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Shale gas wastewater characterization: comprehensive detection, evaluation of valuable metals, and environmental risks of heavy metals and radionuclides

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Abstract: Shale gas wastewater (SGW) has great potential for the recovery of valuable elements, but it also poses risks in terms of environmental pollution, with heavy metals and naturally occurring radioactive materials (NORM) being of major concerns. However, many of these species have not been fully determined. For the first time, we identify the elements present in SGW from the Sichuan Basin and consequently draw a comprehensive periodic table, including 71 elements in 15 IUPAC groups. Thus, we analyze the elements offering recycling opportunities or with risk potential . Most of the metal elements in SGW exist at very low concentrations (< 0.2 mg/L), including rare earth elements, revealing poor economic feasibility for recovery. On the contrary, salts, strontium (Sr), lithium (Li), and gallium (Ga) are in higher concentrations and have impressive market demand, hence great potential to be recovered. As for environmental burdens related to raw SGW management, salinity and Fe, Cu, As, Mn, V pose the highest threats. Nevertheless, Pb, Hg, Cd, Cr, Ni, Sb, and Tl with very high intrinsic ecotoxicity are all in very low concentrations (BDL or < 5 μg/L) and within safety ranges, although their cumulative effect cannot be ignored in the long-term. The gross α activity and gross β activity in SGW range from 3.71-83.4 Bq/L, and 1.62-18.7 Bq/L, respectively, with radium-226 as the main component. Therefore, radioactivity is much higher than the safety range. The advanced combined process "pretreatment-disk tube reverse osmosis (DTRO)" with pilot-scale is evaluated for the safe reuse of SGW. This process has high efficiency in the removal of metals and total radioactivity. However, the gross α activity of the effluent (1.3 Bq/L) is slightly higher than the standard for discharge (1 Bq/L), which is thus associated with potential long-term environmental hazards.

Keywords: shale gas wastewater (SGW), heavy metal elements, naturally occurring radioactive material (NORM), safe disposal, resources recovery

1. Introduction

Abundant reserves of unconventional shale oil and gas have profoundly affected the energy landscape in China (Mayfield et al. 2019). Although the extraction of shale gas in China started ~10 years later than that in the United States, China is witnessing a shale gas boom and has become the third-largest shale gas producer in the world. The Sichuan Basin is the most active and commercially mature shale gas region in China. Fuling, Weiyuan, Changning, and Zhaotong are the four major shale gas blocks in the Sichuan Basin (Wei et al. 2021).

Horizontal drilling and hydraulic fracturing techniques for shale gas extraction rely heavily on water consumption, as 20,000 to 50,000 m^3 water is needed for the exploitation of each well in the Sichuan Basin (Liu et al. 2022). A fraction of 15%-50% of injected water returns to the surface and generates a large amount of shale gas wastewater (SGW). The composition of SGW is very complex due to the long-term interaction with the formation brine, containing high levels of total dissolved solids (TDS), diverse metal elements, a variety of organic compounds, and naturally occurring radioactive materials (NORM) (Chang et al. 2019a, Huang et al. 2020, Liu et al. 2020, Sun et al. 2021, Tang et al. 2020, Xie et al. 2022, Zhong et al. 2021). The new developments to rational SGW management comprise not only the removal of these contaminants but also the recycling of valuable metals, potentially contributing to economic benefits and meeting strategic needs. However, up to now, the types and concentrations of valuable metal elements in SGW have not been comprehensively analyzed. Studies only reported that sodium chloride, lithium (Li), uranium (U), or rare earth elements might have resource recovery potential (Chang et al. 2019b, Emmons et al. 2022, Kumar et al. 2019, Tian et al. 2020). However, the economic feasibility of the recovery of valuable metals from SGW as secondary

raw materials has not been studied. This feasibility is determined by the concentration, market price, extraction cost, and market demand of each element (Shahmansouri et al. 2015).

Reports on the adverse effects of shale gas extraction on infant health (Currie et al. 2017), and the contamination of SGW to local ecosystems from poor management have raised public concerns (Kondash et al. 2018). It is necessary to comprehensively detect harmful substances in SGW, especially heavy metals and NORM. Heavy metals are among the pollutants that disrupt the ecological balance of water, soil, and air. Cr, As, Cd, Hg, Pb, Sb, Tl, Mn are typically hazardous heavy metals with high ecotoxicity, which have been detected in SGW of the Marcellus Shale (Chang et al. 2019a, Zhong et al. 2021), Bakken Shale (Lauer et al. 2016, Xiao 2021), and Denver-Julesburg (DJ) Basin (Rosenblum et al. 2017) in the U.S. Their concentrations vary greatly (BDL to greater than 1 mg/L) in different shale gas regions, due to the different geochemical characteristics of shale formations and brine. However, the analysis of heavy metals in SGW from the Sichuan Basin is very limited, and their environmental impacts and health risks have not been assessed. The same conclusion can be drawn for NORM.

SGW often contains radionuclides from shale formations, including α particles, β particles, potassium (^{40}K), radium (^{226}Ra and ^{228}Ra), cesium (^{137}Cs), lead (^{212}Pb), polonium (^{210}Po), thorium (^{228}Th, ^{230}Th, and ^{232}Th), and uranium (^{234}U, ^{235}U, and ^{238}U) (Sun et al. 2019). However, only one work (Ni et al. 2018) has reported the radioactivity of ^{226}Ra and ^{228}Ra in SGW from Weiyuan in the Sichuan Basin. In the U.S., NORM and their environmental risk assessment in shale gas regions have been determined in the Marcellus Shale (Blondes et al. 2018, Geeza et al. 2018, Gusa and Vidic 2019, Mehta and Kocar 2019), Bakken Shale (Lauer et al. 2016, Xiao 2021), and DJ Basin (Rosenblum et al. 2017). It was found that each radionuclide in DJ Basin was much lower than that in the Marcellus Shale or Bakken Shale. Long-term exposure to

radioactivity can cause major environmental and health problems, including potential negative impacts to freshwater biota and increasing risks of cancer (Geeza et al. 2018, Gusa and Vidic 2019, McMahon et al. 2019, Sun et al. 2019). Therefore, comprehensive detection of the radioactivity of SGW is necessary in the Sichuan Basin, together with assessment of potential associated risks.

Given the high risks associated to SGW management, the wide consensus is that it needs to be treated before discharge. However, despite increasingly stringent standards, treated effluents may still contain salinity or halides, heavy metals, or radionuclides that are then released into surface waters. Research reports have proven that the salinity of the receiving streams and the radioactivity of its sediments can increase, resulting to metals and radium bioenrichment, or even contaminating urban drinking water in Pennsylvania (Geeza et al. 2018, Warner et al. 2013). Therefore, the detection of water quality, including heavy metals and NORM in the effluents from treatment facilities is also of vital importance before reuse or discharge, an effort that however has been vastly neglected so far.

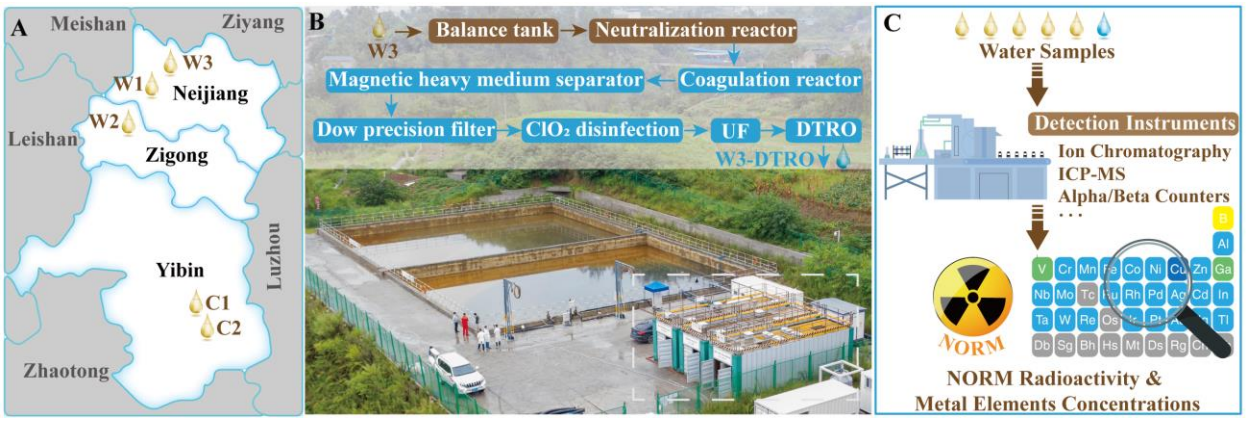
In this work, we analyze SGW from five wells in different locations of Weiyuan and Changning blocks in the Sichuan Basin, China. General water quality, heavy metals, and radionuclides are comprehensively reported to assess the potential for valuable elements recovery or environmental risks. Moreover, a combined “pretreatment-disk tube reverse osmosis (DTRO)” treatment process is discussed with the goal of SGW treatment in Weiyuan, and the quality of its effluent is comprehensively analyzed to evaluate its safety for reuse or discharge.

2. Materials and methods

2.1. Sample collection and description of the pilot-scale treatment facility

Five SGW samples from different shale gas blocks in the Sichuan Basin were collected for detection in 2021. Two of the water samples were from the Changning shale gas block (denoted as C1 and C2). C1 was obtained from Yuhua Village in Gongxian County, and C2 was from Leijiawan Village in Gongxian County. Other three water samples were collected from the Weiyuan shale gas block (denoted as W1, W2, and W3). W1 was obtained from Longhui Village in Weiyuan County, W2 was from Xinlong Village in Rongxian County, and W3 was from Macaoyan Village in Zizhong County. Their sites are depicted in Fig. 1A.

In the location of W3, an advanced process including coagulation, ultrafiltration (UF), and DTRO, etc. for the reuse of SGW was studied by construction and performance evaluation of a pilot-scale system. A photographic image and the schematic of the process train are displayed in Fig. 1B. The facility is framed within the white dotted line in this figure. The raw SGW sample W3 was treated by this combined system, and the effluent of DTRO was denoted as W3-DTRO. All water samples were preserved in sealed plastic buckets and transported to the laboratory (~2 days after collection) for analysis. Each sample was quantified with different instruments to analyze the general quality, metal elements concentrations, and NORM radioactivity (Fig. 1C). Before analysis, all samples were stored at 4 ℃ in the dark.



127 **Fig. 1. (A)** Five SGW samples from different shale gas blocks in the Sichuan Basin, China. Two
128 samples were collected from the Changning shale gas block (denoted as C1 and C2), and other
129 three were from the Weiyuan shale gas block (denoted as W1, W2, and W3). **(B)** Photographic
130 image and flow chart of the combined process for the treatment of raw SGW sample W3; the
131 final effluent is denoted as W3-DTRO. **(C)** Schematic of this study. The composition of all water
132 samples, i.e., C1, C2, W1, W2, W3, and W3-DTRO, was determined with different instruments
133 to analyze the general quality, metal elements concentrations, and NORM radioactivity.

134

135 **2.2. Analytical methods for general water quality, major cations and anions, and trace**
136 **metal elements**

137 The pH was measured with a PB-10 meter (Sartorius Scientific Instruments Co., Ltd.,
138 Germany). Dissolved organic carbon (DOC) and total nitrogen (TN) were both determined with
139 a total organic carbon analyzer (TOC-L CPH CN200, Shimadzu, Japan) after filtration of the
140 samples with 0.45-μm filters (Wanda Co., Ltd., Zhejiang, China). An Ultrameter II 6PFC
141 (Myron L Company, USA) portable multifunctional meter was utilized to acquire the value of
142 TDS and conductivity. The concentrations of major cations and anions (Na^+, K^+, Ca^{2+}, Mg^{2+},
143 Ba^{2+}, Sr^{2+}, Li^+, NH_4^+, and Cl^-, Br^-, F^-, SO_4^{2-}, NO_3^-, NO_2^-) were determined by Dionex
144 Integration HPIC ion chromatography (Thermo Fisher Scientific Inc., USA, with CS12A and
145 AS11-HC chromatographic columns) after filtration of the samples with 0.45-μm filters and
146 100× dilution for the raw SGW, or no dilution for W3-DTRO.

147 The qualitative and quantitative analysis of 57 trace metals, and 4 non-metal elements (total
148 contents in aqueous samples) was performed by inductively coupled plasma-mass spectrometry

149 (ICP-MS, NexION 1000G, Perkin Elmer, Waltham, MA). Samples were prepared in acid-
150 washed glass bottles. Prior to measurements, 13.5 mL of each sample was digested with 1.5 mL
151 of nitric acid (69.3%, UPS, Kelong Chemical Co., Ltd, Chengdu, China) for 8 min at 130 ℃, 5
152 min at 150 ℃, 5 min at 180 ℃. No suspended solids were observed after digestion and holding
153 for at least 12 hours. Therefore, filtration was not required. A field blank was also prepared using
154 the same method used for the samples. At the beginning of the measurement, three cleaning
155 blanks of 2% nitric acid were run to clear any residual contamination from previous runs.
156 Additionally, two cleaning blanks were run between every sample to ensure no crossover
157 between samples and no build-up of contamination within the machine. At least two parallel
158 measurements were run for each sample to take the average result. The concentrations of
159 elements in the field blank were subtracted to get the final results. The detection limits of the
160 elements measured by IPC-MS in this study are given in Table S2 (Supporting Information, SI).

161 **2.3. NORM analysis**

162 Six water samples of 10 L each for radionuclide analysis were collected in polyethylene
163 containers and sent to the Analytical Laboratory of Beijing Research Institute of Uranium
164 Geology for NORM detection. The gross α and β activities were determined on the Alpha/Beta
165 Counters (MPC9604, ORTEC, Tennessee, USA) according to the standards of EJ/T 1075-1998
166 and EJ/T 900-1994, separately. The concentrations of uranium (U) and thorium (Th) were
167 obtained with ICP-MS, as discussed above, following the guide of Water Quality-Determination
168 of 65 Elements-Inductively Coupled Plasma-Mass Spectrometry (HJ 700-2014). The
169 radioactivity of potassium-40 (^{40}K) was measured with an atomic absorption spectrophotometer
170 (Z-2000, Hitachi, Japan) following the guide of Analytical Methods of Potassium-40 in water
171 (GB 11214-1989). The activities of technetium-90m (^{90m}Tc), cesium-137 (^{137}Cs), cobalt-60 (^{60}Co)

and radium-228 (^{228}Ra) were determined on high purity germanium (HPGe) γ-spectroscopy counted 580,000 s with the volume of 0.2 L, referring to the standard of Determination of Radionuclides in Water by Gamma Spectrometry (GB/T 16140-2018). Radium-226 (^{226}Ra) was analyzed by radium radon emanation (PC-2100) using GB 11214-1989. Plumbum-210 (^{210}Pb) was also analyzed by alpha/beta counters with the guide of EJ/T 859-1994. Polonium-210 (^{210}Po), $^{234}U/^{238}U$, and $^{230}Th/^{232}Th$ were measured with α-spectroscopy (OCTE-PLUS) by GB/T 13071-2010.

3. Results and discussion

3.1. General quality of SGW and major ions

The general water quality and concentrations of major cations and anions in raw SGW samples in Sichuan Basin are presented in Table S1 (SI). The TDS and DOC levels were similar to those commonly reported in other research (Chang et al. 2019a, Huang et al. 2020, Liu et al. 2020, Tang et al. 2020, Tang et al. 2021, Zhong et al. 2021), with TDS values between 13,730 mg/L (C2) and 31,090 mg/L (C1), and with relatively low DOC levels of 4.26 (C1) to 26.8 mg/L (C2). The main inorganic ions in SGW were Na^+ and Cl^-, which accounted for 80%-95% of the total TDS. Ca^{2+}, Ba^{2+}, Sr^{2+} and Mg^{2+} were major divalent cations. Li^+ (11.5-33.7 mg/L) was also in medium-to-high concentrations, which may be considered to have recycling potential (Kumar et al. 2019), and this topic will be discussed in the next section. Br^- was another important anion, accounting for 0.4%-0.6% of TDS. Generally, these concentrations were in the same range as those reported before relative to SGW in the Sichuan Basin (Chang et al. 2019a, Huang et al. 2020, Liu et al. 2020, Liu et al. 2021, Shang et al. 2020, Tang et al. 2020, Tang et al. 2021, Zhong et al. 2021). We also report the data associated with the shale gas regions of Bakken, DJ

Basin, and Marcellus in the U.S., for comparison. Although the salinity and organics content in different regions are largely different, the main ion composition is the same.

3.2. Potential to valuable elements recovery

Based on the analyses conducted for major ions (Table S1), trace metals (Table S3, Table S4), and non-metals (Table S5), the average concentration ranges of 71 elements in 15 IUPAC groups in raw SGW samples (C1, C2, W1, W2, W3) are summarized in Fig. 2A. Except for the known dominant elements, other metal elements that existed in SGW are in low concentrations (BDL-2 mg/L). Among them, the elements Ag, Al, Au, Be, Bi, Pb, Se, Sn, Hf, Hg, Ir, Nb, Ta, Te, Pt, Pd, In, Zr, Zn, as well as some rare earth elements, e.g., Ce were below the detection limits, hence unrecoverable. Other valuable metals, such as Li, uranium (U), and other rare earth elements, were found at diverse concentrations. In order to assess their recovery potential, the average concentrations and market prices (Table S6, SI) of the elements higher than detection limits are provided in Fig. 3A (U. S. Geological Survey 2021, https://en.institut-seltene-erden.de/aktuelle-preise-von-seltenen-erden/).

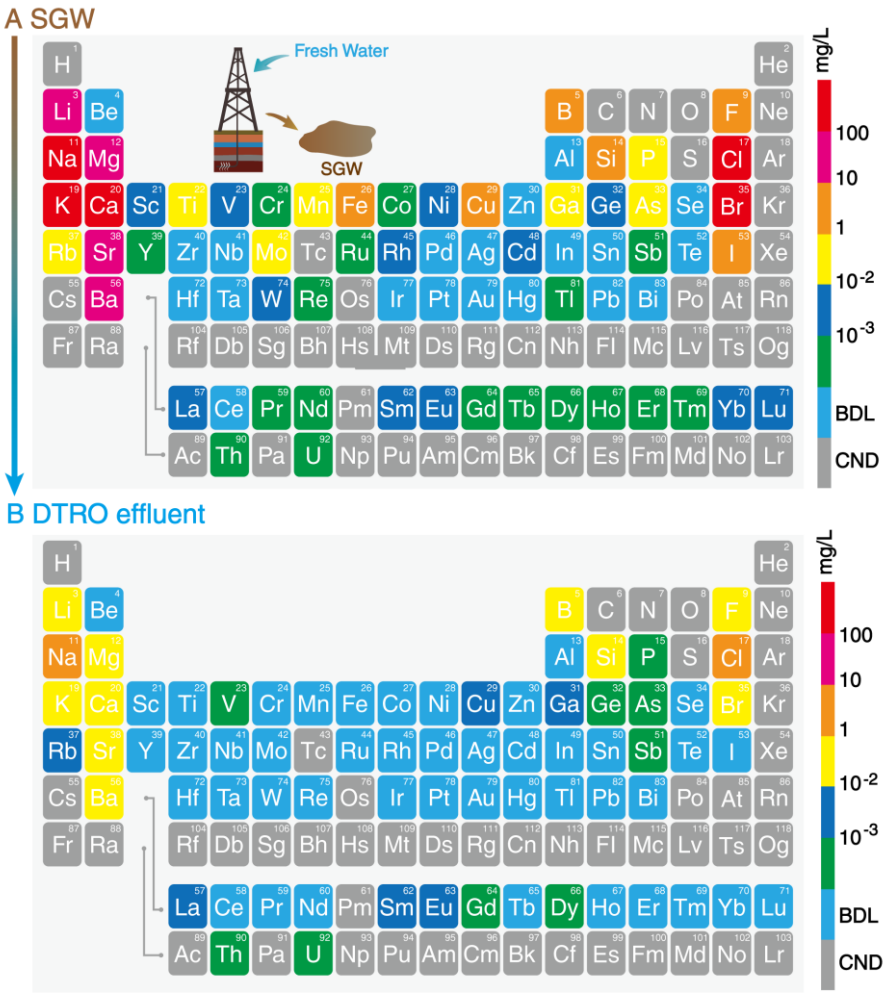


Fig. 2. (A) Periodic table of the average concentration ranges of major and trace elements in raw SGW samples (C1, C2, W1, W2, W3) from the Sichuan Basin. **(B)** Periodic table of the concentration ranges of major and trace elements in the effluent of treated sample (W3-DTRO). "BDL" stands for "below the detection limit", and "CND" stands for "could not analyze". The concentrations of Li, Na, K, Mg, Ca, Sr, Ba, F, Cl, and Br are related to the ionic concentrations.

Generally speaking, the concentration, market price, and extraction cost determine the economic feasibility of recovering an element from SGW, as illustrated by Shahmansouri *et al*.

217 (Shahmansouri et al. 2015). In this study, for simplicity, the extraction cost ratio is normalized to
218 1 for all elements. Thus, if the product cost (market price × average concentration in SGW) of an
219 element is greater than 1, it means that the extraction of this element from SGW may be
220 economically feasible. In Fig. 3A, the elements represented by a red dot may be potentially
221 recovered with economic feasibility, and the dots placed in the top right corner represent the
222 most economical conditions. Although many kinds of metal elements were contained in SGW,
223 from the practical point of view, only a limited number may be feasibly recovered. The recovery
224 of Na, Mg, Ca, Ba, K, and useful nonmetal elements, *e.g.*, Br, which were found in high
225 concentrations in SGW, is technically feasible. At the same time, these elements are in high
226 market demand, illustrating that they are suitable and promising for extraction from SGW. Sr and
227 Li were also in medium-to-high concentrations, as well as in high demand. However, their
228 extraction method from SGW is currently being studied and not mature yet. Electrochemical
229 separation and adsorption are regarded as the most promising techniques (Kumar et al. 2019).

230 Rb and Ga both were found at concentrations higher than 0.2 mg/L, and are associated with
231 high market prices. Ga-based products have been used in defense applications, fifth-generation
232 (5G) networks, cable television transmission, commercial wireless infrastructure, power
233 electronics, and satellite. China is the largest producer of Ga (290 tonnes out of 300 globally).
234 However, as for Rb, although its price is higher, the application demand is low (2 tonnes in the
235 U.S.in 2020). Rb and its salts have little commercial use, and small amounts are produced for
236 research purposes mostly (https://www.lenntech.com/). Therefore, Ga is more suitable for
237 recovery from SGW than Rb. As for Ru, Rh, and Ge, their concentrations and demands were
238 low. Their extraction is costly, technically complex, and not suitable for recovery as of today.

The extraction of elements depicted with the blue dots is not economical, including rare earth elements. However, considering their strategic significance to economy and security, it is necessary to develop extraction technologies from SGW, which may be complex and costly but ultimately advantageous. Among them, Sc (6.46-12.7 μg/L), Sm (4.89-9.54 μg/L), and Eu (3.39-5.98 μg/L) were in relatively higher concentrations and probably the most potentially recyclable ones. Elements that are in low concentrations in raw SGW may be substantially higher in other streams, such as concentrates (*e.g.*, RO concentrate), which would represent better sources for extracting these valuable elements.

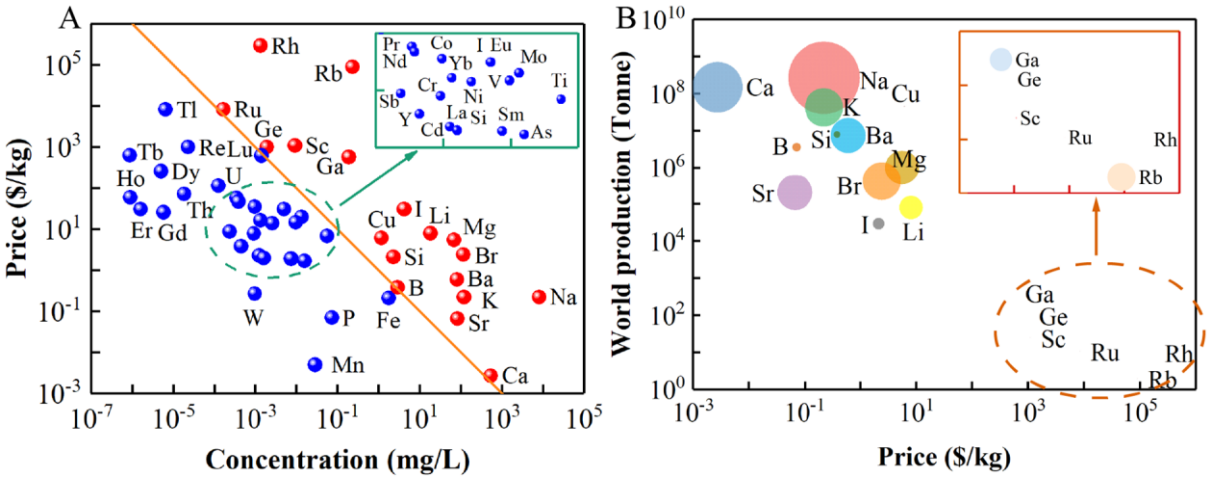


Fig. 3. (A) Average concentration of elements in SGW from the Sichuan Basin and their market prices. The elements shown in the figure do not include those found to be below the detection limits. Element concentration value is the average of five SGW samples. The market prices are based on 2020 USGS metal commodities summaries (U. S. Geological Survey 2021), and the prices for rare earth elements are based on the statistics of The Institute for Rare Earths and Metals AG (https://en.institut-seltene-erden.de/aktuelle-preise-von-seltenen-erden/). The preliminary economic feasibility of recovering an element from SGW is assessed based on its concentration and market price, as well as the extraction cost, and the details are illustrated by

Shahmansouri *et al*. (Shahmansouri et al. 2015). **(B)** Prices, world production, and concentration of elements characterized by economic feasibility of extraction. Bubble sizes represent the logarithm of elements' average concentrations in SGW (U. S. Geological Survey 2021). Note that there is no official data on the world productions of Rb, Ru, or Rh in 2020. Therefore, the corresponding data refer to the consumption in the U.S. Finally, world production of B excludes that in the U.S.

3.3. Potential health and environmental impacts of inorganic compounds in SGW

The salinity, metals, and NORM in SGW would likely cause environmental pollution and harm to human health following spills/leakage into soil, surface water, or groundwater (Sun et al. 2019). We assessed in detail the metal distribution and concentrations (Fig. 2), as well as NORM radioactivity (Fig. 4, Table S7) of SGW from the Sichuan Basin to estimate its potential risks to the environment and to human health. A detailed description of the health effects and environmental impacts of all inorganic compounds above the detection limits in SGW is reported in Table S8 (SI). The high TDS of SGW will increase salinity levels in nearby waters, which has influence on fish and other aquatic species. The concentrations of Cl, F, Ba, B, and NO_3^- in SGW were far higher than the values associated with Drinking Water Standard (GB 5749-2022). The leakage into soil or surface water can do harm to plants and aquatic life. Br^- may also cause ecotoxicity effects (Jiang et al. 2014). The leakage into drinking water sources can cause the formation of carcinogenic disinfection byproducts (Huang et al. 2018).

Regarding heavy metals, their non-degradability and accumulation behavior in organisms may induce lasting environmental impacts. Al, Fe, Cr, Sb, As, Be, Cd, Cu, Pb, Hg, Ni, Se, Ag,

and Zn are listed as primary contaminant metals by the U. S. Environmental Protection Agency (EPA) for their potential biotoxicity and wide-ranging presence. As, Pb, Hg, Cd, Cr, Ni Sb, and Tl are the most harmful ones with high ecotoxicity. In raw SGW from the Sichuan Basin, the composition of heavy metals was varied, but concentrations were generally low. Cu (903-1451 μg/L) and Fe (435-5727 μg/L) were in the highest concentrations among all heavy metals, far higher than the values in the Drinking Water Standard and Integrated Wastewater Discharge Standard (GB 8978-1996). When released into the environment, they may accumulate in soil and surface water and eventually reach plants and animals. Cu has negative effects on microorganisms and earthworms and may reduce plant diversity. The concentrations of As, Mn, and V also exceeded the Drinking Water Standard. The high ecotoxicity of As may increase the chances of alteration of genetic material of fish, and thus element is also readily absorbed by plants. Eventually, it will enter the human body through the food chain, resulting in potential health hazards. Other elements, i.e., Rb, Ga, Ti, and Mo were in relatively high concentrations (> 20 μg/L) in SGW. Rb, Ga, and Ti are related with weak health and environmental risks. Nevertheless, Mo is characterized by high toxicity to humans and animals due to its teratogenicity, but its concentration in SGW was below the Drinking Water Standard, thus associated with potentially impacts. The rare earth elements, Sc, Tm, and Eu with concentrations of ~10 μg/L have no known biological role, and would likely pose no threat to plants or animals. Finally, the elements, Pb, Hg, Cd, Cr, Ni, Sb, and Tl with very high intrinsic ecotoxicity were all in very low concentrations (BDL or < 5 μg/L) and within safety ranges, leading to relatively low environmental impacts in the shale gas region. However, their cumulative effect may not be negligible in the long term. Other heavy metals were below 1 μg/L in SGW, and have low to moderate toxicity, thus inducing negligible environmental impacts.

The presence of NORM represents another significant risk in SGW. Fig. 4 displays the gross α activity and gross β activity that reflect the overall radioactivity levels of raw SGW from the Sichuan Basin, which were in the ranges 3.71-83.4 Bq/L, and 1.62-18.7 Bq/L, respectively. The contribution to gross α activity mainly came from ^{238}U, ^{232}Th, ^{226}Ra, while the gross β activity from ^{40}K (Shi et al. 2021). Their values were much higher than those in Drinking Water Standard and Integrated Wastewater Discharge Standard, implying serious radiation risks. Long-term exposure to radioactivity can cause major health problems related to cancer. Any leak into the environment would induce comprehensive, systematic, and persistent radioactive pollution to the surrounding water and soil, affecting animals and plants around the shale gas regions (Shi et al. 2021). From Fig. S1 (SI), it can be seen that there is some correlation between radioactivity and TDS (R^2=0.5182), because formation brine with higher salinity will promote the dissolution of radioactive material from the shale, as reported by previous research (McMahon et al. 2019, Vengosh et al. 2009).

Specifically, the gross α activity of the water samples had a strong correlation (R^2=0.9745) with Ra isotopes (^{226}Ra + ^{228}Ra), as depicted in Fig. S2 (SI). ^{224}Ra has a short half-life of 3.6 days, so it was not considered in this study. Considering that the radioactivity of ^{228}Ra was below the detection limit (<1.1 Bq/L), ^{226}Ra radioactivity was mostly responsible for the gross α activity of the SGW. Previous research has reported that ^{226}Ra with a half-life of 1600 years was the major component of NORM and also the major contributor of radioactivity in SGW (Gusa and Vidic 2019). The correlation between Ra radioactivity and TDS and alkaline earth metal concentration of Ba is shown in Fig. S3 (SI). The concentration of alkaline earth metal Ba had strong correlation (R^2=0.8318) with the radioactivity of Ra, indicating that Ba is a better predictor of Ra activity than TDS. This phenomenon has also been reported by other reports (Fan

et al. 2018). ^{226}Ra and ^{228}Ra are the decay products in water of ^{238}U and ^{232}Th existing in the shale of Lower Silurian Longmaxi Formation of the Sichuan Basin. The low radioactivity of ^{228}Ra may due to the low concentration of ^{232}Th in the shale. To summarize, ^{226}Ra was the major component of NORM, presented at radioactivity levels as high as 0.31-19.5 Bq/L in all SGW samples from the Sichuan Basin. This result was consistent with the only previous report of radioactivity in SGW in Weiyuan of the Sichuan basin (Ni et al. 2018). This was much higher than the Drinking Water Standard (1 Bq/L), implying that raw SGW would cause Ra pollution to the surrounding water and soil. Plants and animals would likely absorb this element from the soil and water, and accumulate, bio-magnify up the food chain. Eventually, it would likely cause health problems to people in surrounding areas (https://www.lenntech.com/).

Analyzing the numbers in more detail, the concentrations of U and Th in raw SGW were very low and in the ranges 0.067-0.17 μg/L (U) and 0.003-0.064 μg/L (Th), respectively. The concentration of U was much lower than the Drinking Water Standard of 30 μg/L. The data also illustrates for the first time that the radioactivity of ^{210}Po in samples from Weiyuan and Changning had very low value, ranging from 0.011 to 0.259 Bq/L, below the US EPA drinking water guidelines (0.555 Bq/L). However, the values of ^{210}Pb in C2 and W2 were slightly higher than the US EPA guidelines for ^{210}Pb exposure by ingestion (0.115 Bq/L). The radioactivity of ^{210}Pb and ^{210}Po in SGW from the Sichuan Basin were a little higher than that in DJ basin in the U.S. (Rosenblum et al. 2017). Other radioactivity indexes, including ^{90m}Tc, ^{137}Cs, and ^{60}Co, were too low for detection. In general, the radioactivity of SGW in the Sichuan Basin was found to be much lower than that in the Marcellus Shale and Bakken Shale in the U.S., and in a similar range to that in DJ Basin in the U.S. This may be attributed to the presence of low levels of parent radionuclide ^{238}U in the formation and to the low salinity of the formation brine. However, the

radioactivity was still significantly higher than the safe range, potentially posing health and environmental risks in the shale gas regions.

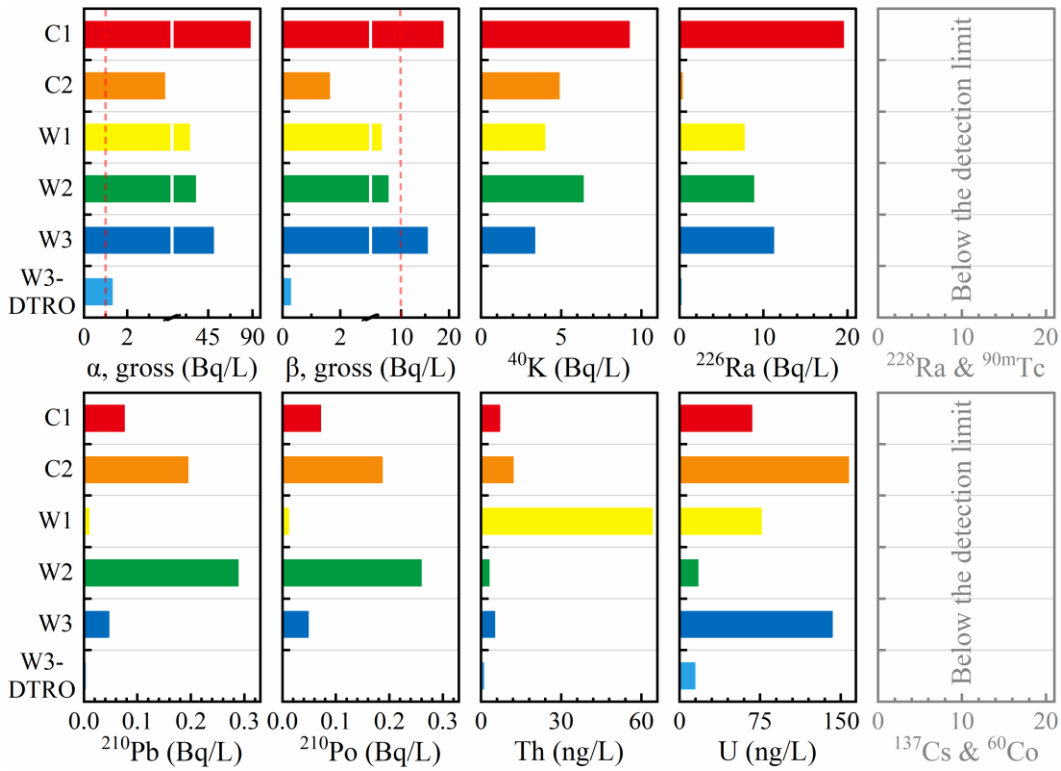


Fig. 4. Radioactivity of NORM in raw SGW samples (C1, C2, W1, W2, W3) and in the effluent treated sample (W3-DTRO). The red dotted line represents the limit value specified by Integrated Wastewater Discharge Standard (GB 8978-1996).

3.4. Safety of the effluent from the "pretreatment-DTRO" treatment system

In order to obtain good effluent quality, advanced DTRO technology with relatively high cost and high energy consumption was investigated. The detailed water quality of the effluent of the combined system (W3-DTRO, Fig. 1B), including general parameters, concentrations of

major ions, and trace metals is summarized in Table S8 (SI), and Fig. 2B. Upon treatment, W3-DTRO had a very low TDS value of 14.9 mg/L, associated with a removal rate >99.9%, with NaCl being the main component left. The concentrations of Cl, F, Ba, B, and NO_3^-, which were higher than the standards in raw SGW, were all within the safety ranges after treatment. The concentration of Br was as low as 0.06 mg/L, lower than the concentrations which can typically lead to the formation of disinfection by-products (0.1 mg/L). As for heavy metals, most were below the detection limits in the effluent, except for Ga (9.97 μg/L), Cu (2.55 μg/L), Rb, La, Sm, Eu with concentrations ~1 μg/L, and As, V, Ge, Gd with concentrations ~ 0.1 μg/L. All the heavy metal indexes were lower than the Drinking Water Standard, indicating negligible ecotoxicity to the environment of shale gas regions.

The radioactivity of W3-DTRO effluent is displayed in Fig. 4. The combined treatment process had the removal rates greater than 95% for all indexes, reaching a gross α activity of 1.3 Bq/L and a gross β activity of 0.27 Bq/L. The gross α activity was a little higher than that of the Drinking Water Standard (0.5 Bq/L) and Integrated Wastewater Discharge Standard (1 Bq/L), and may result in sub-standard discharge to surface water. Continuous discharge may induce persistent radioactive pollution to the surrounding water and soil, thus affecting animals and plants. Opportunely, W3-DTRO had a very low Ra radioactivity of 0.177 Bq/L, meeting the Drinking Water Standard of 1 Bq/L. Moreover, the radioactivity of ^{210}Pb and ^{210}Po in W3-DTRO were 0.002 Bq/L and 0.001 Bq/L, respectively. The radioactivity of ^{210}Pb was below the US EPA guidelines for ^{210}Pb exposure by ingestion (0.115 Bq/L), and the radioactivity of ^{210}Po was even below the US EPA drinking water guidelines (0.555 Bq/L), implying negligible occupational and public health risks.

In general, the advanced "pretreatment-DTRO" combined system was found to be highly efficient in the removal of organics (> 95% of DOC), inorganic contaminants (> 99% of TDS) and NORM radioactivity (> 97% of α activity) from raw SGW in the Sichuan Basin, and the effluent water quality met the Drinking Water Standard and Integrated Wastewater Discharge Standard (Table. S8, SI), except for the index of gross α activity. Long-term exposure to radioactivity can cause major environmental and health problems, including potential negative impacts to freshwater biota and increasing risks of cancer (Geeza et al. 2018, Gusa and Vidic 2019, McMahon et al. 2019, Sun et al. 2019). Therefore, a specific polishing step may be additionally required for this index. Note that the DTRO technology is usually more effective than the traditional and commonly used RO technology in removing various contaminants (Chen et al. 2021). Therefore, the radioactive safety of a possible RO effluent would likely be higher and not meet the required standards.

4. Conclusions

For the first time, our research presented an in-depth analysis of SGW characteristics from different wells in Weiyuan and Changning shale gas blocks of the Sichuan Basin, comprehensively illustrating the composition of major anions, cations, trace heavy metals, and NORM, including 71 elements in 15 IUPAC groups. Although many kinds of valuable elements existed in SGW (including rare earth elements), only a few may be suitable for extraction when considering their concentration, market price, world demand, and extraction difficulty, mainly including common salts, as well as Sr, Li, and Ga. Additional efforts are needed to develop efficient extraction methods, such as electrochemistry and adsorption.

As for the potential risks associated with poor management of SGW, salinity, metals, and NORM are major inorganic compounds that may cause environmental pollution and harm to human health. Considering combined toxicity and concentrations, Fe (>0.5 mg/L), Cu (>0.5 mg/L), As (14.6-18.2 μg/L), Mn (BDL-109.5 μg/L), and V (7.44-11.7 μg/L) may pose the highest risks. Pb, Hg, Cd, Cr, Ni, Sb, and Tl with very high ecotoxicity were all in very low concentrations (BDL or < 5 μg/L), but their cumulative effect may not be ignored in the long term. Also, the gross α activity and gross β activity of the water samples (3.71-83.4 Bq/L and 1.62-18.7 Bq/L, respectively), as well as ^{226}Ra, were far higher than the discharge standards. This may induce persistent radioactive pollution to the surrounding water and soil, affecting animals and plants. By accumulating, and bio-magnifying up the food chain, these elements may eventually influence human health.

In the effluent of "pretreatment-DTRO" combined process, both DOC (0.669 mg/L) and TDS (14.9 mg/L) were very low. However, gross α activity (1.3 Bq/L) was a little higher than the standard for Integrated Wastewater Discharge (GB 8978-1996) of 1 Bq/L. The long-term sub-standard discharge may lead to radioactive contamination in the water environment. The effluent quality of advanced DTRO technology is expected to be of higher quality than any effluent from traditional RO filtration, which raises concerns about the radioactive contamination of SGW effluents treated with RO technology.

CRediT authorship contribution statement

Wancen Xie: Methodology, Validation, Formal analysis, Investigation, Visualization, Writing - original draft. **Lun Tian:** Validation, Formal analysis, Investigation. **Peng Tang:** Methodology, Data curation. **Jianyong Cui:** Investigation**. Tiejian Wang:** Investigation**. Yingming Zhu:** Investigation**. Yuhua Bai:** Methodology. **Alberto Tiraferri:** Formal analysis,

Visualization, Writing - review & editing. **John C. Crittenden:** Writing - review & editing. **Baicang Liu:** Conceptualization, Supervision, Writing - review & editing.

Supporting information.

The supporting information is available free of charge.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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