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Monitoring Arsenic in rice paddies of Malabar Coast, South western India

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Abstract

Arsenic (As) is a naturally occurring toxic metalloid posing the highest morbidity and mortality worldwide. Considering the tropical humid climate and abundance of amorphous Fe minerals in Kerala that may lead to enrichment of As, a study was conducted at Kerala Agricultural University during February 2024 to assess the spatial variability of As in rice ecosystems of Kerala. The Northern coastal agro-ecological units (AEU), namely Northern coastal plain (AEU 2) and *Kaipad* lands (AEU 7) of Malabar Coast were selected and divided in to grids of size 5 x 5 km^2. The grids containing paddy fields were located and 46 geo-referenced surface soil and irrigation water samples from rice fields and nearby canals respectively were collected and analysed. The As content in irrigation waters of AEU 2 (0.03±0.009 µg L^{-1} to 1.56±0.06 µg L^{-1}) and AEU 7 (0.08±0.006 µg L^{-1} to 4.67±0.148 µg L^{-1}) was below the critical limits of 100 µg L^{-1} by the Food and Agriculture Organization and showed a significant (*P≤0.05*) positive correlation (r=0.33*) with the electrical conductivity of water. The available As in soil samples of AEU 2 & AEU 7 varied from 0.67±0.76 to 832.87±3.21 µg kg^{-1} and 0.32±0.56 to1255.20±18.85 µg kg^{-1}, respectively. This study confirms the presence of available As and its interactions with other nutrients in these systems suggesting its chances for bioaccumulation and environmental contamination in near future. Irrespective of the AEUs, Pearson's correlation analysis revealed significant (*P ≤ 0.01*) negative correlations between available As and available Fe (r = - 0.50***) in soil. This finding forms the basis for developing Fe - based As remediation of soil and water in these systems.

Introduction

Arsenic (As) is one of the most toxic elements, for its highest morbidity and mortality risk worldwide. It is known as the "King of Poison and "Poison of Kings" as it was the preferred poison used in many high-profile murders of the royal families in the past. Arsenic poisoning in organisms mainly occurs by the consumption of contaminated drinking water and foodstuffs. Anthropogenic activities like mining, smelting, and usage of arsenic-loaded pesticides and herbicides are attributed as the potential sources of arsenic in the ecosystem (Sanyal et al. 2020). More than 500 million and 50 million people in the world and India, respectively, are at risk of As poisoning (Shaji et al. 2021).

World Health Organization has identified 10 µg L^{-1} as the permissible limit of As in drinking water (WHO, 1993). However, apart from domestic uses, a substantial amount of groundwater is also used for irrigated agriculture in dryland rice cultivation, which accounts for about three fourth of the country's total rice production (Pradhan et al. 2021). Irrigation with arsenic contaminated ground water could transfer 1000 tons of arsenic annually (Roberts et al. 2007) to cultivated land worldwide which could raise the soil arsenic levels by 1 µg g^{-1} per annum as predicted by Meharg and Rahman (2003). This could increase the arsenic load up to five times than that of normal soil (Ahsan et al. 2008). Moreover, the contamination of agricultural produce with arsenic through irrigated water was affected by the distance from irrigation water inlet (Dittmar et al. 2007)) type of soil, plant (Sandil et al. 2021).

Numerous studies have identified that the adsorption of arsenic by soils is primarily due to the presence of iron, manganese, and aluminum oxides, especially the oxalate-extractable (amorphous) iron oxides (Livesey and Huang, 1981; McLaren et al. 1998) which act as source of arsenic in soil and can cause pollution. Weathering of the rocks releases As (III) which are highly mobile in the environment. Three possible mechanisms had been postulated for the arsenic mobility in aquifers of West Bengal and Bangladesh by Bose and Sharma (2002) first being the oxidation of arsenic bearing pyrite, release of arsenic from iron oxy-hydroxides and through competitive exchange with phosphate ions. Among these, under moderately reduced conditions with + 400mV to + 200mV (Patrick and Reddy, 1978) the mobilization of arsenic was predominantly controlled by dissolution of iron oxy hydroxide was reported as the most probable mechanism of arsenic release in submerged soil. The high rainfall and presence of high amorphous iron minerals (Kamarudheen, 2024) could be a promising factor for holding arsenic in soil and could be potential sequester cum contributor of arsenic in the groundwater aquifers of Kerala.

Rice is a staple food of Kerala grown under alternate wetting and drying conditions and is a well-known arsenic accumulator. The accumulation of arsenic in rice parts follows the order roots (85–95 per cent) > straw > grains (Rahman et al. 2023). Moreover, rice grown in contaminated soils resulted in arsenic phytotoxicity through inhibition of ATP formation and oxidative stress which caused lower grain yields (Bhattacharyya et al. 2003). The concentration of arsenic accumulated in rice grains is approximately ten times higher than other cereal crops (Hsu et al. 2012). The entire coastal saline soils of Kerala are mostly mono-cropped with rice where these low lands contribute to 37 per cent of the rice production in Kerala (Joseph, 2016).

Being enriched with amorphous Fe minerals, reductive dissolution from Fe (III) to Fe (II) in rice soils, could potentially lead to increased precipitation of arsenic (Masscheleyn et al. 1991) in these submerged wetland rice soils of Kerala, resulting in arsenic toxicity. Podgorski et al. (2020) predicted that about 0.4 percent of the land area and nearly 77000 people were potentially exposed to arsenic (> 10g L^{-1}) from groundwater through random forest modelling in Kerala.

To account the agroecological variability of climate, land use, geomorphology and soil the Kerala State Planning Board commissioned a project to National Bureau of Soil Survey and land use Planning in 2008 to delineate five Agro Ecological Zones (AEZ) and twenty-three Agro Ecological Units (AEUs) with homogeneous agricultural environment for effective developmental planning and sustainable land use management with administrative boundaries of panchayaths as the spatial bounding units. Among the twenty-three agroecological units, Northern coastal plain (AEU 2) and *Kaipad* lands (AEU 7) under coastal plain AEZ were selected for the study. Northern coastal plain comprises of 77 panchayats spanning along the coast from Thrissur district up to the northern end of Kerala (Kasaragode District). The unit has tropical humid monsoon climate with mean annual rainfall and temperature of 3133–3254 mm and 27.5 ^{o}C respectively. The *Kaipad* lands (AEU 7) lies along the coast of Kozhikode, Kannur and Kasaragod districts covering 16 panchayats.

The elevated levels of geogenic and anthropogenic arsenic are reported along many coastal systems around the world particularly in south and south East Asia (LeMonte et al. 2017). Though the presence of elevated concentrations of arsenic is not reported in soils, sediments, water and agricultural systems, the unmonitored disposal of sewage, industrial, domestic and urban wastes, fertilizers and pesticides might contribute more to the enrichment of available As in the coastal belts of Kerala. Moreover, under conditions where the dissolution of iron was controlled by the amorphous iron minerals in rice growing wetland soils of Kerala, (Kamarudheen, 2024) the possibility of the increased iron mediated arsenic mobilization could not be waived off. Hence, the present study assessed the spatial variability of As in rice growing tracts of Northern coastal plain (AEU 2) and *Kaipad* lands (AEU 7) of Kerala

Materials and methods

2.1 Study area and sampling

Agroecological units 2 and 7 are positioned as nearly level to gently sloping lands along the coast lies between the sea and the midlands. The lowlands of these AEUs are cultivated with rice. The entire northern coastal plain and *Kaipad* lands were divided into uniformly sized grids of 2500 ha (5 x 5 km^2 intervals). Those grids which contain paddy fields were selected for the sampling at a sampling intensity of 1 panchayat from one grid. Out of a total of 60, 46 grids containing paddy fields were thus selected and 46 georeferenced composite surface (0–15 cm) soil and water samples were collected with 38 sampling locations from Northern coastal plain and 8 locations from *Kaipad* lands (Fig. 1.; Table 1 refer supplementary information).

2.2. Chemical analyses of water

Water samples were collected from the irrigation canals in clean plastic bottles, corked tightly, labelled properly and prepared for laboratory analysis. Water samples were characterized for pH and electrical conductivity using pH meter and EC meter, respectively. Arsenic in water samples were analyzed using Inductively Coupled Argon Plasma Mass Spectroscopy (Thermo Scientific, iCAP RQ) from Sophisticated Analytical Instruments Facility, Cochin University of Science and Technology, Kerala.

2.3. Chemical analyses of soil

Soil pH and electrical conductivity was estimated in a 1:2.5 soil: water suspension using a pH meter and conductivity bridge, respectively (Jackson, 1985). Organic carbon (WBC) in soil was determined by wet digestion (Walkley and Black. 1934). Alkaline $KMnO_4$ mineralizable N (available N) was extracted following Subbiah and Asija, (1956), available P was extracted for acid soils with pH < 6.5 by Bray and Kurtz. (1945) and for neutral and alkaline soils with pH > 6.5 by Olsen et al (1954). The available K, Ca and Mg were extracted by 1N ammonium acetate (pH 7.0) (Jackson. 1973) and estimated by flame photometer (Model: Elico CL – 378) and Atomic Absorption Spectroscopy (Model: Varian AA240). The

available S by Williams and Steinbergs (1959), available Fe and Mn by Sims and Johnson (1991) and Lindsay and Norvell (1969) respectively.

The available arsenic (As) in acidic soil with pH < 6.5 was determined by the Modified Morgan extraction (Mcintosh, 1969; Udovic and McBride, 2012) by molar ammonium acetate at pH 4.8 and in alkaline soil with pH > 6.5 was extracted by 0.5M sodium bicarbonate at pH 8.5 (Olsen et al. 1954) and estimated in Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Thermo Scientific, iCAP RQ) from Sophisticated Analytical Instruments Facility, Cochin University of Science and Technology, Cochin, Kerala.

2.4. Data Analysis

The data obtained from the experiments were analyzed using SPSS software (IBM Corp. Released 2021. IBM SPSS Statistics for Windows, Version 28.0. Armonk, NY: IBM Corp).

Results and Discussions

3.1. Chemical properties of irrigation water collected from paddy fields of Northern coastal plain (AEU 2) and Kaipad Lands (AEU 7)

Surface irrigation water samples (0–30 cm depth) were collected from water channels beside the paddy fields and analysed. The mean pH of irrigation water (N = 46) of AEU 2 was 7.71 ± 0.06 and AEU 7 was 8.18 ± 0.08. Irrigation water samples of Northern Coastal plain recorded pH from 5.94 ± 0.04 at Vallikkunnu panchayat to 8.58 ± 0.03 at Udma panchayat and from 7.46 ± 0.04 (Pilicode) to 8.60 ± 0.04 (Cherukunnu and Cheruvathur) in AEU 7 (refer supplementary information Table 2).

However, extraneous values other than 6.5 to 8.4 warrants the presence of a toxic ion or nutritional imbalance (IS 11624, 2019). The electrical conductivity irrigation water of AEU 2 ranged from 0.03 ± 0.01 dSm^{-1} (Chemnad and Mogralputhur) to 4.59 ± 0.02 dSm^{-1} (Tanur) and in AEU 7 the highest EC of 17.04 ± 0.03 dSm^{-1} was recorded from Ezhome and the lowest EC of 0.02 ± 0.01 dSm^{-1} from Pilicode (refer supplementary information Table 2). CSSRI (2022) categorized 60% of the irrigation water as good for irrigation and 26.65% was reported to be marginally alkaline (< 4 dSm^{-1}) and 13% in highly alkaline in Kannur district of Kerala.

The presence of arsenic in groundwater aquifers of Kerala poses a significant threat to both the public and the entire ecosystem. Wu et al. (2021) recently reported that 0.3–0.6 per cent of deaths due to cardiovascular disease could be attributed to the elevated levels of arsenic in groundwater. The origins and kinetics of arsenic in groundwater with elevated arsenic levels are attributed to the dissolution of arsenic-bearing minerals and redox reactions between arsenic bearing sulphide and Fe/Mn - oxyhydroxides with the groundwater (Ju et al. 2014). The leaching of arsenic from dumping materials containing arsenopyrite during heavy rains could lead to the enrichment of arsenic in the ground water aquifers (Hebbar and Janardhana 2016).

Out of 46 irrigation water samples collected, 41 locations recorded the presence of arsenic in the irrigation water and in five locations the content was below detectable limit (BDL) of 0.10 µg ml^{-1} (refer supplementary information Table 2). The arsenic content in irrigation water was ranged from 0.03 ± 0.01 µg L^{-1} at Ramanattukara to 1.56 ± 0.06 µg L^{-1} at Matool panchayat (Table 2) in AEU 2 and from 0.08 ± 0.01 µg L^{-1} (Cheruvathur) to 4.67 ± 0.15 µg L^{-1} (Cherukunnu) in AEU 7. The arsenic content in irrigation water collected from paddy fields of Narath, Madayi, Mangalpady, Manjeswar (AEU 2) and Pallikkara (AEU 7) was below detectable limit of 0.10 µg ml^{-1}(Table 1). In the present study, 89 Percent of the irrigation water samples showed the presence of As. The un-warranted freshwater pumping from overlying saline layers, coupled with saline intrusion, had been reported to contribute up to 14 fold more As concentrations (Seyler and Martin, 1991, Shimod et al., 2022). This is in line with CSSRI (2022) wherein the blocks of Kannur, Panoor, and Thalassery were classified as semi-critical areas with percent ground water extraction from 70 to 90. Cherukunnu lies as coastal areas of Kannur with brackish to saline aquifers and luxurious mangrove cultivation was reported to have saline water intrusion from backwater shallow channels. Irrigation water from cherukunnu panchayat, situated in the coastal belt of Kannur was reported to experience high saline water intrusion from shallow backwater channels (CGWB, 2013), recorded the highest As in the present study. The recent reports of Kumar (2023) on the presence of arsenic in ground water aquifers within 100 m depth and the significant 90 per cent contribution of alluvial aquifers of India in As contamination (Shaji et al., 2021) threw caution on excessive ground water extraction. Although As was detected in irrigation water, it remained well below the critical limit set by the Food and Agriculture Organization (100 µg L^{-1}) and within the permissible limit of Bureau of Indian Standards (10µg L^{-1}).

3.2. Chemical properties of surface soil samples collected from paddy fields of Northern coastal plain (AEU 2) and Kaipad Lands (AEU 7)

The composite surface soil samples collected from AEU 2 were subjected to chemical analysis and pH (N = 38) was ranged from 3.08 ± 0.02 to 7.42 ± 0.03. The highest pH was recorded from Matool and the lowest was from Chavakkad whereas pH of soils of AEU 7 ranged from 4.2 ± 0.03 (Thrikkaripur) to 7.23 ± 0.02 (Cheruvathur). The electrical conductivity of the soil of AEU 2 varied from 0.07 ± 0.02dSm^{-1} to 4.46 ± 0.02dSm^{-1} whereas it ranged from 0.05 ± 0.01 dSm^{-1} to 12.12 ± 0.03 dSm^{-1} in AEU 7 (refer supplementary information Table 3).

The lowest Walkley Black carbon (WBC) in AEU 2 was from Azhikode (0.19 ± 0.03%) whereas the highest WBC was from Chavakkad Municipality (5.33 ± 0.03%) (Refer supplementary information Table 3). The available N ranged from 150.52 ± 1.95 $kgha^{-1}$ to 1329.66 ± 3.92 kg ha^{-1}, available phosphorous from 6.41 ± 0.27 to 276.42 ± 0.20 kg ha^{-1} and available K from 20.13 ± 1.93 to 2548.00 ± 2.87 kg ha^{-1}. The highest AKN was reported from Chavakkad and lowest from Eramala whereas Azhikode recorded the highest available P and Kumbla recorded the lowest available P. Content of available K was the highest at Chavakkad and lowest at Chorodu (refer supplementary information Table 4).

Chavakkad recorded the highest available Ca (1148.75 ± 4.27 mg kg^{-1}), available S (1142.28 ± 2.59 mg kg^{-1}), available Fe (539.7 ± 4.50 mg kg^{-1}) and Mn (71.82 ± 0.37 mg kg^{-1}) in soils of AEU 2 whereas the highest available Mg was reported from Kumbla (228.71 ± 2.42 mg kg^{-1}) (refer supplementary information Tables 5 and 6). Kanhangad recorded the lowest content of available Ca (83.75 ± 3.04 mg kg^{-1}) and available Mg (17.17 ± 1.90 mg kg^{-1}). The content of available S (2.84 ± 0.37 mg kg^{-1}) and available Mn (0.08 ± 0.02 mg kg^{-1}) was the lowest at Kumbla. The lowest available Fe with 132.40 ± 2.86 mg kg^{-1} was reported from Vallikkunnu (refer supplementary information Table 5).

In AEU 7, soils from Ezhome recorded the highest available K (2548.00 ± 2.87 kg ha^{-1}), available Ca (3805.02 ± 6.45 mg kg^{-1}), available Mg (1403.91 ± 3.46 mg kg^{-1}), available S (1241.53 ± 1.68 mg kg^{-1}) and available Fe (573.70 ± 4.61 mg kg^{-1}) (refer supplementary information Tables 4 and 5). Soils from Pilicode showed the lowest electrical conductivity of 0.05 ± 0.01 dS m^{-1}, available Ca (60 ± 2.62 mg kg^{-1}) and available S (2.37 ± 0.38 mg kg^{-1}) and the highest WBC (3.96 ± 0.04 per cent) and AKN (526.84 ± 1.77 kg ha^{-1}) (refer supplementary information Tables 3, 4 & 5). The lowest WBC (0.31 ± 0.03 per cent) and the highest available P (78.41 ± 0.39 kg ha^{-1}) were recorded from Cherukunnu, whereas the lowest pH (4.20 ± 0.03) and AKN (213.24 ± 0.66 kg ha^{-1}) were reported from Thrikkaripur. The highest pH (7.23 ± 0.02) and lowest available K (21.28 ± 2.38 kg ha^{-1}) was recorded at Cheruvathur whereas Pallikkara recorded the lowest available Fe (104.30 ± 2.49 mg kg^{-1}) (refer supplementary information Tables 3, 4, 5 & 6). The collected soil samples were analysed for available arsenic, and it found that out of 38 paddy fields soils sampled, 37 locations had the presence of arsenic in available form. The content of available arsenic ranged from 0.67 ± 0.76 µg kg^{-1} to 832.87 ± 3.21 µg kg^{-1} of soil (refer supplementary information Table 6). The highest available arsenic was reported from Vallikkunnu and the lowest was from Chorodu. The content of available arsenic at Manjeswar was below detectable limit of 0.10 µg ml^{-1}(Fig. 2, refer supplementary information Table 6). In AEU 7, the lowest available arsenic content of 0.58 ± 0.56 µg kg^{-1} was recorded at Pilicode, and the highest was recorded at Pallikkara (1255.20 ± 18.85 µg L^{-1}) (refer supplementary information Table 6)

Most of the soil samples reported an acidic pH and numerous prior studies reported the acidic pH in loamy sand soils of coastal plain and the high saline coastal water intrusion. Very low pH in soil can also be arised due to the application of acid fertilsers, without the application of lime which fails to neutralize the acidity generated (KSPB, 2013). The highest pH was recorded from Matool panchayat may associated with the application of lime during the cropping season prior to soil sample collection and it gives high available Ca content also. Nair and Money (1972) reported that saline soil pH in Kaipad land may varied from 3-6.8 generally. However, an alkaline pH of 7.23 was reported from Cheruvathur, might be due to the application of lime and other fertilisers. The electrical conductivity (EC) of the Northern coastal plain and Kaipad land ranged from non-saline (0.07) to strongly saline (12.12 dSm^{-1}). Almost 86% of soil samples reported a non-saline nature, it could be attributed by the free drainage condition in sandy soil, which leads to loss of mineral salts (Verma et al. 2005). However, the high salinity reported

from *Kaipad* land could be attributed to the high salt content in the inundating saline water intrusion in this area (Purandhar et al. 2022)

The Walkley Black carbon (WBC) in Northern coastal plain and *Kaipad* lands reported low to high level. The coastal loamy sand contains 18.5% of poor organic carbon (< 0.75%). However, 48% of samples recorded high organic carbon content in soil. The organic manure incorporation can increase the organic carbon in soil (Li et al. 2019) as well as microbial activities. Organic carbon in soil measures the nitrogen content in soil as well as the microbial activity. The available N content in soils of Northern coastal plain and Kaipad landvaried from low to high level. The soil containing high organic carbon content like Chavakkad (AEU 2) and Pilicode (AEU 7) also recorded high nitrogen content in soil. Soil containg high organic carbon and nitrogen can enhances the mineralization process by soil microbes. The available phosphorous content in the Northern coastal plain and Kaipad land recorded low to high level. Even though the soils of this area reported an acidic pH, most of the samples reported a high level phosphorous. This could be attributed by the application of phosphatic fertilisers in soil which increases the labile phosphorous pool. Chandramohan and Mohan (2012) recorded the available phosphorous in Kaipad land as 7.2–34.2 kg ha^{-1}, substantiating the phosphorous in Kaipad lands. Samikutty (1977) reported that saline soils of Kerala, including Kaipad soils, generally show deficiency of phosphorous.The available K content in Northern coastal plain and Kaipad land reported a low to high levels in soil. The high potassium content of in soil was limited to only four samples of Northern coastal plain, it might be due to the loamy sand texture of soil in which the retention capacity of nutrients is low, which promotes the leaching loss of most of the nutrients especially the exchangeable cations in soil. The available potassium content in soil exhibit a positive correlation with electrical conductivity and this similar correlation was reported in coastal sandy soils by Behara and Shukla (2014). The high potassium content in soils of Ezhome is associated with the cropping system practices in which the paddy stubbles are incorporated after the rice harvest in field. Samikutty (1977) reported that *Kaipad* soils record higher sodium and potassium content than other paddy systems in Kerala.

The available calcium and magnesium content in the Northern coastal plain and *Kaipad* reported deficiency as well as sufficiency range. However most of the samples reported deficiency of calcium as well as magnesium. In coastal sandy soil associated with high rainfall has less retention capacity of nutrients, leading to calcium and magnesium leaching out in the soil. How ever the highest level of calcium and magnesium content in soils of Ezhome might be associated with rice shrimp farming system in this region. The saline water intrusion in *Kaipad* land also contribute high calcium content in soil. Mini (2015) reported that the unbalanced fertilizer application without the addition of Mg fertilizer can cause Mg deficiency in soil.. Identification of low levels of calcium and magnesium content by soil testing prior to crop cultivation is essential for the proper growth and greater yield from these regions. Most of the soils in Northern coastal plain and Kaipad land containing sufficient level of sulphur in soil. It might be associated with the application of factomphos, which contain sulphur along with high doses of nitrogen and phosphorus. The occurrence of sulphur-bearing parent material like pyrites and Jarosite can also contribute to high sulphur in this soil (Iyer. 1989). Moderately high content of organic matter can also contribute sulphur to soil (Santhi G R, 2017)

The micronutrients in soil including iron and manganese present in sufficient level both in Northern coastal plain and Kaipad land. An investigation conducted by Kamarudheen (2024) revealed the presence of a high concentration of amorphous Fe in Kerala soil. The high rainfall associated with the leaching of basic cations to deeper horizons and Fe bearing parent material in soil could be the reason for contributing the high amount of iron as well as manganese in Kerala soil. However, soil samples collected from Kanchangad, Kumbla and Mangalpady panchayats showed manganese deficiency. The unbalanced fertilizer application of these regions and sandy soil, which causes leaching of nutrients, might be the reason for the deficiency of many nutrients in soils.

3.6. Distribution of available As in soils of Northern coastal plain (AEU 2) and Kaipad lands (AEU 7)

Available arsenic in acidic soils was extracted using 1M ammonium acetate adjusted to pH 4.8 (Modified Morgan reagent) and 0.5M $NaHCO_3$ adjusted to pH 8.5 for available arsenic in neutral to alkaline soils (pH > 6.5). The arsenic extracted through ammonium acetate in soil was considered the most easily exchangeable and, therefore, the most available species and constituted 2 per cent of the total arsenic extracted (Migoni et al. 2021) through sequential fractionation. Ammonium acetate facilitated the extraction of water soluble and carbonate bound and highly exchangeable forms of metals and metalloids (Patinha et al. 2004), predominantly the exchangeable ions in the soils (Minkina et al., 2018). Similarly for alkaline soils, the Olsen-P was extracted using 0.5M $NaHCO_3$ and was found significantly and positively correlated with pH under near neutral soil reaction regime (Giri et al. 2012). Moreover, Giri et al. (2012) established significant positive correlations with arsenic uptake by rice dry matter and $NaHCO_3$ extractable As (r = 0.98*).

Spatial variation of available arsenic content in soil samples collected from paddy fields of 38 panchayats in Northern coastal plains are shown (Fig. 2). Thirty seven locations (97 percent) showed the presence of available arsenic in soils. This form of metals extracted by weak extractants are most easily released fractions from soil to other environmental compartments such as hydrosphere and biosphere (Migoni et al. 2021). These significantly bioavailable fractions are more mobile, dangerous and associated with highest potential toxicity form an ecological point of view. Hence the exchangeable fraction of arsenic could be present in these soils got mineralized from the exchangeable sites under accelerated acidification (pH < 6.5) in these soils, which become more mobile and bioavailable in the presence of organic matter (Fleming et al. 2013). Sixteen percent of soil samples showed the available arsenic content between 0–10 μg L^{-1}. Seven soil samples (18 percent) recorded available As content at the range of 11 μg L^{-1} -100 μg L^{-1}. Seventeen panchayats (45 percent) showed an As at the range of 101 μg L^{-1} -350 μg L^{-1}. Thirteen percent (five) samples showed available arsenic between 351 μg L^{-1} – 700 μg L^{-1} and two panchayats, Vallikkunnu (Malappuram), and Kumbla (Kasaragode) recorded the highest available As the content of 832.87 μg L^{-1} and 786.56 μg L^{-1} respectively and included in the frequency class from 701 μg L^{-1} – 1000 μg L^{-1} of As in soil. Out of the 38 sampling locations, only Manjeshwar shows As in soil below reliable detectable limit of 0.10 μg ml^{-1} of the Inductively Coupled Plasma Mass Spectroscope. Though total arsenic content up to 171.4 μg L^{-1} was reported from

Kovalam (Vineethkumar et al. 2020), only moderate enrichment factor (4.61 (n = 18) was observed for As through crustal materials or natural weathering along the coastal belt of Kerala. The arsenic may be enriched in soil due to human activities such as metallurgical waste disposal, arsenic mining, use of arsenical pesticides. The longterm experimentation by Hartley et al. (2013) in Rothamsted reported that the application of phosphatic fertilizers in soil over a period of 59 years, doubled the arsenic concentration of the initial 10 mg kg^{-1}. Thus, a distant possibility of contamination of arsenic from long-term application of phosphatic fertilizers such as triple super phosphate, single super phosphate and rock phosphate in rice fields could be the reason for arsenic accumulation in the soil of Kerala.

The spatial distribution of As in soils of paddy fields of *Kaipad* lands AEU 7 (Fig. 3; Table 2) was represented by four frequency distribution classes. Two panchayats, Pilicode and Thrikkaripur, reported available arsenic content in the range from 0 to 10 µg L^{-1}. Fifty percent of the soil samples recorded available arsenic content between 1-100 µg L^{1}. The comparatively higher available arsenic content of (208.69 µgL^{-1}) was reported from Valiyaparamb panchayat, Kasaragode district and was classified in the range of 101 µg L^{-1} to 500 µg L^{-1}. The highest arsenic content of 1255.2 µg L^{-1} (range 501 µg L^{-1} to 1500 µg L^{-1}) was recorded at Pallikkara panchayat, Kasaragode district.

Pearson's Correlation analysis of As in irrigation water and soil with chemical properties in Northern coastal plain (AEU 2) and Kaipad lands (AEU 7)

Pearson's correlation analysis of arsenic in water samples collected from Northern coastal plain and *Kaipad* land indicates a significant positive correlation ($p \leq 0.01$) with electrical conductivity of water (r = 0.33**). Smedley and Kinniburgh (2002) reported that water with high salinity and pH can attribute high arsenic content in water, might be attributed by extreme dry climate and evaporation rate. Irrespective of AEUs, the available As was significantly ($p \leq 0.01$) negatively correlated with available Fe (-0.501**) whereas, significant correlations were obtained between available As with available Fe (r = -0.369*), P (r = − 0.351*), Ca (r = 0.384*), Mg (r = 0.432**) and Mn (r = − 0.366*) in AEU 2.

Table 1
Correlation matrix of As with chemical properties of irrigation water and soil in Northern coastal plain (AEU 2) and *Kaipad* lands (AEU 7)

Irrigation water	
Chemical parameter	Electrical Conductivity (dSm^{-1})
As (µg L^{-1})	0.33**
Soil	
Chemical parameter	Available Fe
Available As (µg kg^{-1})	-0.501**

Table 2
Correlation matrix of As with chemical properties of soil in Northern coastal plain (AEU 2)

Chemical parameter	Available Fe	Available P	Avaiable Ca	Avaialable Mg	Available Mn
Available As (µg kg^{-1})	-0.369*	− 0.351*	0.384*	0.432**	− 0.366*

The interaction between iron and manganese with arsenic in soil was described by various researchers, mentioned as the adsorption of arsenic by soils is influenced by the presence of Fe especially the oxalate-extractable (amorphous) iron oxides (Livesey and Huang., 1981; McLaren et al., 1998). Niazi et al. (2018) also reported that in aerated soils, the inorganic form of arsenic (arsenate) is dominant and primarily associates with iron (Fe(III)) (oxy)(hydr)oxides. Maguffin et al (2020) documented that As mobilization in paddy soil is influenced by biogeochemical cycling of redox sensitive elements like Mn and Fe under fluctuating condition. However, the adsorption rate of As on Mn oxides is less than the adsorption of As on Fe oxides (Suda and Makino. 2016). Strawn (2018) concluded that As and P are chemical analogue, which shows similar chemical property in similar environmental behaviour. Both the elements involve in adsorption/desorption (Neupane et al, 2014), precipitation (Xu et al. 2010), and competitive absorption in plant and microbial systems (Anawar *et al*. 2017).

Saalfield and Bostick (2010) reported that the adsorption of Ca or Mg along with bicarbonate causes arsenic to be released from ferrihydrite, which is greater than from competition alone, particularly in dynamic flow conditions. This desorption could play a significant role in As mobilization in As affected, circumneutral aquifers, especially those experiencing rapid organic matter mineralization that leads to calcite dissolution and the generation of dissolved calcium and bicarbonate. So et al (2008) demarked that the precipitation of calcium (or magnesium) carbonates on the surface of iron oxide may restrict arsenic access to the oxide. However, the newly formed carbonates create an additional surface area for arsenic adsorption.

Conclusions

The research findings presented highlight a critical issue concerning As contamination in groundwater and soils of Kerala, particularly in the Northern coastal plains and *Kaipad* lands. This article documents the first report of available As in rice fields of the northern coastal lands of Kerala. Elevated levels of As in both groundwater and irrigation water pose significant health risks, as evidenced by studies linking As exposure to cardiovascular diseases. The spatial distribution of arsenic reveals the presence in substantial majority of sampled areas, even though it occupies below critical limit in water by the Food and Agriculture Organization (100 µg L^{-1}) and Geological Survey of India (12 mg kg^{-1}) in soil. The factors contributing to arsenic mobilization include geological conditions, such as the dissolution of arsenic-bearing minerals and anthropogenic activities, particularly the leaching from industrial waste and the over-extraction of groundwater. The presence of arsenic in irrigation water could have severe implications for agricultural practices, potentially affecting food safety and public health. The study

identifies correlations between As levels with other soil nutrients, indicating complex interactions that could influence As mobility and availability in soil. Hence addressing the As contamination in Kerala requires a multi-faceted approach, including comprehensive monitoring, effective waste management practices, sustainable groundwater management and the adoption of safer agricultural practices are crucial to mitigating the impacts of As on health and the environment. Further research is needed to fully understand the long-term effects of As exposure and to develop strategies for remediation and prevention.

Declarations

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Authors' Contributions

All authors contributed to the study. Conception and design, Conceptualization and methodology, Mayadevi Mullasseril Ramachandran Nair and Sandeep Sasidharan Nair.; formal chemical analysis, Rashbi Jahan Vellari; data curation, Mayadevi Mullasseril Ramachandran Nair and Sandeep Sasidharan Nair, Divya Vijayan Vattekat, Beena Viswanathan Nair. Indirabai Amma and Subin Kaniyamattathil Jose; writing—original draft preparation, Rashbi Jahan Vellari, Mayadevi Mullasseril Ramachandran Nair and Sandeep Sasidharan Nair; writing, review and editing, Mayadevi Mullasseril Ramachandran Nair and Sandeep Sasidharan Nair, Divya Vijayan Vattekat, Beena Viswanathan Nair. Indirabai Amma and Subin Kaniyamattathil Jose. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript."

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability Statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Figures

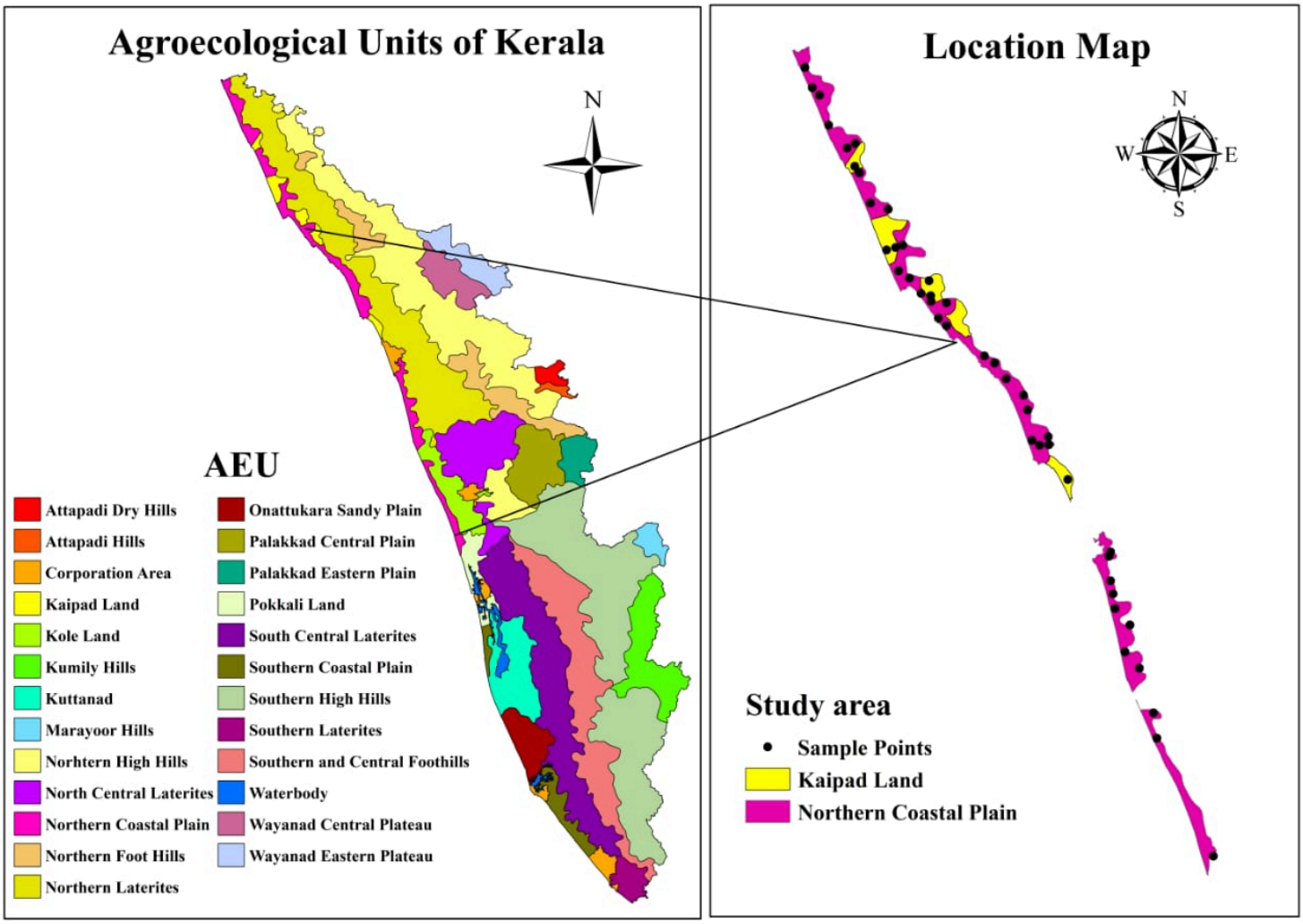


Figure 1

Location map indicating study area. Map outlines adopted from [Survey of India]

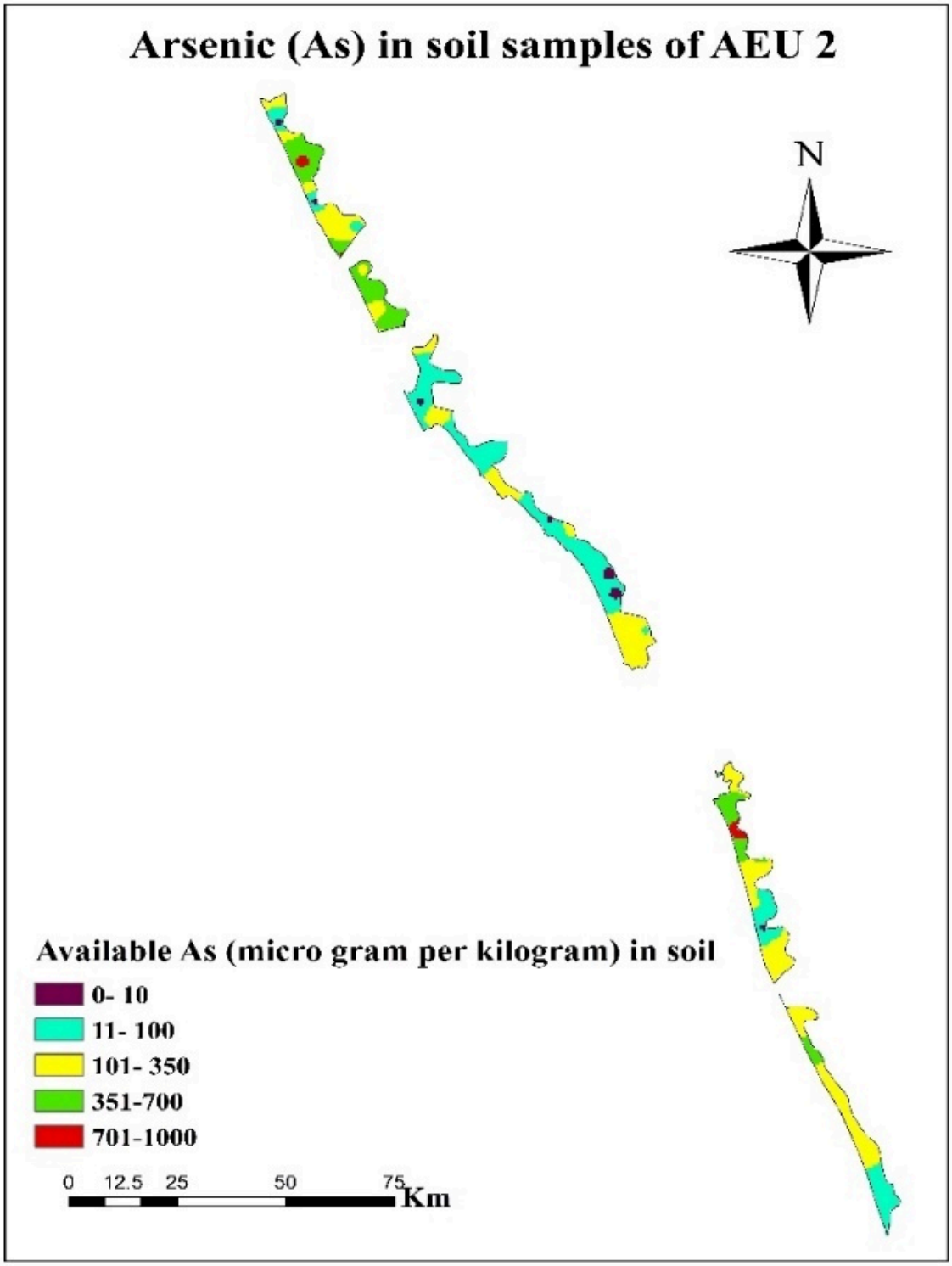


Figure 2

Spatial distribution of As in soils of AEU 2

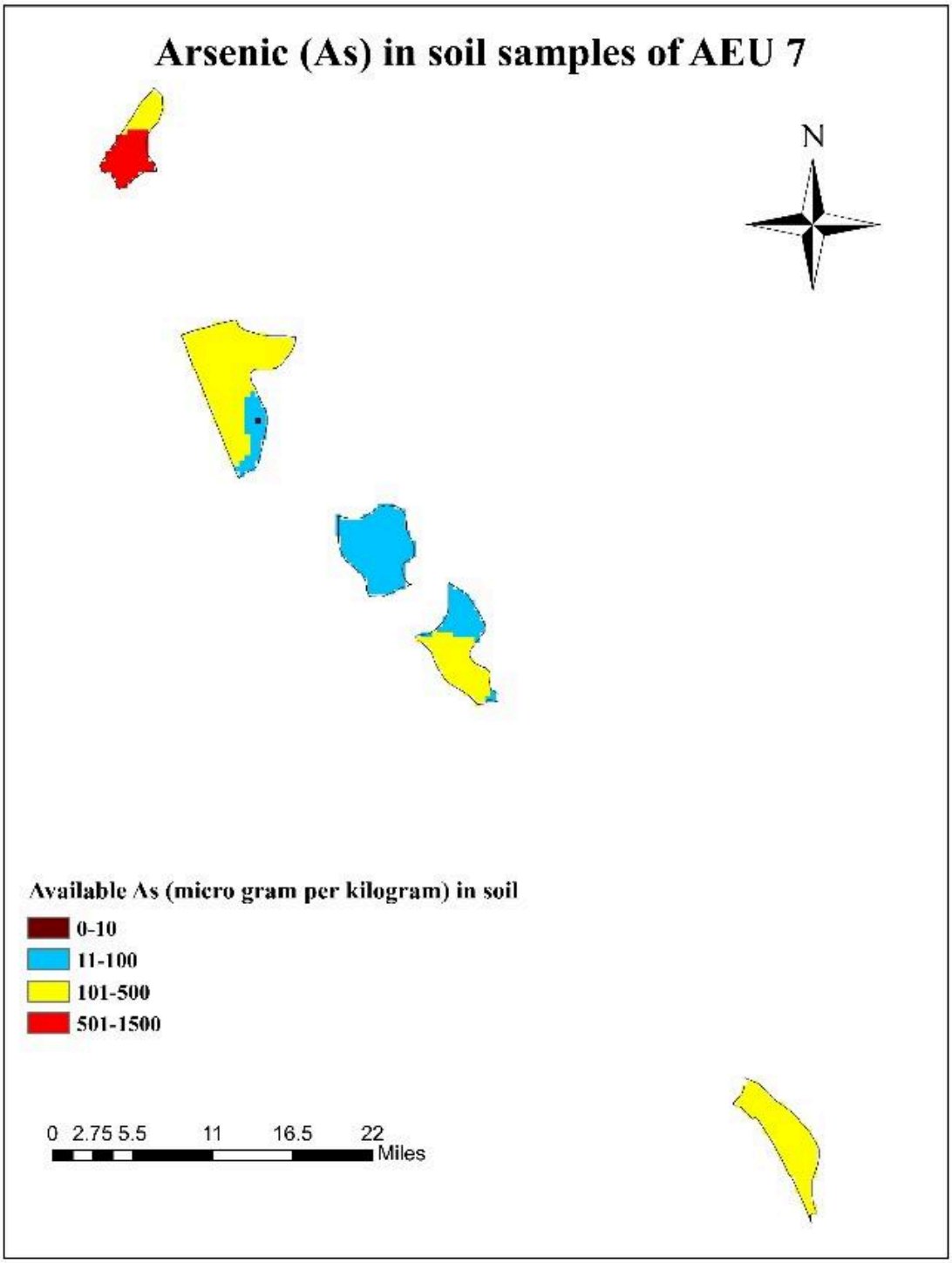


Figure 3

Spatial distribution of As in soils of AEU 7

Supplementary Files

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