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Investigation of arsenic contamination in groundwater using hydride generation atomic absorption spectrometry

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Abstract The validated hydride generation atomic absorption spectrometry (HG-AAS) method has been used to investigate total arsenic in groundwater. Under optimal experimental conditions, the concentration of arsenic in groundwater can be analysed in the range of 0.5 to 50 µg/L, with a method detection limit of 0.15 µg/L. Its recovery in the field is from 96.3 to 99.8%, with high repeatability. The method was used to observe the total arsenic pollution in groundwater collected in Phu Tho Province, Vietnam. A total of 364 groundwater samples were analysed. The results showed that arsenic pollution was significant, with 15.93% of the samples higher than the maximum permissible level of arsenic. About 20.69% of the contaminated samples had a total arsenic ten times higher (100 µg/L) than the maximum permissible level of arsenic. The pollution source was also considered by comparing the arsenic level in the groundwater with arsenic in the surface water in the same areas. Thus, the use of the high-accuracy and sensitive method, HG-AAS, supplies valuable data on groundwater pollution for water resources management and environmental protection.

Keywords HG-AAS · Arsenic · Groundwater · Pollution · Natural toxicant

Introduction

Arsenic (As) is one of the representative hazardous elements that cause significant health complications, such as liver disease (Hsu et al., 2016), cardiovascular disease (Navas-Acien et al., 2019), respiratory disease (Sancheza et al., 2016), type 2 diabetes mellitus (Beck et al., 2017) and cancers (Martinez et al., 2011; Wei et al., 2019). As exposure occurs primarily through ingestion of contaminated food and drinking water, besides inhalation and absorption through the skin. Arsenic in drinking water is a direct cause of human health problems and thus, is a severe worldwide human health concern. The amount of arsenic in drinking water accumulates over time, and if the dose is large enough, it will cause disease (Hong et al., 2014).

Arsenic pollution in groundwater has both natural and anthropogenic causes. The natural causes are geological and sedimentary processes under the influence of oxidation, reduction or biochemical processes (Bissen & Frimmel, 2003). The primary natural

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sources include geological formations (e.g. sedimentary deposits/rocks, volcanic rocks and soils), geothermal fluids, coal and volcanic activities (Missimer et al., 2018; Smedley & Kinniburgh, 2002). Anthropogenic sources include anthropogenic activities such as coal burning, emissions, As-containing wastewater, pesticides, irrigation water and industrial waste (Nriagu et al., 2007; Shankar et al., 2014).

There have been many reports of arsenic poisoning from drinking water, nearly 50% of the raw water of which is supplied by groundwater. According to Smith et al. (2000) and Flanagan et al. (2012), estimated tens of millions of people in Bangladesh have been exposed to arsenic-contaminated water, resulting in approximately 24,000 deaths each year. Kwanyuen et al. (2017) reported that in Ron Phibun town, Thailand, about 1000 people had been diagnosed with As-related skin disorders. Alarcón-Herrera et al. (2013) claimed that 8.81 million people were exposed to a high level of arsenic in groundwater. Ravenscroft et al. (2009) revealed that South American countries such as Guatemala and El Salvador have high As content in their water resources, detected from volcanogenic.

Vietnam has one of the highest levels of natural contamination of arsenic in groundwater (Shaji et al., 2020). Nguyen et al. (2018, 2020) reported that in Thai Nguyen Province, 75% of groundwater samples had more than the permissible limit of arsenic in groundwater set by the World Health Organization. Winkel et al. (2011) and Stopelli et al. (2020) also found arsenic-contaminated groundwater in deep aquifer exploitation areas in Ha Noi and in the Red River delta. Although several studies have observed the level of arsenic contamination in groundwater, the fulfillment data in many areas in Vietnam, especially in mineral-rich regions, mountainous areas and highlands, have not been thoroughly studied yet.

In this study, a validated method based on HG-AAS was used to investigate total arsenic contamination in groundwater in Phu Tho Province, Vietnam. This province has many pegmatite mines of original hydrothermal and sulphide, such as kaolin, fenspat, mica, quartzite, pyrite and iron, which can be the natural sources of arsenic in groundwater. About 40 wards in most communes in Phu Tho province, especially in mineral areas with over 360 groundwater samples, will be collected for the observation. Surface water samples will also be collected at the arsenic-contaminated location to find out if the cause of the pollution is natural or artificial. The research results can provide reliable data for managing and using groundwater resources most safely.

Materials and methods

Materials and reagents

All the reagents used in this study were of analytical grade. Arsenic standard solution (1000 mg/L As^{V}) traceable to SRM from NIST (H_3AsO_4 in 0.5 mol/L HNO_3) was purchased from Merck (Merck, Darmstadt, Germany). Potassium iodide (purity $\geq$ 99.5%), L-ascorbic acid (99% purity) and hydrochloric acid (36.5–38%) were purchased from Sigma-Aldrich (Singapore). All the solutions were prepared and diluted using ultra-pure water with an electrical resistivity > 18.3 MΩ·cm produced by the Barnstead Water Purification Systems.

Groundwater sampling

Groundwater was sampled according to ISO 5667–11: 2009 (ISO, 2020). The samples were collected from water wells that were used for drinking and living. The water wells were either dug wells (depth: 15–20 m) or drilled wells (depth > 25 m). Groundwater was pumped out for 10–15 min from the drilled wells and drained for 5–10 min from the dug wells before the sampling. The groundwater samples were collected in 1-L polypropylene cans and acidified with 1 mL of concentrated nitric acid before they were brought to the laboratory for storage, sample preparation and analysis. The sampling position is presented in Fig. 1.

Sample preparation and analysis

The samples were prepared in the following three steps according to ISO 17378–2:2014 (ISO, 2019). First, 20 mL of hydrochloric acid ($\rho = 1.15$ g/mL) was added to 4 mL of a mixed solution of potassium iodide and ascorbic acid [3 g potassium iodide KI and 5 g L (+) − ascorbic acid in 100 mL of water] in a round-bottom flask that contained 50 mL of

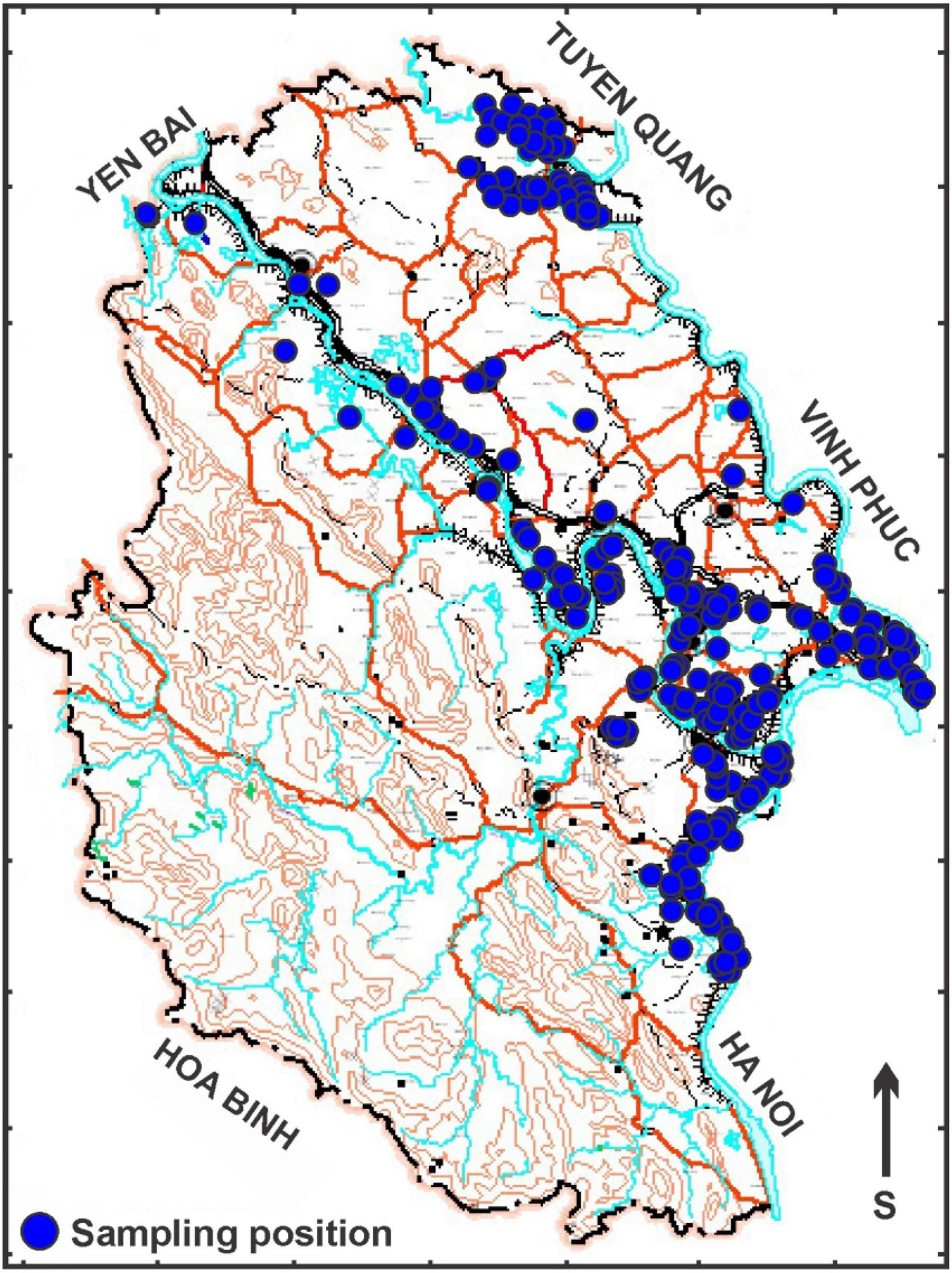

Fig. 1 Groundwater sampling for arsenic determination in Phu Tho Province

groundwater sample. Second, this mixture was gently heated for 15 min at 50 °C to convert all the arsenic into the As^{III} form. Finally, the solution was cooled to room temperature, transferred to a volumetric flask and diluted to a final volume of 100 mL. A total of 0.5 mL of this solution was injected into the flow injection hydride generator (Perkin Elmer FIAS 100 Flow Injection for AAS) and analysed using atomic absorption spectrometry (Perkin Elmer AAnalyst 800, USA) at the operating conditions, as shown in Table 1. The calibration curve was prepared in the same way as the sample, except that the sample was replaced with a blank matrix (arsenic-free) spiking various amounts of As^{V}.

Results and discussion

HG-AAS method verification

To confirm the accuracy of the HG-AAS method that was used in this study, its merits such as linearity, method detection limit (MDL), accuracy and precision were sequentially evaluated, according to the standards of the Association of Official Analytical Chemists (AOAC, 2016) and ISO/IEC 17,025–2017 (ISO, 2017).

The linearity was observed with various concentrations of As^{III}, from 0.5 to 50 µg/L. The calibration curves obtained with the coefficient correlation (R^2) were higher than 0.997. R^2 was stable on 3 different days. The MDLs in the determination of arsenic were calculated from the three-time standard deviation (SD) that was calculated from 11 repetitive analysis spiked samples. As shown in Table 2, the average MDL for As determination ranged from 0.10 to 0.15 µg/L, whereas the published MDL of this method was 0.15 µg/L. According to the maximum permissible As limit of 10 µg/L, the obtained MDLs were highly sensitive to the determination of arsenic in groundwater. The average concentration to the MDL value, from 5.7 to 6.5, confirmed that the spike level in the experiments had high concordance.

Table 1 Operating conditions of HG-AAS for determination total arsenic in groundwater

Instrument parameter	
Atomic absorption spectrometer Perkin Elmer A800	
Wavelength	193.7 nm
Spectral band-pass	0.7 nm
Lamp	EDL
Lamp current setting	380 mA
Cell temperature	900 °C
Hydride generation Perkin Elmer FIAS 100	
Reducing agent	0.2% (w/v) $NaBH_4$ in 0.05% (w/v) NaOH
Carrier solution	HCl solution 10%
Carrier gas	Argon, 100 mL/min flow rate
Pump	120 rpm
Loop sample	0.5 mL

The accuracy of the method was evaluated based on the recovery value, repeatability and intermediate reproducibility. By repeatedly analysing the sample with different spiking concentrations of arsenic, the recovery value and the relative standard deviation (*RSD*) percentage were calculated and are shown in Table 2. The recoveries varied from 96.3 to 99.8%, much better than the required value (60 to 115% at the corresponding level). This demonstrated the high trueness of the quantification. The maximum *RSD* in the arsenic determination was 3.69%. According to the RSD Horwitch function or the AOAC, the obtained *RSD* was much lower than the maximum acceptable value for a concentration of 100 µg/L (15%). Therefore, the method exhibited excellent repeatability precision for determining arsenic in groundwater.

The uncertainty was measured based on a combination of "top-down" and "bottom-up" approaches (ISO/IEC, 2008; EURACHEM/CITAC, 2012). From the primary sources of uncertainty of the method, which were precision, bias and reference standard purity, the uncertainty measurement was 10.52%. The merits are summarised in Table 2.

Table 2 The merits of the HG-AAS validated method

Parameters	Value
Calibration range	0.5–50 µg/L
Correlation coefficient, R^2	>0.997
MDL	0.15 mg/kg
Intra-laboratory reproducibility, % recovery	96.3–99.8%
Repeatability within-day, *RSD*, $n=6$	1.74–3.69%
Repeatability inter-day, *RSD*, $n=6$	2.91–4.88%
Uncertainty measurement (%), $k=2$	11.52%

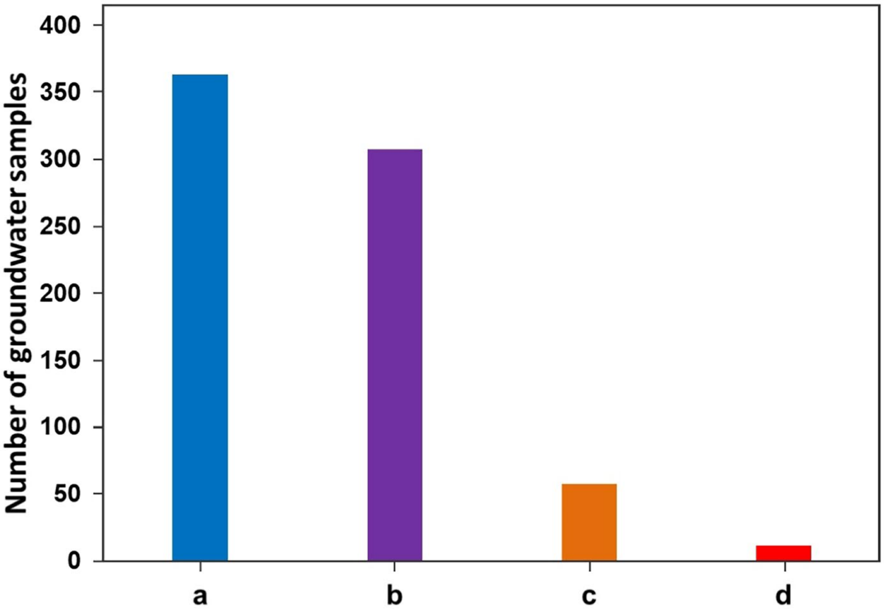

Fig. 2 Groundwater samples for arsenic detection and measurement. **a** Total samples; **b** positive samples; **c** contaminated samples (> 10 µg/L); and **d** seriously contaminated samples (> 100 µg/L)

Observation of arsenic pollution in groundwater

Arsenic pollution in groundwater was observed in the 364 samples collected in 36 wards in Phu Tho Province. It was found that 84.61% of the samples were positive for As (>0.5 µg/L). The arsenic contamination of the groundwater was 15.93%, which exceeded the maximum permissible level of 10 µg/L. The samples with As concentrations 10 times higher than the allowable threshold accounted for 20.69% of the contaminated water samples (Fig. 2; Table S1 in Supporting Information), with the highest concentration reaching 267 µg/L. In 10 of the 36 areas (27.78%), the groundwater had an arsenic concentration above the maximum permissible level (Fig. 3).

Source of arsenic contamination of groundwater

To assess the source of the arsenic in the groundwater, 56 surface water samples (from ponds, lakes and rivers) near the 14 groundwater sampling areas, where the groundwater had arsenic concentrations higher than 5 µg/L, were

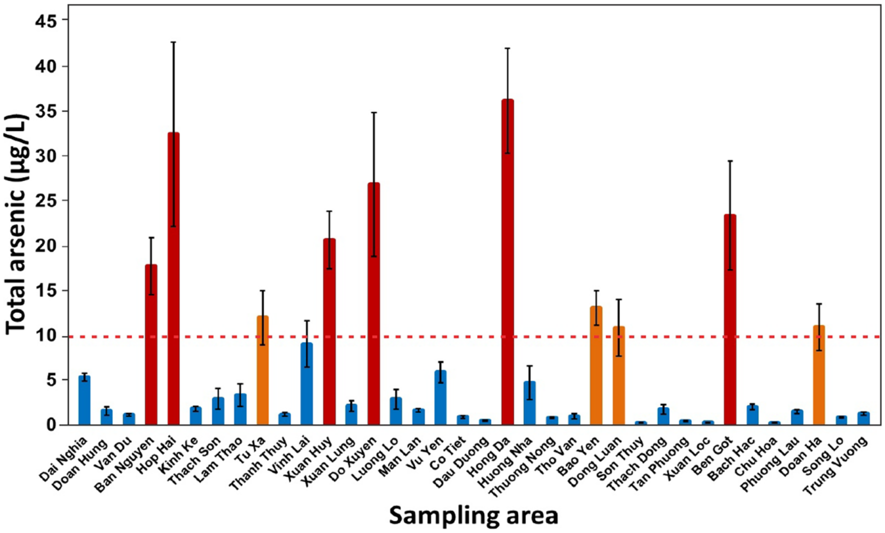

Fig. 3 The contamination of arsenic in groundwater in Phu Tho Province. The arsenic-contaminated samples were lower than 10 µg/L (in dark blue), slightly higher than 10 µg/L (in orange) and much higher than 10 µg/L (in red)

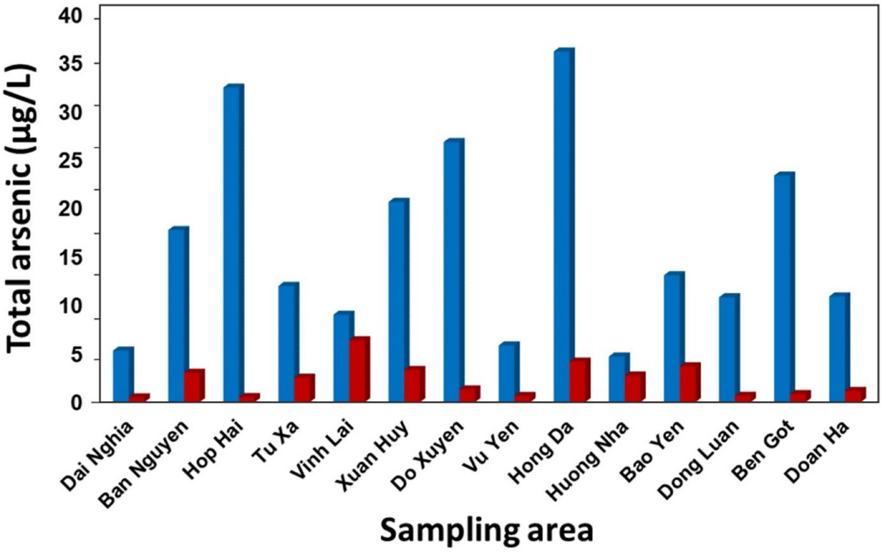

Fig. 4 Comparison of arsenic contamination of groundwater (in blue) and surface water (in red) at the same sampling area in Phu Tho, Vietnam

also observed. Anthropogenic sources usually cause arsenic pollution in the surface water as agricultural, industrial and other human activity wastes. Although the surface water samples positive for arsenic (>0.5 µg/L) were 76.78% of the total of 56 surface water samples, the samples that had arsenic concentrations higher than 10 µg/L accounted for only 3.57%.

The difference between the arsenic contamination in groundwater samples (total arsenic higher than 5 µg/L), and the surface water samples at the same sampling position was significant (Fig. 4). The paired *t*-test results for the mean between the surface water and the groundwater samples yielded a *p*-value (two-tail) of 0.00065, which is much smaller than 0.05, confirming that the arsenic contaminations in the two studied aquatic environments were entirely different (Table 3).

Table 3 Paired *t*-test for arsenic contamination in groundwater and surface water

Parameters	Groundwater	Surface water
Mean	16.7692458	2.341300366
Variance	109.2242529	3.260101744
Observations	13	13
Pearson correlation	−0.002173728	
Hypothesized mean difference	1	
df	12	
t Stat	4.563277411	
$P(T<=t)$ one-tail	0.000325508	
t Critical one-tail	1.782287556	
$P(T<=t)$ two-tail	0.000651017	
t Critical two-tail	2.17881283	

Six areas with concentrations much higher than 10 µg/L (red column in Fig. 3) are low-lying areas stretching along the Red River, where porous aquifers have loose, soft formations. These results are consistent with those of previous research on groundwater pollution in the downstream area of the Red River (Stopelli et al., 2020; Winkel et al., 2011). The high groundwater abstraction from peat-rich aquifers may enhance the dissolution of arsenic-rich iron oxyhydroxides and, thus, increase arsenic concentrations (Winkel et al., 2011). All these results prove that the source of arsenic pollution cannot be from human activity and industrial waste. Thus, we can conclude that the arsenic in the groundwater is from natural sources.

Conclusion

This study is the first complete study on arsenic pollution in groundwater in Phu Tho, the northern midland mountainous province of Vietnam. There are many mineral deposits and peat-rich aquifers in the province that may cause groundwater pollution. Based on the validated HG-AAS method, this work assessed the arsenic-contaminated level in groundwater in 36 areas. The results showed that the level of pollution was considerable. There were 27.78% sampling areas that had average arsenic concentrations higher than the maximum permissible level. It is recommended that groundwater in these areas be arsenic-treated before it is used for drinking, for health safety. The sources of arsenic pollution were also examined in this study by comparing the concentrations of arsenic in the surface water with groundwater in arsenic-contaminated areas. Almost of the surface water samples were not arsenic-contaminated, which demonstrated that the sources of the pollution were natural and underground. All the results prove valuable data for environmental management and technology.

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Author contribution All the authors contributed to the study conception and design. Dinh Vu Le designed the study, analysed the data, wrote and submitted the manuscript. Pham Thi Kim Giang evaluated the experimental procedures and results. All the authors read and approved the final manuscript.

Data availability All the data generated or analysed during this study are included in this published article (and its supplementary information files).

Declarations

Conflict of interest The authors declare no competing interests.

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