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Analysis Of Fe, Ni, Li Trace Metal Concentration In An Edible Indian Squid *Loligo Duvacelii* Collected From Chennai.

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Abstract

The current study attempted to assess the amount of key trace element (Fe, Ni, Li) found in squid *Loligo duvacelii* purchased from Ennore and Royapuram, the two most prominent markets on the Chennai coast. Lithium, nickel, and iron, was determined using the ICP- OES. Metal concentrations fluctuated in the study area, which might be attributed to a variety of environmental conditions. The research findings contribute to the development of a dataset of seafood quality in this region and give a scientific foundation for management planning for improved protection and sustainable development of aquaculture in the study area.

Keywords – Squid Loligo duvacelii, Ennore and Royapuram, trace element (Fe, Ni, Li), muscle tissues and human health.

Introduction

Trace metals are elements found in very low concentrations in the environment, such as chromium, cobalt, copper, iron, magnesium, selenium, and zinc. Because of their significant functions in living things, manganese (Mn), iron (Fe), zinc (Zn), and copper (Cu) are referred to as essential metals (Maret, 2016). According to National Research Council, 1989, certain of them are acknowledged to be nutritionally necessary. Most trace elements work as catalysts in enzyme systems, but some metallic ions—like iron and copper—take part in energy metabolism's oxidation-reduction processes. All trace elements are harmful if taken in significant quantities over an extended period of time (National Research Council, 1989). Molluscs obtain it via sediments and water. When these mollusks are ingested by higher trophic-level creatures (such as fish and mammals) in the food chain, heavy metals accumulate in them and are biomagnified (Singh and Gupta, 2021).

Squid is a staple in the Mediterranean diet because of its remarkable sensory and nutritional features, such as large concentrations of muscle proteins, omega-3 fatty acids, and vitamin E (Moreiras *et al*., 2013 & Lucas *et al*., 2022). Squid is an abundant source of protein; and the advantage of this cephalopod muscle comprises its high processing output, low-fat content, fine flavour and extremely white meat (Raman and Mathew, 2014). As demand for marine resources increases, squid can provide a high protein alternative to fish stocks, particularly in those regions where other fish stocks may have become reduced by overfishing (Anusha and Fleming, 2014). Compared to merely analyzing water or sediment, research on the accumulation of heavy metals in aquatic animals can provide a more accurate picture of metal contamination in the aquatic ecosystem (Lorenzon *et al*., 2000). Concerns about the health benefits and dangers of food consumption have prompted a focus on the concentration of essential metals in ecosystems and their component creatures, with a special focus on pollutants in marine animals. Therefore, the purpose of the study is to provide current baseline concentrations of some essential trace metals (Li, Fe and Ni) in the muscle tissues of *Loligo duvacelii* of moderate size that were purchased from the fish markets in Ennore and Royapuram.

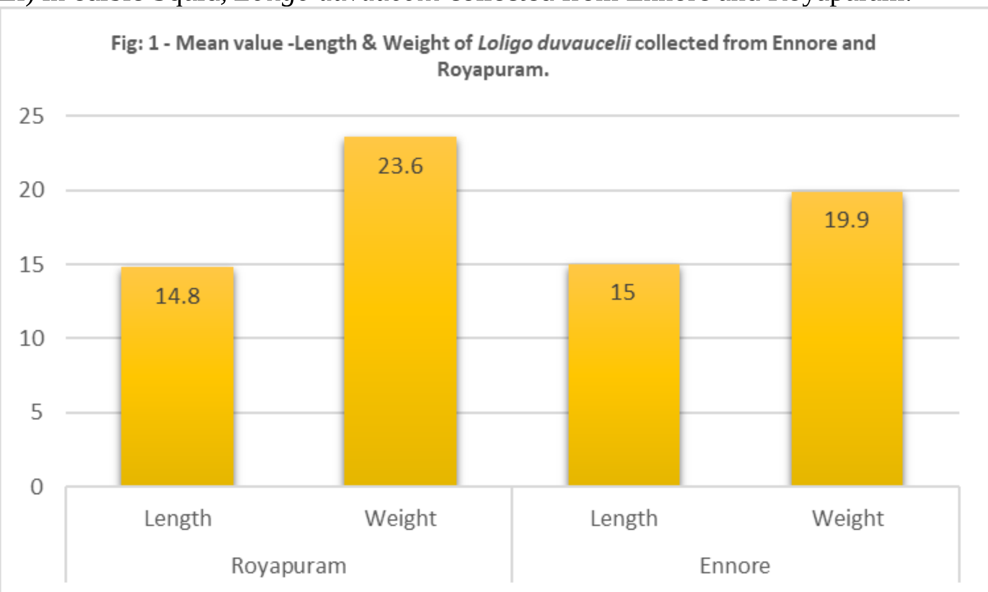
Materials and Methods

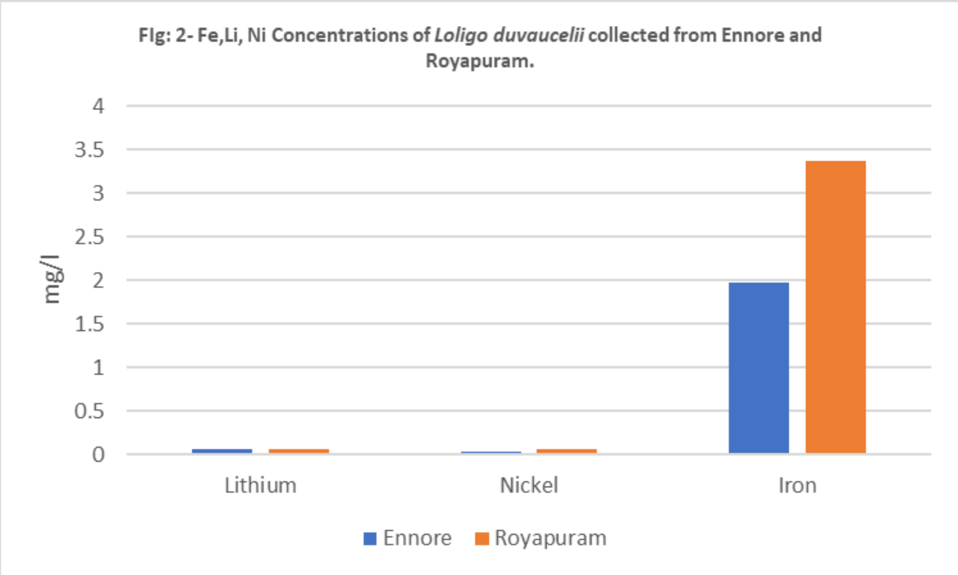
Fresh squid samples were purchased directly from fish markets located in Ennore and Royapuram. The samples were randomly selected, collected samples were tagged and kept in separate sterile polythene bags, immediately iced and brought to the laboratory in insulated boxes. To eliminate dirt, samples were rinsed in running water. The total length (TL) was measured in cm and the total body weight (TBW) in gm. After measuring the physical parameters (length and weight), the samples were covered with sterilized polythene bags and kept at -20°C in a deep freezer until further examination. At the laboratory, frozen Squid samples were allowed to thaw at room temperature and processed for analysis. Samples of two locations were carefully dissected; the muscle tissues were isolated for the current study. The tissues collected were cleaned and sterilized with Saline water (sodium chloride), 2g of muscle tissue was weighed and homogenized manually using mortar and pestle and aliquots were taken for wet digestion. The heavy metals concentration of essential metals (Fe, Li, Ni) were determined using the inductively coupled plasma mass spectrometry (ICP- OES) (Supriya *et al*., 2020).
Statistical analysis - Data were categorized and analyzed using SPSS version 24 after being loaded into an Excel spreadsheet for Microsoft Office 2007. ANOVA was used to determine whether heavy metal concentrations varied significantly between sites, ($P < 0.05$) considered as statistically significant.

Results and Discussion

Limited samples of moderate size edible Squid, *Loligo duvaucelii* (ranged from 12 to 17 cm of its total length and 20 to 30 gm of total body weight) randomly collected from Ennore and Royapuram where the length and weight were higher in Royapuram samples than the samples collected from Ennore. Trace metal concentration (Fe, Ni, Li) in muscle tissue, varied in *Loligo duvaucelii*, Royapuram showed highest concentration compared to Ennore. The results showed that heavy metal contamination in the tissues sampled were in an increasing order of Lithium, Nickel and Iron in both locations.

Figure 1 depicts mean value of length & weight, Fig 2 represents the concentrations of trace metals (Fe, Ni, Li) in edible Squid, *Loligo duvaucelii* collected from Ennore and Royapuram.





Seafood is regarded as a healthy and protein-rich diet that contain elements such as Zn, Fe, Cu, etc. for human health which have the ability to absorb and collect trace metal elements in their bodies, which consequently damage human health when individuals consume seafood (Da Le *et al*., 2021) The Indian squid *Loligo duvacelii* (Orbigny, 1848) is the leading species among squids, accounting for around 97% of all catches in Indian waters (Supriya *et al*., 2020). According to the research, males and females are in equal proportion. It grows in sizes ranging from 4 to 28 cm for males and 4 to 18 cm for females. Squid juveniles are less than 4 cm long (Sujitha and Shoba, 2006). The target organ for measuring metal accumulation potential in this investigation was muscle tissue from *Loligo duvacelii* as a large portion of muscular tissue is consumed. It has been demonstrated that the amount of metal in an animal's tissues is significantly influenced by its size. The variability in the total length and body weight of *Loligo duvacelii*, in this study of two sites is considered a normal difference due to the variation in age, sex, and size. Mineral buildup is influenced by animal characteristics (species, variety, body size, age, specific tissues and organs) as well as environmental factors influencing animal food, particularly water pollution in fisheries (Duysak and Ugurlu, 2017). Since squid are a carnivorous species with a limited metabolic capacity and a propensity to collect minerals, the animal diet would be especially significant among these (Torrinha *et al*., 2014, Vieira *et al*., 2020, Lucas *et al*., 2022), because of their short life cycle, and accumulate lower levels of toxic elements than some commonly-consumed fish (Storelli, 2008).
Squid can also accumulate trace amounts of other minerals, such as Ca, Mg, Zn, Cu, Fe, or Mn, among others, because marine waters and sediments may also include other salts ((Torrinha *et al*., 2014). Because of their conservative character, heavy metals accumulate and become more potent as they move up the food chain. According to Kilgour (1997), organisms that have a tight association with sediment have relatively high body concentrations of metals, and crustaceans and squids are suitable markers for long-term monitoring of metal contamination in the marine environment. This can be attributed to a variety of reasons, including habitat, dietary uptake, pollutant bioavailability, and the main factor for heavy metal uptake in crustaceans via food, which is mostly fed by sediments, which are regarded as the main source of pollution (Younis *et al*., 2014). Various researchers such have reported that the ecological requirements, sex, size, and molt of marine animals were also found to affect metal accumulation in their tissues (Canli and Atli, 2003). In the highest recorded trace metal accumulated in both sites is iron (Fe) where the nickel to be the least which is in contrast to the study of heavy metal concentrations in sea food from three selected landing centers of Chennai coast (Supriya *et al*., 2020). Assessment of various Metal levels in squids varied substantially between species and between various locations of the same species of *Loligo duvacelii* (Prafulla *et al*., 2001).

Nickel (Ni)

Nickel plays an important role in several enzymatic systems, stimulating enzymes involved in glucose breakdown and utilization and in hormone, lipid and cell membrane metabolism (Venu Babu *et al*., 2022). The Ni content in Squid muscle was below the tolerance limit, with a mean value of 0.027 & 0.056 ppm collected from Ennore and Royapuram regions. Ni levels in Squid *Loligo duvacelii* edible muscle were several orders of magnitude lower than those reported by Prafulla *et al*. (2001). Ichihashi *et al*. (2001) discovered that the concentration of Ni was higher in adults of the squid *Sthenoteuthis oualaniensis* than in juveniles while studying the link between Ni concentration and squid specimen size. Excess nickel (Ni) is hazardous to aquatic creatures and persists in the aquatic environment. A requirement for nickel has not been conclusively demonstrated in humans. According to Supriya *et al*. (2020), increased nickel concentrations recorded at all study sites were brought about by petroleum industries, stainless steel industries, electroplating facilities, smelting plants, nickel-cadmium battery plants, and nickel smelters in this geographical region. Nickel is also utilized in jewelry, ceramics, disinfectants, and batteries, and its levels have been found to be more concentrated in crowded environments. According to Cempel and Nikel (2006), nickel concentrations in the environment (air, water, soil, and food) ought to stay within regulatory limits and be considered detrimental to the general population. Environmental pollution from nickel may be due to industry, the use of liquid and solid fuels, as well as municipal and industrial waste. However, everyone should keep in mind that, despite nickel has not been extensively discharged into the environment, it may pose a risk to human health.

Lithium

Li occurs naturally in surface waters, primarily in ionic form (Szklarska and Rzymski, 2019). It is unknown how Li impacts ecosystems, as with humans, Li may be beneficial to organism health (Thibon *et al.*, 2021) and some authors consider Li to be an essential trace element, recommending a daily Li intake of 14.3 g/kg (Schrauzer, 2002). Our current study reveals lithium values in Ennore and Royapuram were 0.057- 0.065 mg kg-1, which were higher than the values reported by Supriya *et al*. (2020), in squid samples collected from three different regions of the Chennai coast; Pattinapakkam and Royapuram recorded higher than Ennore, which supports the current results. However, anthropogenic activities, namely those related to recent technology advancements, are responsible for an extra Li input into the environment (Won and Kim, 2017). Because of the unequal distribution of Li in the Earth's crust, its concentrations may differ depending on geographical region and its estimated consumption in populations around the world varies greatly (Schrauzer, 2002). Because Li is highly reactive with oxygen and water, it does not exist free in its pure metallic state in nature. Indeed, various types of Li (mainly Li2CO3) have been used as the primary treatment for bipolar disorder since 1949 because Li has a neuroprotective impact form (Szklarska and Rzymski, (2019), Thibon *et al.*, (2021) and Machado-Vieira, 2018).

Several investigations have found Li in freshwater, coastal and marine, sediments, and biota (Aral and Vecchio-Sadus, 2008; Gaspers *et al*., 2021; Kszos and Stewart, 2003; Millot and Negrel, 2021; Rezaee, 2021). Lithium concentrations in cephalopods ranged from 0.06 g/g (Pacific Ocean) to 0.55 0.09 g/g (Barbosa *et al*., 2023). Supriya *et al*. (2020), reported that permissible levels for seafoods were not available for comparison. Furthermore, urban runoff and industrial wastewater discharges, urban and industrial activities contribute to Li contamination (Barbosa *et al*., 2023). Li contained in water may undergo significant bioaccumulation and its environmental toxicity is low if any (Kavanagh *et al*., 2017).

Iron

Fe is an essential nutrient for many organisms, especially for humans. Many proteins and enzymes required for health are iron-dependent (Institute of Medicine, 2006). Iron is a component of proteins in humans that transport oxygen (Dallman, P.R., 1986) and is also required for cell formation and differentiation regulation (Bothwell, 1979 and Niketa *et al*., 2020). Low iron levels restrict cells from receiving enough oxygen, resulting in fatigue, poor work performance, and decreased immunity (Institute of Medicine, 2006). The movement of oxygen from the environment to the tissues is one of the key functions of iron. The majority of life forms on earth rely on iron (Fe), one of the most abundant metals, for optimal human physiology. Protein is essential for rapid growth and maintenance of animal muscle tissue (Okuzumi & Fujii, 2000 and Niketa *et al*., 2020). Protein is vital in a variety of physiological functions in animals, including catalysis, transportation, immune system protection, movement generation, nerve impulse control, and growth (Sudhaker *et al*., 2011; Fredrick *et al*., 2013 and Niketa *et al*., 2020). High protein content is required for the continuance and stability of various biological processes throughout life (Okuzumi & Fujii, 2000; Kanwal & Saher, 2016 and Niketa *et al*., 2020).

As demand for marine resources grows, squid can provide a high protein alternative to fish supplies, particularly in areas where other fish stocks have been had been depleted. Da Le *et al.* (2021) recorded that the average contents of Fe were quite high, 51.23 ± 13.81 mg·kg−1 for fish, 89.92 ± 58.65 mg·kg−1 for crustaceans, and 113.14 ± 65.91 mg·kg−1 for mollusc samples, where Supriya *et al.* (2020) Fe recorded in Royapuram 0.002 mg/kg results were contrast to the present study where the concentration ranged from 1.967 in Ennore and 3.3724 mg/kg in Royapuram. Da Le *et al.* (2021) noted that there is no available regulation for the permissible value of Fe content in fishery seafood. The difference in trace metal element contents in seafood may reflect the water and sediment quality which are impacted by both point and dispersal wastes sources (Da Le *et al.* (2021).

Conclusion

Seafoods remain a major source of food consumption and are easily obtainable in terms of required nutrients for human consumption, it is imperative to explore their potential for containing critical metals, which are crucial for the body's normal functioning. The variations in the concentrations of metals observed during this study might have been owed to a range of issues, notably physical attributes like age, size, and sex, or geographic location. Metal pollution, which is largely caused by mining activity and industrial effluent and has catastrophic impacts on every living creature, including humans, is one of the most prevalent threats to the environment. To sum up, regular trace element analysis serves as essential for greater insight of human nutrition.

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