Cave ventilation is influenced by variations in the CO_2-dependent virtual temperature

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Abstract: Dynamics and drivers of ventilation in caves are of growing interest for different fields of science. Accumulated CO_2 in caves can be exchanged with the atmosphere, modifying the internal CO_2 content, affecting stalagmite growth rates, deteriorating rupestrian paintings, or creating new minerals. Current estimates of cave ventilation neglect the role of high CO_2 concentrations in determining air density – approximated via the virtual temperature (T_v) –, affecting buoyancy and therefore the release or storage of CO_2. Here we try to improve knowledge and understanding of cave ventilation through the use of T_v in CO_2-rich air to explain buoyancy for different values of temperature (T) and CO_2 content. Also, we show differences between T and T_v for 14 different experimental sites in the vadose zone, demonstrating the importance of using the correct definition of T_v to determine air buoyancy in caves. The calculation of T_v (including CO_2 effects) is currently available via internet using an excel template, requiring the input of CO_2 (%), air temperature (ºC) and relative humidity (%).

INTRODUCTION

There is currently growing interest in characterizing storage and ventilation of CO_2 in caves, both from external (atmospheric) and internal (speleological) perspectives. Measurements of rising atmospheric CO_2 by Keeling (1960) since the mid-20th century reveal that anthropogenic activities are causing CO_2 accumulation in the atmosphere and forcing global warming. Soils are a large pool of terrestrial carbon (C), estimated to contain 2344 Pg C in solid form in the top 3 m (Jobbagy & Jackson, 2000) – three times the aboveground biomass C reservoir and double that of the atmosphere (Schlesinger, 1997) – and also have an enormous capacity to store gaseous CO_2 in subsurface cracks, pores and cavities. The vadose zone is enriched in CO_2 and some caves often exceed 5% (volumetric CO_2 fraction of 50,000 ppm; Ek & Gewelt, 1985; Howarth & Stone, 1990; Denis et al., 2005; Batiot-Guilhe et al., 2007; Benavente et al., 2010) representing important air compositional differences with respect to the external atmosphere, currently near 395 ppm. Accumulated CO_2 in caves

can be exchanged with the atmosphere (Weisbrod et al., 2009; Serrano-Ortiz et al., 2010; Sanchez-Cañete et al., 2011), modifying the internal CO_2 content and affecting stalagmite growth rates (Banner et al., 2007; Baldini et al., 2008), deteriorating rupestrian paintings (Fernández et al., 1986) and creating new minerals (Badino et al., 2011). However due to the complexity and peculiarity of caves, as well as the variety of meteorological conditions that determine the degree and timing of ventilation (Fairchild & Baker, 2012), such exchanges are not well understood and their contributions to regional atmospheric CO_2 budgets remain unknown.

Estimation of cave ventilation can be realized by a number of means, the most common of which has traditionally neglected the role of high CO_2 concentrations and requires refinement. The drivers implicated in the cave ventilation can be classified as either dynamic or static (Cigna, 1968). Dynamic drivers are defined by moving fluids such as water or wind (Nachshon et al., 2012), while static drivers include variations of pressure, temperature or air composition (water vapor, CO_2, CH_4, etc.). Ventilation rates can be measured directly using anemometers,

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estimated indirectly through variations in Radon content (Hakl et al., 1997; Faimon et al., 2006), or other tracer gases (de Freitas et al., 1982) or variations in air density. Most commonly, air density variations are approximated to evaluate buoyancy according to temperature differences between the internal (T_{int}) and exterior atmosphere (T_{ext}), neglecting air composition (Fernàndez-Cortes et al., 2006; Baldini et al., 2008; Liñan et al., 2008; Milanolo & Gabrovšek, 2009; Faimon et al., 2012). Faimon et al. (2012) modelled the airflows into a cave, and found that the temperature explained more than 99% of variations in air density; therefore, temperature could be used as an alternative airflow predictor. However, de Freitas et al. (1982) concluded that reversal of airflow occurs when the densities in the cave and the exterior are equal, rather than when thermal conditions of the cave and external air are the same. For this reason, they suggest that the gradient in virtual temperature (T_v) between the cave and outside air would be the appropriate indicator. In this sense, Kowalczk & Froelich (2010), improved the determination of internal /external air densities by including the influence of water vapor, using the traditional definition of the virtual temperature. Nevertheless, in cases where CO_2 molar fractions of internal air exceed atmospheric values by an order of magnitude or more, it is necessary to take into account the heaviness of CO_2 when calculating the virtual temperature (Kowalski & Sanchez-Cañete, 2010).

Whereas high CO_2 values registered in cave air have been attributed most often to the seepage of CO_2-enriched water from the root zone, the possibility of sinking flows of dense, CO_2-rich air should also be considered. Biological CO_2 is produced near the surface by respiration of plant roots and microorganisms (Kuzyakov, 2006); in most caves, isotopic studies confirm a clear biological origin of cave CO_2 (Bourges et al., 2001, 2012). Soil CO_2 generally increases with depth, from near-atmospheric concentrations at a few centimeters to an order of magnitude more a few meters down (Amundson & Davidson, 1990, Atkinson, 1977). High concentrations of CO_2 at depth have been explained in terms of shallow CO_2 dissolution, downward transport by seepage, and subsequent precipitation from water in deeper layers (Spötl et al., 2005), whereas surface layers are depleted in CO_2 by exchange with the atmosphere. At depth and for caves in particular, another input of CO_2 could be due to the injection of dense, CO_2-rich air, flowing down through fissures due to differences in buoyancy, whose characterization is poorly known and requires information regarding T_v. This virtual temperature has been little applied to soils and caves, but could explain why CO_2 accumulates at depth yielding concentrations much higher than those in the atmosphere.

Here we show the error produced in determining the virtual temperature when not taking into account CO_2 effects, and demonstrate its repercussions for the determination of air buoyancy in caves. We try to improve knowledge and understanding of cave ventilation through the use of virtual temperature

in CO_2-rich air. Accurate determinations of virtual temperature allow numerical evaluation of buoyancy, and thus can determine exactly when ventilation is possible, and therefore when a cave can release or store CO_2. Also we represent T_v -explaining the relative buoyancy relevant for cave ventilation- for different values of T and CO_2 content. Then, we show differences between T and T_v, -calculated both with and without accounting for CO_2 content- for 14 different experimental sites in the vadose zone, demonstrating the importance of using the correct definition of T_v to determine air buoyancy in caves.

DERIVATIONS AND DEFINITIONS

For purposes of characterizing air buoyancy, meteorologists define the virtual temperature (T_v) as the temperature that dry air must have to equal the density of moist air at the same pressure. The virtual temperature for the atmosphere is approximated as (see appendix A):

$$T_v = T(1 + 0.61r) \tag{1}$$

where T and T_v are the absolute temperature (K) and virtual temperature (K) respectively and r is the mixing ratio (dimensionless), defined as the ratio of the mass of water vapor to that of dry air.

Thus variations in the virtual temperature serve as a proxy for those in air density (Stull, 1988), which can be obtained through the equation of state for moist air:

$$p = \rho R_d T_v \tag{2}$$

where p, ρ and R_d are the pressure (Pa=J m^{-3}), air density (kg m^{-3}) and particular gas constant for dry air (286.97 J kg^{-1} K^{-1}) respectively. Equation (2) makes clear that, for a given altitude level (pressure), air density is related directly to T_v, which serves therefore as a surrogate variable for determining buoyancy.

Equation (2) is only valid for the free atmosphere, while for caves or soils it should not be used due to high concentrations of CO_2 in the air. This equation, normally used for assessing the buoyancy of an air mass by changes in its density, is valid in the atmosphere because the molar mass of dry air (m_d) is very constant, 0.02897 kg·mol^{-1}, since air composition is very constant once water vapor has been excluded. However the air composition in soils or caves differs from that of the atmosphere due to higher amounts of CO_2.

The correct equations to calculate the virtual temperature including CO_2 effects were developed by Kowalski & Sanchez-Cañete (2010). Frequently caves exhibit values exceeding 0.4% in volumetric fraction of CO_2, ten times the atmospheric concentration (Howarth & Stone, 1990; Denis et al., 2005; Batiot-Guilhe et al., 2007; Benavente et al., 2010). This CO_2 increment with respect to atmospheric concentrations provokes changes in the composition of dry air and its molar mass (m_d) so that the definition of the virtual temperature in eq. (1) is inappropriate. An approximation to calculate the virtual temperature (T_v) including CO_2 effects is via the following equation (see appendix):

$$T_v = T + (1 + 0.6079r_v - 0.3419r_c) \quad \text{(3)}$$

where r_v and r_c are the water vapour and carbon dioxide mixing ratios respectively (dimensionless).

Therefore for determining air density in caves or soils including CO_2 effects, the virtual temperature can be used in the ideal gas law with the particular gas constant (R_{noa}, 287.0 J K^{-1} kg^{-1}) for the mixture of nitrogen (N_2), oxygen (O_2), and argon (Ar).

$$p = \rho \cdot R_{noa} \cdot T_v \quad \text{(4)}$$

This parameter can be computed exactly using an excel template found at http://fisicaaplicada.ugr.es/pages/tv/!/download, where it is only necessary to enter values of CO_2 (%), air temperature (°C) and relative humidity (%).

RESULTS AND DISCUSSION

The difference between internal (cave) and external (atmosphere) virtual temperatures can be used to determine the potential for buoyancy flows. The virtual temperature is a variable used traditionally by meteorologists to determine air buoyancy. Knowing the internal and external virtual temperatures allows determination of air densities (using equation 4) and therefore calculation of the possibility of buoyancy flows. The following results are organized into two sections. First, general differences between T and T_v, including CO_2 effects and comparing the interior and exterior environments, are presented to highlight the importance of using the appropriate variable (T_v) to characterize air density. Then, differences are shown for the conditions of specific caves selected from the literature.

Quantifying T_v-T for caves in general

Differences between air temperature (T) and virtual temperature (T_v) (eq. 3) at different volumetric fractions of CO_2 are shown in Fig. 1, assuming 100% relative humidity (RH) as is typical for internal conditions. To give an example, a cave with 3% CO_2, and 10°C would have a T_v 3°C lower than T (see dashed lines). Positive values (orange color) indicate that the virtual temperature is higher than the temperature due to the dominant influence of water vapor on compositionally determined air density (for low CO_2 concentrations). This is greater for higher temperatures since warm air can store more water vapor than cold air, decreasing the molar mass below that of dry air (28.96 g mol^{-1}) due to the increased importance of water vapor (18 g mol^{-1}), thus reducing the density.

Figure 2 shows that whenever the internal and external atmospheres have the same temperature and relative humidity, higher values of CO_2 inside the cave explain stagnation of the cave environment. For example, a cave with 3% CO_2 and exterior and interior temperature of 10°C would have a virtual temperature 4.3°C colder than that of the external air; consequently the internal air is denser than the exterior and therefore stagnant.

Whereas differences between external and internal virtual temperatures are necessary for the correct interpretation of cave ventilation, the difference between external and internal temperatures is commonly used (Spötl et al., 2005; Fernàndez-Cortes et al., 2006, 2009; Baldini et al., 2008; Liñan et al., 2008; Milanolo & Gabrovšek, 2009; Faimon et al., 2012). Thus, with similar values of T_{ext} and T_{int}, the differences between virtual temperatures can be more than 10°C (Fig. 2).

Fixing the internal CO_2 content (e.g., at 3% to continue with the example presented above), we can analyze differences between external and internal virtual temperatures (Fig. 3) at different temperatures. Negative values indicate that the interior air is denser than the exterior and therefore stagnant. For example, a cave with 3% CO_2, 100% RH and 10°C presents neutral buoyancy when the external temperature is approximately 6°C. Consistent with the results of Fig. 2, when both cave and external atmosphere are at 10°C, T_v is lower than T by 4.3°C. Higher values of the external temperature imply stagnant air inside the cave.
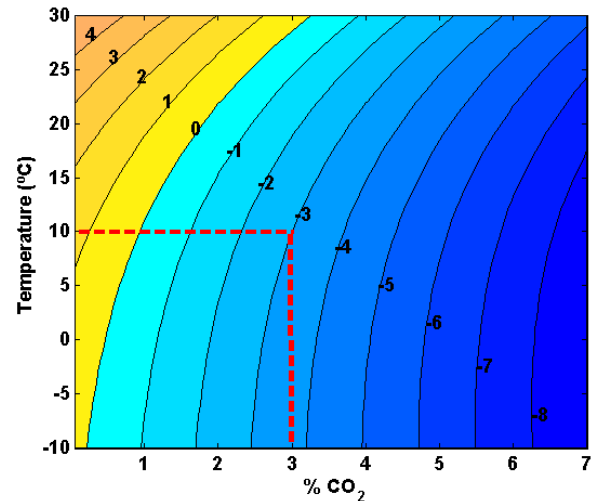

Fig. 1. Isopleths of the difference between the virtual temperature and temperature (T_v - T), as a function of volumetric fraction CO_2 (1% = 10.000 ppm) and temperature, for 100% of RH.
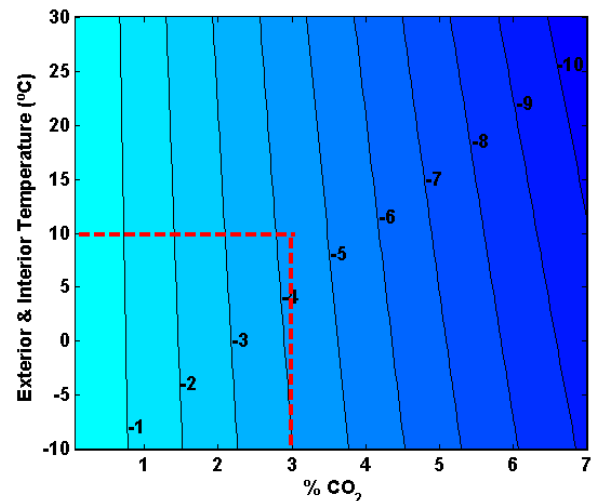

Fig. 2. Isopleths of the difference between virtual temperatures of exterior and interior (Tv_{int} - Tv_{ext}) both with identical temperature and 100% of RH, as a function of temperature and volumetric fraction CO_2. The exterior is considered to contain 0.0395% CO_2.
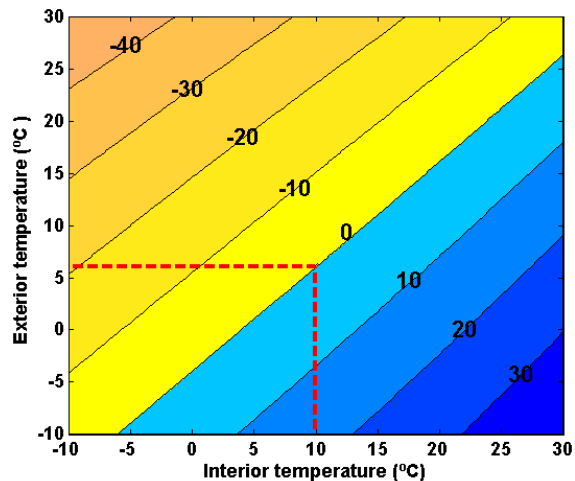
Fig. 3. Isopleths of the difference between the virtual temperature of interior and exterior with 3% CO_2 ($Tv_{int} - Tv_{ext}$), each at 100% of RH, as a function of the internal and external temperatures.

Quantifying T_v–T for specific caves

To determine when buoyancy flows are possible, scientists must compare the differences between external and internal virtual temperatures. Thus, if virtual temperatures are equal (independent of the amount of water vapor or CO_2) both air masses will be in equilibrium. On the other hand, if air mass A has a virtual temperature higher than air mass B, then air mass A will have the lower density. In this way, comparing the virtual temperatures of air masses specifies their relative densities (from eq. 4) and thus the tendency to float or sink.

Maximum CO_2 values and mean temperatures of 14 caves and boreholes of the world are shown in Table 1. These published data were taken as examples to calculate the differences between the virtual temperature and temperature. Although such differences also depend on the temperature, caves in excess of 1% CO_2 generally present negative differences between T_v and T, while lower values of CO_2 present positive differences (Fig. 4). However, for example, the subtropical Hollow Ridge cave (D) presents more positive values of T_v-T than does the temperate Císařská cave (C), despite similar volumetric fractions of CO_2 (0.42 and 0.4%, respectively). Such differences are

due to differences in water vapor content, according to temperature (19.6 versus 9.6° C in Hollow Ridge and Císařská cave, respectively).

Virtual temperature differences between the exterior and interior are compared to distinguish between periods of stagnant versus buoyant cave air for each experimental site, using their maximum values of CO_2 and the mean T (Fig. 5). Differences between the virtual temperatures (T_{v_ext}-T_{v_int}) increase with increasing CO_2 molar fraction and therefore higher CO_2 implies greater differences between internal and external densities, with the internal air denser than the external air and therefore causing stagnation (in the case of a cave lying below its entrance). For example, the Natural Bridge Caverns (I) with 4% CO_2 presents a difference of 6 °C between the (mean annual) external and internal virtual temperatures. Therefore, the internal air is denser than that of the external atmosphere (on average), inducing its stagnation and explaining the storage of CO_2. In the Nerja cave borehole (M), with 6% and 0.0395% CO_2 for the internal and external atmosphere, respectively, the virtual temperature in the borehole is 8.9°C lower than the outside (Fig. 5). This difference in T_v implies that the internal air is denser, inhibiting convective ventilation. Therefore, researchers who use differences between exterior/interior air temperatures to determine ventilation, may find differences between virtual temperatures close to 9 °C, when the exterior/interior air temperature is the same in both, and therefore over- or under-estimate the ventilation periods.

Differences between virtual temperatures in two air masses indicate density differences between both, and thus the potential for ventilation due to buoyancy. However, two possible issues must be considered that hamper or facilitate ventilation of the cave. The first includes atmospheric conditions such as the wind (Kowalczk & Froelich, 2010) and pressure changes (Denis et al., 2005; Baldini et al., 2006) inside and outside of the cave. The relevancy of buoyancy-induced cave ventilation is greatest on days with atmospheric stability, where there are little pressure changes and low winds. During these days static processes (Cigna, 1968) are dominant. The second issue is the number

Table 1. Published carbon dioxide concentrations in cavity airspaces (*visual estimates).

| Country	Cave/ Soil	Name	% vol. CO2 (Maximum)	Mean temperature (ºC)	ID	Source
Italy	Cave	Grotta di Ernesto	0.170*	8*	A	(Frisia et al., 2011)
Bosnia and Herzegovina	Cave	Srednja Bijambarska Cave	0.220	6.2	B	(Milanolo & Gabrovšek, 2009)
Czech Republic	Cave	Císařská Cave	0.4	9.6*	C	(Faimon & Licbinska, 2010)
USA (Florida)	Cave	Hollow Ridge Cave	0.422	19.6	D	(Kowalczk & Froelich, 2010)
Spain	Cave	Cave Castañar de Ibor	0.44	17	E	(Fernández-Cortes et al., 2009)
Ireland	Cave	Ballynamintra Cave	0.65	11.5	F	(Baldini et al., 2008)
Spain	Borehole	Sierra de Gádor	1.5	12	G	(Sanchez-Cañete et al., 2011)
France	Cave	Aven d'Orgnac	3.5	13	H	(Bourges et al., 2001)
USA(Texas)	Cave	Natural Bridge Caverns	*4	20*	I	(Wong & Banner, 2010)
Spain	Cave	Cova de les Rodes	4.9	17.2 (other sources)	J	(Ginés et al., 1987)
Australia	Cave	Bayliss Cave	5.9	26	K	(Howarth & Stone, 1990)
France	Skinhole	Causse d'Aumelas	6	15.3 (other sources)	L	(Batiot-Guilhe et al., 2007)
Spain	Borehole	Cave of Nerja	6	21	M	(Benavente et al., 2010)
France	Cave	Cave of Lascaux	6	17.6 (other sources)	N	(Denis et al., 2005)
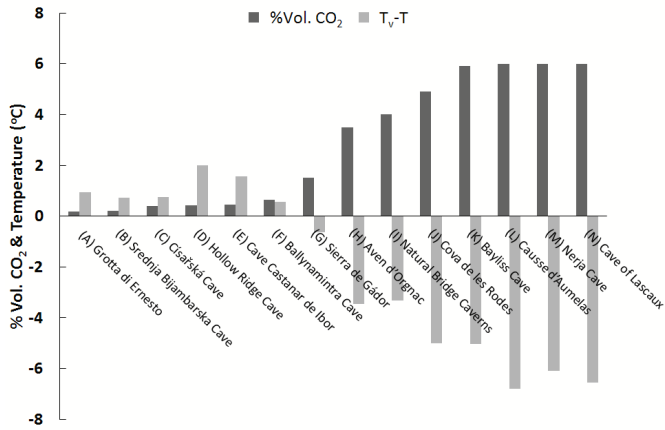
Fig. 4. Volumetric fraction of CO_2 (%, dark gray) and differences between virtual temperature (Tv) and temperature (T), (ºC, light gray) in the different cavities.

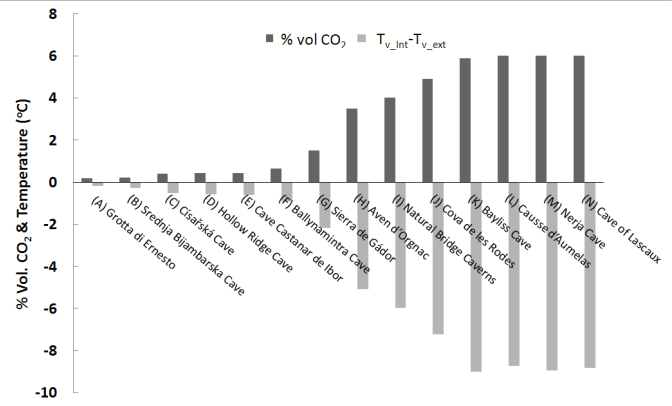Fig. 5. Volumetric fraction of CO_2 (%, dark gray) and differences between the virtual temperature of interior and an exterior (Tv_int -Tv_ext in ºC, light gray) in the different cavities. Both internal and external air are assumed to have the same temperature, which is the annual mean for the cave.

of entrances to the cave and their different altitudes and orientations (up or down). In caves with a single entrance the air will flow inward along the floor or roof, and return outward along the roof or floor, according to the sign of the density difference. However if the cave has many entrances at different levels, it may be necessary to monitor more than one entrance (Cigna, 1968). Due to the strong spatial variability of the temperature, simply knowing T_v at a single point inside (and outside) the cave may not necessarily be sufficient for determining the potential for ventilation.

CONCLUSIONS

We used the information of several caves together with gas law to demonstrate that the difference between external and internal virtual temperatures including CO_2 effects determines the buoyancy and should be used for the correct interpretation of cave ventilation. Often scientists estimate ventilation neglecting CO_2 effects, but this can cause errors close to 9 °C in the difference between external and internal virtual temperatures when the air temperature is the same in both. Thus, the common use of the difference between external and internal temperatures could over- or under-estimate the existence of ventilation processes, depending on CO_2 content and relative humidity.

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REFERENCES

Amundson R. G. & Davidson E. A., 1990 - *Carbon dioxide and nitrogenous gases in the soil atmosphere.* Journal of Geochemical Exploration, **38**: 13-41. http://dx.doi.org/10.1016/0375-6742(90)90091-N

Atkinson T. C., 1977 - *Carbon-dioxide in atmosphere of unsaturated zone - important control of groundwater hardness in limestones.* Journal of Hydrology, **35**: 111-123. http://dx.doi.org/10.1016/0022-1694(77)90080-4

Badino G., Calaforra J. M., Forti P., Garofalo P. & Sanna L., 2011 - *The present day genesis and evolution of cave minerals inside the Ojo de la Reina Cave (Naica Mine, Mexico).* International Journal of Speleology, **40**: 125-131. http://dx.doi.org/10.5038/1827-806X.40.2.5

Baldini J. U. L., Baldini L. M., McDermott F. & Clipson N., 2006 - *Carbon dioxide sources, sinks, and spatial variability in shallow temperate zone caves: Evidence from Ballynamintra Cave, Ireland.* Journal of Cave and Karst Studies, **68**: 4-11.

Baldini J. U. L., McDermott F., Hoffmann D. L., Richards D. A. & Clipson N., 2008 - *Very high-frequency and seasonal cave atmosphere P(CO2) variability: Implications for stalagmite growth and oxygen isotope-based paleoclimate records.* Earth and Planetary Science Letters, **272**: 118-129. http://dx.doi.org/10.1016/j.epsl.2008.04.031

Banner J. L., Guilfoyle A., James E. W., Stern L. A. & Musgrove M., 2007 - *Seasonal variations in modern speleothem calcite growth in Central Texas, USA.* Journal of Sedimentary Research, **77**: 615-622. http://dx.doi.org/10.2110/jsr.2007.065

Batiot-Guilhe C., Seidel J. L., Jourde H., Hebrard O. & Bailly-Comte V., 2007 - *Seasonal variations of CO2 and Rn222 in a mediterranean sinkhole - spring (Causse d'Aumelas, SE France).* International Journal of Speleology, **36**: 51-56.

Benavente J., Vadillo I., Carrasco F., Soler A., Liñan C. & Moral F., 2010 - *Air Carbon Dioxide Contents in the Vadose Zone of a Mediterranean Karst.* Vadose Zone Journal, **9**: 126-136. http://dx.doi.org/10.2136/vzj2009.0027

Bourges F., Genthon P., Genty D., Mangin A. & d'Hulst D., 2012 - *Comment on "Carbon uptake by karsts in the Houzhai Basin, southwest China" by Junhua Yan et al.* Journal of Geophysical Research-Biogeosciences, **117**: G03006.

Bourges F., Mangin A. & d'Hulst D., 2001 - *Carbon dioxide in karst cavity atmosphere dynamics: the example of the Aven d'Orgnac (Ardeche).* Comptes Rendus de l' Académie des Sciences, Serie II Fasc. a, Sciences de la Terre et des Planètes, **333**: 685-692.

Cigna A.A., 1968 - *An analytical study of air circulation in caves.* International Journal of Speleology, **3**: 41-54.

De Freitas C. R., Littlejohn R. N., Clarkson T. S. & Kristament I. S., 1982 - *Cave climate: Assessment of airflow and ventilation.* Journal of Climatology, **2**: 383-397. http://dx.doi.org/10.1002/joc.3370020408

Denis A., Lastennet R., Huneau F. & Malaurent P., 2005 - *Identification of functional relationships between atmospheric pressure and CO2 in the cave of Lascaux using the concept of entropy of curves.* Geophysical Research Letters, **32**: L05810. http://dx.doi.org/10.1029/2004GL022226

Ek C. & Gewelt M., 1985 - *Carbon dioxide in cave atmospheres. New results in Belgium and comparison with some other countries.* Earth Surface Processes and Landforms, **10**: 173-187. http://dx.doi.org/10.1002/esp.3290100209

Faimon J. & Licbinska M., 2010 - *Carbon dioxide in the soils and adjacent caves of the Moravian karst.* Acta Carsologica, **39**: 463-475.

Faimon J., Stelcl J. & Sas D., 2006 - *Anthropogenic CO2-flux into cave atmosphere and its environmental impact: A case study in the Cisarska Cave (Moravian Karst, Czech Republic).* Science of the Total Environment, **369**: 231-245. http://dx.doi.org/10.1016/j.scitotenv.2006.04.006

Faimon J., Troppova D., Baldik V. & Novotny R., 2012 - *Air circulation and its impact on microclimatic variables in the Cisarska Cave (Moravian Karst, Czech Republic).* International Journal of Climatology, **32**: 599-623. http://dx.doi.org/10.1002/joc.2298

Fairchild I. J. & Baker A., 2012. *Speleothem Science: From Process to Past Environments*, Wiley-Blackwell, Chichester, 450 p.

Fernández-Cortes A., Calaforra J. M. & Sanchez-Martos F., 2006 - *Spatiotemporal analysis of air conditions as a tool for the environmental management of a show cave (Cueva del Agua, Spain).* Atmospheric Environment, **40**: 7378-7394. http://dx.doi.org/10.1016/j.atmosenv.2006.06.045

Fernández-Cortes A., Sanchez-Moral S., Cuezva S., Cañaveras J. C. & Abella R., 2009 - *Annual and transient signatures of gas exchange and transport in the Castanar de Ibor cave (Spain).* International Journal of Speleology, **38**: 153-162.

Fernández P. L., Gutierrez I., Quindós L. S., Soto J. & Villar E., 1986 - *Natural ventilation of the Paintings Room in the Altamira cave.* Nature, **321**: 586-588. http://dx.doi.org/10.1038/321586a0

Frisia S., Fairchild I. J., Fohlmeister J., Miorandi R., Spötl C. & Borsato A., 2011 - *Carbon mass-balance modelling and carbon isotope exchange processes in dynamic caves.* Geochimica Et Cosmochimica Acta, **75**: 380-400. http://dx.doi.org/10.1016/j.gca.2010.10.021

Ginés A., Hernández J., Ginés J. & Pol A., 1987 - *Observaciones sobre la concentración de dióxido de carbono en la Atmósfera de la Cova de les Rodes.* Endins, **13**: 27-38.

Hakl J., Hunyadi I., Csige I., Geczy G., Lenart L. & Varhegyi A., 1997 - *Radon transport phenomena studied in karst caves - International experiences on radon levels and exposures.* Radiation Measurements, **28**: 675-684. http://dx.doi.org/10.1016/S1350-4487(97)00163-7

Howarth F. G. & Stone F. D., 1990 - *Elevated carbon dioxide levels in Bayliss Cave, Australia: implications for the evolution of obligate cave species.* Pacific Science, **44**: 207-218.

Jobbagy E. G. & Jackson R. B., 2000 - T*he vertical distribution of soil organic carbon and its relation to climate and vegetation.* Ecological Applications, **10**: 423-436. http://dx.doi.org/10.1890/1051-0761(2000)010[0423:TVDOSO]2.0.CO;2

Keeling C. D., 1960 - *The concentration and isotopic abundance of carbon dioxide in the atmosphere.* Tellus, **12**: 200-203. http://dx.doi.org/10.1111/j.2153-3490.1960.tb01300.x

Kowalczk A. J. & Froelich P. N., 2010 - *Cave air ventilation and CO2 outgassing by radon-222 modeling: How fast do caves breathe?* Earth and Planetary Science Letters, **289**: 209-219. http://dx.doi.org/10.1016/j.epsl.2009.11.010

Kowalski A. S. & Sanchez-Cañete E. P., 2010 - *A New Definition of the Virtual Temperature, Valid for the Atmosphere and the CO2-Rich Air of the Vadose Zone.* Journal of Applied Meteorology and Climatology, **49**: 1692-1695.

Kuzyakov Y., 2006 - Sources of CO2 efflux from soil and review of partitioning methods. Soil Biology & Biochemistry, **38**: 425-448. http://dx.doi.org/10.1016/j.soilbio.2005.08.020

Liñan C., Vadillo I. & Carrasco F., 2008 - *Carbon dioxide concentration in air within the Nerja Cave (Malaga, Andalusia, Spain).* International Journal of Speleology, **37**: 99-106.

Milanolo S. & Gabrovšek F., 2009 - *Analysis of Carbon Dioxide Variations in the Atmosphere of Srednja Bijambarska Cave, Bosnia and Herzegovina.* Boundary-Layer Meteorology, **131**: 479-493. http://dx.doi.org/10.1007/s10546-009-9375-5

Nachshon U., Dragila M. & Weisbrod N., 2012 - *From atmospheric winds to fracture ventilation: Cause and effect.* Journal of Geophysical Research-Biogeosciences, **117**: G02016.

NOAA, 1976. U. S. Standard Atmosphere, 1976. NASA and USAF.

Sanchez-Cañete E. P., Serrano-Ortiz P., Kowalski A. S., Oyonarte C. & Domingo F., 2011 - *Subterranean CO2 ventilation and its role in the net ecosystem carbon balance of a karstic shrubland.* Geophysical Research Letters, **38**: L09802.

Schlesinger W. H., 1997. *Biogeochemistry: An Analysis of Global Change.* Academic Press, San Diego, 588 p.

Serrano-Ortiz P., Roland M., Sanchez-Moral S., Janssens I. A., Domingo F., Godderis Y. & Kowalski A. S., 2010 - *Hidden, abiotic CO2 flows and gaseous reservoirs in the terrestrial carbon cycle: Review and perspectives.* Agricultural and Forest Meteorology, **150**: 321-329. http://dx.doi.org/10.1016/j.agrformet.2010.01.002

Spötl C., Fairchild I. J. & Tooth A. F., 2005 - *Cave air control on dripwater geochemistry, Obir Caves (Austria): Implications for speleothem deposition in dynamically ventilated caves.* Geochimica Et Cosmochimica Acta, **69**: 2451-2468. http://dx.doi.org/10.1016/j.gca.2004.12.009

Stull R. B., 1988. *An introduction to Boundary Layer Meteorology.* Kluwer Academic Publishers, Dordrecht, The Netherlands, 667p.

Weisbrod N., Dragila M. I., Nachshon U. & Pillersdorf M., 2009 - *Falling through the cracks: The role of fractures in Earth-atmosphere gas exchange.* Geophysical Research Letters, **36**: L02401. http://dx.doi.org/10.1029/2008GL036096

Wong C. & Banner J. L., 2010 - *Response of cave air CO2 and drip water to brush clearing in central Texas: Implications for recharge and soil CO2 dynamics.* Journal of Geophysical Research-Biogeosciences, **115**: G04018.

Appendix

The starting point for deriving the virtual temperature is the ideal gas law:

$$pV = nR^*T$$
(A1)

where *p, V, n, R** and *T* are the pressure (Pa), volume (m³), number of moles (moles), universal gas constant (8.314 m³ Pa K⁻¹ mol⁻¹) and absolute temperature (K) of the gas, respectively. Since the number of moles (*n*) is equal to the mass (*m*, in kg) divided by the molar mass (*M*, in kg mol⁻¹), equation 1 can be written as:

$$pV = \frac{m}{M}R^*T$$
(A2)

By substituting the density, $\rho = m/V$ this can be rewritten in the form:

$$p = \rho \frac{R^*}{M}T$$
(A3)

When defining the particular gas constant (*R*) as R=R*/M, the equation of state for the atmosphere can be written in the form convenient for meteorologists as:

$$p = \rho RT$$
(A4)

where *p, ρ, R* and *T* are the pressure (Pa=J m⁻³), density (kg m⁻³), particular gas constant (J kg⁻¹ K⁻¹) and absolute temperature (K) of the gas, respectively.

The individual gas laws for any gas (suffix "i"), including the mixture defined as dry air (suffix "d"), water vapor (suffix "v") and another mixture defined as moist air (suffix "m") are described in the following equations

$$p_i = \rho_i R_i T$$
(A5.a)

$$p_d = \rho_d R_d T$$
(A5.b)

$$p_v = \rho_v R_v T$$
(A5.c)

$$p = \rho_m R_m T$$
(A5.d)

Dry air

The equation of state for dry air is shown in equation (A5.b), where water vapor is excluded from the air mass. Here, R_d is the gas constant for dry air, which can be determined by using the principle of mass conservation

$$\rho = \sum \rho_i$$
(A6)

and Dalton's law of partial pressures:

$$p = \sum p_i$$
(A7)

By combination of equations A5.a, A6 and A7 we obtain

$$p = T\sum \rho_i R_i$$
(A8),

which compared with equation A5.b yields

$$R_d = \frac{\sum \rho_i R_i}{\sum \rho_i}$$
(A9)

Replacing the density ($\rho = m/V$) in equation A9

$$R_d = \frac{\sum \frac{m_i}{V} R_i}{\sum \frac{m_i}{V}}$$
(A10)

and eliminating volume, which is identical for both the mixture and any individual component, it is found that:

$$R_d = \frac{\sum m_i R_i}{\sum m_i}$$
(A11)

showing that the effective particular gas constant for a mixture (such as dry air) can be calculated by the (mass) weighted combination of the particular constants for the individual components. To determine R_d it is necessary to know the composition of the dry atmosphere, by mass (Table A1).

Table A1. Components of dry air with their particular gas constants and fractional contribution by mass (NOAA et al., 1976).

Gas	Individual gas constant Ri (J kg-1 K-1)	% Mass
N₂	296.7	75.52
O₂	259.8	23.15
Ar	208.1	1.28
CO₂	188.9	0.05

Substituting into equation A11:

$$R_d = \frac{75.52 \cdot 296.7 + 23.15 \cdot 259.8 + 1.28 \cdot 208.1 + 0.05 \cdot 188.9}{100} = 286.97 \cong 287 JKg^{-1}K^{-1}$$

Moist air

The equation of state for moist air is given in equation A5.d. The moist air density can be written using equation A6:

$$\rho_m = \frac{m_v + m_d}{V} = \rho_v + \rho_d$$
(A12)

where ρ_v and ρ_d are the densities of water vapor and dry air respectively. Using equations A11 and A12, and the principle that the effective particular gas constant for the mixture (now moist air) is the (mass) weighted combination of the particular constants for the individual components, yields the gas constant of moist air (R_m),

$$R_m = \left(\frac{m_v R_v + m_d R_d}{m_v + m_d}\right)$$
(A13)

Multiplying by

$$\left(\frac{1/m_d}{1/m_d}\right)$$

produces

$$R_m = \left(\frac{\frac{m_v}{m_d} R_v + \frac{m_d}{m_d} R_d}{\frac{m_v}{m_d} + \frac{m_d}{m_d}}\right)$$
(A14)

Considering that the mixing ratio (*r*) is defined as the ratio of the mass of water vapor (m_v) to that of dry air (m_d) $r \equiv \frac{m_v}{m_d}$, and substituting this into equation A14 gives

$$R_m = \left(\frac{r R_v + R_d}{r + 1}\right)$$
(A15)

To simplify, equation A15 is multiplied by $\left(\frac{1-r}{1-r}\right)$ to give:

$$R_m = \frac{r R_v - r^2 R_v + R_d - r R_d}{r - r^2 + 1 - r}$$
(A16)

The denominator of equation A16 can be approximated as unity when recognizing that every second-order term is several orders of magnitude smaller. The numerator can be similarly simplified, leading to the following approximation:

$$R_m = R_d + r R_v - r R_d$$
(A17).

To simplify, the second term is multiplied by

$$\left(R_d \middle/ R_d \right)$$

$$R_m = R_d + r\frac{R_v}{R_d}R_d - rR_d \tag{A18}$$

Substituting the gas constants of dry air (R_d=287 J kg^{-1} K^{-1}) and water vapor (R_v=461.51 J kg-1 K-1), equation A18 can be written and organized as:

$$R_m = R_d + rR_d 1.61 - rR_d \tag{A19}$$

$$R_m = R_d(1 + 1.61r - r) \tag{A20}$$

$$R_m = R_d(1 + r(1.61 - 1)) \tag{A21}$$

$$R_m = R_d(1 + 0.61r) \tag{A22}$$

Substituting into equation A5.d we can write the equation of state for moist air

$$p = \rho_m R_d(1 + 0.61r)T \tag{A23}$$

Rather than associating the varying water vapor effect (1+0.61r) with the gas constant (and thus producing a variable constant), meteorologists traditionally associate this term with the temperature. Thus, through equation A23, the virtual temperature for the atmosphere is defined as:

$$T_v = T(1 + 0.61r) \tag{A24}$$

CO$_2$ rich-air

Equations to calculate the virtual temperature including CO$_2$ effects were developed by Kowalski & Sanchez-Cañete (2010). An approximation to calculate the virtual temperature (T_v) including CO$_2$ effects is via the following equation:

$$T_v = T + (1 + 0.6079r_v - 0.3419r_c) \tag{A25}$$

Where T_v is the virtual temperature (K), and r_v and r_c are the water vapour and carbon dioxide mixing ratios respectively (dimensionless).

The errors that arise when using equation A25 as an approximation to T_v (including CO$_2$ effects) were evaluated explicitly for the range of gas concentrations typically found in terrestrial caves and found to be less than 0.1% (0.3 K) for volumetric CO$_2$ fractions of up to 5%.

For a calculation without error, the virtual temperature should be defined using the particular gas constant for the mixture of moist air including high concentrations of CO$_2$, denoted as R$_{mc}$ and defined as:

$$R_{mc} = \frac{R_{noa} + r_c R_c + r_v R_v}{1 + r_c + r_v} \tag{A26}$$

where R_{noa} is the particular gas constant for the mixture of nitrogen (N$_2$), oxygen (O$_2$), and argon (Ar) (287.0 J K^{-1} kg^{-3}), R_c is the particular gas constant for CO$_2$ (188.9 J K^{-1} kg^{-3}), R_v is the particular gas constant for water vapor (461.5 J K^{-1} kg^{-3}), r_v is the water vapor mixing ratio (dimensionless), and r_c is the carbon dioxide mixing ratio (dimensionless).

The exact expression for T_v is then

$$T_v = T\left(\frac{\dfrac{R_{noa} + r_c R_c + r_v R_v}{1 + r_c + r_v}}{R_{noa}} \right) \tag{A27}$$

which is programmed in an Excel file freely available at http://fisicaaplicada.ugr.es/pages/tv/!/download

Therefore for determining air density in caves or soils including CO$_2$ effects, the virtual temperature can be used in the ideal gas law with the particular gas constant for the mixture of nitrogen (N$_2$), oxygen (O$_2$), and argon (Ar)

$$p = \rho \cdot R_{noa} \cdot T_v \tag{A28}.$$