Complex mechanism of sulphane odour production in water heating and suitable remedial measures

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ABSTRACT

Drinking or heated water can have a wide range of disturbing odours which have many various causes. A well known example is sulphane (hydrogen sulfide) odour, reminiscent of rotten eggs, which naturally occurs in some underground waters. Less known and hitherto unexplained is this odour arising from hot water in water heaters. As a response to complaints by consumers we investigated 14 sites and thanks to experimental work in one of these recognised a complex mechanism at work. For production of sulphane to occur in a water heater the following conditions must be met: presence of sulphate-reducing bacteria, presence of sulphates, reduction properties of water indicated by a very low nitrate content (highest value was 10 mg/L, mostly <2 mg/L), and presence of sacrificial magnesium anode. We identified four possible remedial measures, some of which are less effective or only short term, or have an undesirable side-effect (corrosion). The most effective measure was replacement of the magnesium anode for an aluminium or zinc anode, which retains the anticorrosion protection of the heater.

Key words: anode, hydrogen sulfide, rotten egg odour, water heater

HIGHLIGHTS

• Sulphane in drinking or hot water is a cause of annoying odour.
• Sulphane may originate in water source or distribution networks, including water heaters.
• Production of sulphane in hot water is a complex process which involves specific chemical properties of water, sulphur bacteria present and the type of water heater.
• The article analyses the major factors involved in the production of sulphane and offers remedial measures.

INTRODUCTION

Although drinking or heated water is objectively safe from a health standpoint it may be unacceptable for the consumer in a sensory or aesthetic sense if it has an unusual or unpleasant smell. For this reason, increasing attention has been given to this issue in recent years. Individual odours are precisely identified and associated with potential sources, and remedial measures are proposed (Burlingame et al. 2011; Lauer 2014).

One of the well known water-borne odours is the stench of rotten eggs caused by the presence of sulphane, or hydrogen sulphide. This odour can manifest in cold (drinking) water or hot water and the place of incidence represents an important diagnostic marker of the source. If the odour persists in cold and subsequently in hot water the usual source is an aquifer (well water). The cause may be organic pollution but is commonly of natural origin, based on the interaction of special geochemical conditions in the bedrock and the activities of certain sulphur or sulphate-reducing bacteria. Historically, such sulphurous mineral waters have been used for therapeutic purposes (Carbajo & Maraver 2017) but if they are to be used as domestic water supplies it is necessary to remove the hydrogen sulphide content by water treatment (Lemley et al. 1999; McFarland & Provin 1999; MDH 2013). A less common source is proliferation of sulphur or sulphate-reducing bacteria in metal pipes, resulting in sulphane production and corrosion (Hack 1981; AWWA 2004; MDH 2013). In such an instance the odour is most noticeable on opening the water tap, and disappears or weakens when the water has run off; or fluctuates noticeably in the course of time.
If odour is detected in hot, but not cold, water then the source is the hot water heater. Although this effect has been described in a number of countries we have found no peer-reviewed articles that have specifically targeted and analysed the conditions of sulphane production, and pertinent counter-measures, with the exception of a brief technical article (Hack 1981) and several short recommendations by public authorities (NCHD n. d.; NSE 2008; MDH 2013).

In warm water – an environment with minimum oxygen content – sulphane is produced by sulphate-reducing bacterial species. These are spherical, spiral, oval or vibrioid, sized 0.4–3.0 μm and strictly anaerobic, occurring in minimally oxygenated environments (Holt et al. 1994). Growth of sulphate-reducing bacteria gives rise to the formation of slime which supports the development of other bacteria in water systems, particularly iron bacteria (AWWA 2004). All such microorganisms may play a role in the creation of odour (albeit different to that of sulphane) and contribute to corrosive processes (Štěpánek & Jiřík 1979; AWWA 2004). Sulphate-reducing bacteria include Desulfovibrio desulfuricans which are frequently present in soil and water. Their optimum growth temperature is 25–40 °C with an optimal pH of 6.6–7.5.

Sulphates or other oxygenated inorganic sulphur compounds can be reduced by a number of steps to sulphane (H2S). A ‘bacterial catalyst’ is required for sulphate reduction (bacterial enzymes – specific dehydrogenases). For sulphate-reducing bacteria to act as catalysts they require an external source of energy, in the form of oxidised elementary hydrogen (Štěpánek & Jiřík 1979; Hack 1981; Rajagopal & LeGall 1989). Aside from the above-mentioned hydrogen oxidation process, sulphate-reducing bacteria are capable of acquiring energy by oxidation of organic compounds such as sugars, organic acids, hydrocarbons or amino acids. However, because the volume of organic matter in drinking or hot water is low we surmise that only oxidation of elementary hydrogen is at play, specifically hydrogen ions or protons (Štěpánek & Jiřík 1979; Sarin et al. 2004).

Elementary hydrogen is formed in water to varying degrees as a result of corrosion in water distribution networks and ancillary equipment (Cord-Ruwisch & Widdel 1986; Lorowitz et al. 1992). Nonetheless, it is primarily found in water heaters which contain anti corrosion systems. Although the inner surfaces of the heaters are enameled, they are rarely free of tiny cracks; such cracks may also occur during installation and operation. For this reason, storage water heaters are fitted with anti corrosion technology which comprises a magnesium metal anode which gradually dissolves in water, releasing magnesium ions (Mg2+), where two electrons are released for each magnesium ion, resulting in an oxidation–reduction reaction. The electrons are absorbed in water by either dissolved oxygen, hydrogen ions, chlorine or other chemical oxidants used for disinfection. Hot water usually contains hydrogen ions only, which are formed by dissociation of water molecules, and which react with electrons to form elementary hydrogen (Sarin et al. 2004).

This is the basis of the so-called electrochemical corrosion protection, which is achieved by creation of a strong electrochemical cell with suitable polarisation. The anode is a so-called sacrificial electrode made of a less noble material, i.e. with a lower electrode potential than the material being protected – the steel outer jacket of the heater – which becomes the cathode and is thus corrosion resistant. The highest potential difference (and strongest electric cell) is formed by magnesium and iron, i.e. the steel jacket of the heater (Lower 2020). This why magnesium is the preferred material for anodes, and less frequently zinc, aluminium or titanium.

The magnesium anode produces more electrons than necessary for protection of the steel surface. These ‘superfluous’ electrons that are not used up on the metal inner surface of the heater by electrochemical reaction and are what provides the necessary energy to the sulphate-reducing bacteria that produce sulphane (NCHD n. d.; Hack 1981). However, the anode and associated sulphate-reducing bacteria are not the sole causative agents of the problem: a specific role is played by the chemical composition of the heated water and its physical–chemical properties, which have as yet not been discussed or described in the literature.

Because our National Reference Laboratory, engaged in water quality issues, has been approached by a number of people requesting advice pertaining to the odour issue, we have, in the majority of reported cases, visited the facility in question, and collected and analysed water samples. In one instance we were able to conduct various intervention measures and experimentally evaluate their effectiveness. The main aim of this work was to ascertain the conditions that promote sulphane odour in heaters and test possible remedial measures in practice.

**METHODS**

**Analytical methods**

Two methods have been used for the determination of sulphate-reducing bacteria in water: (a) an older national method on agar medium according to Brys (Štěpánek et al. 1982); and (b) American Standard Method 9240D, 5. Sulphur Bacteria
Both methods can be used in an MPN (most probable number) version, which allows quantification of bacteria in a specified volume of water examined, e.g. 100 mL used by us, with a very low detection limit (1 MPN/100 mL).

Nitrates and sulphates were analysed according to the ISO 10304-1 and the ISO 7890-3 standards, respectively.

Detection of hydrogen sulfide was sensorial, performed on site by the sampling personnel (in all cases), and a panel of trained evaluators in the laboratory (in selected cases if samples could be delivered quickly to the laboratory). All assessors were trained according to the EN ISO 8586 Sensory analysis – general guidelines for the selection, training and monitoring of selected assessors and expert sensory assessors. To assess the odour intensity, we used the method prescribed by the Czech National Standard ČSN 75 7340 Water quality – Methods of approximate sensory analysis, providing a six grade scale, which can be seen in the footnote of Table 1.

**Statistical analysis**

Stata, statistical software release 14.2 (Stata Corp LP, College Station, TX, USA) was used for statistical analysis. The relationship between selected variables of the set of localities was evaluated by Spearman’s correlation coefficient ($r_s$) and significance test. Mann–Whitney $U$-test test was used to compare chemical parameters existing in the monitored set against the control (public and commercial wells in the Czech Republic). Results with $p$-values less than 0.05 were considered statistically significant.

**On-site inspections**

During our local investigations, conducted in 2015–2019, we focused on the water source (depth of well, water quality, treatment if applicable), the method of water heating (heater type and age, anode type, electric current on anode) and incidence/intensity of odour over time. We gathered data on 14 sites in 13 different communities with an incidence of sulphane odour in hot water only; in the majority of cases we collected samples ourselves or had samples collected by a local laboratory.

Although we investigated several dozen sites just 14 sites were selected for our survey (see Results). At the other sites the sulphane odour was detectable in cold water or was a different type of odour (musty, with a slight sulphurous edge) which was caused by domestic water softening and/or iron removal treatment units.

**Anode rods**

Origins and compositions of the anode rods installed in water heaters by its producers or in our interventions: magnesium anode (product of Polish origin, company unknown; Mg 91.5%; Al 5.3%; Zn 2%; Mn 1.2%), zinc anode (product of Swedish origin, company unknown; Zn 95%, Al 4%, Cu 1%), and aluminium anode (producer Suburban, Dayton, TN, USA; Al 95%; Zn 5%).

Anode current (between anode and earthing pin) was measured using Digital multimeter DT9205A (producer: Dongguan Xinghongwei Precision Measuring Instrument Technology Co., Guangdong, China) with a sensitivity of 0.001 mA. Oxidation–reduction potential (ORP) was measured by ORP Tester 10 (producer: OAKTON Instruments, Vernon Hills, IL, USA); range up to 1,000 mV, accuracy $±$ 2 mV, resolution 1 mV, temperature measuring range 0–50 °C; the reference electrode was silver chloride in 3.5 M KCl.

Anode current cannot be directly measured without special modification of the water heater, and was therefore measured with the assistance of a field service engineer only in heaters in our experimental locality.

**RESULTS AND DISCUSSION**

In 13 cases the water was sourced from privately owned wells, untreated with no disinfection. In the greater proportion of cases the wells had been drilled. We also studied the case of one community where the odour problem was reported in several households, with a public mains connected to untreated and unchlorinated underground water from a deep bore hole. A breakdown of these sites is shown in Table 1. All water heaters with detected sulphane odour were equipped with a magnesium anode.

Sulphate-reducing bacteria are widely spread in the environment; they were present in water at all sites with sulphane odour (usually in counts of 10–500 MPN/100 ml, but also with a maximum spike of up to 1,100 MPN/100 mL, which corresponded with the strong sulphane odour in Location 1; see Table 1 for individual results). They were detected in hot water in every single case, and in some cases in cold water as well. In view of the fact that we had never registered complaints of sulphane odour arising in centrally heated hot water in large residential buildings, we collected hot water samples from several...
Table 1 | Incidence and intensity of odour in hot water, sulphate and nitrate content, oxidation–reduction potential (ORP) value and counts of sulphate-reducing bacteria in water source from selected localities

<table>
<thead>
<tr>
<th>Location (region)</th>
<th>Sulphane in hot water</th>
<th>Intensity of sulphane odour (degrees)</th>
<th>Sulphate (mg/L)</th>
<th>Nitrate (mg/L)</th>
<th>ORP&lt;sub&gt;h&lt;/sub&gt;/ORP&lt;sub&gt;l&lt;/sub&gt; (mV)</th>
<th>Sulphate-reducing bacteria (MPN/100 mL)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location 1; old source (dug well 5 m depth), Central Bohemia Region</td>
<td>NO (all 4 heaters)</td>
<td>0</td>
<td>86</td>
<td>80–125</td>
<td>172/387</td>
<td>210 (cold water)</td>
<td>Heaters: OKC 125, OKCV 160, OKHE 125, Enersan 80P</td>
</tr>
<tr>
<td>Location 1; new source (borehole 55 m); Central Bohemia Region</td>
<td>YES (3 heaters: OKC 125, OKCV 160, OKHE 125)</td>
<td>5</td>
<td>99</td>
<td>&lt; 2 (4 analyses)</td>
<td>12/227</td>
<td>240 (cold kitchen)</td>
<td>1,100 (hot water, kitchen)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>240 (hot, bathroom)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO (heater ENERSAN 80P)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>150 (hot, another bathroom)</td>
<td></td>
</tr>
<tr>
<td>Location 2; dug well 13 m; Central Bohemia Region</td>
<td>NO</td>
<td>0</td>
<td>299</td>
<td>10.2–13</td>
<td>237/452</td>
<td>48 (cold)</td>
<td>48 (hot)</td>
</tr>
<tr>
<td>Location 2; borehole 55 m; Central Bohemia Region</td>
<td>YES</td>
<td>4</td>
<td>332</td>
<td>&lt; 2</td>
<td>5/220</td>
<td>240 (cold)</td>
<td>240 (hot)</td>
</tr>
<tr>
<td>Location 3, borehole 35 m; Central Bohemia Region</td>
<td>YES</td>
<td>4</td>
<td>480</td>
<td>&lt; 2</td>
<td>N.M.</td>
<td>75 (cold)</td>
<td>240 (hot)</td>
</tr>
<tr>
<td>Location 4, dug well 13 m; Central Bohemia Region</td>
<td>YES</td>
<td>4</td>
<td>40</td>
<td>&lt; 2–3.6</td>
<td>N.M.</td>
<td>210 (hot)</td>
<td></td>
</tr>
<tr>
<td>Location 5, dug well 7 m; Central Bohemia Region</td>
<td>YES</td>
<td>4</td>
<td>80</td>
<td>&lt; 2</td>
<td>N.M.</td>
<td>210 (hot)</td>
<td></td>
</tr>
<tr>
<td>Location 6, borehole 30 m; Central Bohemia Region</td>
<td>YES</td>
<td>4</td>
<td>232</td>
<td>4–6.9</td>
<td>N.M.</td>
<td>210 (hot)</td>
<td></td>
</tr>
<tr>
<td>Location 7, borehole 93 m; Central Bohemia Region</td>
<td>YES</td>
<td>3</td>
<td>139–172</td>
<td>2.3–10</td>
<td>181/396</td>
<td>N.M.</td>
<td>Source water for municipal water supply</td>
</tr>
<tr>
<td>Location 7, outlet from the storage reservoir; Central Bohemia Region</td>
<td>YES</td>
<td>3</td>
<td>dtto</td>
<td>dtto</td>
<td>217/432</td>
<td>N.M.</td>
<td>Municipal water supply</td>
</tr>
<tr>
<td>Location 8, dug well 9 m; Central Bohemia Region</td>
<td>YES</td>
<td>4</td>
<td>217</td>
<td>&lt; 2</td>
<td>N.M.</td>
<td>N.M.</td>
<td></td>
</tr>
<tr>
<td>Location 9, borehole 27 m; South Bohemia Region</td>
<td>YES</td>
<td>4</td>
<td>&lt;2</td>
<td>N.M.</td>
<td>N.M.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location 10 (combination private borehole 30 m + public supply), Vysocina Region</td>
<td>occasionally</td>
<td>0–3</td>
<td>46 (public supply) 42 (private well)</td>
<td>17 (public supply) &lt;2 (private well)</td>
<td>N.M.</td>
<td>N.M.</td>
<td>Joining pipes from the well and municipal water supply; sulphane odour changes in time according to the extent of water mixing in kitchen and bathroom</td>
</tr>
<tr>
<td>Location 11, borehole 15 m; Moravian-Silesian Region</td>
<td>YES</td>
<td>5</td>
<td>261</td>
<td>&lt;2</td>
<td>N.M.</td>
<td>250 (cold) 0 (hot w. 65 °C)</td>
<td></td>
</tr>
<tr>
<td>Location 12, borehole 12 m; Olomouc Region (Middle Moravia)</td>
<td>YES</td>
<td>4</td>
<td>85</td>
<td>&lt;2</td>
<td>N.M.</td>
<td>N.M.</td>
<td></td>
</tr>
<tr>
<td>Location 13, borehole 30 m; Zlín Region (Eastern Moravia)</td>
<td>YES</td>
<td>4</td>
<td>50</td>
<td>3.2</td>
<td>N.M.</td>
<td>N.M.</td>
<td></td>
</tr>
<tr>
<td>Location 14, dug well 20 m; Zlín Region (Eastern Moravia)</td>
<td>YES</td>
<td>4</td>
<td>165</td>
<td>&lt;5</td>
<td>N.M.</td>
<td>N.M.</td>
<td></td>
</tr>
</tbody>
</table>

**ORP**... the potential, expressed in hydrogen scale.
**ORPm**... the potential, measured with a reference electrode (silver chloride in 3.5 M KCl) at pH 7 and a temperature of 10 °C.
**N.M.**... not measured.

*The scale used (see the Methods for reference): 0 – none, no odour detected; 1 – very slight, barely discernible; 2 – weak; 3 discernible, odour could cause negative evaluation of the water; 4 – pronounced, odour is off putting for water consumption; 5 – very strong, odour degrades water quality.

*Range of values means interval of detected values from two or more measurements.
diverse buildings in Prague. Sulphate-reducing bacteria were not detected in any of these buildings (unpublished data). In all cases drinking water was heated having undergone comprehensive treatment, including chlorination and ozonation.

One of the monitored sites (Location 1) served as an experimental object, by kind permission of the owners, due to the uniqueness of the situation. The building was an ex-farmstead, situated on the outskirts of the local community, with its own wells. It contained four housing units, each with its own water heater. As long as the owners had used the old dug well (5 m depth), which was chemically and microbiologically polluted, there had been no sulphane odour issues. However, the problem arose when a new bore well (55 m depth) with untainted water began to be used instead. The odour problem occurred in hot water only, from three heaters (types: OKC 125, OKCV 160, OKHE 125). Water from the remaining heater, which was the oldest and from a different manufacturer (Enersan 80P) had no such issue. The new and old wells were situated 50 m apart but drew water from separate aquifers with different chemical composition. A comparable situation was seen in a detached house about 2 km away (Location 2) which had two wells of varying depth (13 and 55 m, about 10 m apart) and where odour was detected in hot water from the deeper well only. However, at the farmstead site we installed various types of anode into the heaters with sulphane odour: (a) the original magnesium anode for comparison, later replaced by aluminium; (b) zinc anode; and (c) aluminium anode. We then heated the water in each heater to 80 °C to kill the sulphate-reducing bacteria and set identical baseline conditions, with the new bore hole as the common water source. The heaters were then set to a standard regimen at approximately 50 °C. The presence of sulphane in hot water was monitored sensorially by the users and several times per year by laboratory staff. The odour threshold for hydrogen sulphide in water has been estimated to be as low as 0.05 mg/L (WHO 2003). The anode current measurements taken are presented in Table 2.

Measured values of anode current show that the current in the magnesium electrodes is higher by about one order of magnitude against the current generated by the anodes from other materials. The magnesium anodes in these heaters were from the MAMgAl6Zn3 group with EN 12438 standard (CEN 2017). They primarily contained magnesium with a mix of 5–7% Al, 2–4% Zn, 0.2–1% Mn and other metals at 0.1–0.01% content. The chemical composition of the anode was responsible for the intensity of the generated current and amount of generated electrons which in excess reduce sulphates to sulphane. As we shall see, the simplest remedial measure is to remove the magnesium anode and replace it with anodes made of another metal in order to retain some anti corrosive properties.

From the outset we monitored 10–15 indicators which are used as standard as a basic set for examining well water quality. In all localities we monitored chemical oxygen demand (COD-Mn), nitrate, sulphate, iron, manganese, water hardness and pH and other selected parameters (nitrite, chloride etc.). Microbiological parameters monitored comprised colony counts, coliform bacteria and faecal indicators. Deviations from normal well water findings were at first sight exceptional concentrations of nitrate (unusually low) and sulphate (unusually high).

For the purposes of statistical evaluation we used a comparison set of all public and commercial wells in the Czech Republic (a total of 2,544 sites) in which water quality is regularly monitored and their data are accessible in the national database of drinking water quality (IS PIVO 2021). Comparison data from 2018 were used (number of results for individual indicators ranged from 1,425 to 4,769) because there were no significant changes in year-on-year chemical results. Statistically

<table>
<thead>
<tr>
<th>Type of heater</th>
<th>Type of anode</th>
<th>Anode current (mA)</th>
<th>Water temperature (°C)</th>
<th>Sulphane formation (sensually detected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OKC 125</td>
<td>Zinc (Zn &gt; 90%)</td>
<td>0.330 (9.6.2017)</td>
<td>50</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.140 (28.11.2017)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.300 (26.4.2018)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>OKCV 160 (exchange Mg anode for Al one)</td>
<td>Magnesium (Mg 91.5%)</td>
<td>4.260 (9.6.2017)</td>
<td>50</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.840 (28.11.2017)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.050 (26.4.2018)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>OKHE 125</td>
<td>Aluminium (95% Al + 5% Zn)</td>
<td>0.034 (18.10.2018)</td>
<td>15</td>
<td>NO</td>
</tr>
<tr>
<td></td>
<td>Aluminium (95% Al + 5% Zn)</td>
<td>0.140 (26.4.2018)</td>
<td>15</td>
<td>NO</td>
</tr>
</tbody>
</table>

All heaters were originally fitted with magnesium anodes and emitted sulphane odour.

Notes: in the fourth heater (Enersan 80 P) the anode current could not be measured for technical reasons; sulphane odour was never detected from this heater in heated water from either of the wells. The hot water temperatures were very low in some cases because heaters were switched off when no people were present.
Significant results were detected not only for nitrate and sulphate, but also iron, manganese and water hardness. Conversely, no significant differences were seen in COD-Mn and pH. The evaluation is presented in Table 3. Whereas the nitrate values in our localities were significantly lower than is common in well water nationwide, the detected values for sulphate, water hardness, iron and manganese were much higher. As such, this describes the typical profile of water which tends to producing sulphane odour: underground water with a high content of total dissolved solids, iron, manganese but with a low oxygen content and reductive character. In terms of microbiology the water in the monitored localities fulfilled the necessary standards for drinking water.

We further investigated if the degree of sulphane odour correlated with nitrate content or sulphate-reducing bacteria, albeit they were not monitored in all of our localities. Spearman’s correlation coefficient for nitrate was $r_s = -0.686$, $p = 0.001$ (lower nitrate concentrations are associated with increased sulphane odour). The coefficient for sulphate-reducing bacteria was $r_s = 0.900$, $p = 0.002$ (higher bacterial counts were associated with more intensive odour from hot water), although this result should be viewed with reserve. We recorded a case of very intensive odour with zero bacterial count (Location 11) when the water was heated to 65 °C (this water temperature at the heater output is beyond the vitality profile of these bacteria; while in other parts of the heater with cold water in-flow the bacteria may survive) and conversely we detected tens to hundreds of sulphate-reducing bacteria in wells with no record of odour from either cold or hot water. The first case can be explained by the mechanism of boilers in which water is gradually heated to the set temperature throughout the capacity of the storage tank. When heated water is run from the boiler it is replaced by cold water which mixes with the warm water in the lower parts of the boiler and creates a favorable environment for bacterial growth and survival. We detected that in our case the cold water contained sulphate-reducing bacteria at 250 CFU/100 mL, so that the boiler was effectively supplied by the necessary bacteria for multiplication and production of sulphane in its lower section. However, with a water temperature of 65 °C at the outlet the bacteria were inactivated and subsequent hot water analysis failed to detect them. In the second case (presence of sulphate-reducing bacteria without odour) the cause may be that the necessary chemical conditions in water for sulphane production were absent.

We realized only during the final phases of our investigation and evaluation that measurement of the oxidation–reduction potential (ORP) could be suitable for characterisation of water in which sulphane is produced during heating. Unfortunately, we were able to conduct these measurements in only five localities, including the experimental farmstead object. Of these, valid results were acquired from three localities where it was possible to conduct measurements at the site of sample collection. Laboratory measurements distorted the result because the ORP value can change during transport. Despite this, the results suggested that problems occur in water with a reductive properties, or low ORP. In our set of localities the ORP values had a certain correlation with nitrate values: the lower the ORP values, the nitrate values were correspondingly lower as well (Spearman’s correlation coefficient $r_s = 0.707$; $p = 0.050$; if we take only wells with odour issues then the coefficient is even $r_s = 0.975$).

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Monitored localities with odour</th>
<th>Public and commercial wells in the Czech Republic</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median</td>
<td>IQR</td>
<td>Median</td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>2.05</td>
<td>2.20</td>
<td>2.50</td>
</tr>
<tr>
<td>Sulphate (mg/L)</td>
<td>155.50</td>
<td>182.00</td>
<td>37.00</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>0.34</td>
<td>0.69</td>
<td>0.03</td>
</tr>
<tr>
<td>Manganese (mg/L)</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Hardness (mmol/L)</td>
<td>4.40</td>
<td>2.56</td>
<td>1.50</td>
</tr>
<tr>
<td>COD-Mn (mg/L)</td>
<td>0.32</td>
<td>0.56</td>
<td>0.72</td>
</tr>
<tr>
<td>pH</td>
<td>7.20</td>
<td>0.05</td>
<td>7.10</td>
</tr>
</tbody>
</table>

Mann–Whitney U-test was used for comparison; whole data sets were used for calculations.
IQR, interquartile range.
The ‘protective’ effect of higher ORP values – a higher nitrate content against sulphane production in heated water – can be explained on the basis of bacterial physiology, hydrochemistry and electrochemistry (Pitter 2009). The ORP value has marked significance for biological processes as it yields a proportional representation of individual oxidation levels of a given element in water and is also dependent on the surrounding pH. During a regular range of ORP values (value for standard hydrogen electrode) in waters +500 mV to −500 mV there is the possibility of reduction of specific compounds in water as follows: reduction starts with oxygen, followed by manganese, the Mn IV and Mn III forms are reduced to Mn II, then by reduction of NO3 to N2, and then reduction of Fe III to Fe II. After this the sulphates and organic substances are reduced to sulphide sulphur, methane and carbon dioxide. Sulphate and organic substances reduce under anaerobic conditions (low or even negative ORP values) and so the formation of foul-smelling sulphane can only occur in water after depletion of not only oxygen but also the oxidisable forms of Fe and Mn, nitrites and nitrates. Therefore, the biochemical reduction of sulphate in a neutral and slightly alkaline environment requires markedly negative ORP values. This is why nitrates reduce to elementary nitrogen sooner than sulphate to sulphide. Nitrates in water are stable at relatively high ORP values and at slightly positive values (anoxic conditions) will reduce to nitrites and elementary nitrogen; in a mix of sulphate and nitrate, nitrate is reduced first (Pitter 2009). In view of the fact that Mn, Fe and nitrite concentrations in drinking water usually occur in tenths of mg/l, reduction mainly affects nitrate and, subsequently, with a significantly lower ORP value, sulphate. Figure 1 shows the chain of reactions starting with the disintegration of the magnesium anode and concluding with sulphane formation in hot water.

These findings allow us to answer two basic questions with which we were confronted at the start of our study of the experimental locality: 1. Why did the sulphane problem paradoxically occur when the original poor water source was replaced by a better one? 2. Why did this problem affect only three of the four heaters?

The new and old wells had a similar sulphate content (99 versus 86 mg/L) but very different oxidation-reduction conditions, indicated by the ORP values (12 versus 172 mV) and nitrate values (<10 versus approximately 100 mg/L). Water polluted by nitrate (content 80–125 mg/L) in the old dug well had oxidational properties which prevented the presence of sulphane, because instead of sulphate reduction there occurred a prior reduction of nitrate without ensuing sensorially detectable by-products. Conversely, water from the new well and deeper externally uncontaminated aquifer had reductive properties (nitrate content 1–2 mg/L, or below the limit of quantification) so that sulphate was reduced to sulphane.

The three heaters (OKC 125, OKCV 160 and OKHE 125) which were relatively new or almost new and which began producing foul-smelling water were fitted with fully functional magnesium anodes. The protective anode on the fourth, and

**Figure 1** | Scheme of sulphane formation in hot water in water heaters (adapted from Lorowitz et al. 1992; Sarin et al. 2004).
oldest, heater (Enersan 80P) had been fully used up and never replaced, as was confirmed during later replacement of the heater. The reason why there had never been any corrosion problems with this heater is probably because the inner enamelled surface was of exceptional quality and without cracks where corrosion occurs.

It is therefore evident that the formation of sulphane in water heaters is a complex process involving numerous factors. Nevertheless, various remedial measures can be considered. However, not each of the following interventions will be equivalently effective or permanent:

1. The simplest solution is overheating the water in the heater at 70–80 °C for several hours to kill the sulphate-reducing bacteria, followed by a thorough flushing of the hot water pipes to remove sulphane residua. Because sulphate-reducing bacteria are virtually omnipresent it would be only a matter of time before the heater is colonised again. In our experience, this one-off intervention will limit sulphane production for 1–2 weeks after which the odour problem recurs. Maintaining this temperature constantly is usually financially unfeasible. Perhaps a UV lamp or mechanical antibacterial filter placed in front of the heater would be effective, but we have not had the possibility of verifying this.

2. The second simplest but also rapid and effective measure is to remove the magnesium anode from the heater. However, by doing this we remove the anti corrosion protection and unless the inner surface of the heater is perfectly enamelled then within a few weeks corrosion problems will occur (rust-coloured water), as verified in our experimental object. Conversely, such a solution was used successfully without negative impact in several of our locations. This depends on the inner surface quality of a given heater, and cannot be anticipated.

3. An effective, permanent and therefore recommended measure is to exchange the magnesium anode for an anode from a different material which generates less electrons: it will not create such a strong electrochemical cell with the steel jacket of the heater as magnesium (Fe-Mg). We found aluminium or zinc anodes to be effective in that they did not give rise to sulphane odour but did provide anticorrosive protection (NCHD n.d.; Hack 1981; MDH 2013). Although this approach is suitable it is not accessible to all consumers because the majority of manufacturers do not offer replacement anodes from any other material than magnesium. Aluminium anodes which are for sale online have screw fittings that are not universal. A requisite aluminium rod serving as an anode is relatively cheap and available but requires a locksmith to custom fit. Some of the new types of heater use different anticorrosion measures – so-called active cathodic protection which uses anodes from electrically conductive but relatively sparingly soluble material (titanium) which is directly connected to a source of DC current from an outside source. We have not come across an instance of this type of heater producing sulphane odour despite the fact that some were installed under conditions which had the potential for sulphane odour problems.

4. A further possibility is to change the water properties to be more oxidising. This could be achieved by continual disinfection with chlorine or another oxidant. This option simultaneously addresses two of the critical points in the sequence of sulphane odour formation: it kills or inhibits the growth of sulphate-reducing bacteria and elevates ORP (prevents the creation of elementary hydrogen). If this measure is applied, it is necessary to control and prevent excessive formation of disinfection by-products. However, to raise ORP it is not always necessary to use aggressive chemical oxidants, if the consumer wishes otherwise. In one of our locations (no. 7) it sufficed to aerate the water: the water system operator achieved this by installing an aerator (a larger version of the common device used in aquariums). This resolved sulphane issues in all of the supplied households, and is also the reason why there are practically no problems in public water mains: the water in public systems usually passes through water towers where it is aerated and its reductive properties are reduced.

**CONCLUSIONS**

Our tests and literature studies have revealed that formation of sulphane in water heaters is a complex process which manifests under a series of concurrently activated conditions, at least the following ones:

(a) presence of a magnesium sacrificial anode producing excess electrons,
(b) presence of sulphate-reducing bacteria,
(c) reductional properties of water indicated by very low nitrate content (under 10 mg/L, ideally below the limit of detection) and lower ORP values – this particular condition can be fulfilled only in the case of underground water from certain hydro-ecological structures without further modifications and disinfection,
(d) higher sulphate content in water (ideally over 100 mg/L).
This helps to explain why the phenomenon is apparently not global, and is not recognised in all countries (we have come across mentions of it in France, the USA and Canada). The problem does not occur if the local water does not have reductive properties or local manufacturers of water heaters do not use magnesium anodes, or if people use continuous flow heaters. Conversely, sulphate-reducing bacteria appear to be omnipresent in undisinfected water and mostly have no negative effects aside from corrosion. However, if and when the problem does arise, consumers are hard-pressed to find advice and solutions. Understanding the mechanisms underlying sulphane in hot water has enabled us to propose four remedial measures of varying efficacy.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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