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Geochemical fractionation of trace elements in ostreid and gastropod shells: A potential proxy for heavy metal pollution in Ghana's coastal environment

Fraccionamiento geoquímico de elementos traza en conchas de ostreidos y gasterópodos: Un indicador potencial de contaminación por metales pesados en ambientes costeros de Ghana

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ABSTRACT

The content of trace elements from *Crassostrea tulipa* (Ostreidae, Bivalvia) from four localities (Pra Estuary, Densu Estuary, Kpone Beach, and Anyanui Creek) along the coast of Ghana has been used as a bioindicator of environmental pollution. The lowest values of heavy metals correspond to the *Crassostrea* shells from Densu Estuary and Anyanui Creek, whereas the highest contents are recorded in the shells from Pra Estuary and Kpone Beach. Densu Estuary and Anyanui Creek are located in areas not affected by major industries, and only Densu is located in a densely urbanized setting. *Crassostrea* shells from Densu Estuary are only enriched in Ni. However, the Total Organic Carbon content of the sediments of the Densu Estuary indicates anthropogenic organic pollution not evidenced by the composition of *Crassostrea* shells. The *Crassostrea* shells from the Pra Estuary show enrichment in most of the analysed trace elements (Li, Be, V, Cu, Cr, Zn, Ga, Y, Sn, Pb, U, Th, ∑REE, and As) compared with other studied sites. This enrichment is related to heavy metals influx to the Pra River by the mining activities, extensive forest clearance, and loss of soil minerals. The *Crassostrea* shells from Kpone Beach present comparatively high content of some trace elements (Be, Ba, Cu, Zn, Nb, Pb, and REE). The metal pollutants are related to the input of the Heavy Industrial Area of Tema (located around 3.5 km west of Kpone Beach) and urban effluents from the Greater Accra Region. The high content of Ba, Cu, Zn, and Pb in *Crassostrea* is directly related to high phytoplankton productivity (mainly for diatoms) linked to the input of trace metals transferred into the marine food webs. In addition, some analyses of gastropod shells from Kpone Beach indicate that *Cerithium* and *Nerita* are more sensitive to accumulating Ni and As than *Crassostrea*. The values of trace metals from the *Crassostrea* shells of the Densu Estuary and Anyanui Creek are comparatively low. Considering the role of *Crassostrea* shells as bioindicators for heavy metals pollution, the less polluted localities are Anyanui Creek and Densu Estuary, whereas Pra Estuary and Kpone Beach are affected by anthropic activities such as mining, urban effluents, and industry.

Keywords: *Crassostrea*; trace metals; pollution; mangrove.

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RESUMEN

El contenido en elementos traza de *Crassostrea tulipa* (Ostreidae, Bivalvia) de cuatro localidades (Estuario del Río Pra, Estuario del Río Densu, Playa Kpone y Arroyo Anyanui) a lo largo de la costa de Ghana ha sido utilizado como un bioindicador de contaminación ambiental. Los valores más bajos en metales pesados corresponden a las conchas de *Crassostrea* del Estuario del Densu y el Arroyo Anyanui, mientras que los más altos se han registrado en las conchas el Estuario del Río Pra y Playa Kpone. El Estuario del Río Densu y el Arroyo Anyanui se localizan en áreas no afectadas por grandes industrias, y únicamente el Estuario del Densu se localiza en un área densamente urbanizada. Las conchas de *Crassostrea* del Estuario del Densu presentan enriquecimiento principalmente de Ni. Sin embargo, el contenido total en carbono orgánico en el sedimento en el Estuario del Densu indica polución orgánica de origen antropogénico, pese a no existir evidencias en la composición de elementos traza en las conchas de *Crassostrea*. Los especímenes procedentes del Estuario del Pra muestran enriquecimiento en la mayoría de los elementos traza estudiados (Li, Be, V, Cu, Cr, Zn, Ga, Y, Sn, Pb, U, Th, ∑REE y As). Este enriquecimiento está relacionado con el aporte de metales pesados al Río Pra en relación con las actividades mineras, la deforestación extensiva y la consecuente pérdida de suelos. Las conchas de *Crassostrea* de Playa Kpone presentan un comparativamente alto contenido en algunos elementos traza (Be, Ba, Cu, Zn, Nb, Pb, y ∑REE). Los contaminantes metálicos están relacionados con los aportes del Área de Industria Pesada de Tema (localizada a unos 3.5 km al oeste de Playa Kpone) junto con los residuos urbanos del área metropolitana de Accra. El alto contenido en Ba, Cu, Zn, y Pb en *Crassostrea* está directamente relacionado con la alta productividad de fitoplancton (principalmente diatomeas) que transfiere metales traza a la red trófica marina. Además, algunos análisis realizados en conchas de gasterópodos de Playa Kpone indicant que *Cerithium* y *Nerita* son más sensibles a la acumulación de Ni y As que *Crassostrea*. Teniendo en cuenta la utilidad de las conchas de *Crassostrea* como bioindicadores de contaminación por metales pesados, los ecosistemas menos contaminados corresponden a las localidades de Arroyo Anyanui y Estuario del Río Densu, mientras que el Estuarío del Río Para y la Playa Kpone están afectados por actividades antrópicas tales como la minería, los vertidos urbanos y los industriales.

Palabras clave: *Crassostrea*; metales traza; contaminación; mangler.

Introduction

Pollution of the marine environment with trace metals, present toxic impact on the ecological functioning of their ecosystems as well as the well-being of people that depend on these marine environments for food, especially coastal and estuarine ecosystems (Du et al., 2011; Mahu et al., 2016). The pollution ranks among the topmost problems that coastal environments face globally, and Ghana's Coast is no exception to this. Heavy metal pollution of Ghana's coastal environments is a major problem because increasingly, people are becoming adamant about the need to engage in sustainable environmental activities to lessen land-based discharge of heavy metal effluents into the coastal environment. The recent increase in illegal extraction of gold from bearing rocks using unacceptable methods such as amalgamation with mercury and direct disposal of untreated effluents into major river bodies has triggered the increase of heavy metals input into the ocean (Babut et al., 2003; Amonoo-Neizer et al., 1996; Armah et al., 2014). Additionally, the country's inability to enforce regulations and the existence of several systemic barriers, including lack of data hinder the implementation of sound ocean health policies resulting in an exacerbation of the problem. While works have recorded high levels of toxic metals such as Cd, As, Hg, and Pb in water, sediment, and muscle of fish (Donkor et al., 2005; Fianko et al., 2007, Adokoh et al., 2011; Mahu et al., 2015; Afum & Owusu, 2016; Duncan et al., 2018; Effah et al., 2021; Nyarko et al., 2023), such studies only date back to the last 50 years (Mahu et al., 2016). The lack of historical and baseline data makes it difficult to reference national or regional background levels to formulate policies that inform better decision-making. This lack of historical data is fostered by a lack of capacity and resources to implement long-term coastal environmental monitoring programmes. However, in the absence of long-term monitoring data, the shells of invertebrate marine organisms have proven beyond doubt to be reliable predictors of past environmental conditions (Thébault et al., 2009; Yan et al., 2020).

The content of trace elements in the mollusc shells is mainly controlled by the mineralogy of the shell: i.e. high-Mg calcite, low-Mg calcite, and aragonite. In addition, vital effects related to the metabolism play a key role in the adsorption and co-precipitation of trace elements in the shells, particularly for Ba, Sr, and Zn. According to Smrzka et al. (2019), aragonite and calcite readily incorporate trace elements during precipitation. The carbonate minerals are very prone to incorporate important amounts of trace elements (Veizer, 1983; Du et al., 2011; Reolid et al., 2023) via co-precipitation and adsorption (Zachara et al., 1991; Paquette & Reeder, 1995). Invertebrate skeletons grow in equilibrium with the chemical composition of their surrounding water, making the chemical composition of their skeletons a proxy of past environmental conditions, including pollution by heavy metals. The chemical compositions of invertebrate shells have been typically used proxies for palaeoclimatic and palaeoecological and pollution reconstructions (e.g. Rosales et al., 2004; Wanamaker et al., 2008; Schone et al., 2011; de Winter et al., 2020). Most of these geochemical works are focused on well-known taxonomic groups such as bivalves (e.g. Van der Putten et al., 2000; Usero et al., 2005; Markulin et al., 2019; Tarique et al., 2019), belemnites (e.g. Rosales et al., 2004; Benito & Reolid, 2012; Ullmann et al., 2022), corals (e.g. Wyndham et al., 2004; Montagna et al., 2005; Raddatz et al., 2014; Raddatz & Rüggeberg, 2019), and brachiopods (e.g. Brand et al., 2003; Azmi et al., 2011; Clark et al., 2016; Roda et al., 2021).

Crassostrea tulipa, Lamarck 1819, the mangrove oyster of West Africa, is a widespread mollusc found along the coastal environment of Ghana and along the West to Central coast of Africa. The oyster is essentially a brackish water organism that occurs in estuaries, backwaters, mangrove roots, and in open coastal waters. The unique positioning of these oysters within these transitional waters and its widespread nature make them an excellent species for studying environmental contamination. The reason being that the estuaries and other nearshore areas inhabited by oysters are also the preferred locations for an ever-growing human population globally, hence, affected by varied human activities (Mil-Homens et al., 2009; Mahu et al., 2016; Chevrollier et al., 2022).

After metals arrive to the marine ecosystem, they can be bioaccumulated in soft tissues and biomineralized in shells of the oysters and other macroinvertebrates (Zhang et al., 2020). The soft tissue of *C. tulipa* has been studied extensively to document its potential to bioaccumulate heavy metals. This is particularly important for establishing connections to human health as well as serving bioindicators of ecosystem health in recent (Joiris et al., 2000; Otchere, 2003; Otchere et al., 2003; Rebelo et al., 2005; Sidoumou et al., 2006; Obodai et al., 2011). Woelke (1967) and His & Maurer (1988) proposed the study of biochemical composition of *Crassostrea gigas* could be employed to identify any deterioration of the environment. Unlike the shells, tissue studies do not address the challenge of bridging historical and baseline data gaps in regions where the capacity for environmental monitoring is limited. Yet, only, a few works have analysed the metal composition of the shell of oysters (e.g. Carriker et al., 1982; Huanxin et al., 2000; Edwards et al., 2009; Goodwin et al., 2013). The filter-feeding ability of *C. tulipa* plays a role in its biomineralization process which is closely related with the activity of primary producers (Thébault et al., 2009; Goodwin et al., 2013). In shallow water habitats, such as estuaries, changes in nutrient inputs from natural and anthropogenic origin results in seasonal phytoplankton blooms that change the chemical properties of the waters (Cabrita et al., 2020). Nutrient enrichment of aquatic environments is commonly associated to contamination with hazardous pollutants, which can be accumulated in significant amounts in marine organisms through the food web (Wang, 2002, Ali et al., 2019). Filter feeders, such as *Crassostrea*, ingest large amounts of phytoplankton and precipitate their shells in equilibrium with these waters (Goodwin et al., 2013). Thus, trace metals may be added to their shells through metabolism (mainly feeding) and directly from the interaction of the calcitic/aragonitic shells with water.

The main purpose of the present study is to test if the analysis of the trace element contents of *Crassostrea* shells collected from different estuaries, beaches, and intertidal environments on the Ghanaian coast is a useful proxy of water contamination. In addition, in this preliminary work shells of different genera of gastropods have been collected and analysed from one locality for comparing the chemical fractionation and biomineralization potential in the two different taxonomic groups.

Materials and Methods

Study areas

Live macroinvertebrate samples were collected from four locations (i.e., Pra Estuary, Densu Estuary, Kpone Beach, and Anyanui Creek) spanning the west to the east Coast of Ghana (Fig. 1A, B).

The Pra Estuary (5°01'19.3"N 1°37'28.4"W) is located at the mouth of the Pra River (Fig. 1C) which takes its source from the Kwahu Plateau. The main tributaries are Birim and Offin rivers. Pra River enter in the Gulf of Guinea at Shama in the Western Region of Ghana. It is one of the largest rivers in Ghana with an estimated mean annual discharge of about 214 m^3 s^{-1}, with a catchment area of 29,000 km^2 (WRC, 2012). The river drains several gold mining towns including Bogoso, Dunkwa, Fosu, Obuasi, Praso, Tarkwa, and Twifo in the upper to middle reaches and Aboadze, Aboso, Inchaban, Nsuta, Sekondi Takoradi, and Shama in its lower reaches. The Pra River and its estuary is severely impacted by small-scale mining activities with unacceptably high loads of suspended sediments which are evident physically and from satellite images.

The Densu Estuary (5°30'58.1"N 0°18'23.4"W) is located at the mouth of the Densu River (Fig. 1D) which takes its source from the Atewa-Atwiredu mountain range near Kibi, in the Eastern Region of Ghana. The Densu River, whose main tributaries are the Adeiso, Nsakyi, Dobro, and Kuia rivers, is approximately 116 km long with a drain a total area of 2,564 km^2 (Debrah, 1999). The river drains through numerous towns counting Akwadum, Old Tafo, New Tafo, Koforidua, Suhum, Nsawam, Adaiso, Asuhoe, Mangoase, Bepowase in the upper to middle reaches which are underlain by Birimiam and Dahomeyan basement rocks; and Bortianor, Pokuase, Weija, Kokrobite and Nyanyanu townships in the lower reaches underlain by the Togo series rocks. While there is some mining happening along the Densu (Hagan et al., 2011), the level of pollution arising from mining is very minimal compared to the Pra River. The estuary is however situated in an urbanized location with several residents and some industries with significant effluent discharges.

The Kpone Beach (5°41'23.5"N 0°03'52.9"E) is located within the heavy industrial belt of Ghana to the East of the Tema Port (Fig. 1E). The beach is mostly sandy with rock patches and stretches about 2.7 km and fed with sediment and other associated inputs through the eastward-moving littoral drift. Mainly, such inputs are from the Tema Harbour and adjacent industries and the Laloi River. This part of Ghana is the most industrialized with documented impacts of the industrial process on the quality of seawater (Botwe et al., 2017a, 2017b).

The Anyanui Creek (5°47'38.02"N 0°42'46.53"E) is located between the estuary of the Volta River to the West and the Keta Lagoon and stretches about 27 km (Fig. 1F). The creek receives input from the Lower Volta during the low tide and from the ocean during the high tide. Unlike the estuaries to the West, the Volta estuary is not impacted by mining activities and industrial activities. The only significant impacts on the creek come from agricultural activities within its watershed.

Specimen collection and trace element determination

Live macroinvertebrate samples were collected from the study location between October and December 2021 (Table 1) for chemical analysis. A total of 19 ostreids of the species *Crassostrea tulipa* were sampled from the four locations (4 from Pra Estuary, 4 from Densu Estuary, 6 from Kpone Beach, and 5 from Anyanui Creek). Additionally, 13 gastropods belonging to the genera *Turritella*, *Stramonita*, *Nerita*, *Cerithium*, and *Patella* were collected from Kpone Beach (Table 2).

Shells were washed under distilled water and submitted to ultrasound bath for deleting potential particles of clay minerals. Subsequently, a part of the shells were ground to powder and homogenized in a tungsten carbide ring mill for 4 to 6 seconds to obtain a grain size < 53 µm at the Department of Geology of the University of Jaén. In the case of ostreids the part of the shell selected for analyses was around the commissure of the lower valve. In the gastropod specimens the selected part was mainly the last whorl, except in *Turritella* where the complete shells were employed considering the small size and thin shell wall.

The determination of trace-elements was done by inductively coupled plasma-mass spectrometry (ICP-MS) with a NexION 300D (Perkin Elmer) spectrometer in the Centro de Instrumentación Científica of the University of Granada, after HNO_3 + HF digestion of 0.1000 g of powder sample in a Teflon-lined vessel at 180°C and 200 p.s.i during 30 min, evaporation to dryness, and subsequent dissolution in 100 mL of 4 vol.% HNO_3. Instrument measurements were carried out using Rh as the internal standard. Precision was better at 5% for analyte concentrations of 10 ppm.

In addition, two sediment cores of 40 cm depth were studied in the Pra and Densu estuaries for

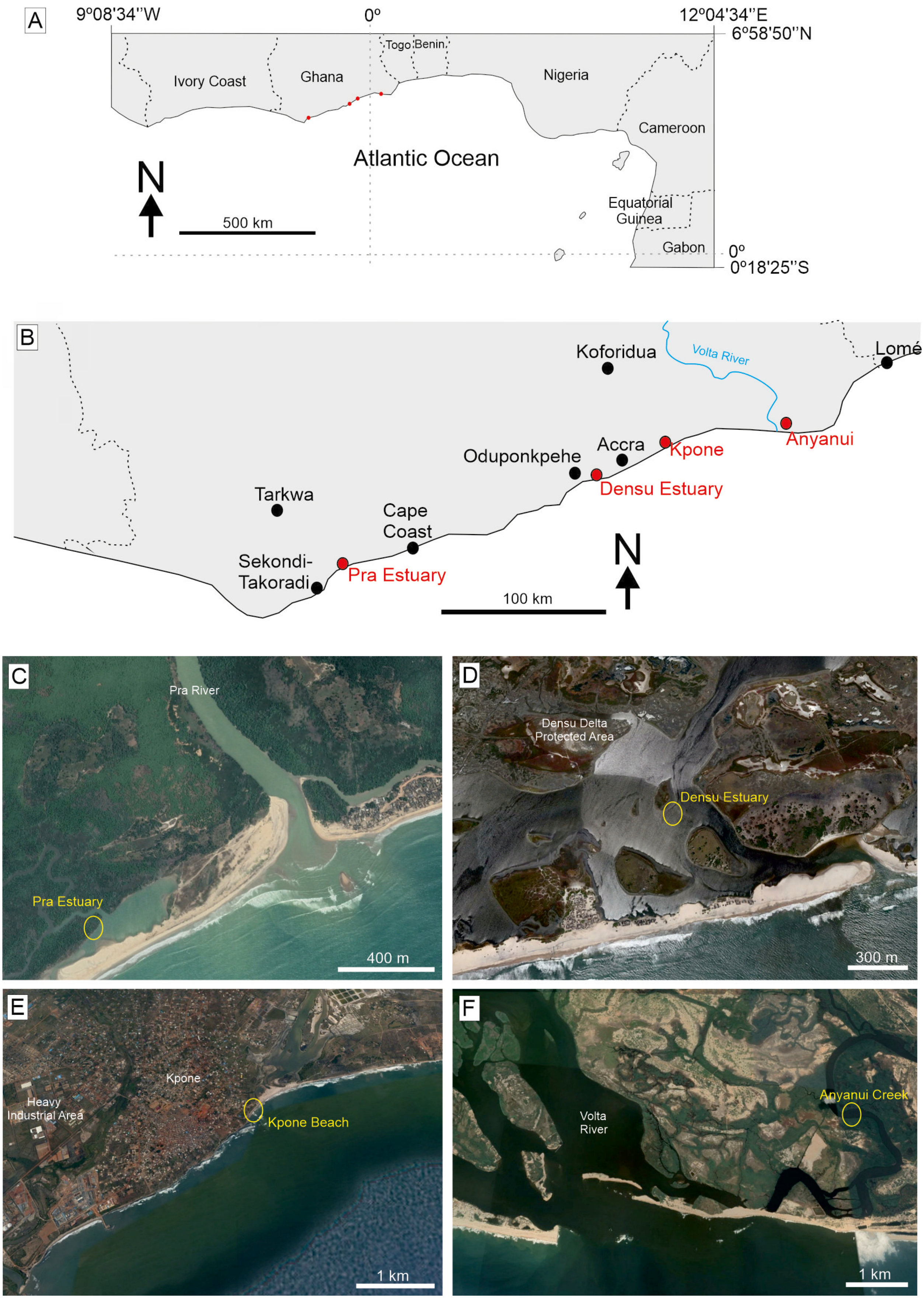

Figure 1.— Location of the sampling sites. A and B. General position of the sampling sites (red points) in the Coast of Ghana. C-F. Detailed location of the sampling sites (yellow circles) on satellite images of GoogleEarth ®.

Table 1. Content of selected trace elements (ppm) in the different *Crassostrea* samples studied from Pra Estuary, Densu Estuary, Kpone Beach and Anyanui Creek.

Reference	Site	Li	Rb	Be	Sr	Ba	V	Cr	Co	Ni	Cu	Zn	Y	Nb	Sn	Pb	As	Zr	La	Ce	SUM REE
PRA-1	**Pra Estuary**	7.11	1.17	0.11	804.15	17.56	5.06	6.33	1.4	18.25	16.07	63.02	0.65	0.94	3.6	1.4	0.909	5.18	2.14	3.16	8.21
PRA-2	**Pra Estuary**	12.23	2.52	0.15	984.45	22.54	5.98	8.54	1.74	19.59	27.21	61.12	0.86	1.07	4.14	1.48	1.536	6.99	2.59	3.99	10.02
PRA-3	**Pra Estuary**	8.47	3.29	0.23	814.25	33.22	5.05	34.89	1.55	21.77	56.67	179.11	2.93	1.16	5.34	2.47	1.756	8.31	2.74	4.07	10.56
PRA-4	**Pra Estuary**	2.78	2.34	0.06	918.97	6	1.18	1.47	0.69	16.21	30.53	15.6	0.08	0.72	3.01	0.62	0.496	3	1.36	1.58	4.6
DS-3	**Densu**	2.24	1.04	0.07	921.44	12.29	1.67	1.76	1.13	25.19	4.85	10.39	0.2	0.79	1.19	0.68	0.053	19.39	1.4	1.73	4.96
DS-4	**Densu**	3.11	0.99	0.08	916.1	15.1	1.69	1.96	1.09	25.7	3.55	11.44	0.27	0.81	0	0.81	0.824	6.19	1.53	2.08	5.79
DS-1	**Densu**	2.06	0.96	0.06	951.58	12.17	3.53	20.04	7.24	24.77	1.81	12.07	0.04	0.71	0.1	0.53	0	3.52	1.19	1.34	4.1
DS-2	**Densu**	2.55	0.66	0.06	941.54	6.74	0.52	1.25	0.93	19.9	1.83	12.3	0.09	0.68	0	0.99	0.048	4.17	1.23	1.36	4.16
KP-14	**KponeBeach**	3.34	0.45	0.09	720.89	31.91	1.34	1.53	0.83	19.36	7.05	4.83	0.69	1.22	1.73	0.58	0.141	3.16	1.68	2.26	6.38
KP-14.2	**KponeBeach**	1.74	0.3	0.13	686.48	83.78	0.54	1.04	0.76	16.74	2.2	5.87	0	1.46	0	1.02	0	9.11	2.35	2.5	7.97
KP-14.3	**KponeBeach**	0.79	0.67	0.14	580	101.21	1.07	2.86	1.02	14.79	82	61.65	0.05	1.56	0	4	0.044	6.4	2.7	2.91	9.1
KP-14.4	**KponeBeach**	0.22	0.16	0.16	636.95	532	1.46	2.59	0.86	17.59	1.92	86	0	1.81	0	1.16	0	10.49	2.95	3.11	9.99
KP-14.5	**KponeBeach**	0.72	0.42	0.11	710.83	108.47	1.28	2.38	2.13	16.51	24.25	18.26	0.21	1.26	0	1.15	0.023	5.43	2.25	2.4	7.54
KP-15	**KponeBeach**	6.11	3.21	0.19	869.95	106.17	5.26	30.06	1.65	16.67	51.7	110.79	0.97	1.35	5.12	2.73	0.507	5.31	1.95	2.78	7.72
GL-1	**Anyanui Creek**	0.93	0.73	0.06	763.66	4.6	0.32	0.65	0.63	21.44	13.71	87.63	0.03	0.68	1.28	1.57	0.118	3.62	1.2	1.29	4.02
GL-2	**Anyanui Creek**	2.39	0.74	0.06	929.94	179.14	0.67	0.64	0.6	19.1	1.24	9.46	0.05	0.79	1.72	0.81	0.042	7.36	1.19	1.37	4.13
GL-3	**Anyanui Creek**	4.05	0.83	0.09	857.44	14.87	1.75	2.13	0.84	18.4	1.65	22.82	0.39	0.89	2.99	0.95	0.178	4.66	1.63	2.38	6.4
GL-4	**Anyanui Creek**	0.82	0.23	0.06	1469.64	100.52	0.5	0.79	1.1	18.77	1.42	64.03	0.12	0.71	1.61	0.41	0	2.76	1.3	1.42	4.33
GL-5	**Anyanui Creek**	2.82	0.67	0.08	1248.73	20.7	2.01	2.74	1.84	18.37	7.91	17.45	0.56	0.83	3.03	1.61	0.058	4.88	3.76	6.47	15.29
Average		2.202	0.64	0.07	1053.882	63.966	1.05	1.39	1.002	19.216	5.186	40.278	0.23	0.78	2.126	1.07	0.079	4.356	1.816	2.586	6.834

Table 2. Content of selected trace elements (ppm) in the different genera of gastropods and *Crassostrea* from Kpone Beach.

Sample	Taxa	Li	Rb	Cs	Be	Sr	Ba	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Y	Nb	Zr	Mo	Sn	Pb	As	SUM REE
KP-12	Cerithium	0	0.3	5.45	0.06	1063.11	1.56	0.24	0.26	1.15	0.57	25.04	5.88	6.87	0.45	0	0.67	2.77	0.07	1.97	0.64	0.127	4.1
KP-13	Cerithium	0.7	0.46	0.1	0.06	1504.87	5.85	0.36	2.14	1.45	0.77	25.23	6.52	8.89	0.11	0.27	0.78	3	0.01	1.68	1.26	0.686	5.54
KP-10	Nerita	0.68	1.02	1.63	0.06	1338.59	2.25	0.2	0.3	0.42	0.63	24.56	9.79	5.12	0.03	0.03	0.68	2.58	0.53	1.62	1.73	0.151	5.11
KP-7	Nerita	4	0.35	0.09	0.1	1682.17	140	0.26	0.27	23.16	0.77	20.87	31.79	79.74	0.25	0.41	0.88	7.72	0.25	4.53	1.32	0	4.43
KP-8	Nerita	6.33	0.34	0.07	0.09	1125.47	53.27	0.23	0.27	6.72	0.68	20.44	24.01	49.35	0.17	0.14	0.79	3.76	0.14	3.54	1.16	0.129	4.38
KP-9	Nerita	0	0.15	0.06	0.06	1540.96	4.17	0.36	0.33	0.21	0.66	17.46	2.56	10.22	0	0.14	0.78	2.8	0	3.23	1.05	0.17	5.36
KP-1	Patella	2.95	0.8	1.07	0.06	1451.38	1.93	0.27	0.17	0.31	0.59	19.48	0.27	6.34	0.11	0	0.67	3.46	0.09	1.66	0.56	0.073	3.81
KP-2	Patella	2.55	0.42	0.06	0.05	1466.37	1.59	0.36	0.19	0	0.56	15.86	0	0.62	0	0	0.93	2.78	0.17	3.87	0.35	0.112	3.78
KP-6	Patella	1.72	0.41	0.07	0.06	1442.53	1643.24	0.21	0.49	0.42	0.57	18.2	3.64	19.47	0	0.2	0.68	2.66	0.02	3.58	0.58	0.167	4.01
KP-11	Stramonita	0.07	0.36	0.11	0.05	1696.67	2.67	0.2	0.18	0.22	0.82	24.27	2.22	3.01	0	0	0.7	3.52	0.02	1.34	0.47	0.102	3.8
KP-3	Turritella turbona	0.98	1.99	0.11	0.11	1323.68	32.89	3.1	11.81	4.99	1.58	13.91	4.8	11.79	1.11	2.85	1.53	10.19	0.1	4.32	1.65	1.546	9.18
KP-4	Turritella turbona	0	0.39	0.06	0.06	1477.16	1.74	0.53	0.39	0	0.61	16.37	0	2.79	0	0.04	1.62	2.67	0.01	4.57	0.58	0.223	5.92
KP-5	Turritella turbona	0	0.37	0.06	0.06	1258.45	1.56	0.58	0.28	0	0.62	16.69	2.39	4.45	0	0.01	1.37	2.73	0.03	5.04	0.43	0.215	3.94
KP-14	Crassostrea tulipa	3.34	0.45	0.1	0.09	720.89	31.91	0.26	1.34	1.53	0.83	19.36	7.05	4.83	0.3	0.69	1.22	3.16	0.36	1.73	0.58	0.141	6.38
KP-14.2	Crassostrea tulipa	1.74	0.3	0.17	0.13	686.48	83.78	0.3	0.54	1.04	0.76	16.74	2.2	5.87	0	0	1.46	9.11	0.52	0	1.02	0	7.97
KP-14.3	Crassostrea tulipa	0.79	0.67	0.37	0.14	580	101.21	0.4	1.07	2.86	1.02	14.79	82	61.65	0	0.05	1.56	6.4	0.63	0	4	0.044	9.1
KP-14.4	Crassostrea tulipa	0.22	0.16	0.24	0.16	636.95	532	0.32	1.46	2.59	0.86	17.59	1.92	86	0	0	1.81	10.49	2.54	0	1.16	0	9.99
KP-14.5	Crassostrea tulipa	0.72	0.42	0.23	0.11	710.83	108.47	0.32	1.28	2.38	2.13	16.51	24.25	18.26	0	0.21	1.26	5.43	2.15	0	1.15	0.023	7.54
KP-15	Crassostrea tulipa	6.11	3.21	0.19	0.19	869.95	106.17	0.45	5.26	30.06	1.65	16.67	51.7	110.79	0.83	0.97	1.35	5.31	1.21	5.12	2.73	0.507	7.72

analysing the organic matter content through %C and %N in each core at 2 cm depth intervals. Analyses of the total organic carbon (TOC) and total nitrogen (TN) were carried out at Moss Landing Marine Laboratories using a CE Model 440 Elemental Analyzer after treating the samples with 1 N HCl.

Results

Chemical composition of ostreid shells

The studied shells of *Crassostrea tulipa* show a variable pattern of distribution of the trace element contents related to the studied site (Fig. 2). Averagely, the highest content of trace elements is in decreasing order: Sr, Ba, Zn, Cu, Ni, Li, Zr, Cr, and V. The content of other trace elements (i.e., Sn, Pb, La, Ce, Mo, Rb, Cs, Co) was usually lower but locally reached values > 2 ppm.

The samples with the highest content of metals are those from Pra Estuary and Kpone Beach (Fig. 2). The shells from Pra Estuary are enriched relative to the other sites in Li, Rb, Be, V, Cr, Cu, Zn, Ga, Y, Sn, Pb, U, Th, ∑REE and As (Fig. 2 and Table 1). The oyster shells from Kpone Beach present relatively high content in Be, Ba, Cu, Zn, Nb, Pb and ∑REE.

The *Crassostrea* shells from Anyanui and Densu are comparatively more pristine with relatively low levels of trace metals compared with those from Pra Estuary and Kpone Beach (Fig. 2). Average-wise, the distribution of trace elements that are > 1 ppm in the shell of the oysters followed the patterns below.

- Pra Estuary: Sr > Zn > Cu > Ba > Ni > Cr > Li > Zr > V > Sn > Ce > Rb > La > Pb > As > Y > Co
- Densu Estuary: Sr >Ni >Ba > Zn > Zr > Cr > Cu > C > Li > V > Ce > La
- Kpone Beach: Sr > Ba > Zn > Cu > Ni > Cr > Zr > Ce > La > Li > V > Pb > Nb > Co > Sn
- Anyanui creek: Sr > Ba > Zn > Ni > Cu > Zr > Ce > Li > Sn > La > Cr > Pb > V > Co

The comparison of the distribution of trace elements in *Crassostrea* shells from the different sites, indicates very high values of Sr > 600 ppm, with the highest mean values in Anyanui Creek (1,053 ppm, σ = 295 ppm) whereas the lowest mean values correspond to the samples from Kpone Beach (700 ppm, σ = 97 ppm) and Pra Estuary (880 ppm, σ =86 ppm) (Figs. 2 and 3). The Ba is the next most abundant trace element in the oyster shells (Fig. 2). The highest value of Ba was recorded in the shells from Kpone Beach (mean value 161, σ = 180 ppm), and the lowest values were found in the shells from the Pra (mean 20, σ = 11.3 ppm) and Densu (mean 11, σ = 3.5 ppm) estuaries (Fig. 2). High variabilities were obtained for Zn levels across the different sites as well, with Pra shells recording the highest contents (mean 80.0, σ = 69.8 ppm) and the Densu shells recording the lowest (mean 11.5 ppm, σ = 0.8 ppm) (Figs. 2 and 3). Contrary to Sr, Ba and Zn, Ni showed a near homogenous distribution across the sites ranging from 14.7 ppm (σ = 1.5 ppm) in shells from Kpone Beach, to 25.7 ppm (σ = 2.6 ppm) corresponding to Densu Estuary (Figs. 2 and 3). Copper content is particularly high in ostreids from Pra Estuary (mean value 32.6 ppm) and Kpone Beach (mean value 28.2 ppm), whereas the lowest mean values are recorded in Anyanui Creek (5.2 ppm) and Densu (3.0 ppm) (Figs. 2 and 3). Lithium content is especially high in the Pra Estuary (mean 7.6 ppm, σ =3.9 ppm) but nearly homogenous and low in Densu (2.5 ppm, σ =0.4 ppm), Anyanui creek (2.2 ppm, σ = 1.3 ppm), and Kpone Beach (2.1 ppm, σ = 2.2 ppm) (Fig. 2). Similar to Ni, the content of Zr presents a near homogeneous content across the studied sites, with the highest mean value corresponding to Densu Estuary (8.3 ppm, σ = 7.4 ppm) and the lowest one to Anyanui Creek (4.4 ppm, σ = 1.7 ppm). Chromium and vanadium values are clearly higher in the shells from Pra Estuary (mean Cr = 12.8 ppm, V = 4.3 ppm), intermediate in Kpone Beach (Cr = 6.7 ppm, V = 1.8 ppm) and Densu (Cr = 6.2 ppm, V = 1.8 ppm), and very low in the samples from Anyanui Creek (Cr = 1.4 ppm, V = 1.0 ppm) (Fig. 2).

Other trace elements such as Sn, Rb, La, Ce, Pb, Nb, Y, and Be show the highest values in the Pra Estuary and Kpone Beach (Figs. 2 and 3, Table 1). Commonly the lowest values for these elements correspond to *Crassostrea* shells from Anyanui Creek and Densu Estuary. The Sn is especially high in the oyster shells from Pra Estuary with average values of 4.0 ppm (σ = 0.9 ppm), whereas in Densu is very low (0.3 ppm, σ = 0.5 ppm) (Figs. 2 and 3). The As content is also highest in the shells from Pra Estuary with a mean value of 1.2. ppm (σ = 0.5 ppm), but < 0.2 ppm in the other studied sites (Figs. 2 and 3). The Pb presents the highest values in Kpone Beach and Pra Estuary (mean value 1.8 and 1.5 ppm respectively) (Fig. 3). Uranium and Hg are exclusive to only the shells from Pra Estuary with values < 0.04 ppm (Table 1). The REE presents the

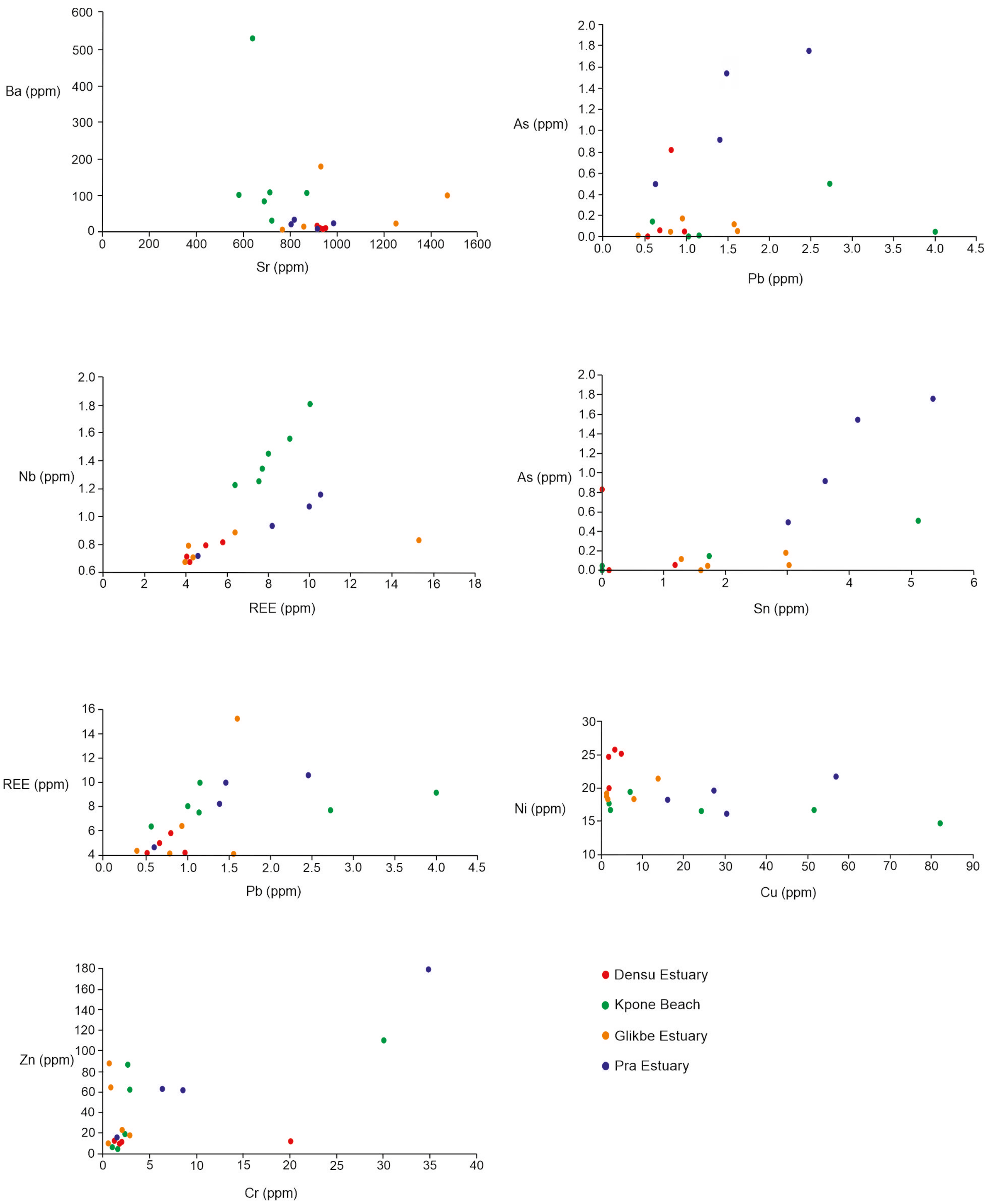

Figure 2.— Cross plots for the content of selected trace elements of *Crassostrea* from the studied sites. See the different content of trace elements according to the distinct studied areas in the Coast of Ghana. The highest contents of As, Sn and Pb (highly toxic elements) are commonly in samples from Kpone Beach and Pra Estuary.

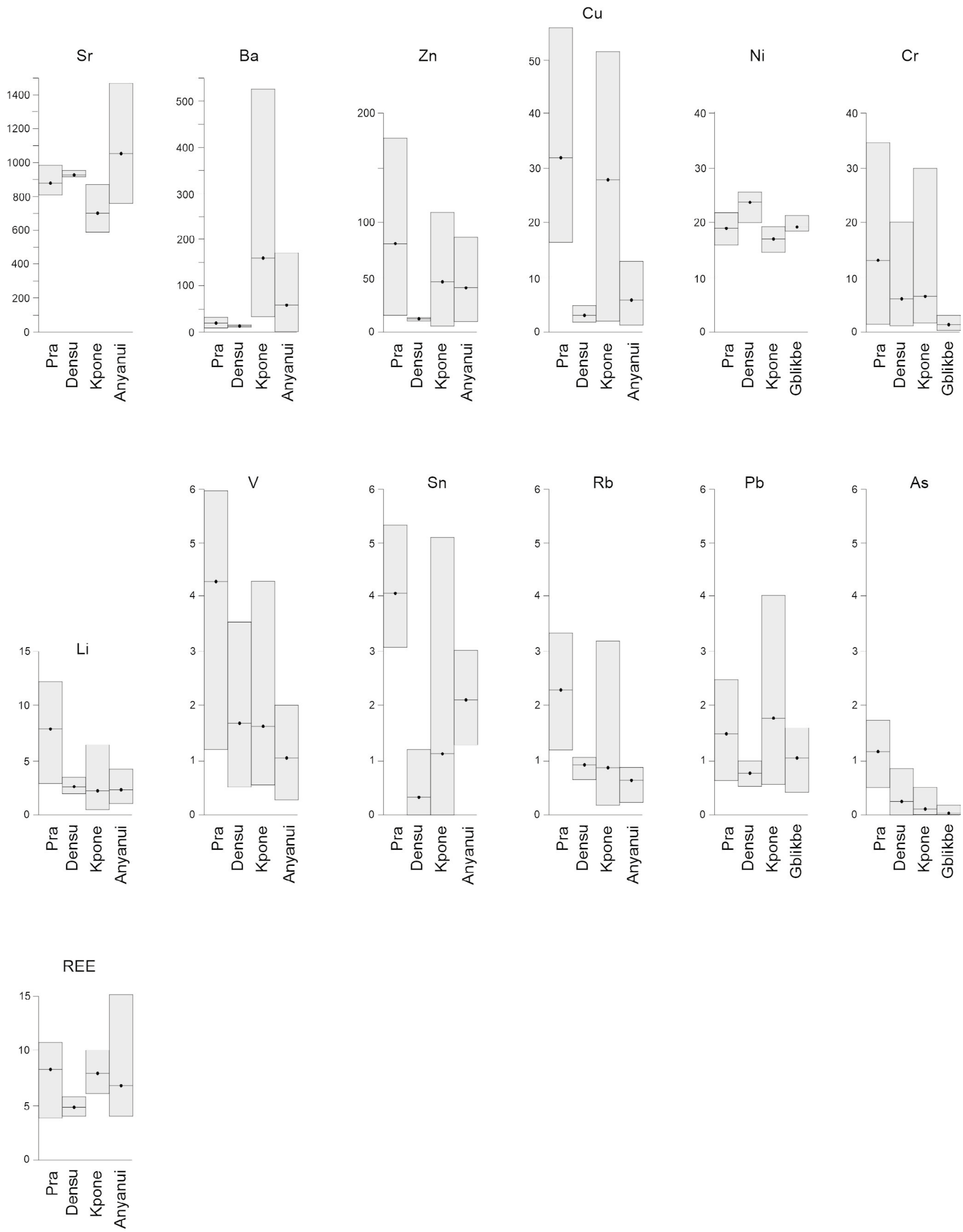

Figure 3.— Boxplot diagram representing the concentration of the trace elements in *Crassostrea* shells from all the analysed localities. Boxes range from lower to upper values, and the average value is shown with a horizontal line inside the box.

highest values in the shells from Pra Estuary (mean 8.3 ppm, σ = 2.6 ppm) and Kpone Beach (mean 8.1 ppm, σ = 1.2 ppm), especially in the case of La and Ce (Fig. 3, Table 1). In general, the content of REE is again low in shells of *Crassostrea* from Densu and Anyanui (Fig. 3). However, one sample (GL-5) from Anyanui shows very high values in REE content, and mainly La (3.8 ppm) and Ce (6.5 ppm). The correlation coefficient for some trace elements is very high in Kpone Beach (Nb vs REE, R^2 = 0.92; As vs Sn, R^2= 0.98) and Pra Estuary (Nb vs REE, R^2 = 0.99; As vs Sn, R^2= 0.87; Pb vs REE, R^2 = 0.78), and locally for Densu Estuary (Nb vs REE, R^2 = 0.86) (Fig. 2).

Chemical composition of gastropods from Kpone Beach

Here, we present the trace element contents in gastropod shells collected from Kpone Beach only to understand the level of fractionation and biomineralization in the two taxonomic groups of molluscs. The highest contents of trace metals are recorded in the shells of oysters and epifaunal gastropods of the genera *Cerithium* and *Nerita* (Table 2). The lowest content of Li, Cu, and Ni corresponds to *Turritella* (infaunal gastropod).

The Sr content of the aragonitic shells of the gastropods is higher (mean 1413, σ = 98 ppm) than in the calcitic shells of ostreids (701 ppm, σ = 189 ppm) (Fig. 4). The Ni content in gastropods is also slightly higher (mean value 19.9 ppm, σ = 3.8 ppm) than in *Crassostrea* (16.9 ppm, σ = 1.5 ppm) (Fig. 4). The As content is also higher in gastropods (0.3 ppm) than in the oyster shells (0.1 ppm), especially in the case of *Turritella* (ranging from 0.2 to 1.5 ppm). The Sn content is also higher in gastropods (mean 3.2 ppm) than in ostreids (1.1 ppm) (Fig. 4), with the highest values in *Turritella* (4.3 – 5.0 ppm) (Table 2). The content in Co, Cr, Cu, Mo, Pb, Zn, Zr, and REE are clearly enriched in the ostreid shells compared to the gastropod shells (Fig. 4).

Organic carbon from sediment cores

The TOC values of Pra Estuary range from 0.77 to 1.85 wt.% (average 1.17 wt.%) whereas TN ranges from 0.05 to 0.14 wt.% (average 0.09 wt.%). As a general trend TOC and TN increase from the sediment surface downward, with the highest values of TOC reaching from 30 to 34 cm depth, and maximum values of TN reaching from 28 to 34 cm depth (Fig. 5). The C/N ratio ranges from 10.02 to 15.51 (average 12.19).

The organic matter content at Densu Estuary is higher than in Pra Estuary. TOC values of Densu Estuary range from 0.98 to 4.01 wt.% (average 1.66 wt.%) whereas TN ranges from 0.04 to 0.27 wt.% (average 0.10 wt.%). As a general trend TOC and TN decrease from the sediment surface to downward, with the highest values of TOC reached in the first centimetres (Fig. 5). The C/N ratio ranges from 12.93 to 26.62 (average 16.71) with the highest values recorded from 34 to 40 cm depth.

Discussion

Incorporation of trace elements into mollusc shells

The high-Mg calcite, low-Mg calcite, and aragonite are susceptible to incorporate significant amounts of trace elements (e.g. Zachara et al., 1991; Du et al., 2011; Raddatz & Rüggeberg, 2019). In addition, the content of trace metals in mollusc shells depends on charge and ionic radius (more or less similar to Ca^{2+}), the growth rate and the shell surface structure (e.g. Reeder et al., 1999; Reolid et al., 2023). Trace elements with charge and size similar to Ca^{2+} such as Co and Zn, will be more susceptible to be incorporated within calcite crystal structure via co-precipitation (Morse & Mackenzie, 1990). Some elements commonly present in the shells such as Sr, Ba, and U (e.g. Russell et al., 1994; Thébault et al., 2009; Pérez-Huerta et al., 2013; Keul et al., 2013; Reolid et al., 2023), present higher coordination number and replace Ca via adsorption of cations. According decreasing ionic radius, the adsorption is favoured with the incorporation of free metals ions for divalent cations, or as complexed aqueous species for trivalent cations (see Zachara et al., 1988; Cheng et al., 1999). The adsorption within the lattice starts with an early rapid surface uptake, followed by slower removal from solution (Comans & Middelburg, 1987; Stipp & Hochella, 1991). However, larger ions such as Sr, Ba, and U are favourably incorporated into aragonite where Ca is with a higher coordination number than in calcite (Morse et al., 2007).

Metabolism plays a main role in the vital effect that affect the trace elements in the shell of filter feeders such as *Crassostrea* that includes phytoplankton and

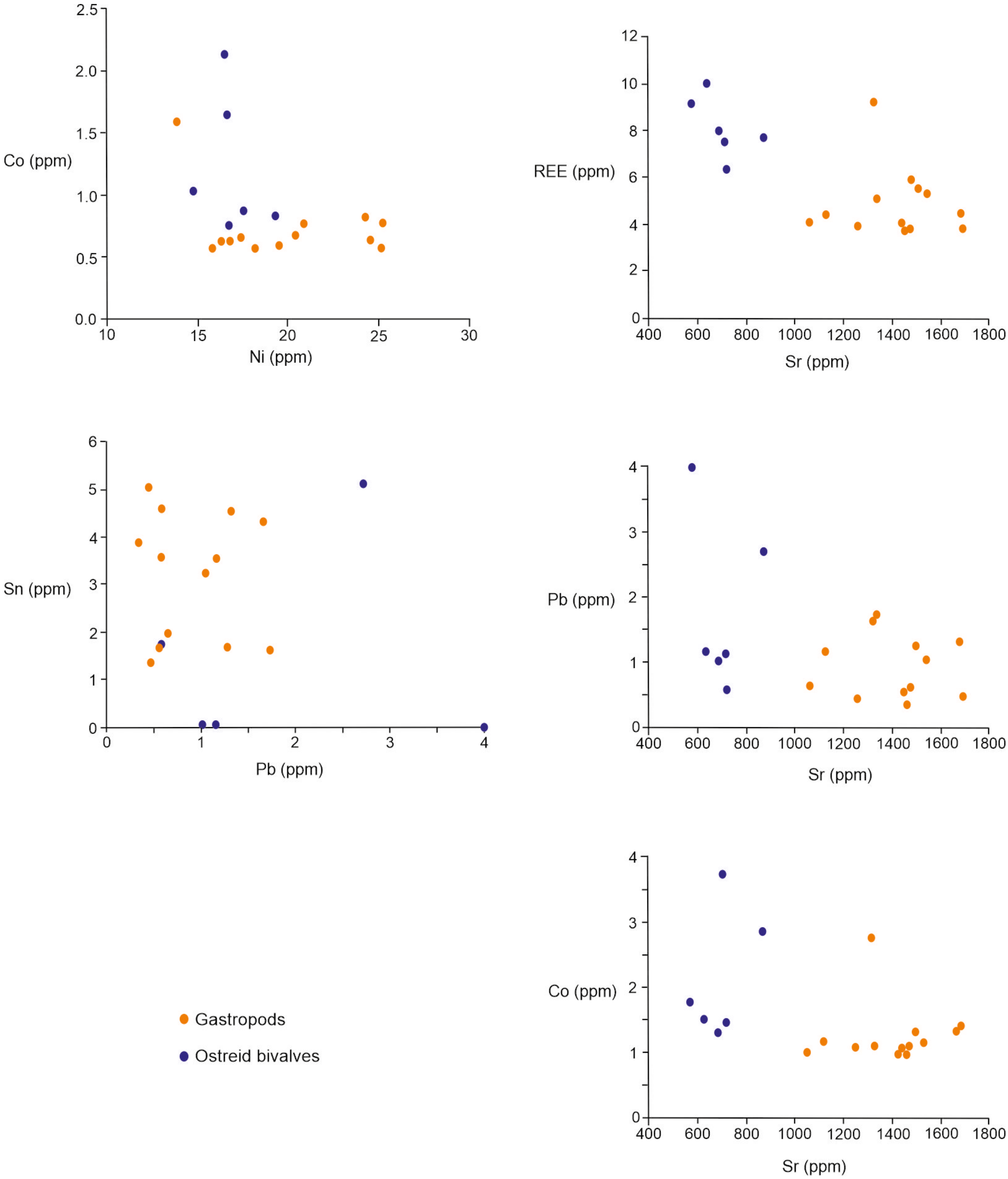

Figure 4.— Cross plots for the content of selected trace elements of different gastropod genera and *Crassostrea* from Kpone Beach. The content of trace metals is clearly differentiated in two populations.

decaying algal flocs in the diet (e.g. Galimany et al., 2017; Weissberger & Glibert, 2021). Phytoplankton is very sensitive to inputs of heavy metals (e.g. González-Dávila, 1995; Chevrollier et al., 2022; Szymanska-Walkiewicz et al., 2022) that are bioaccumulated in soft tissues and shell of benthic molluscs (Huanxin et al., 2000; Edward et al., 2009; Goodwin et al., 2013).

The element Sr is the most abundant in the studied shells, both in *Crassostrea* and the different genera

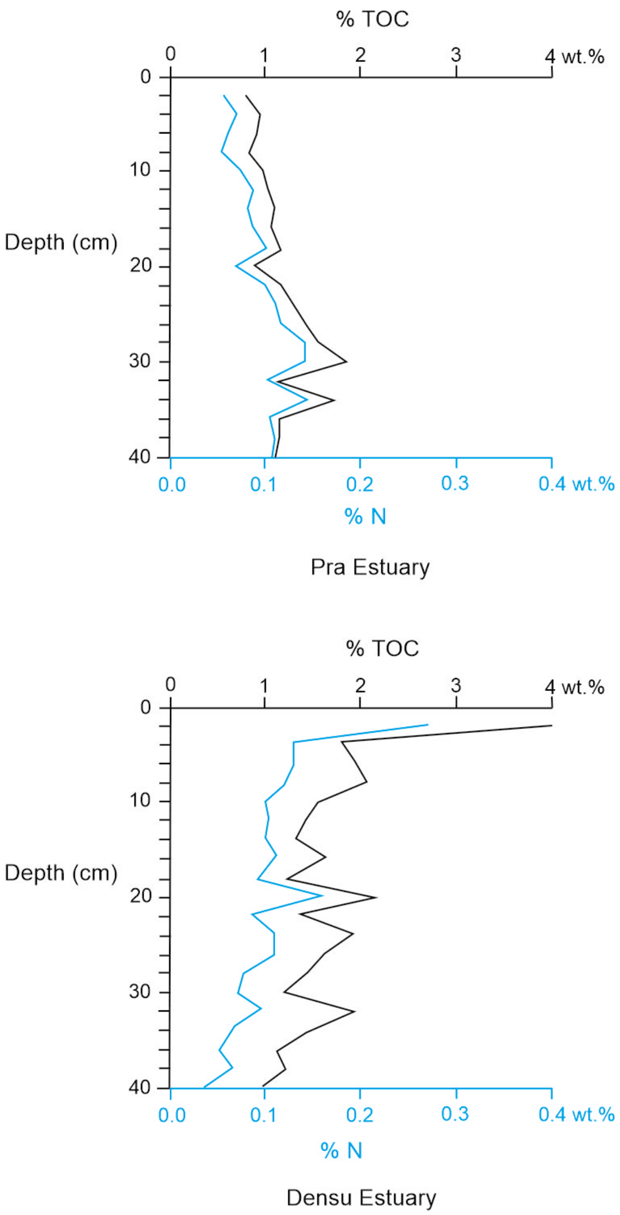

Figure 5.— Profiles of %TOC and %N in the sediment cores of 40 cm depth studied in the Pra and Densu estuaries for analysing the organic matter content.

of gastropods. Sr substitutes Ca via adsorption of cations in the lattice with an early surface uptake (Comans & Middelburg, 1987; Smrzka et al., 2019). The high content of Sr is congruent with the results from other calcitic shells (de Winter et al., 2019; Baeza-Carratalá et al., 2021; Reolid et al., 2023). The highest values of Sr occur in the aragonitic shells of gastropods. Considering the samples from Kpone Beach, where both oysters and gastropods were analysed, the average content of Sr of gastropods (1413 ppm) is double of *Crassostrea* (700 ppm). According to Morse et al. (2007), Sr is preferentially incorporated in aragonite crystals which explains the highest values in the aragonitic gastropods.

Crassostrea specimens from Pra Estuary (20 ppm) and Densu (11 ppm) record the lowest values of Ba whereas the highest values correspond to samples from Kpone Beach (average 161 ppm). The Ba content is comparatively low in the different gastropod taxa from Kpone Beach. Comparatively, high enrichment of Ba is expected in the aragonitic shells of gastropods since it has a high coordination number (Gillikin et al., 2006; Findlater et al., 2014), however, this was not recorded in the Kpone Beach samples. According to Reolid et al. (2023) vital effect interferes on Ba fractionation and is superimposed to expected fractionation considering the shell mineralogy. The main source of Ba to marine environments is river runoff (Schoepfer et al., 2015). Phytoplankton incorporates Ba by metabolic uptake or adsorption assimilated intracellularly (Bertram & Cowen, 1997; Tribovillard et al., 2006; González-Muñoz et al., 2012). Many works examined the connexion between primary productivity and biogenic Ba abundance (e.g. McManus et al., 1999; Jeandel et al., 2000; Prakash Babu et al., 2002; Schoepfer et al., 2015). In addition, Ba may be obtained by calcifiers through feeding on phytoplankton and decaying algal flocs (that also include microphytobenthic algae) according to Brannon & Rao (1979) and Stecher et al. (1996). They are among the natural diet of *Crassostrea* (e.g. Gerdes, 1983; Cognie et al., 2001; Galimany et al., 2017; Weissberger & Glibert, 2021).

The highest Zn values are recorded in *Crassostrea* shells from Pra Estuary (80 ppm), whereas the lowest ones are from Densu samples (11.5 ppm). Cations Ca^{2+} and Zn^{2+} present the same charge and a comparable size, hence Zn^{2+} can easily be incorporated into calcite crystals (Morse & Mackenzie, 1990). The Zn is an essential trace element for animals, however its excess accumulation in organisms gives rise to severe metabolic disorders (Nordberg et al., 2002). Generally, the Zn content of gastropods of Kpone Beach is lower than in *Crassostrea*, and only the largest specimens of *Nerita* present relatively high values. The different content of Zn among the studied taxa of molluscs is independent of shell type and is only related to vital effect.

The highest average value of Ni content corresponds to Densu Estuary (23.9 ppm) and the lowest to Kpone Beach (16.9 ppm). Nickel is a micronutrient required by phytoplankton for growth

(Calvert & Pedersen, 1993; Dupont et al., 2010), hence, can be incorporated by the filter-feeding process of *Crassostrea*. However, gastropods from Kpone Beach show higher values of Ni in the shells (mainly for *Cerithium*, *Nerita* and *Stramonita*). *Cerithium* was described as tolerant to high concentrations of heavy metals (Nicolaidou & Nott, 1999). Studies of soft tissue and shells of *Nerita lineata* indicate that Ni and other elements (Cu and Pb) are bioaccumulated in environments and sediments rich in these trace metals (Yap & Cheng, 2009; Haris et al., 2020).

Copper content is mainly high in the ostreids from Pra Estuary (mean 32.6 ppm) and Kpone Beach (28.2 ppm). In Kpone Beach, Cu is higher in *Crassostrea* and *Nerita*. Copper is an critical nutrient for marine plankton as well and it is a component of several enzymes (Moore et al., 1996; Rainbow, 2002). The high values of Cu in the *Nerita* shells compared with other gastropods agree with the sensitivity of this genus to incorporate heavy metals in the soft tissue and shell according to Yap et al. (2009). *Nerita* is an herbivorous grazer of microalgae and probably obtains Cu from feeding.

The Li content of *Crassostrea* is higher in the Pra Estuary (7.6 ppm) than in the rest of the sites (mean Li < 2.5 ppm). The values from gastropods are very variable but within the range of *Crassostrea*. Ca and Mg can be substituted by Li in the calcitic shells, and Li/Mg and Li/Ca ratios decline with temperature (Marchitto et al., 2018). However, a strong biological control on Li incorporation is possible (Raddatz & Rüggeberg, 2019).

The Zr and Cr in marine settings are related with terrigenous detrital input. There is not a clear pattern of distribution in the studied shell, except that the lowest values of these metals in *Crassostrea* are from shells of Anyanui Creek (Zr = 4.4 ppm and Cr = 1.4 ppm). This confirms that the input of metals in Anyanui Creek is sensibly lower than in other studied localities.

The lowest values of V were obtained in shells of Anyanui Creek (1.0 ppm). Vanadium is an essential nutrient for marine plankton and it is a constituent of several enzymes (e.g. Nalewajko et al., 1995; Moore et al., 1996; Smrzka et al., 2019), occurring as dissolved phase under oxic conditions ($VO_2(OH)_3^{2-}$ and H_2VO^{4-}).

The Pb, As and Sn are elements with high toxicity that in marine settings are related to terrigenous detrital input or anthropogenic discharges (Mahu et al., 2016). These elements present the highest values in the Pra Estuary and Kpone Beach and the lowest values in *Crassostrea* from Anyanui and Densu localities. The Sn is particularly high in the shells from Pra Estuary (mean 4.0 ppm) and very low in Densu Estuary (0.3 ppm). Concentrations of these elements are very indicative of water anthropogenic pollution. The correlation coefficient for some trace elements (As, Sn, Pb and REE) is very high in Kpone Beach and Pra Estuary, and generally very low in Anyanui Creek and Densu Estuary samples, pointing to a similar source of pollution and similar way of incorporation in the bivalve shells in Kpone Beach and Pra Estuary.

Trace elements as proxies for pollution on the Ghana coast

From west to east, the different localities show very different values for trace elements and represent different environmental contexts. The maximum content of heavy metals is found in the *Crassostrea* shells from Pra Estuary and Kpone Beach, and the lowest values of heavy metals come from shells of Densu and Anyanui Creek. This is directly related to the human activity in the watershed of the different rivers and tributaries as well as the direct discharge of heavy metals by industry and mining. Considering the use of mollusc shells as bioindicators for heavy metals pollution (Carell et al., 1987; Richardson, 2001; Edward et al., 2009; El-Sorogy & Youssef, 2015; Dar et al., 2018), the less polluted localities are Anyanui Creek and Densu.

In the westernmost site analysed, the shells of ostreids from the Pra Estuary, show enrichment with respect to the other sites in most of the analysed trace elements (Li, Rb, Be, V, Cr, Cu, Zn, Ga, Y, Sn, Pb, U, Th, ∑REE and As). The Pra river is one of the most heavily impacted waterbodies in Ghana by small-scale mining (Donkor et al., 2006; Seth & John, 2016; Awotwi et al., 2018; Duncan et al., 2018) and the extensive deforestation for settlement, mining, and infrastructural expansion, among other sources. The turbid waters observed from satellite images result from artisanal (mostly illegal) mining activities that discharge heavy metals into the river (Donkor et al., 2006) and the significant loss of soil minerals and succeeding high sediment transport by the Pra River and its tributaries (Seth & John, 2016), which ends up in the estuary in the locality of Shama where the samples are coming from. The relatively high content of Cu in the shells (> Ba) is congruent with the high values reported by the Shama locality by Seth and John (2016).

Although the Densu Estuary is placed in a highly urbanized setting, these are mostly residents. The city of Accra covers a wide part of the catchment containing river channels and floodplains. There are no major industries in this part of the country to have such negative impacts on the estuary waters. Mostly, effluents are discharged from domestic sources. Densu Estuary is among the most significant coastal drainage basins of Ghana. However, Gildeeva et al. (2021) recorded relatively high values of Zn, Cr, Ni, Cu, and As in some samples of sediments of the Densu Estuary. These authors also found elevated values of organic carbon within the sediment that related to extreme anthropogenic organic pollution. Our analyses of TOC from the top 40 cm of sediments at the bottom of Densu Estuary indicate that organic matter accumulated in the sediment (0.98 to 4.01 wt.%) is higher than in Pra Estuary (0.71 to 1.85 wt.%) (Fig. 5). The N content is also higher in Densu Estuary (average 0.11 wt.%). This is congruent with anthropogenic organic pollution. It is curious that studied Densu shells of *Crassostrea* are not strongly contaminated by urban effluent. *Crassostrea* shells from Densu Estuary are only enriched in Ni with respect to the other studied sites. Akita et al. (2020) analysed heavy elements in the sediments of an area of the Densu Estuary and found low contamination for Zn, Hg, and Cu, but high contamination of Pb. However, this contamination by Pb is not recorded in the ostreid shells (0.5 – 1.0 ppm). In general, the content of trace metals in the studied *Crassostrea* shells indicates a comparatively low contaminated environment if compared with Pra Estuary and Kpone Beach.

Kpone Beach is in the highly industrialized part of Ghana, therefore it is consistent that we are seeing this interesting trend in the enrichment of the samples with the metal pollutants. *Crassostrea* shells are relatively enriched in trace metals such as Be, Ba, Cu, Zn Nb, Pb, and REE. This is the result of the input of urban effluents from Kpone as well as some industries located in Kordjor River whose effluents arrive at the Kpone beach. Indeed, the Heavy Industrial Area of Tema is located around 3.5 km west of the sampling site. This area includes aluminum and iron companies, oil refineries, thermal plants, and others. In addition, to the west of Kpone Beach, there are more than 50 km of urbanized coast constituted by Accra and surrounding localities (Greater Accra Region). Considering that the Guinea Current is a warm surficial current that flows to the east along the Guinea Gulf Coast, we can hope that different pollutants coming from industry and urban effluents can be recorded in the composition of the shells. High levels of Cd, As, Hg, Pb, Zn, and Cu have been reported from lagoons and estuaries close to the cities of Accra and Tema (Tay et al., 2009; Gbogbo & Otoo, 2015). Nyarko et al. (2014) reported the enrichment of Cd, As, Cu, Ni and V in the sediments of Tema Port. Taking into account the gastropod shells, *Nerita* and *Cerithium* are more sensitive to accumulating Ni and As than *Crassostrea*. The input of trace metals from the industry, as well as fertilizers from agriculture, can result in seasonal phytoplankton blooms (Thébault et al., 2022). The high values of Ba in *Crassostrea* can be related to high phytoplankton productivity due to phytoplankton incorporating Ba by metabolic uptake or adsorption (Bertram & Cowen, 1997; González-Muñoz et al., 2012). The high content of Ba in *Crassostrea* shells is directly related to the ingestion of high amounts of phytoplankton in this context. Several studies have suggested a link between phytoplankton blooms and Ba content in shells (Lazareth et al., 2003; Goodwin et al., 2013), especially in the case of diatom blooms (Thébault et al., 2009, 2022). Phytoplankton blooms are significant biological sinks of trace metals such as Cr, Co, Ni, Cu, Zn, Cd, and Pb, (Cabrita et al., 2020) that are bioaccumulated into the marine food web, including by molluscs.

Finally, the Volta River which connects to Anyanui Creek, where the oysters were collected, is considered less impacted by anthropogenic pollution from industries because, the river and its tributaries do not flow through the country's industrialized region. The lowest values of heavy metals from shells of Anyanui Creek are consistent with lower pollution.

From the trace element data obtained from different study areas globally, it is clearly demonstrated that molluscs such as bivalves and gastropods, are efficient trace element bioaccumulators, useful as bioindicators of heavy metal pollution (Boening, 1999; Gupta & Singh, 2011; Wang & Lu, 2017). Considering the results from Kpone Beach, the different taxa show distinct trace element fractionation. *Crassostrea* bivalve is more susceptible to incorporating elements such as Ba, Co, Mo, and REE, whereas *Nerita* and *Cerithium* gastropods are more susceptible to incorporating Ni. This agrees with Yap & Cheng (2009) and Haris et al. (2020), iterating that *Nerita* bioaccumulates Ni in the shell when values are high in the environment. With respect to the other trace metals, there is not a clear preferential distribution.

The shells of the mollusc *Crassostrea tulipa*, indeed indicated high heavy metals pollution in the known polluted waters of the Pra Estuary and Kpone Beach and lower heavy metals in the least polluted study areas (i.e., the Densu Estuary and Anyanui Creek). Pollution of Ghana's coastal waters together with other factors such as climate change, water channel modification, and habitat degradation put further stress on marine organisms including oysters. According to Mahu et al. (2022) *Crassostrea tulipa* is among the marine organisms that are extremely vulnerable to global change impacts such as ocean acidification, potential sea-level rise and fluctuations in salinity and temperature controlled by variabilities in precipitation related to the climatic change. The preferred habitat of *Crassostrea tulipa*, i.e., mangrove ecosystems is subjected to enormous pressures (20-30% of mangroves in Ghana lost during the last decades (Ajonina et al., 2008). For example, Mahu et al. (2022) attributed high mortalities in the Densu Estuary and Anyanui Creek to the influx of freshwater from the Densu and Volta rivers respectively. The adult *Crassostrea tulipa* can survive in freshwater for > 10 days with the shell valves closed by adductor muscles contracted, but metabolism is severely affected (Dimock, 1967). Climate-induced factors such as temperature and salinity fluctuations may affect the incorporation of trace elements into the shell lattices of *Crassostrea*. Future research efforts should be further directed at understanding the effects of salinity and temperature fluctuations on the incorporation of trace elements in the *Crassostrea* shells.

Conclusions

The fractionation of trace elements from *Crassostrea tulipa* collected from the Pra Estuary, Densu Estuary, Kpone Beach, and Anyanui Creek has been used as a proxy for environmental pollution. This preliminary work shows the highest values of heavy metals correspond to the *Crassostrea* shells from Pra Estuary and Kpone Beach, whereas the lowest values of heavy metals were obtained from shells from Densu and Anyanui Creek.

The shells from the Pra Estuary show enrichment with respect to the other study areas in most of the analysed trace elements (Li, Rb, Be, V, Cr, Cu, Zn, Ga, Y, Sn, Pb, U, Th, ∑REE, and As). The Pra river is among the heavily impacted waterbodies in Ghana by the discharge of heavy metals related to mining activities but also the extensive forest clearance, the substantial loss of soil minerals, and succeeding high sediment transport by the Pra River, which ends up in the Pra Estuary where the samples are coming from.

The other highly polluted area, according to the content of trace elements in the *Crassostrea* shells, is Kpone Beach. *Crassostrea* shells are relatively enriched in trace metals such as Be, Ba, Cu, Zn, Nb, Pb, and REE. The recorded enrichment in metal pollutants is the result of the input of urban effluents from the Greater Accra Region as well as the Heavy Industrial Area of Tema (located around 3.5 km west of the studied area). Notable, is the high content of Ba in *Crassostrea* directly related to high phytoplankton productivity due to phytoplankton incorporating Ba by metabolic uptake and adsorption. Phytoplankton productivity (mainly for diatoms) is related to the influx of trace metals (such as Cr, Co, Ni, Cu, Zn, Cd, and Pb), which are transferred into the marine food chains, including in molluscs. In addition, the content of trace metals of gastropods shells from Kpone Beach was analysed for comparing with the composition of *Crassostrea*. Analyses of gastropod shells from Kpone Beach indicate that genera *Nerita* and *Cerithium* are more sensitive to accumulating Ni and As than *Crassostrea*.

The values of trace metals from the *Crassostrea* shells of the Densu Estuary and Anyanui Creek are comparatively low. Considering the use of mollusc shells as bioindicators for heavy metals pollution, the less polluted localities are Anyanui Creek and Densu. Although the Densu Estuary is located in a densely urbanized setting, there are mostly residents and there are no major industries. *Crassostrea* shells from Densu Estuary are only enriched in Ni with respect to Pra Estuary and Kpone Beach. With respect to the Anyanui Creek that connects with the Volta River, this area is not polluted by any major industries.

This work demonstrates that the study of content of trace elements in mollusc shells, and specially *Crassostrea*, is a useful tool to approach the environmental pollution in coastal environments. Next research steps will advance in systematic analysis of coastal environments with large number of specimens.

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The authors of this article declare that they have no financial, professional or personal conflicts of interest that could have inappropriately influenced this work.

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