Cave ventilation is influenced by variations in the CO$_2$-dependent virtual temperature

Enrique P. Sánchez-Cañete$^{1,2,*}$, Penélope Serrano-Ortiz$^{1,2}$, Francisco Domingo$^{1,3}$, and Andrew S. Kowalski$^{2,4}$

$^1$ Departamento de Desertificación y Geo-ecología, EEA-CSI, Ctra. Sacramento s/n, 04120, La cañada de San Urbano, Almería, Spain
$^2$ Centro Andaluz de Medio Ambiente (CEAMA), 18006, Granada, Spain
$^3$ Departamento de Física Aplicada, Universidad de Granada, Av. Fuentenueva s/n, 18071 Granada, Spain
$^4$ Universidad Almería, Departamento Biología Vegetal & Ecología, E-04120 Carrera Sacramento s/n, 04120, Almería, Spain

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 (%).

Keywords: buoyancy; carbon dioxide; caves; soil ventilation; ventilation; virtual temperature

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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-20$^{th}$ 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-Guille 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, 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 ($T_m$) and exterior atmosphere ($T_{ex}$), neglecting air composition (Fernández-Cortes et al., 2006; Baldini et al., 2008; Liňan 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, Kowalczyk & 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):

$$ T_v = T \left( 1 + 0.61 r \right) $$

(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:

$$ p = \rho R T_v $$

(2)

where $p$, $\rho$, and $R$ 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 ($m_g$) 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 ($m_g$) 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):

$$ T_v = T + \left( 1 + 0.6079 r_r - 0.3419 r_c \right) $$

(3)

where $r_r$ and $r_c$ are the water vapour and carbon dioxide mixing ratios respectively (dimensionless).
Therefore for determining air density in caves or soils including CO₂ effects, the virtual temperature can be used in the ideal gas law with the particular gas constant \( R_{\text{noa}} \) 287.0 J K\(^{-1}\) kg\(^{-1}\) for the mixture of nitrogen (N\(_2\)), oxygen (O\(_2\)), and argon (Ar).

\[
p = \rho \cdot R_{\text{noa}} \cdot T_v
\]

This parameter can be computed exactly using an Excel template found at http://fisicaaplicada.ugr.es/pages/tv/1/download, where it is only necessary to enter values of CO₂ (%), 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 CO₂ 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 CO₂ are shown in Fig. 1, assuming 100% relative humidity (RH) as is typical for internal conditions. To give an example, a cave with 3% CO₂ 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 CO₂ 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 CO₂ inside the cave explain stagnation of the cave environment. For example, a cave with 3% CO₂ 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; Fernández-Cortes et al., 2006, 2009; Baldini et al., 2008; Linan et al., 2008; Milanolo & Gabrovšek, 2009; Faimon et al., 2012). Thus, with similar values of \( T_{\text{int}} \) and \( T_{\text{ext}} \), the differences between virtual temperatures can be more than 10°C (Fig. 2).

Fixing the internal CO₂ 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% CO₂, 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.

### Quantifying \( T_v - T \) for specific caves

To determine when buoyancy flows are possible, scientists must compare the differences between
Table 1. Published carbon dioxide concentrations in cavity airspaces (*estimates).

<table>
<thead>
<tr>
<th>Country</th>
<th>Cave/Soil</th>
<th>Name</th>
<th>% vol. CO₂ (Maximum)</th>
<th>Mean temperature (°C)</th>
<th>ID</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Italy</td>
<td>Cave</td>
<td>Grotta di Ernesto</td>
<td>0.170*</td>
<td>8*</td>
<td>A</td>
<td>(Frisia et al., 2011)</td>
</tr>
<tr>
<td>Bosnia and Herzegovina</td>
<td>Cave</td>
<td>Srednja Bijambarska Cave</td>
<td>0.220</td>
<td>6.2</td>
<td>B</td>
<td>(Milanolo &amp; Gabrovšek, 2009)</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>Cave</td>
<td>Čísařská Cave</td>
<td>0.4</td>
<td>9.6*</td>
<td>C</td>
<td>(Faimon &amp; Licbinska, 2010)</td>
</tr>
<tr>
<td>USA (Florida)</td>
<td>Cave</td>
<td>Hollow Ridge Cave</td>
<td>0.422</td>
<td>19.6</td>
<td>D</td>
<td>(Kowalczyk &amp; Froelich, 2010)</td>
</tr>
<tr>
<td>Spain</td>
<td>Cave</td>
<td>Cave Castañar de Ibor</td>
<td>0.44</td>
<td>17</td>
<td>E</td>
<td>(Fernández-Cortes et al., 2009)</td>
</tr>
<tr>
<td>Ireland</td>
<td>Cave</td>
<td>Bailynamintra Cave</td>
<td>0.65</td>
<td>11.5</td>
<td>F</td>
<td>(Baldini et al., 2008)</td>
</tr>
<tr>
<td>Spain</td>
<td>Borehole</td>
<td>Sierra de Gádor</td>
<td>1.5</td>
<td>12</td>
<td>G</td>
<td>(Sanchez-Canete et al., 2011)</td>
</tr>
<tr>
<td>France</td>
<td>Cave</td>
<td>Aven d’Orgnac</td>
<td>3.5</td>
<td>13</td>
<td>H</td>
<td>(Bourges et al., 2001)</td>
</tr>
<tr>
<td>USA (Texas)</td>
<td>Cave</td>
<td>Natural Bridge Caverns</td>
<td>*4</td>
<td>20*</td>
<td>I</td>
<td>(Wong &amp; Banner, 2010)</td>
</tr>
<tr>
<td>Spain</td>
<td>Cave</td>
<td>Cova de les Rodes</td>
<td>4.9</td>
<td>17.2 (other sources)</td>
<td>J</td>
<td>(Ginés et al., 1987)</td>
</tr>
<tr>
<td>Australia</td>
<td>Cave</td>
<td>Bayliss Cave</td>
<td>5.9</td>
<td>26</td>
<td>K</td>
<td>(Howarth &amp; Stone, 1990)</td>
</tr>
<tr>
<td>France</td>
<td>Skinhole</td>
<td>Causée d’Aumelas</td>
<td>6</td>
<td>15.3 (other sources)</td>
<td>L</td>
<td>(Batiot-Guille et al., 2007)</td>
</tr>
<tr>
<td>Spain</td>
<td>Borehole</td>
<td>Cave of Nerja</td>
<td>6</td>
<td>21</td>
<td>M</td>
<td>(Benavente et al., 2010)</td>
</tr>
<tr>
<td>France</td>
<td>Cave</td>
<td>Cave of Lascaux</td>
<td>6</td>
<td>17.6 (other sources)</td>
<td>N</td>
<td>(Denis et al., 2005)</td>
</tr>
</tbody>
</table>

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 CO₂ and the mean T (Fig. 5). Differences between the virtual temperatures (Tᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥ$v Troll $(TV_{v Troll})$ increase with increasing CO₂ molar fraction and therefore higher CO₂ 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% CO₂ 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 CO₂. In the Nerja cave borehole (M), with 6% and 0.0395% CO₂ 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 Tᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥᵥ$v Troll$ 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 (Kowalczyk & 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 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,
Fig. 4. Volumetric fraction of CO₂ (%, dark gray) and differences between virtual temperature ($T_v$) and temperature ($T$, °C, light gray) in the different cavities.

Fig. 5. Volumetric fraction of CO₂ (%, dark gray) and differences between the virtual temperature of interior and an exterior ($T_v$ - $T_{v,ext}$ in °C, 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.

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 CO₂ effects determines the buoyancy and should be used for the correct interpretation of cave ventilation. Often scientists estimate ventilation neglecting CO₂ 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 CO₂ content and relative humidity.

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Cave ventilation is influenced by the virtual temperature


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

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

where $p$, $V$, $n$, $R^*$ and $T$ are the pressure (Pa), volume ($m^3$), number of moles (moles), universal gas constant ($8.314 \text{ m}^3\text{ Pa K}^{-1}\text{ mol}^{-1}$) 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:

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

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

$$p = \rho R^* T \quad (A3)$$

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:

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

where $p$, $\rho$, $R$ 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:

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

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

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

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

**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:

$$\rho = \rho_0 = \rho_i \quad (A6)$$

and Dalton’s law of partial pressures:

$$p = \sum \rho_i \quad (A7)$$

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

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

which compared with equation A5.b yields:

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

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

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

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

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

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>
<thead>
<tr>
<th>Gas</th>
<th>Individual gas constant Ri (J kg$^{-1}$ K$^{-1}$)</th>
<th>% Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>296.7</td>
<td>75.52</td>
</tr>
<tr>
<td>O$_2$</td>
<td>259.8</td>
<td>23.15</td>
</tr>
<tr>
<td>Ar</td>
<td>208.1</td>
<td>1.28</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>188.9</td>
<td>0.05</td>
</tr>
</tbody>
</table>

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

Substituting into equation A11:

$$R_d = 25.52 + 296.7 + 259.8 + 208.1 + 0.05 \approx 287.7 \text{ J kg}^{-1}\text{ K}^{-1}$$

**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:

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

where $\rho_v$ and $\rho_d$ 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 ($R_m$):

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

Multiplying by produces:

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

Considering that the mixing ratio ($r$) is defined as the ratio of the mass of water vapor ($m_v$) to that of dry air ($m_d$), using A11 and A12, and substituting this into equation A14 gives:

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

To simplify, equation A15 is multiplied by giving:

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

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:

$$R_m = R_d + r R_v - r R_d \quad (A17).$$
To simplify, the second term is multiplied by
\[
\left( \frac{R_v}{R_d} \right)
\]

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

\[
R_m = R_d + r \frac{R_v}{R_d} R_d - r R_d
\]  
(A18)

\[
R_m = R_d(1 + r(1.61 - 1))
\]  
(A20)

\[
R_m = R_d(1 + 0.61r)
\]  
(A22)

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

\[
p = \rho_m R_d (1 + 0.61r) T
\]  
(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:

\[
T_v = T(1 + 0.61r)
\]  
(A24)

**CO\textsubscript{2} rich-air**

Equations to calculate the virtual temperature including CO\textsubscript{2} effects were developed by Kowalski & Sanchez-Cañete (2010). An approximation to calculate the virtual temperature \((T_v)\) including CO\textsubscript{2} effects is via the following equation:

\[
T_v = T + (1 + 0.6079r_v - 0.3419r_c)
\]  
(A25)

Where \(T\) 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\textsubscript{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\textsubscript{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\textsubscript{2}, denoted as \(R_{ma}\), and defined as:

\[
R_{ma} = \frac{R_{noa} + r_c R_c + r_v R_v}{1 + r_c + r_v}
\]  
(A26)

where \(R_{noa}\) is the particular gas constant for the mixture of nitrogen (N\textsubscript{2}), oxygen (O\textsubscript{2}), and argon (Ar) \((287.0 \text{ J K}^{-1} \text{ kg}^{-1})\). \(R_c\) is the particular gas constant for CO\textsubscript{2} \((188.9 \text{ J K}^{-1} \text{ kg}^{-1})\). \(R_v\) is the particular gas constant for water vapor \((461.5 \text{ J K}^{-1} \text{ kg}^{-1})\). \(r_c\) is the water vapor mixing ratio (dimensionless), and \(r_v\) is the carbon dioxide mixing ratio (dimensionless).

The exact expression for \(T_v\) is then

\[
T_v = T \left(\frac{R_{noa} + r_c R_c + r_v R_v}{R_{noa} + r_c + r_v}\right)
\]  
(A27)

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

Therefore for determining air density in caves or soils including CO\textsubscript{2} effects, the virtual temperature can be used in the ideal gas law with the particular gas constant for the mixture of nitrogen (N\textsubscript{2}), oxygen (O\textsubscript{2}), and argon (Ar)

\[
p = \rho \cdot R_{noa} \cdot T_v
\]  
(A28).