Natural radioactivity and radiation hazard assessment of industrial wastes from the coastal phosphate treatment plants of Gabes (Tunisia, Southern Mediterranean Sea)

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Abstract

This work is a first contribution to the knowledge of natural radionuclides (^{226}Ra, ^{238}U, ^{40}K, and ^{232}Th) activities in phosphate rock (NORM), phosphogypsum, and phosphogypsum foam (TENORM) from the coastal fertilizer plants of Gabes (Southeastern Tunisia) and the assessment of their radiation hazards on human health and the surrounding environment. In the three studied materials, activities were found to be in the range of 35.4 (^{40}K)-375.1 (^{226}Ra), 10.0 (^{40}K)-220.2 (^{226}Ra), and 79.2 (^{232}Th)-1168.6 Bq kg^{-1} (^{226}Ra), respectively. Considering the studied radionuclides and materials, the corresponding decreasing activity orders were found to be ^{226}Ra>^{238}U>^{40}K>^{232}Th and PGF>PR>PG, respectively. All human health hazard indices exceeded the worldwide recommended safety limits, which shows that the workers in Gabes phosphate fertilizer plants as well as the neighboring human community may potentially be exposed to significant radiation, which may cause several diseases and malformations. It is therefore recommended to avoid and/or reduce the potential fertilizer industry radioactive impact in the area.

***Keywords*:** Phosphate rock; Phosphogypsum; Phosphogypsum foam; Tunisian Chemical Group; Natural radioactivity; Radiation hazard assessment.

Human body is continuously exposed to terrestrial (rocks, soils, water, building materials, and atmosphere) and extraterrestrial (cosmic rays) sources of natural radiations (Amanjeet et al., 2017). However, it may be differently affected depending on the radiation types (α, β, or γ), received doses (low or effective dose), exposure times (acute, intermediate, and chronic), and exposure routes (ingestion, dermal, or inhalation) (ATSDR, 1990; INRS, 2012). The International Agency for Research on Cancer (IARC) classified all types of these ionizing radiations as carcinogenic to humans (Group 1; IARC, 2012). However, the development of human health effects due to radiation may take years (Lenntech, 2018). For example, exposure to thorium can affect lungs, bone marrow, bone surface, and gonads (INRS, 2013), while exposure to uranium affects the liver, bone marrow, bone surface, lungs, colon, and gonads (INRS, 2014). Within the same context, the Agency for Toxic Substances and Disease Registry (ATSDR) reported that the long-term exposure to U and Ra inhalation could lead to serious diseases including acute leucopoenia, chronic lung diseases, mouth necrosis, and anemia (ATSDR, 1990, 1999, 2012a). For instance, humans exposed to radon inhalation can develop lung cancer; those exposed to radium inhalation can develop numerous cranial, nasal, and bone tumors (ATSDR, 1990, 1992). Exposure to thorium was also reported to be at the origin of different cancers (lung, hepatic, pancreas, bone, kidney, and blood; ATSDR, 1992). Several human activities, especially mining activities, have allowed the dispersion of radionuclides into the environment (Hilal et al., 2014), thus leading to its radiological contamination, as it is the case for phosphate mines and the associated agricultural fertilizer production industrial activities (Sahu et al., 2014; Gaafar et al., 2016). Therefore, both phosphate mining and phosphate industrial processing increase the exposure risks on workers, inhabitants, and natural environments to these naturally radionuclides (Sahu et al., 2014). Presently, it is important to evaluate these radiation hazards to protect the natural environment in general and human health in particular.

Sedimentary origin phosphate rocks (PR) are considered as naturally occurring radioactive materials (NORM) because they contain uranium (^{238}U) and thorium (^{232}Th) radioisotope series and natural ^{40}K (Gaafar et al., 2016; Rutherford et al., 1994; Uosif et al., 2014). The uranium series predominate in PR because U^{4+} replaces Ca^{2+} in calcium phosphate ($Ca_3(PO_4)_2$; Sabiha-Javied and Asghar Tufail, 2010). Indeed, this type of PR can contain up to 1500 Bq kg^{-1} of ^{238}U series (UNSCEAR, 1993) and in some other ores up to 20×10^3 Bq kg^{-1} of U_3O_8 (Paschoa and Godoy,

2002). The manufacturing fertilizer industrial process allows concentration of PR radioactive elements in the product (phosphoric acid, PA) and by-product (phosphogypsum, PG) (Rutherford et al., 1994; UNSCEAR, 2008). Additionally, this industrial process generally produces some particles and gaseous emissions enriched with ^{226}Ra and ^{238}U (Gaafar et al., 2016). Therefore, PR processing is considered one among numerous industrial activities that produce Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM; Egidi and Hull, 1999). Thus, they represent a potential source of natural radionuclides contaminating the environment (Sahu et al., 2014) and posing a threat to human health. However, despite their potential risks to the environment and public health in workplaces and neighborhood of factories, TENORM wastes of fertilizer factories, such as PG (USEPA, 2002), are worldwide poorly managed (Sahu et al., 2014). Indeed, only 15% of PG worldwide production is recycled (Tayibi et al., 2009), and between 85 and 238×10^6 t of untreated PG are annually stored in nonweathering process-protected stockpiles (like Gafsa and Sfax in Tunisia and Huelva in Spain) or discharged directly into the aquatic environment (river or sea), like in the Gulf of Gabes (Southeastern Tunisia). PG radioactivity, which is mostly due to ^{226}Ra and its progeny radionuclides (Rutherford et al., 1994), constitutes the main environmental challenge for several phosphate-producing countries (e.g., China, USA, Russia, Morocco, and Tunisia).

In the 70s, the Tunisian Chemical Group (GCT) began its industrial activities in Gabes (Fig. 1a). These factories used sulfuric acid in a dehydrated wet process to transform Tunisian PR to PA, with production of by-products of huge PG quantities ($\approx30\times10^3$ t day^{-1} of untreated humid PG; El Zrelli et al., 2018a). Although the dehydrated wet process used is economic, it by-produces large quantities of polluted PG (5 t of PG for each ton of PA produced; Rutherford et al., 1994). Indeed, every year, nearly 10.5×10^6 t of this untreated TENORM wastes, which contain 8.41 of U and 3.89 t of Th, are dumped directly into the Gabes Sea (El Zrelli et al., 2018b). During the last 40 years, this potentially high radio-pollutant load has been progressively dispersed into the Gabes Gulf, as shown by Muller et al. (2009) and El Zrelli et al (2019a). In addition to PG wastes, huge quantities of untreated PR are dumped in Chatt Essalam Beach (Fig. 1b), close to the phosphate fertilizer factories of Gabes (El Zrelli et al., 2019a). Numerous studies were carried out recently on the effects of discharged PG on the marine environment and life in Gabes, concluding that the industrial discharges caused serious environmental damages including

biodiversity loss (Rabaoui et al., 2010, 2015; El Kateb et al., 2016), degradation of seawater (Darmoul, 1988; Rabaoui et al., 2014; El Zrelli et al., 2018a), and sediment quality (Ayadi et al., 2014; El Zrelli et al., 2015, 2019a; Rabaoui et al., 2015; El Kateb et al., 2018) and regression of key habitats such as *Posidonia oceanica* meadows (El Zrelli et al., 2017). However, all these latter studies focused only on the effect of metallic pollution and did not consider the radioactive impact generated by the local factories. To the best of our knowledge, despite their potential radiological effects, no studies were carried out thus far on the concentration and dispersion of radioactive pollutants related to Gabes phosphate industry, NORM and TENORM, neither on their impact on human health. This work is the first study conducted with regard to this purpose. It aims *i*) to determine the activities of ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U in PR, PG, and PG foams (PGF; formed after PG marine dissolution; El Zrelli et al., 2019b; Fig. 1c) from the local factories and *ii*) to assess their radioactivity risks on humans in the central area of Gabes Gulf, using various human health assessment indices. This study can be a useful baseline for future projects on monitoring and protection of the Gabes Gulf environment from the phosphate industry-related pollution and management of PG wastes in other countries with phosphate fertilizer industry.

PR, PG, and PGF composite samples were collected from the same phosphate fertilizer industrial site (Gabes factories) during September-October 2014 (for more details, see El Zrelli et al., 2018b, 2019b). To consider the spatial variability in the three different materials, 3 PR subsamples from trucks load transporting the fertilizer production raw ores, 4 PG subsamples from the filter of the phosphoric acid processing chain, and 10 PGF subsamples from the littoral discharge of industrial wastes were separately collected, mixed, and homogenized to produce 3 final representative composite samples. In the laboratory, samples were separately oven-dried, at 50°C for 5 days, to constant weights, milled to fine powder, and homogenized. Three specimens were thereafter packed in cylindrical plastic box (85.82 g of PR; 47.77 g of PG; and 34.85 g of PGF) and sealed under vacuum to prevent any radon loss. The samples were analyzed six months after preparation to ensure that the secular equilibrium between ^{226}Ra and its short-lived daughters is reached and that the ^{234}Th analyzed in the samples can be related to ^{238}U (i.e., no remaining excess of ^{234}Th in the samples).

The samples were analyzed at LAFARA (LAboratoire de mesure des FAibles RAdioactivités) underground laboratory, located in the tunnel of Ferrières (Ariège, French Pyrénées, France; van Beek et al., 2013). We used a high-purity germanium detector (semi-planar, p-point contact, detector; ORTEC-AMETEK PROFILE-FX series) with a diameter of 85 mm and a thickness of 33.2 mm (volume of 183 cm^3). This gamma-ray spectrometer is placed under 85 m of rock (ca. 215 m water equivalent), which protects the detector from cosmic rays, thus reducing the background.

^{226}Ra activities were determined from the γ photo peaks of ^{214}Pb and ^{214}Bi (295, 352, and 609 keV). ^{40}K activities were determined using the 1460 keV peak. The 2615 keV peak of ^{208}Tl was used to estimate the activity of thorium-232, assuming that ^{208}Tl is in secular equilibrium with ^{232}Th in the samples (Ademola and Olatunji, 2013; Ademola et al., 2014). ^{238}U activities were determined from the ^{234}Th ($T_{1/2}$= 24.1 d) activities (using the 63.3 keV peak), which are in secular equilibrium with ^{238}U.

We used three internationally provided standards (RGU-1, RGTh-1, and IAEA-375) to calibrate the LAFARA gamma-ray spectrometer detector, similarly to Li et al. (2017). RGU-1 and RGTh-1, provided by IAEA (International Atomic Energy Agency), are reference materials prepared using U and Th ores, respectively, and diluted with floated silica powder. It deals in fact with ^{238}U, ^{235}U, and ^{232}Th standards, with all the series' daughters being in secular equilibrium to determine the detection efficiencies associated with gamma-ray lines produced by gamma-ray emitters of ^{238}U, ^{235}U, and ^{232}Th series (mainly ^{210}Pb, ^{234}Th, ^{226}Ra, ^{223}Ra, ^{214}Pb, ^{214}Bi, ^{228}Ac, ^{212}Bi, and ^{208}Tl). The IAEA-375 standard was used to determine the detection efficiencies for ^{40}K.

To assess the human health radiological hazards associated with the exposure to radiations emitted by natural radionuclides present in PG, PR, and PGF samples, 4 different indices were taken into consideration. These indices include the following:

- Outdoor absorbed gamma dose rate (D_{out})

D_{out} was proposed to estimate the total outdoor (UNSCEAR, 2000) absorbed dose rates at 1 m above the ground surface, due to γ-ray emission in air from ^{226}Ra, ^{232}Th, and ^{40}K. This index can be calculated as follows:

$D_{out} = 0.462\ C_{Ra} + 0.621\ C_{Th} + 0.0417\ C_K$(in nGy h^{-1}) (1)

where 0.462, 0.621, and 0.0417 and C_{Ra}, C_{Th}, and C_K are the dose rate factors (in nGy·h^{-1}/Bq kg^{-1} (E.C., 1999; UNSCEAR, 2000)) and the activities (in Bq kg^{-1}) of radium, thorium, and potassium, respectively.

- Outdoor annual effective dose equivalent ($AEDE_{out}$)

As proposed by UNSCEAR (2000), $AEDE_{out}$ can be determined as follows:

$AEDE_{out} = D_{out} \times T \times F \times 20\%$ (2)

$AEDE_{out} = D_{out} \times 1.226$ (in μSvy^{-1}) (3)

where D_{out} is the outdoor absorbed gamma dose rate (in $nGyh^{-1}$); T is the time to convert from year to hour (8760 hours); F is the conversion factor, which is equal to 0.7 $\mu SvGy^{-1}$ for adults and 20% are the outdoor stay times, respectively.

- Annual gonad dose equivalent (AGDE)

The gonads, active bone marrow, and bone surface cells are the most sensitive human organs to radiations and are thus considered as organs of interest by the UNSCEAR (1988). AGDE can be calculated following the equation proposed by Mamont-Ciesla et al. (1982):

$AGDE = 3.09\ C_{Ra} + 4.18\ C_{Th} + 0.314\ C_K$(in Bq kg^{-1}) (4)

where C_{Ra}, C_{Th}, and C_K are the activities in Bq kg^{-1} of ^{226}Ra, ^{232}Th, and ^{40}K, respectively.

- Outdoor Excess lifetime cancer risk ($ELCR_{out}$)

Outdoor exposure to ionizing radiations, in particular β and γ rays, increases the likelihood of developing cancer in humans. This risk can be estimated by the $ELCR_{out}$, which is calculated using the following formula (Qureshi et al., 2014):

$ELCR_{out} = AEDE_{out} \times DL \times RF$ (in $mSvy^{-1}$) (5)

where $AEDE_{out}$, DL, and RF are the outdoor annual effective dose equivalent, average lifetime duration (75 years for Tunisian people), and fatal risk factor per Sievert (0.05 Sv^{-1}) (ICRP, 2008), respectively.

The activities of the studied naturally occurring radionuclides in PR, PG, and PGF samples are shown in Table 1, with the values represented in Bq kg^{-1} of dry weight. For the three materials analyzed, the highest and lowest activities were recorded with ^{226}Ra and ^{232}Th, respectively. Radionuclides' activities in PR, PG, and PGF ranged from 35±4 (^{40}K) to 375±1 (^{226}Ra), 10±2 (^{40}K) to 220±1 (^{226}Ra), and 79±3 (^{232}Th) to 1169±3 (^{226}Ra) Bq kg^{-1}, respectively. PGF was found to be the most enriched in radionuclides (2011±5 Bq kg^{-1}), followed by PR (671±3 Bq kg^{-1}) and PG (253±2 Bq kg^{1}). These wide differences of radioactive contents are most likely due to the variability of chemical, physical, and geochemical properties between the studied materials (Sam et al., 1998) and also to the different chemical behaviors of radionuclides that may concentrate (or not) into one specific phase compared to others. For instance, the variable organic matter content between the three materials analyzed is one of the key factors explaining the variability in radionuclide load. In fact, El Zrelli et al. (2018b, 2019b) reported that the organic matter concentrations in Tunisian PR, PG, and PGF are equal to 2.99±0.11%, 0.50±0.02%, and 24.70±1.24% of dry weight, respectively. According to Chuang et al. (2015), organic compounds have high chelating affinity to radionuclides through particular strong binding sites (e.g., −OH, −O=POOO−, −COOH, and −R-S-R−). This property plays an important role in PGF radionuclide overload and also in the dispersion of these radioactive pollutants in the Gulf of Gabes through the marine migration of these industrial foams (El Zrelli et al., 2019b), as shown in Fig. 1.

$^{232}Th/^{238}U$ activity ratios of PR and PGF were found to be lower than 1, indicating that these 2 materials are uranium-enriched. This is in concordance with the results of El Zrelli et al. (2018b, 2019b). The U enrichment of Tunisian PR is mainly due to its sedimentary origin (Gaafar et al., 2016; Sabiha-Javied and Asghar Tufail, 2010), whereas that of PGF is due to its high concentration of organic matter (El Zrelli et al., 2019b). For PG, $^{232}Th/^{238}U$ ratio activity was found to be equal to 1, indicating that PG is U-impoverished. This impoverishment in U is explained by the fact that PR uranium load concentrates primarily into PA following the PR sulfuric acid attack (Rutherford et al., 1994), thus leading to the accumulation of only 5% of PR uranium in PG (UNSCEAR, 2008). The U impoverishment of PG is therefore mainly due to the uranium chemical fractionation in favor of PA. Thus, U enrichment/impoverishment resulting from the chemical process is responsible for the

radioactive disequilibrium observed between uranium and its progenies with which the $^{238}U/^{226}Ra$ ratio was below unity (Table 1).

Table 2 compares the activities of ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U between Tunisian PR and PG and those from other regions. ^{226}Ra PR activity concentrations reported herein were found to be higher than those found in Italy (Righi et al., 2005) and Finland (Mustonen, 1985) but lower than those recorded in Egypt (El-Bahi et al., 2017), India (Sahu et al., 2014), America (Guimond and Hardin, 1989), Saudi Arabia (AlZahrani et al., 2011), Morocco (Guimond, 1990), and Nigeria (Jibiri and Fasae, 2012). ^{232}Th activity of Tunisian PR appeared to be similar to that of Saudi Arabian PR (AlZahrani et al., 2011), lower than those of Egyptian (El-Bahi et al., 2017), Indian (Sahu et al., 2014), American (Guimond and Hardin, 1989), and Nigerian (Jibiri and Fasae, 2012) PRs, and higher than those of Italian (Righi et al., 2005), Moroccan (Guimond, 1990), and Finnish (Mustonen, 1985) PRs (Table 2). Tunisian PR was found to be less concentrated in ^{40}K than the PR of other countries, except for India and Morocco (Table 2). ^{238}U in Tunisian PR was lower than that in PR of other countries, with limited reports (Table 2). Taking into account ^{226}Ra, Tunisian PG was found to be less concentrated than the PG of other countries, except for Brazil (Borges et al., 2013). PGs of all other countries, except for Brazil (Borges et al., 2013) and Egypt (El-Bahi et al., 2017), were found to be less concentrated in ^{232}Th than the Tunisian PG (Table 2). In the case of ^{40}K, only Serbian (Rajkovic and Toskovic, 2002) and Indian (Sahu et al., 2014) PGs showed lower activities than the Tunisian PG. Tunisian PG is the least rich in ^{238}U compared to that in the PG of all other countries (Table 2). The differences in PR and PG radionuclide activities are most likely due to the different origins of PR (sedimentary or igneous), PA production processes (e.g., PR reactivity, properties of added reagents), and PG age (fresh or old) (Sabiha-Javied and Asghar Tufail, 2010; El-Bahi et al., 2017; Gaafar et al., 2016; El Zrelli et al., 2018b).

The calculated values of radiation hazard indices taken into consideration are listed in Table 3. For D_{out}, the obtained values were found in the range of 109.04 (PG)-594.79 $nGyh^{-1}$ (PGF), with an average of 300.96 $nGyh^{-1}$. D_{out} calculated values were found to be higher than the global averages, that is, 59 $nGyh^{1}$ (UNSCEAR, 2000; Table 3). $AEDE_{out}$ ranged from 0.13 (PG) to 0.73 $mSvh^{-1}$(PGF). The mean value of $AEDE_{out}$ was found to be 0.37 $mSvh^{-1}$. The obtained values were higher than the worldwide average, that is, 0.07 $mSvh^{-1}$(UNSCEAR, 2000; Table 3). AGDE

ranged from 0.73 for PG to 3.99 $mSvy^{-1}$ for PGF with a mean value of 2.02 $mSvy^{-1}$. The calculated AGDE values were found to be very high compared to the worldwide average value (i.e., 0.3 $mSvy^{-1}$; Mamont-Ciesla et al., 1982; Table 3). Finally, we found that the obtained $ELCR_{out}$ values ranged from 0.50×10^{-3} (PG) to 2.73×10^{-3} (PGF), with an average of 1.38×10^{-3}. All calculated values were very high compared to the worldwide average, which is equal to 0.29×10^{-3} (Taskin et al., 2009; Table 3).

Fig. 2 shows a comparison of the 4 calculated radiological hazard indices in the three materials analyzed with worldwide permissible limits. The descending order of hazard values, with regard to the analyzed material types, is as follows: PGF>PR>PG. Our results exceeded most of the safety limits recommended by several international commissions (UNSCEAR, EC, and ICPR). With some indices such as AGDE, the values found for PR, PG, and PGF were 343%, 143%, and 1230% higher than the standard safety limits, respectively (Table 3). With the lack of official studies on phosphate industry environmental and human health impacts, these results provide a clear idea about the NORM and TENORM potential radiological hazards related to the phosphate fertilizer plants of Gabes. According to the higher $ELCR_{out}$ values found herein (Table 3), humans who are in continuous contact with PR, PG, or PGF (workers, fishermen, and inhabitants) are probably exposed to total effective doses that may be responsible for several carcinogenic diseases (El Zrelli et al., 2019b). Within this context, Mahjoubi et al. (2000) reported average ^{222}Rn concentrations equal to 1785 and 3855 Bq m^{-3} in the phosphoric acid plant of Sfax and M'dhilla PG stockpiles, respectively. These values are extremely high compared to the safety limit recommended by the International Commission on Radiological Protection (i.e., 200 Bq m^{-3}; ICRP, 1993). It is worth noting that ^{222}Rn is a harmful radioactive gas produced by ^{226}Ra of PG (Rutherford et al., 1994), which is responsible for serious damages of human internal organs (USEPA, 2002), in particular lung cancer (ATSDR, 1990, 2012b). Moreover, human gonads are among the most sensitive organs to radiation (UNSCEAR, 1988), which may cause, depending on the received doses, serious potential genetic effects (Lejeune, 1985). According to NRC (1990) and ICRP (1977), the estimated risk of serious birth defects in the future progenies of parents, irradiated with an annual dose of 10^4 µSv, ranges between 2×10^{-3} and 3×10^{-3}%. Based on the average AGDE recorded herein (2.02 $mSvy^{-1}$), a 30-year old man must have accumulated a gonad dose equivalent to 6.06×10^4 µSv. This is likely to

correspond to a risk of birth defects in future progenies, which is estimated to be between 12.04×10^{-3} and 18.8×10^{3}%. These values are 6 times higher than the risk values calculated with the recommended AGDE safety limit (1.8×10^{-3} to 2.7×10^{-3} of risk). Various diseases and illnesses observed with locals (e.g., birth defects, cancers, repetitive abortion, infertility, impotence, paralysis, cardiovascular, and chronic respiratory diseases; El Zrelli et al., 2019b) may be linked to the potential hazards of industrial pollutants (El Zrelli et al., 2019b; Rabaoui et al., 2014 and 2017).

Table 4 provides estimates of the annual releases of ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U from PR, PG, and PGF in the working and natural environment of Gabes fertilizer factories. Radionuclides were found to be more released from PR than from PG and PGF, with total released amounts equal to 2008.0, 1328.7, and 214.0 x 10^{9} Bq y^{-1}, respectively. According to Righi et al. (2005), the atmospheric release of particulate matter from plant smokestacks could increase the release amount of radionuclide in the environment surrounding the factory. In our case study, PR is stocked in GCT plants (Fig. 3a), occasionally discharged in the marine environment, and consequently accumulated in Chatt Essalam Beach (Fig. 3b; see also El Zrelli et al., 2019b). Thus, PR represents a potential source of radiological hazards to workers and neighboring inhabitants. The exposure to radiological risks could be enhanced by irradiation and/or internal (by inhalation or ingestion of windborne PR fine particles) and external (by deposition of PR fine particles on the skin or clothes) contamination. The radiological effects of GCT factories on the coastal environment are mainly due to the huge marine discharges of untreated PG (a cumulative quantity of more than 200 million tons since 1972; El Zrelli et al., 2018b). In addition, the marine migration of PGF allows to disseminate the industrial radionuclide contaminants toward other Mediterranean areas (El Zrelli et al., 2019b). Within this context, it is worth noting that changing the currently used phosphate fertilizer production process in GCT (based on wet process phosphoric acid, WPA) with a less harmful one has the potential to drastically reduce the annual fluxes of radionuclides (Table 4), as already shown in other factories such as Ravenna plants in NE Italy (Righi et al., 2005). For instance, replacing the sulfuric acid (H_2SO_4) by nitric acid (HNO_3) during PR acid attack will prevent the formation of PG, which is considered one of the main causes of radioactive pollution related to phosphate fertilizer production (Haridasan et al., 2001;

Righi et al., 2005). This can be more enhanced with the prevention of outdoor PR storage and/or PR discharges in the local marine environment.

From an environmental point of view, no studies on the effects of radiation on local marine and terrestrial organisms were conducted thus far. El Zrelli et al. (2018a) recently reported fish skeletal malformations in Chatt Essalam Beach, which can be probably linked to radioactive pollution, as pointed out in other studies (Trapeznikov et al., 1994; Bogutskaya et al., 2011). In the same sense, Ayadi et al. (2015) noted the presence of numerous test morphological abnormalities with some benthic foraminiferal species, near Gabes phosphate factories. Seagrass abundance was also reported to drop close to Gabes phosphate fertilizer plants (El Zrelli et al., 2017). During this study, several dead and malformed marine organisms (Fig. 4) were observed, between 2017 and 2018, along Chatt Essalam Beach (Fig.1b).

This is the first assessment of radiological hazards related to natural radioactivity of Gabes phosphate fertilizer factories (NORM and TENORM). Activity concentrations of ^{226}Ra, ^{238}U, ^{40}K, and ^{232}Th in PR, PG, and PGF were measured by γ ray-spectrometry. All radiological indices appeared to exceed the safety limits recommended by international commissions, leading to deduce that NORM and TENORM materials from local phosphate fertilizer plants may pose potential radiation hazards to neighboring community and marine environment. More investigations and continuous monitoring programs are therefore needed to avoid and/or reduce these potential radiation risks and limit their effects on the environment and human health. According to these results, untreated phosphogypsum wastes should not be directly thrown into the natural environment, neither reused nor stored on stockpiles, unless their hazardous load has been removed. The following recommendations are suggested:

- Ban dumping of PG discharges and other liquid and solid phosphate industry wastes into the marine environment of Gabes Gulf.
- Program and conduct a rapid and effective decontamination plan of the impacted marine environment.
- There is necessity to conduct epidemiological and environmental studies on the potential effects of the hazardous phosphate industry wastes on the local environment and human community.

- Limit the exposure of the local population to the potential radiation risk through the establishment of an exclusion zone in which all human activities (such as fishing and swimming) are prohibited.
- Monitor the radioactivity levels and ionizing radiation exposure levels of workers in fertilizer plants. Wherever necessary, protect the workers in fertilizer plants against the potential radiation hazards.
- Prohibit the industrial overexploitation of groundwater to avoid any marine intrusion that may be responsible for a potential radioactive contamination of the waters used mainly in agriculture and potability.
- Prohibit the use of PR and untreated PG as agriculture fertilizers in Gabes agricultural areas.
- Modernize the phosphate fertilizer factories and adopt a non-phosphogypsum-producing process.

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677 **Table 1**. Activity concentrations (Bq kg^{-1}) of ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U in phosphate
678 rock (PR), phosphogypsum (PG), and phosphogypsum foam (PGF) samples. The total
679 concentrations of the radionuclides (∑ of radionuclides), as well as the ratios
680 $^{232}Th/^{238}U$ and $^{238}U/^{226}Ra$ are also given. *(UNSCEAR, 2000).
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Radionuclides/Ratios	**PR**	**PG**	**PGF**	**Average**	**Worldwide***	
					Average	**Range**
^{226}Ra	375±1	220±1	1169±3	588±2	35	17-60
^{40}K	35±4	10±2	137±6	61±4	400	140-850
^{232}Th	39±2	11±1	79±3	43±2	30	11-64
^{238}U	221±5	12±3	626±10	286±6	35	16-110
∑ of radionuclides	671±3	253±2	2011±5	978±3	500	184-1084
$^{232}Th/^{238}U$	0.2	1.0	0.1	0.4	-	-
$^{238}U/^{226}Ra$	0.6	0.1	0.5	0.4	-	-

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689 **Table 2.** Comparison of activity concentrations of ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U ($Bqkg^{-1}$) in Tunisian phosphate rock (PR) and phosphogypsum
690 (PG) with the finding of other studies in other countries.

Material	Countries	^{226}Ra	^{40}K	^{232}Th	^{238}U	References
PR	Tunisia	375.1±1.4	35.4±3.8	39.1±1.8	221.3±5.0	Present work
	Egypt	786	765	85	1031	El-Bahi et al. (2017)
	India	1.29×10^3	0.01×10^3	0.09×10^3	1.34×10^3	Sahu et al.(2014)
	Italy	120	4000	3.5	-	Righi et al. (2005)
	USA	780	200	49	-	Guimond and Hardin (1989)
	Saudi Arabia	513	242	39	-	AlZahrani et al. (2011)
	Morocco	1600	10	20	1700	Guimond (1990)
	Finland	54	3200	11	-	Mustonen (1985)
	Nigeria	1038	536	257	-	Jibiri and Fasae (2012)
PG	Tunisia	220.2±1.0	10.0±1.7	11.1±0.9	11.5±2.9	Present work
	Korea	618	24	9	-	Song et al. (2011)
	Jordan	376	40	4	-	Al-Jundi et al. (2008)
	Serbia	439	8.7	8.7	-	Rajkovic and Toskovic (2002)
	India	0.3×10^3	0.005×10^3	0.01×10^3	0.03×10^3	Sahu et al. (2014)
	Spain	647	33	8	-	Oueñas et al. (2010)
	Brazil	95	99	131	36	Borges et al. (2013)
	Egypt	550	870	79	663	El-Bahi et al. (2017)
	Syria	259	-	1.9	33	Attar et al. (2011)

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692 **Table 3.** Values of radiation hazard indices calculated based on the results of activity
693 radionuclides in phosphate rock (PR), phosphogypsum (PG), and phosphogypsum
694 foam (PGF) collected from Gabes phosphate fertilizer plants. *UNSCEAR (2000),
695 **Mamont-Ciesla et al. (1982), ***Taskin et al. (2009).

Radiation Hazard Indices	**PR**	**PG**	**PGF**	**Average**	**Permissible limits**
D_{out} ($nGyh^{-1}$)	199.05	109.04	594.79	300.96	59.0*
$AEDE_{out}$ ($mSvh^{-1}$)	0.24	0.13	0.73	0.37	0.07*
AGDE ($mSvy^{-1}$)	1.33	0.73	3.99	2.02	0.30**
$ELCR_{out}$ ($\times 10^{-3}$)	0.92	0.50	2.73	1.38	0.29***

Table 4. Estimated annual releases of ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U from phosphate rock (PR), phosphogypsum (PG), and phosphogypsum foam (PGF) in the working and natural environment of Gabes fertilizer plants. *Average 1990-2015.

	Annual quantities	**Radionuclide (10^9 Bq y^{-1})**			
		^{226}Ra	**^{40}K**	**^{232}Th**	**^{238}U**
PR	2 993 10^3 t*	1 122.7	106.0	117.0	662.4
PG	5 256 10^3 t	1 157.4	52.6	58.3	60.4
PGF	106.4 10^3 t	124.3	14.6	8.4	66.6

713 **Figure Captions**

714 **Fig. 1.** Figure showing the locations of the phosphate treatment plants in Gabes, southeastern
715 Tunisia (**a**) and industrial littoral discharge in Chatt Essalam Beach (between the commercial
716 and fishing ports of Gabes) (**b**) and the marine migration of phosphogypsum foam (**c**).

717 **Fig. 2.** Comparison (%) of calculated radiological hazard indices with worldwide permissible
718 limits.

719 **Fig. 3.** Photograph showing the outdoor phosphate (PR) storage in GCT factories (**a**) and its
720 accumulation along Chatt Essalam Beach (**b**).

721 **Fig. 4.** Photographs of some organisms often found dead, between 2017 and 2018, in Chatt
722 Essalam Beach (Fig. 1). *Caretta caretta* (**1a**, **1b,** and **1c**), *Tursiops truncatus* (**2**),
723 *Phalacrocorax carbo* (**3**), *Podiceps cristatus* (**4**), *Liza aurata* with skeletal malformations (**5**).

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Italy
Tunisia
Mediterranean Sea
Algeria
Libya
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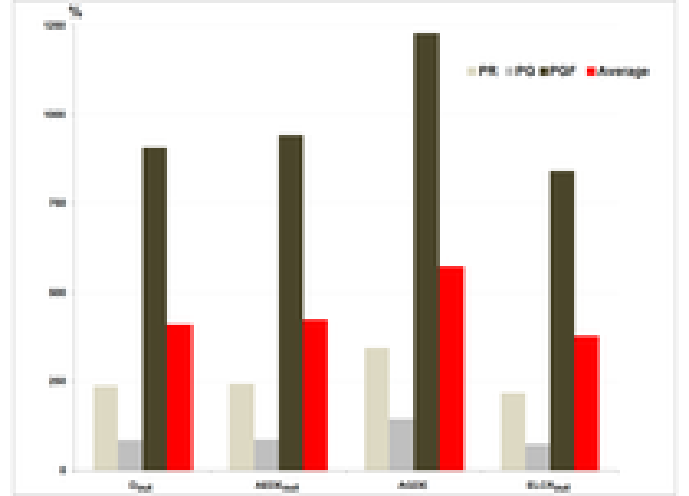
Gulf of Gabes
Commercial harbor
GCT
Industrial littoral discharge
PGF
Chatt Essalam beach
Fishing harbor
c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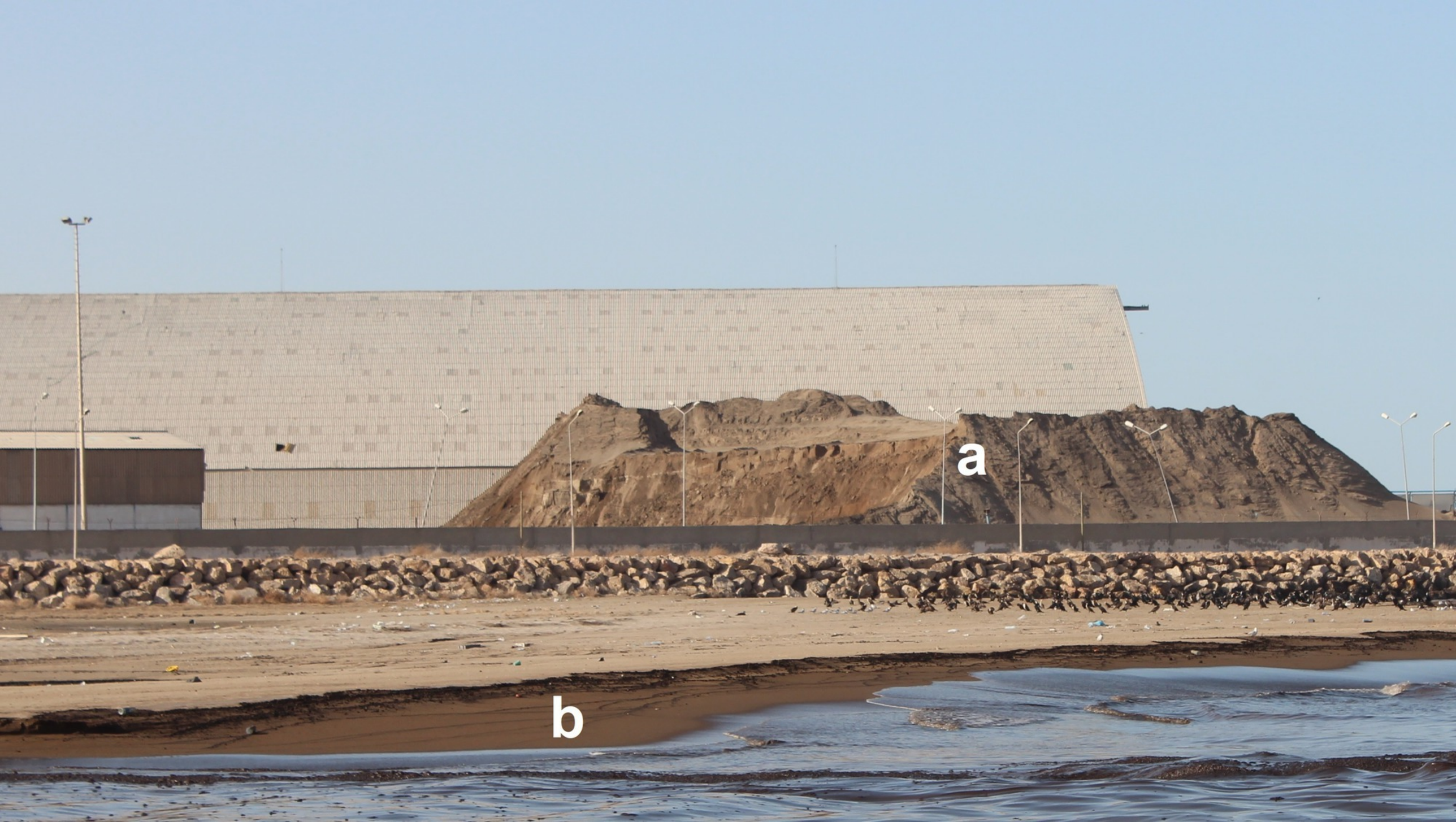
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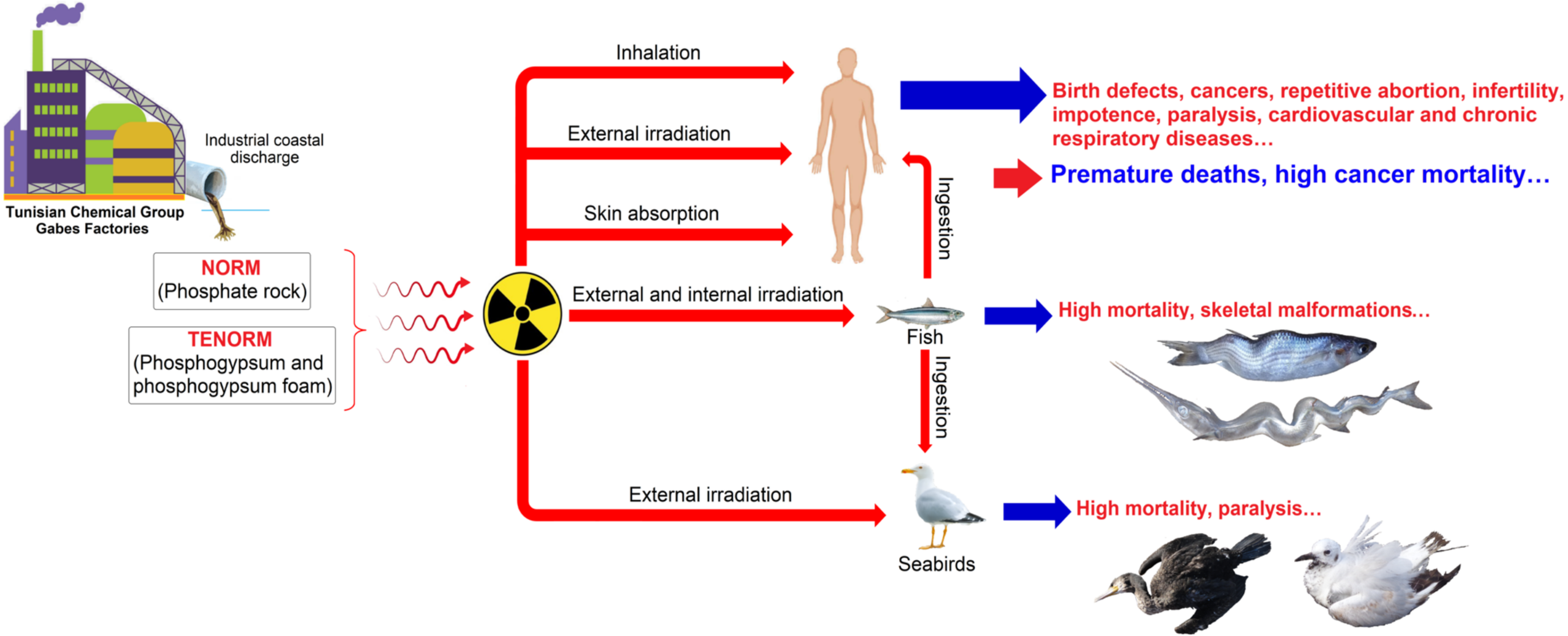
Industrial coastal discharge
Tunisian Chemical Group
Gabes Factories
NORM
(Phosphate rock)
TENORM
(Phosphogypsum and phosphogypsum foam)
Inhalation
External irradiation
Skin absorption
External and internal irradiation
External irradiation
Ingestion
Ingestion
Fish
Seabirds
Birth defects, cancers, repetitive abortion, infertility, impotence, paralysis, cardiovascular and chronic respiratory diseases…
Premature deaths, high cancer mortality…
High mortality, skeletal malformations…
High mortality, paralysis…