ASSESSMENT OF GODAVARI ESTUARINE MANGROVE ECOSYSTEM THROUGH TRACE METAL STUDIES

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Abstract

Trace metals (Fe, Mn, Cu, Co, Ni. Pb, Cd & Cr) analyses in particulate matter and sediments were carried out at sixteen different stations in the Godavari mangrove ecosystem covering the three regions viz., Kakinada (KKD) bay, Goutami-Godavari estuary (GGE) and Coringa & Gaderu mangrove environments (CGME). High concentrations of trace metals in particulate matter and in sediments in the mangrove environment compared to the KKD bay and GGE region reveals the significance of mangrove environment as a source for these trace metals. The significant correlations observed between several couples of metals in different regions as well as between numbers of heavy metals (Fe, Mn, Zn) with Total Suspended Matter (TSM) in particulate organic matter indicating that complexation with organic materials may play an important role in the distribution pattern of these metals. Significant correlations between organic carbon (OC) and Cr, Co, Pb, Cu and Mn in sediments of all the three regions indicate that organic matter is acting as a metal carrier. The values of Pollution Load Index (PLI) were found to be very low, and varied between 0.34-0.60 in KKD bay, 0.47-0.97 in GGE and 0.62-1.03 in CGME indicating that this estuarine ecosystem is not a pollution concern in the present scenario.

Key words: Mangrove, Trace metals, Water quality, Estuary

Introduction

Mangrove forests are considered to be highly productive tropical ecosystems (Clough, 1992). It is a widespread view that the mangrove forests represent an important carbon and nutrient source to the adjacent lagoonal and coastal systems (Odum & Heald, 1972, 1975; Twilley, 1988; Wattayakorn *et al.*, 1990; Robertson *et al.*, 1992). The Coringa River mangrove ecosystem is the second largest coastal ecosystem in the east coast of India, connected to Kakinada bay on its north and to the Gautami-Godavari on its south. Presence of numerous canals, river tributaries along with dense mangrove vegetation makes it a unique habitat. Increasing pressure on mangrove forests due to urbanization, industrialization and intensive aquaculture in this area poses a threat to this ecosystem. It is therefore crucial to understand the possible role of mangroves in maintaining high productivity in adjacent

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waters. Even though some biological studies (Bouillon *et al.*, 2000; Dehairs *et al.*, 2000; Ranga Rao *et al.*, 2003) and chemical studies on nutrients and chlorophyll (Tripathy *et. al.*, 2004) in Godavari estuarine mangrove ecosystems were made earlier, detailed assessment on trace metal studies were not reported so far. An attempt has been made in this paper to understand the biogeochemistry and water quality assessment through trace metal studies of the Gautami-Godavari mangrove estuarine ecosystem.

Materials and methods

Seawater samples were collected (once) at sixteen different stations in Kakinada bay, Gautami-Godavari estuarine region and Coringa and Gaderu mangrove environments (Fig.1) during September 2001 (SW monsoon). Water samples were collected from all the stations were subjected to the analyses of particulate matter, trace metals and total suspended matter. An aliquot (1 l) of the seawater samples were immediately filtered using preweighed 0.45 µm membrane (Milipore) filters. Filters containing suspended matter were dried in a vacuum desiccator over silica gel and weighed to an accuracy of 0.01 mg. Filter containing particulate matter and blanks were digested with a mixture of perchloric acid and nitric acid and evaporated to almost dryness. The residues after dilution to 25 ml with HCL (0.1N) were then subjected to trace metal analysis using Perkin Elmer (Model 3110) Atomic Absorption Spectrophotometer (AAS) with air-acetylene fuel mixture. The concentrations of trace metal elements were computed from calibration curves. The precision of the method determined from replicate analyses and expressed in terms of percent coefficient of variation is 10, 8.8, 7.2, 5.5, 5.0, 12.0, 5.0 and 6.8 respectively for Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb. The particulate trace metals in water were expressed as µg.dm⁻³. Sediment samples collected in the study area were estimated for trace metals after digesting with a mixture of hydrofluoric acid and aqua regia and using Atomic Absorption Spectrophotometric method (Loring and Rantala, 1977). The coefficient of variation for Pb, Cd, Zn, Cu, Co, Ni, Cr, Fe and Mn were 2.0, 0.7, 0.6, 0.77, 0.67, 0.53, 1.2, 2.8 and 4.5 respectively. The trace metal concentrations in sediments were expressed in µg.g⁻¹.

Study area

The study area (Fig. 1) comprises the area between Kakinada (KKD) bay (station K_1 - K_5), Gautami-Godavari (GG) estuarine region (station G_6 - G_9) and the Gaderu River (station M_{10} - M_{11}) and Coringa River mangrove environment (station M_{12} - M_{16}). The Gaderu and Coringa are the branches of river Godavari, the second largest river in India with a mean annual discharge of 1.1 x 10^{11} m³, of which 93-96 % occurs during wet monsoon seasons.

The extensive estuarine areas to the north of Gautami-Godavari (82° 15' and 82° 22' E; 16° 43' and 17° 00' N; area = 132 km²) open into Kakinada bay via the main branches Gaderu (length = 11 km) and Coringa (length = 26 km). The area between Gautami-Godavari and Kakinada bay has dense vegetation of mangrove forests and mudflats belong to Coringa Wildlife Sanctuary. The shallow Kakinada bay (area = 150 km²) opens into the sea on its northern side and is bordered along most of its eastern length by a narrow sand bar. Tides are semi diurnal and tidal amplitude in the Bay varies between 2.3 and 4.5 m, but in the mangrove covered area the tidal amplitude value is comparatively less (Sreenivas, 1998).

Results and discussions

Trace metals in particulate matter

In order to understand the factors controlling geochemical processes in these estuarine mangrove ecosystems, the distribution of particulate trace metals and their possible interaction with TSM is discussed. The range and average concentration of trace metals in particulate matter of the three aquatic systems are given in Table 1. From the data in Table 1 it is obvious that mangrove area containing high TSM contains high concentrations of trace metals compared to Kakinada Bay and estuarine region. Fe (3136.0 µg.dm⁻³) & Mn (98.1 ug.dm⁻³) values are observed to be at least 5 to 10 times higher in mangrove systems and these high concentrations may be due to the non-anthropogenic sources such as weathering of rocks from the up streams of rivers and high organic resources from mangrove litter and leaves. Fe & Mn leached from the planktonic and leaf material in the mangrove systems may be quickly converted into colloidal hydroxide at the pH (7.0 - 8.0) prevailing in the water column and may be adsorbed onto particulate matter, which in turn get transported to sediments. High concentrations of other metals such as cobalt (2.5, 5.68, 7.4 µg.dm⁻³), copper (30.1, 30.1, 43.8 µg.dm⁻³) and zinc (16.3, 9.5, 41.1 µg.dm⁻³) in KKD bay, GGE region and CGME area respectively may be associated with this hydrous iron oxide or iron oxide coating on the preexisting particles (Lambert et al., 1981; Murray & Gill, 1978). High concentrations of Cd (6.0, 6.75, 7.42 µg.dm⁻³) & Pb (2.06, 3.44, 3.10 µg.dm⁻³) in KKD bay, GGE region and CGME area respectively may be due to anthropogenic inputs and wastes through runoff into these aquatic environments. The high concentrations of particulate trace metals (Cu, Co, Ni, Zn) in estuarine and mangrove environments may be due to the remineralization from sediments and organic matter in the low salinity range. In this estuarine mangrove environment as fresh water mixes, nutrient and particle removal are the dominant features and reflect high primary production, flocculation and particle scavenging. In order to

understand the importance of these particulate trace metals, the total data set was subjected to the regression analysis and the correlation matrix is given in Table 3. The significant correlationships were observed between several couples of metals in different regions as well as between numbers of heavy metals (Fe, Mn, Zn) with total suspended matter indicating that complexation with organic materials may play an important role in the distribution pattern of these metals. The poor correlations between other metals (Cu, Co, Ni, Zn) indicate the possible extra loads from the anthropogenic sources especially in Kakinada Bay and Coringa mangrove areas. Further the enrichment of these metals may be attributed that their major contribution to terrigenous origin and partly to the biological production especially uptake of particulate trace metals by phytoplankton as reported earlier (Knaner and Martin, 1973). No correlations between Pb and Cd with other metals showed that these metals are having a discrete source but not contributed significantly from the terrestrial runoff.

Trace metals in sediments

The range and average concentrations of trace metal and organic carbon in surficial sediments were given in Table 2. An increasing order in concentrations of the metals was observed from KKD Bay, GG estuarine region and mangrove area except in the case of two metals (Fe & Mn) because of contamination from the local sources. High concentrations of organic carbon in mangrove sediments (especially Coringa mangrove environment) are due to the decomposed mangrove detritus and anthropogenic inputs. High concentrations of Mn in sediments in mangrove environment and GG estuarine region is mainly due to the detrital materials, ferromanganese minerals, clay minerals and accessory sulphide minerals. The enrichment of biogenic element (Cu) in the sediments may be due to its association with organic matter thereby increasing planktonic production in the mangrove environment. Copper which has biological importance for making frustules of plants contributes to high planktonic production through increase of Organic matter in the underlying sediment. But the KKD Bay experiences high concentration of Co and Ni could be due to the discharge of agricultural and industrial wastes though Kakinada canal. However the waters of mangrove environment show comparatively high concentrations of Cd and Cr. Chromium is primarily derived from the process of continental weathering, however generally it exists as CrO₄²⁻ in the oxidized mud, which is relatively soluble (Elderfield, 1970) with the continuous accumulation of sediment.

Significant correlations (0.61, 0.33, 0.59, 0.52 and 0.55 for n=16, p<0.01) were observed (Table 4) between organic carbon and Cr, Co, Pb, Cu and Mn respectively in all the three regions, which indicates organic matter is acting as a metal carrier. Significant correlation (0.32) between Fe and Mn implies its origination from detrital mineral and anthropogenic inputs and incorporated in sediment in the form of iron oxide and hydrous manganese. Accordingly, an insight into the correlation matrix broadly divided these trace metals into three combinations viz., (i) Fe, Mn and Cr; (ii) Cu, Co and Ni; (iii) Pb and Cd. Positive correlations between Fe and Mn may be due to their strong association as oxides or oxyhydroxides in the aquatic environment. Cu, Co, Ni also showed positive correlations with Fe & Mn in the study region reveals their adsorption on to the oxyhydroxides of Fe & Mn and also their complexation with organic material playing an important role in their distribution patterns (Samuel & Phillips, 1988). High concentrations of these trace metals in mangrove sediments indicate that the mangrove systems are physical traps for fine material and their transported load of metals constitute of chemical group of metals from selection (Harbison, 1986).

In order to understand the contamination state of trace metals, the trace metals values were utilized to find contamination factor (CF). While computing the CF of sediments of the study region, world average concentrations of these elements reported for Shale (Turkian and Wedephol, 1961) were taken as the background values. However the pollution level in trace metals was calculated by a simple method based on Pollution Load Index (Tomlinson *et al.*, 1980).

$$CF = C_{metal} / C_{background \ value}$$

$$PLI = \sqrt[n]{(CF_1 \ X \ CF_2 \ X \ CF_3 \ X \X \ CF_n)}$$

Where,

CF = contamination factor, n = number of metals

C _{metal} = metal concentration in polluted sediments

C Background value = background value of that metal

The study result shows that the CF values of most of the metals such as Fe, Mn, Cu, Co, Cr and Ni in the study area are low (<1). But, CF values for metals like Pb and Cd shows higher (>1) values due to the influence of external discrete sources like agricultural runoff

and anthropogenic inputs. The values of Pollution Load Index (Table 5) were found to be very low (<1) in all the three regions. Even through the PLI values are <1 in mangrove environment, it appears that these values are relatively higher than both KKD bay and GG estuarine region. An overall view indicates that at present this mangrove estuarine ecosystem is considered to be of no pollution concern but attention should be brought due to that fast development of industries and habitation in this area.

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Table 1: Range & average of trace metal concentrations in particulate matter of the study area

| Parameters | KKD bay | GGE region | Mangrove area |
|---------------------------------|---------------|----------------|----------------|
| TSM (mg.dm ⁻³) | (36.0-89.6) | (40.8-84.4) | (38.4-264) |
| 15M (mg.um) | 52.3 | 69.0 | 167.0 |
| Fe (μg.dm ⁻³) | (110.0-935.0) | (180.0-1320.0) | (925.0-4595.0) |
| re (μg.uiii) | 321.0 | 659.0 | 3136.0 |
| Mn (μ g.dm ⁻³) | (4.52-25.0) | (8.04-32.5) | (17.5-143.0) |
| Min (μg.din) | 13.6 | 15.8 | 98.1 |
| Cu (µg.dm ⁻³) | (28.5-32.5) | (28.0-31.0) | (26.5-39.0) |
| Cu (µg.um) | 30.1 | 30.1 | 43.8 |
| Co (μg.dm ⁻³) | (0.51-10.0) | (3.05-9.01) | (2.02-12.0) |
| Co (µg.uiii) | 2.50 | 5.68 | 7.40 |
| Ni (µg.dm ⁻³) | (12.5-25.0) | (29.0-36.0) | (5.50-35.0) |
| M (μg.uiii) | 21.5 | 31.9 | 27.3 |
| $Zn (\mu g.dm^{-3})$ | (8.51-37.0) | (5.05-16.5) | (4.01-55.5) |
| Zii (µg.uiii) | 16.3 | 9.50 | 41.1 |
| Pb (μg.dm ⁻³) | (0.51-5.02) | (0.53-7.00) | (0.52-5.50) |
| Po (μg.uiii) | 2.06 | 3.44 | 3.10 |
| Cd (µg.dm ⁻³) | (5.02-7.03) | (5.52-8.05) | (6.01-8.50) |
| Cu (μg.uiii) | 6.00 | 6.75 | 7.42 |

Table 2: Range & average of trace metal concentrations in sediments of the study area

| Parameters | KKD bay | GGE region | Mangrove area |
|---|-----------------|-----------------|-------------------|
| $OC(ugg^{-1})$ | (0.11-2.90) | (0.03-3.36) | (0.04-3.23) |
| $OC (\mu g.g^{-1})$ | 1.12 | 1.17 | 1.64 |
| $E_{\alpha}(u_{\alpha} a^{-1})$ | (4499.0-4934.0) | (3817.0-4777.0) | (4461.0 - 4697.0) |
| Fe (μ g.g ⁻¹) | 4701.0 | 4254.0 | 4575.0 |
| $\mathbf{M}_{\mathbf{p}} \left(\mathbf{u}_{\mathbf{q}} \mathbf{q}^{-1} \right)$ | (225.0-768.0) | (101.0-1150.0) | (439.0-3253.0) |
| Mn ($\mu g.g^{-1}$) | 446.0 | 429.0 | 1059.0 |
| $C_{\rm tr} \left(\log \alpha^{-1} \right)$ | (30.0-51.0) | (12.0-61.0) | (34.0-58.0) |
| Cu (μg.g ⁻¹) | 42.4 | 40.2 | 47.8 |
| Co (µg.g ⁻¹) | (26.0-50.0) | (23.0-51.0) | (21.0-44.0) |
| Co (µg.g) | 32.4 | 30.7 | 28.8 |
| Ni (μg.g ⁻¹) | (13.0-60.0) | (9.00-41.0) | (7.50-52.0) |
| NI (μg.g) | 44.5 | 20.7 | 25.7 |
| Db $(u \circ e^{-1})$ | (2.51-38.0) | (33.0-65.0) | (16.0-95.0) |
| Pb ($\mu g.g^{-1}$) | 18.2 | 46.7 | 55.8 |
| Cd (µg.g ⁻¹) | (0.51-6.02) | (7.50-12.0) | (6.00-17.0) |
| Cu (µg.g) | 4.12 | 9.00 | 10.9 |
| $Cr(ugg^{-1})$ | (0.80-1.36) | (1.30-2.56) | (1.45-2.70) |
| Cr (μg.g ⁻¹) | 1.02 | 1.73 | 2.20 |

TSM= Total Suspended Matter, OC=Organic Carbon, Fe= Iron, Mn=Manganese, Cu= Copper, Co= Cobalt, Ni=Nickel, Zn=Zinc, Pb=Lead, Cd=Cadmium

Table 3: Correlation matrix of particulate trace metals in mangrove area (n=32)

| | TSM | Fe | Mn | Cu | Co | Ni | Zn | Pb | Cd |
|-----|------|------|------|------|------|------|-------|------|-------|
| TSM | 1.00 | 0.89 | 0.81 | 0.57 | 0.57 | 0.28 | 0.51 | 0.20 | 0.37 |
| Fe | | 1.00 | 0.96 | 0.54 | 0.54 | 0.05 | 0.72 | 0.19 | 0.49 |
| Mn | | | 1.00 | 0.58 | 0.46 | 0.04 | 0.70 | 0.14 | 0.48 |
| Cu | | | | 1.00 | 0.35 | 0.43 | 0.24 | 0.44 | 0.15 |
| Co | | | | | 1.00 | 0.22 | 0.26 | 0.26 | 0.25 |
| Ni | | | | | | 1.00 | -0.29 | 0.43 | -0.04 |
| Zn | | | | | | | 1.00 | 0.02 | 0.47 |
| Pb | | | | | | | | 1.00 | 0.05 |
| Cd | | | | | | | | | 1.00 |

Table 4: Correlation matrix of trace metals in sediments of the three study area (n=16)

| | OC | Fe | Mn | Cu | Co | Ni | Pb | Cd | Cr |
|----|------|------|------|------|------|-------|-------|-------|-------|
| OC | 1.00 | 0.42 | 0.55 | 0.52 | 0.33 | -0.02 | 0.59 | 0.25 | 0.61 |
| Fe | | 1.00 | 0.32 | 0.30 | 0.59 | 0.55 | -0.13 | 0.04 | 0.06 |
| Mn | | | 1.00 | 0.43 | 0.68 | 0.20 | 0.38 | -0.08 | 0.48 |
| Cu | | | | 1.00 | 0.46 | 0.29 | 0.20 | 0.09 | 0.32 |
| Co | | | | | 1.00 | 0.54 | 0.05 | -0.27 | 0.14 |
| Ni | | | | | | 1.00 | -0.55 | -0.32 | -0.32 |
| Pb | | | | | | | 1.00 | -0.19 | 0.87 |
| Cd | | | | | | | | 1.00 | 0.68 |
| Cr | | | | | | | | | 1.00 |

Table 5: Concentration, contamination factor and pollution load index of metals in sediments in three regions

| Stn. | Fe | | M | In | (| Cu | Co | | Ni | | Pb | P b | (| Cd | (| Cr | PLI |
|----------|-------|------|------|------|----|------|------|---------|--------|---------|--------|------------|-----|------|------|------|------|
| | A | В | A | В | A | В | A | В | A | В | A | В | A | В | A | В | |
| | | | | | | | V | VORLD S | SHALE | AVERAC | ЭE | | | | | | |
| | 46000 | - | 800 | - | 45 | - | 19 | - | 68 | - | 20 | - | 0.3 | - | 90 | - | |
| | | | | | | | | KAŁ | INADA | BAY | | | | | | | |
| K_1 | 4934 | 0.11 | 666 | 0.83 | 51 | 1.14 | 50 | 2.63 | 60 | 0.88 | 2.5 | 0.13 | 2.5 | 8.34 | 1.05 | 0.01 | 0.48 |
| K_2 | 4806 | 0.10 | 285 | 0.36 | 49 | 1.09 | 27 | 1.42 | 47 | 0.69 | 6.0 | 0.30 | 0.5 | 1.67 | 0.80 | 0.01 | 0.34 |
| K_3 | 4499 | 0.09 | 225 | 0.28 | 34 | 0.75 | 26 | 1.37 | - | - | 6.5 | 0.33 | 5.5 | 18.3 | 0.85 | 0.01 | 0.39 |
| K_4 | 4544 | 0.09 | 285 | 0.36 | 30 | 0.67 | 30 | 1.58 | 13 | 0.19 | 38 | 1.90 | 6.0 | 20.0 | 1.05 | 0.01 | 0.48 |
| K_5 | 4722 | 0.10 | 768 | 0.96 | 48 | 1.07 | 29 | 1.52 | 35 | 0.51 | 38 | 1.90 | 6.0 | 20.0 | 1.36 | 0.02 | 0.68 |
| | | | | | | GA | UTAM | I-GODAV | ARI ES | STUARIN | IE REG | ION | | | | | |
| G_6 | 4197 | 0.09 | 194 | 0.24 | 28 | 0.63 | 23 | 1.21 | 17 | 0.25 | 33 | 1.65 | 7.5 | 25.0 | 1.30 | 0.01 | 0.47 |
| G_7 | 3817 | 0.08 | 101 | 0.13 | 60 | 1.34 | 24 | 1.26 | 9.0 | 0.13 | 41 | 2.05 | 12 | 40.0 | 1.35 | 0.02 | 0.48 |
| G_8 | 4226 | 0.09 | 272 | 0.34 | 12 | 0.27 | 25 | 1.31 | 16 | 0.23 | 48 | 2.40 | 8.5 | 28.3 | 1.70 | 0.02 | 0.49 |
| G_9 | 4777 | 0.10 | 1150 | 1.43 | 61 | 1.36 | 51 | 2.68 | 41 | 0.60 | 65 | 3.25 | 8.0 | 26.7 | 2.65 | 0.03 | 0.47 |
| | | | | | | | | MAN | GROVE | AREA | | | | | | | |
| M_{10} | 4624 | 0.10 | 542 | 0.68 | 45 | 1.00 | 32 | 1.68 | 36 | 0.53 | 27 | 1.35 | 7.0 | 23.3 | 1.45 | 0.02 | 0.64 |
| M_{11} | 4598 | 0.09 | 819 | 1.02 | 52 | 1.16 | 30 | 1.58 | 52 | 0.76 | 16 | 0.80 | 6.0 | 20.0 | 1.70 | 0.02 | 0.67 |
| M_{12} | 4488 | 0.09 | 439 | 0.55 | 34 | 0.76 | 24 | 1.26 | 9.0 | 0.13 | 49 | 2.45 | 17 | 56.7 | 2.20 | 0.02 | 0.62 |
| M_{13} | 4571 | 0.10 | 525 | 0.66 | 48 | 1.07 | 26 | 1.37 | 24 | 0.35 | 53 | 2.65 | 14 | 46.7 | 2.35 | 0.03 | 0.75 |
| M_{14} | 4587 | 0.10 | 488 | 0.61 | 49 | 1.09 | 21 | 1.10 | - | - | 61 | 3.05 | 9.5 | 31.7 | 2.45 | 0.03 | 0.79 |
| M_{15} | 4697 | 0.10 | 3253 | 4.07 | 58 | 1.29 | 44 | 2.31 | 7.5 | 0.11 | 95 | 4.75 | 9.0 | 30.0 | 2.70 | 0.03 | 0.93 |
| M_{16} | 4461 | 0.09 | 1350 | 1.68 | 49 | 1.09 | 25 | 1.31 | - | - | 90 | 4.50 | 14 | 46.7 | 2.50 | 0.03 | 1.03 |

A = Metal concentration (ppm),

B = Contamination Factor,

PLI = Pollution Load Index

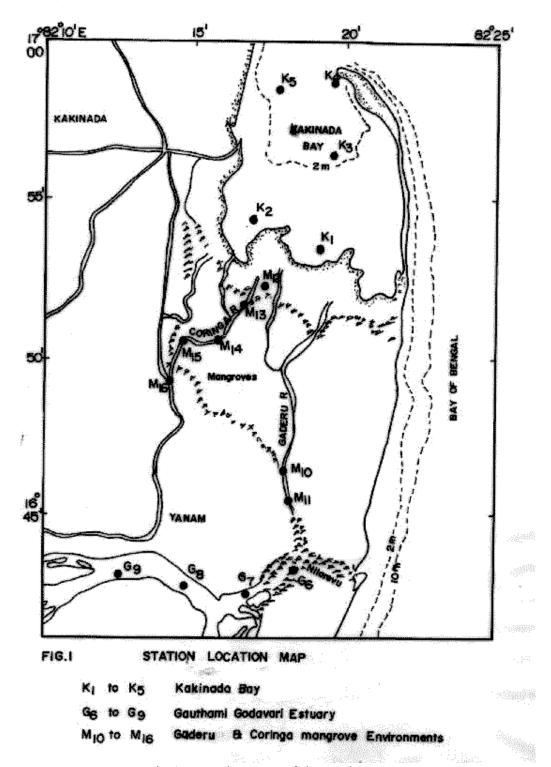


Fig.1: Location map of the study area