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# Spatial Distribution and Pollution Assessment of Trace Elements Pb, Cu, Ni, Fe and As in the Surficial Water of Staring Bay, Indonesia

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Staring Bay has long been used by the local community for fisheries and fishing activities; however, the rapid population growth and industrial activities around the bay in recent years are predicted to contribute significantly to the increase of waste entering the bay. This particular study was aimed to provide baseline levels of trace elements Pb, Cu, Ni, Fe, and As in this bay. Concentration and spatial distribution of trace elements were analyzed to determine the pollution status of the bay. An inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify elements content. The concentrations of trace elements varied from 0.049-0.685 µg $L^{-1}$ (average: 0.261 ± 0.163 µg $L^{-1}$) for Pb, 0.170-1.278 µg $L^{-1}$ (0.475 ± 0.252 µg $L^{-1}$) for Cu, 0.375-1.469 µg $L^{-1}$ (0.754 ± 0.258 µg $L^{-1}$) for Ni, 0.544-69.290 µg $L^{-1}$ (8.036 ± 13.779 µg $L^{-1}$) for Fe, and 0.952-1.721 µg $L^{-1}$ (1.366 ± 0.168 µg $L^{-1}$) for As. The present study suggests that Staring Bay has been highly contaminated by trace elements Pb and Fe relative to their normal oceanic levels. The contaminated areas were found in the estuaries due to terrestrial anthropogenic inputs from industrial and agricultural activities, residential areas and brackish ponds.

**Keywords:** Staring Bay, trace element, pollution status

## Introduction

The current rapid human population growth followed by an increase in industrial activities have led to a decrease in water quality, including seawater. One of the constituents that can reduce the quality of seawater is the trace element that accumulates in water bodies and causes pollution.[1-4] Trace elements enter the coastal areas through naturally occurring substances (biogenic) and by several human activities (anthropogenic) discharges, such as domestic waste, agricultural activities and industrial practices.[5,6] Anthropogenic processes of trace elements have been noted to go beyond the natural fluxes for some elements.[7] The toxic trace elements entering the ecosystem may lead to geo-accumulation, bioaccumulation, and biomagnifications. Trace elements like Fe, Cu, Zn, Ni and others are important for the proper functioning of biological systems and their deficiency or excess could lead to some disorders.[8] Food chain contamination by trace elements has become a burning issue in recent years because of their potential accumulation in bio-systems through contaminated water, soil and air.[9,10] The presence of trace elements in the marine environment has received a lot of attention from environmental researchers because of its toxicity, the fact of being easily absorbed by marine organisms' tissues and can experience biologic intensification.[11-13]

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Staring Bay, located in the South Konawe Regency, Province of Southeast Sulawesi, Indonesia, is one of the most valuable natural resources and plays a critical role in communities around the area. The bay has ecological benefits for fish as it serves as spawning, nursery and fishing ground for commercial and non-commercial fishing.[14] However, during recent decades, there has been rapid development and urbanization around this area. The rapid development increased the urbanization process, including industrial activities which contribute to pollutants such as trace elements in aquatic environment.[15] Environmental pollution is the result of rapid industrialization and technological advancement and unprecedented increase in population.[8]

There are several rivers spread in the western, southwestern and southeastern parts of the bay which carry industrial, agricultural, and urban domestic waste into the seawater system. For example, the Kunikuni Moramo River and Laonti River are two big river system flows that connect directly to the southwestern and southeastern parts of the bay. These may become a source for the input of trace elements to the bay. However, no report has been published concerning how trace elements behave on the surface seawater of Staring Bay. This study aimed to provide baseline levels of trace elements Pb, Cu, Ni, Fe and As in the Staring Bay through investigating their spatial distribution and pollution status.

## Experimental

### Study location and sampling site

Geographically, Staring Bay is located at 4°02’40”-4°08’53” S and 122°40’03”-122°48’02” E and has an area of 193.23 km$^2$. The depth of the Staring Bay ranges from 0 to 75 m. It connects to the Banda Sea through Wawonii Island to the northeast (Figure 1). During recent decades industrial and urban development have surrounded the area which was a consideration when deciding on sampling sites in the present study (Table 1).

### Sampling

All polyethylene vessels used to collect and store water samples were pre-washed by 10% nitric acid

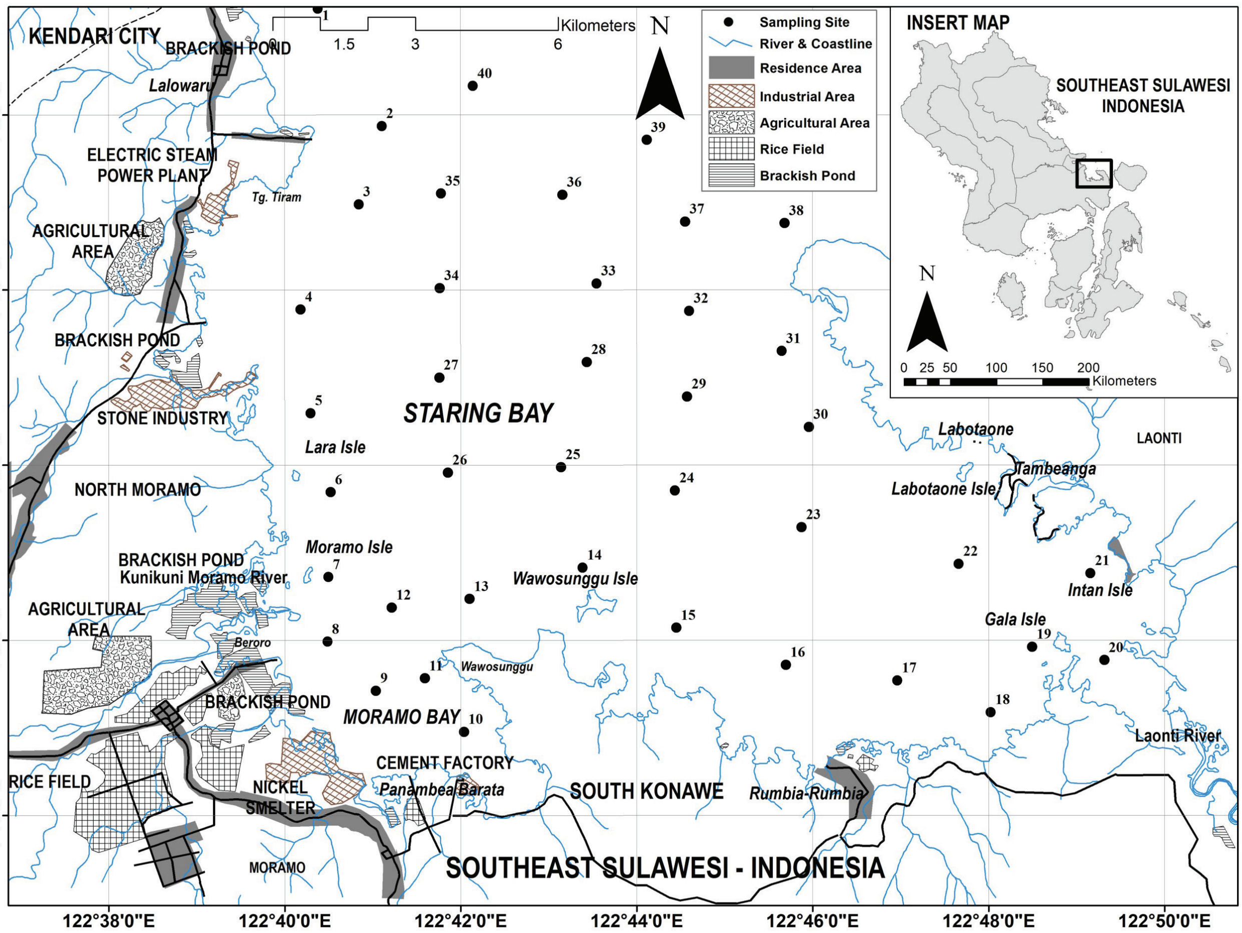

**Figure 1.** Geographic location of Staring Bay, Indonesia. The sampling sites are shown by filled circles.

**Table 1.** Regional representative of forty sampling sites in Staring Bay

| Site | Region |
|---|---|
| 1, 2 | residence, estuary, and agricultural activity (brackish pond) |
| 3, 4 | industry (electric steam power plant), estuary, and agricultural activities (brackish pond and rice field) |
| 5 | stone industry, estuary, and agricultural activities (brackish pond and rice field) |
| 6-8 | residence, estuary of Kunikuni Moramo River and agricultural activities (brackish pond and rice field) |
| 9 | residence, estuary, industry (nickel smelter) and brackish pond |
| 10, 11 | residence, estuary and industry (cement factory) |
| 12-17 | estuary |
| 18-20 | estuary of Laonti River |
| 21, 22 | estuary and residence area |
| 23-37 | inner bay |
| 38-40 | outer bay |

(Kanto Chemical Co., Inc., Tokyo, Japan) and rinsed with deionized water with resistivity of 18.2 MΩ cm before they were oven-dried at 40 °C. Water samples were collected at high tide during the dry season in September 2018 from forty sampling sites (Figure 1) and representative of eleven regions of the bay (Table 1). All samples were filtered through a Millipore HA filter (0.45 µm pore size), added with concentrated nitric acid (Kanto Chemical Co., Inc., Tokyo, Japan) to meet the final solution of 1% nitric acid, and then preserved at 4 °C until analysis. Geographic coordinates of the sampling sites were recorded using a Global Positioning System (Garmin GPSMap 64s, Taiwan). During sampling, water parameters (i.e., temperature, pH, and salinity) were measured directly by a portable pH/conductivity meter (JENWAY 430, UK) (Table 2).

### Analysis

Direct analysis of trace elements in seawater samples was performed using an inductively coupled plasma mass spectrometry (ICP-MS, XSERIES 2, Thermo Fisher Scientific, Bremen, Germany) and collision cell technology (CCT) in conjunction with the FAST sample introduction system from ESI (Elemental Scientific Inc., Omaha, NE, USA) to overcome both spectral and non-spectral interferences. The ICP-MS system was configured following parameters listed in Table 3 with the sample introduction system in combination with an autosampler. An internal standard of $^{115}$In (2 ppb solution) was used for the entire measurement of $^{208}$Pb, $^{65}$Cu, $^{60}$Ni, $^{56}$Fe and $^{75}$As. The multi-elemental standard solution of SPEX XSTC-331 (SPEX CertiPrep®, New Jersey, USA) was used to quantify trace element concentrations by calibration curve method. Each sample measurement was read 3 times producing the precision values (relative standard deviation, RSD) of 2.09 (for Pb), 1.23 (Cu), 1.04 (Ni), 1.16 (Fe), and 1.68% (As). The limits of detection were defined from 3 standard deviations of 10 blank runs and found to be 0.003, 0.010, 0.035, 0.051, and 0.025 µg L$^{-1}$, for Pb, Cu, Ni, Fe, and As, respectively. CASS-6, the certified reference material (CRM) of seawater produced by National Research Council (NRC), Canada, was utilized to assess the accuracy of the quantification and found good recoveries (Table 4). Pearson correlation analysis was performed to measure the relationship between variables of trace element concentrations and seawater parameters. The distribution of trace elements among sampling sites, where the concentrations were expressed in a similar unit, was examined by principal components analysis (PCA) and hierarchical clustering analysis (HCA). All statistical analyses were accomplished using the computer software of Statistical Analysis System (SAS) 9.4.[16] The pattern of surface seawater current during sampling was analyzed by a numerical model using the flow mesh flexible model.[17]

## Results and Discussion

### Seawater parameters and spatial distribution of trace elements

Table 2 shows seawater parameters during sampling. Sea surface temperature (SST) was almost similar at each sampling site with a variation of 30.0-30.7 °C (average = 30.3 ± 0.2 °C). The high SST in Staring Bay could not be separated from the geographical position of Indonesia in the equatorial region, which is the area that receives the most solar heat. The equatorial region has a warm SST that is triggered by continuous heating throughout the year. Sampling conducted in September 2018 during the dry season offered a significant contribution to the invasion of atmospheric temperature into the water system of Staring Bay. A previous study[18] has underlined that high temperatures increased the trace element contents in the marine environment due to an increased reaction rate of the formation of trace element ions.

The high temperature will trigger the evaporation process in the water body to rise which may influence the salinity value.[19] Salinity in Staring Bay ranged from 32.21-35.98‰ (Table 2) and changed as a linear function of SST with a correlation coefficient ($r^2$) of 0.594. The distribution of seawater salinity is influenced by various factors such as evaporation, water circulation pattern, rainfall, and river flow.[20] The high salinity (saline water)

**Table 2.** Geographic coordinates of sampling sites and water parameters

| Site | Geographic coordinate | | Water parameter | | |
|---|---|---|---|---|---|
| | Longitude | Latitude | Temperature / °C | Salinity / ‰ | pH |
| 1 | 122°40’22.72” E | 4°0’47.24” S | 30.7 | 35.27 | 7.91 |
| 2 | 122°41’6.44” E | 4°2’7.79” S | 30.3 | 34.90 | 8.03 |
| 3 | 122°40’50.62” E | 4°3’1.36” S | 30.2 | 34.50 | 7.92 |
| 4 | 122°40’10.96” E | 4°4’13.36” S | 30.2 | 34.70 | 8.11 |
| 5 | 122°40’17.68” E | 4°5’24.39” S | 30.2 | 34.63 | 7.91 |
| 6 | 122°40’31.28” E | 4°6’18.56” S | 30.7 | 35.20 | 8.10 |
| 7 | 122°40’29.86” E | 4°7’16.69” S | 30.7 | 35.57 | 8.11 |
| 8 | 122°40’29.26” E | 4°8’0.95” S | 30.2 | 34.32 | 8.19 |
| 9 | 122°41’2.20” E | 4°8’34.61” S | 30.0 | 32.67 | 7.95 |
| 10 | 122°42’2.19” E | 4°9’2.77” S | 30.1 | 32.43 | 8.01 |
| 11 | 122°41’35.55” E | 4°8’26.12” S | 30.0 | 33.30 | 7.98 |
| 12 | 122°41’12.96” E | 4°7’37.58” S | 30.1 | 33.70 | 7.93 |
| 13 | 122°42’6.02” E | 4°7’31.71” S | 30.2 | 33.61 | 7.90 |
| 14 | 122°43’23.20” E | 4°7’10.34” S | 30.4 | 33.70 | 8.00 |
| 15 | 122°44’27.01” E | 4°7’51.49” S | 30.5 | 34.60 | 8.02 |
| 16 | 122°45’41.74” E | 4°8’16.89” S | 30.5 | 34.12 | 7.96 |
| 17 | 122°46’57.83” E | 4°8’27.56” S | 30.2 | 34.90 | 7.95 |
| 18 | 122°48’1.43” E | 4°8’49.37” S | 30.1 | 32.45 | 7.94 |
| 19 | 122°48’29.66” E | 4°8’4.59” S | 30.0 | 32.21 | 7.92 |
| 20 | 122°49’18.90” E | 4°8’13.66” S | 30.1 | 32.83 | 8.12 |
| 21 | 122°49’9.41” E | 4°7’14.18” S | 30.0 | 33.21 | 8.10 |
| 22 | 122°47’39.56” E | 4°7’7.75” S | 30.1 | 34.12 | 7.91 |
| 23 | 122°45’52.41” E | 4°6’42.61” S | 30.0 | 33.20 | 7.93 |
| 24 | 122°44’26.20” E | 4°6’17.44” S | 30.6 | 35.14 | 8.01 |
| 25 | 122°43’8.43” E | 4°6’1.42” S | 30.3 | 33.20 | 7.93 |
| 26 | 122°41’51.27” E | 4°6’5.17” S | 30.6 | 35.41 | 7.91 |
| 27 | 122°41’45.48” E | 4°5’0.16” S | 30.7 | 35.32 | 8.02 |
| 28 | 122°43’26.07” E | 4°4’49.45” S | 30.6 | 35.24 | 7.89 |
| 29 | 122°44’34.40” E | 4°5’13.08” S | 30.6 | 35.17 | 7.93 |
| 30 | 122°45’57.55” E | 4°5’33.92” S | 30.2 | 34.77 | 8.03 |
| 31 | 122°45’38.95” E | 4°4’41.90” S | 30.3 | 35.10 | 7.96 |
| 32 | 122°44’35.97” E | 4°4’14.46” S | 30.2 | 35.11 | 7.92 |
| 33 | 122°43’32.83” E | 4°3’55.62” S | 30.5 | 35.32 | 8.02 |
| 34 | 122°41’45.70” E | 4°3’58.80” S | 30.3 | 35.24 | 8.01 |
| 35 | 122°41’46.63” E | 4°2’53.96” S | 30.5 | 35.17 | 7.93 |
| 36 | 122°43’9.47” E | 4°2’54.87” S | 30.3 | 34.77 | 8.03 |
| 37 | 122°44’33.17” E | 4°3’13.27” S | 30.5 | 35.10 | 8.01 |
| 38 | 122°45’40.92” E | 4°3’14.33” S | 30.4 | 34.12 | 7.92 |
| 39 | 122°44’6.92” E | 4°2’17.30” S | 30.5 | 35.98 | 7.93 |
| 40 | 122°42’8.42” E | 4°1’40.27” S | 30.8 | 35.87 | 7.93 |

with an average of 34.40 ± 1.03‰ in the studied area might be due to the high evaporation at day time of the dry season during samples collection. However, water circulation pattern in the estuary areas around Kunikuni Moramo River at the southwestern part (sampling sites 9 and 10) as well as the influence of freshwater arising from the mouth of Laonti River at the southeastern part of the bay (sampling sites 18-20) possibly yielded salinities decreased to ca. 32‰ (Table 2). The increase of salinity level is often associated with high chloride content. Under certain circumstances, chloride may have an important role in determining the distribution of trace elements in the aquatic environment through the formation of the element-chloride species.[21] In addition, trace elements, which usually sink in marine sediments through adsorption and successive sedimentation, can be released back into seawater when the salinity of the environment changes.[22]

**Table 3.** ICP-MS settings for measurement

| ICP-MS configuration | |
|---|---|
| Nebulizer | ESI PFA-ST MicroFlow nebulizer |
| Spray chamber | cyclonic spray chamber |
| Torch | demountable torch with 2.5 mm diameter |
| Interface | Xt-Ni cone |
| Spread temperature / °C | 2 |
| Additional gas | 2% methane in Ar at 100 mL min$^{-1}$ |
| Nebulizer gas / (L min$^{-1}$) | 1-1.1 |
| RF power / W | 1500 |
| CCT gas | 8% hydrogen in helium at 5 mL min$^{-1}$ |
| CCT mode | +2 V kinetic energy discrimination |
| Tube color | sample = orange-green;<br>internal standard = black-black |
| Dilution ratio of sample:internal standard | 1:4 |
| Sampling loop / µL | 500 |
| Carrier solution | 0.3 M $HNO_3$ |
| Analytical parameter | |
| Internal standard isotope | $^{115}$In (2 ppb solution) |
| Number of replicates *per* sample | 3 |
| Scan mode | peak jumping |
| Sample uptake time / s | 3 (2 mL sample) |
| Washing delay / s | 10 |
| Total time *per* sample / s | 30 |

ICP-MS: inductively coupled plasma mass spectrometry; RF: radio frequency; CCT: collision cell technology.

**Table 4.** Measurement results of the CRM CASS-6 in comparison to the certified values

| Element | CASS-6 concentration / (µg L$^{-1}$) | | Recovery / % |
|---|---|---|---|
| | Measured (n = 5) | Certified | |
| Pb | 0.0096 ± 0.0006 | 0.0104 ± 0.0040 | 92 ± 5 |
| Cu | 0.509 ± 0.021 | 0.520 ± 0.032 | 98 ± 4 |
| Ni | 0.422 ± 0.036 | 0.410 ± 0.040 | 103 ± 9 |
| Fe | 1.664 ± 0.057 | 1.53 ± 0.12 | 109 ± 4 |
| As | 0.966 ± 0.027 | 1.02 ± 0.10 | 95 ± 3 |

CASS-6: certified reference material (CRM) of seawater produced by National Research Council (NRC), Canada.

Seawater pH at the sampling sites varied from 7.9 to 8.19 (Table 2) with an average value of 7.98 ± 0.07, which was a typical characteristic of modern seawater pH. The pH of seawater controls the speciation of dissolved trace elements, which in turn influences their solubility in coastal waters by the carbonate system.[23] Changes in pH may cause both an increase and a decrease in the trace element contents by several degrees. Lower pH values can encourage the solubility of trace element compounds; as the level of hydrogen ions increases, most cations are released into the water instead of being in adsorbed forms.[24] Generally, a decrease in pH will increase the concentration of dissolved trace element cations, whereas the high pH tends to promote the precipitation of the elements in the form of hydroxides.

The distribution of trace elements in the coastal water of Staring Bay at each sampling site is tabulated in Table 5. The concentrations of dissolved trace elements Pb, Cu, Ni, Fe, and As varied from 0.049 to 0.685 µg L$^{-1}$ (average = 0.261 ± 0.163 µg L$^{-1}$), 0.170 to 1.278 µg L$^{-1}$ (average = 0.475 ± 0.252 µg L$^{-1}$), 0.375 to 1.469 µg L$^{-1}$ (average = 0.754 ± 0.258 µg L$^{-1}$), 0.544 to 69.290 µg L$^{-1}$ (average = 8.036 ± 13.779 µg L$^{-1}$), and 0.952 to 1.721 µg L$^{-1}$ (average = 1.366 ± 0.168 µg L$^{-1}$), respectively.

Figure 2 shows the spatial distribution of trace elements in Staring Bay superimposed with the surface seawater current direction at high tide. Spatial distribution pattern was used to perceive the trace elements fluctuation levels and their possible causes. As shown in Figure 2, except for As, spatial distribution of trace elements Pb, Cu, Ni, and Fe had a relatively similar pattern, where the higher concentrations were found in the western part of the bay; suggesting a similar source of input, which might come from related types of terrestrial anthropogenic activities, such as fish pond cultivations, residential areas, as well as industrial and agricultural activities (Table 1). Moreover, based on the data from Geospatial Information Agency of Indonesia,[25] Staring Bay is surrounded by thirty-three watercourses that empty into the bay; nineteen watercourses spread from northwest to southwest, including the Kunikuni Moramo River flow, nine watercourses span from south to southeast, including the large flow of Laonti River, and the remaining five are in the eastern part of the bay. Therefore, the high content of trace elements recorded in the western part of the bay was probably due to the large number of tributaries in the area, allowing the input of pollutants from various anthropogenic activities on the land through their streams. This phenomenon was supported by the high tide current direction that moved from northeast (the mouth of the bay) to west (Figure 2), with the result that trace elements were more concentrated in the west, while elements dispersion was likely to run slowly to the center of the bay. It is suggested that the distribution of trace elements in the marine environment is affected not only by the littoral pollutants but also by the hydrodynamic characteristics,[26] one of which is the seawater current.

The maximum Pb concentrations were found at sites 4, 6, and 7 (ca. 0.6 µg L$^{-1}$) and the highest one was at site 9 (ca. 0.7 µg L$^{-1}$). Those sites were representatives of

**Table 5.** Concentrations of trace elements Pb, Cu, Ni, Fe, and As in the surficial water of Staring Bay

| Sampling site | Trace element concentration / (µg $L^{-1}$) | | | | |
|---|---|---|---|---|---|
| | Pb | Cu | Ni | Fe | As |
| 1 | 0.197 ± 0.011 | 0.310 ± 0.060 | 0.638 ± 0.162 | 2.058 ± 0.041 | 1.253 ± 0.143 |
| 2 | 0.277 ± 0.030 | 1.278 ± 0.040 | 0.990 ± 0.167 | 4.957 ± 0.102 | 1.328 ± 0.380 |
| 3 | 0.053 ± 0.002 | 0.222 ± 0.036 | 0.729 ± 0.090 | 0.608 ± 0.122 | 1.475 ± 0.362 |
| 4 | 0.639 ± 0.009 | 0.928 ± 0.065 | 0.858 ± 0.102 | 19.92 ± 1.065 | 1.447 ± 0.112 |
| 5 | 0.169 ± 0.001 | 0.433 ± 0.092 | 0.658 ± 0.097 | 0.815 ± 0.141 | 1.206 ± 0.146 |
| 6 | 0.618 ± 0.032 | 0.727 ± 0.071 | 0.990 ± 0.112 | 27.04 ± 0.956 | 1.344 ± 0.262 |
| 7 | 0.593 ± 0.031 | 0.795 ± 0.050 | 1.050 ± 0.177 | 47.59 ± 1.292 | 1.508 ± 0.123 |
| 8 | 0.055 ± 0.013 | 0.979 ± 0.127 | 1.469 ± 0.129 | 69.29 ± 0.200 | 1.517 ± 0.312 |
| 9 | 0.685 ± 0.050 | 0.269 ± 0.068 | 1.157 ± 0.183 | 1.900 ± 0.171 | 1.064 ± 0.185 |
| 10 | 0.157 ± 0.015 | 0.220 ± 0.022 | 1.299 ± 0.128 | 0.962 ± 0.059 | 0.952 ± 0.359 |
| 11 | 0.328 ± 0.012 | 0.500 ± 0.078 | 1.169 ± 0.046 | 11.23 ± 0.826 | 1.405 ± 0.219 |
| 12 | 0.161 ± 0.024 | 0.358 ± 0.084 | 1.221 ± 0.147 | 4.178 ± 0.056 | 1.126 ± 0.107 |
| 13 | 0.175 ± 0.017 | 0.307 ± 0.013 | 0.859 ± 0.077 | 3.038 ± 0.237 | 1.241 ± 0.391 |
| 14 | 0.358 ± 0.012 | 0.643 ± 0.067 | 0.865 ± 0.073 | 7.758 ± 0.467 | 1.396 ± 0.312 |
| 15 | 0.300 ± 0.012 | 0.817 ± 0.109 | 0.797 ± 0.133 | 6.524 ± 0.460 | 1.618 ± 0.377 |
| 16 | 0.249 ± 0.013 | 0.551 ± 0.053 | 0.815 ± 0.120 | 5.113 ± 0.186 | 1.721 ± 0.087 |
| 17 | 0.118 ± 0.013 | 0.291 ± 0.043 | 0.802 ± 0.058 | 0.672 ± 0.068 | 1.465 ± 0.106 |
| 18 | 0.248 ± 0.010 | 0.412 ± 0.107 | 0.772 ± 0.089 | 5.641 ± 0.496 | 1.650 ± 0.262 |
| 19 | 0.247 ± 0.007 | 0.568 ± 0.043 | 0.735 ± 0.078 | 7.002 ± 0.176 | 1.507 ± 0.133 |
| 20 | 0.356 ± 0.029 | 0.739 ± 0.071 | 0.803 ± 0.099 | 27.48 ± 1.300 | 1.265 ± 0.106 |
| 21 | 0.273 ± 0.012 | 0.459 ± 0.087 | 0.871 ± 0.051 | 19.44 ± 0.486 | 1.606 ± 0.166 |
| 22 | 0.095 ± 0.009 | 0.281 ± 0.047 | 0.730 ± 0.124 | 0.928 ± 0.101 | 1.292 ± 0.273 |
| 23 | 0.251 ± 0.012 | 0.554 ± 0.089 | 0.767 ± 0.113 | 5.367 ± 0.389 | 1.307 ± 0.139 |
| 24 | 0.429 ± 0.024 | 0.698 ± 0.028 | 0.708 ± 0.189 | 11.46 ± 1.064 | 1.326 ± 0.148 |
| 25 | 0.127 ± 0.013 | 0.343 ± 0.016 | 0.407 ± 0.003 | 0.773 ± 0.123 | 1.370 ± 0.159 |
| 26 | 0.152 ± 0.007 | 0.256 ± 0.017 | 0.437 ± 0.078 | 1.076 ± 0.174 | 1.149 ± 0.186 |
| 27 | 0.437 ± 0.024 | 0.656 ± 0.046 | 0.453 ± 0.062 | 5.608 ± 0.374 | 1.204 ± 0.396 |
| 28 | 0.234 ± 0.011 | 0.308 ± 0.041 | 0.410 ± 0.169 | 1.159 ± 0.069 | 1.309 ± 0.179 |
| 29 | 0.215 ± 0.015 | 0.302 ± 0.014 | 0.375 ± 0.057 | 1.166 ± 0.096 | 1.550 ± 0.313 |
| 30 | 0.117 ± 0.009 | 0.206 ± 0.076 | 0.474 ± 0.139 | 0.663 ± 0.046 | 1.421 ± 0.351 |
| 31 | 0.171 ± 0.017 | 0.263 ± 0.033 | 0.569 ± 0.152 | 1.236 ± 0.198 | 1.140 ± 0.088 |
| 32 | 0.109 ± 0.006 | 0.311 ± 0.022 | 0.553 ± 0.073 | 0.817 ± 0.113 | 1.272 ± 0.125 |
| 33 | 0.346 ± 0.014 | 0.349 ± 0.083 | 0.584 ± 0.168 | 2.928 ± 0.042 | 1.472 ± 0.495 |
| 34 | 0.396 ± 0.007 | 0.515 ± 0.032 | 0.593 ± 0.125 | 4.731 ± 0.287 | 1.528 ± 0.231 |
| 35 | 0.067 ± 0.011 | 0.224 ± 0.028 | 0.558 ± 0.094 | 0.567 ± 0.035 | 1.177 ± 0.187 |
| 36 | 0.371 ± 0.030 | 0.582 ± 0.071 | 0.538 ± 0.165 | 3.657 ± 0.060 | 1.471 ± 0.157 |
| 37 | 0.274 ± 0.002 | 0.637 ± 0.067 | 0.703 ± 0.092 | 4.196 ± 0.310 | 1.451 ± 0.233 |
| 38 | 0.145 ± 0.004 | 0.201 ± 0.022 | 0.562 ± 0.106 | 0.663 ± 0.048 | 1.417 ± 0.260 |
| 39 | 0.193 ± 0.024 | 0.319 ± 0.039 | 0.640 ± 0.108 | 0.672 ± 0.110 | 1.268 ± 0.112 |
| 40 | 0.049 ± 0.006 | 0.170 ± 0.010 | 0.555 ± 0.165 | 0.544 ± 0.107 | 1.415 ± 0.378 |
| Average | 0.261 ± 0.163 | 0.475 ± 0.252 | 0.754 ± 0.258 | 8.036 ± 13.779 | 1.366 ± 0.168 |
| RSD / % | 63 | 53.19 | 34.26 | 171.47 | 12.28 |

RSD: relative standard deviation.

anthropogenic activities on the land. For example, site 4 was marked by the presence of an electric steam power plant as well as agricultural area, sites 6 and 7 belonged to the mouth of Kunikuni Moramo River, while site 9 was dominantly marked by a nickel smelter (Table 1). The high Pb concentrations found in those areas might also arise from combustion and road-side dust which were transported from the atmosphere to the water body during runoff and rainy season.[1] The highest Cu concentration was found at site 2 (ca. 1.3 µg $L^{-1}$), which might be affected by the waste from residence and brackish pond activities. Site 8, which was located close to the mouth of Kunikuni Moramo River and was also associated with residence and agricultural activities (brackish pond and rice field) on the

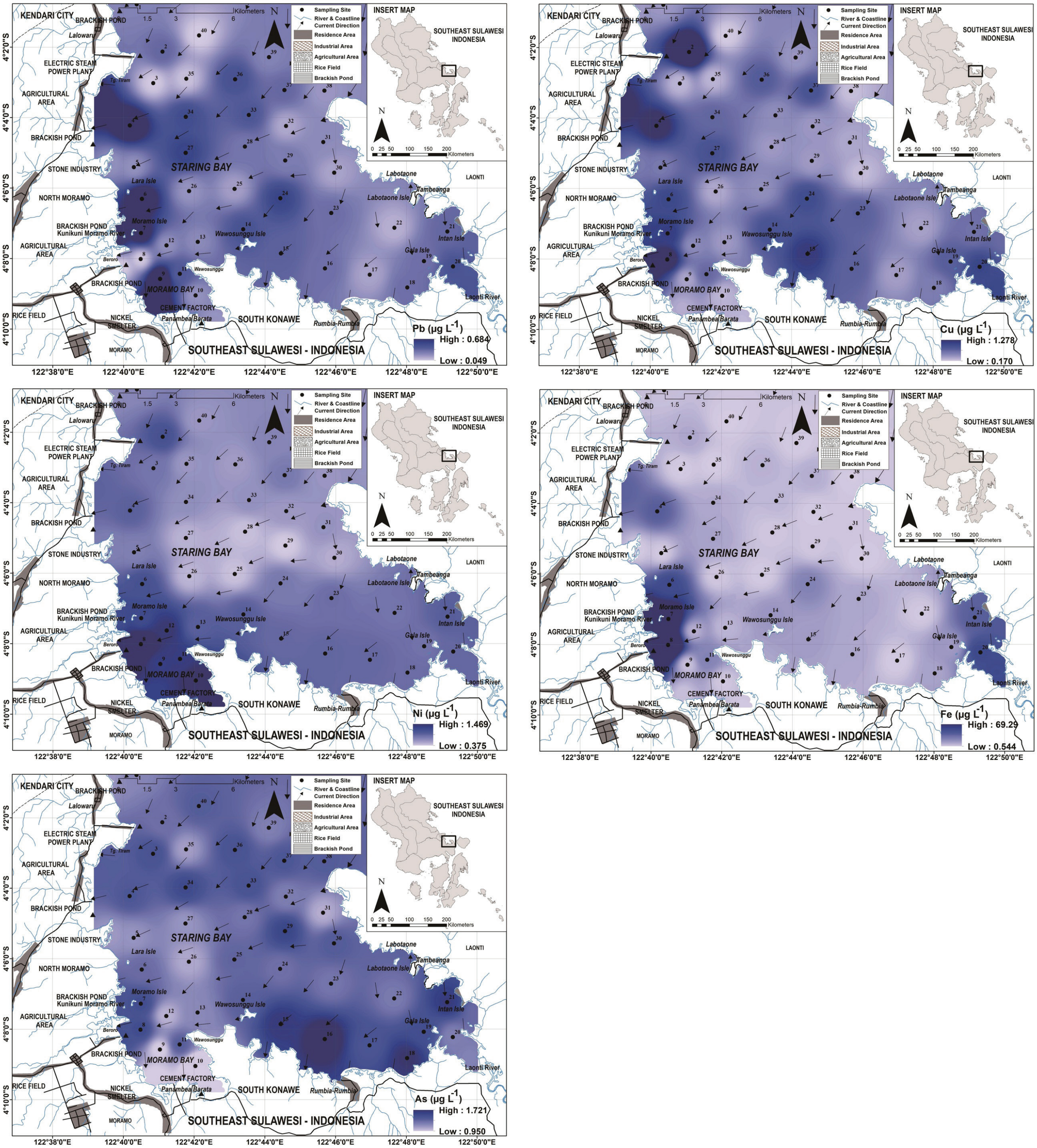

**Figure 2.** Spatial distribution of trace elements Pb, Cu, Ni, Fe, and As in Staring Bay overlaid by surface seawater current pattern.

land, contained the highest concentrations of Ni and Fe of ca. 1.5 and ca. 69 μg L$^{-1}$, respectively.

Table 5 further shows that the lowest concentrations of trace elements Pb, Cu and Fe were found at site 40, which was the outer part of the bay. The low concentrations of these elements in the outermost part of the bay might be due to washing or mixing seawater with the Banda Sea, which would dilute the concentrations of trace elements. The lowest concentration of trace element Ni (ca. 0.4 μg L$^{-1}$) was found at the sampling sites 25-29. Such sites were located in the middle of the bay where the movement of seawater mass away from the source of pollution during low tide and the presence of seawater mass mixing with the outer bay were possibly the reason for the low concentration of Ni. The lowest concentration of trace element As (0.952 μg L$^{-1}$) was recorded at site 10, which was an estuary.

It is important to note that about half of forty sampling sites, i.e., sampling sites 1 to 22, were regions affected by estuaries. The result of direct field observation found that the estuary area of Staring Bay was surrounded by mangrove ecosystem along the coast. It is well known that mangroves can absorb trace element from their growth environment into their bodies; known as phytoremediation. Therefore, most estuarine regions have low element concentrations because of the influence of such phytoremediation processes.[27-31] However, the trend of low element concentrations was not discovered in estuary areas compared to the outer regions in Staring Bay, except for trace element As. It is suggested that the behavior of elements in estuaries is a complex phenomenon and can vary from one estuary to another and/or from one region to another. Non-conservative behavior of the trace elements in the mixing zone of an estuary may be due to ion exchange, variation of ionic strength, adsorption and biological uptake.[32]

The relative standard deviation (RSD, %) was used to analyze the diversity of trace elements among forty sampling sites.[26] Table 5 shows that the highest diversity occurred in the distribution of trace element Fe (RSD = ca. 171%), followed by Pb (ca. 63%), Cu (ca. 53%), and Ni (ca. 34%). The very high variability of Fe in Staring Bay was related to the addition-removal processes of this element in the marine environment. Apart from anthropogenic sources, which is a concern of the present study, addition of Fe in the surface water of Staring Bay might come from other external sources as well as regenerated sources recycled *in situ* from diverse particulate phases, including: deposition of atmospheric aerosols, vertical mixing and upwelling, input from bottom sediments, and biogenic recycling of cellular Fe in surface water. Meanwhile, Fe removal could occur through several mechanisms, such as: sorption and precipitation, biological assimilation, aggregation of inorganic or organic colloids, and sinking of mineral and biogenic particles.[33] A special case is addressed to the trace element As, where its concentration in Staring Bay was almost distributed evenly throughout the sampling sites (RSD = ca. 12%). Taking into consideration that its concentrations in the whole sites were below the normal oceanic concentration (2.6 μg L$^{-1}$),[34] the natural processes possibly controlled the distribution of As, such as current movement and removal by stronger adsorption process to the particulate matter in the marine system. Moreover, a previous study[35] underlined that the concentration of dissolved As will be greatly reduced in waters containing high content of free sulfide due to the formation of sulfide minerals containing coprecipitated As at neutral and alkaline pH.

Pearson correlation analysis was carried out to determine the extent of the relationship among the analyzed trace elements, as well as between elements and seawater pH and salinity (Table 6). Table 6 shows that there were significant positive linear relationships between trace elements Pb and Cu, Cu and Ni, Ni and Fe, and Fe and Cu with coefficient values of 0.492, 0.403, 0.571, and 0.605, respectively. This suggested that these elements might have similar sources of pollution or they underwent similar migration processes in the bay.

Table 6 further informs that pH was positively linear correlated to the element concentrations of Pb, Cu, Ni, and Fe with coefficient values of 0.483, 0.695, 0.464, and 0.797, respectively. Based on a chemical point of view, a decrease in pH will be followed by an increase in element solubility in the aquatic system.[23] It has to be noted that the pH of Staring Bay during sampling was found to be

**Table 6.** Pearson correlation matrix among variables

| | | Pb | Cu | Ni | Fe | As | pH | Salinity |
|---|---|---|---|---|---|---|---|---|
| Pb | Pearson[a] | 1 | | | | | | |
| | *P*-value | | | | | | | |
| Cu | Pearson[a] | 0.492[b] | 1 | | | | | |
| | *P*-value | 0.001 | | | | | | |
| Ni | Pearson[a] | 0.234 | 0.403[b] | 1 | | | | |
| | *P*-value | 0.147 | 0.010 | | | | | |
| Fe | Pearson[a] | 0.294 | 0.605[b] | 0.571[b] | 1 | | | |
| | *P*-value | 0.065 | 0.000 | 0.000 | | | | |
| As | Pearson[a] | 0.059 | 0.302 | –0.088 | 0.263 | 1 | | |
| | *P*-value | 0.719 | 0.058 | 0.590 | 0.101 | | | |
| pH | Pearson[a] | 0.483[b] | 0.695[b] | 0.464[b] | 0.797[b] | 0.275 | 1 | |
| | *P*-value | 0.002 | 0.000 | 0.003 | 0.000 | 0.086 | | |
| Salinity | Pearson[a] | –0.026 | 0.015 | –0.442[b] | –0.029 | 0.035 | 0.013 | 1 |
| | *P*-value | 0.876 | 0.927 | 0.004 | 0.858 | 0.829 | 0.938 | |

[a]Pearson correlation coefficient ($P < 0.05$); [b]correlation is significant at the 0.01 level (2-tailed).

not too fluctuating and was at a slightly alkaline pH at each sampling point (Table 2). In such modern seawater pH, the carbonate system is responsible for the solubility of almost all elements due to the formation of element-carbonate complexes with different magnitudes for each element.[23] Accordingly, high concentrations of trace elements within the seawater pH background of Staring Bay, and exceeding normal levels of pristine seawater[34] for several sampling sites, indicate that those elements were in the free ionic forms and that their presence was likely to result from the accumulation of inputs from activities on the land around the bay. The increase of commercial vessel traffic, such as shipping and fishing vessels, might also contribute significantly to the increase in elements accumulation in this region. Salinity was noticed to only affect the distribution of trace element Ni through a negative linear relationship (coefficient = –0.442) (Table 6), indicating a conservative behavior for this element. The estuaries of Staring Bay, with lower salinity values than those of recorded at inner and outer areas (Table 2), might act as sources for trace element Ni. In addition to pH and salinity, the hydrodynamic factors, such as: tidal forcing, wind condition, waves, strength and direction of seawater current can have different effects on the process of addition-removal of elements in seawater.[36]

PCA and HCA were performed on the data comprising forty sampling sites and five trace elements (Pb, Cu, Ni, Fe, and As). Five principal components have been taken out. The first two principal components PC1 and PC2 can expose suitably the distribution of forty sites in Staring Bay with 69.39%, thus the plot score between the principal components of PC1 and PC2 can describe quite well the spread of five trace elements concentrations (Figure 3) and the distribution at forty sampling sites (Figure 4). Figure 3 shows that Cu and Fe have a similar characteristic from forty sampling sites since their plot points are close to each other. This is supported by the high Pearson correlation coefficient of 0.605 (Table 6), suggesting they were probably originated from the same source of terrestial input. An earlier study[37] has emphasized that the presence of Fe and Cu strongly affected the inorganic redox chemistry where both elements were in a linear relationship in modern seawater pH. However, the distribution of trace element As does not correlate with those of four other elements (Figure 3), verified by quite poor correlation coefficients among them (Table 6).

Figure 4 shows the results of the PCA. Sites 2, 4, 6, 7, 8, 11, 14, 20, 23, 24 and 27 have similar characteristics on the Pb, Cu, Ni, Fe and As distribution which is indicated by positive PCA1 and relatively low positive PCA2 values. Sites 9, 10 and 12 have different characteristics from other sites, characterized by much higher positive PCA2 values and isolated from other sites. Sites 15, 16, 18, 19, 21, 33, 34, 36 and 37 have equal characteristics with negative PCA1 and PCA2 values. Finally, sites 1, 3, 5, 13, 17, 22, 25, 26, 28, 29, 30, 31, 32, 33, 35, 38, 39 and 40 have same characteristics of the trace elements distribution, indicated by negative PCA1 values.

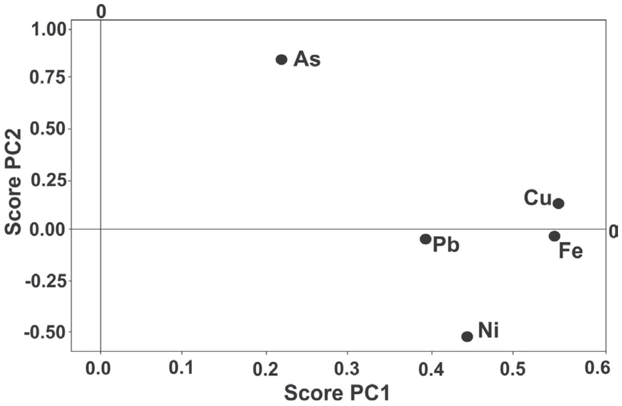

**Figure 3.** Loads of variables on the two principal components PC1 and PC2.

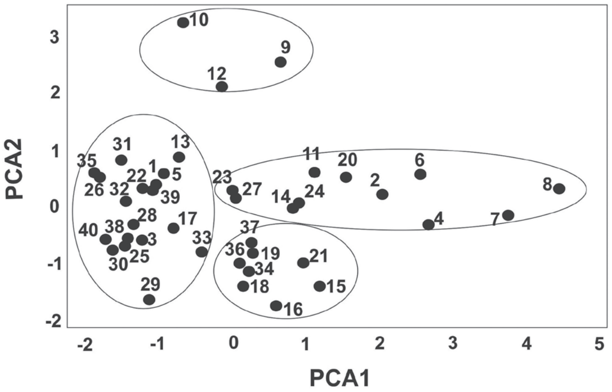

**Figure 4.** Scatter plot of PCA1 and PCA2 values on the distribution of trace elements Pb, Cu, Ni, Fe and As at forty sampling sites in Staring Bay.

HCA using Ward's method which is depicted in the dendrogram of sampling sites (Figure 5) shows that there are four groups having homogeneity on Pb, Cu, Ni, Fe and As concentrations. The first group is composed of sites 9, 10 and 12; the second group includes sites 2, 4, 6, 7, 8, 11, 14, 20, 23, 24 and 27; the third group consists of sites 15, 16, 18, 19, 21, 33, 34, 36 and 37; and the fourth group is composed of sites 1, 3, 5, 13, 17, 22, 25, 26, 28, 29, 30, 31, 32, 35, 38, 39 and 40. Both PCA and HCA produce a clustering of sampling sites that mutually support each other. It is important to note that both of these statistical analyses show that samples collected at sites 9, 10 and 12 have characteristics of Pb, Cu, Ni, Fe and As concentrations different from other sites. This illustrates that anthropogenic activities occurred around those sampling sites (i.e., nickel smelter and cement factory) requiring serious attention because they may have a significant contribution to the accumulation of trace elements in Staring Bay coastal waters.

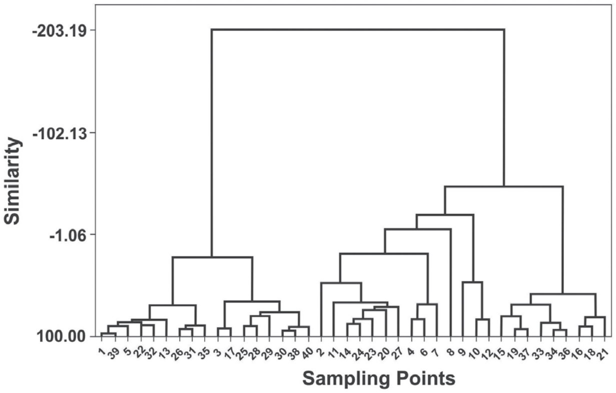

**Figure 5.** Dendrogram of HCA for forty sampling sites based on trace elements Pb, Cu, Ni, Fe and As concentrations in Staring Bay.

### Pollution status

The aquatic system is considered to be polluted when contaminants are introduced into the water environment, usually as a result of anthropogenic activities, thus rendering water unfit for intended use. The status of trace element pollution in Staring Bay was determined in three ways, first was by using the water pollution index (WPI) method, the second was to use pollution load index (PLI) and the last was by comparing the element concentrations observed in the study area with those of Indonesian seawater quality standards, National Oceanic and Atmospheric Administration (NOAA) threshold regulation, and their normal concentration in the pristine seawater.

WPI has been widely used as an indicator for the quality of seawater and river water according to an equation:[38]

$$\mathrm{WPI} = \sum_{n=1}^{n} \frac{A_i}{T} \times \frac{1}{n} \qquad (1)$$

where $A_i$ is measured concentration of element i in the study area, T is the threshold level of element i in the country of the study area, and n indicates the number of measured parameters. Water quality according to WPI is classified into six classes, those are class I (very pure) if WPI ≤ 0.3, class II (pure) if WPI = 0.3-1.0, class III (moderately polluted) if WPI = 1.0-2.0, class IV (polluted) if WPI = 2.0-4.0, class V (impure) if WPI = 4.0-6.0, and class VI (heavily impure) if WPI > 6.0. Measurement results using trace element concentrations data in Table 5 and the threshold level according to the seawater quality standards of Indonesia (listed in Table 7) obtained WPI values of 0-0.1 in the entire sampling sites, which means that Staring Bay is practically pure (class I).

PLI was calculated to provide information on the extent to which the pollution load at each sampling site was different compared to the permitted concentration of trace elements. In this study we modified the PLI on five trace elements analyzed based on their ratio to the background concentrations following the equation:[39]

$$\mathrm{PLI} = \sqrt[5]{\mathrm{CF}_{\mathrm{Pb}} \times \mathrm{CF}_{\mathrm{Cu}} \times \mathrm{CF}_{\mathrm{Ni}} \times \mathrm{CF}_{\mathrm{Fe}} \times \mathrm{CF}_{\mathrm{As}}} \qquad (2)$$

where CF is a contamination factor obtained from the ratio of measured element concentration to its background level (i.e., normal oceanic concentration, tabulated in Table 7). PLI has been used as an index to consider whether or not there is anthropogenic influence in a coastal area. An aquatic system is supposed to be polluted (anthropogenic) if PLI > 1, while PLI < 1 (natural) refers to no pollution.[4] Calculation results of forty sampling sites found that PLI values varied from 0.3 to 1.9. PLI values greater than 1 (or polluted sites) were obtained at eleven sites, including sites 2 (PLI = 1.1), 4 (1.6), 6 (1.6), 7 (1.9), 8 (1.4), 11 (1.1), 14 (1.1), 15 (1.1), 20 (1.4), 21 (1.2) and 24 (1.2). This result implies that such polluted sites in Staring Bay might be originated from anthropogenic sources around the bay.

**Table 7.** Trace elements Pb, Cu, Ni, Fe and As concentrations in Staring Bay in comparison with the seawater quality standard of Indonesia, National Oceanic and Atmospheric Administration (NOAA) regulation, as well as the normal concentration of seawater

| Reference | Source | Concentration / ($\mu$g L$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | | Pb | Cu | Ni | Fe | As |
| Present study | Staring Bay | 0.261[a] | 0.475[a] | 0.754[a] | 8.036[a] | 1.366[a] |
| MNLH[40] | seawater quality standards of Indonesia[b] | 100 | 10 | NR | NR | NR |
| | | 5 | 50 | 75 | NR | 25 |
| | | 8 | 8 | 50 | NR | 12 |
| Buchman[41] | NOAA[c] | 210 | 4.8 | 74 | 300 | 69 |
| | | 8.1 | 3.1 | 8.2 | 50 | 36 |
| Broecker and Peng[34] | normal oceanic concentration | 0.03 | 0.9 | 6.6 | 3.4 | 2.6 |

[a]Mean concentration; [b]first row: seawater threshold of port waters, second row: seawater threshold of marine tourism area, third row: seawater threshold for marine biota; [c]first row: acute level, second row: chronic level. MNLH: State Minister of the Environment of the Republic of Indonesia; NR: not regulated; NOAA: National Oceanic and Atmospheric Administration.

The remaining sites were practically unpolluted since their PLI values < 1. However, it should be noted that PLI (and also WPI) values less than 1 do not necessarily indicate there was no pollution from anthropogenic sources or other enhancement over the background.[42]

The trace elements concentrations of Staring Bay in comparison with the Indonesian seawater quality standards, NOAA standard and their normal concentration in seawater are tabulated in Table 7. It is important to note that the water quality standards of Indonesia, according to the Decree of the Minister of Environment of the Republic of Indonesia Number 51 of 2004,[40] regulates seawater quality standards of three designations, i.e., seawater threshold of port waters, marine tourism area, as well as marine biota.

Table 7 shows that the average concentrations of trace elements Pb, Cu, Ni, Fe and As dissolved in surface seawater of Staring Bay were within the acceptable limits in comparison to the Indonesian seawater quality standards,[40] as well as the threshold level of NOAA.[41] However, special attention should be given to the sampling site 8 with Fe content = ca. 69 µg $L^{-1}$ (Table 5) because it has exceeded the threshold of iron regulated by NOAA for chronic level, and to the sampling site 7 with dissolved iron of ca. 48 µg $L^{-1}$, which is very close to the threshold. Those both sites were located close to the mouth of the Kunikuni Moramo River in the southwest and were linked to densely populated and agricultural activities (brackish ponds and rice fields) occurred on the land. Once the concentrations of trace element were compared to their normal levels in seawater,[34] the trace elements Pb and Fe had much higher concentrations (i.e., 8.7 and 2.4 folds, respectively) relative to their normal concentrations in the sea, suggesting high contamination. Comparing our data to the other regions, the Pb concentration in Staring Bay (0.261 µg $L^{-1}$) is much lower relative to seawater both in Tianjin Bohai Bay, China (7.18 µg $L^{-1}$) and Jinzhou Bay, China (0.61 µg $L^{-1}$).[26,43] Local characteristics and movement of seawater currents in the two bays in China caused Pb contamination in water bodies by 239 and 20 folds, respectively, relative to normal levels in seawater. Actual high concentration was found in the Kepez Harbor of Canakkale, Turkey (9.39 mg $L^{-1}$) due to residues from existing facilities around the harbor.[44] In the case of Fe, the concentration found in Arabian Gulf, Saudi Arabia (3.54 µg $L^{-1}$) was 13 times greater than that measured in Staring Bay which was possibly triggered by the dust storms from the surrounding deserts,[45] yet the ship breaking activities governed the quite high level of Fe (28.4 mg $L^{-1}$) along the Bay of Bengal, Bangladesh.[46] The present study recommends that the management of the marine environment around Staring Bay is quite significant to be carried out by the local government to minimize anthropogenic activities around the bay and also to protect the marine environment from trace element pollution, particularly Pb and Fe.

## Conclusions

Staring Bay is a bay located in Southeast Sulawesi Province, Indonesia and is surrounded by rapid industrial and lively agricultural activities, as well as high population growth. This study examines the spatial distribution and pollution status of trace elements Pb, Cu, Ni, Fe and As dissolved in the water system in Staring Bay. The concentrations of trace elements were obtained at 0.049-0.685 µg $L^{-1}$ (average = 0.261 ± 0.163 µg $L^{-1}$), 0.170-1.278 µg $L^{-1}$ (average = 0.475 ± 0.252 µg $L^{-1}$), 0.375-1.469 µg $L^{-1}$ (average = 0.754 ± 0.258 µg $L^{-1}$), 0.544-69.290 µg $L^{-1}$ (average = 8.036 ± 13.779 µg $L^{-1}$), and 0.952-1.721 µg $L^{-1}$ (average = 1.366 ± 0.168 µg $L^{-1}$) for Pb, Cu, Ni, Fe and As, respectively. The highest concentration was found in trace element Fe, followed successively by As, Ni, Cu and Pb. Referring to the relative standard deviation values of the total forty samples being examined, trace element Fe had the highest variability relative to the other four elements, affected by addition-removal processes of this element anthropogenically and naturally. The lowest diversity of trace element As, where the concentration was below the normal oceanic level, was possibly controlled by natural processes. Examination result of the pollution status summarized that Staring Bay has been highly contaminated by trace elements Pb and Fe relative to their normal level in pristine seawater, especially in the estuary area located to the west. Such contamination is likely to originate from anthropogenic waste resulting from industrial and agricultural activities, residential areas and brackish pond practices on the land. Handling this contamination requires to be performed immediately by the local government to maintain the continuity of marine life in the Staring Bay.

## Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

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