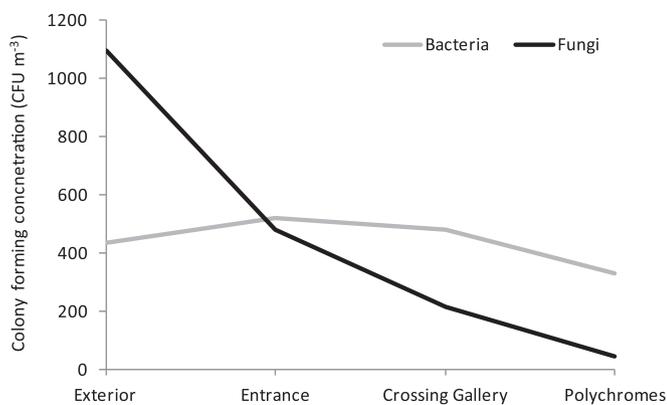


Fig. 23. Airborne bacteria and fungi aerosol concentrations expressed as colony forming units per m³ of air in Altamira Cave, Spain. Data displayed is averaged from four cave visits on the same day 7:18–7:57 am, 9:29–10:05 am, 11:49 am–12:17 pm and 2:57–3:27 pm. During this time monitoring was only exposed to the influence of the operator.

Actinobacteria, forming grey spots in the cave surface near the entrance, can use the captured CO₂ to dissolve the rock and subsequently generate crystals of CaCO₃ in periods of lower humidity and/or CO₂ (Cuezva et al., 2012). Likewise, bacteria are also involved in the formation of calcitic moonmilk deposits in this cave (Sanchez-Moral et al., 2012). In some instances the aerosol contribution to speleothem could be significantly increased as a result of secondary feedback concentrating processes and provide a proxy for emissions events which would not be detectable otherwise.

Monitoring of suspended fungi and bacteria was undertaken in Altamira Cave to determine the spatial distribution of microbial aerosols throughout the cave network, the results of which are displayed in Fig. 23. Fungi demonstrate the same distribution observed in the suspended aerosol counts carried out during the same fieldwork period indicating the same ventilation driven distribution mechanism as other aerosols. It should be noted that fungi may associate with larger particles which were not detected by the particle counter. However, bacteria demonstrate a pervasive but spatially independent distribution. This is coherent with the distribution of intermediate to coarser aerosols observed from suspended aerosol monitoring, as bacterial aerosols are typically of 0.3–10 μm in size (as shown in Fig. 2). The aerial distribution of suspended bacteria differs to the observations of bacterial colonisation, which is dominant nearest the cave entrance. It is plausible that the relationship between bioaerosols and cave surface colonisation is controlled by the distribution of inorganic aerosols which provide a nutrient flux creating conditions suitable for sustaining microbial production. Therefore colonisation differences occur as a consequence of relatively high nutrient fluxes to cave surfaces rather the direct deposition of bacteria.

6. Conclusions

A range of cave aerosol issues have been explored in this review providing the first synthesis of cave aerosol literature combined with the presentation of cave aerosol monitoring data highlighting topics of key importance.

Methodologies have been outlined for the analysis and identification of aerosols. Surrogate surface and particle counting methods have been shown to offer the most suitable methods for cave dry deposition and suspended aerosol sampling respectively. Subsequent to aerosol capture a wealth of geochemical, morphological and quantitative information can be obtained through both inorganic and organic analytical techniques such as ICP-MS, SEM and GC-MS respectively.

Data has shown that cave aerosols are internally and externally sourced from both natural and anthropogenic processes. Monitoring data demonstrates that cave visitor disruptions release aerosols to levels orders of magnitude greater than that of the natural background. Cave environment degradation from combustion emissions and cave visitors is becoming increasingly common and is developing as a cave management problem. Cave preservation practices involving ventilation control and visitor number restrictions have been shown to reduce the introduction of cave aerosols and their detrimental impacts.

Cave aerosols are sensitive to environmental conditions and will therefore exhibit temporal and spatial variations. A range of cave processes can be investigated by measurement of suspended aerosol loads, aerosol deposition and aerosol type. Data has shown that cave atmosphere aerosol transport is predominantly controlled by cave ventilation and anthropogenic disturbances. As aerosol monitoring instruments become more widely available, aerosols may become a preferable environmental monitoring indicator providing greater sensitivity over more commonly used indicators such as cave air CO₂ and temperature.

Aerosol introduction, distribution, deposition and incorporation are complex and variable processes dictated heavily by the specific cave situation. Cave morphology has been shown to influence cave aerosol deposition to speleothem through the control of ventilation forced air flow rates and creation of turbulence. Monitoring data displays evidence of progressive aerosol deposition with significant fallout within the entrance region of caves. Hydrological aerosol production has been shown to be of significance and may provide notable additions to speleothem geochemistry in proximity to active water flows. The distribution of aerosol deposition as a consequence of cave morphological effects, internal aerosol production and subsequent variable potential contribution to speleothem geochemistry throughout caves demonstrates the need in some cases to consider aerosol deposition distributions when choosing speleothem for palaeoenvironmental investigations.

Calculations have demonstrated that the ultimate contribution of aerosols to speleothem geochemistry is predominantly dependent on growth rates, deposition flux, and aerosol incorporation factors. Results have shown that aerosol contributions to speleothem chemistry will commonly be of low significance; but, in certain instances aerosols may provide considerable additions. Comparisons of dry deposition flux rates to speleothem geochemistry have demonstrated that in the case of Obir Cave (Austria) a >99.9% reduction in drip water flow rates is required to reduce trace element supply quantities to equal that of aerosol supply. In some scenarios aerosol contributions may contaminate samples for some geochemical analytical techniques, such as radiogenic isotope studies, or skew drip water environmental signatures. Conversely, with greater understanding, aerosols through speleothem incorporation may provide a novel environmental indicator not yet constrained by existing proxies especially in the identification and interpretation of speleothem growth hiatus events.

Aerosol deposition contributions to speleothem surfaces may not be sufficient to influence speleothem chemistry directly to a significant degree. However, microbiological processes may provide a positive feedback to aerosol deposition. The presence of deposits may facilitate and sustain microbial communities which subsequently, through bio-accumulative processes, result in inorganic concentration horizons of notable levels.

To summarise, the key situations where aerosol deposition may provide noteworthy contributions to speleothem are:

- Hiatus events (ceased/very slow speleothem growth).
- Very high deposition flux rates as a result of a combination of efficient aerosol transport and large external suspended loads.

- Secondary microbial feedback processes resulting in increased concentrations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.quascirev.2012.11.016>.

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