

Quality change mechanism and drinking safety of repeatedly-boiled water and prolonged-boil water: a comparative study

Yuanzheng Zhai, Jingwen Yang, Yaguang Zhu, Qingqing Du, Wenzhen Yuan and Hong Lu

ABSTRACT

Quality, safety and potability of repeatedly-boiled water (RBW) and prolonged-boil water (PBW) lead to concern and even misgivings in the public from time to time, especially in China, and other societies have a habit of drinking boiled water, with improvements of living standards and owing to increasing concerns for human health. This phenomenon is mainly attributed to the fact that the conclusions drawn from existing scientific experiments could not respond well to the concerns. In order to make up for this deficiency, tap water was selected to carry out RBW and PBW experiments independently. The quality changes of RBW and PBW show very similar trends that are not as great as might be imagined, and both are impacted by the tap water quality and the physiochemical effects. The dominating physiochemical effects are the water evaporation and the resulting concentration of unreactive components (most dissolved components), which can be easily explained by the existing evaporation-concentration theory. The results show that tap water will be still safe and potable after being frequently boiled or after having undergone prolonged boiling, as long as it satisfies the sanitary standards of drinking water prior to heating. Therefore, there is no need to worry about drinking RBW or PBW in daily life.

Key words | drinking water quality, human health risk, prolonged-boil water, repeatedly-boiled water

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HIGHLIGHTS

- Experiments testing repeatedly-boiled water and prolonged-boil water were made.
- Water quality changes are similar and are not as great as might be expected.
- Potability of the water was assessed and compared with that of tap water.
- Physicochemical effects controlling the boiling process were identified.
- It will be helpful for dispelling public misgivings related to boiled water quality.

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INTRODUCTION

Due to habits or history, residents in some countries such as China have developed a habit of drinking boiled water rather than drinking tap water directly (Pan *et al.* 2014; Zhang *et al.* 2015; Shi *et al.* 2017). Drinking warm or cool boiled water is considered to be more beneficial to human health compared to directly drinking tap water (Alasdair *et al.* 2017; Jiri *et al.* 2017) and is thus considered a better habit because boiling can not only effectively kill pathogenic microorganisms in the water (Pan *et al.* 2014), but can also reduce the concentration of residual disinfectants (Wu *et al.* 2001; Krasner & Wright 2005; Wang *et al.* 2019). However, due to the evolution of water heating facilities and changes in lifestyle, extremes are seen: for instance, boiling drinking water more than once or unconsciously for a long period or even constantly in daily life (Luo 2017). Water that is boiled many times and is cooled to normal temperatures after each time is often called ‘repeatedly-boiled water’ (RBW), while water that is boiled for a long duration is often called ‘prolonged-boil water’ (PBW). The presence of RBW and PBW is quite normal and even inevitable in drinking fountains at home or in public (Luo 2017), which are seen everywhere in the daily life of Chinese people (Figure 1). This raises a practical issue: whether the quality of RBW or PBW is safe for drinking, which has attracted increasing public attention with the improvement in people’s living standards and the increasing concerns for human health (Song *et al.* 2017; Troldborg *et al.* 2017; Ma *et al.* 2019; Neil *et al.* 2019). Indeed, controversies remain among the public regarding this issue (Shen & Zhang 2011), while the

academic community has not yet provided an adequate systematic and authoritative explanation for this issue.

The idea that RBW and PBW are not potable or are even carcinogenic has spread among the public of China in recent years and is even occasionally seen in news reports and in ‘scientific tips’ in newspapers and on the internet (Shen & Zhang 2011; Luo 2017), which has caused psychological burdens and anxiety for the public. However, it is not difficult to find that almost all of the conclusions in these reports come from ‘perceptual knowledge’ or even ‘parrot’ ideas rather than relying on rigorous scientific experiments. This is a situation that neither the public nor the academic community would like to see. These perceptions are generally based on the following logic: RBW and PBW can quickly cause an increase in salinity (known as TDS), hardness and heavy metals attributed to rapid water loss and thus the concentration of the solutes because of intensive water evaporation; a significant increase in trinitrogen ($\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$), especially NO_2 , induced by the concentration and the chemical transformation, and that trinitrogen can be further transformed into carcinogens (nitrosamines) after entering the human body; and an increase in Fe, Mn and possibly other heavy metals caused by the increasing dissolution of the boiler (usually iron or stainless steel) into the water. This reasoning is easy to understand and has been accepted by the public because it uses certain scientific reasoning on the surface and its scientific principles are relatively simple and easy to understand. Nevertheless, our profound understanding of such changes



Figure 1 | Common household and public water heaters. (a) and (b) are common water boilers in Chinese households: (a) is an electric kettle which is usually heated once and (b) is a water dispenser which can be heated multiple times; and (c) and (d) are generally used in some public places in China such as schools, hospitals, airports, etc.

in water should be based on rigorous scientific experiments rather than on assumptions or conjecture.

Fortunately, in order to make up for this deficiency, a few researchers carried out experiments in response to this issue in recent years. Liang & Chen (2007) carried out an RBW experiment in which bottled mineral water was boiled 52 times, during which 11 samples were collected for analysis, and they found that the concentration of NO_2^- -N was far below the low levels stipulated by the quality standards for drinking water, although these levels gradually increased as the experiment progressed. Shen & Zhang (2011) carried out an RBW experiment that boiled tap water five times and found that NO_3^- -N and hardness increased by the concentrating effect, but no NO_2^- -N was detected throughout the experiment. Both the mutual transformation of trinitrogen and the biochemical effects of nitrogen-related carcinogens were considered to be an impossible occurrence in the experiment. Luo (2017) carried out an RBW experiment where tap water was boiled 120 times and sampled six times for analysis and found that all measured ions (including major ions, trinitrogen and some common heavy metals) were far below the limiting values stipulated in the quality standards for drinking water, although they did increase gradually as the experiment progressed. It is worth mentioning that no NO_2^- -N was detected throughout the experiment. In general, it can be seen that the existing scientific reports related to this topic are very limited in number, and their conclusions are not completely consistent. More importantly, these studies have not revealed the mechanism of water quality change. Therefore, it should be said that these studies are not good enough to respond well to public concerns, or at least not enough to completely dispel doubts.

The lack of case studies may be largely attributed to the fact that this type of research does not have high academic value because it does not involve a profound scientific theory, nor does it need advanced research methods. It may also be attributed to the fact that in only a few countries, such as China, does the public care about this issue because of their living habits. However, it is still worthwhile conducting case studies to supplement the scientific evidence related to the social concerns mentioned above and the high complexity and spatiotemporal

heterogeneity of chemical components of drinking water worldwide. Furthermore, it can also be seen from the above analyses that there are still problems to be solved. For example, the existing experiments perhaps cannot fully reflect the possible extreme situations in daily life because the frequency of boiling or the boiling duration was insufficient. The data obtained cannot describe the entire experimental process well because the number of samples in the experimental process is relatively small (only the early and late stages are generally concerned without sufficient attention paid to the middle stage). The general state of water quality cannot be well known because the number of the monitored water quality indicators was relatively limited, especially as most of the existing studies focused only on trinitrogen. What is more, the existing conclusions were only obtained directly from the available monitoring data, neither with the mechanism analyses of physical, chemical and biological effects in the process, nor with any reliability demonstrated on the credibility of the conclusion from the view of experimental conditions and the daily habits of boiling and drinking. Thus, the credibility and generalizability of the conclusions are limited, and are not enough to be used to dispel misgivings.

Based on the above considerations, we identified the aim of this study, which is to reveal the water quality change process and its mechanism of repeatedly-boiled water and prolonged-boil water, and further to determine the potability and safety for drinking of these two kinds of water in daily life. We sincerely hope that our efforts in this regard will be helpful for dispelling the misgivings of the public.

MATERIALS AND METHODS

Experimental procedures

The boiling water experiments were carried out in the laboratory, and involved two independent experiments to emulate two common boiling habits of drinking water in daily life: RBW experiment (No. I) and PBW experiment (No. II), respectively. The experimental water (raw water) was taken directly from the urban tap water of Beijing,

China, which entered the urban water distribution network after chlorination disinfection in the water plant. The boiling water container was a 15 L stainless steel steamer (Figure 2) and was newly purchased for this experiment, and the heating device was a household induction cooker with a power of 2 kW. Before each experiment, the steamer was washed thoroughly using distilled water and then dried before adding the experimental water.

The RBW experiment (No. I) was carried out first, in which the water was heated to boiling for a total of 18 times until the water in the 15-L steamer boiled dry. The container was heated without a cover throughout the experiments. The water was cooled to a normal temperature (25 °C) before each subsequent episode of heating to boiling, and each boiling period lasted approximately 3 minutes, during which the water sample was collected in a beaker and put into a 500 mL sampling bottle. The water in the steamer had dried up after the last sampling because of the quick loss induced by the intense evaporation and the sampling in the experiment. Finally, a total of 19 water samples were collected, including one sample from the tap water used for the experiment. The RBW experiment lasted approximately 15 hours.

The PBW experiment (No. II) was carried out next, in which the boiling period was approximately 6 hours, lasting until the water in the 15-L steamer boiled dry. The container was heated without a cover throughout the experiments. The first sampling took place shortly after boiling, after which samples were collected in a 500 mL sampling bottle with a beaker every 20–25 minutes until the end of the experiment. The volume of each sample was 500 mL. The water in the steamer remained at boiling from the first sample to the last. Finally, a total of 17 water samples were collected,



Figure 2 | Experimental apparatus.

including one sample from the tap water used for the experiment.

A total of 36 water samples were collected for analysis during the two experiments.

Indicators and measurements

The selection of water quality indicators for monitoring in the experiment is very important, because the potability and drinking safety of water are determined by the species and concentrations of solutes in it. The monitoring indicators were selected from standards for drinking water quality released by China, the World Health Organization and the European Union, considering that there are many existing standards around the world and they are similar to each other in indicator species. The monitoring indicators involve the conventional water quality indicators, trinitrogen, heavy metals, trace organic substance indicators, microbial indicators, toxicological indicators, sensory traits and radioactive indicators. Disinfection by-products are also involved considering the use of the disinfection process in water plants and physicochemical properties of disinfectants, which are usually harmful to human health.

Based on these considerations, a total of 44 water quality indicators were measured and analyzed: pH, TDS, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2+} , HCO_3^- , $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, $\text{NO}_2^-\text{-N}$, Fe, Mn, Al, Ba, Zn, As, Cd, Cr, Cu, Ni, Sb, Hg, Se, Pb, CN^- , F^- , CHCl_3 , CHCl_4 , COD_{Mn} , chroma, turbidity, smell and taste, visible to the naked eye, volatile phenols, anionic synthetic detergent, total alpha radioactivity, total coliform, heat-resistant coliform, *Escherichia coli*, total colony number, total beta radioactivity and chlorine and free chlorine preparation (disinfection by-products).

Values for pH were measured directly at the experimental site using a portable multi-parameter rapid water quality analyzer (HANNA-HI9828) (Table 1) to obtain more accurate data, because results are labile over time. To obtain more accurate data for other indicators, all collected water samples were measured immediately after the samples were collected. Every sample was divided into three replicate samples and subsequently measured individually in the laboratory in order to reduce uncertainty. The other indicators were measured using the instruments in the chemical analysis laboratory (Table 1). TDS was determined using a gravimetric

Table 1 | Measuring methods of parameters and detectable limits

No.	Parameter (unit)	Measuring method	Detectable limit
1	pH (/)	Portable multi-parameter rapid water quality analyzer (HANNA-HI9828)	/
2	TDS (total dissolved solids) (mg/L)	Gravimetric method (Electronic scales FA2104B)	/
3	Na ⁺ (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.005 mg/L
4	K ⁺ (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.030 mg/L
5	Mg ²⁺ (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.002 mg/L
6	Ca ²⁺ (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.01 mg/L
7	Cl ⁻ (mg/L)	Ion chromatography (Thermo ICS-2100)	0.02 mg/L
8	SO ₄ ²⁺ (mg/L)	Ion chromatography (Thermo ICS-2100)	0.09 mg/L
9	HCO ₃ ⁻ (mg/L)	Acid-base titration (0–50 mL burette)	0.0001 mg/L
10	NH ₄ ⁺ -N (mg/L)	Ion chromatography (Thermo ICS-2100)	0.025 mg/L
11	NO ₃ ⁻ -N (mg/L)	Ion chromatography (Thermo ICS-2100)	0.01 mg/L
12	NO ₂ ⁻ -N (mg/L)	Ion chromatography (Thermo ICS-2100)	0.003 mg/L
13	Fe (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.03 mg/L
14	Mn (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.010 mg/L
15	Al (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.0005 mg/L
16	Ba (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.0618 mg/L
17	Zn (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.0008 mg/L
18	As (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.0012 mg/L
19	Cd (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.0005 mg/L
20	Cr (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.0005 mg/L
21	Cu (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.001 mg/L
22	Ni (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.00248 mg/L
23	Sb (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.00025 mg/L
24	Hg (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.001 mg/L
25	Se (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.01 mg/L
26	Pb (mg/L)	ICP-AES (PerkinElmer Optima 8000)	0.01 mg/L
27	δD (‰)	Liquid water isotope analyzer (LGR912-0008)	/
28	δ ¹⁸ O (‰)	Liquid water isotope analyzer (LGR912-0008)	/
29	CN ⁻ (mg/L)	Ion chromatography (Thermo ICS-2100)	0.05 mg/L
30	F ⁻ (mg/L)	Ion chromatography (Thermo ICS-2100)	1.0 mg/L
31	CHCl ₃ (mg/L)	Meteorological chromatography (Agilent7890A)	0.06 mg/L
32	CHCl ₄ (mg/L)	Meteorological chromatography (Agilent7890A)	0.002 mg/L
33	COD _{Mn} (mg/L)	Spectrophotometry (TU-1810DAPC)	3
34	Volatile phenols (mg/L)	Spectrophotometry (TU-1810DAPC)	0.002 mg/L
35	Anionic synthetic detergent (mg/L)	Spectrophotometry (TU-1810DAPC)	0.3 mg/L
36	Total alpha radioactivity (Bq/L)	Liquid scintillation counting	0.5 Bq/L
37	Total beta radioactivity (Bq/L)	Liquid scintillation counting	1 Bq/L
38	Chlorine and free chlorine preparation (mg/L)	Enzyme substrate method	0.05 mg/L
39	Chroma (platinum cobalt color unit)	Platinum cobalt colorimetry	15

(continued)

Table 1 | continued

No.	Parameter (unit)	Measuring method	Detectable limit
40	Turbidity (NTU)	Photoelectric colorimetry (GDS-3)	1
41	Smell and taste	/	Not checked out
42	Visible to the naked eye	/	Not checked out
43	Total coliform (MPN/100 mL)	Enzyme substrate	Not checked out
44	Heat-resistant coliform (MPN/100 mL)	Enzyme substrate	Not checked out
45	<i>E. coli</i> (MPN/100 mL)	Enzyme substrate	Not checked out
46	Total colony number (CFU/mL)	Plate colony counting	100 CFU/mL

method (electronic scales FA2104B); Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe, Mn, Al, Ba, Zn, As, Cd, Cr, Cu, Ni, Sb, Hg, Se and Pb were determined using ICP-AES (PerkinElmer Optima 8000); Cl⁻, SO₄²⁻, NH₄⁺-N, NO₃⁻-N and NO₂⁻-N were determined using ion chromatography (Thermo ICS-2100); HCO₃⁻ was determined using acid-base titration (0–50 mL burette); CHCl₃ and CHCl₄ were determined using meteorological chromatography (Varian CP-3800); COD_{Mn}, volatile phenols and anionic synthetic detergent were determined using spectrophotometry (TU-1810DAPC); chroma was determined using platinum cobalt colorimetry; turbidity was determined using photoelectric colorimetry (GDS-3); smell and taste were determined through smell and taste; visible to the naked eye was determined through direct observation; total alpha radioactivity was determined using low background total alpha monitoring; total beta radioactivity was determined using a thin sample method; chlorine and free chlorine preparation (disinfection by-products) were determined using N, N-diethyl-p-phenylenediamine. In addition, the stable isotopes of water hydrogen and oxygen (D and ¹⁸O) were also determined using a liquid water isotope analyzer (LGR912-0008) (Table 1) to reveal the water evaporating process.

The equilibrium of anion and cation charge of each water sample was calculated to check the reliability of the measured data, and data were considered potentially valid only if the calculated result was neutral. The maximum difference of the replicate samples of all the samples was less than 0.5%, and thus all the measured data were valid. The average value of the replicate samples was assigned to the corresponding sample for analyses. Thus, a total of 46 indicators/parameters (Table 1) were obtained for all collected samples and a total of 1,656 measured data points were obtained for analysis.

Analysis methods

The analysis methods in the study involved statistical analysis, time series analysis and the linear regression method. AquaChem software was used for the analysis of hydrochemistry type, and the GMWL (Global Meteoric Water Line; Craig 1961) of D and ¹⁸O was used to constrain the evaporation processes in the experiments. Standards for Drinking Water Quality of China (GB 5749-2006) was adopted as the reference standard in this study to determine the potability of the water, which referred to the relevant standards of the USA, Japan, EU and WHO when established. The standard for NO₂⁻-N referred to the standard of WHO because of the absence of it in the standard of China. Water should be considered to be potable if the concentrations of all the water quality indicators measured do not exceed the acceptable levels (or the acceptable range such as pH) regulated by the standard. The details of all these methods and standards are omitted here given that they are very common and easily located, and related references can be used.

The relative value (relative to initial concentration) of the concentrating speed of chemical components in water during the test is explained by concentration ratio (CR₁). The concentration rate (CR₂) is used to calculate the absolute value of the concentrating speed of chemical components in water during the test. The concentration rate (CR₂) is equal to the concentration ratio (CR₁) times the initial concentration. The two distinct equations of CR₁ and CR₂ can be written as:

$$CR_1 = (FC-IC)/(IC \times N) \quad (1)$$

$$CR_2 = (FC-IC)/N \quad (2)$$

where CR_1 is the concentration ratio (%); CR_2 is the concentration rate (ML^{-3}); FC is the final concentration (ML^{-3}); IC is the initial concentration (ML^{-3}); and N is the test count.

RESULTS

Change trends of the indicators

Of the 44 measured water quality indicators (Table 2), Fe, Mn, Al, Ba, Zn, As, Cd, Cr, Cu, Ni, Sb, Hg, Se, Pb, CN^- , F^- , $CHCl_3$, CCl_4 , COD_{Mn} , volatile phenols, anionic synthetic detergent, total alpha radioactivity, total beta radioactivity, smell and taste, visible to the naked eye, total coliform, heat-resistant coliform and *E. coli* were always below the detectable limits in the experiments as well as the tap water, so their change trends could not be analyzed. Total colony number and chlorine and free chlorine could only be detected in the tap water, and their contents in the tap water were within the acceptable levels. In other words, their contents could not be detected after the first boiling

until the end of the experiment, so their change trends could also not be analyzed. Chroma and turbidity never changed from the tap water to the end of the experiment and were always within the acceptable levels. The other 12 water quality indicators (pH, Na^+ , K^+ , Mg^{2+} , Cl^- , TDS, NO_3^- -N, NO_2^- -N, Ca, HCO_3^- , SO_4^{2-} and NH_4^+ -N), D and ^{18}O were always detectable and showed clear variations (Figure 3) and thus could be analyzed quantitatively.

It is worth noting that the same indicators from the two experiments generally presented similar change trends (Figure 3) and had similar value ranges (Table 2), indicating that they had undergone similar processes. All of the detectable indicators in the two experiments could be classified into two types according to their change trends: increasing indicators (Figure 3(a)–3(g)) and decreasing indicators (Figure 3(h)–3(l)). D and ^{18}O presented similar trends to those indicators with increasing trends (Figure 3(m) and 3(n)).

The increasing indicators were pH, Na^+ , K^+ , Mg^{2+} , Cl^- , TDS, NO_3^- -N and NO_2^- -N, while the decreasing indicators were Ca^{2+} , HCO_3^- and SO_4^{2-} (Table 2). Generally, the

Table 2 | Standard for drinking water quality, statistical information on the measured parameters, and linear relationship between parameter and sampling times

Parameter (mg/L)	Limited value	Value range		Mean		r	
		I	II	I	II	I (n = 18)	II (n = 16)
(a) Increasing dominated by physical effect (water evaporation and solute concentration)							
pH (/)	6.5–8.5	7.63–8.95	7.63–8.84	8.42	8.29	0.74	0.39
$Na^+ + K^+$	200	15.10–32.35	14.41–25.93	19.71	17.03	0.77	0.75
Mg^{2+}	/	12.91–26.26	11.75–19.96	16.50	14.14	0.78	0.68
Cl^-	250	21.61–47.04	19.62–38.70	28.88	25.10	0.79	0.60
TDS	1,000	156.70–225.00	153.60–193.70	171.64	166.95	0.06	0.00
TDS-($Ca^{2+} + 1/2HCO_3^-$)	/	64.92–179.42	29.74–144.89	102.06	84.79	0.82	0.74
NO_3^- -N	20	9.76–20.54	9.17–17.42	12.66	11.38	0.80	0.51
NO_2^- -N	3 ^A	1.26–2.72	1.24–2.47	1.64	1.56	0.77	0.49
(b) Decreasing dominated by chemical effect (thermal decomposition and precipitation)							
Ca^{2+}	/	44.12–17.21	42.75–21.06	25.71	30.29	-0.87	-0.97
HCO_3^-	/	152.55–54.91	183.06–42.71	93.14	115.22	-0.90	-0.94
SO_4^{2-}	250	2.53–0.06	2.65–0.26	0.81	1.40	-0.76	-0.95
$Ca^{2+} + HCO_3^-$	/	195.56–66.02	211.88–63.77	114.19	137.45	-0.92	-0.88
NH_4^+ -N	0.5	0.27–0.14	0.25–0.13	0.19	0.21	-0.33	-0.60

Limited value: the potable limit stipulated by the Standard for Drinking Water Quality of China (GB 5749-2006); A: the potable limit stipulated by the Standard for Drinking Water Quality of World Health Organization (WHO); I: repeatedly-boiled water; II: prolonged-boil water; and r: the linear correlation coefficient between parameter and sampling times, and '-' before it represents the negative correlation.

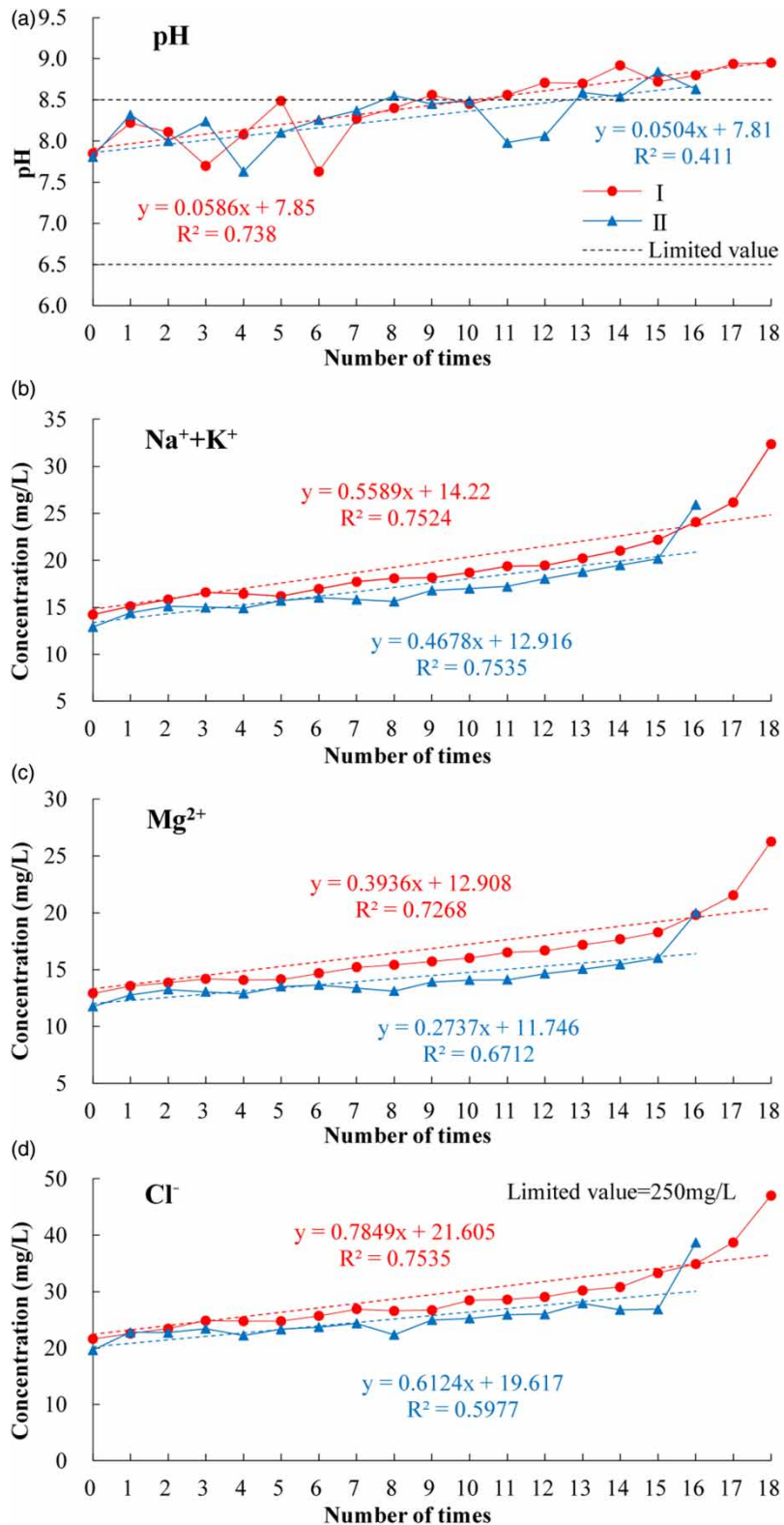


Figure 3 | Changes of the measured indicators in the experiments. (Continued.)

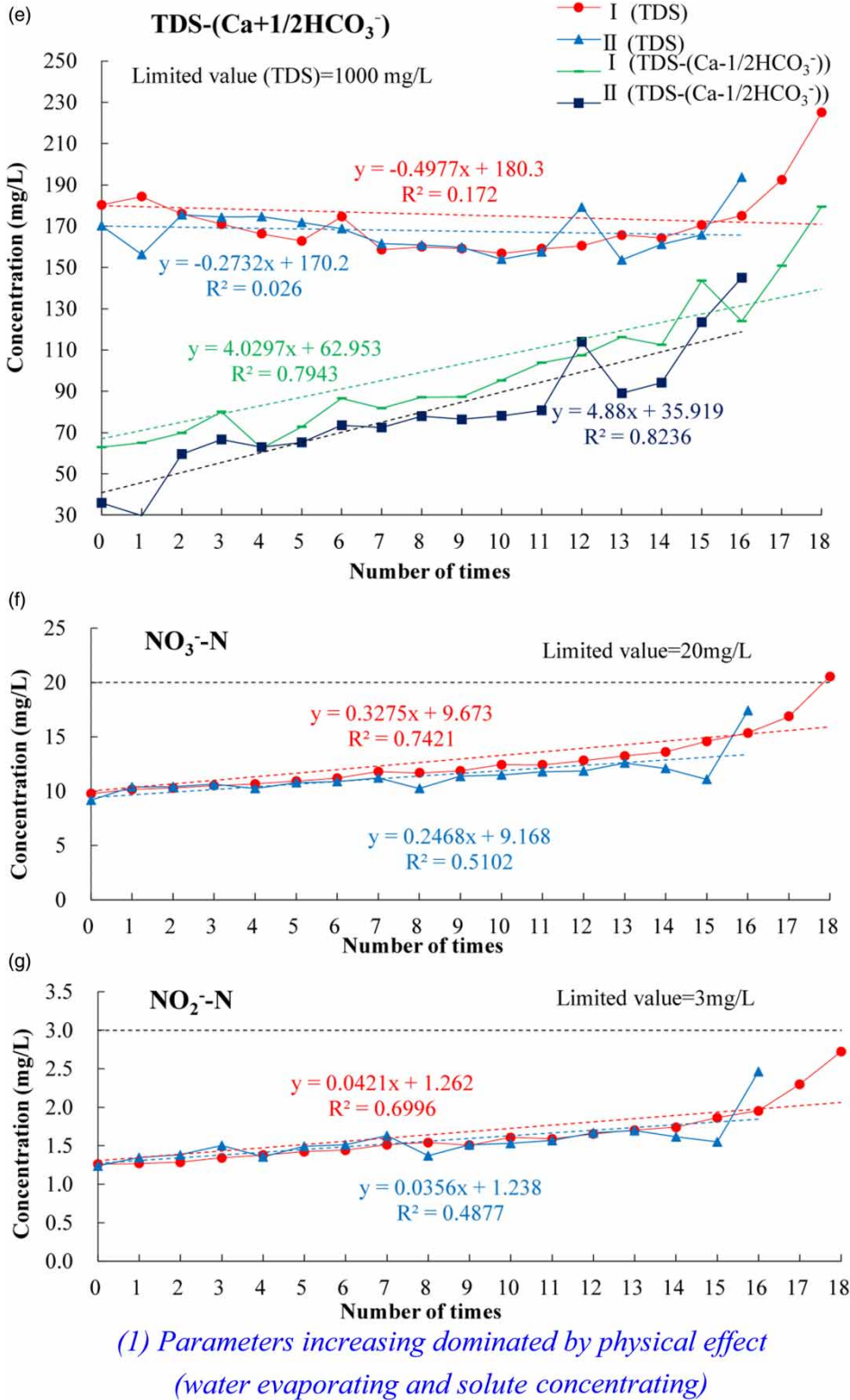


Figure 3 | Continued.

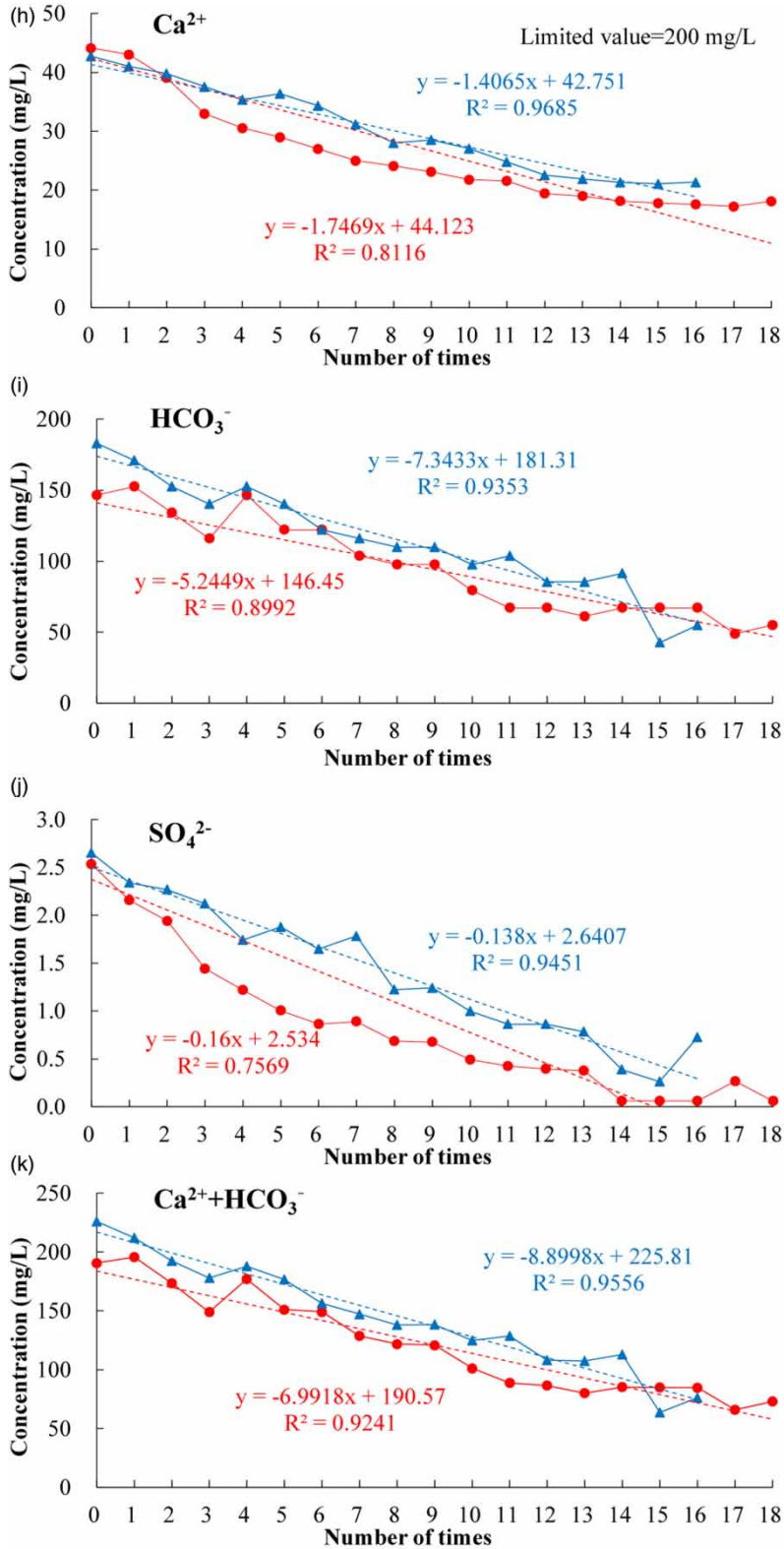
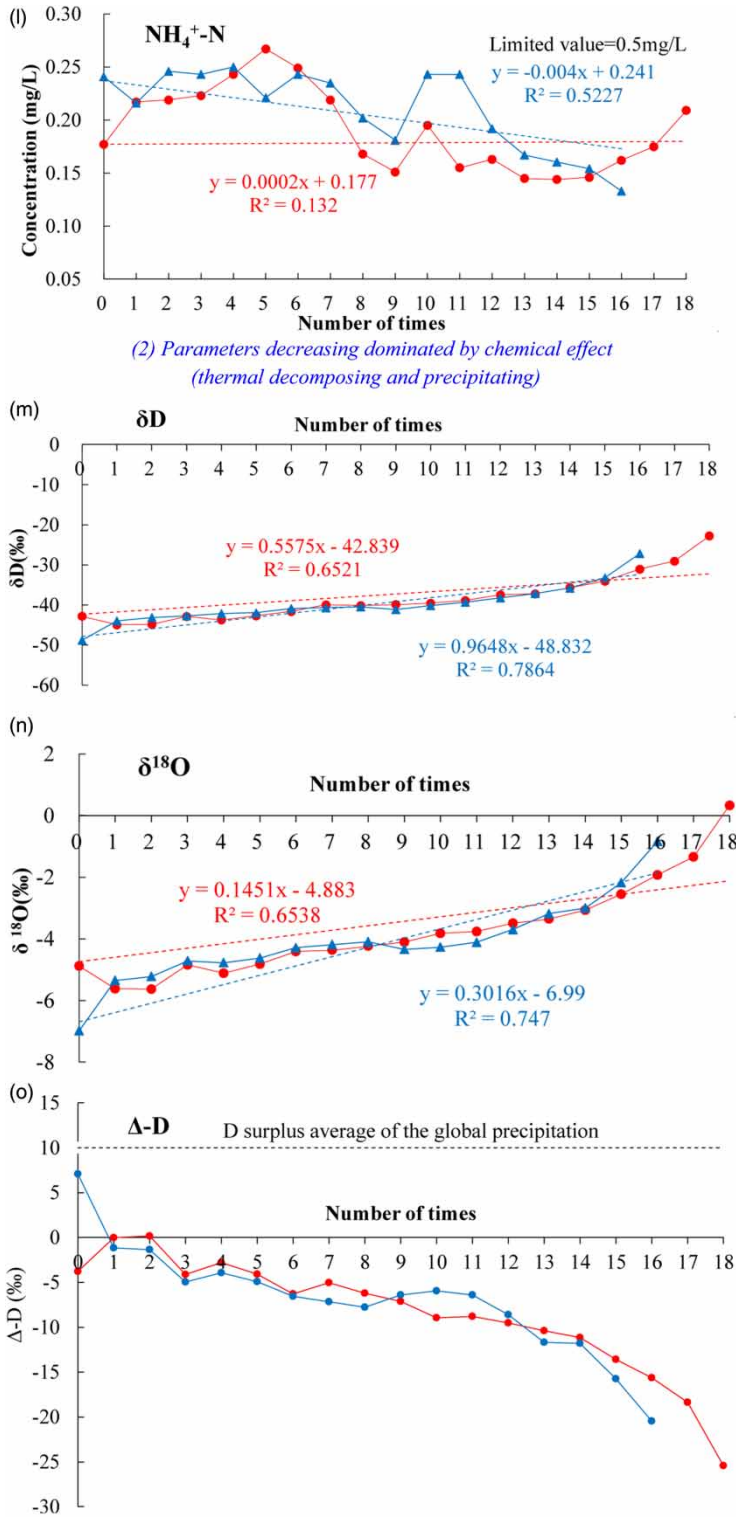


Figure 3 | Continued.



I : repeatedly-boiled water; II : prolonged-boil water; "0" at the x-axis represents the raw water.

Figure 3 | Continued.

changes in all measured indicators originated from the tap water, thus the levels of the indicators in the early stages of the experiments were close to those in the tap water. Nevertheless, the levels deviated increasingly more from those of the tap water as the experiments progressed.

The milligram equivalent concentrations of the anions and the cations in the tap water of the two experiments were in the following order: $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- \text{-N} > \text{SO}_4^{2-}$ and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ + \text{K}^+$ and the hydrochemical type was $\text{HCO}_3\text{-Ca-Mg}$. However, the relative relationships among the ion concentrations gradually changed as the experiments progressed (Figure 4). For the anions, Cl^- and $\text{NO}_3^- \text{-N}$ increased gradually while HCO_3^- and SO_4^{2-} decreased gradually, and the order of their concentrations gradually changed to $\text{NO}_3^- \text{-N} > \text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. Meanwhile, for the cations, Ca^{2+} decreased gradually while Na, K and Mg increased gradually, and the order of their concentrations gradually changed to $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ + \text{K}^+$. Thus, the hydrochemical type of the water of the two experiments gradually changed from $\text{HCO}_3\text{-Ca-Mg}$ to $\text{Cl}\cdot\text{HCO}_3\text{-Mg-Ca}$.

The maximum values of pH, $\text{Na}^+ + \text{K}^+$, Mg^{2+} , Cl^- , TDS, and $\text{TDS}\cdot(\text{Ca}^{2+} + 1/2\text{HCO}_3^-)$ for the two experiments were 1.17 (I) and 1.15 (II), 2.14 (I) and 1.80 (II), 2.03 (I) and 1.70 (II), 2.18 (I) and 1.97 (II), 1.44 (I) and 1.26 (II), and 2.76(I) and 4.87 (II) times the corresponding values of the tap water, respectively (Figure 5(a)). The minimum values of Ca^{2+} , HCO_3^- , SO_4^{2-} , $\text{Ca}^{2+} + \text{HCO}_3^-$ and $\text{NH}_4^+ \text{-N}$ of the two experiments were 39% (I) and 49% (II), 36% (I) and 23% (II), 2% (I) and 10% (II), 34% (I) and 30% (II), and 52% (I) and 52% (II) of the corresponding values of the tap water, respectively (Figure 5(a)). The maximum values of $\text{NO}_3^- \text{-N}$, $\text{NO}_2^- \text{-N}$ and trinitrogen in the two experiments were 2.11 (I) and 1.90 (II), 2.16 (I) and 2.00 (II), and 2.10 (I) and 1.88 (II) times the corresponding values of the tap water, respectively (Figure 5(a)). It could also be seen that, for the components that increased (the comprehensive water quality indicators were excluded), the concentrations were 1.7 times to 2.18 times compared with the tap water and for the components that decreased, the decreasing values of concentrations ranged from 48 to 98%. In other words, the multiples of the increase of all chemical components were close to each other. For trinitrogen, the amplitudes of the variations were between 48% and 1.16 times with respect to the tap water. The comparative

analyses indicated relatively slight, and thus very limited, changes in the chemical components in the experiments, regardless of whether trinitrogen or the other components were being considered.

Drinking safety of the water

It can be seen from 'Change trends of the indicators' above that Fe, Mn, Al, Ba, Zn, As, Cd, Cr, Cu, Ni, Sb, Hg, Se, Pb, CN^- , F^- , CHCl_3 , CCl_4 , COD_{Mn} , chroma, turbidity, smell and taste, visible to the naked eye, volatile phenols, anionic synthetic detergent, total alpha radioactivity, total beta radioactivity, total coliform, heat-resistant coliform, *E. coli*, total colony number and chlorine and free chlorine (disinfection by-products) were always within the acceptable levels regulated in the standard for drinking water quality and thus the water in different stages in the experiment was safe for drinking considering these indicators of water quality.

For the other water quality indicators, pH reached 8.95 in the later stages of the experiment and slightly exceeded the acceptable upper limit (8.5), and Cl^- , TDS and SO_4^{2-} were always far below the acceptable levels and thus satisfied the standard. For the hydrochemical components of most concern, $\text{NH}_4^+ \text{-N}$, $\text{NO}_3^- \text{-N}$ and $\text{NO}_2^- \text{-N}$ were also always below the acceptable levels and thus satisfied the standard except for the one value of $\text{NO}_3^- \text{-N}$ (20.54 mg/L; the last sample of the RBW experiment) that slightly exceeded the acceptable value (20 mg/L). Na^+ , K^+ , Ca^{2+} , Mg^{2+} and HCO_3^- were not regulated by the standard and thus were not considered separately here because they had been reflected in the comprehensive water quality indicators such as TDS and hardness which were regulated by the standard. Hardness also satisfied the standard according to the calculated values based on Ca^{2+} and Mg^{2+} , although it was not measured directly in the experiments. Thus, we could say that the water in all the stages of the experiment, as well as the tap water, satisfied the standard for drinking water quality (Table 2), therefore the water is safe for drinking.

DISCUSSION

We carried out two independent experiments to observe the quality changes of RBW and PBW, simulating two different

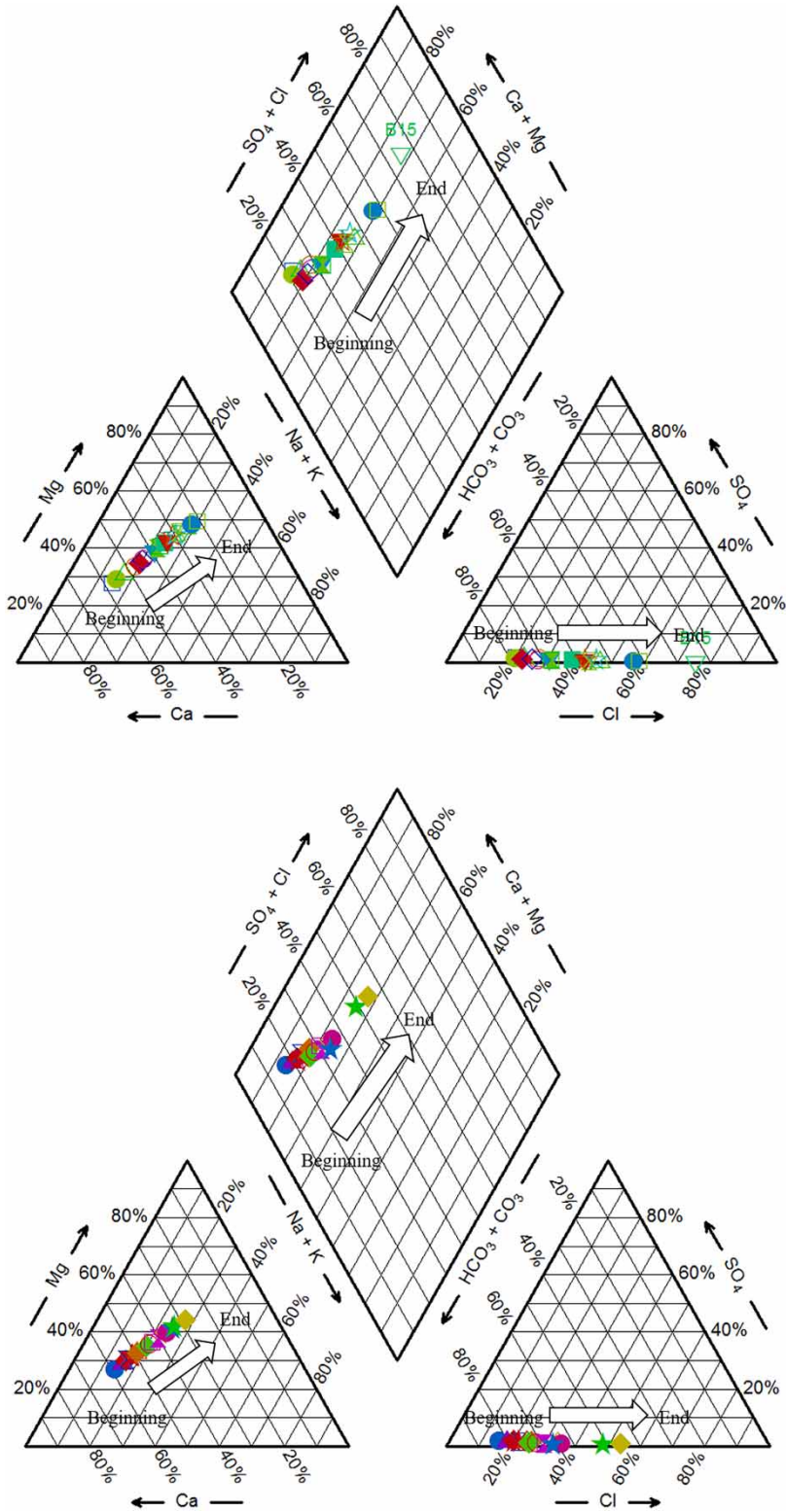
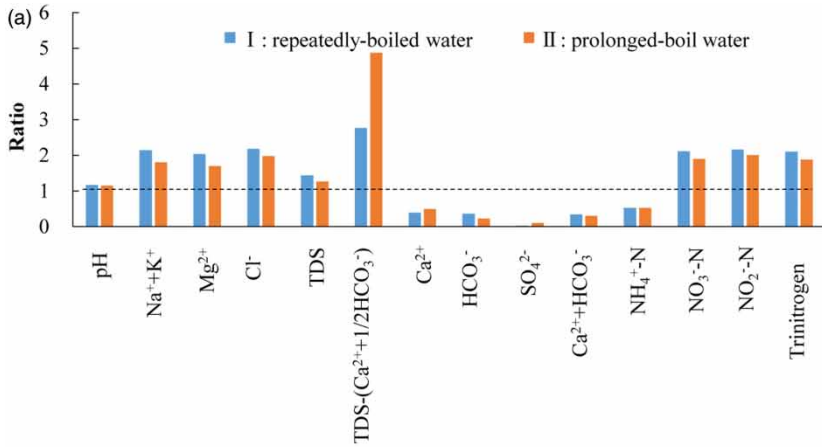
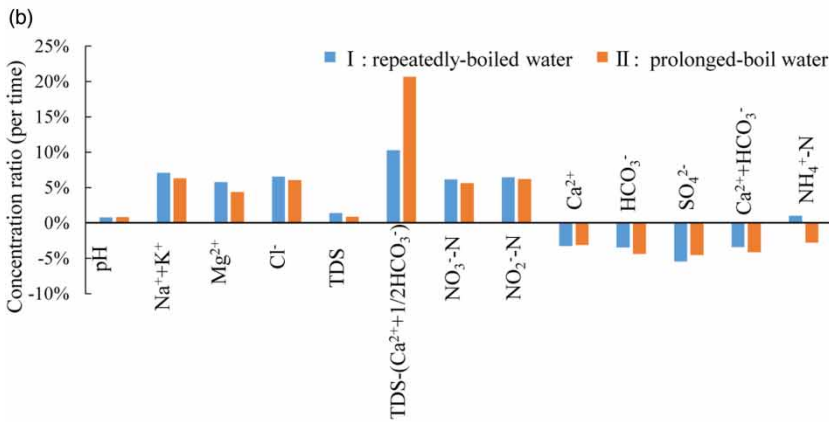


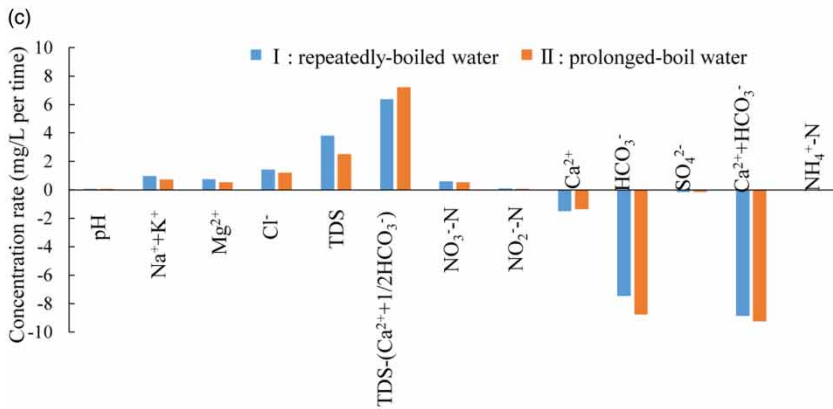
Figure 4 | Piper diagrams reflecting the hydrochemical types and evolution of the water in the experiments.



Change rates of the parameters in the experiments relative to the raw water



Concentration ratio of the parameters in the experiments



Concentration rate of the parameters in the experiments

Figure 5 | Change rates of the parameters relative to the tap water and the concentration ratio and rate of the parameters in the experiments. (a) Ratio refers to the ratio of the maximum (increasing parameter) or the minimum (decreasing parameter) of the parameter in the experiments to the corresponding value of the raw water; ratio < 1 means the concentration decreased in the experiments; and ratio > 1 means the concentration increased in the experiments; (b) <0 refers to the concentration decreased in the experiments; % refers to the rate of change compared with the value of the raw water; (c) mg/L refers to the quantity of change compared with the value of the raw water.

yet common habits of boiling drinking water. The drinking safety of the water in the experiments was then evaluated with reference to the sanitary standards for drinking water. Both the boiling times of RBW and the boiling duration of PBW in the experiments were generally considered to be sufficient to reflect the worst habit in daily life, viewing it from the effects in water quality. However, it is in fact impossible to consider all worst-case scenarios through experimentation because of the limitations of the experimental conditions, such as the boiling times, the boiling durations and even the quality of the tap water for experiment. Thus, it is necessary to determine the mechanisms of water quality change in the process of heating/boiling water and subsequently to demonstrate the credibility of the conclusions obtained by the two experiments to effectively dispel public misgivings.

Mechanism of water quality change

Water quality is commonly controlled by physical, chemical and microbial effects (Hu et al. 2011; Mu et al. 2016; Liu et al. 2017; Salari et al. 2018; Pichel et al. 2019; Zhu et al. 2019). Nevertheless, any microbial effects in the experiments should be neglected considering the water temperature. Thus, the revelation of the mechanism of quality change of repeatedly-boiled water and prolonged-boil water will proceed from the physical and chemical effects.

Physical effects

It can be confirmed that intensive water evaporation processes took place in the experiments through observing the changes in D, ^{18}O and $\Delta\text{-D}$ ($=\delta\text{D}-8\delta^{18}\text{O}$) (Figure 3(m)–3(o)), which are excellent tracers when tracking the process of water evaporation and fractionation (Zhai et al. 2013; Hao et al. 2019). The curves from the two experiments show that the water underwent almost the same evaporation process in the two experiments, in which both D and ^{18}O increased linearly as the two experiments progressed, and the increasing levels of D were 22.15‰ (I) and 21.65‰ (II) and the corresponding values of ^{18}O were 5.3‰ (I) and 6.15‰ (II). Nevertheless, $\Delta\text{-D}$ decreased linearly as the two experiments progressed because of the impacts of heterogeneous evaporation of the two isotopes (Hao et al. 2019) and the decreasing levels were 25.60‰ (I) and 27.54‰ (II). Also impacted by heterogeneous evaporation, the linear relationship (known as the evaporation line) between D and ^{18}O are obviously different from the GMWL (Figure 6), and the slopes of the lines of the two experiments are 3.5079 (I) and 3.7993 (I). Generally, the heavy isotopes in water molecules (D and ^{18}O) constantly fractionated and thus accumulated in the steamer with experimental progression, the processes of which were much more intensive compared with those occurring in the natural environment (Zhai et al. 2013).

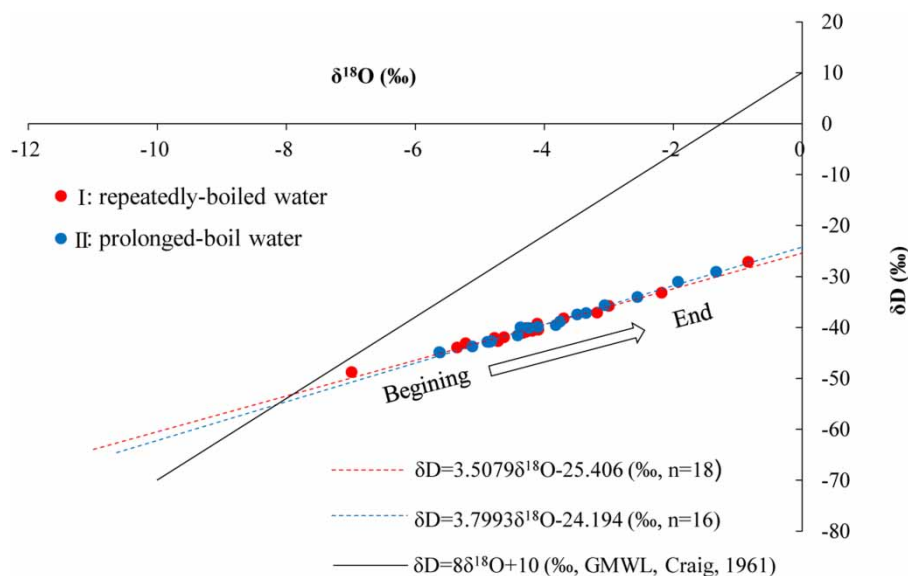


Figure 6 | Linear relationship between δD and $\delta^{18}\text{O}$ of the experimental water indicating the intensive evaporating processes.

Associated with the water evaporation processes, the concentrations of unreactive chemicals dissolved in the water showed inevitable increases. The unreactive chemical components refer to those chemical substances not exhibiting volatilization, chemical reaction, or precipitation in hot and boiling water. All the components showing increasing trends in the experiments (Na^+ , K^+ , Mg^{2+} , Cl^- , NO_3^- -N and NO_2^- -N) not only underwent similar processes (Table 3) but also exhibited very similar increasing amplitudes (Figure 5(a)). For example, the correlation coefficient of NO_3^- -N and Cl^- of both experiments reached 0.99. Meanwhile, all components with decreasing trends in the experiments (Ca^{2+} , HCO_3^- and SO_4^{2-}) not only underwent similar processes (Table 3) but also had relatively similar decreasing amplitudes (Figure 5(a)). For example, the correlation coefficient of Ca^{2+} and HCO_3^- for the two experiments reached 0.79 (I) and 0.89 (II), respectively (Table 3). Furthermore, the linear correlations between the increasing and decreasing components were also clear (Table 3). Regarding the comprehensive water quality indicators (pH and TDS), the law of correlation is complicated because of the complexities of their changes which are determined by the chemical components of the water. It can be seen that the change trends of the water isotopes and increasing components (Na^+ , K^+ , Mg^{2+} , Cl^- , NO_3^- -N and NO_2^- -N) in the experiments fully proved the existence of evaporation and concentration effects, which is the decisive or even the only factor in controlling the increases in the concentrations of those unreactive components. The concentration ratios (CR_1) of the unreactive components ($\text{Na}^+ + \text{K}^+$, Mg^{2+} , Cl^- , NO_3^- -N and NO_2^- -N) ranged from 4.37 to 7.08% per boil relative to the tap water (Figure 5(b)), and their corresponding concentration rates (CR_2) ranged from 0.08 mg/L (known as NO_2^- -N) to 1.41 (known as Cl^-) mg/L (Figure 5(c)).

For the decreasing components (Ca^{2+} , HCO_3^- and SO_4^{2-}) in the experiments, it is clear that the phenomenon cannot be fully explained by physical effects but must be explained by considering chemical effects.

Chemical effects

First, it is well known that Ca^{2+} and HCO_3^- in water will undergo a thermal decomposition reaction when water is heated, in which CaCO_3 precipitates and CO_2 volatilizes

($\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 \uparrow + \text{CaCO}_3 \downarrow$). Thus, the concentrations of Ca^{2+} and HCO_3^- of the water decrease quickly as the experiments progress, and are the highest cation and anion concentrations in the tap water, respectively. CR_1 of Ca^{2+} of the two experiments are -3.27% (I) and -3.13% (II) compared with the tap water, and the corresponding values of HCO_3^- are -3.47% (I) and -4.38% (II) (Figure 5(b)). Second, it is well known that Ca^{2+} and SO_4^{2-} in water precipitate ($\text{Ca}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4 \downarrow$) when water is heated because of their low solubility (Havlica & Sahu 1992). Thus, the concentration of SO_4^{2-} also decreases in a manner similar to Ca^{2+} and HCO_3^- as the experiments progress. CR_1 of SO_4^{2-} of the two experiments are -5.43% (I) and -4.54% (II) compared with the tap water (Figure 5(b)).

It is also well known that NH_4^+ could be in the form of NH_3 (known as ammonia gas) (Wang *et al.* 2002). Thus, the measured concentrations of NH_4^+ -N contain both NH_4^+ and NH_3 , which is more complicated than and thus different from the case of Ca^{2+} , HCO_3^- and SO_4^{2-} (discussed above) due to the existence of gas. NH_4^+ and HCO_3^- in water also occur in a thermal decomposition reaction when the water is heated, in which both NH_3 and CO_2 volatilize as the products ($\text{NH}_4^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{NH}_3 \uparrow + \text{CO}_2 \uparrow$). Thus, the concentration of NH_4^+ -N does not increase like NO_3^- -N and NO_2^- -N. CR_1 of NH_4^+ -N in the two experiments are 1.00% (I) and -3.00% (II) compared with the tap water (Figure 5(b)).

The temporary hardness value also decreases quickly and is determined by Ca^{2+} and HCO_3^- . Therefore, it is beneficial to reduce the temporary hardness through boiling the drinking water, as temporary hardness is also considered to be one of the harmful indicators if the concentration is relatively high in the drinking water. Different from the chemical components and the temporary hardness discussed above, TDS shows a fluctuation change rather than a trend change (Figure 3(e)). The phenomenon is synthetically and simultaneously determined by the concentration, and the volatilization and precipitation effects, of which the former causes a TDS increase, while the latter two cause TDS to decrease.

After the above analyses, the physicochemical effects controlling the experiments are successfully identified: the evaporation of the water and thus the concentration of the unreactive chemical components (most dissolved solutes) as the physical effects, and both the precipitation and the

Table 3 | Linear relationship (*r*; before it represents the negative correlation) between the parameters

Parameter	pH	Na ⁺ + K ⁺	Mg ²⁺	Cl ⁻	TDS	TDS-(Ca ²⁺ + 1/2HCO ₃ ⁻)	NO ₃ ⁻ -N	NO ₂ ⁻ -N	Ca ²⁺	HCO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺ + HCO ₃ ⁻	NH ₄ ⁺ -N	δD	δ ¹⁸ O
pH	1.00	0.37	0.34	0.22	-0.06	0.31	0.21	0.21	-0.39	-0.53	-0.39	-0.51	-0.02	0.43	0.48
Na ⁺ + K ⁺	0.55	1.00	<u>0.99</u>	<u>0.87</u>	0.13	<u>0.84</u>	<u>0.86</u>	<u>0.84</u>	-0.63	-0.74	-0.60	-0.73	-0.03	<u>0.95</u>	<u>0.90</u>
Mg ⁺	0.56	<u>0.99</u>	1.00	<u>0.89</u>	0.18	<u>0.80</u>	<u>0.89</u>	<u>0.87</u>	-0.54	-0.67	-0.50	-0.65	-0.04	<u>0.93</u>	<u>0.87</u>
Cl ⁻	0.54	<u>0.84</u>	<u>0.80</u>	1.00	0.17	<u>0.80</u>	<u>0.99</u>	<u>0.96</u>	-0.42	-0.47	-0.34	-0.47	-0.04	<u>0.76</u>	<u>0.70</u>
TDS	0.03	0.29	0.28	0.40	1.00	0.15	0.19	0.24	0.01	-0.01	0.01	-0.01	-0.05	0.09	0.06
TDS-(Ca ²⁺ + 1/2HCO ₃ ⁻)	0.57	<u>0.77</u>	0.72	<u>0.93</u>	0.30	1.00	0.61	0.65	-0.75	-0.88	-0.71	-0.87	-0.05	<u>0.88</u>	<u>0.87</u>
NO ₃ ⁻ -N	0.57	<u>0.85</u>	<u>0.81</u>	<u>0.99</u>	0.41	<u>0.93</u>	1.00	<u>0.97</u>	-0.41	-0.46	-0.32	-0.46	-0.05	<u>0.75</u>	0.69
NO ₂ ⁻ -N	0.55	<u>0.84</u>	<u>0.80</u>	<u>0.99</u>	0.42	<u>0.92</u>	<u>0.99</u>	1.00	-0.38	-0.47	-0.29	-0.46	-0.06	<u>0.75</u>	<u>0.70</u>
Ca ²⁺	-0.57	-0.41	-0.37	-0.53	0.01	-0.59	-0.52	-0.50	1.00	<u>0.89</u>	<u>0.95</u>	<u>0.92</u>	0.01	-0.70	-0.72
HCO ₃ ⁻	-0.62	-0.54	-0.50	-0.59	-0.01	-0.77	-0.59	-0.72	<u>0.79</u>	1.00	<u>0.87</u>	<u>0.99</u>	0.04	-0.82	-0.85
SO ₄ ²⁻	-0.58	-0.42	-0.37	-0.54	-0.01	-0.61	-0.53	-0.51	<u>0.98</u>	<u>0.78</u>	1.00	<u>0.90</u>	-0.01	-0.86	-0.70
Ca ²⁺ + HCO ₃ ⁻	-0.63	-0.53	-0.49	-0.60	-0.01	-0.76	-0.59	-0.57	<u>0.86</u>	<u>0.99</u>	<u>0.85</u>	1.00	0.03	-0.81	-0.84
NH ₄ ⁺ -N	-0.35	-0.18	-0.19	-0.09	-0.03	-0.20	-0.11	-0.09	0.25	0.44	0.22	0.42	1.00	-0.02	-0.03
δ	0.58	<u>0.83</u>	<u>0.79</u>	<u>0.97</u>	0.35	<u>0.93</u>	<u>0.98</u>	<u>0.97</u>	-0.55	-0.63	-0.56	-0.64	-0.16	1.00	<u>0.98</u>
δ ¹⁸ O	0.56	<u>0.80</u>	<u>0.76</u>	<u>0.97</u>	0.33	<u>0.94</u>	<u>0.97</u>	<u>0.97</u>	-0.58	-0.65	-0.58	-0.66	-0.16	<u>0.99</u>	1.00

The data in the lower left are from the repeatedly-boiled water experiment (I; *n* = 18), and those in the upper right are from the prolonged-boil water experiment (II; *n* = 16).

volatilization induced by the thermal decomposition reaction as the chemical effects. The physical effects increase the concentrations of some chemical components, while the chemical effects decrease the concentrations of the other chemical components. The combined impacts of the physical effects and the chemical effects causes TDS fluctuations in the experiments, while TDS also increases gradually similar to the unreactive chemical components if Ca^{2+} and HCO_3^- are excluded (labeled as $\text{TDS}-(\text{Ca}^{2+} + 1/2\text{HCO}_3^-)$; Figure 3(e)). The concentration ratios of $\text{TDS}-(\text{Ca}^{2+} + 1/2\text{HCO}_3^-)$ in the two experiments are 10.28% (I) and 20.56% (II), while the corresponding values of $\text{Ca}^{2+} + \text{HCO}_3^-$ are -3.43% (I) and -4.14% (II) (Figure 5(b)).

Considering the undetectable components in the experiments, these phenomena at least indicate that these components do not increase significantly caused by concentration effect or physicochemical dissolution from the wall of the steamer, or their concentrations were always too low to be detected although an increase actually took place.

Possible increases of harmful substances

Although the above has revealed the mechanism of water quality change, the public may still have doubts because of the absence of poisonous and harmful substances above, which are discussed in this section. The discussion is divided into two parts considering the actual results: inorganic and organic nitrogen species and other poisonous and harmful

substances including heavy metals, trace organic substances, pathogenic microorganisms and radioactive substances.

N species

It is well known, or at least viewed by the public, that the concentration of nitrogen will obviously increase if the drinking water is boiled often or boiled for a long time (Liang & Chen 2007; Luo 2017). This is discussed in detail here based on experimental data. The possibility of an increase in harm from nitrogen is also discussed here considering the public concerns and misgivings and the complexity of the biochemical properties of nitrogen. The analysis in 'Mechanism of water quality change' above has shown that NO_3^- -N and NO_2^- -N present the same increasing trends as the other unreactive components in the experiments. CR_1 of NO_3^- -N of the two experiments are 6.13% (I) and 5.62% (II), and the corresponding values of NO_2^- -N are 6.43% (I) and 6.20% (II) (Figure 5(b)). CR_1 of NH_4^+ -N of the two experiments are 1.00% (I) and -3.00% (II) compared with the tap water, respectively (Figure 5(b)). CR_1 of trinitrogen of the two experiments are 6.08% (I) and 5.50% (II), respectively. That is, trinitrogen levels did not appear to be abnormal except for a gradual increase during the experiments (Figure 7). Thus, we have to say that the changing law of trinitrogen is not different from the other components discussed above.

In addition to the physicochemical effects discussed above, it is necessary to further demonstrate the possibility of trinitrogen transformation or trinitrogen formation of

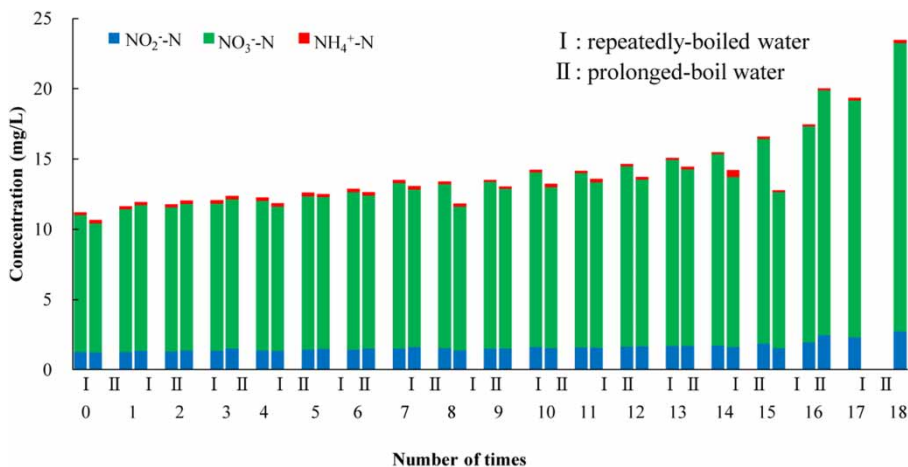


Figure 7 | Changes of trinitrogen in the experiments.

other harmful substances, perhaps even carcinogens. It is well known that trinitrogen can transform into its other forms under certain conditions (Kuypers *et al.* 2018; Xin *et al.* 2019). For example, $\text{NH}_4^+\text{-N}$ can be transformed to $\text{NO}_3^-\text{-N}$ and subsequently to $\text{NO}_2^-\text{-N}$ by nitrification, and $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ can be transformed to gaseous nitride and N_2 by denitrification (Kuypers *et al.* 2018). These effects can occur either in nature or in the laboratory. However, neither nitrification nor denitrification is possible in the present experiments considering the biochemical and redox conditions. For example, both nitrification and denitrification require the participation of microorganisms (such as nitrobacteria and denitrifying bacteria) (Massara *et al.* 2017; Kuypers *et al.* 2018) and the transformation of $\text{NO}_2^-\text{-N}$ to $\text{NO}_3^-\text{-N}$ requires the existence of a strong oxidant (Kuypers *et al.* 2018), neither of which is possible in the experiments. It is also not necessary to worry about the transformations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ to $\text{NO}_3^-\text{-N}$ because $\text{NO}_3^-\text{-N}$ accounts for approximately 87% of trinitrogen, which means both $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ levels are almost negligible compared with $\text{NO}_3^-\text{-N}$ (Figure 7). In the standard, the acceptable value of $\text{NO}_3^-\text{-N}$ is 40 and 6.7 times of those of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$, respectively.

Only the $\text{NO}_2^-\text{-N}$ species of trinitrogen is toxic, but it is not carcinogenic (Zhai *et al.* 2017; Wang *et al.* 2018). Trinitrogen cannot be transformed into other harmful substances or carcinogens because of the limitations of the biochemical conditions in the experiments.

The above analyses show that trinitrogen cannot be produced in water by air, and the existing trinitrogen in water will not transform into other forms forming new toxic or harmful chemicals, nor will it react to produce other toxic, harmful or carcinogenic substances. The truth is as follows: (1) $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ concentrate at the starting point of the tap water only because of water evaporation, and their concentrations increase continuously, but their increased amplitudes are very limited (with CR_1 of 5.9 and 6.3% relative to the tap water, respectively); (2) the variation in $\text{NO}_3^-\text{-N}$ mostly reflects the variation in trinitrogen because the concentration level of $\text{NO}_3^-\text{-N}$ in the tap water is generally 1–2 orders of magnitude higher than for $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$; and (3) most importantly, no carcinogens transformed from trinitrogen are produced in the water, no matter how many times it is boiled or how long it is boiling.

Other harmful substances

In addition to nitrogen species, there may be substances in the water that may have an impact on human health, such as heavy metals, trace organic substances, pathogenic microorganisms and radioactive substances. Heavy metals are easily dissolved under acidic conditions (Li *et al.* 2016a), and increasing alkaline conditions in the test cannot promote their dissolution. In fact, heavy metals will undergo an evaporation and concentration process similar to Na^+ during the test as discussed above under ‘Mechanism of water quality change’, while other physiochemical and biological effects will not occur. Therefore, the law of the concentration increases of heavy metals will be at least similar to, if not the same as, that of Na^+ .

High temperature is conducive to volatilization and degradation of trace organic substances (Li *et al.* 2016b), so there is no doubt that boiling water is conducive to improving water quality. Moreover, the longer the boiling time is, the more obvious the improvement effect. As for the pathogenic microorganisms that may remain in tap water, they will be killed in the boiling process (Stijn *et al.* 2018), so we should not worry about it. As for radioactive substances, the situation will not be worse than that of heavy metals, because their decay is not affected by temperature, physiochemical and biological effects.

General applicability of the study findings

To make the results of this study more applicable and more broadly instructive, it is indispensable to demonstrate the credibility of the results obtained by this study. It can be seen from the above analyses that the water quality of RBW and PBW are determined by both the quality of the tap water (such as tap water) and the boiling habits. Therefore, demonstration of the credibility of the results for guiding practices will also proceed from these two factors.

Representativeness of the municipal sample used in the experiment

Undoubtedly, the water quality change in both RBW and PBW originates from the tap water. If the tap water for boiling is from tap water, its quality is controlled by both the

incoming water and by the treatment process of the supply plant. In other words, the quality of the tap water varies from one plant to another. To verify the representativeness of the experimental water used in this study, water quality data from six urban plants in China were collected (Table 4). These cities cover both northern and southern China and their water sources include rivers, reservoirs and groundwater. Thus, the plants cover all common types. It can be seen that the concentration levels of the water quality parameters from different plants have no significant difference, and the concentration levels of some harmful components of city water, such as NO_3^- -N, are even lower than those of the tap water used in the experiments. Thus, the results obtained in the experiments are reliable when considering the tap water used compared with the drinking water in daily life.

Viewing the credibility from the manner of boiling

Water boilers in daily life may be electric kettles or pots at home, or drinking fountains at home or in public, such as in an office or outdoors, and are usually heated directly by electricity, with some heated by an electric furnace or stove. In some cases, a steamer may be used to heat water, such as in the experiments. The manners or habits of adding water into the boiler can be classified into three types: the single-time type (Type I), the pulsed addition type (Type II) and continuous type (Type III). Type I means that water is added into the boiler only once for

boiling before drinking, and no new water is added during heating or boiling. Type II means that new water is added into the boiler once or episodically during heating or boiling. Type III means that new water is added continuously as long as there is space in the boiler. All the new water refers to the tap water, the quality of which is deservedly considered to satisfy the sanitary standards for drinking water.

As for Type I, the water in the boiler will decrease quickly during heating and boiling because of the limited volume and the intensive evaporation of the water. The remaining water available for drinking in the boiler will be limited if it is boiled for a certain number of times (known as the RBW) or boiling for a longer time (known as the PBW). Using experiment No. I as an example, 40% of the water in the volume of a 15 L steamer evaporated after being boiled 18 times, and the concentrations of the harmful components such as NO_3^- -N and NO_2^- -N in the remaining water doubled compared with those of the tap water (Table 2). The results of experiment No. II were similar to those of experiment No. I (Table 2). In fact, it seldom occurs in daily life that water is boiled in such a large vessel and people drink the remaining limited water after a significant amount has evaporated. For Types II and III, commonly seen in drinking fountains at home or in public, new water is added automatically or manually in a timely manner to compensate for the loss of water in the boiler because of evaporation and intake for drinking. The newly added water dilutes the concentrations of the harmful components of the RBW or the PBW in the boiler. In other

Table 4 | Comparison of water quality of urban tap water from several typical cities of China and that of the raw water used in the experiment

City Water source	Limited value	This study	North China				South China	
			Beijing Multi-sources	Tianjin River	Harbin Reservoir	Xi'An Groundwater	Guangzhou River	Shenzhen Reservoir
pH (/)	6.5–8.5	7.8	7.2–8.0	7.5–7.9	6.8–7.0	7.9–8.1	7.7–7.9	7.2–7.6
Cl^- (mg/L)	250	20–22	13–60	9–26	9–12	5–91	11–26	10–14
TDS (mg/L)	1,000	170–180	166–514	164–218	50–102	127–551	125–200	50–114
NO_3^- -N (mg/L)	20	9.2–9.8	1.2–9.3	0.6–1.0	1.2–1.4	0.2–3.9	2.0–2.6	0.2–1.7
SO_4^{2-} (mg/L)	250	2.5–2.7	25.4–83.6	26.4–40.0	7.0–20.0	16.1–139.3	17.0–27.4	5.7–12.0
NH_4^+ -N (mg/L)	0.5	0.18–0.24	–	<0.02–0.40	–	–	<0.05	0.02–0.04
Total hardness (mg/L as CaCO_3)	450	155–163	120–354	127–143	30–150	76–230	38–48	30–56
Heavy metals	/	Far below the limited values or even below the detectable limits						

The data are adopted from the official websites of the water supply plants of these cities.

words, the quality of the water obtained from these two types will be significantly better than that of the Type I.

To describe the issue quantitatively, the times of boiling water required for the concentrations of chemical components in tap water to exceed the corresponding acceptable levels are calculated. The larger values of the concentration ratios (per time compared with the value of the tap water) obtained by the experiments (Figure 5(b)) were adopted for calculation in order to reflect the worst scenario. TDS is largely determined by the macro components ($\text{Na}^+ + \text{K}^+$, Ca^{2+} , Mg^{2+} , HCO_3^- , Cl^- and NO_3^- -N), out of which $\text{Na}^+ + \text{K}^+$ and Cl^- are the fastest concentrated cations and anions, respectively (Figure 5(b)). It is necessary to boil the tap water 268 and 152 times, respectively, in order to make the concentrations of $\text{Na}^+ + \text{K}^+$ and Cl^- in the tap water (11.73 and 21.61 mg/L) exceed the acceptable levels (200 and 250 mg/L). The corresponding times required for TDS is 73 if only the increasing components (known as $\text{TDS}-(\text{Ca}^{2+} + 1/2 \text{HCO}_3^-)$) are considered, and the number will be much larger if the decreasing components are also considered. As to Fe, Mn and other possible heavy metals, the number of times cannot be calculated directly because they were always below the detectable limits in the experiments. In order to carry out the calculation, we assume that the concentrations of these heavy metals exactly equal the detectable limits (Table 4), and their concentration processes in the boiling process are similar to that of Na^+ . Furthermore, we take the heavy metal with the smallest multiple between the acceptable value and the detectable limit as an example in order to reflect the worst scenario, and the heavy metal is Fe and the multiple is 10. Thus, the calculation for heavy metals can be performed and the corresponding number of times is 140. The corresponding numbers of times of NO_3^- -N and NO_2^- -N are 18 and 22, respectively. It can be seen from the above calculation that NO_3^- -N and NO_2^- -N are the easiest components to exceed the acceptable levels, because the numbers of times required of them are one order of magnitude smaller than those of the salinity and heavy metals. That is to say, the RBW and the PBW are potable as long as the concentrations of NO_3^- -N and NO_2^- -N do not exceed the acceptable levels. In fact, the concentrations of NO_3^- -N and NO_2^- -N in tap water are generally lower than those of the experimental water (Table 4). Thus, more boiling time

is required for the tap water in daily life compared with the tap water used in the experiments.

It can be seen from the above analyses that the quality of the boiled water for drinking in daily life cannot be worse than that of the water obtained by the experiments, regardless of how the water is boiled at home or in public. Thus, the results obtained from the experiments are reliable when considering the manner of boiling (including boiling times and boiling durations) designed in the experiments compared with boiling habits in daily life.

CONCLUSIONS

The two experiments (repeatedly-boiled water and prolonged-boil water experiments) successfully imitated two common habits of boiling water in daily life. The tap water used in the experiments was boiled for many more times than may happen in daily life, and the boiling time was also much longer. The water quality changes of the two experiments were very similar, which were modest in general and not as great as may be imagined by the public. The water quality initially depended on the quality of the tap water, but was gradually dominated by the physiochemical effects occurring in the boiling water container with the experiments going on. The main physiochemical effects were the water evaporation and the resulting concentration of unreactive components, which involved most dissolved chemicals. The other effects contained the precipitation of calcium carbonate and calcium sulfate, and the volatilization of carbon dioxide and ammonia. Dominated by these effects, the salinity (TDS) did not increase gradually but fluctuated because of the offsetting effect between the increasing and decreasing factors. Temporary hardness, sulfate and ammonia decreased gradually in the experiments; concentration effects of nitrate, nitrite and heavy metals, as well as other unreactive chemicals, indeed occurred but was very limited. In fact, no other complicated or mysterious effects took place except the effects discussed above which could be explained by the existing simple evaporation-concentration theory. The theory can be expressed simply as, how much percentage of the water in the boiling container is evaporated, and how much percentage of the concentrations of the unreactive components in the water will

increase accordingly. In general, the changes in the amplitudes of all dissolved chemicals in the water, including those harmful to human health, will be very limited, without degrading the water quality grade. That is, the quality of the tap water will still be safe for drinking after being frequently boiled or after prolonged boiling, as long as it satisfies the sanitary standards of drinking water prior to heating. Therefore, there is no need to worry about drinking repeatedly-boiled water or prolonged-boil water in daily life.

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