



JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics
Sector of Neutron Activation Analysis
and Applied Research

FINAL REPORT ON THE SUMMER STUDENT PROGRAM

*Geochemistry of the Egyptian Mediterranean Coastal
Sediments and Their Contamination with Heavy Metals
Using Instrumental Neutron Activation Analysis*

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Abstract

The Egyptian Mediterranean coastal area is a dynamic ecosystem. It receives water from the two estuaries of the Nile River (Rosetta and Damietta), the outlets of the coastal lakes (Mariout, El-Manzala, El-Burullus, and Edku), and the drains. 114 horizontal coastal sediments profiles were collected from the coastal area extending from East Port Said to Alexandria covering the breaker zone in this area. Also suspended matter filters were collected from the same area. The content of heavy metals will be determined by instrumental neutron activation analysis. The extent of pollution will be quantified using different indices: geoaccumulation factor, Non-lithogenic metal values, Degree of Contamination, Contamination Factor, Enrichment Factor, Potential Sediment Contamination Impact Using PEL-Q and ERM-Q Methods, Potential Ecological Risk Index, Sediment Pollution Index and Prospective Ecological Risk Assessment. The results will also be treated geostatistically to understand the behavior of heavy metals. These results will be useful for coastal management and protection in Egypt.

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1. Introduction

Although heavy metals are natural constituents of the Earth's crust and are present in all ecosystems, their concentrations have been dramatically increased by human activities¹⁻⁴. Consequently, considerable attention has been given to understand the adverse effects of heavy metals on various ecosystems over the past two decades. The marine environment is a major recipient of heavy metals released both land-based and sea-based sources^{5,6}. It receives domestic, agricultural and industrial untreated wastewaters. Due to changing inputs and practices, and to transport and transfer processes within the marine environment, levels of heavy metals can vary significantly, both spatially and with time. These changes are important for countries, which rely on marine resources, as they can have economic, social, and human health and environmental impacts. So a continuous monitoring program of heavy metals is very important in these countries.

The heavy metals monitoring program has two main concerns that determine its output. The first concern is the media used for monitoring. This media may be geological like sediments and suspended matter⁷, biological like fishes and algae (mainly used for bioavailability measurements)^{3,4}, synthetic passive samplers like chemcatchers⁸ and diffusive gradients in thin film techniques(DGT)⁹ (used for speciation and bioavailability measurements) and water. The second concern is the analytical tool used for the measurement of the heavy metals concentration in the collected sample. Fig.1. Summarizes the different analytical techniques with their limits of detection.

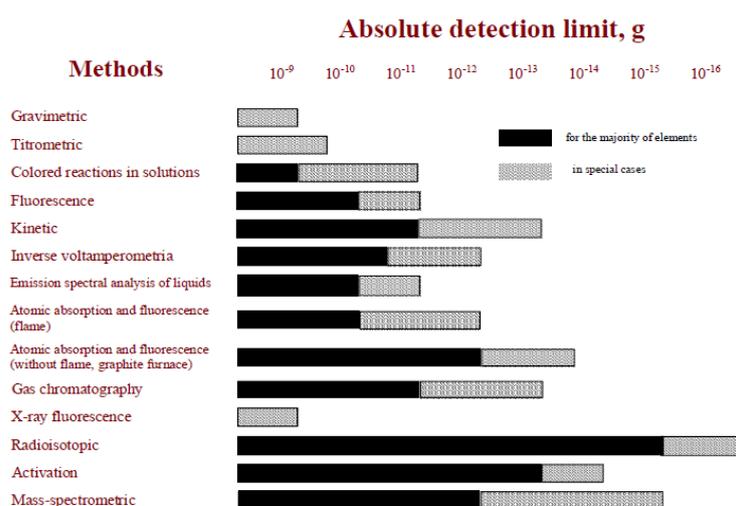


Fig.1. Detection limits of elemental analysis techniques

1.1. Sediments as a monitoring tool

In 1980, the International Council for the Exploration of the Sea (ICES) has considered the physical, chemical and biological characteristics of sediments as well as the processes that contribute to their role as a monitoring tool⁷. Undisturbed surface sediment samples can provide an immediate assessment of the present levels of contamination in the area in relation to the textural and geochemical characteristics of the sediment. Heavy metals and other toxic substances could be absorbed from the water column onto surfaces of fine particles and usually move thereafter with the sediments¹⁰⁻¹². Sediments can act as a true “sink” for heavy metals, making the analytical determination of their concentrations easier and supplying time-integrated information about the ecosystem’s health^{13,14}. Fixed heavy metals to sediments may be recycled back to the water column via chemical and biological processes¹². The most crucial property of metal ions is that they are bio-available and non-biodegradable in the environment and that their uptake by benthic organisms depends largely on their mobility, total concentration, and chemical forms.

1.2. Neutron activation analysis

Amongst the various elemental analysis techniques, neutron activation analysis (NAA) is still the reference method (reference method). It is a sensitive and accurate analytical method that identifies and quantifies elements in a sample through analysis of characteristic gamma rays emitted during radioactive decay after being irradiated by neutrons and converted into radioactive nuclei. NAA procedure consists of three main consecutive steps: (i) activation via irradiation with reactor neutrons, (ii) measurement of the gamma-radiation after one or more decay times and (iii) interpretation of the resulting gamma-ray spectra in terms of elements and concentrations¹⁵.

1.2.1. Activation

The activation with neutrons is the first stage in a NAA procedure. Its purpose is to convert some of the stable nuclei in radioactive nuclei emitting radiation that can be used for analytical purposes. Insight into the reactions that may take place during activation facilitates the identification of the relation between the observed radioactive nucleus, its target nucleus and associated element. Insight into the reaction rates is of importance for the quantitative analysis and for a priori estimates of the feasibility of an analysis.

Each atomic nucleus can capture a neutron during irradiation. A nuclear reaction results, in which often the nuclear mass changes; immediately after the capture ('promptly') excess energy in the form of photons and/or particles will be emitted. The newly formed nucleus may be unstable. When unstable, already during activation it starts to decay to a stable state by the emission of radiation through one or more of the

following processes: β^- -decay, β^+ -decay, electron capture, α -decay, or internal transition decay. In most cases γ and X-radiation will be emitted too. The capture of a neutron by a atomic nucleus and the resulting reaction may be illustrated, in the case of a cobalt target nucleus as $^{59}\text{Co} (n,\gamma) ^{60}\text{Co}^{15}$.

The most common reaction occurring in NAA is the (n,γ) reaction, but also reactions such as (n,p) , (n,α) , (n,n') and $(n,2n)$ are important. Some nuclei, like ^{235}U are fissionable by neutron capture and the reaction is denoted as (n,f) yielding fission products and fast neutrons.

The cross section and the neutron flux are neutron energy dependent. In nuclear research reactors -which are intense sources of neutrons- three types of neutrons can be distinguished as illustrated in Fig.2.

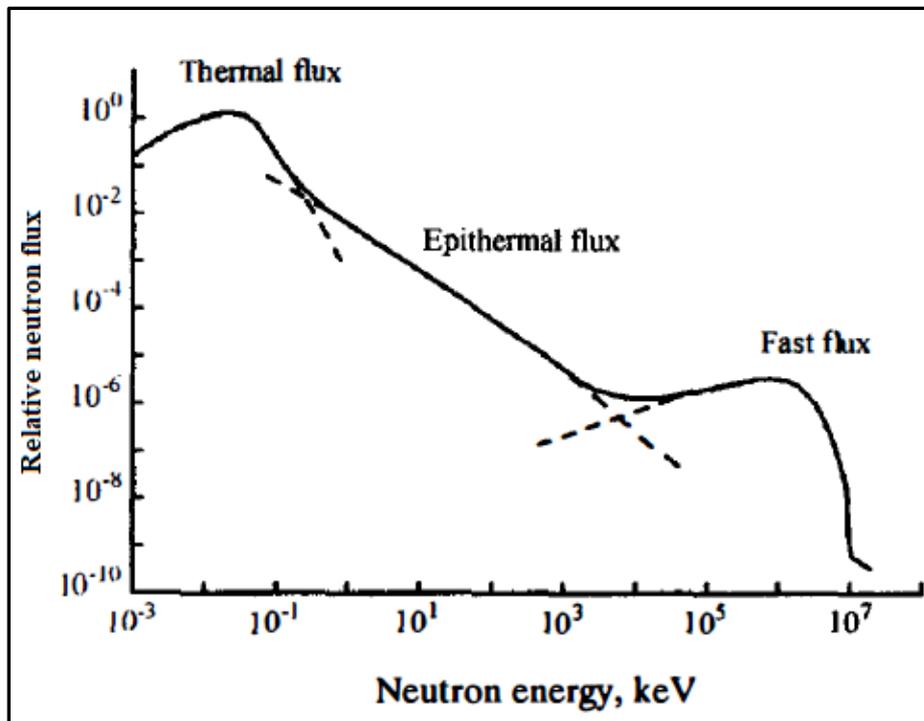


Fig.2. Schematic representation of the neutron flux spectrum in a nuclear reactor.

Reactions of the (n,γ) and (n,f) type have the highest cross section (typically in the order of 0 . 1 - 100 barn) for thermal neutrons whereas the other reactions ((n,p) , (n,α) , (n,n') , $(n,2n)$) mainly occur with fast neutrons at cross sections 2 or 3 orders of magnitude lower. In several cases nuclear reactions result into the conversion of a stable nucleus into another stable nucleus¹⁶.

In the majority of NAA procedures thermal neutrons are used for the activation. Sometimes activation with epithermal reactor neutrons is preferred to enhance the activation of elements with a high ratio of resonance neutron cross section over thermal neutron cross section relatively to the activation of elements with a lower such a ratio¹⁷.

1.2.2. Advantages and limitations of NAA

In common with most analytical techniques, neutron activation analysis has advantages and limitations relative to other methods. The major advantages and limitations are listed below¹⁸.

I. Advantages:-

1. Sensitivity: The method has very high sensitivity for many elements, in some instances to 10^{-10} g.
2. Matrix effects: The fact that nuclear reactions are involved results in the chemical or physical nature of the matrix being unimportant, (exceptions occur where a major matrix element has a high absorption cross section). Thus samples and standards do not have to have similar bulk compositions.
3. Contamination: As the only operations performed on environmental samples prior to irradiation are usually collection and preparation, there is no reagent blank and the possibility of contamination from apparatus or reagents is greatly reduced or eliminated.
4. Multielement technique: For many applications the method is non-destructive and multielement. For example, as many as 28 elements may be determined in air particulates (80). Even where radiochemical separations are necessary, groups of elements can often be separated rather than individual elements.
5. Isotopic ratios: Where an element possesses several stable isotopes, isotopic ratios may be measured in certain cases by activation analysis.
1. Non-destructive technique: Materials can be activated in any physical state, viz. solid, liquid or gaseous. There is no fundamental necessity to convert solid material into a solution prior to activation.

II. Limitations:-

1. Not all elements possess suitable radioactive nuclides; either formation cross sections are low or half-lives are very long or very short, resulting in poor sensitivity.
2. In INAA methods for environmental samples, decay periods of up to one month may be necessary to allow the determination of some long-lived nuclides. Hence, the method will have a time lag for some results.
3. Not all laboratories have access to a nuclear reactor.

The purposes of this study are to determine the concentration of heavy metals in sediments across the Egyptian Mediterranean coast using instrumental neutron activation analysis (INNA), to assess the ecological risks for heavy metals using different methodologies, to identify the sources of the heavy metals, and to sketch the implications for decision making and to provide suggestions for future watershed management.

2. Experimental

INNA is not a push-button technique. The main procedures of the INNA are carried out according to the scheme in fig.3.

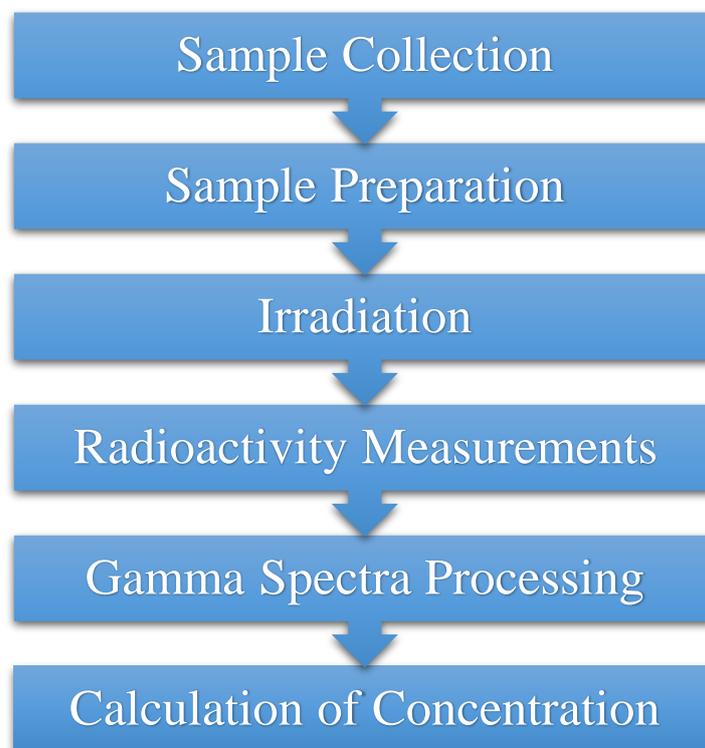


Fig.3. Procedure of INNA

2.1. Area of study and sampling:

The coastal zone is that part of the land surface influenced by marine processes. It extends from the landward limit of tides, and windblown coastal dunes, and seaward to the point at which waves interact significantly with the seabed. The coastal zone is a dynamic part of the Earth's surface where both marine and atmospheric processes produce beaches and dunes, barriers and tidal inlets, rocky coasts, and shape deltas¹⁹. Due to the dynamic nature of the coastal zone, Horizontal profile sampling approach is adopted. Sampling area was the coastal zone from East Port Said to Abu Qir bay (Fig.4) Surface sediment samples were collected using Ekman grab sampler from the breaker zone during October 2016 to June 2017. Surface sediment profiles extending

perpendicular to the baseline are collected to a depth of 6 m or a distance from the offshore of 1400 which nearer is. The sediment samples are collected every 400 meters. The collected samples are separately washed by distilled water to remove soluble salts and then air dried and sieved from shell and debris. Water parameter pH, Conductivity, TDS, ORP and others are measured in-field using CTD.



Fig.4. Map of the coastal area from East Port Said to Abu Qir bay showing sampling places.

Sample collection was accomplished by the research stations of the Coastal Research Institute in Egypt as the following:-

1. Abu Qir Research Station: It is responsible for the study of the coastal region of Abu Qir bay extending to the outlet of Lake Edku and the Estuary of Rashid branch and the adjacent coastal area. 28 profiles are collected(72 samples) (Fig.5).

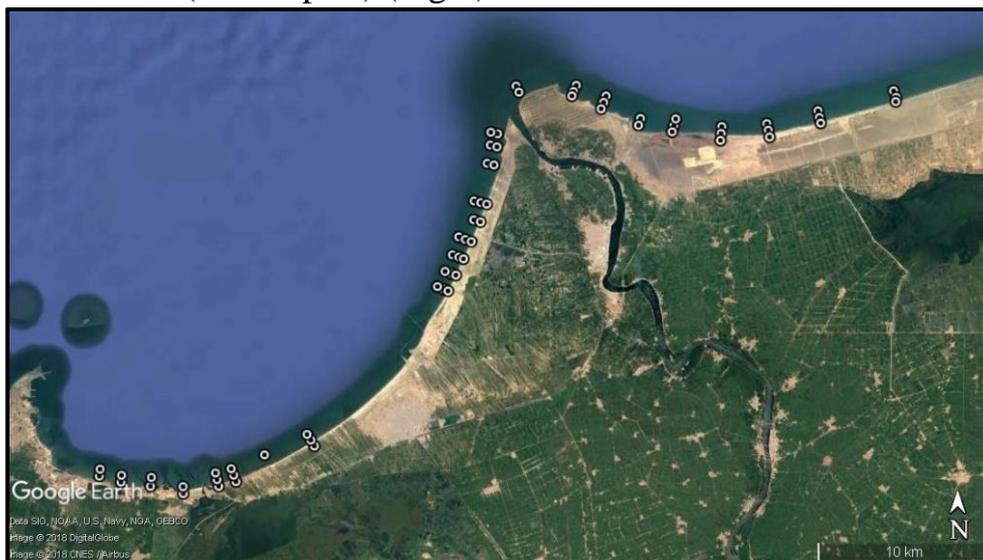


Fig.5. Abu Qir Research Station coastal profiles

2. Elbrullus Research Station: It is responsible for the study of the coastal region around the outlet of Lake Elbrullus and the adjacent coastal area including the outlet of Kitchener Drain. The sector of Ras El-Bar contains 28 coastal profiles(115 samples) (Fig.6).



Figure.6. Elbrullus Research Station coastal profiles

3. Ras Elbar Research Station: It is responsible for the study of the coastal region of Port Said west to Suez Canal extending to the outlet of Lake Manzala and the Estuary of Damietta branch and the adjacent coastal area. The sector of Ras El-Bar contains 58 coastal profiles(215 samples) (fig.7).

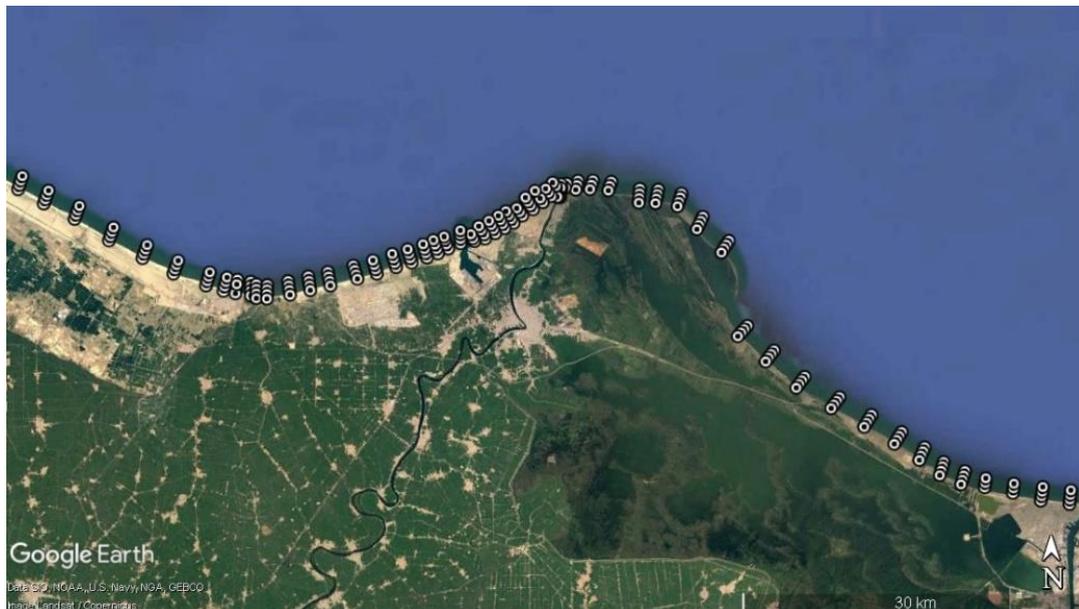


Figure.7. Ras Elbar Research Station coastal profiles

Suspended matter filter samples from selected areas across the same sampling area were also collected as shown on the map (fig. 8).

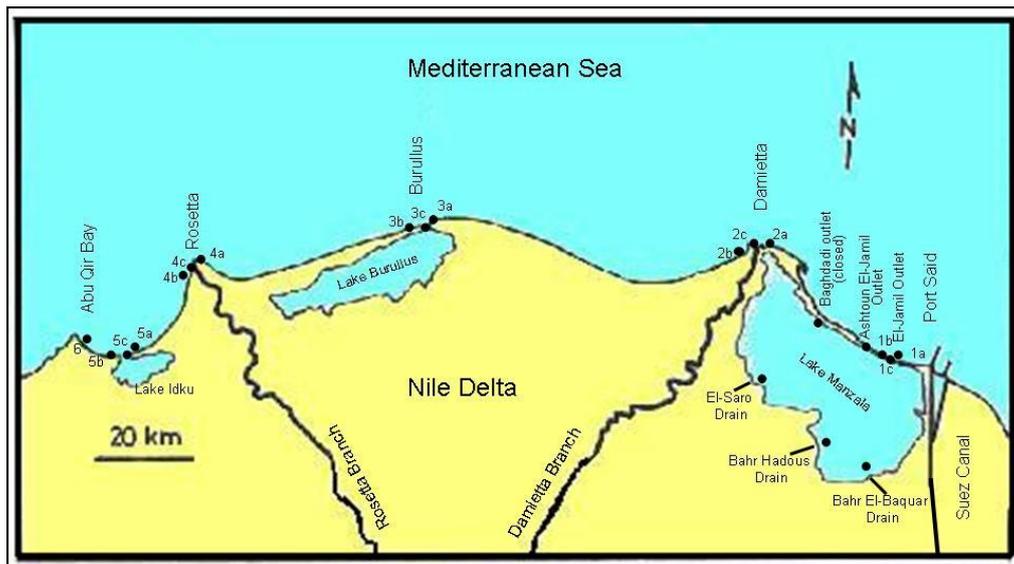


Fig.8. Suspended matter sampling locations.

2.2. Sample preparation:

Small amounts of the sediments are pelletized in press-forms and precisely weighed. The suspended matter filters are also pelletized in press-forms and precisely weighed as they are.

Short-term irradiation samples are heat-sealed in polyethylene foil bags, while the samples for long-term irradiation ones are packed in aluminum cups. Also samples of certified reference materials (CRMs) are pelletized and packed in the same way to be irradiated and measured with the samples. It is used later for the calculation of the concentrations using the comparative method.

2.3. Irradiation of samples:

Samples are packed in transport containers made of polystyrene for short time irradiation and aluminum for long time irradiation (Fig.9). Transport containers containing the samples are irradiated at REGATA; the pneumatic system used for irradiation at Pulsed fast reactor IBR-2M.



Fig.9. Transport containers used for irradiation: aluminum at the left and polystyrene at the right.

IBR-2M is a PuO_2 – fueled pulsed fast reactor. its unique technical approach produces one of the most intense neutron fluxes at the moderator surface among the world's reactors: $\sim 10^{16}$ n/cm²/s, with a power of 1850 MW in pulse (Fig.10). Its reactivity is modulated by the movement of two mechanical parts: the main movable reflector and the auxiliary movable reflector in opposite directions. When the two reflectors meet at the core, the reactor status changes from a subcritical on to a supercritical one²⁰.

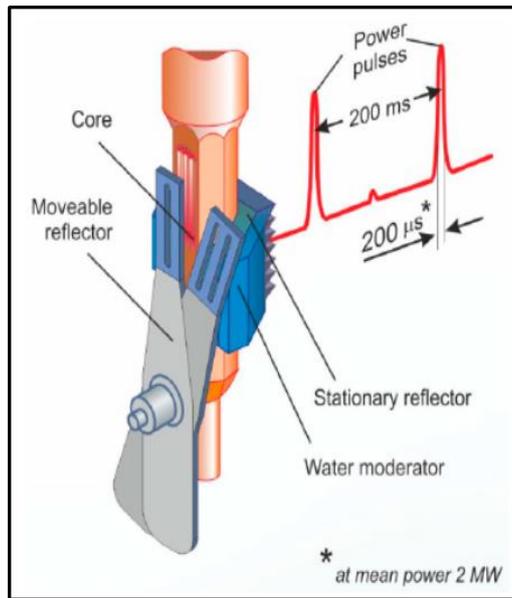


Fig.10. IBR-2M pulsed fast reactor core with the movable reflectors.

The REGATA experimental setup for INAA at the reactor IBR-2M (Fig.10) consists of four channels for irradiation (Ch1-Ch4), the pneumatic transport system (PTS) and gamma-spectrometers.

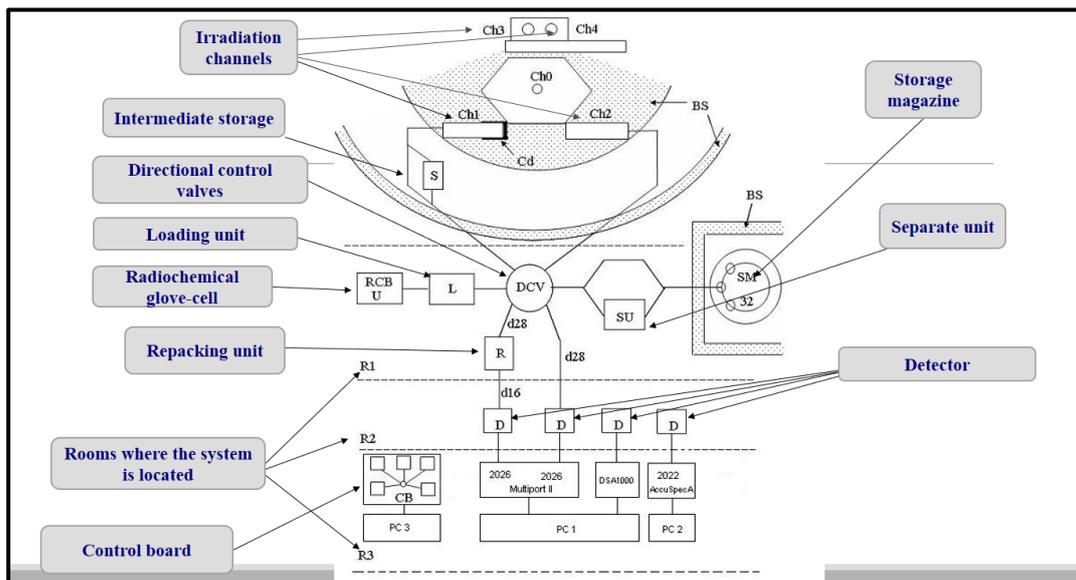


Fig.11. REGATA experimental set up

The main parameters of the irradiation channels are presented in Table 1. The channels Ch3, Ch4 are cooled by water, and the channels Ch1, Ch2, connected with the pneumatic transport system, are cooled by air. That is why the temperature in channels Ch3 and Ch4 is lower than the temperature in channels Ch1 and Ch2 in spite of the greater neutron flux density. The time of sample irradiation in channels Ch3, Ch4 depends on the operation cycle duration of the reactor and is equal to 10-12 days as a rule. The irradiation channels Ch1 and Ch2 are the same, but Ch1 is Cd-coated.

Table.1. Irradiation channels characteristics

Irradiation site	Neutron flux density (n/cm ² s)×10 ¹²			T (°C)	Channel Diam. (mm)	Channel length (mm)
	<i>Thermal</i>	<i>Resonance</i>	<i>Fast</i>			
Ch1	Cd-coated	3.31	4.32	70	28	260
Ch2	1.23	2.96	4.1	60	28	260
Ch3	Gd-coated	7.5	7.7	30-40	30	400
Ch4	4.2	7.6	7.7	30-40	30	400

Up to 7 containers can be simultaneously loaded in each channel for long irradiation. The neutron flux density is controlled by monitors (Au, Zr, etc.). Containers are transported by compressed air. Acoustic detectors, placed on the «flight pipe» of irradiation channels behind the first ring of a biological shield, allow one to determine the time of container arrival and departure accurately.

The intermediate storage (S) (Fig.11) is used to reduce the activity of aluminum containers after long irradiation. It is located between two rings of the biological shield of the reactor. There is also a magazine to store highly activated samples with 32 cells (SM) (Fig.11). It is surrounded with the biological shield made of lead and concrete blocks.

PTS has loading (L) and unloading (U) units (Fig.11) to load and to extract containers from the system. To provide radiation safety the unloading unit is placed into a glove-cell. All devices of the pneumatic system are equipped with photosensors and end-switches for indication of the container position in the system and for correct operation of all mechanisms²¹.

2.4. Radioactivity measurements

REGATA radioanalytical complex deals with a large number of samples, so a fully automated system is implemented. Figure.12 shows the block diagram for the automatic system of spectra measurements.

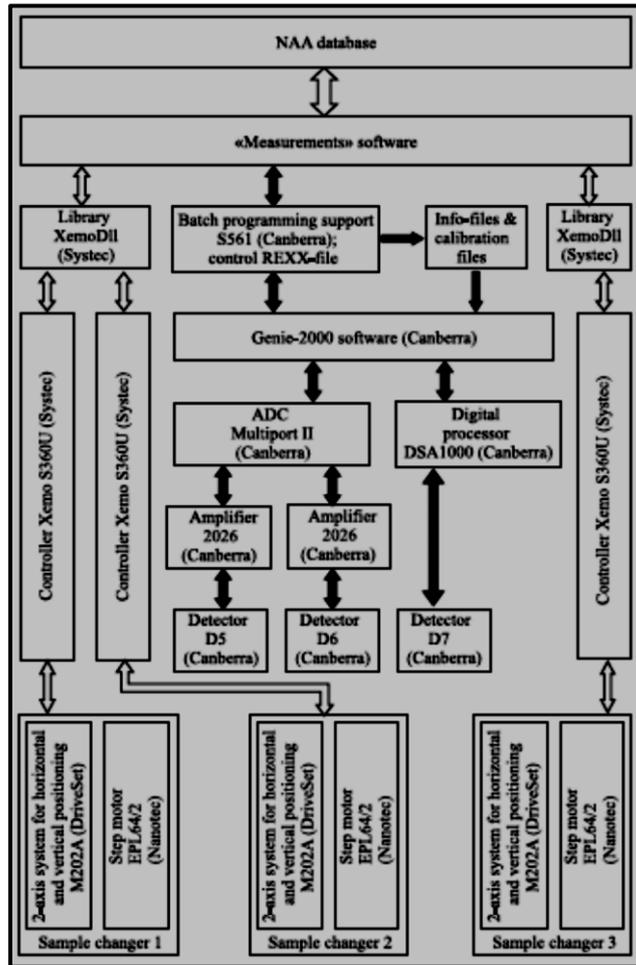


Fig.12. The block diagram of automatic system of spectra measurement

The system consists of three HPGe detectors with spectrometric electronics, three sample changers and the original control software. Each sample changer consists of two-axis linear positioning module M202A by DriveSet (DriveSet.de) company and disk with 45 slots for containers with samples (fig.13). Further details about the system are discussed elsewhere²².

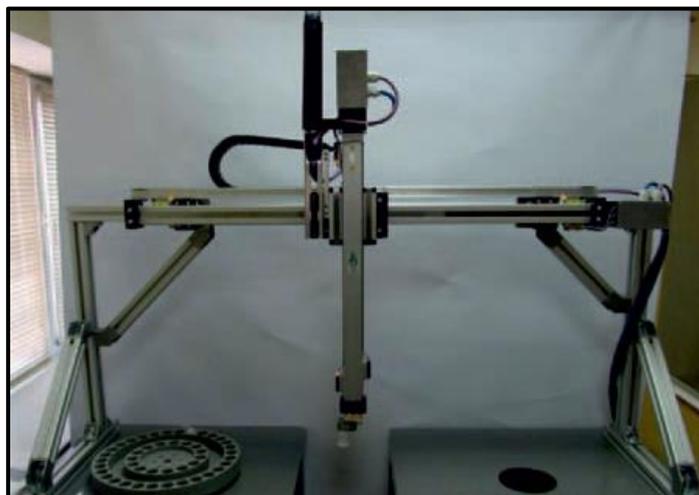


Fig.13. Sample changer

2.5. Gamma spectra analysis and calculation of concentration

The Genie-2000 program developed by Canberra with an additional interactive peak fitting module S506 is used for processing of the spectra obtained. Calculation of elemental concentrations in the samples is performed by a relative method using the Concentration program^{23,24}.

3. Results

Results of the concentrations of heavy metals will be available after long and short irradiation and data processing. Obtained results will be published. Sediments contamination will be assessed using the following indices:

- 1- Non-Lithogenic Metal Calculation: Non-lithogenic metal values were calculated as shown in (Eq.1):

$$M_{NL}(\%) = \left[M_{e\ Total} - \left(\frac{M_e}{Al} \right)_{crustal} \times Al_{Total} \right] \times 100 / M_{e\ Total} \quad (\text{Eq.1})$$

Negative values explain metal concentrations of sediment, which are lower than that of the values that came from crustal²⁵.

- 2- Geo-accumulation Index: Geo-accumulation index (I_{geo}) is a common approach that estimates the enrichment of metal concentrations above background or baseline concentrations and can be calculated using (Eq.2)^{25,26}. This index is basically a single-metal approach to quantify metal pollution in sediments when the concentration of toxic heavy metal is 1.5 or more times greater than their lithogenic background values²⁷. The geo-accumulation index consists of seven grades ranging from unpolluted to very highly polluted. Class 6 indicates a 64-fold enrichment above the background value²⁸.

$$I_{geo} = \log_2 \frac{C_n}{1.5 B_n} \quad (\text{Eq.2})$$

where, C_n is the measured concentration of the element n and B_n is the geochemical background value element n in average crust²⁹.

- 3- Contamination Factor: Contamination factor describes the contamination of a given toxic substance in a basin³⁰. Contamination factor (C_f) is the ratio of the concentration of the element in sediment (C_e) to preindustrial reference value for the element (C_{pi}) (eq 3).

$$C_f^i = C_e / C_{pi} \quad (\text{Eq.3})$$

C_f classes are summarized in Table.2

Table.2. Classes of contamination factor

Contamination Factor	Contamination Factor categories
$C_f < 1$	low contamination factor
$1 \leq C_f < 3$	3 moderate contamination factor
$3 \leq C_f < 6$	Considerable contamination factor
$C_f > 6$	very high contamination factor

4- Degree of Contamination: The degree of contamination (C_d) in sediment is defined as the sum of all various contaminant factors in heavy metals (Eq.4) ²⁵.

$$C_d = \sum_i^n C_f^i \quad (\text{Eq.4})$$

C_d scale is given in table.3.

Table.3. Degree of Contamination scale

Degree of contamination value	scale
$C_d < 8$	low degree of contamination
$8 \leq C_d < 24$	moderate degree of contamination
$24 \leq C_d < 48$	considerable degrees of contamination
$C_d > 48$	very high degree of contamination

5- Enrichment Factor: Assessment of heavy metal pollution in marine sediments requires knowledge of preindustrial metal concentrations to act as a reference against which the measured values can be compared ³¹. Therefore, to better understand the sediment quality in the studied area, levels of metal pollution were evaluated with different techniques for environmental assessment that should be considered. One of them is the ‘‘enrichment factor (EF)’’, which is a powerful tool to distinguish between anthropogenic and naturally occurring sources of heavy metals. The EF technique is used in the area of atmospheric aerosols, sediments, soil, and solid wastes to determine the degree of modification in the composition ²⁵. The EF of metals is defined as follows using aluminum as a reference element (Eq.5).

$$EF = \frac{(C_x/C_{Al})_{\{Sample\}}}{(C_x/C_{Al})_{\{Background\}}} \quad (\text{Eq.5})$$

where, $(C_x/C_{Al})_{\{sample\}}$ is the ratio of metal and Al concentrations of the sample and $(C_x/C_{Al})_{\{background\}}$ is the ratio of metal and Al concentrations of background. Table.4. outlines the EF scale.

Table.4. Degree of Contamination scale

Enrichment factor (EF)	EF Categories
$EF \leq 2$	Depletion to minimal enrichment
$2 < EF \leq 5$	Moderate enrichment
$5 < EF \leq 20$	Significant enrichment
$20 < EF \leq 40$	Very high enrichment
$EF > 40$	Extremely high enrichment

- 6- Potential Sediment Contamination Impact Using PEL-Q and ERM-Q Methods: The sediments' potential for causing adverse biological effects of the tested sediments was evaluated by calculating the probable effects level (PEL) quotient (PEL-Q) based on the published guideline values for coastal waters, namely the threshold effects level (TEL) and PEL, according to ³². The PEL-Q index was calculated for each contaminant, according to the formula described by ³³ (Eq.6):

$$PEL - Q_i = C_i / PEL_i \quad (\text{Eq.6})$$

where, PEL_i is the guideline value for each contaminant i and C_i is the measured concentration of the same contaminant. The sediment quality guide line quotient index (SQG-Q) was developed to compare sites affected by contaminant mixtures and can be calculated as follows in eq.7 ³³:

$$SQG - Q = \frac{\sum_{i=1}^n PEL - Q_i}{n} \quad (\text{Eq.7})$$

where, n is the total number of contaminants under analysis. sediment quality guide line quotient index is classified into: ($SQG - Q < 0.1$) is unimpacted, ($0.1 \leq SQG - Q < 1$) is moderately impacted and ($SQG - Q \geq 1$) is highly impacted ^{34,35}.

The mean effect range medium (ERM) quotient (mERMQ) method for the measurement of adverse effect caused by specific chemicals ³⁶ can be expressed by Eqs. 8 and 9 ^{37,38}.

$$ERM - Q_i = C_i / ERM_i \quad (\text{Eq.8})$$

$$mERMQ = (\sum_{i=1}^n ERM - Q_i) / n \quad (\text{Eq.9})$$

where, ($ERM - Q$) is the effects range-median quotient; C_i is the measured concentration of the examined metal (i). Four levels of mERMQ were used for the assessment: (1) lowest priority sites, ($mERMQ < 0.1$); (2) medium-low priority ($0.11 \leq mERMQ < 0.5$); (3) high-medium priority sites, ($0.51 \leq mERMQ < 1.5$); and (4) high priority sites, ($mERMQ \geq 1.5$). These levels were toxic in amphipod survival bioassays ^{37,39}.

7- Potential Ecological Risk Index Method: Potential ecological risk index method (PERI) was proposed by ²⁹. The method was widely applied to evaluate the harm of heavy metals in the sediments and was described as follow ⁴⁰:

- a. Pollution Index: Pollution index (C_f^i) evaluates the pollution of heavy metals in the sediments. It does not reveal to the ecological effects and hazards and it can be calculated from the following in (Eq 10):

$$C_f^i = C_{surface}^i / C_{reference}^i \quad (\text{Eq.10})$$

where, C_f^i is the pollution index of a single heavy metal (i) in the sediments. $C_{surface}^i$ and $C_{reference}^i$ are the measured and background (reference) values of the same heavy metal in surface and earth's crust sediments, respectively²⁹.

- b. Potential ecological risk index for the single heavy metal pollution (E_f^i): The formula for E_f^i for the single heavy metal pollution is expressed as follows (Eq 11):

$$E_f^i = C_f^i \times T_f^i \quad (\text{Eq.11})$$

where, T_f^i is the response coefficient for the toxicity of the single heavy metal (i). The formula reveals to the hazards of heavy metals on the human and aquatic ecosystem and reflects the level of heavy metal toxicity and ecological sensitivity to the heavy metal pollution ³⁰.

- c. Potential toxicity response index for various heavy metals in the sediments (RI): Its formula is illustrated as follows (Eq 12):

$$RI = \sum E_f^i \quad \text{Eq.12}$$

The grading standards of potential ecological risk of heavy metals are in Table.5.

Table.5. Relationship among RI, E_f^i , and pollution levels in sediments

Scope of E_f^i	Ecological risk level of single-factor pollution	Scope of RI	General level of potential ecological risk
$E_f^i < 40$	low	$RI < 150$	Low grade
$40 \leq E_f^i < 80$	Moderate	$150 \leq RI < 300$	Moderate grade
$80 \leq E_f^i < 160$	Higher	$300 \leq RI < 600$	severe
$160 \leq E_f^i < 320$	High	$RI \geq 600$	serious
$E_f^i \geq 320$	serious		

8- Sediment Pollution Index(SPI):- It is a multi-metal approach for the assessment of sediment quality with respect to trace metal concentrations along with metal toxicity, and its developed formula can be expressed as (Eqs. 13 and 14) ⁴¹:

$$SPI = \sum (EF_m \times W_m) / \sum W_m \quad \text{Eq.13}$$

$$EF_m = C_n / C_R \quad \text{Eq.14}$$

where, EF_m is the ratio between the measured metal concentration (C_n) and the reconstructed background metal concentration (C_R) instead of the average metal concentration in shale. W_m is toxicity weight. The following classification is given for the (SPI: 0 – 2 = natural sediment), (2 – 5 = low polluted sediment), (5 – 10 = moderately polluted sediment), (10 – 20 = highly polluted sediment), and (>20 = dangerous sediment).

9- Prospective Ecological Risk Assessment :- This assessment can measure or predict the levels of environmental parameters that are likely to cause harm to targets of interest. It can be achieved by comparing the measured environmental concentrations (MECs) with appropriate threshold values (PNECs) to get risk quotients (RQs) (Eq. 15) ⁴².

$$RQ = MEC / PNEC \quad \text{Eq.15}$$

When RQ value is less than 1, it is presumed that the likelihood of adverse effects is low. When RQ value is greater than 1, there is a likelihood of adverse effects with the magnitude that increases with the increase in RQ.

10- Statistical Analyses: The objective of the geostatistical study is to accurately understand the contaminants' behavior so a contamination mapping can be plotted in order to visualize the pollution migration. A geostatistical study is conducted as indicated in Fig.14.

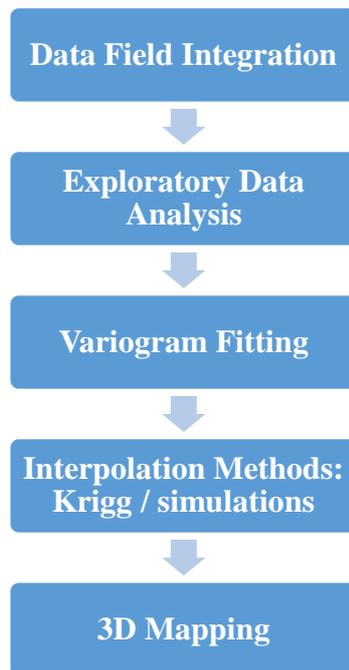


Fig.14. Steps of Geostatistical analysis

1. Data field integration: This step is made in the previous sections.
2. Exploratory data analysis: During this step, raw data are pretreated using multivariate techniques including a grouping analysis, cluster analysis (CA), and principal component analysis (PCA). CA and PCA are appropriate to

evaluate relationships between variables and the general behavior of the data. Limit of detection (LD) values will be used for concentration values equal to zero in the CA and PCA. CA and PCA enable evaluations of the concentration of metals by station sampled. These techniques were recently applied to interpret the data from marine sediment metals⁴³⁻⁴⁶. An experimental variogram will be generated.

3. Variogram fitting: The experimental variogram is fitted⁴⁷.
4. Interpolation and 3D mapping: the fitted variogram is interpolated and a 3D map is generated.

4. Conclusion

In this study, the spatial distribution of heavy metals in the breaker zone of the Egyptian Mediterranean coasts will be studied and assessed using instrumental neutron activation analysis. Sediments contamination will be assessed using the following indices: geoaccumulation factor, Non-lithogenic metal values, Degree of Contamination, Contamination Factor, Enrichment Factor, Potential Sediment Contamination Impact Using PEL-Q and ERM-Q Methods, Potential Ecological Risk Index, Sediment Pollution Index and Prospective Ecological Risk Assessment. ArchGis technology and geostatistical methods will be used to study the behavior of heavy metals. The obtained results would serve as a reference database to assess the future impacts of human activities. Also, these results would be used as a contribution to the knowledge and rational management and to take drastic decisions to solve the problems of pollution on aquatic life.

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6. References

1. Uluturhan, E., Kontas, A. & Can, E. Sediment concentrations of heavy metals in the Homa Lagoon (Eastern Aegean Sea): Assessment of contamination and ecological risks. *Mar. Pollut. Bull.* **62**, 1989–1997 (2011).
2. Neşer, G. *et al.* Heavy metals contamination levels at the Coast of Aliğa (Turkey) ship recycling zone. *Mar. Pollut. Bull.* **64**, 882–887 (2012).
3. Khaled, A., El Nemr, A. & El Sikaily, A. Heavy metal concentrations in biota of the mediterranean sea: a review, part I. *Blue Biotechnol. J.* **2**, 79–133
4. Khaled, A., El Nemr, A. & El Sikaily, A. Heavy metal concentrations in biota of the mediterranean sea: a review, part II. *Blue Biotechnol. J.* **2**, 191–249
5. Windom, H. L. Contamination of the marine environment from land-based sources. *Mar. Pollut. Bull.* **25**, 32–36 (1992).
6. Tornero, V. & Hanke, G. Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas. *Mar. Pollut. Bull.* **112**, 17–38 (2016).
7. Loring, D. H. & Rantala, R. T. T. Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Rev.* **32**, 235–283 (1992).
8. Aguilar-Martínez, R. *et al.* Assessment of Chemcatcher passive sampler for the monitoring of inorganic mercury and organotin compounds in water. *Int. J. Environ. Anal. Chem.* **88**, 75–90 (2008).
9. Søndergaard, J., Bach, L. & Gustavson, K. Measuring

- bioavailable metals using diffusive gradients in thin films (DGT) and transplanted seaweed (*Fucus vesiculosus*), blue mussels (*Mytilus edulis*) and sea snails (*Littorina saxatilis*) suspended from monitoring buoys near a former lead–zinc mine in West Greenland. *Mar. Pollut. Bull.* **78**, 102–109 (2014).
10. Hwang, D.-W. *et al.* Monitoring of trace metals in coastal sediments around Korean Peninsula. *Mar. Pollut. Bull.* **102**, 230–239 (2016).
 11. El Nemr, A. M., El Sikaily, A. & Khaled, A. Total and Leachable Heavy Metals in Muddy and Sandy Sediments of Egyptian Coast Along Mediterranean Sea. *Environ. Monit. Assess.* **129**, 151–168 (2007).
 12. Yang, Y. *et al.* Comprehensive assessment of heavy metal contamination in sediment of the Pearl River Estuary and adjacent shelf. *Mar. Pollut. Bull.* **64**, 1947–1955 (2012).
 13. Zhang, Z., Juying, L., Mamat, Z. & QingFu, Y. Sources identification and pollution evaluation of heavy metals in the surface sediments of Bortala River, Northwest China. *Ecotoxicol. Environ. Saf.* **126**, 94–101 (2016).
 14. Weber, P. *et al.* Metals in the water, sediment, and tissues of two fish species from different trophic levels in a subtropical Brazilian river. *Microchem. J.* **106**, 61–66 (2013).
 15. Bode, P. *Instrumental and organizational aspects of a neutron activation analysis laboratory.* (DEN HAAG, 1996).
 16. Simonits, A., Corte, F. & Hoste, J. Single-comparator methods in reactor neutron activation analysis. *J. Radioanal. Chem.* **24**, 31–46 (1975).
 17. De Bruin, M. & Korthoven, P. J. M. Computer oriented system for nondestructive neutron activation analysis. *Anal. Chem.* **44**, 2382–2385 (1972).
 18. Beck, J. N. & Lamberty, C. M. Thermal neutron activation analysis—an important analytical tool. *Appl. Spectrosc. Rev.*

- 37**, 19–55 (2002).
19. Masselink, G., Hughes, M. G. & Hughes, M. G. *An Introduction to Coastal Processes and Geomorphology*. (Routledge, 2014). doi:10.4324/9780203783740
 20. Shvetsov, V. Neutron Sources at the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research. *Quantum Beam Sci.* **1**, 6 (2017).
 21. Frontasyeva, M. Scientific Reviews: Radioanalytical Investigations at the IBR-2 Reactor in Dubna. *Neutron News* **16**, 24–27 (2005).
 22. Pavlov, S. S., Dmitriev, A. Y. & Frontasyeva, M. V. Automation system for neutron activation analysis at the reactor IBR-2, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. *J. Radioanal. Nucl. Chem.* **309**, 27–38 (2016).
 23. Dmitriev, A. Y. & Pavlov, S. S. Automation of the quantitative determination of elemental content in samples using neutron activation analysis on the IBR-2 reactor at the Frank laboratory for neutron physics, joint institute for nuclear research. *Phys. Part. Nucl. Lett.* **10**, 33–36 (2013).
 24. Pavlov, S. S., Dmitriev, A. Y., Chepurchenko, I. A. & Frontasyeva, M. V. Automation system for measurement of gamma-ray spectra of induced activity for multi-element high volume neutron activation analysis at the reactor IBR-2 of Frank Laboratory of Neutron Physics at the joint institute for nuclear research. *Phys. Part. Nucl. Lett.* **11**, 737–742 (2014).
 25. Özkan, E. Y. A New Assessment of Heavy Metal Contaminations in an Eutrophicated Bay (Inner Izmir Bay, Turkey). *Turkish J. Fish. Aquat. Sci.* **12**, 135–147 (2012).
 26. Muller, G. Index of Geoaccumulation in Sediments of the Rhine River. *GeoJournal* **2**, 108–118 (1969).
 27. Gaur, V. K., Gupta, S. K., Pandey, S. D., Gopal, K. & Misra, V. Distribution of heavy metals in sediment and water of river

- Gomti. *Environ. Monit. Assess.* **102**, 419–433 (2005).
28. Förstner, U., Ahlf, W., Calmano, W. & Kersten, M. in *Sediments and Environmental Geochemistry* 311–338 (Springer Berlin Heidelberg, 1990). doi:10.1007/978-3-642-75097-7_18
 29. Martin, J.-M. & Meybeck, M. Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* **7**, 173–206 (1979).
 30. Hakanson, L. An ecological risk index for aquatic pollution control. a sedimentological approach. *Water Res.* **14**, 975–1001 (1980).
 31. Abraham, G. M. S. & Parker, R. J. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environ. Monit. Assess.* **136**, 227–238 (2007).
 32. Macdonald, D. D., Carr, R. S., Calder, F. D., Long, E. R. & Ingersoll, C. G. Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* **5**, 253–278 (1996).
 33. Long, E. R. & MacDonald, D. D. Recommended Uses of Empirically Derived, Sediment Quality Guidelines for Marine and Estuarine Ecosystems. *Hum. Ecol. Risk Assess. An Int. J.* **4**, 1019–1039 (1998).
 34. MacDonald, D. D. *et al.* Development, Evaluation, and Application of Sediment Quality Targets for Assessing and Managing Contaminated Sediments in Tampa Bay, Florida. *Arch. Environ. Contam. Toxicol.* **46**, 147–161 (2004).
 35. Costa, P. M. *et al.* Assessment of the genotoxic potential of contaminated estuarine sediments in fish peripheral blood: Laboratory versus in situ studies. *Environ. Res.* **111**, 25–36 (2011).
 36. Long, E. R., MacDonald, D. D., Severn, C. G. & Hong, C. B. Classifying probabilities of acute toxicity in marine sediments

- with empirically derived sediment quality guidelines. *Environ. Toxicol. Chem.* **19**, 2598–2601 (2000).
37. Long, E. R., Field, L. J. & MacDonald, D. D. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environ. Toxicol. Chem.* **17**, 714–727 (1998).
 38. Long, E. R. Calculation and Uses of Mean Sediment Quality Guideline Quotients: A Critical Review. *Environ. Sci. Technol.* **40**, 1726–1736 (2006).
 39. Yan, C., Li, Q., Zhang, X. & Li, G. Mobility and ecological risk assessment of heavy metals in surface sediments of Xiamen Bay and its adjacent areas, China. *Environ. Earth Sci.* **60**, 1469–1479 (2010).
 40. Martin, J.-M. & Meybeck, M. Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* **7**, 173–206 (1979).
 41. Aguiar, J. E., de Lacerda, L. D., Miguens, F. C. & Marins, R. V. The geostatistics of the metal concentrations in sediments from the eastern Brazilian continental shelf in areas of gas and oil production. *J. South Am. Earth Sci.* **51**, 91–104 (2014).
 42. PEMSEA. *Manila Bay: Initial Risk Assessment*. PEMSEA Technical Information Report No. 2001/01; Global Environment Facility/United Nations Development Programme/International Maritime Organization Regional Programme on Building Partnerships in Environmental Manage. (2001).
 43. Aguiar, J. E., de Lacerda, L. D., Miguens, F. C. & Marins, R. V. The geostatistics of the metal concentrations in sediments from the eastern Brazilian continental shelf in areas of gas and oil production. *J. South Am. Earth Sci.* **51**, 91–104 (2014).
 44. Badawy, W. M., El-Taher, A., Frontasyeva, M. V., Madkour, H. A. & Khater, A. E. M. Assessment of anthropogenic and geogenic impacts on marine sediments along the coastal areas of Egyptian Red Sea. *Appl. Radiat. Isot.* **140**, 314–326 (2018).

45. Badawy, W. M., Ghanim, E. H., Dului, O. G., El Samman, H. & Frontasyeva, M. V. Major and trace element distribution in soil and sediments from the Egyptian central Nile Valley. *J. African Earth Sci.* **131**, 53–61 (2017).
46. Arafa, W. M. *et al.* Geochemistry of sediments and surface soils from the Nile Delta and lower Nile valley studied by epithermal neutron activation analysis. *J. African Earth Sci.* **107**, 57–64 (2015).
47. Hu, B. *et al.* Heavy Metal Pollution Delineation Based on Uncertainty in a Coastal Industrial City in the Yangtze River Delta, China. *Int. J. Environ. Res. Public Health* **15**, (2018).