

Comment on “Carbon uptake by karsts in the Houzhai Basin, southwest China” by Junhua Yan *et al.*

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[1] In a recent paper Yan *et al.* [2011] estimate the carbon uptake in the Houzhai Basin due to dissolution of carbonate by rainwater using dissolved carbon measurements on this basin. Since both the surface and the underground river networks are known to converge toward a single outlet, this could be achieved with one hydrological station, monitoring water discharge and providing water for chemical analyses. From a nearly monthly record over the 1986–2007 period, they were able to monitor the seasonal variations of dissolved carbon uptake and to compute a mean yearly uptake of $20.7 \text{ g C m}^{-2} \text{ yr}^{-1}$ for the Houzhai Basin, which is further extended to estimate the total carbon uptake by karst in south China. Since several karstic basins are located in China, the study by Yan *et al.* is of great interest for the scientific community. Our concern is that it neglects the gaseous component of the carbon budget. However, it is known that karstic voids contain a few percent volume of CO_2 , and we will present below evidence that this CO_2 is drained downward with rainwater from organic soils, collected by karstic voids and finally advected toward the Earth’s atmosphere, which can significantly alter the carbon budget computed by Yan *et al.* As the conclusions presented by Yan *et al.* are designed to constrain global atmospheric models, we suggest that the gaseous CO_2 should also be considered in the estimates of the budget of carbon flowing through the Houzhai Basin.

[2] Our team has accumulated more than 20 years’ research experience on this topic. Our studies were mainly motivated by the conservation of caves, including prehistoric painted caves, which requires the stability of the inner atmosphere. It is well known that the CO_2 concentration can reach a few percent volume in the cave atmosphere [James, 1977], and we monitored its concentration in a large set of French caves [Bourges *et al.*, 2001, 2006]. We have strong indications that this CO_2 is mainly biogenic and produced in

soils. This inference is supported by numerous $\delta^{13}\text{C}$ measurements in the Villard Cave (SW France) with a mean $\delta^{13}\text{C}$ of $\text{CO}_2 = -22.7\text{‰}$ (50 samples from 2005 to 2010), where its variation has been correlated with the CO_2 air concentration [Genty, 2008], and in the Chauvet Cave (SE France) with a mean $\delta^{13}\text{C}$ of $\text{CO}_2 = -22.7\text{‰}$ (20 samples from 2000 to 2010). There is also growing evidence that CO_2 is transported downward both as dissolved species and in biphasic flow with water seeping toward the phreatic zone [Atkinson, 1977; Bourges *et al.*, 2006; Mudry *et al.*, 2008; Milanolo and Gabrovšek, 2009]. One of our most original results is that the cave atmosphere is not at rest but is continuously flowing toward the Earth’s atmosphere through large openings [Bourges *et al.*, 2001]. Our interpretation is that soil air enriched with CO_2 is dragged downward both in biphasic flow and as dissolved species during infiltration of rainwater and collected as gaseous CO_2 by the network of macroscopic voids including fissures and caves. Our results indicate that a significant part of this CO_2 is directly drained to the outside atmosphere through open fissures and large cave openings. This interpretation is now widely accepted by scientists working on caves [Baldini *et al.*, 2006; Serrano-Ortiz *et al.*, 2010]. After reviewing CO_2 data gathered by the flux tower community and showing an anomalously high CO_2 rate escaping from karst terrains toward the atmosphere, Serrano-Ortiz *et al.* [2010] proposed an explanation similar to ours, involving a downward infiltration of CO_2 with rainwater followed by an outflow of gaseous CO_2 toward the terrestrial atmosphere. In some instances, winds flowing on permeable soils can further enhance the exchanges of CO_2 between the cave atmosphere and the Earth’s atmosphere [Sanchez-Cañete *et al.*, 2011; Cuezva *et al.*, 2011].

[3] We were able to observe the outward flow of CO_2 on several occasions and to estimate the annual flow of gaseous CO_2 at one French cave: the Aven d’Orgnac network (Figure 1). In winter, the outside air is colder and denser than the cave atmosphere, and the cave is therefore ventilated by downward flow of the outside air; then, in most parts of the cave the CO_2 content is similar to that of the terrestrial atmosphere [Bourges *et al.*, 2006; Kowalski and Sanchez-Cañete, 2010]. This was shown with temperature, CO_2 concentration and Rn concentration profiling along the cave system. Due to this thermo-compositional venting, the CO_2 derived from soils and conveyed to the cave would be efficiently transferred to the Earth’s atmosphere. However, direct measurements of CO_2 flux were impossible in winter,

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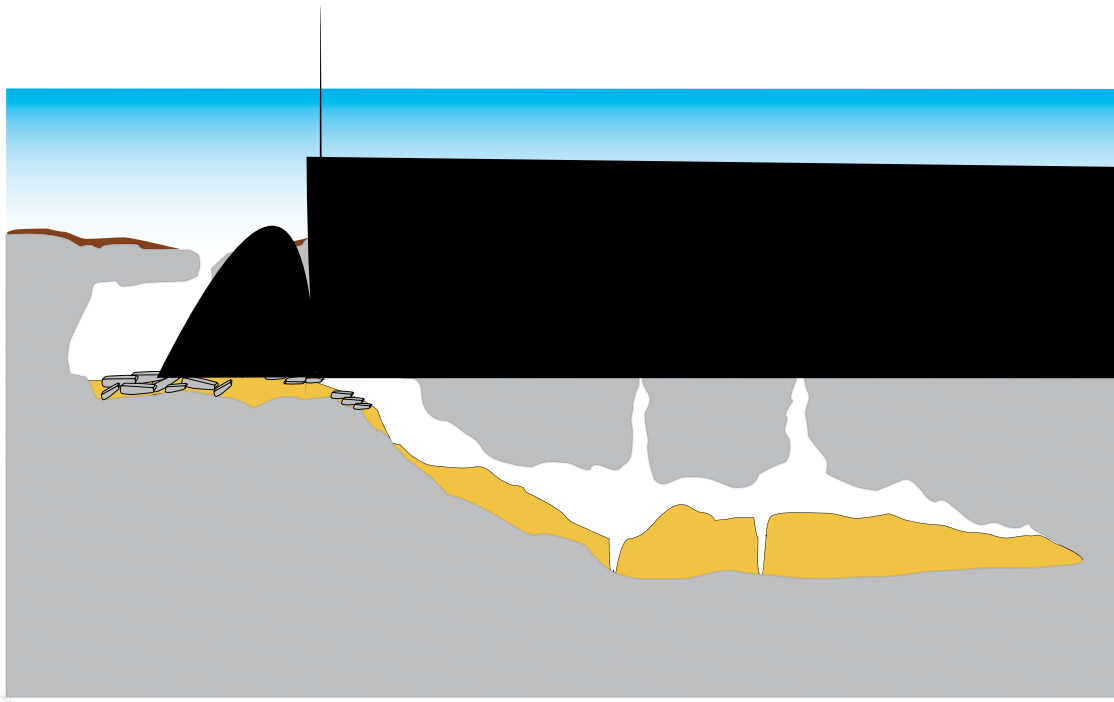
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and the stability of the cave atmosphere permitted reliable flux measurements at the cave opening only during summer. First radial profiling with one anemometer allowed us to define the air velocity distribution at the opening. Then, both air velocity and CO₂ concentration were continuously monitored during four 24-h time periods at selected points. This allowed us to compute that a mean of 1.9 t of CO₂ was escaping from the cave at its opening during each summer day. The stability of the atmosphere composition in the remote parts of the cave suggests that inflow of soil CO₂ into the cave occurs at a more or less constant rate and therefore that these measurements made in summer can be extrapolated to the entire year. The CO₂ exported yearly toward the Earth's atmosphere through the opening of the Aven

d'Orgnac thus amounts to 693 t. The surface drained by this cave network and aerodynamically related to its main opening has been estimated by drawing above each contour point of the cave a cone with a 60° aperture toward the Earth's surface. This 60° opening is a crude estimate of the area from which the flow lines of the infiltrating rainwater will converge toward the cave. On the other hand, the cave has been defined as the volume that is aerodynamically connected to the opening, and some remote parts of the cave, connected to the main cave through a narrow opening where no significant airflow was observed, were excluded. The resulting surface amounts to 0.56 km² (Figure 1), which implies that, near Orgnac, the carbon flux toward the Earth's atmosphere amounts to 343 g C m⁻² yr⁻¹. Similar

calculations at the Chauvet Cave considering a surface of 0.4 km² yield a carbon flux of 337 g C m⁻² yr⁻¹. Due to uncertainties about the surface area drained into the cave and to the seasonality of the CO₂ flux at its opening, these estimates rely on approximations; but they are 16 times larger than the carbon flux transported by surface and underground water on the Houzhai Basin as reported by Yan *et al.* [2011]. Kowalczk and Froelich [2010] recently published similar results obtained from a ²²²Rn and CO₂ budget in the Hollow Cave (Florida, USA). Their computations of the CO₂ escaping from the cave toward the Earth's atmosphere yield a yearly carbon export of 180 g C m⁻² yr⁻¹, with a CO₂ concentration in the cave atmosphere nearly one order of magnitude lower than ours. Even if this estimate is lower than ours—which indicates that further work is required on the CO₂ exchanges of cave atmosphere—it is still nearly one order of magnitude larger than the carbon flux computed by Yan *et al.* [2011]. These estimates apply only to the part of infiltrating CO₂ that is directly connected to a large cave system. The CO₂ infiltrating with rainwater would likely not depend on the presence of a cave at depth. According to our interpretation, a large part of this CO₂ would cross macroscopic voids and then be brought back at the surface toward the Earth's atmosphere, which is what is measured by tower flux experiments in karstic terrains and reported in Serrano-Ortiz *et al.* [2010].

[4] We suggest that the CO₂ dragged with rainwater infiltrating toward the aquifer should be included in the carbon budget of the Houzhai karstic basin CO₂. Its aerodynamic regime during its return to the Earth's atmosphere could be monitored using commercial anemometric and CO₂ sensors disposed at the opening of caves or by including the Houzhai karst in a flux tower network.

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