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Identification of Major Interfering Substances for Heavy Metal Determination in Northern Sea Areas of Sri Lanka

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

This study investigated the physicochemical characteristics of seawater from five locations along the northern Sri Lankan coast, encompassing areas with varying degrees of anthropogenic activity. The analysis revealed significant variations in several parameters, potentially influenced by human influences. The results reveal significant variations in several parameters. For instance, turbidity levels varied from 1.88 NTU in Thalaiyadi to 13.3 NTU in Pannai, with Pannai, Myliddy, and Kakkaithivu exceeding the recommended limit of 5 NTU. Total suspended solids (TSS) ranged from

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3 mg/L in Thalaiyadi to 83 mg/L in Pannai, surpassing the recommended limit of 30 mg/L. Electrical conductivity (EC) ranged from 45,700 µS/cm in Nainathivu to 49,500 µS/cm in Pannai, exceeding the typical seawater range. Nitrate levels ranged from 10.4 mg/L in Thalaiyadi to 19.1 mg/L in Myliddy. Major cations such as calcium (361 mg/L to 417 mg/L), magnesium (1,222 mg/L to 1,327 mg/L), and sodium (10,140 mg/L to 10,530 mg/L) also showed significant differences across locations. These findings highlight the need for continuous monitoring and effective management strategies to mitigate the negative impacts of anthropogenic activities on these coastal ecosystems. Furthermore, the complex seawater matrix presents challenges for heavy metal determination using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) due to spectral interferences from major cations, non-specific matrix effects, and interferences from organic matter, turbidity, and suspended solids. Careful consideration of these factors through background correction techniques, matrix modifiers, sample pre-treatment, and optimization of analysis parameters is crucial for accurate heavy metal determination in these environments. This study contributes to a better understanding of the environmental conditions and emphasizes the need for further research on heavy metal contamination and the development of robust analytical methods tailored to address the challenges posed by the complex seawater matrix in northern Sri Lanka.

Keywords: Sea water; matrix interferences; anthropogenic activity; heavy metal.

1. INTRODUCTION

The northern sea areas of Sri Lanka, encompassing regions like Pannai, Gurnagar, Kaakai Theevu, Thalaiyadi, Myliddy, and Nainathivu, harbor critically important marine ecosystems [1]. These ecosystems provide a rich tapestry of marine life, serving as breeding and feeding grounds for commercially valuable fish species, thereby significantly contributing to local fisheries [1]. Additionally, they offer recreational opportunities and support coastal communities by bolstering tourism and other maritime activities. However, anthropogenic activities such as industrial development, urbanization, and agricultural practices pose a growing threat to the pristine nature of these environments [2-4]. These activities can introduce various contaminants, including heavy metals, into the seawater, potentially disrupting the delicate ecological balance and jeopardizing the health of marine life [5]. Heavy metals are a particular concern due to their persistence and bioaccumulative nature. They tend to accumulate in organisms over time and magnify as they move up the food chain, ultimately posing a threat to human health through seafood consumption [6]. Accurate determination of heavy metal concentrations in seawater is crucial for effective environmental monitoring and management strategies. However, seawater analysis presents a unique challenge due to its complex matrix of dissolved salts and other inorganic substances. These inorganic interferences can significantly impact analytical techniques such as Graphite Furnace Atomic Absorption Spectrometry (GF-AAS), leading to inaccurate results [7].

Previous attempts to utilize GF-AAS in regional laboratory of the National Water Supply and Drainage Board, Jaffna for heavy metal analysis in the aforementioned sea areas have yielded unreliable results, often generating false positive or false negative signals. This is likely due to the interference of dissolved salts and inorganic and organic compounds present in the seawater matrix. Therefore, identification and characterization of these interfering substances are crucial for developing reliable methods for heavy metal analysis in these marine environments. This research aims to address this critical gap by identifying and characterizing the major inorganic substances present in the seawater of the designated northern Sri Lankan Sea areas that may interfere with the accurate determination of heavy metal concentrations. Understanding these interferences is essential for developing reliable methods for heavy metal analysis, ultimately enabling effective environmental monitoring and management strategies for the protection of these vital marine ecosystems. The specific objectives of this study are: To analyze the total composition of seawater in the designated regions, focusing on major cations and anions, total dissolved solids (TDS), total hardness, turbidity, and suspended particles, using standard methods outlined by the American Public Health Association (APHA, 2021), to identify and characterize the major inorganic substances that may interfere with the determination of heavy metals using standard analytical techniques like GF-AAS.

2. METHODOLOGY

2.1 Study Area Selection

The study focused on two distinct areas within the northern Sri Lankan coastal seas (Fig. 1). The first set of sampling locations (Pannai and Kaakai Theevu) were chosen due to their proximity to known anthropogenic activities, suggesting a higher potential for heavy metal contamination. The second set of locations (Thalaiyadi, Myliddy, and Nainathivu) were selected as areas with less anticipated influence from human activities.

2.2 Sample Collection and Preservation

Water samples were collected following the guidelines outlined in Table 1060:I of the American Public Health Association [8]. Standard sampler was used for sample collection. This ensured proper sample collection, preservation, and transportation to the laboratory for analysis.

2.3 Analysis of Water Samples

A comprehensive analysis was conducted on the collected water samples, encompassing physical and chemical parameters. All testing procedures adhered to established standards: Sri Lankan Standards SLS 614:2013 and APHA guidelines [8]. Physical parameters such as Color was measured using a Spectrophotometric method while Turbidity was determined through a Nephelometric approach. Chemical Parameters such as Electrical Conductivity (EC) and pH were analyzed using instrumental methods. Spectrophotometry with a HACH DR6000 spectrophotometer quantified Nitrates, Nitrites, Total Iron, Total Phosphate, and Fluoride. Titrimetric methods were employed for Chloride (Argentometric titration), Total Alkalinity (Acid base titration), Total Hardness (EDTA Titration), Magnesium (EDTA Titration), and Calcium (EDTA Titration) analysis while Sulfate was measured using a turbidometry method. Total Dissolved salts was analyzed by gravimetric method. Finally, Sodium and Potassium were determined by the flame technique of Atomic Absorption Spectrometry (AAS). All the testing are conducted at Regional Laboratory, National Water Supply and Drainage board Jaffna.

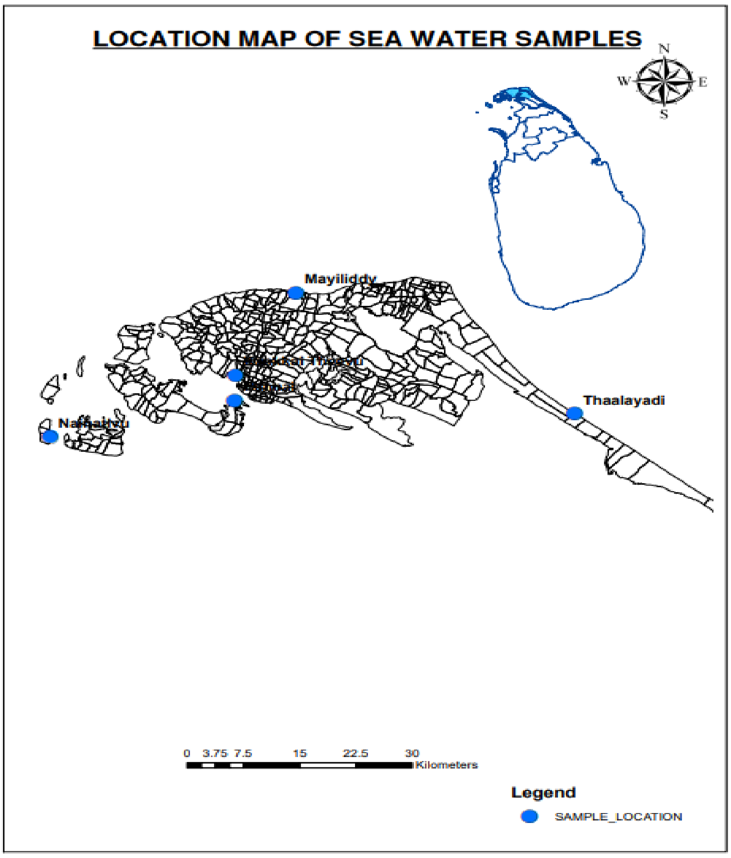

Fig. 1. Sample location

3. RESULTS AND DISCUSSION

This study investigated the physicochemical characteristics of seawater samples collected from five designated locations within the northern Sri Lankan coastal seas, encompassing areas with varying degrees of anthropogenic activity (Fig. 1). The findings revealed notable variations in several parameters, potentially influenced by human influences in the region.

Table 1 represents the physical and chemical quality of the sea water collected from Nainathivu, Myliddy, Thalaiyadi, Pannai and Kakkaithivu.

3.1 Physical Parameters

Color values ranged from 5 Pt-Co units (Nainathivu) to 39 Pt-Co units (Kaakai Theevu) While most locations exhibited color within the natural seawater range of 5-20 Pt/Co units (Jerlov, 1968), the significantly higher value observed in Kaakai Theevu suggests the presence of elevated organic matter content, potentially linked to anthropogenic activities in this area, which is known to have higher human influence compared to others Mikunthan et al., [2], Joshua et al.,[9].

Turbidity levels varied between 1.88 NTU (Thalaiyadi) and 13.3 NTU (Pannai). Although Thalaiyadi and Nainathivu displayed turbidity within the recommended limit of 5 NTU for good quality seawater [10], Pannai, Myliddy and Kaakai Theevu exceeded this threshold, indicating the presence of suspended particles likely originating from resuspension of bottom sediments or discharge of effluents from human activities [11]. Consistent with the turbidity findings, Total Suspended Solids (TSS) levels ranged from 3 mg/L (Thalaiyadi) to 83 mg/L (Pannai) exceeding the recommended maximum limit of 30 mg/L for good quality seawater [10]. The elevated TSS in Pannai further corroborates the influence of anthropogenic activities on this location.

3.2 Chemical Parameters

The pH values across all locations were slightly alkaline (7.78-8.17), falling within the typical range for natural seawater (7.5-8.2) [12].

Table 1. Physical and chemical quality of the sea water

Parameters	Nainathivu	Myliddy	Thalaiyadi	Pannai	Kakkaithivu
Physical Parameters					
Colour, Pt/Co	5	10	7	14	39
Turbidity, NTU	2.95	9.31	1.88	13.3	6.41
Total Suspended Solid, TSS, mg/L	4	7	3	83	53
Chemical Parameters					
pH	8.15	8.12	8.17	8.13	7.78
Electrical Conductivity, EC, µS/cm	45700	46900	48000	49500	47600
Chloride as Cl^-, mg/L	19598	18953	19251	20343	19747
Bicarbonate, mg/L	168	160	166	161	218
Alkalinity as $CaCO_3$, mg/L	138	131	136	132	179
Nitrate as NO_3^-, mg/L	14.2	19.1	10.4	18.3	12.5
Nitrite as NO_2^- , mg/L	0.302	0.133	0.001	0.503	0.004
Fluoride as F^-, mg/L	1.82	1.81	1.89	1.91	1.91
Phosphate as PO_4^{3-}, mg/L	0.54	0.53	0.21	0.65	0.66
Total Dissolve solid, TDS, mg/L	39431	37352	33600	37621	37798
Hardness as $CaCO_3$, mg/L	6306	6156	6356	6507	6056
Total Iron as Fe^{2+}, mg/L	0.36	0.16	0.04	0.08	0.17
Sulphate as SO_4^{2-}, mg/L	3125	3594	3094	3875	2831
Calcium as Ca^{2+}, mg/L	409	361	393	417	409
Magnesium as Mg^{2+}, mg/L	1283	1276	1305	1327	1222
Sodium, mg/L	10400	10290	10140	10530	10210
Potassium, mg/L	538	529	538	569	549

Electrical Conductivity (EC) values ranged from 45700 µS/cm (Nainathivu) to 49500 µS/cm (Pannai), exceeding the typical range of 30000 to 40000 µS/cm for seawater [13]. This increase in EC suggests potentially higher salinity due to lower freshwater input or evaporation in areas like Pannai with higher anthropogenic activity [5]. It is important to note that seawater quality in the Indian Ocean exhibits regional variations. Studies on the Indian Ocean have reported salinity levels ranging from 33.0 to 37.3 g/L Kumar et al., [14], which is consistent with the EC values observed in this study. However, further detailed comparisons with specific Indian Ocean regions would require considering factors like local oceanographic conditions and proximity to freshwater inputs. Total Dissolved Solids (TDS) levels ranged from 33600 mg/L (Thalaiyadi) to 39431 mg/L (Nainathivu), exceeding the average seawater concentration of 35000 mg/L [13]. This elevation in TDS could be attributed to a combination of factors, including natural variations in salinity, lower freshwater input and the influence of anthropogenic activities that contribute to dissolved salts.

Chloride concentrations varied from 18953 mg/L (Myliddy) to 20343 mg/L (Pannai), exceeding the average seawater concentration of 19000 mg/L [13]. This indicates some level of enrichment, possibly due to anthropogenic sources or natural variations in local geology. Bicarbonate, Alkalinity, and Hardness values varied slightly across locations but generally remained within the expected ranges for natural seawater [15].

Nitrate levels ranged from 10.4 mg/L (Thalaiyadi) to 19.1 mg/L (Myliddy), while nitrite levels were generally low across all locations (0.001 mg/L to 0.503 mg/L)) Phosphate concentrations varied between 0.21 mg/L (Thalaiyadi) and 0.66 mg/L (Kakkaithivu). While these values fall within the natural ranges for seawater [16], localized variations could be linked to agricultural runoff or sewage discharge, especially in areas with higher anthropogenic activity [17].

Iron concentrations ranged from 0.04 mg/L (Thalaiyadi) to 0.36 mg/L (Nainathivu). Calcium levels varied between 361 mg/L (Myliddy) and 417 mg/L (Pannai). Magnesium concentrations ranged from 1222 mg/L (Kakkaithivu) to 1327 mg/L (Pannai). Sodium levels varied from 10140 mg/L (Thalaiyadi) to 10530 mg/L (Pannai). Potassium levels ranged from 529 mg/L (Myliddy) to 569 mg/L (Pannai). While these values generally fall within the expected ranges for seawater [18], localized variations could be linked to specific geological conditions or anthropogenic influences. These major cations displayed variations across the locations, potentially influenced by factors like salinity and seawater circulation patterns.

The elevated levels of color, turbidity, TSS, EC, TDS, and certain nutrients observed in Pannai and Kaakai Theevu, compared to other locations, suggest a stronger influence of human activities in these areas. The significant variations in turbidity, total suspended solids (TSS), electrical conductivity, and concentrations of major cations across different sites, particularly in regions with higher anthropogenic activity, point to increased pollution levels [19]. Potential sources of these contaminants include industrial effluents, agricultural runoff, and sewage discharge. These findings underscore the need for continuous monitoring and the implementation of effective management strategies to mitigate the adverse effects of human activities on the coastal ecosystems of northern Sri Lanka. Further research is essential to evaluate the concentrations of heavy metals and other potential contaminants, particularly in areas with known anthropogenic influences, to better understand the environmental and health risks posed by these pollutants.

Challenges in Heavy Metal Determination by GFAAS in Northern Sri Lankan Seawater.

Physical and chemical parameters of seawater samples from the northern Sri Lankan sea areas highlights several potential challenges for heavy metal determination using GF-AAS. The presence of major ions in seawater can significantly interfere with the accurate measurement of heavy metals using GFAAS.

3.3 Spectral Interferences

Spectral interferences are particularly important in GFAAS, where the overlap of absorption lines from the matrix elements can cause significant errors in quantifying trace metals [20]. The secondary absorption band of Ca at 223.5 nm overlaps with the primary absorption lines of several heavy metals, including Cd, Zn, and Pb [21]. This necessitates careful background correction techniques like Zeeman background correction or the use of matrix modifiers to minimize spectral overlap. Iron (Fe) exhibits strong absorption bands at wavelengths commonly used for heavy metal analysis, such as 213.9 nm for Cd and 213.8 nm for Pb [21]. Similar to Ca, background correction or matrix modifiers are crucial for mitigating spectral interference. While Mg interference is less pronounced compared to Ca and Fe, its secondary absorption band at 202.2 nm can potentially interfere with the determination of As [21].

3.4 Non-Specific Matrix Effects

High Dissolved Solids (TDS): Elevated levels of TDS, observed in the study area, can lead to increased background absorption and reduced sensitivity for heavy metal analysis. This necessitates dilution of samples or the use of matrix modifiers to minimize non-specific effects [20]. High Cl concentrations, exceeding the average seawater values, can enhance analyte volatility during atomization in the graphite furnace, leading to underestimation of heavy metal concentrations. High concentrations of matrix elements, such as sodium and magnesium, can cause non-specific absorption, leading to inaccurate results (Willie, S. N., & Sturgeon, R. E. [22]. Using matrix modifiers like ammonium phosphate can alleviate this issue [20]. The elevated organic matter content observed in Kaakai Theevu can pose challenges during sample preparation. Organic matter can form complexes with heavy metals, reducing their availability for analysis. Pretreatment steps like acid digestion or the use of chelating agents are often necessary to break down these complexes and release the bound metals [23]. High turbidity and suspended solids levels, exceeding recommended limits in Pannai and Kaakai Theevu, can lead to clogging of the graphite furnace and signal suppression. Pre-filtration or centrifugation steps might be required to minimize these interferences [22].

Several studies have addressed the challenges of heavy metal determination in seawater using GFAAS. GFAAS has emerged as a powerful technique for direct cadmium determination in seawater, offering high sensitivity and selectivity [24]. However, challenges such as spectral interferences and matrix effects necessitate the development of robust methodologies for accurate heavy metal quantification [25]. Pre-concentration techniques, such as cloud point extraction [26]. chelation and extraction Sperling, [27], Sturgeon et al., [28], ion exchange Bruland, [29], Kingston et al., [30], and electrodeposition Lund and Larsen, [31] and solid-phase extraction [32]. have been employed to increase the sensitivity of the analysis by concentrating trace metal ions. Additionally, matrix modifiers, including palladium and magnesium nitrates Wang, X., et al. [33], have been utilized to mitigate matrix effects and improve analytical precision. Selective volatilization, as demonstrated by Lundgren et al. [31], offers a direct approach to heavy metal determination in seawater by atomizing at temperatures below the vaporization temperature of NaCl, thereby separating the metal signal from the salt matrix. Modified furnace programs, such as optimized heating ramps and temperature programs Tian, M., et al. [34], have been implemented to enhance sensitivity and reduce background noise, thereby improving the detection limits for heavy metal in seawater [35]. Kumar et al. (2010) highlighted the matrix interferences caused by Ca, Mg, and Na in the analysis of Cd, Pb, and Cu in seawater samples from the Gulf of Mannar, India [36]. They employed background correction and matrix modifiers to overcome these interferences [37]. Arulmozhi et al. (1998) investigated the influence of organic matter on heavy metal determination in coastal seawater samples. They emphasized the importance of proper sample digestion techniques to release metals bound to organic complexes. A study by Wijesekera et al. [4] analyzing heavy metals in coastal Sri Lankan waters emphasized the importance of matrix modification with ammonium phosphate to overcome interferences from Ca and Mg during Pb analysis [38].

The provided data on the seawater composition of the northern Sri Lankan Sea areas suggests that GFAAS analysis of heavy metals will likely encounter challenges due to: Spectral interferences from major cations like Ca, Fe, and Mg, Non-specific matrix effects caused by high TDS and Cl concentrations, Potential interferences from organic matter, particularly in areas like Kaakai Theevu, Signal suppression due to high turbidity and suspended solids in Pannai and Kaakai Theevu [39]. Therefore, careful consideration of these factors is crucial for accurate heavy metal determination using GFAAS. Employing background correction techniques, matrix modifiers, appropriate sample pre-treatment (digestion, filtration), and optimization of analysis parameters are essential to overcome these challenges and achieve reliable results [40,41].

4. CONCLUSION AND RECOMMENDATION

This study analyzed the physicochemical characteristics of seawater samples from five locations in the northern Sri Lankan coastal seas. The findings revealed significant variations in several parameters, particularly in areas with higher anthropogenic activity. Elevated levels of turbidity, total suspended solids, color, electrical conductivity, total dissolved solids, and certain nutrients in Pannai and Kaakai Theevu compared to other locations, indicating potential environmental degradation linked to human influences. Major cations like calcium, iron, and magnesium displayed variations across the locations, potentially influenced by factors like salinity and seawater circulation patterns.

These findings suggest that: Continuous monitoring and effective management strategies are crucial to mitigate the negative impacts of anthropogenic activities on these coastal ecosystems. Further investigations are necessary to assess heavy metal concentrations, particularly in areas with known anthropogenic influences, for a comprehensive understanding of potential environmental and health risks.

The study highlights potential challenges for heavy metal analysis using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) due to the presence of major ions in seawater: Spectral interferences from calcium, iron, and magnesium can be mitigated using background correction techniques and matrix modifiers. Non-specific matrix effects from high dissolved solids, chloride, organic matter, turbidity, and suspended solids can be addressed through dilution, matrix modifiers, sample pre-treatment, and optimization of analysis parameters. Therefore, careful consideration of these factors is essential for accurate heavy metal determination using GFAAS in these northern Sri Lankan sea areas. This study contributes to a better understanding of the environmental conditions in these marine environments and emphasizes the need for further research on heavy metal contamination and the development of robust analytical methods to address the challenges posed by the complex seawater matrix.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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