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Assessment of the Heavy Metals and Natural Radioactivity in Phosphate Mines and Occupational Health Effects at Some Egyptian Regions

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Abstract

In this work the specific activities of natural radionuclides namely (^{238}U series, ^{232}Th series and ^{40}K) has been measured in collected sedimentary phosphate deposits samples from El-Hamraween, El-Quser and Safaga phosphate mines in Egypt. HPGe γ-spectrometry was used. This study was undertaken to estimate the radiation hazard indices in phosphate mining at the studied mines on their occupational workers, and to establish correlation relationships between the some measured heavy metals such as As, Cd and Pb in blood workers and their concentration in phosphate rock ores. As well as determination the biomarkers in the blood workers such as malondialdehyde (MDA) and superoxide dismutase (SOD). The phosphate mine sample of El-Hamrawein has the lowest activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in compared to the phosphate mine samples of El-*Quseir* and Safaga (El-Hamrawein<El-*Quseir*<Safaga). The activity concentrations of all analyzed investigated radionuclides considerably fluctuated; for ^{226}Ra activity concentrations varied from 222.4 to 255.8 Bq kg^{-1}, 122.4 to 188.3 Bq kg^{-1} and 115.4 to 165.8 Bq kg^{-1} for Safaga, El-Quseir and El-*Hamrawein,* respectively. For ^{232}Th activity concentrations varied from 135.6 to 212.3 Bq kg^{-1}, 112.8 to 167.4 Bq kg^{-1} and 132.8 to 188.6 Bq kg^{-1} for Safaga, El-Quseir and El-*Hamrawein,* respectively. For ^{40}K activity concentrations varied from 225.2 to 312.8 Bq kg^{-1}, 168.7 to 268.9 Bq kg^{-1} and 95.2 to 155.8 Bq kg^{-1} for Safaga, El-Quseir and El-*Hamrawein* respectively. The workers of old ages have higher concentration of the investigated heavy metals than young ages. There is a good relation between the concentration of the investigated metals in phosphate mine samples and their concentration in blood of the occupational workers in these mines.

Keywords: Superoxide dismutase; Malondialdehyde; Natural radionuclides; Heavy metals; Phosphate; Occupational workers; Health effects

Introduction

Studies of natural environmental radiation and radioactivity are great importance and interest for environmental chemistry as well as many other disciplines. Environmental radiation originates from a number of naturally occurring and human-made sources. The estimation of exposure to ionizing radiation is an important goal of regulatory authorities and radiation protection scientists. Thus knowledge of the background radiation level is of paramount importance [1,2]. Radioactive materials occur naturally everywhere in the environment (e.g., uranium series, thorium series and potassium-40). By far the largest proportion of human exposure to radiation comes from natural sources from external sources of radiation, including cosmic and terrestrial radiation, and from inhalation or ingestion of radioactive materials. The global average annual human exposure from natural sources is 2.4 mSv/year. Some sources (e.g., uranium) can be concentrated during extraction by mining and other industrial activities [3]. The phosphate rock extractions are man-made sources of air- and water borne radionuclide releases to the environment. Phosphate rocks contain relatively high concentrations of naturally occurring radioactive materials from uranium series and thorium series (^{238}U and ^{232}Th). Mining, milling, transportation of phosphate ores, manufacturing of phosphate fertilizers containing uranium are ways in which the workers, public and the environment are exposed to enhance natural radioactivity [4]. Man is exposed to ionizing radiation with or without his consent. Because of the lethal effects of ionizing radiation, the practice has been to monitor and assess the levels of exposure and keep one's exposure to ionizing radiation as low as reasonably achievable (also known as the ALARA principle). In Egypt, phosphate formations are established in different sites. Three locations of phosphate mines have been selected for this study and they are *Safaga* (33° 57′E 26° 44′N), *El-Quseir*(34° 17′E 26° 06′N) and El-*Hamrawein (35° 12′E 26° 15′N).* The terrestrial gamma radionuclides cause the major contribution to the annual average doses of radiation exposure of the world's population [3]. Natural environmental radioactivity series mainly from primordial radionuclides, such as the nuclides from both ^{238}U and ^{232}Th series and their decay products as well as ^{40}K are occur at trace levels in all ground formations [5]. Exposure of workers and the public to radiation from phosphate rock is therefore unlikely. The European Commission has issued a draft proposal for revision of the Basic Safety Standards for the protection of workers and the general public against the dangers of ionizing radiation [6]. Mined phosphate poses concerns due to levels of heavy metals that may present in phosphate rock. Trace heavy metals constitute the main oxidative stress factor in mammals by the production of free radicals which cause the cardiovascular diseases [7]. The heavy metals oxidize lipids and proteins to form deterioration products with high radical activity which produces Reactive Oxygen Species (ROS) [8]. So, oxidative stress is an imbalance for the production of ROS which lead to an increased oxidation of cellular components [9].

This work aims to measure the specific activities of natural radionuclides namely (^{226}Ra (^{238}U) series, ^{232}Th series and ^{40}K) in collected sedimentary phosphate deposits samples from El-Hamraween, El-Quser and Safaga phosphate mines in Egypt. And to establish

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correlation relationships between some heavy metals such as As, Cd and Pb in blood workers and their concentration in phosphate rock ores. As well as determination the biomarkers in blood of occupational workers such as malondialdehyde (MDA) and superoxide dismutase (SOD) in addition to the hematological parameters (Hemoglobin concentration, red blood count, white blood count and platelets count). This work can be considered as a step toward investigating natural radioactivity in phosphate hills in Egypt which considered a part of the Egyptian's radiological baseline map. The experimental results will be used as guides for decision makers in solving some natural environmental problems which may be found in those areas of phosphate mines. On the other hand, the radiation safety measures and radiation safety standers should be account into consider for workers and environmental ecosystems in phosphate mines areas.

Materials and Methods

Sampling and sample preparation

In Egypt, phosphate formations are established in different sites. Three locations of open-pit phosphate mines have been selected for this study. These samples were collected by services partner (Baltic Control Company). El-*Hamrawein (35° 12/ E 26° 15/ N)*, *El-Quseir* (34° 17/ E 26° 06/ N) and *Safaga* (33° 57/ E 26° 44/ N) locations. Phosphate sampling was carried out in the months of April, May and December 2014. Twelve samples were collected from each mine; four samples were collected from the subsurface phosphate horizon (subsurface samples), four samples were collected from the exposed lower phosphate horizon (surface samples lower bed) and four samples were collected from the exposed upper phosphate horizon (surface samples upper bed). The collected samples were transferred to labeled polyethylene bags, closed and transferred to the laboratory for preparation and measurements. The collected samples were dried at room temperature for a week. The quartering technique was used to get a representative sample for each horizon. So, there are three representative samples for each mine. The Phosphate samples were prepared and analyzed as reported in [10].

Radioactivity measurements

The activity concentration of the natural ^{238}U series, ^{232}Th series and ^{40}K in the investigated samples were determined using a high-resolution HPGe γ-spectrometry system with 30% counting efficiency. These investigations were carried out in the Laboratory of Egyptian Nuclear and Radiological Regulatory Authority. This was performed by taking 250 cm^3 counting vials filled up to a height of 7 cm, which correspond to 170 cm^3. The measurement duration was up to 80,000 sec. The obtained spectra were analyzed. The determination of the presence radionuclides and calculation of their activities were based on the following gamma-ray transitions (in keV): the ^{226}Ra activities (or ^{238}U activities for samples assumed to be in radioactive equilibrium) were estimated from ^{234}Th (92.38 keV, 5.6%), while γ-energies of ^{214}Pb (351.9 keV, 35.8%) and ^{214}Bi (609.3, 45%), 1764.5 keV, 17%) and ^{226}Ra (185.99 KeV, 3.5%) were used to estimate the concentration of ^{226}Ra. The Gamma- ray energies of ^{212}Pb (238.6 keV, 45%), and ^{228}Ac (338.4 keV, 12.3%), (911.07 keV, 29%), (968.90 keV, 17%) were used to estimate the concentration of ^{232}Th. The activity concentrations of ^{40}K were measured directly by its own gamma rays (1460.8 keV, 10.7%). In order to determine the background distribution due to naturally occurring radionuclides in the environment around the detector, an empty polystyrene container was counted in the same manner as the samples. The activity concentrations were calculated after measurement and subtraction of the background. The activities were determined from measuring their respective decay daughters. The activity concentrations were calculated from the intensity of each line taking into account the mass of the sample, the branching ratios of the γ-decay, the time of counting and the efficiencies of the detector [11,12].

Determination of heavy metals in phosphate samples

Atomic Absorption Spectrophotometer (AAS) is a simple and well available technique for the determinations of heavy metals in the soil samples. Heavy metals in sediments were determined according to [12]. These investigations were carried out in National Research Center, Cairo, Egypt. The metal ions were determined by Atomic Absorption Spectrophotometer, Perkin Elmer model Analyst 100 which is manufactured in USA. The sediments were digested with 5: 1 mixture of HF and $HClO_4$ acids; 1 g (dry weight) sample was digested by 2 ml $HClO_4$ and 10 ml HF to near dryness, subsequently a second addition of 1 ml of $HClO_4$ and 10 ml of HF and evaporated to near dryness. Finally, 1 ml of $HClO_4$ alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12N HCl and diluted to 25 ml with de-ionized water, the results obtained were determined according to [13].

Measurements of heavy metals in blood workers

Whole blood (1 ml) was transferred into screw capped polypropylene tubes and 5 ml nitric acid solution was added. After 10 minutes; it diluted with 5 ml deionized water, digested was continued in a microwave oven. In this digestion procedure, the temperature was increased gradually from 85°C to 230°C through 15 minutes. The sample preparation was completed with addition of 5 ml deionized water and 3 ml HCl 70% conc. Inductively-Coupled Plasma-Mass Spectroscopy (ICP-MS) (Agilent 7700X, USA) at (National Research Center, Cairo, Egypt) was used for the analysis of metals in collected samples. The standards for ICP-MS were prepared from stock solutions of lead, cadmium, arsenic at 10 mg/L concentrations obtained from Sigma-Aldrich, Australia, and labeled as Fluka Trace Cert Ultra Plasma with purity was higher than 99.999%. Calibration was performed by aqueous multi-element standard solutions. The method was validated by analysis of certified reference materials (Seronorm Trace Elements, Billingstad, Norway). Accurate results were obtained for all elements according to [14].

Hematological measurements

Ninety phosphates mine workers were taken from the three studied sites (Safaga site, El-Hamrawein site and El-Quseir site) in addition to a control group worker for investigations. All workers were divided according their age into three groups (first group 20-30 years, second group 30-40, third group 40-50 years) and 10 people as a control group was selected from non-phosphate mine workers (mean age 30 years). Hematological assessment Blood samples (5 mL) were collected by venepuncture of the cubital vein in the antecubital fossa by using a 5 mL disposable syringe. A part of the blood sample was then transferred to sterile vacuum tubes containing an anticoagulant Ethylene Diamine Tetra acetic Acid (EDTA), for whole blood analysis. The remaining blood was collected in sterile vacuum tubes with no added anticoagulant and was kept at room temperature for 2 h, where it was allowed to clot, as this was designated for serum separation for superoxide dismutase (SOD) and Malondialdehyde (MDA). The tubes were transported to a laboratory (Biomedical Lab, National Research Center, Egypt) for analysis by using hematological investigations consisting of the Hemoglobin (Hb) concentration, RBC count, WBSc, platelets count, hematological investigations were estimated in an automated blood counting machine (SYSMEX XE-2100; Sysmexbiomedical Lab, National Research Center, Egypt, Accurate results were obtained for all elements according to [15].

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Determination of SOD and MDA

Superoxide dismutase (SOD) activity determination and Malondialdehyde (MDA) determination were performed at Biomedical Lab, National research center, Egypt. SOD determined according to the method of [16], and MDA determined according to method adopted by [17]. The samples were analyzed by spectrophotometer (Milton Roy spectronic 3000 ARRAY double beam spectrometer, manufactured in Germany.

Results and Discussion

Radioactivity measurements in phosphate samples

Activity concentrations of the natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) were measured for the investigated phosphate mines samples by HPGe gamma spectrometry. According to the International Atomic Energy Agency, one kilogram of soil typically contains the following amounts of the following three natural radioisotopes 370 Bq of ^{40}K (typical range 100-700 Bq), 25 Bq of ^{226}Ra (typical range 10-50 Bq), 25 Bq of ^{238}U (typical range 10-50 Bq) and 25 Bq of ^{232}Th (typical range 7-50 Bq). The activity concentrations of these radionuclides in different layers of the investigated samples are shown in Table 1. It is recognize from the Table 2 that there is a clear variation in activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in layer samples (Subsurface, Surface upper bed and Surface lower bed) in every investigated mine and also in the different mines. As can be seen, activity concentrations of all analyzed radionuclides considerably fluctuated; for ^{226}Ra activity concentrations varied from 222.4 to 255.8 Bq kg^{-1}, 122.4 to 188.3 Bq kg^{-1} and 115.4 to 165.8 Bq kg^{-1} for Safaga, El-Quseir and El-Hamrawein, respectively and these concentrations are 5 to 10 times higher than that value recommended by IAEA. For ^{232}Th activity concentrations varied from 135.6 to 212.3 Bq kg^{-1}, 112.8 to 167.4 Bq kg^{-1} and 132.8 to 188.6 Bq kg^{-1} for Safaga, El-Quseir and El-Hamrawein, respectively and these concentrations are 5 to 8 times higher than that value recommended by IAEA 2000. For ^{40}K activity concentrations varied from 225.2 to 312.8 Bq kg^{-1}, 168.7 to 268.9 Bq kg^{-1} and 95.2 to 155.8 Bq kg^{-1} for Safaga, El-Quseir and El-Hamrawein, respectively and these concentrations are lower than that value recommended by IAEA. Also the obtained results indicate that the phosphate mine sample of El-Hamrawein has the lowest activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in compared to the phosphate mine samples of El-*Quseir* and Safaga (El-Hamrawein<El-*Quseir*<Safaga). This can be discussed in the light of increasing concentration of P_2O_5 as shown in Table 3. In all investigated mines, the remarkable highly activity concentrations are record in surface lower bed samples and this can be discussed as the deep site has more phosphate ore rocks which contains more highly percentage of P_2O_5 conjugated with uranium, thorium and potassium isotopes [10], were reported that phosphate mine in Safaga has relatively high levels of ^{226}Ra. The average activity ratio (range) of ^{226}Ra/^{228}Ra in the region of Safaga– Quseir–Marsa Alam city (sample codes from 510 to 549) was 2.25 (0.83-5.33). The increases of these ratios, exceeding unity, could be attributed to the phosphate mining in Safaga-Quseir region and/or their geo-chemical behavior in the environment [10].

Concentration of heavy metals in the studied phosphate samples

In this study the concentration of some famous hazardous heavy metals which reflected the impacts on their environmental sites, workers in phosphate mines rocks ores and phosphate industry phopsphgysoium which directly these products into plants and agricultures ecosystem. Table 2 shows the heavy metals concentration in Safaga, *Al Quseir* and EL- Hamrawein sites, where the Co was recorded (11.2, 17.8 and 15.2 ppm) respectively, also AS was recorded in Safaga, *Al Quseir* and EL-Hamrawein (24.9, 26.8 and 20.2 ppm) respectively. As well as the Cd was recorded (0.88, 0.98 and 1.2 ppm) respectively. Also Pb was recorded 28.2, 22.3 and 26.7 ppm) respectively. These data revealed some variations in heavy metals concentration according to phosphate mines site. The data recoded increased levels of Pb concentrations in Safaga site in compared to *Al Quseir* and El-Hamrawein sites, as well as Cd in *Al Quseir* and Safaga sites in compared to *Al Quseir* site, these results were acceptable when compared to global ratio of heavy metals in phosphate rocks. The concentration of cobalt phosphate rocks widely, generally ranging from about 1 to 40 ppm [18]. On the other hand, soils near cobalt-containing mineral deposits, mining and smelting facilities, or industries manufacturing or using cobalt alloys

Samples	The selected natural radionuclide's in phosphate mine at *Safaga*(33° 57' E 26° 44' N) (Bq kg^{-1})			Activity of the investigated radionuclide's at El-*Quseir* (34° 17' E 26° 06' N) (Bq kg^{-1})			Activity of the investigated radionuclide's at El-*Hamrawein (35°12' E 26° 15' N)* (Bq kg^{-1})		
	^{226}Ra	^{232}Th	^{40}K	^{226}Ra	^{232}Th	^{40}K	^{226}Ra	^{232}Th	^{40}K
Subsurface samples	222.4 ± 7.2	135.6 ± 4.7	225.2 ± 11.5	122.4 ± 5.8	112.8 ± 7.3	168.7 ± 6.5	115.4 ± 5.9	95.2 ± 4.8	132.8 ± 6.8
Surface samples upper bed	235 ± 7.8	198.2 ± 7.1	264.7 ± 12.3	154.6 ± 7.1	132.7 ± 6.2	212.5 ± 9.7	135.2 ± 6.2	122.7 ± 8.3	145.2 ± 7.8
Surface samples lower bed	255.8 ± 9.3	212.3 ± 9.2	312.8 ± 12.8	188.3 ± 7.6	167.4 ± 8.4	268.9± 10.2	165.8 ± 6.6	155.8 ± 9.4	188.6 ± 8.7

Table 1: Activity concentrations of the selected natural radionuclides in the investigated phosphate samples.

Phosphate samples	Heavy metals (ppm)		
	As	Cd	Pb
Safaga	24.9	0.88	28.2
El-*Quseir*	26.8	0.98	22.3
El-Hamrawein	20.2	1.2	26.7

Table 2: Concentration of some heavy metals in the investigated phosphate samples.

Site	P_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
El-Hamrawein	28	14.5	0.74	4.2	45	0.9	0.8	0.9
El-*Quseir*	30	15.3	0.52	3.1	47	1.1	0.6	1.3
Safaga	33	11.2	0.33	2.3	41	0.8	1.1	1.2

Table 3: Mean percentage of metal oxides in the investigated phosphate samples.

or chemicals may contain much higher levels of cobalt. Available studies of the carcinogenic effects of cobalt in occupationally-exposed humans have reported mixed results, with both positive and negative results. Lifetime inhalation of cobalt sulfate resulted in increased tumor incidences in both rats and mice [19]. The most common problem causing cationic metals (metallic elements whose forms in soil are positively charged cations e.g., Pb^{2+}) are mercury, cadmium, lead, nickel, copper, zinc, chromium, and manganese [20]. Nonessential metals such as As, Pb and Cd are toxic even in trace amounts. Intake of cadmium above safe limit causes high blood pressure, liver disease and nerve or brain damage. The essential metals can also produce toxic effects at higher concentrations. They tend to bio-accumulate, cause toxicity to plants and contaminate the food chain [21]. Only a few metals of proven hazardous nature are to be completely excluded in food for human consumption. Thus, only three metals, namely lead, cadmium and mercury, have been included in the regulations of the European Union for hazardous metals [22].

Percentage of metal oxides in phosphate ores

The chemical analysis of phosphate samples were carried out for showing the correlation between oxides of heavy metals regarding phosphate mine and their hazardous on the occupational workers. As shown in Table 3 Safaga mine sample has high content of P_2O_5 and Na_2O while it has low content of SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO in compared to the other two investigated samples. El-Hamraweinhas low content in P_2O_5 and K_2O while it has higher content of Al_2O_3 and Fe_2O_3 than the other two investigated samples. *Al-Quseir* mine sample has moderate contents of the investigated metal oxides except SiO_2, CaO, MgO and K_2O are higher values.

The obtained results revealed increasing of siliceous ores which have impact health hazards in workers. The workers exposures to these particles may have many artificial and hematological diseases. Inhalation of silica causes risk of tuberculosis, lung cancer and some autoimmune diseases such as scleroderma and rheumatoid arthritis. Freshly fractured silica dust appears to be more reactive and more hazardous than old or stale dust. This may be a consequence of a relatively higher surface charge on freshly formed particles [23].

Concentration of some heavy metals in blood workers

The obtained results of investigated heavy metals in blood of occupational workers at phosphate mines are shown in Table 4. From Tables 4 and 5, it is clear that there is a good relation between the concentration of the investigated metals (As, Cd and Pb) in phosphate mine samples and their concentration in blood of the occupational workers in these mines. Generally, Table 6 shows that the concentrations of the heavy metals in all ages of the occupational workers are higher than that of the control sample. Also it shows that old ages have higher concentration of these metals than young ages and this agreement with Ref. [24], which reported that Cd and Pb concentrations in the blood of aging workers are more than youngest workers. Workers *at* El-*Hamrawein mine* have low concentration of Arsenic (As) than other workers at *both of Safaga* and *El-Quseir* mines. Workers *at Safaga mine* have low concentrations of Cd than other workers at *both of* El-*Hamrawein* and *El-Quseir* mines. *Workers at El-Quseir mine* have low concentrations of Pb than other workers at *both of* EL-*Hamrawein* and *Safaga* mines. The variation of the investigated heavy metals between the workers at the different sites agrees with their concentrations in the phosphate mines. The enhancement of As, Cd and Pb in blood workers could be due to their accumulation through the inhalation of phosphate dust which may be released into the environment during mining process.

Heavy metal (µg/dL)	Control Mean ± SD n, 8	Workers *at Safaga*			Workers *at* El-*Hamrawein*			Workers *at* El-*Quseir*		
		Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)	Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)	Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)
As	0.046 ± 0.011	0.076 ± 0.015	0.121 ± 0.019	0.128 ± 0.039	0.077 ± 0.007	0.116 ± 0.032	0.123 ± 0.040	0.078 ± 0.021	0.149 ± 0.016	0.152 ± 0.008
Cd	0.086 ± 0.021	0.164 ± 0.027	0.162 ± 0.023	0.192 ± 0.060	0.181 ± 0.011	0.204 ± 0.018	0.224 ± 0.054	0.171 ± 0.025	0.194 ± 0.027	0. 214 ± 0.023
Pb	0.362 ± 0.068	0.994 ± 0.105	1.244 ± 0.027	1.662 ± 0.180	0.882 ± 0.161	1.218 ± 0.075	1.196 ± 0.227	0.868 ± 0.077	1.121 ± 0.088	1.068 ± 0.171

Table 4: Concentration of some heavy metals in blood workers (Mean ± SD and n, 10).

Parameters	Control Mean ± SD n, 10	Workers *at Safaga*			Workers *at* El-*Quseir*			Workers *at* El-*Hamrawein*		
		Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)	Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)	Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)
SOD U/g Hb	4.22 ± 0.85	8.91 ± 2.63	10.44 ± 2.89	11.54 ± 3.1	12.48 ± 3.11	15.49 ± 3.22	18.22 ± 3.89	7.22 ± 0.46	8.24 ± 0.97	10.83 ± 2.33
MDA U/L	10.22 ± 0.92	28.43 ± 2.32	32.58 ± 2.78	35.66 ± 2.98	24.35 ± 0.57	32.58 ± 3.11	38.75 ± 2.13	40.66 ± 3.44	46.75 ± 3.22	42.83 ± 3.89

Table 5: Concentration of SOD and MDA in blood workers (Mean ± SD and n, 10)

Blood Parameters	Control	Workers *at Safaga*			Workers *at* El-*Quseir*			Workers *at* El-*Hamrawein*		
		Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)	Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)	Age of 20 to 30 (year)	Age of 30 to 40 (year)	Age of 40 to 50 (year)
Hemoglobin mg/dl	12.55 ± 0.31	11.96 ± 0.21	11.02 ± 0.32	10.38 ± 3.3	12.46 ± 0.11	11.56 ± 0.33	10.4 ± 0.065	12.8 ± 0.14	11.27 ± 0.25	9.4 ± 0.13
Red cell count × 10^6/ cmm^3 mil	5.21 ± 0.09	4.34 ± 0.05	4.04 ± 0.08	3.96 ± 0.06	4.3 ± 0.02	4.14 ± 0.04	3.72 ± 0.073	21.6 ± 0.23	3.71 ± 0.024	3.38 ± 0.042
Leucocytic count/cmm	6450 ± 9.1	6744 ± 8.3	5830 ± 5.2	7300 ± 5.1	5819 ± 7.84	5770 ± 6.94	6360 ± 7.36	6970 ± 8.53	6750 ± 9.66	6300 ± 6.22
Platelet count × 10^3/ cmm	290 ± 3.8	185 ± 4.3	181.2 ± 2.3	152.2 ± 2.3	239 ± 2.48	187.6 ± 5.28	173.2 ± 4.22	237 ± 4.88	166 ± 2.85	115.4 ± 2.84

Table 6: Concentration of some blood characteristics for workers (Mean ± SD and n, 10).

Determination of hematological parameters

The prevalence of occupational health hazards for phosphate mine workers in *Safaga*, *Al Quseir* and EL-*Hamrawein*. The experimental study were designed according to three different age stage were start from (20-30 y), (30-40 y) and (40-50 y) male workers selected in three phosphate mine sites and were undergo to hematological studying and other biochemical studies. In this study the results in Table 4 shows the hematological parameters in Safaga phosphate mine workers at age (20-30) the Hemoglobin, Red cell count, Leucocytic count / and Platelet count recoded 11.96 mg/dl, 4.34 × 10^6/ cm^3 mil, 6744 cm^3 and 185 × 10^3 /cm^3 respectively. On the hand phosphate mine workers in safaga at age (30-40 y) recorded in Hb, RBC, WBCs and PLTC 11.02 mg/dl, 4.04 × 10^6/ cm^3 mil, 5830/cm^3 and 181.2 × 10^3/cm^3. Also mine workers in safaga at age (40-50) recorded in Hb, RBCs, WBCs and PLTC 10.38 mg/dl, 3.96 × 10^6/cm^3 mil, 7300 cm^3 and 152.2 × 10^3/cm^3. The interpretation of these results was concepts for the duration time and intervals periods for the phosphate mine workers. It was clear when the workers increased in intervals and progress in life age the hematological functions decreased. The phosphate mine workers were stress under the effects of inhalable particles of heavy metals, chemicals compounds and radioactive nuclides in phosphate rocks and ores, which leads to different types of occupational hazards diseases. This result was conformed with the results of [25], which observed on workers in phosphate mines were exposed to inhalable heavy metals and radionuclide for a long time lead to hematological disorders. The hematological disorders were take place in phosphate mine works undergoes the oxidative stress factors. Oxidative damage is one of the results of this imbalance, comprising oxidative modification of cellular macromolecules. It has long been recognized that ROS are harmful for cells, because they injure hemoglobin and RBCs, which leads to structural and functional impairments [8,9]. On the other hand hematological parameters in Al Quseir phosphate mine workers shows in Table 4 Hb, and RBCs, WBCs and Platelet count in workers revealed that normal limits in Hb% and RBCs, WBCs and platelet count for workers at age 20-30 y. Also workers at age 30-40 y recorded moderate level for hematological parameters. On the other hand workers at age from (40-50 y) recorded decreased in hematological parameters. The interpretation of the data was due to the interval period and long time for workers duration in phosphate mine. Also the age and life spine of workers it is notable in these data the oldest age workers do not have any resistance against oxidative stress and losses of antioxidant.

Determination of SOD and MDA

In this study it is evident that phosphate miners were exposed to oxidative stress emitted from the particles of heavy metals and radionuclides. The oxidative stress plays a role in damage of immune system and makes a hematological disorder for phosphate workers. These symptoms were very clear in oldest workers than youngest works. The results in Table 5 show the concentration of Supper Oxide Dismutase (SOD) and Malonaldyhde in blood of phosphate mine workers. The SOD and MDA recorded in safaga phosphate mine workers age (20-30 y) 8.91 ± 2.63 U/g Hb and 10.22 ± 0.92 U/L compared to control non-workers 4.22 ± 0.85 U/g Hb and 10.22 ± 0.92 respectively. This results was confirmed of results [26], he recorded that increased level of SOD activities in phosphate miners. Reduction in SOD activity as observed by us may be due to an increased endogenous production of ROS as evidenced by increased SOD. This decrease in antioxidant enzyme may be related to the consumption of activated enzymes against oxidative stress.

Table 5 shows the concentrations of SOD and MDA in Al Quseir and EL-Hamrawein phosphate mine workers. The data revealed highly increased SOD in Al Quseir phosphate mine workers at all age stage in compared to control group non workers. On the other hand data in Table 5, recorded slightly increased in SOD activity at EL-Hamrawein phosphate mine workers. Also MDA in EL-Hamrawein phosphate mine workers recorded highly activity for all interval age (20-30), (30-40 y) and (40-50 y) where 40.66 ± 3.44, 46.75 ± 3.22 and 42.83 ± 3.89 U/L) respectively in compared to non-workers control group 10.22 ± 0.92. These results was confirmed with [22], where recorded that MDA levels are increased in phosphate mine workers, due to exposure to particles of heavy metal and radionuclide. These toxic particles lead to oxidative stress. Increased oxidative stress generation free radicals and increased Reactive Oxygen Species (ROS). However, direct evidence for oxidative stress is often obscure following long-term and environmentally-relevant for workers in phosphate mines.

Conclusion

This study raveled that MDA and SOD acting as smart biomarkers for determination types and category of health impacts in phosphate miners workers during exposures to heavy metals and natural radioactivity. An increased serum MDA level in phosphate miners may indicate a general oxidant effect of phosphate heavy metals dust and natural radioactive nuclides. Also, decreased SOD activity in phosphate miner might be a marker of diminished antioxidant defense system which was caused by heavy metals and natural radioactivity.

The workers in phosphate miner's plants are more susceptible to health problems. MDA, SOD and hematological tests acting specific tests to confirm the effect of phosphate miner's pollutants can be carried out. This study investigation also occupational and heavy metals exposure in the phosphate miners. On the other hand we need to implement radiation regulations and standards through improving the working conditions to reduce the occupational radiation exposure to the accepted levels recommended by ICRP-and IAEA-Safety standard.

Radiological and environmental safety should be considered in phosphate mines. Regulations should be issued and applied by the administration of these sites. Radiological follow up should be a routine. Medical follow up system should be applied. Occupational health monitoring should be taken into consideration according to US EPA 2010 and WHO 2006 standard and regulation for health measurements in occupational mines.

The activity concentrations of the investigated radionuclides considerably fluctuated in the studied mines. The concentrations of ^{226}Ra are 5 to 10 times higher than that value recommended by IAEA 2000. The concentrations of ^{232}Th are 5 to 8 times higher than that value recommended by IAEA 2000. The ^{40}K concentrations are lower than that value recommended by IAEA 2000. The concentrations of the investigated heavy metals (As, Cd and Pb) in old ages of the occupational workers are higher than that of young ages, while these metals are concentrating in all ages more than the control people sample.

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