Spatial distribution and extent of environmental risks of strontium metal concentration in water and bottom sediments of Nile River, Egypt

Moutaz Khalifa
Menofia
zozo elsadani (zozoelsadani@yahoo.com)
zagazig university

Wang Ming Qi
china university of geoscience, Beijing

Research Article

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Abstract

Strontium is one of the rare heavy metals found in the sediments and water of the Nile River. By examining the metal concentration in 69 sampling points along the river between two Nile banks and the Middle, we could throw further light on its dispersion in the current study. High Sr concentrations were found in the eastern>western>middle regions with average concentrations of 344.3, 338.39, and 327.57 ppm, respectively, due to the point sources such as industrial activities, sewage discharge, and agricultural discharge. High Sr concentrations were found in the West and East of Cairo (Samarut and Beni Suef) (395, 397, and 392 ppm). Various pollution indices, such as the Geo-accumulation index, Contamination factor, and Enrichment factor depiction, were used to determine the pollution level caused by this metal, ranging from low to moderate contamination. According to the extraction fractions, the occurrence nature of the element is as follows: Acid soluble > residual > Fe-Mn oxhydroxides (reducible) > organic (oxidizable). The risk assessment code based on the Acid soluble fraction indicates moderate to high risk. Renal failure and baby bone growth problems are common in Egypt, impacting Sr concentration in sediments. The average Sr concentration in water is around (221.58 µg/l), indicating that the water is perfectly safe to drink. The study's findings are useful in determining the extent of Sr metal pollution in the river. If not monitored, Sr concentration will be an issue in Egypt and Ethiopia following dam construction. After the dam is built, this study will serve as a baseline.

Introduction

Strontium is a lithophile metallic element in group two of the Periodic Table (heavy metal). Natural strontium is not radioactive and exist in four stable isotopic forms: Sr\(^{88}\) (82.6%), Sr\(^{86}\) (9.9%), Sr\(^{87}\) (7.0%) and Sr\(^{84}\) (0.6%) representing 0.02-0.03% of the earth's crust with an average 200-300 mg/kg. It exists in igneous and metamorphic rocks, including granites and sedimentary rocks; it mainly enters the water through leaching from limestone as hydrated Sr\(^+2\) and can move down into groundwater (Malina, 2004) or by natural weathering of rocks and soils. Strontium is easily mobilized during weathering, especially in oxidizing acid environments. It is incorporated in clay minerals and strongly fixed by organic matter, so it is highly related to unweathered feldspar minerals because the feldspar is the top Sr carrier. Sr can replace Ca in both silicates and non-silicate Ca minerals due to the significant similarity of their ionic radii and replace potassium in silicates and Barium in sulfate minerals. Extraction of Strontium from its ore naturally as the minerals celestite (SrSO\(_4\)) and strontianite (SrCO\(_3\)). These minerals are concentrated into strontium carbonate or other chemicals formed by a series of chemical processes used in making glass products and ceramics, pyrotechnics, paint pigments, fluorescent lights, color television tubes, ferrite magnets, zinc refining, medicines, and other products. The radioactive isotope Sr\(^{90}\) is used as cancer therapeutics to alleviate bone pain while Sr\(^{85}\) in medical applications. Air deposition (0.1 µg/m\(^3\)) from coal-burning and phosphate fertilizers can also contribute smaller amounts (de Beers Canada, 2013; WHO, 2010). (IARC); The International Agency for cancer research) and EPA. has illustrated that radioactive Strontium is carcinogenic to humans because it emits beta radiation and is deposited inside the body. The biological effects of Strontium are related to its chemical similarity to calcium that is taken into bone instead of calcium that grows bones were weakened, especially in infants; Strontium is readily accumulated in opercula of fish (ATSDR, 2004). The inhalation of stable Strontium in smoke from an ignited roadside affects cardiovascular in humans (Federman & Sachter, 1997). The anthropogenic activities of industrialized human society have led to the increased local concentration of Strontium (ATSDR, 2004). Sr is accumulated in chronic renal failure patients, an association between osteomalacia and increased bone strontium concentration in dialysis patients (D’Haese et al., 1997, 2000). According to (Soliman et al., 2012) increasing renal failure in Egypt) and bone weekend growth of children let us focus on this metal in water and sediments of the main Nile River stream.

This study aims to monitor Sr metal in bottom sediments and the overlying water of the Nile River in Egypt before the operation of the GERD. This research will be repeated after the GERD operation to investigate the potential subsequent environmental changes on the river due to flow reduction and sediment retention at the GERD. Providing the concentration, distribution, and potential sources of Strontium as a critical heavy metal in the sediments and water of the Nile River mainstream, assess the degree of Strontium contamination by using different pollution indices, determine the mode of occurrences and identify the bioavailability of Strontium based on sequential extraction fractions, focus on the west, Middle, and East of this natural stream, related to anthropogenic sources. No specific scientific investigations regarding the fractionation and concentration distribution of Strontium in Nile sediments, Egypt, have been conducted.

Materials And Methods

1.1 Study area

The Nile is the longest river globally, with about 6700 km in length. The Nile water in Egypt comes from the Ethiopian highlands > 85%, while from the East African Lake Plateau 15%. The Nile River enters Egypt at its southern boundary with Sudan and runs through a narrow valley (1000 km long) which varies from 2 to 20 km in width. Subsequently, it is bifurcated at 25 km (north of Cairo) into the Rosetta and Damietta branches forming a delta with its base on the Mediterranean Seashore.

Sediments supplied to the Nile are derived from the basaltic Ethiopian Highlands, Precambrian basement rocks of the Arabian–Nubian Shield and Saharan Metacraton, and Phanerozoic sedimentary a contribution from aeolian sources, Red Sea Hills of Egypt also contribute to the River Nile drainage basin (Garzanti et al., 2006, 2015; Padoan et al., 2011; Schneiderman, 1995; Stanley and Wingerath, 1996b). About 65% of the industrial water needs are supplied by Nile while receives > 57% of its effluents. Besides the natural sources of toxic waste are the drains during the seasonal flash flood. The Nile receives enormous amounts of agricultural wastewater that carry various chemical pollutants related to the widespread use of agrochemicals. Furthermore, a significant quantity of industrial, municipal, and domestic wastes and street contaminants are drained, directly or indirectly, into the Nile.

Heavy metals in Nile River sediments with toxic limit derived from anthropogenic sources as water treatment plants, heavy traffic, mining, paper, pulp, iron and steel, electric power plants, cement, Chlor-alkali, fertilizers, Sugar refining, oil, and detergents factories, and nitrogen fertilizer plants, (El-Kammar et al., 2009; Badr et al., 2013; Abdel-Satar et al., 2017; Badawy et al., 2017, 2020 and Hasaballah et al., 2019) along the riverbank. (Häggroth & Höglund, 1961) found
that the vegetables have the highest concentration of Sr related to foliar retention of fall-out and aerosol, salt water samples from red sea contain arseable amounts of Sr, while the human adult femur and vertebra were found to indicate a very small value of Sr in Egypt. (Panahifar et al., 2019) showed that two elements deposited in the areas of active bone turnover such as growth plates and trabecular bone in rats.

### Sampling and geochemical analysis:

About 23 composite samples were collected from Cairo to Aswan using a grab sampler (Ekman type) washed between sites using distilled Water then river water. A subsample was taken using a plastic spoon, placed into clean sealed polyethylene bags, and then stored at a low temperature inside the icebox. Sediments were dried entirely in an oven at 70°C for around 24 h and preserved for chemical analysis. The sampling sites’ coordinates and elevation were recorded using a GPS tracker (Garmin eTrex 10, Lenexa, KS, US). Representative sediment samples were being homogenized for sieve analysis. For trace elements concentration (acid digestion) treatment, 0.25g dry sediment was digested using a mixture of 2mL HCl, 6mL HNO₃, and 2mL HF. Then digestion solutions were treated using ICP-AES (Agilent 5110, USA) and ICP-MS (Agilent 7900, USA) respectively at ALS CEMEX (Guangzhou) Co Ltd-China. The standard calibration solutions were prepared from Agilent multielement calibration standard 8500-6944 (Agilent Technologies, USA). A standard solution containing Rh was used as an internal standard to monitor signal drift during counting. Equipment condition monitoring and quality control were performed by measuring a standard solution after every eight samples analysis. All reagents are used of analytical grade chemicals.

According to water samples, about 23 representative water samples in September 2019 under the water surface about (20-40) cm at the same location of sediments. The pH, temperature, and total dissolved solids (TDS) were measured in situ using a HI98129.HI98130 waterproof PH/EC/TDS and Temperature portable meter (HANNA, USA). Before measurement, the meters were calibrated by standard Solutions in addition to Oxidation-reduction potential (ORP) was also measured in situ using HI98190, a professional waterproof portable PH/ORP Meter, HANNA, USA. All samples were acidified with ultrapure nitric acid in a 30 ml LDPE bottle (prewashed with 10% nitric acid, ultra-pure Water, and Nile water). The acid used was analytically pure, and the Water was ultra-pure. All water samples were stored at low temperature (4°C) until laboratory analysis. Sr contents were determined by inductively coupled plasma mass spectrometry (Table1).

#### 2.2. Sequential fractionation methods

Many different sequential extraction techniques have been developed for metal partitioning. Sequential extraction determines trace elements’ origin, mobility, and biological and physicochemical availability in solid samples and sediments (du Laing et al., 2007). Single extractions are thus generally used to provide a rapid evaluation of the exchangeable metal fraction in soils and sediments (Rao et al., 2007; Sahuquillo et al., 2003; Salomons, 2006). Several speciation schemes for trace elements in soils or sediments with environmental applications. The most widely used methods are those proposed by (Campanella et al., 1995; Rauret, 1998; Tessier et al., 1979). Chemical fractionation of Sr in sediments was extracted according to the European “Community Bureau of Reference” (BCR) sequential extraction procedure which was proposed (Quevauviller et al., 1997; Ure et al., 1993)(Fig.2). This method has been used widely in determining specific chemical forms of heavy metals in various environmental media, including sediments. This method has been validated using a sediment certified reference material BCR-701 (Rauret & López-Sánchez, 2006). This method was applied and accepted by many specialists (Davutluoglu et al., 2011; Fernández-Ondoño et al., 2017; Fiedler et al., 1994; Nemati et al., 2011; Pueyo et al., 2008; Usero et al., 1998; Zimmerman & Weindorf, 2010), although other short steps of extraction (Ramos et al., 1994), Sediments were completely dried in an oven at 40°C for around 48 h before the BCR procedure. The KS 4000 ic control shaker (IKA, Germany) was used to agitation the sediments at room temperature for 16 h. We used composite samples from three sides. The extraction of fractions from residue in each step was centrifuged at 3000 rpm for 20 min, and the fraction was put in a polyethylene centrifuge tube. The residue was washed with 20 mL deionized water for 15 minutes in the mechanical shaker then centrifuged at 3000 rpm for 20 min. The fraction(supernatant) was decanted, and the residue was subjected to the next step. This separation is operated at super clean and advanced geochemistry laboratory of China university of geoscience.

All supernatants were decanted into polyethylene containers and refrigerated before analysis. Samples were washed between extraction using 10mL ultrapure Water. All the glassware and polypropylene ware were soaked overnight in dilute nitric or hydrochloric acid, then rinsed with deionized water before use. The residual part of the samples was digested by a mixture of acid (HNO₃+HF+HClO₄) (Bai et al., 2011). All the reagents and standard solutions used were of guarantee grade. The concentration of metals was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500, USA). The results were recovered ranging from 94 to 102 (n=4). The extraction method is summarized in the flow chart scheme (Fig.2).

#### 1.2 Environmental pollution indices

Many techniques have been used to estimate metal pollution in sediments. In this study, pollution levels have been determined using pollution indices as contamination factor, enrichment factor, Index of geo-accumulation, pollution. The selection of background value is the essential parameter to interpret valuable geochemical data, so (Salminen et al., 2005) is chosen to be the background.

**A. The geo-accumulation index (I_{geo}):**

This index is a single metal approach to evaluate the sediment contamination with heavy metals and quantify the intensity of heavy metal contamination in terrestrial, aquatic, and marine environments (Gaur et al., 2005; Moshood N. & Shinichi, 2009; Ozkan & Buyukisik, 2012). Geo-accumulation index (I_{geo}) is considered the metal concentrations related to reference or pre-industrial sediments of the study area. It is calculated using the following relations (Muller, 1969).

1) $I_{geo} = \log_2 \left( \frac{C_i}{1.5 \times B_n} \right)$
Where $C_n$: concentration of the metal in the sediments, $B_n$: Geochemical background of the element according to (Salminen et al., 2005), and 1.5 is the background matrix correction in factor due to lithogenic effects. $I_{geo}$ values classified as followed: $I_{geo}<0$: no pollution, $I_{geo}(0-1)$: no to moderate pollution, $I_{geo}(1-2)$: moderate pollution, $I_{geo}(2-3)$: moderate to heavy pollution, $I_{geo}(3-4)$: heavy pollution, $I_{geo}(4-5)$: heavy to extreme pollution and $I_{geo}>$ extreme pollution from unpolluted to very extremely polluted (Muller, 1969).

B. The contamination factor (CF):

It is an indicator to assess the contamination status of sediments in aquatic ecosystems (Abraham & Parker, 2008; Rabajczyk et al., 2011) and is used to express the contamination degree with a single metal. The contamination factor calculated according to this equation:

$$2) \text{CF}=C_n/B_n$$

$C_n$ is the concentration of metal and $B_n$ is the background. The contamination degrees can be categorized according to their values to: CF<1 (low pollution), 1<CF3 (moderate pollution), 3<CF<6 (high pollution) and CF>6 (very high pollution), (Hakanson, 1979).

C. Enrichment factor, EF.

It was calculated to determine the anthropogenic origins (contamination) levels of metals in sediments. Geochemical normalization of the heavy metals data to a conservative element, such as Al, Fe, was employed to identify abnormal metal concentrations. Many authors used Al to normalize heavy metal contaminates. In this study also, Al was used as well to differentiate natural from anthropogenic components. The metal EF is calculated as follow (Ergin et al., 1991):

$$3) \text{EF}=(M/Al)_{\text{sample}}/(M/Al)_{\text{background}}$$

Where M: is the metal concentration. Ef values are classified to EF ≤ 2 (low enrichment), EF range from 2 to 5 is moderate enrichment, EF (5-20) is high enrichment, EF range (20-40) very enrichment and EF>40 is extremely enrichment according to (Diop et al., 2015).

Results And Discussion

2.1 Distribution and assessment pollution of Strontium:

In the present study, the distribution of Strontium in Sixty-Nine sampling locations of about twenty-three positions along the river from West, Middle, and East (Fig. 1) and (Table 1). The average concentration of Sr is (336.75ppm) and ranges from (187-397ppm). The highest value was recorded at the sample of Cairo from the west and the East of Samalut and Beni Suef with values (395, 397, and 392 ppm) respectively. Strontium average at East>West>Middle with values (344.3, 338.39, and 327.57ppm) respectively, indicating the high potential anthropogenic sources at two sides of Nile (Fig.3) and (Table 1). The upper continental crust (UCC) value of Sr is (316ppm) according to (Wedepohl, 1995), is lower than the maximum and higher than the minimum of this study value indicating the depletion of Sr at selected locations and also enrichment at specific sites, while about 450mg/kg (Mason & Moore, 1982). Its average in granite is 285mg/kg and in basalt 465mg/kg according to (Bowen, 1979) while high concentrations (1000 mg/kg) have been mainly recorded in anorthite (Wedepohl, 1995), a crustal average of (384 mg/kg) (Mielke, 1979). The median strontium concentration was 126 mg/kg in European stream sediments, while the average in worldwide soil is about 240mg/kg (ATSDR, 2004). The lowest value for Strontium recorded by the geochemical atlas of Europe (Finland) is about 171ppm (Salminen et al., 2005). At River Kortalaiyar, India, Strontium is moderate pollution with concentration (22-512ppm) (Jerin & Periakaruppan, 2015). According to (El-Sorogy et al., 2018), the Sr enrichment factor is about (98.87), implying anthropogenic sources in Al-Jubail industrial city, at Dammam, Saudi Arabia. The negative correlation between Sr with some principal oxides as (SiO$_2$, Al$_2$O$_3$, MnO, K$_2$O, and P$_2$O$_5$) (-0.48, -0.08, -0.31, -0.58, and -0.61) respectively, slightly positive with CaO) (0.42) and no relation with (TiO$_2$, Fe$_2$O$_3$, MgO, Na$_2$O, and clay%), (Table) indicated its anthropogenic and geogenic source. High concentration of CaO and Sr concentration at Samalut eastern sample with value (18.96 and 397 ppm) showing the high substitution between them. The upstream from (Kom Umbo to Tahta) about (8602 ppm), Middle stream from (Sohag-Minya) about (7782 ppm) and downstream from (Biba-Cairo) about (6193 ppm). There is an increase from downstream to upstream (North to South) in the strontium concentration, which is contrary to other heavy metals according to (Abou El-Anwar et al., 2018). The enrichment of the metal may lead to pollution. The pollution by the metal is best assessed using various pollution indices as the Geo-accumulation index ($I_{geo}$), Enrichment factor (E.F.), and Contamination factor (CF). The average $I_{geo}$ value of Sr in the sampling locations is shown in (Table 1) and Fig. (4), elucidating no to moderate pollution according to (Muller, 1969) (Table 4). All values were calculated less than one, and the highest discount (0.61 and 0.63) at the eastern of (Samalut and Beni Suef). The CF average of Sr is (1.97) with a range from 1.09 to 2.32 (Table 2) and Fig. (4). The CF of East>West,middle. Cairo west and Beni Suef East recorded the highest value of CF (2.29 and 2.32). Since the CF index for Sr is between (1-3) in all sampling locations, the moderate level of contamination is ascertained according to (Hakanson 1979), Table (3). The EF average is (1.89) with a range from 2.92 to 1.27 illustrating low to moderate enrichment according to (Diop et al., 2015) (Table 4). The Eastern samples of Edfu and Samalut recorded the highest value of EF (2.8 and 2.92) (Table 2) and Fig. (4) due to the proximity of the ferrosilicon industry and the phosphate company, in addition to domestic and agricultural wastes. The EF of East>West>Middle. The Strontium pollution may affect bone growth in children. And cause a change in the structure of dental. In adults, Sr may increase the bone density and badly affect renal failure patients. The isotope Sr$^{90}$ is very carcinogenic, causing bone cancer and leukemia. It is evident from the pollution indices that the Nile River is at the average of pollution by Sr. The present study reveals that the slightly enriched of Sr concentration in the river. The enrichment if not monitored may progress. A survey in Turkey suggested a relationship between strontium exposure and childhood rickets.

2.2 Sequential extraction:
Strontium is found in small amounts as well as the largest sources of exposure to Strontium are Food and drinking water. Due to the nature of Strontium, some of it gets into fish, vegetables, and livestock. Leafy vegetables, grain, and dairy products contribute the greatest percentage of dietary Strontium to humans. Strontium acts like calcium in the body when entering the bloodstream and is distributed throughout the body; it enters and leaves cells quite easily. The bioaccumulation availability, reactivity, and mobility are determined by the metal chemical form making the chemical speciation study necessary (Morrison, 1989). The different chemical forms of Strontium can affect the solubility and mobility of the metal from sediments. Metals bound to the exchangeable fraction are available, whereas those included in the carbonate/adsorbed phases become more mobile and easily available with increasing acidity. The residual fraction represents the unreactive phase. The order of strontium fractions is as follow: Acid soluble > residual > Fe-Mn oxy-hydroxides (reducible) > organic (Oxidizable) (Fig.5). The fractions are in ranges as follow (26.22-70.28%) for Acid soluble (exchangeable and carbonate), (4.59-13.68%) for Fe-Mn oxyhydroxide, (0.09-0.49%) for organic and (22.47-64.18%) for residual fractions (Table 5). At (Minya, Tahta, Qena, and Edfu), Strontium was mostly concentrated in the residual fraction >60%. According to the Risk assessment code (RAC), it represents exchangeable fraction and carbonate percent (Acid soluble). Nile sediments samples are medium to high risk, except Cairo, Helwan, Giza, and Esna are very high risk (Fig.6). This metal species posed a medium-high risk and easily can enter the food chain. By hetero ionic exchange at high strontium concentrations, the element may replace calcium in bone (Mattar, 1979; Querido et al., 2016). Incorporating the greater-sized strontium ions in the bone will affect a mild crystal lattice distortion (Eisenberg E, 1973).

Accumulation of Sr in chronic renal failure patients an association between osteomalacia and increased bone Sr concentrations in dialysis patients (Salminen et al., 2005) of Finland atlas, the strontium concentration in water is about (1463.7 µg/L). There is a slight increase from downstream to upstream in the Sr concentration following sediment concentration. Sr in seawater is about eight mg/L (ATSDR, 2014). Based on the Canada health review (2018), the proposed guideline for Sr in drinking water is a maximum acceptable concentration (MAC) of 7.0 mg/L. Dissolved Sr loads in the world's river waters have been reported by (Gaillardet et al., 2003) ranged from few ng/L to nearly (100 µg/L) with an average (60µg/L). According to (Salminen et al., 2005) of Finland atlas, the strontium concentration in water is about 0.327mg/L. The quality water parameters were measured using advanced tools like (PH, Oxidation-reduction potential (ORP), Temperature, and Total dissolved solids (TDS.)). O.R.P ranged from 239 to 441 with an average (345.87) at studied samples less than WHO (2011) limit value (700 MV). The Temperature ranged from 26°C to 31.3°C with an average (28.08°C), PH. ranged from 7.9 to 9 with an average (8.4); however, PH. according to (WHO, 2011),(EPA, 2018) and Egyptian regulation (6.5-8), (6.5-8.5) and (7-8.5), respectively. The highest PH. (9) was recorded at Qena. T.D.S. ranges from (146 -188) with an average (158.39) less than values limits of Egyptian regulation and (EPA, 2018) (500 mg/g) (Table 5). Strontium is positively correlated with (TDS, ORP and Temp) (0.75, 0.22, and 0.41) respectively and negatively with PH (-0.54) (Table 6). EPA recommends that stable strontium levels in drinking water should not be more than (4 mg/L). Most forms of radioactive and stable Strontium are dissolved in water. Most Strontium dissolved in water comes from Strontium in rocks and soil that water runs over, so it may be move deeper into the ground and enter the groundwater. Strontium dust from the air represents a small part of the Strontium found in water. Some strontium is suspended in water. The strontium concentration in water is less than EPA value(EPA, 2012; US EPA, 2013); 4mg/l and 1.5mg/l, so it is safe, but it will be severe if not monitored because many kids in Egypt suffer from bone weakness.

Conclusion
The present study focusses on Sr in Nile River sediment and water indicating that the concentration of Sr isn't very significant. It warns us of the condition shortly, so we need a common way towards monitoring the enrichment of Strontium. The pollution indices illustrate low to moderate pollution degree while Cluster analysis depicts three anthropogenic sources of Sr. Strontium fractions: Acid soluble > residual > Fe-Mn oxy-hydroxides (reducible) > organic (Oxidizable). The risk assessment of Sr from moderate to high according to the exchangeable fraction percent except Cairo, Helwan, Giza, and Esna are very high risk. The Sr water concentration is safe. Near to the agricultural effluents and industrial point source, the pollution must be checked in a determined manner, especially before and after the Ethiopian dam operation. Must continue Monitoring pollution because of Sr's lousy effect on renal failure patients and the bone strength of infants to solve the two problems faced in Egypt.

Declarations
References


**Tables**

Tables 1, 2, 4, and 5 are available in the supplementary files section.

Tables 3 and 6 are not available with this version.

**Figures**

Figure 1

Location map of sampling stations along main river stream.
Figure 2
Flowchart of sequential extraction procedures.

Figure 3
Crossed map of strontium concentration (ppm) of the Nile river main stream sediments from West, Middle and East.

Figure 4
Box plot of Contamination factor (CF), geo-accumulation index (Igeo) and enrichment factor (EF) of Nile River sediments.
Figure 5
Fractions distribution of Sr in the Nile sediments. **F1:** Acid soluble; **F2:** Reducible; **F3:** Oxidizable fraction; **F4:** Residual fraction.

Figure 6
Risk assessment code (RAC) at samples location along Nile River main stream.

Figure 7
Dendrogram showing cluster of variables on the basis of similarity of strontium.

Supplementary Files
This is a list of supplementary files associated with this preprint. Click to download.

- supplementaryforSr.docx
- Tables.docx