What happened to the stink? Changes in the hydrogen sulfide content of Hévíz thermal lake

V. Vajda[1], J. Mátyási[1], Gy. Németh[2], D. Szieberth[1]

[1]Budapest University of Technology and Economics Department of Inorganic and Analytical Chemistry, H-1111 Budapest, Szent Gellért tér 4. Tel.: +361-463-4056

[2]Hévíz Spa and St. Andrew's Hospital for Rheumatology

MŰEGYETEM 1782

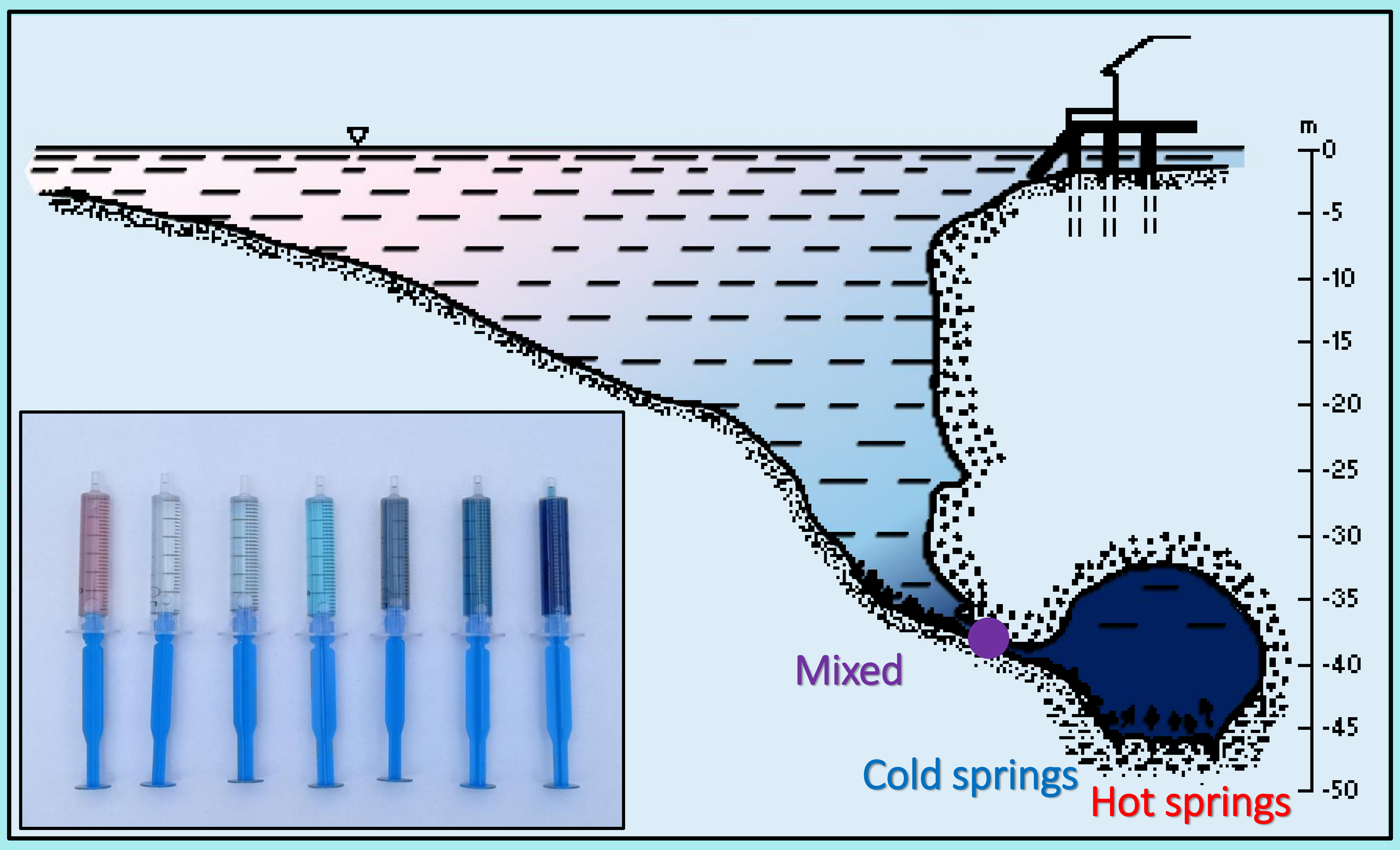
Introduction

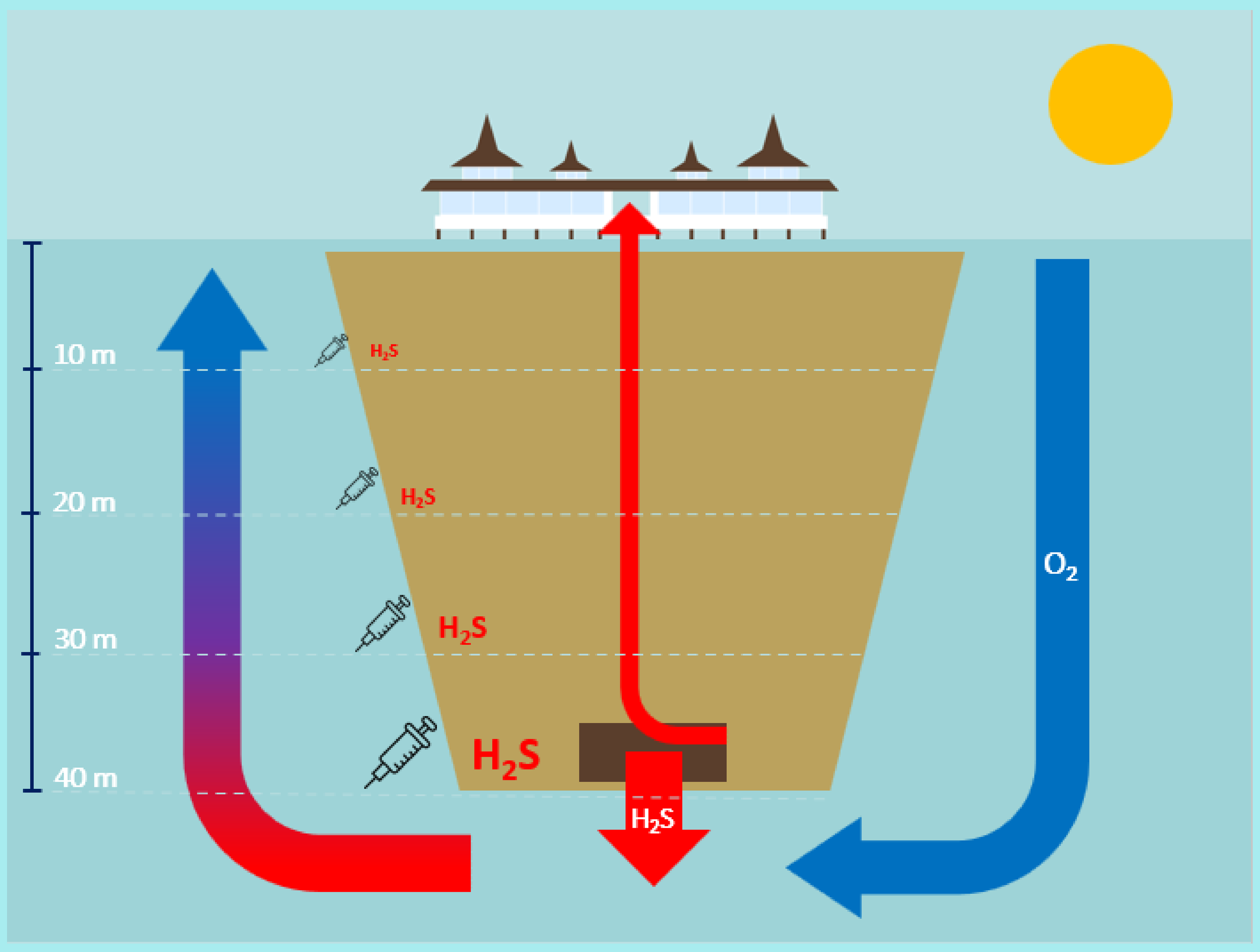
Lake Hévíz is the largest thermal lake in Europe and was already known in Roman times. Its water has a curative effect on various rheumatic diseases and the healing power of the water is partly attributed to its dissolved hydrogen sulfide content. The lake is fed by a cluster of springs located in the spring cave that opens at the bottom of the lake at the depth of 38m. While a part of the spring water arrives to the cave on a shallow and relatively short route ("cold springs", ~22 °C) from the nearby Keszthely Mountains, thermal (~38 °C) water travels on a longer route from the deep aquifer of the Transdanubian range.

By the end of the 1980s due to decades of mining activity, a significant decrease in the karst water levels was observed in the area affecting Hévíz lake. The discharge of the springs nearly halved, and the water temperature dropped. The cessation of mining activity in the 1990s led to an increase in karst water levels. The original discharge and temperature was restored by 2010.

Results and discussion

In the last few years spa guests regularly commented on the decreasing sulfide odor of the lake, raising concern about the possibly diminishing healing properties. Our goal was to study the different forms of sulfur that are present in the lake, including hydrogen sulphide, sulfite, sulfate, thiosulfate, sulphide, polysulfides and to determine which sulfur form is dominant in the spring cave and in the lake. Sampling methods applied earlier are unsuitable for the determination of the different species of sulfur, since the oxygen contained in the breathing gas used to displace water from the sample container oxidizes the unstable sulfur forms.We have tested several sampling methods implemented by scuba divers. For the determination of sulfide content a technique involving sampling with syringes pre-filled with a reagent mixture giving a color reaction with sulfides was developed, providing a semi-quantitative information at the time of sampling followed by accurate spectrophotometric detection in the laboratory.

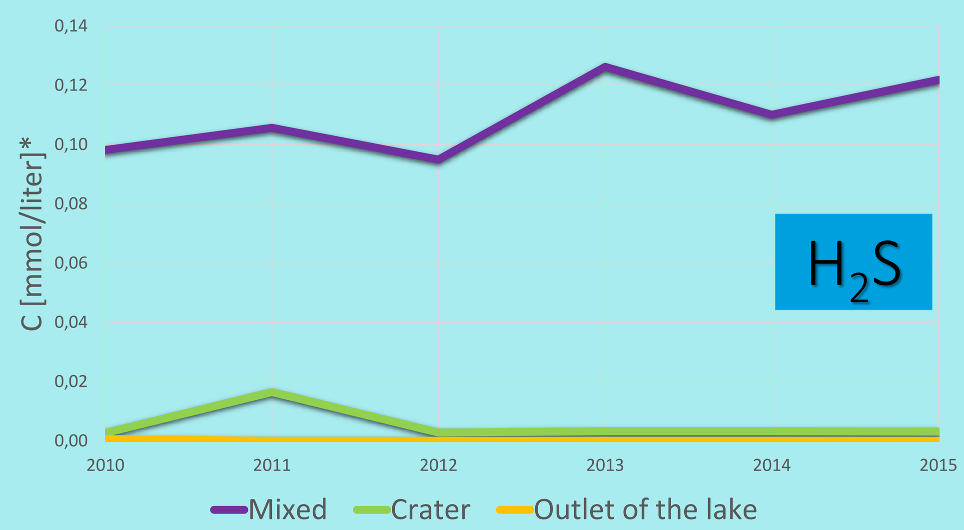


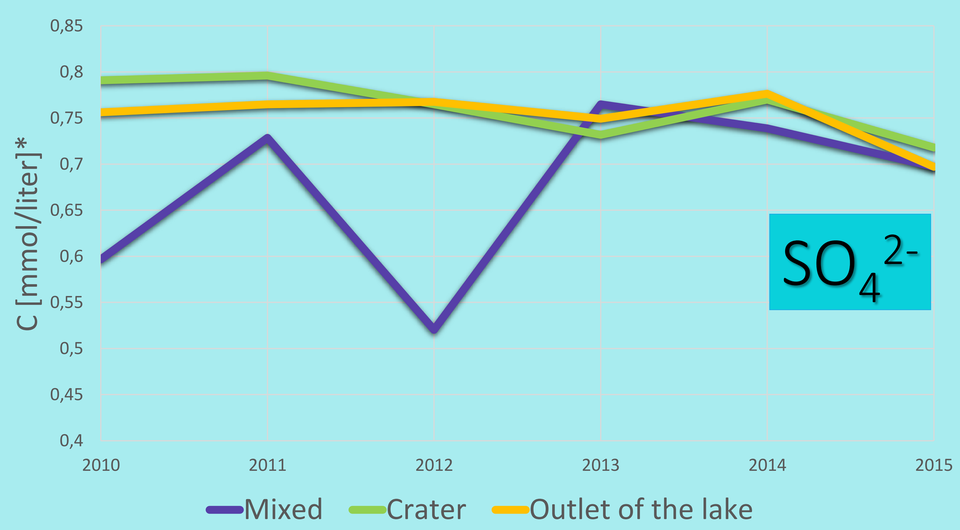


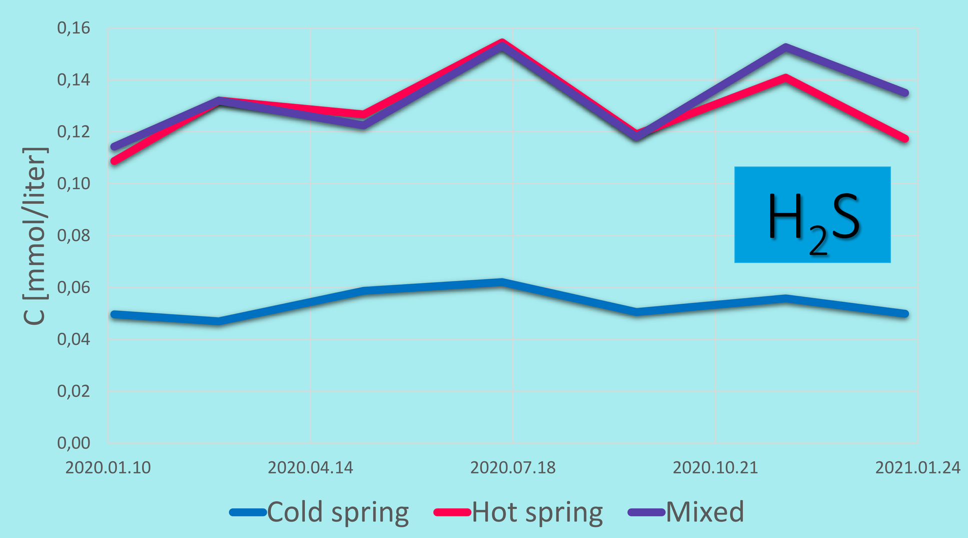
Summary

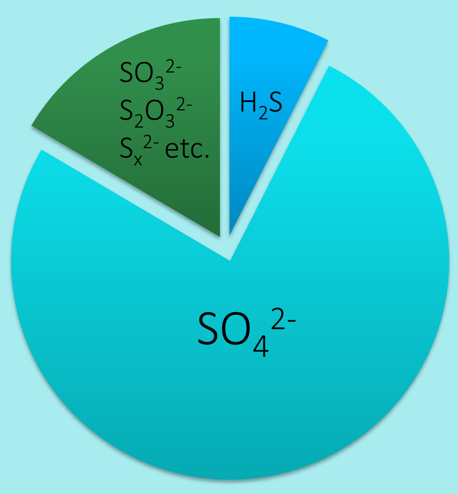
A new reliable sampling method was developed to obtain information on the sulphide concentration at the time of sampling. Information on the hydrogen sulfide content of the cold and hot springs of the spring cave was reported for the first time. The strong current exiting the cave induces a circular flow in the crater. At the western side of the crater wall a strong vertical current carries the oxygenated water from the surface. The oxygen-rich flow mixes with the sulfide-rich cave water immediately as it exits the cave, oxidizing the sulfide immediately. As a result, the higher concentration of sulfide and its healing power presumably can be felt only in the water coming through the pipe directly from the cave to the bath. The measurement results show that other forms of sulfur are also present in significant amounts, but their oxidation takes place quickly, which makes them difficult to quantify. According to the available data and our measurements the sulfide content of the mixed water is stable in the last 10 years. Thus the decreasing sulfide smell is probably the consequence of the changing flow pattern in the lake.

The sulfide content of the water was analyzed both in the lake and in the cave. Inside the cave the hottest and coldest springs were also analyzed besides the mixed water. Two data sets were used but these are the results of different sampling techniques. Compared to previous years there was no significant change in the hydrogen sulphide content in the case of the „mixed" water that exits the cave - containing the water of the 10 different temperature springs. The difference in sulfate concentration between „mixed" and „outlet of the lake" is the result of oxidation of non-sulfate sulfur forms. The water exiting the cave contains a considerable amount of dissolved H_2S, but in samples from the lake the concentration is under the detection limit.





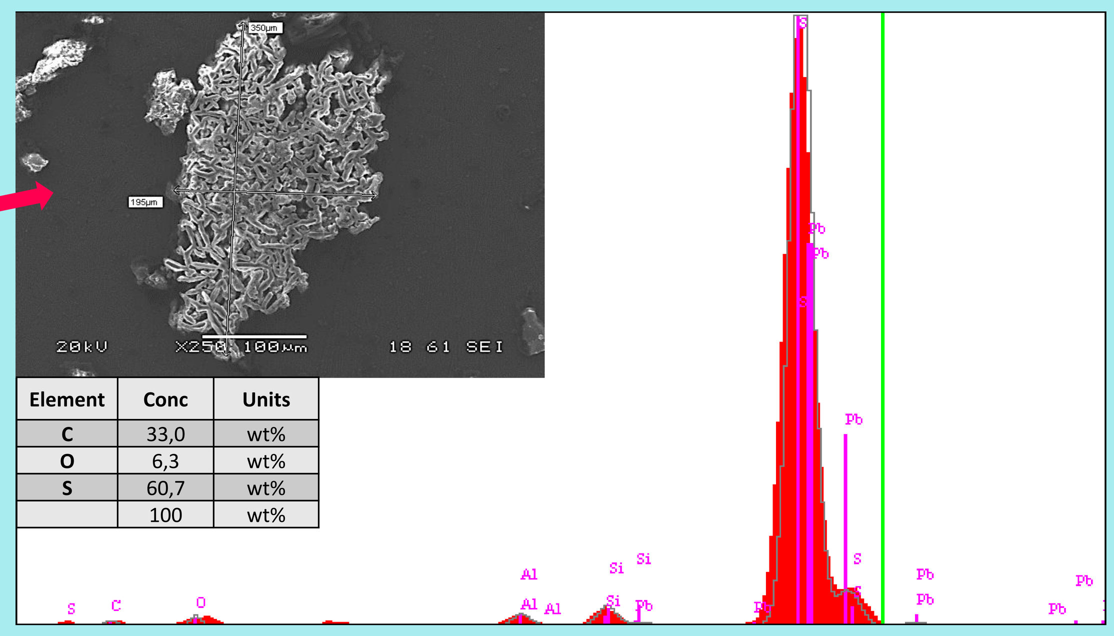




*Data measured by Bálint Analytics.

Based on the measured hydrogen sulfphide and sulfate concentrations, the amount of other sulfur forms can be estimated.

Besides oxidation caused by the intensive flows, oxidation processes of sulphides by microbes also takes place, as a result of this sulfur also appears on the crater wall and in the cave as well. Electron microscopic images confirmed the presence of floating sulfur forms.



References

[1] CLINE, J. D. (1969). SPECTROPHOTOMETRIC DETERMINATION OF HYDROGEN SULFIDE IN NATURAL WATERS1. Limnology and Oceanography, 14(3), 454–458.