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Disinfection of therapeutic water – balancing risks against benefits: case study of Hungarian therapeutic baths on the effects of technological steps and disinfection on therapeutic waters

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ABSTRACT

Thermal therapeutic pools in most countries are operated in a manner similar to swimming pools: with water circulation, filtration and disinfection. However, in some countries, including Hungary, therapeutic pools are traditionally not treated this way, in order to preserve the therapeutic qualities of the water. However, dilution and frequent water replacement applied in these pools are often insufficient to ensure adequate microbial water quality, posing a risk of infection to the bathers. In the present case study, the impact of water treatment (including chemical disinfection by hypochlorite or hydrogen peroxide) was investigated on the therapeutic components of the water in seven Hungarian spas of various water composition. Microbial quality was improved by both disinfectants, but hypochlorite reduced the concentration of the therapeutic components sulfide, bromide, and iodide ions by 40–99%, and high levels of disinfection by-products were observed. Hydrogen peroxide only affected sulfide ion (91% reduction). Other technological steps (e.g., transport or cooling by dilution) were found to have significant impact on composition, often outweighing the effect of disinfection. The current case study demonstrated that thermal waters may be treated and disinfected with minimal loss of the therapeutic compounds, if an adequate treatment procedure is selected based on the water composition.

Key words: disinfection, hydrogen peroxide, hypochlorite, therapeutic water, thermal water

HIGHLIGHTS

- Disinfection of therapeutic pools is necessary to maintain adequate water quality.
- Due to the diversity of therapeutic waters, there is no universal method of disinfection.
- Hypochlorite reduce concentration of therapeutic components sulfide, bromide and iodide ion.
- Hydrogen-peroxide reduce only concentration of sulfide ion.
- Health gain from better microbial quality is likely to counteract the loss of therapeutic effect.

INTRODUCTION

Balneotherapy is an increasingly popular field of complementary therapy and a main attraction in health tourism. Therapeutic waters have been shown to be effective for many diseases and conditions, mainly different rheumatic complaints (Geytenbeek 2002; Bender *et al.* 2014). In addition to those seeking recovery, an increasing number of guests visit spas for rest and relaxation.

The therapeutic effect in balneotherapy is traditionally linked to the presence of certain inorganic chemical components of the water (ISO 2018), although recently the role of organic constituents is also being investigated (Szabó & Varga 2020). In Hungary, therapeutic effect is inferred based on the chemical composition of mineral waters and confirmed by clinical trial (Hungarian Ministerial Decree 1999). The total mineral content of the water should exceed 1,000 mg/l or 500 mg/l if the water contains at least one of the following therapeutic components in sufficient quantity (in brackets): lithium ion (5 mg/l), sulfide ion (1 mg/l), bromide ion (5 mg/l), iodide ion (1 mg/l), metasilicic acid (50 mg/l), radon (37 Bq/l), and carbon dioxide (1,000 mg/l).

Bathing can also pose a risk of infection if the microbiological quality of pool water is inadequate (Barna & Kádár 2012; Germinario *et al.* 2012). Since one of the intended uses of thermal waters is therapeutic, many of the bathers are elderly with underlying health conditions, and therefore more prone to infection than the general population. Thermal pools have been associated with a wide range of infections, including folliculitis and ear infection associated with *Pseudomonas aeruginosa* (Mena & Gerba 2009; Germinario *et al.* 2012), pneumonia caused by non-tuberculotic mycobacteria or *Legionella* (Costa *et al.* 2010; Walczak *et al.* 2013; Ahmed & Mustfa 2014; Leoni *et al.* 2015), or even fatal primary amoebic meningitis due to *Naegleria fowleri* (Heggie 2010). Warm temperature and the often high concentration of organic and inorganic nutrients supports the survival or growth of microorganisms in thermal pools. It has been argued that the autochthonous microbial community of thermal waters can eliminate external microbial contamination (Varga 2019). While this might be true for natural thermal lakes or ponds with low bather load, it is clearly not the case in enclosed pools filled with thermal water. Most regulations therefore require disinfection of these pools; in fact, the Centers for Disease Control and Prevention (CDC) suggests higher than average chlorine levels for hydrotherapy pools due to their warm temperature and the increased vulnerability of the exposed population (Rutala & Weber 2008).

Microbiological safety of pool waters is usually achieved by chemical disinfection. However, disinfectants, especially traditional chlorine-based chemicals, may react with the chemical elements (e.g., sulfide, iodide, and bromide ions) that are traditionally considered natural healing factors (Hungarian Ministerial Decree 1999; ISO 2018; Varga 2019). This effect was demonstrated previously for sodium-hypochlorite and hydrogen peroxide: both are able to oxidize iodide ion (Liebhafsky 1932; Kumar *et al.* 1986; Schmitz 2001) and bromide ion (Bray & Livingston 1923; Kumar & Margerum 1987), although conditions of the reaction were different from those typical for therapeutic waters. Sulfide ion can also be oxidized by pool treatment chemicals (Choppin & Faulkenberry 1937; Hoffmann 1977; Azizi *et al.* 2015).

While in most countries thermal pools are operated using the same treatment technologies as other pools, there are some notable exceptions, such as Italy, Turkey, and Hungary, among others. In Hungary, most therapeutic pools operate in fill-and-drain mode (i.e., without recirculation) and without disinfection to preserve the biologically active constituents. Continuous water replenishment is used to preserve the microbial quality of pool water. Compliance is assessed against national standards, which apply less stringent quality requirements to fill-and-drain pools (MSZ 13690-3:1989; Hungarian Government Decree 1996; Hungarian Ministerial Decree 1996; MSZ 15234:2012). Most international regulations for pool water quality are stricter than these values (e.g., DIN 2012; PWTAG 2013), and the tolerable levels in fill-and-drain pools may already constitute a risk to immunocompromised bathers.

Despite the frequent water exchange, non-compliance rates in the therapeutic pools are much higher than in disinfected pools. The national summary report of monitoring by the public health authorities in 2013 shows 75% non-compliance in therapeutic pools vs 22% in other type of pools, e.g., swimming pools (Vargha *et al.* 2015). Data for 2017–2019 – available at National Public Health Center – shows very similar trends: non-compliance rates were 72, 78, and 73% in therapeutic pools vs 22, 21, and 26% in other types of pool.

Based on these experiences, introduction of disinfection seems inevitable. At the same time, designing appropriate water treatment is challenging due to the complex water composition, the need to preserve the therapeutic effect and, in some cases, the high temperature and organic matter content of these waters. Several alternative methods have been suggested for the treatment of therapeutic pools, including chemical and physical methods, for example, ozone, hydrogen peroxide, treatment with nanomaterials, ultrafiltration, and UV treatment (Sisti *et al.* 2014; Leoni *et al.* 2015; Valeriani *et al.* 2018).

Recently, several spas in Hungary introduced water treatment and disinfection in therapeutic pools. The aim of the present case study was to demonstrate that disinfection of therapeutic pools can improve microbial safety without materially altering the composition of the water, and thus serve as a basis for future recommendation on the operation of thermal pools in Hungary. The study did not extend to the clinical investigation of changes in the therapeutic effect.

MATERIALS AND METHODS

Investigated spas – site description and sampling

Seven therapeutic pools in public spas were investigated in different parts of Hungary between 2017 and 2019. All pools were (partly or exclusively) filled with certified therapeutic water of different composition. All fill waters were deep groundwaters from confined aquifers. The total mineral content was high in all wells (1.493–12.580 mg/l), and the pH was usually slightly alkaline. Of the therapeutic components listed in the national regulation, lithium ions, sulfide ions, bromide ions, iodide ions, and metasilicic acid were investigated (Hungarian Ministerial Decree 1999). Radon and free carbon dioxide, which are very rare in Hungarian therapeutic waters, were not present in the investigated spas.

The pools belonged to three groups, based on the applied water treatment. The first group (Spa II and VI) applied the general pool treatment technology: water was circulated and disinfected with sodium-hypochlorite. In the second group (Spa V and VII) pool water was also circulated, but the disinfectant was a commercial product based on hydrogen peroxide and a quaterner ammonium polymer (hereinafter referred to as hydrogen peroxide). The third type of pools (Spa I, III, and IV) operated in fill-and-drain mode, disinfected with the same product. In one of the latter pools, Spa IV, pool water was recirculated during the day. The disinfectants were dosed automatically in every spa, adjusted to the volume of fill water. Disinfectant levels were checked regularly by the pool operators or by an online monitoring system. All the investigated pools were indoor thermal sitting pools, used for therapeutic and recreational purposes. The characteristics of the investigated facilities are summarized in Table 1.

Sampling points were designated to track changes in the water composition from the water source to the pools: well water, technological steps (where applicable), and pool water were sampled in every facility (Table 1).

A total of 39 sampling points were selected. Every spa was sampled three times, between April 2017 and June 2019; water samples were taken on different days in the afternoon, at peak bather load of the pools. Sampling and the sample preparations were carried out according to the corresponding guidelines and relevant standards (Table 2).

Analytical methods

Temperature, electrical conductivity, pH, and residual disinfectants levels (titration in acidic media with $KMnO_4$ for hydrogen peroxide, LOD 0.1 mg/l and DPD titration method according to the ISO 7393-1:1985 and ISO 7393-3:1990 for hypochlorite, LOD: 0.05 mg/l) were measured on site. Microbiological quality parameters were colony count (ISO 6222:1999), *Escherichia coli* and coliform number (ISO 9308-1:2000), total cocci (MSZ 13690-2:1989), fecal *Enterococci* (ISO 7899-2:2000) and *Pseudomonas aeruginosa* (ISO 16266:2006). Total mineral content water is a sum parameter,

Table 1 | Characteristics of the investigated spas

	Spa I	Spa II	Spa III	Spa IV	Spa V	Spa VI	Spa VII
Applied disinfectant	Hydrogen peroxide	Hypochlorite	Hydrogen peroxide	Hydrogen peroxide	Hydrogen peroxide	Hypochlorite+UV	Hydrogen peroxide
Disinfectant concentration in pool (mg/l)	0.4–4.4	<0.05–2.5	7.1–95	4.3–12	18–298	<0.05–1.4	138–365
Operation mode	Fill-and-drain	Circulated	Fill-and-drain	Combined	Circulated	Circulated	Circulated
Pool volume (m^3)	54	9	25	63	80	68	626
Full water exchange	Daily	Every six months	Daily	Daily	Every three months	Every six months	Every six months
Average residence time of pool water	7 h	18 day	7.7 h	18 h	3.4 day	20.2 day	12 day
Technological steps							
Transport	S	S	X	X	S	S	X
Mixing with cold water	S	X	S	X	–	–	–
Degassing	–	–	X	–	S	X	X
Iron removal	–	–	–	–	S	–	X
Filtering	–	S	–	S	S	S	S
UV treatment	–	–	–	–	–	S	–
Disinfectant dosing	S	X	S	S	S	S	S

X = technological step present, but cannot be sampled; S = technological step present and sampled.

Table 2 | Chemical compounds, analytical methods and standards used for characterization of water samples

Compound	Analytical method	Standard	Detection limit
Alkalinity (hydrogen carbonate, carbonate, hydroxyl ion)	Acid-base titration	MSZ 448-11:1986; ISO 9963-1:1994; ISO 9963-2:1998	0.1 mmol/l
Hardness	Complexometry	MSZ 448-21:1986	1.0 mg/l CaO
Total dissolved material (at 105 and 180 °C)	Weighing	MSZ 448-19:1986	23 mg/l
Ammonium ion	Spectrophotometry	ISO 7150-1:1984	0.02 mg/l
Anions (Br^-, I^-)	Ion chromatography	ISO 10304-1:2007, ISO 10304-3:1997	Br^- 0.05 mg/l, I^- 0.03 mg/l
Metasilicic acid	Spectrophotometry	MSZ 448-26:1991	2.0 mg/l
Sulfide ion	Spectrophotometry	MSZ 448-14:1990	0.1 mg/l
Total organic carbon (TOC)	Thermal oxidation, IR detection	EN 1484:1997	0.3 mg/l
Trihalomethanes (THMs)	GC-MS	MSZ 1484-5:1998	1.0 μg/l
GC-MS fingerprints	Extraction with DCM at pH 2, 7 and 10; GC-MS Scan, compound identification based on NIST-MS database	non-standardized method	–

expressing the total amount of dissolved ions, calculated as follows:

$$\text{Total mineral content} = \frac{c_{HCO_3^-}}{2} + \text{ evaporation residue } (180^\circ\text{C})$$

The analyzed chemical compounds, the analytical methods, and the standards are summarized in Table 2.

Monitoring data

To supplement the measured data, regular water quality monitoring results were obtained from the local public health authorities and the operators for the sampled pools and the period of the study duration. Long-term monitoring results were available for some microbial parameters (*E. coli* and total cocci) and disinfectant levels.

RESULTS

Disinfectant levels in pools

Hypochlorite was applied in Spa II and VI. The concentration of free chlorine in pool samples was between <0.05 and 2.5 mg/l, with a mean value was 0.85 mg/l. Measured values for combined chlorine were between <0.2 and 0.95 mg/l, with a mean value of 0.48 mg/l. Free chlorine concentration exceeded the parametric value (1 mg/l) once in both pools, while combined chlorine was above parametric value (0.5 mg/l) in 50% of the samples (Table 3). In two cases, the observed free and combined chlorine levels imply that free chlorine was consumed completely by naturally occurring (geological) ammonium ion present in the well water (0.4 ± 0.04 and 14 ± 0.06 mg/l in Spa II and VI, respectively).

Free and combined chlorine concentrations were available in 72% of the monitoring data sets provided by public authorities and operators. Concentrations were generally lower than the range measured in the current study: mean concentration of free chlorine and combined chlorine was 0.45 and 0.13 mg/l, respectively. All values met the regulatory requirements.

The detected hydrogen peroxide concentration varied widely, both within and between pools.

There is no legal regulatory requirement for hydrogen peroxide dosing, with the recommended concentration for pool water in the national technical standard being 25–100 mg/l (MSZ 15234:2012). In fill-and-drain pools (Spa I, III, and IV), the applied hydrogen peroxide concentration was generally below this range, with a mean value of 17.9 mg/l (SD 30.3 mg/l), while in circulated pools (Spa V and VII), it was often exceeded (mean value: 191.9 mg/l, SD 138.6 mg/l). In the monitoring data provided by public authorities and operators, disinfectant concentration was only available in 48% of the data sets. Mean values were similar to those observed in the present study: 23.4 ± 21.4 mg/l in fill-and-drain pools and

Table 3 | Concentrations of disinfection-related parameters in spa pools disinfected with hypochlorite

Spa	Free chlorine (mg/l)	Bound chlorine (mg/l)	Ammonium ion (mg/l)	Chlorite (mg/l)	Chlorate (mg/l)	Bromate (mg/l)	$CHCl_3$ (μg/l)	$CHCl_2Br$ (μg/l)	$CHClBr_2$ (μg/l)	$CHBr_3$ (μg/l)	Total THM (μg/l)
Detection limit	0.2	0.2	0.02	0.03	0.05	0.03	1	1	1	1	1
Regulatory value	1	0.5	–	1	3[a]	–	–	–	–	–	50
Spa II/1	BDL	0.6	0.12	BDL	0.69	BDL	1	1.1	1.6	2.7	6.4
Spa II/2	0.8	0.25	BDL	BDL	0.56	BDL	2.8	6.2	12.4	16.6	38
Spa II/3	2.5	BDL	BDL	BDL	0.72	BDL	1.0	1.1	3.3	8.1	14
Spa VI/1	BDL	0.95	1.7	BDL	140	0.34	3.3	1.3	1.8	1.1	7.5
Spa VI/2	1.38	0.55	0.04	BDL	63	0.1	140	13	3.7	BDL	157
Spa VI/3	0.4	0.4	BDL	BDL	49	0.12	32.8	14.1	16.0	4.8	68

The parallels are indicated by Spa X/n, where X is the identification number of the spa, and n is the serial number of sampling.
BDL, below detection limit.
[a]Guideline value (MSZ 15234:2012 2012).

125 ± 77.3 mg/l in circulated pools. The results indicate that maintaining a stable residual hydrogen peroxide level is more difficult than for hypochlorite.

Microbial water quality

Three-quarters of the pool water samples collected during our project (16/21) were compliant with the microbial quality requirements (Supplementary Material, Table S1). The reason for non-compliance was mostly (3/5) the presence of *Pseudomonas*, and two cases were related to intestinal *Enterococci.* Three of the affected pools operated in fill-and-drain mode, and in two of them water was circulated. All non-compliance was associated with unsatisfactory or low levels of disinfectant.

In the pools circulated and treated with hypochlorite, intestinal *Enterococci* was found once (in Spa VI, 1 CFU/100 ml), and *Pseudomonas* was detected once in Spa II and once in Spa VI in low numbers (1 and 8 CFU/100 ml, respectively).

Of the pools disinfected with hydrogen peroxide, one of the fill-and-drain pools (Spa I) was contaminated by *Pseudomonas* (>200 CFU/100 ml) on one occasion, when hydrogen peroxide level was very low (below LOD). The same level of contamination was observed once in one circulated pool (Spa V), despite the higher hydrogen peroxide concentration (18 mg/l), extending to other parts of the circulation system (water storage tanks and filter). *Pseudomonas* was also detected at different technological steps in other spas (Spa III, V, and VI). In every case of detected non-compliance, the operator was duly informed and appropriate steps were taken to prevent further contamination.

In Spa VI, a UV lamp (254 nm) was applied as a complementary disinfection to hypochlorite dosing. The UV irradiation reduced the heterotrophic plate count at 37 °C, but was not effective against *Pseudomonas* bacteria on the occasion when it was detected in multiple sampling points.

According to the personal communication of the spa operator, rapid and significant deposit formation can be detected on the UV lamp. The removal of the deposit requires a technological shutdown, and therefore is only possible intermittently. The deposit formation can significantly reduce the penetration depth and thus the efficiency of the UV lamp (Lin *et al.* 1997).

According to the long-term (three months to three years) monitoring data provided by the operators and the authorities (available only for *E. coli* and total cocci), the compliance rates in the fill-and-drain pools were similar to those observed in the present study (8.0% and 0% non-compliant, 22.7% and 33.3% tolerable), while all circulated pools, regardless of the choice of disinfectant, were fully compliant. Disinfectant concentrations, as described in the previous section, were within the range observed in the current study.

Changes in the chemical composition of therapeutic water

Effect of disinfection

In the two spas applying hypochlorite as disinfectant (Spa II and VI), significant losses (40–99% reduction) of the therapeutic components iodide, bromide, and sulfide were observed after the addition of the disinfectant (Supplementary Material,

Table S2). Sulfide ion, which was only present in Spa II (mean concentration 0.63 ± 0.17 mg/l), and iodide (mean concentration 0.12 mg/l and 0.82 mg/l in Spa II and VI, respectively) decreased below the detection limit (0.1 and 0.03 mg/l, respectively) after hypochlorite dosing, regardless of the concentration of the disinfectant. Bromide ion concentration also decreased considerably (by 52 ± 10 and 96 ± 5%, respectively). The concentration of metasilicic acid and total mineral content remained unchanged in both spas. Lithium ions were present in low concentrations in both spas. In Spa VI, concentration of lithium ions decreased by about 65% during recirculation, while in Spa II it was unchanged. This phenomenon can result from the uncertainty of measurement at low concentrations, but may require further investigation.

In Spa VI, UV treatment was applied as a secondary disinfection method. UV irradiation did not alter the concentration of the therapeutic components present (lithium ion, bromide ion, and metasilicic acid).

No significant (i.e., larger than 20%) changes were observed in the concentration of lithium ion, metasilicic acid, total mineral content, iodide and bromide ions in the spas using hydrogen peroxide, regardless of the applied technology (fill-and-drain or circulated pools). One exception was a sampling event in Spa III, where iodide ion levels decreased by 66% (Supplementary Material, Table S2, Spa III/3). Since the latter was accompanied by the presence of combined chlorine and trihalomethanes (THMs) in pool water, it is assumed that hypochlorite was also added to the pool water on this occasion, although it was not indicated by the operator.

Sulfide ion was present in three wells in spas applying hydrogen peroxide. However, its concentration was reduced below the limit of detection prior to disinfection, during preceding technological steps, i.e., transport (evaporation) and mixing with cold water (dilution) in Spa III and IV. In the remaining case, Spa I operating in fill-and-drain mode, sulfide ion was fully eliminated (below 0.1 mg/l) during disinfection by hydrogen peroxide, from a mean concentration of 1.04 mg/l (SD 0.38 mg/l).

Effect of other technological steps

Besides disinfection, other technological steps, especially dilution with cold drinking water or well water for cooling purposes, had a significant effect on the chemical composition of the waters. The temperature of therapeutic well waters is often high (up to 60–70 °C in the studied spas, see Table 4), and it is necessary to reduce it to a suitable range for bathing. This is usually achieved by mixing the thermal water with cold tap or well water, as practiced occasionally or continuously at six of the seven present study sites. The total mineral content decreased by an average of 21%, in some cases up to 30–49%. In Spa III, the concentration of therapeutic components iodide ion and metasilicic acid decreased below the minimum level required for therapeutic water certification as a result of dilution. Where dilution was used for cooling, this had the most significant impact in the overall composition of the water.

Table 4 | Characteristics of investigated well waters (mean values)

	Detection limit	Spa I	Spa II	Spa III /1.	Spa III /2.	Spa IV	Spa V	Spa VI	Spa VII
T (°C)	–	44.2	43.2	65.9	67.0	53.4	37.3	30.1	41.7
pH	–	6.7	6.8	8.1	8.1	8.3	7.3	7.2	7.9
Conductivity (μS/cm^2)	–	1,713	1,547	2,170	2,250	2,037	18,770	8,460	1,864
TOC (mg/l)	0.3	1.2	0.7	8.6	5.5	3.8	15.0	2.4	2.6
Hardness (mg/l CaO)	1	394	400	13.5	16.1	11.4	297	209	28.0
Ammonium ion (mg/l)	0.02	0.59	0.40	9.7	6.7	8.2	46	14	8.5
Total mineral content (mg/l)	23	**1,598**	**1,493**	**1,969**	**1,927**	**2,114**	**12,580**	**5,718**	**3,361**
Li^+ (mg/l)	0.04	0.57	0.40	0.06	0.06	0.04	0.69	0.97	0.06
S^{2-} (mg/l)	0.1	**1.04**	0.68	0.29	0.36	0.24	0.11	0.15	BDL
Br^- (mg/l)	0.05	0.36	0.29	1.45	1.98	0.65	**20.47**	**7.03**	1.05
I^- (mg/l)	0.03	0.08	0.12	0.95	**1.10**	0.19	**3.53**	0.82	0.23
H_2SiO_3 (mg/l)	2	40	37	**59**	**54**	40	**93**	49	34

Values that exceeded required minimum concentrations for therapeutic water certification are marked in bold.
BDL, Below detection limit.

Figure 1 compares the effects of different cooling and disinfection methods on iodide and bromide ions' concentrations for three different scenarios: disinfection with hydrogen peroxide and cooling by mixing with cold water (Spa III); disinfection with hydrogen peroxide, and cooling with heat exchangers (Spa V); and disinfection with hypochlorite, without dilution (Spa II).

Hydrogen peroxide did not affect the concentration of iodide and bromide ions even at peroxide concentrations as high as 200 mg/l. When it was combined with cooling by heat exchanger, the iodide and bromide ions remained within 10% fluctuation through the entire treatment process (Figure 1(a)). Cooling by mixing with cold water (Figure 1(b)) diluted bromide and iodide ion concentrations by 33 and 38%, respectively, while hydrogen peroxide did not have any further effect. In the third case (Figure 1(c)), disinfection with hypochlorite in itself had a negative effect (loss of 60% for bromide ion and 89% for iodide ion).

Disinfection by-products

THMs were detected in both spas (Spa II and VI) using hypochlorite, in different concentrations. In Spa II, concentration of THMs was always below the regulatory value (50 μg/l) (Hungarian Ministerial Decree 1996), while in Spa VI, the concentration was significantly higher (mean concentration 78 ± 75 μg/l), and non-compliant two times out of the three samplings (Table 3).

Brominated THM species were dominant in Spa II, while in Spa VI, chloroform was detected in the highest concentration, but the other species appeared as well. Besides THMs, in Spa VI, significant chlorate and bromate formation was observed,

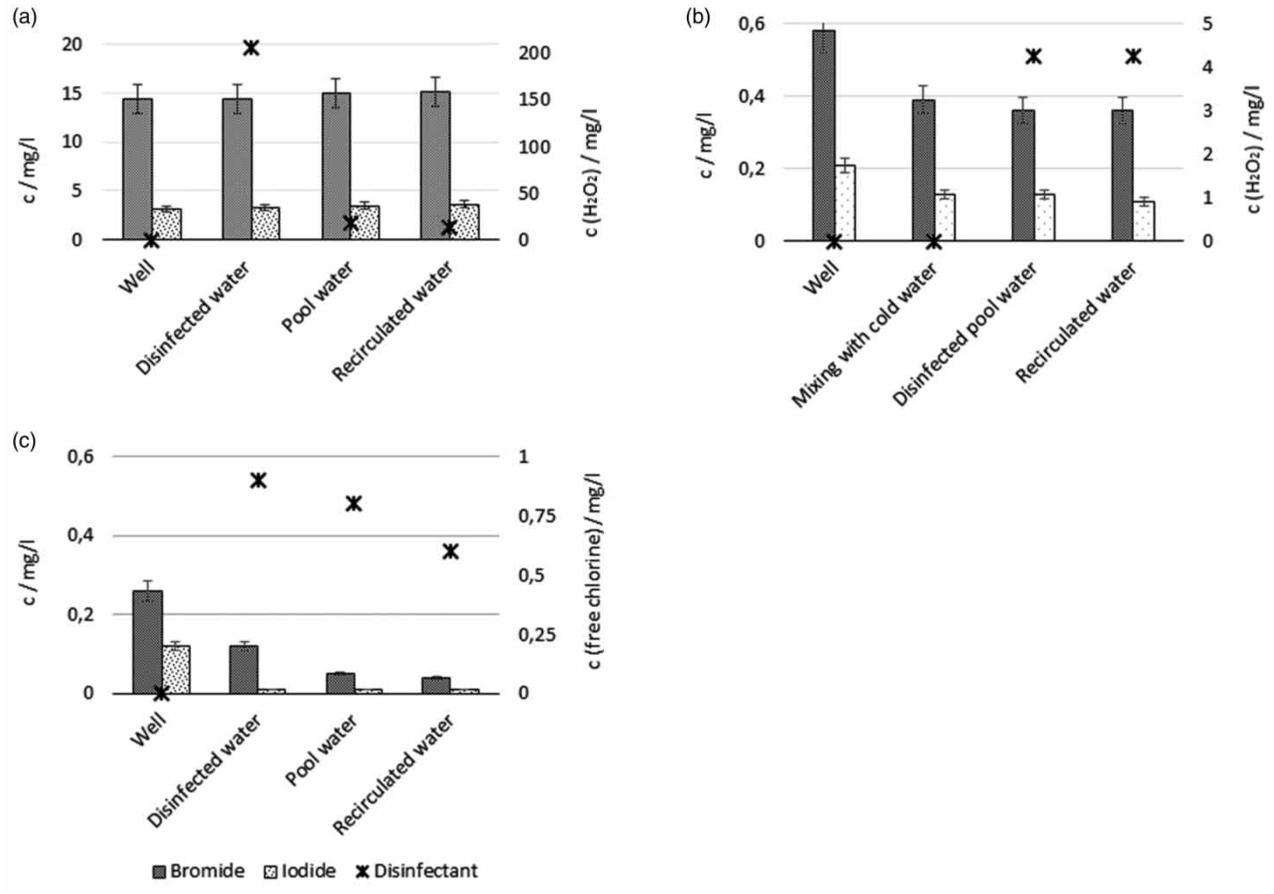

Figure 1 | Effect of different water treatment steps on the concentration of bromide and iodide ions, as therapeutic components of thermal waters: (a) disinfection with hydrogen peroxide and cooling by mixing with cold water (Spa IV); (b) disinfection with hydrogen peroxide, and cooling with heat exchanger (Spa V); and (c) disinfection with hypochlorite, without mixing (Spa II).

and other compounds (haloacetic acids and halogenated acetonitriles) were identified from the GC-MS fingerprint measurements. In Spa II, chlorate was present in low levels.

UV treatment was shown previously to be effective in decomposing by-products (Hansen *et al.* 2013). However, in the present study, inorganic by-products (combined chlorine, chlorate, and bromate ions) were not affected by the treatment, and THMs only decreased slightly (7–17%). The limited efficiency was probably the result of deposit formation on the surface of the lamp.

Identification of potential disinfection by-products of hydrogen peroxide was also attempted, by comparing GC-MS scan fingerprints of treated and untreated water samples, but no components were observed in significant quantities in the differential analysis.

DISCUSSION

To achieve the most possible benefit from using thermal waters, potential adverse health effects also need to be considered. The major health risk is infection due to the presence of indigenous or bather-related microorganisms.

Several methods have been proposed to improve microbial water quality in thermal pools (Valeriani *et al.* 2018). Chemical disinfection is the most convenient for the operator, since they generally already have experience with its application.

The microbiological water quality of the disinfected thermal pools in this study was significantly better than the general quality of therapeutic pools (24% vs 75% non-compliance, respectively) regardless of the applied water treatment. All observed non-compliance was linked to unsatisfactory or low levels of disinfectant indicating that with proper water treatment and disinfection good water quality can be ensured.

The main reason for non-compliance in the present study was the presence of *Pseudomonas*, which may indicate formation of biofilms (Rice *et al.* 2012). Both the high mineral content of thermal waters depositing along the waterlines and their high nutrient (TOC and ammonia-nitrogen) concentration support the formation of biofilms. This phenomenon also underlines the need for continuous disinfection, although it cannot be a substitute for appropriate cleaning and maintenance of each water treatment unit.

However, the current study, while confirming the efficiency of disinfection in improving microbial water quality, also indicated some of the limitations and factors to consider.

Investigating the effect of disinfectants on the chemical composition, hypochlorite was found to react with several potentially therapeutic components, including sulfide, iodide, and bromide ions. Hydrogen peroxide has a higher standard electrode potential ($E_0 = 1.76$ V) than hypochlorite ($E_0 = 0.89$ V), indicating a stronger oxidative force; nevertheless, the results showed that the former was much less reactive under the current circumstances, decreasing only the concentration of sulfide ions. This contradiction may be explained with kinetically inhibited reactions at near-neutral pH (Gulaboski *et al.* 2019). According to the literature, the main products formed by hypochlorite from iodide and bromide ions are iodate ion (Bichsel & Von Gunten 1999) and hypobromate ion (Kumar & Margerum 1987). When oxidizing sulfide ion by either disinfectant, the products are elemental sulfur and sulfate ions. Excess of the oxidizing agent promotes the formation of the latter (Choppin & Faulkenberry 1937). The oxidization of the therapeutic components reduces their concentration, while oxidized species are generated. However, this does not necessarily means loss of therapeutic effect, as dose–response relationships are mostly unknown for the individual components.

Hypochlorite generated unacceptable levels of disinfection by-products in Spa VI, where the ammonium ion concentration of the water was high (14 ± 0.06 mg/l). The presence of ammonium ions also leads to excess disinfectant consumption due to the formation of chloramines. Monochloramine also has some disinfecting effect (Wolfe *et al.* 1984), but the adverse health effect of chloramines is well characterized (Thickett *et al.* 2002; Kaydos-Daniels *et al.* 2008). In swimming pools using chlorine-based disinfection, ammonia-nitrogen is usually removed by breakpoint chlorination, but that is not an option for therapeutic pools. The water temperature of therapeutic pools is usually higher (30–37 °C) than in swimming pools. By-products' formation is enhanced by increasing temperature (Zhang *et al.* 2013). Therapeutic waters often contain bromide ions favoring the formation of bromine-containing THMs. These species pose a greater risk to human health, compared to those containing only chlorine (Zwiener *et al.* 2007; Sharma *et al.* 2014). These factors hinder the use of hypochlorite in therapeutic pools.

Hydrogen peroxide could be a better choice for preserving the chemical composition of the water, as it only reduced sulfide ion concentration in the present study. The efficiency of hydrogen peroxide was not affected by the presence of ammonium ion, so it could be an option for treating therapeutic waters with high ammonium ion concentration. No disinfection by-products were observed during hydrogen peroxide treatments and none have been reported in the literature (Pedahzur *et al.* 1995; Nabizadeh *et al.* 2008). However, maintaining a stable and, therefore, efficient disinfectant level is clearly a challenge. The concentration of hydrogen peroxide should be adjusted to a minimum of 50 mg/l at the first loading, and 150–200 mg/l after recirculation for efficient disinfection.

Other technological steps may also inadvertently change water composition. Water transport to the pools decreases the mineral content through deposition, while volatile compounds such as radon may evaporate. In the present study, the major adverse impact on the concentration of therapeutic components was the dilution of well water with cold (tap or well) water for cooling purposes, far exceeding the effect of disinfection in the case of hydrogen peroxide. The ratio of mixing was adjusted according to the required temperature, between 10 and 40%. The waters used for cooling did not contain free chlorine above the detection limit (0.2 mg/l), but their bromide and iodide concentration was low, which effect is attributed to dilution rather than oxidation. The concentration of metasilicic acid and lithium ion, which were found to be relatively stable in the pool environment during disinfection, was only affected by dilution. Heat exchangers as a complete or partial solution for cooling can be a better option for preserving therapeutic components.

The mechanism of the healing effect of therapeutic waters, especially in relation to their composition, is not yet understood. Although traditionally the healing effect is linked to selected inorganic components, recently, the potential role of organic compounds was also suggested (Szabó & Varga 2020). Further research is necessary to investigate if changes in chemical composition due to disinfection alter the therapeutic effect. However, clinical investigation was outside the scope of the present study.

CONCLUSIONS

The present case study covered only a limited number of pools, since disinfection is not practiced widely in Hungarian thermal spas. For the same reason, it was not possible to investigate a wider range of different water compositions. In pools applying more complex technologies, it is not always possible to discriminate the effect of disinfection from other water treatment steps (e.g., recirculation).

In spite of these limitations, the study has shown that by careful operation of the proper water treatment system, adequate water quality can be ensured in therapeutic pools, despite the adverse circumstances, e.g., high temperature, nutrient-rich water, and high number of bathers.

The selection of appropriate water treatment technology (including disinfection) should take into account the water composition, temperature, and the characteristics of the facility. Applying chlorine-based disinfectants, the health risks posed by the appearance of by-products must also be considered. Hypochlorite disinfection can only be recommended for thermal waters containing a low quantity of organic compounds or ammonium ion, and non-oxidizable therapeutic components such as metasilicic acid, lithium ion, or high total mineral content. Hydrogen peroxide is a more flexible option regarding chemical composition, but care should be taken to maintain the optimal level of disinfection, and the operational costs are usually higher. Chlorine-free methods could be more acceptable for bathers in a therapeutic pool. The by-products of hydrogen peroxide disinfection are not yet known, but that does not mean that they do not exist, and this issue requires further research. UV treatment is one of the chemical-free disinfection methods often recommended for therapeutic treatments. However, according to the spa operators, its efficiency could be hindered by the turbidity of the water or the high concentration of minerals depositing on the surface of the lamp. Besides, as physical methods do not have a residual disinfecting effect to provide protection against bacteria entering the pool from bather shedding, it can only be applied as a secondary method.

The case study indicated that, in terms of most therapeutic components, a carefully designed treatment system does not necessarily materially alter the water composition, especially compared to unavoidable changes during abstraction, transport, and cooling. Further research is necessary to investigate the relative efficiency of treated and untreated therapeutic water on various conditions. Previous clinical studies – while confirming the beneficial effect of therapeutic waters – failed to establish the dose–response relationship between the concentration of therapeutic components and the healing effect (Morer *et al.* 2017). The health benefits of maintaining high microbiological water quality may still compensate for the potentially reduced therapeutic effect. However, it is more likely that, considering the additional benefits of temperature and relaxation, the slight changes in water composition will not be reflected in the clinical outcomes. For those waters that cannot be effectively treated, the use of individual therapeutic tubs filled with untreated well water is also an option. Based on the results of the current study, recommendations will be issued to pool operators to introduce disinfection in further therapeutic pools.

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DATA AVAILABILITY STATEMENT

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

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