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## Gas hazard related to CO<sub>2</sub> degassing at Loutra Ypatis, Greece

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#### Introduction

Earthquakes and volcanic eruptions represent a hazard. However, the impact of gases released in geodynamically active areas should not be underestimated. It is commonly known that geogenic sources release great amounts of gases, which, apart from having an important influence on the global climate, can also have a strong impact on human health causing both acute and chronic effects. In particular, CO<sub>2</sub> and sulphur gases (mainly H<sub>2</sub>S and SO<sub>2</sub>) are the main compounds responsible for acute mortality due to their asphyxiating and/or toxic properties. One of the most known and also worst episodes occurred, took place on the 21th of August 1986 at Lake Nyos, Cameroon, when about 1700 people were killed and 850 injured by a massive CO<sub>2</sub> release (D'Alessandro, 2006).

Like other geodynamically active areas, Greece is also affected by a large number of geogenic gas manifestations (Daskalopoulou *et al.*, 2018a). These occur either in the form of point sources (fumaroles, mofettes, bubbling gases) or of diffuse soil gas emanations (Daskalopoulou *et al.*, 2018b). D'Alessandro and Kyriakopoulos (2013) made a preliminary estimation of the risk related to geogenic gases in Greece for the time period of 1992-2011; the whole population of the country was considered. In that period, at least two fatal episodes with a total of three victims took place, likely caused to the exposure to geogenic gases (specifically  $CO_2$ ). This would give a risk of  $1.3 \times 10^{-8}$  fatality from geogenic gas manifestations per annum. This value, although probably underestimated, is much lower than many other natural or anthropogenic risks. Since deaths due to natural gases are often wrongly attributed, it cannot be excluded that some fatal episode has not been recognized and thus that the risk is somewhat higher than assessed. Although very low, this risk should not be neglected, not only because it is possibly underestimated, but also because simple countermeasures could be adopted for risk reduction. Dangerous areas could be easily identified and delimited by geochemical prospecting and their hazards properly highlighted.

Apart from the sites where fatal episodes occurred, many other hazardous sites have been recognized in Greece. Here we present data collected at Loutra Ypatis (central Greece).

#### Study area

Sperchios Basin – Evoikos Gulf Graben is a 130 km long actively spreading graben in Central Greece (1 cm/a). The high geothermal gradient of the area is evident by the presence of many thermal springs with temperatures that vary from 24 to 82 °C. In the waters of these springs, discharging along the normal faults bordering the graben, an abundant gas phase is bubbling. Loutra Ypatis is one of the emerging springs and its waters (31 °C) are exploited by a spa. The water is currently drained by a gallery and therefore the water level is about 5 m below ground at the bottom of a funnel-like hole (Fig. 1 left). For safety reasons the hole was covered by a closed building (Fig. 1 left and center). The gas, which is vigorously bubbling in the spring, is mostly (> 96%) composed of CO<sub>2</sub> (D'Alessandro *et al.*, 2014). The walls of the hole are covered of sulfur that derives from the partial oxidation of the H<sub>2</sub>S (2500 ppm) contained in the released gas (D'Alessandro *et al.*, 2014).







Figure 1. The thermal spring inside the building (left); Measurements of the atmospheric concentrations of CO<sub>2</sub> outside the building in October 2015 (center); A dead bird close to a small opening of the building (right).

#### Methods

In October 2015 atmospheric concentrations of  $CO_2$  were measured with a Licor LI820 NDIR spectrometer (range 0 to 20,000 ppm, accuracy of 2%), whilst in April 2016, the atmospheric concentrations of  $CO_2$  and  $H_2S$  were measured with a Multi-GAS analyser manufactured by INGV-Palermo equipped with Licor LI-840 NDIR spectrometer ( $CO_2$  0-20,000 ppm) and an EZ3H electrochemical sensor by City Technology Ltd. ( $H_2S$  0–100 ppm). Simultaneous  $CO_2$ ,  $CH_4$  (both 0-100%), CO,  $H_2S$  (both 0-500 ppm) and  $O_2$  (0 – 25%) concentrations within the building were measured with a portable gas analyser GA2000 (Geotechnical Instruments).

#### **Results and discussion**

Due to the fact that a building covers the thermal spring, the intense bubbling activity of its waters creates a strong gas accumulation inside. The main component of the released gases is  $CO_2$ , which has a higher density with respect to atmospheric air, thus creating the conditions for gas accumulation. About 2 m above the water level,  $CO_2$  concentrations of >95% and non-detectable  $O_2$  concentrations were measured. At higher levels above the water,  $CO_2$  concentrations were decreased but never below 50%. Such concentrations within the building are lethal for both animals and human beings. Of course, access is forbidden, but as the building is not perfectly sealed, the gases permeate to the outside through fissures and cracks. Figure 2 shows the  $CO_2$  concentrations measured in the air on October 2015 at 1.5 m height while walking around the walls of the edifice at about 2 m distance. Leaking of  $CO_2$  from the edifice is made evident by concentrations reaching values of more than 6000 ppm. The highest values were measured close to the entrance of the edifice were fissures and cracks are concentrated. Due to the tendency of  $CO_2$  to accumulate at lower levels, in this place, close to the ground,  $CO_2$  levels lethal to small animal can be reached. This was made evident by a dead bird found in that occasion (Fig. 1).

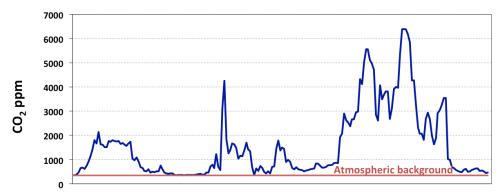


Figure 2. Atmospheric CO<sub>2</sub> concentrations at 1.5m height around the building of Fig. 1 in October 2015

In April 2016, due to the much windier conditions,  $CO_2$  concentrations at the same places reached values never exceeding 1000 ppm while  $H_2S$  was always below 1 ppm. These values sharply increased getting closer to the fissures around the main entrance of the building and reached saturation of the sensors ( $CO_2 > 20,000$  ppm and  $H_2S > 100$  ppm) at a distance of few centimeters.

The intense CO<sub>2</sub> degassing observed at Loutra Ypatis may be responsible for elevated levels that can have an impact on human beings. It is worth noting that values measured in the atmosphere close to the building exceed the Occupational Recommended Exposure Limit of 5000 ppm (NIOSH, 2005). In closed spaces lethal levels can be easily reached. An older inhabitant of the close by village told us that in his childhood a playmate died by going inside the gallery that drains the thermal water out of the spa due to the high CO<sub>2</sub> levels. Such episode underscores the need not to disregard the gas hazard created by intense natural gas manifestations like the thermal spring of Loutra Ypatis.

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