A PROTOCOL FOR RADIOLOGICAL EVALUATION OF NORM INDUSTRIES

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INTRODUCTION (I)

Based in the experience gained during 15 years by both research groups in the radiological evaluation of NORM industries in Spain.

Formed by two sections devoted to the occupational and environmental radiological evaluation in each industry, respectively.

Each section is formed by different phases in such a way that the protocol has to be applied in a sequential form, being not necessary the application of all the phases in all cases.

In the great majority of NORM industries will be enough with the application of the first phases if the conclusions derived from their application is that occupational effective doses are clearly lower than 1 mSv/year, and the environmental radiological impact is quite limited.

Only in specific cases, where the application of the first phases conduit to the possibility of occupational and/or environmental doses near or even higher than 1 mSv/y, the final phases of the protocol with a detailed radiological evaluation should be applied.

INTRODUCTION (II)

With the proposed "graded approach" the efforts are optimized and the economic impact of these studies for the industries is minimized.

Practical Implementation

(1) **Industry devoted to the production of phosphoric acid using sedimentary phosphate rock.**

(2) Industry devoted to the production of titanium dioxide pigments by the sulphate method.

OCCUPATIONAL PROTOCOL

The protocol in its occupational side is formed by three different phases to be applied in a sequential form.

A priori only obligatory the application of the first one in all the chemical industries that can be considered affected by the Title VII of the European BSS.

First phase

- **Identification of the different materials involved in the production process of the industry under evaluation**

- **Detailed information about the management processes applied to the raw materials, final products, co-products and residues.**

- **Detailed design of a flux diagram reflecting the production process of the industry under evaluation**

- **Precise quantification of the amounts of materials involved in the production process**

OCCUPATIONAL PROTOCOL

First phase (cont)

Identification of the places inside the industry where the raw materials, co-products, final products and wastes are stored.

Sampling of representative aliquots of the raw materials co-products and wastes and determi… t.

Cl

- Uranium isotopes: ^{238}**U**, ^{234}**U**
- Thorium isotopes: ^{232}**Th**, ^{230}**Th**, ^{228}**Th**
- Radium isotopes: ^{226}**Ra**, ^{228}**Ra**
- Lead isotopes: ^{210}**Pb**
- Polonium isotopes: ^{210}**Po**
- Potasisium Isotopes: ^{40}**K**

All industries qualified as a no NORM industries, should repeat the application of this first phase every time that the production process experiment significant changes or the origin and main characteristics of the raw materials change.

If the industry is not classified as NORM, then the protocol can be considered finished. If is classified as NORM, then the next step of the protocol should be applied.

OCCUPATIONAL PROTOCOL

IMPLEMENTATION FIRST PHASE IN THE LOCAL INDUSTRIES

Phosphoric acid plant

. Activity concentrations (Bq/kg)			
Sample type	^{238}U	^{226}Ra	^{228}Ra
Raw PR	1840 ± 130	1560 ± 80	22 ± 2
Buk milled PR	1640 ± 90	1722 ± 90	20 ± 2
Optimum size PR	1630 ± 90	1780 ± 90	22 ± 2

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NORM INDUSTRY

In opinion of the authors of this work, all the industries using raw materials with activity concentrations for the components of the uranium and thorium series higher than 1 Bq/g should be evaluated radiologically with high detail.

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OCCUPATIONAL PROTOCOL

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IMPLEMENTATION FIRST PHASE IN THE LOCAL INDUSTRIES

Titanium Dioxide plant

ILLMENITE (Bq/Kg)					
	^{238}U	^{234}U	^{226}Ra	^{228}Ra	^{228}Th
ILM-1	118.5 ± 5.5	135.7 ± 6.4	93 ± 7	296 ± 20	306 ± 21
ILM-2	119.8 ± 5.6	154.9 ± 6.6	69 ± 6	260 ± 21	250 ± 21
ILM-3	108.2 ± 5.5	130.9 ± 6.2	79 ± 6	260 ± 23	252 ± 21
ILM-4	121.8 ± 5.8	146.5 ± 6.5	91± 6	325 ± 22	306 ± 21
ILM-5	123.5 ± 5.0	124. 7 ± 5.0	96 ± 4	365 ± 31	375 ± 30

But in the TiO_2 industrial process there exist a series of processes (digestion of the raw material with sulphuric acid, filtration of lixiviated materials, etc) where easily can be generated by-products or residues clearly more enriched in some natural radionuclides, will all the dosimetric implications associated

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NORM INDUSTRY

OCCUPATIONAL PROTOCOL

Second phase

- Refined collection of representative aliquots of raw materials, intermediate products, commercial final products, co-products and residues, and determination of the activity concentrations of the radionuclides of interest.

-If in the industrial process is generated fine material susceptible to be inhaled, design of an aerosol sampling campaign in strategic locations of the factory*, determining in them* the activity concentrations of the radionuclides of interest.

-Measurements of the ^{222}Rn concentrations with active systems during at least one week in areas of the industries where radon can experiment accumulation, and where the working time expended by the workers cannot be evaluated as negligible.

-Localization along the industrial process, if exists, of points where superficial scales can be formed or where sludge can be deposited- If theses scales or sludge are localized, the total amount should be determined, representative aliquots should be analyzed and the external effective doses in the points where scales were detected should be measured.

OCCUPATIONAL PROTOCOL

Second phase (cont)

With basis in the information and results obtained, the second phase of the occupational protocol should finish with an estimation of the effective doses received by the workers in the industry under analysis.

If the estimation shows that via external radiation and via inhalation the total effective doses are clearly lower than 1 mSv/y, and at the same time the activity concentrations of ^{222}Rn along the industry are clearly lower than 400 Bq/m^{3}, the protocol in its occupational side could be considered closed.

It would not be necessary the adoption of corrective actions in order to decrease the exposures of the workers, and it would not be necessary to take radiological protection measurements.

If it is not the case, it will be imperative to continue with the application of the occupational protocol, entering in the development of the third and final phase.

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OCCUPATIONAL PROTOCOL

IMPLEMENTATION SECOND PHASE IN THE LOCAL INDUSTRIES

Titanium Dioxide plant, Phosphoric Acid plant

Along the industrial process the secular equilibrium between the radionuclides from the same series is disrupted, following different routes according to their chemical behaviour.

Under normal running conditions, the occupational exposures by external radiation are quite moderate and clearly lower than 1 mSv/y.

The inhalation route has clearly less influence that the external irradiation route in the occupational exposure increments.

^{222}Rn levels inside the TiO_2 factory are of non concern.

From the radiological point of view, only some precautions need to be taken in specific points of the factory during maintenance operations: cleaning of crystallizers, changes of Moore filters, etc.

OCCUPATIONAL PROTOCOL

Third phase

If via external radiation and via inhalation the total effective dose estimated for the workers is not clearly lower than 1 mSv/y, it is necessary the performance of the following additional studies in the third and last phase of the occupational protocol.

Tasks

- Construction of a detailed dosimetric map of the external dose rates measured "in-situ" in all the places of the industry under evaluation. Special resolution will have this dosimetric map in the areas where is known the possible presence of enriched amounts of natural radionuclides .

-To perform a more detailed sampling campaign (in locations and time) of aerosols, with the posterior determination of their radioactive content, as a basis for a more refined estimation of the committed effective doses by inhalation received by the workers.

-To carry out a study with very high resolution of the ^{222}Rn activity concentrations, if in the previous studies in the second phase, were not clearly lower than 400 Bq/m^3. It is recommended to perform these studies with passive detectors, in order to extend the sampling period for obtaining representative values.

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OCCUPATIONAL PROTOCOL

Third phase (cont.)

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The analysis and evaluation of the results obtained in this third phase will allow taking in consideration the need or not of adopting radiological protection countermeasures.

The justification and explanation of the possible countermeasures, does not constitute the objective of this paper, and for that reason will be not detailed and justified.

However, and with basis in our previous experience in the field, we can indicate that in many cases the adoption of very simple and economic countermeasures can produce an appreciable decrease in the exposures received by the workers.

IMPLEMENTATION THIRD PHASE IN THE LOCAL INDUSTRIES

The third phase of the occupational protocol does not need to be applied in the industries devoted to the production of phosphoric acid and to the production of titanium dioxide pigments.

In its occupational side, no radiological protection countermeasures should be taken in the P_2O_5 and the TiO_2 industries in order to decrease the worker exposures.

ENVIRONMENTAL PROTOCOL

INITIAL POINT: **If the industry under study in the application of the occupational protocol was not considered after the first phase as a NORM industry, it is not necessary to apply the environmental protocol.**

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THE FIRST ENVIRONMENTAL PHASE ONLY APPLICABLE IN THE INDUSTRIES WHERE AT LEAST THE SECOND OCCUPATIONAL PHASE SHOULD BE APPLIED

ENVIRONMENTAL PROTOCOL

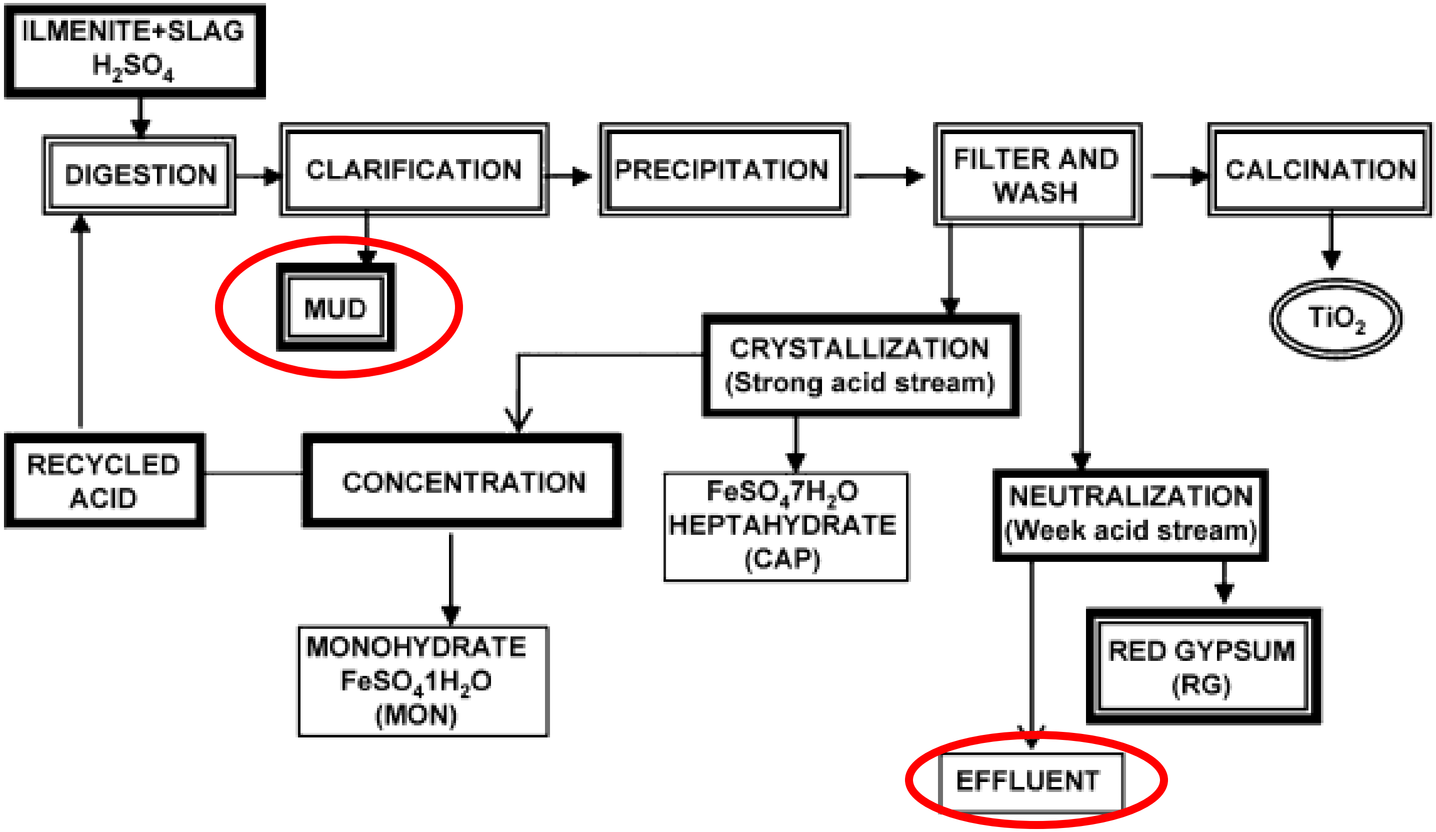
First phase

•From the determinations performed in the second phase of the occupational protocol in residues, wastes and releases, estimation of of the radioactivity fluxes released to the environment

•Identification, if it possible of radioactive markers, in the solid and liquid effluents and in the gaseous emissionss, that are quite different that the found ones in the surrounding environment before starting the industrial activity. These markers can allow the identification of their signals and evaluate the impact in the environment.

WITH BASIS IN THE DETERMINED FLUXES, IF THE ENVIRONMENTAL IMPACT CAN BE EVALUATED AS NEGLIGIBLE, THE ENVIRONMENTAL PROTOCOL CAN BE CONSIDERED CLOSED. IF NOT, THE SECOND PHASE OF THE ENVIRONMENTAL PROTOCOL SHOULD BE APPLIED

FIRST PHASE
TITANIUM DIOXIDE INDUSTRY.



FIRST PHASE
TITANIUM DIOXIDE INDUSTRY.

UNATTACKED MUDS

25000 TONNES PER YEAR

LODOS INATACADOS (Bq/Kg)						
	^{238}U	^{234}U	^{226}Ra	^{232}Th	^{228}Ra	^{228}Th
MUD-1	286 ± 10	296 ± 10	914 ± 52	444 ± 25	2689 ± 167	802 ± 40
MUD-2	230 ± 10	268 ± 11	831± 45	339 ± 23	2472 ± 153	716 ± 36
MUD-3	140 ± 16	167 ± 19	820 ± 47	317 ± 31	2575 ± 151	670 ± 36
MUD-4	164 ± 12	215 ± 17	766 ± 45	367 ± 30	2440 ± 150	677 ± 34
MUD-5	238 ± 10	252 ± 11	744 ± 44	299 ± 27	2472 ± 150	656 ± 34

MANAGEMENT: TRANSLATED IN WET FORM FROM THE PLANT TO AN INETIZATION PLANT. NO ENVIRONMENTAL IMPLICATIONS. OCCUPATIONAL PROTOCOL SHOULD BE APPLIED IN THE INERTIZATION PLANT

FIRST PHASE
TITANIUM DIOXIDE INDUSTRY.

LIQUID EFFLUENTS

WATERS PRACTICALLY FREE OF RADIONUCLIDES

Radionuclide concentrations even lower than the found ones in the waters of the Huelva estuary where are released.

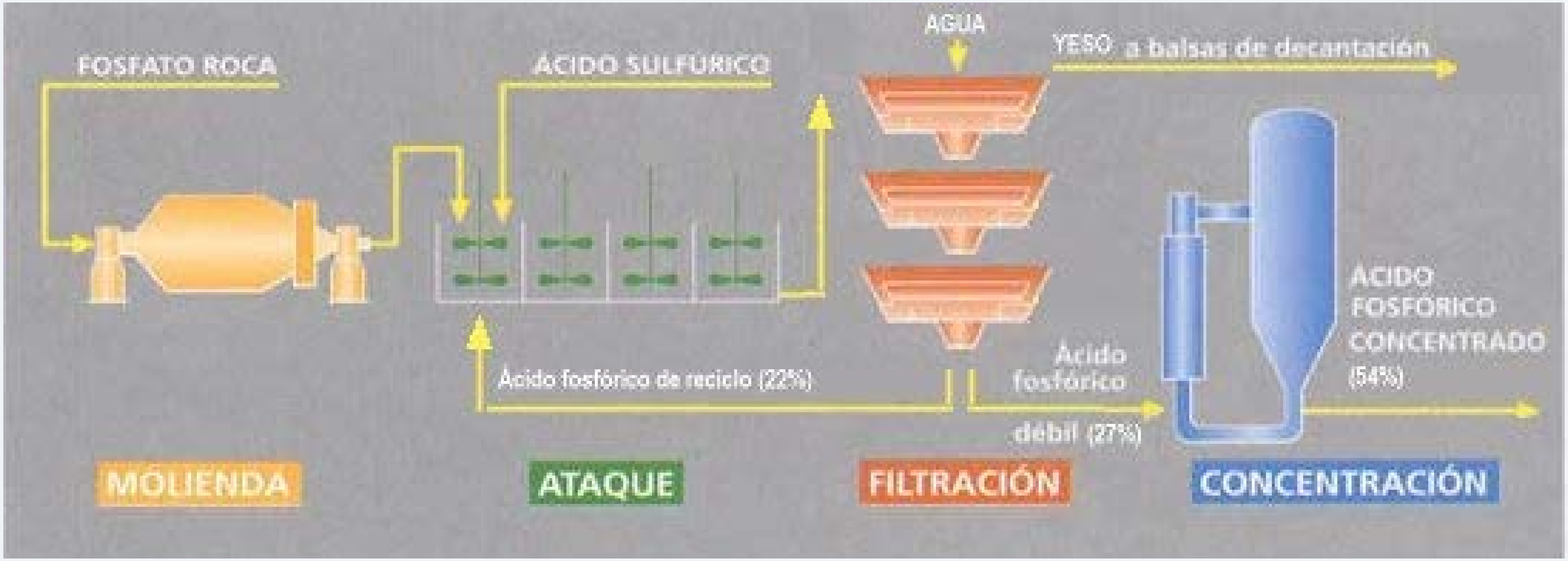
NULL ENVIRONMENTAL IMPACT

CONCLUSION

THE APPLICATION OF THE SECOND PHASE IS NOT NEEDED

IT IS NOT NECESSARY TO ADOPT RADIOLOGICAL PROTECTION COUNTERMEASURES

FIRST PHASE
PHOSPHORIC ACID PRODUCTION.



Roca fosfatica (PR) + Acido sulfúrico (SA) ⟹ Acido fosfórico (PA) + Fosfoyeso (PG)

$$Ca_{10}(PO_4)_6F_2CO_3Ca + 11H_2SO_4 + 21H_2O \rightarrow 6H_3PO_4 + 11CaSO_4 \cdot 2H_2O + 2FH + CO_2$$

FIRST PHASE
PHOSPHORIC ACID PRODUCTION.

GENERATED RESIDUE: PHOSPHOGYPSUM

	^{210}Po (Bq/kg)	^{226}Ra (Bq/kg)		^{210}Po (Bq/kg)	^{226}Ra (Bq/kg)
YZ1-P1	718 (15)	1191 (22)	**YZ2-P1**	423 (9)	435 (47)
YZ1-P2	616 (13)	1018 (14)	**YZ2-P2**	521 (11)	876 (94)
YZ1-P3	1078 (23)	896 (12)	**YZ2-P3**	518 (11)	716 (77)
YZ1-P4	711 (15)	970 (13)	**YZ2-P4**	671 (15)	818 (88)
YZ1-P5	653 (14)	992 (15)	**YZ2-P5**	554 (12)	438 (37)

2 Milllons Tonnes of Phosphogypsum generated annually
Stored in big piles near the production plants
Possible interaction of the PG piles with the neighbouring environment

PHOSPHOGYPSUM MANAGEMENT HISTORY

1968-1997:

- 20% RELEASED DIRECTLY TO THE ODIEL RIVER
- 80% STORED IN PILES OVER MARSHLANDS OF THE TINTO RIVER

(the sea waters used to transport the PG to the piles drained to the Tinto river)

1998- :

- DIRECT RELEASES TO THE NEARBY ENVIRONMENT FORBIDDEN
- NEAR 100% STORED IN THE PILES (the fresh waters used to transport the PG follows a closed circuit)

SINCE THE BEGINNING OF THE NINENTIES

SOME OF THE INACTIVE STACKS WERE RESTORED. THE NAKED STACKS WERE COVERED WITH A SOIL LAYER 30-40 cm THICKNESS.

FIRST PHASE
PHOSPHORIC ACID PRODUCTION.

GENERATED RESIDUES: PHOSPHOGYPSUM

CONCLUSION

POSSIBLE ENVIRONMENTAL RADIOACTIVE IMPACT THAT IT IS NECESSARY TO EVALUATE WITH MORE DETAIL

APLICATION OF THE SECOND PHASE OF THE ENVIRONMENTAL IMPACT

RADIOACTIVE MARKERS:

ISOTOPIC RATIOS $^{226}Ra/^{228}Ra$ $^{230}Th/^{232}Th$

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ENVIRONMENTAL PROTOCOL: SECOND PHASE

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The second phase has two parts that, if it is necessary, can be applied independently and in paralell,

SECOND PHASE PART A

A) If there are gaseous emissions, with significant radionuclide content, compilation of

D) If the atmospheric emissions can be potentially enriched in Rn-222, it is necessary to determine experimentally its levels, and to evaluate its radiological importance,

the second phase is considered closed.

B) Having in consideration the information gained in A), performance of a sampling

Important: The sampling campaigns for aerosols and radon should have a sufficient duration , and they should be performed specially in the months less favourables from the point of view of inmission (at least one month for aerosols and 3 months for radon)

elected radioactive markers)

SECOND PHASE PART A
PHOSPHORIC ACID INDUSTRY.

APPLICABLE IN A SELECTIVE WAY, WITH BASIS IN THE CONCLUSIONS OBTAINED IN THE APPLICATION OF THE FIRST PHASE.

FUNDAMENTS

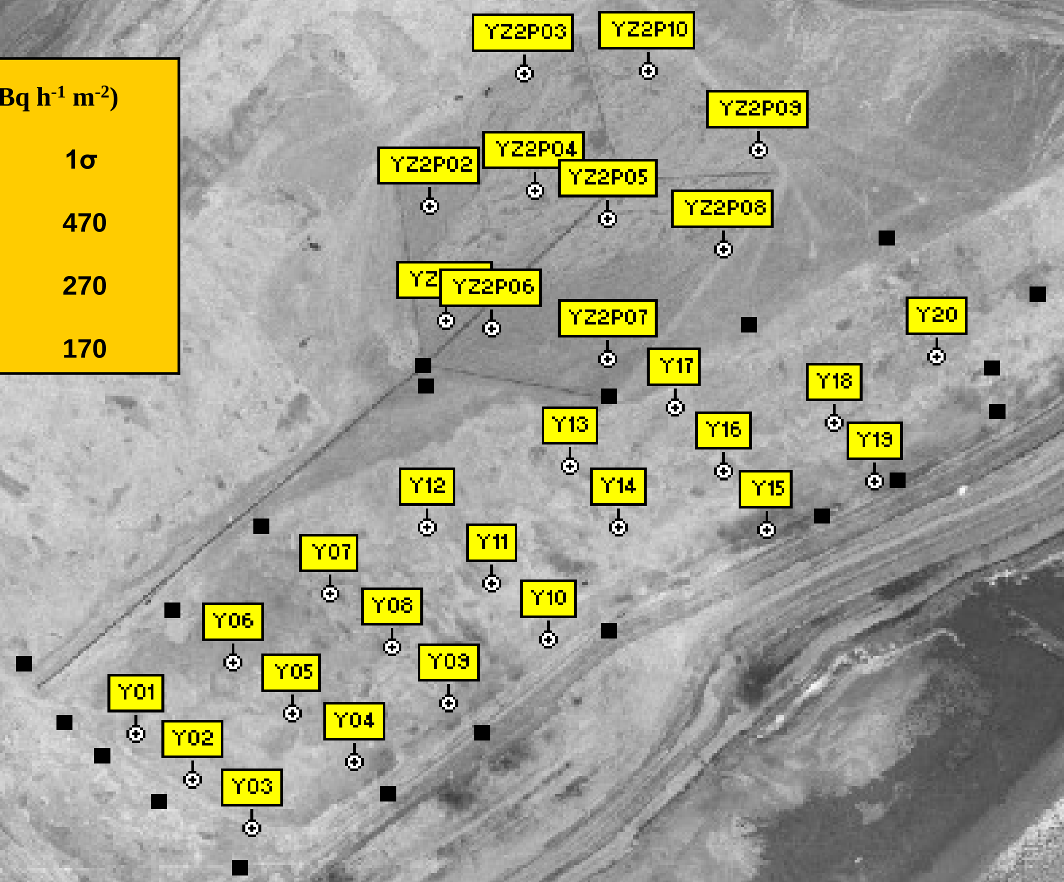
The atmospheric emissions of the plants contain negligible amounts of natural radionuclides, as it was deduced from the occupational study. IT IS NOT NECESSARY TO STUDY THEIR IMPACT IN THE SURROUNDINGS OF THE PLANTS .

The Phosphogypsum piles can be a source of particulate matter to the environment. Particulate matter should be collected in vicinity of the piles, their radionuclide content determined and their iradiological implications should be evaluated.

The naked phosphogypsum piles can be a source of ^{222}Rn to the environment. ^{222}Rn determinations should be performed in the vicinity of the piles and their radiological implications evaluated.

^{222}Rn exhalation rates in the phosphogypsum piles

	Rn Exhalation (Bq h^{-1} m^{-2})		
ZONE	Average		1σ
1	510	±	470
2	250	±	270
3	360	±	170



ENVIRONMENTAL PROTOCOL

SECOND PHASE PART B

A) **If there are solid or liquid releases with a significative radionuclide content, it is necessary to perform a sampling in the receptor compartament** (litosphere, hydrosphere) searching for the collection of good indicators of radioactive impact (sediments, algae, suspended matter in waters, etc) . Posterior application of the points B and C. **If there are no these type of releases, the part B of the second phase can be considered closed.**

B) **Determination of the radioactive content in the samples oollected**, with special emphasis in the study of the radioactive markers identified.

C) If from B, it is concluded the existence of a significative radioactive impact, evaluation of the radiological implications through the trophic chain.

SECOND PHASE PART B
TITANIUM DIOXIDE PIGMENT INDUSTRY

NOT APPLICABLE, WITH BASIS IN THE CONCLUSIONS OBTAINED AFTER IMPLEMENTATION OF THE FIRST PHASE

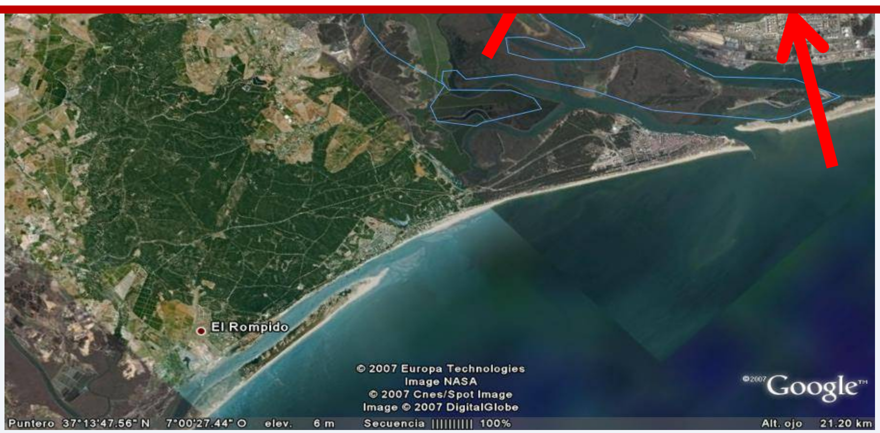
FUNDAMENTS

BE CAREFUL ¡¡¡¡

No solid releases, no piling of residues

Liquid effluents free

NULL ENVIRONMENTAL I

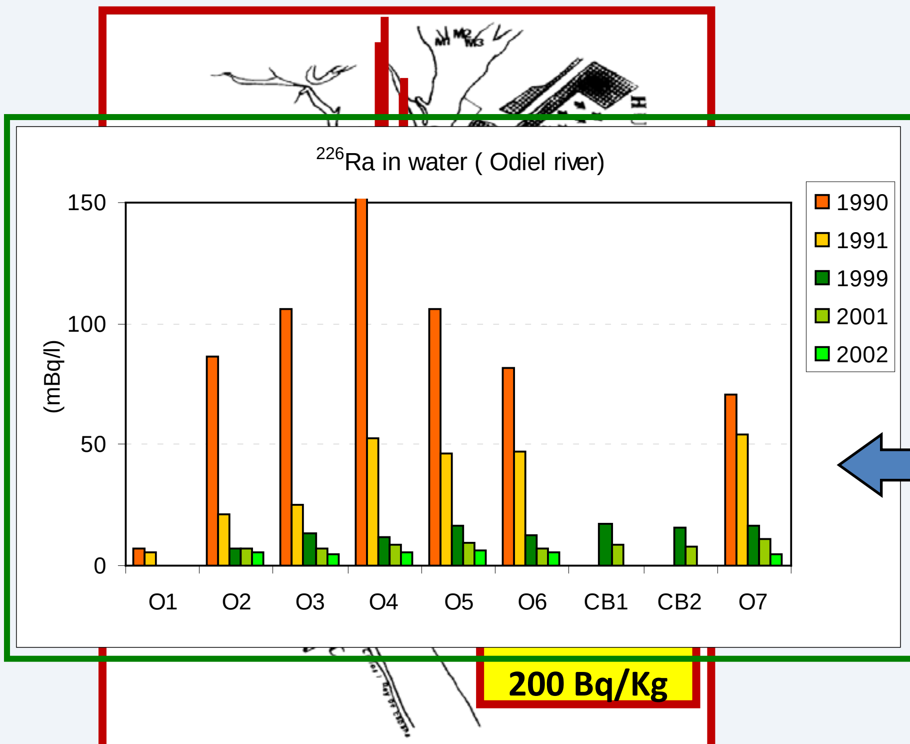


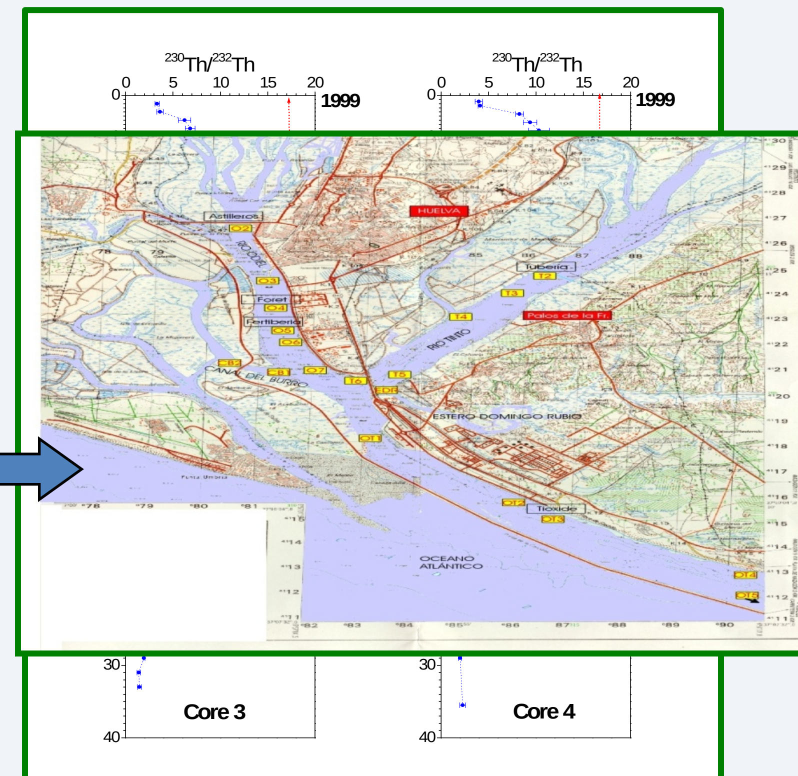
Be careful with the spatial overlapping of possible radioactive impacts..

To identify the origin, there are essential the radioactive markers which characterize each potential source of contamination.

SECOND PHASE PART B
PHOSPHORIC ACID INDUSTRY

APPLICABLE, BECAUSE HISTORICALLY PHOSPHOGYSUM WAS RELEASED TO THE HUELVA ESTUARY . NOWADAYS THERE ARE LIQUID EFFLUENTS COMING FROM LIXIVITATIONS ORIGINATED IN THE OLD PILES .





SECOND PHASE PART B
PHOSPHORIC ACID INDUSTRY.

SHRIMPS				
MARISMAS DEL ODIEL				
CODE	^{210}Po (Bq/kg)	^{210}Pb (Bq/kg)	[U] (μg/kg)	[Th] (μg/kg)
CO1	2.9 ± 0.1	< 0.13	4.5 ± 0.3	1.8 ± 0.2
CO2	3.1 ± 0.1	0.71 ± 0.10	2.0 ± 0.2	1.0 ± 0.2
CO3	6.5 ± 0.2	< 0.24	6.7 ± 0.4	0.5 ± 0.1
CO4	6.4 ± 0.2	< 0.23	5.8 ± 0.5	1.1 ± 0.4
MARISMAS DE CARRERAS (CONTROL)				
CODE	^{210}Po (Bq/kg)	^{210}Pb (Bq/kg)	[U] (μg/kg)	[Th] (μg/kg)
CA1	6.2 ± 0.5	< 0.63	5.6 ± 1.3	6.1 ± 1.0
CA2	6.5 ± 0.5	< 0.65	5.9 ± 0.4	8.9 ± 0.9

BIVALVES		
LOCATION	^{210}Po (Bq/kg f.w.)	^{210}Pb (Bq/kg f.w.)
Punta Umbría (end of Huelva esturay)	20-30	8-15
Andalusian Mediterranean Coast	15-60	5-40
Andalusian Atlantic Coast	15-70	5-40

FINAL POINT OF THE PROTOCOL

Once the radiological evaluations associated to the environmental study have been performed in the second phase, and if it is necessary, the needed radiological protection countermeasures should be taken.

These countermeasures can even imply some changes in the waste management policy followed by the industry under study.

ESO ES TODO AMIGOS¡¡¡¡¡