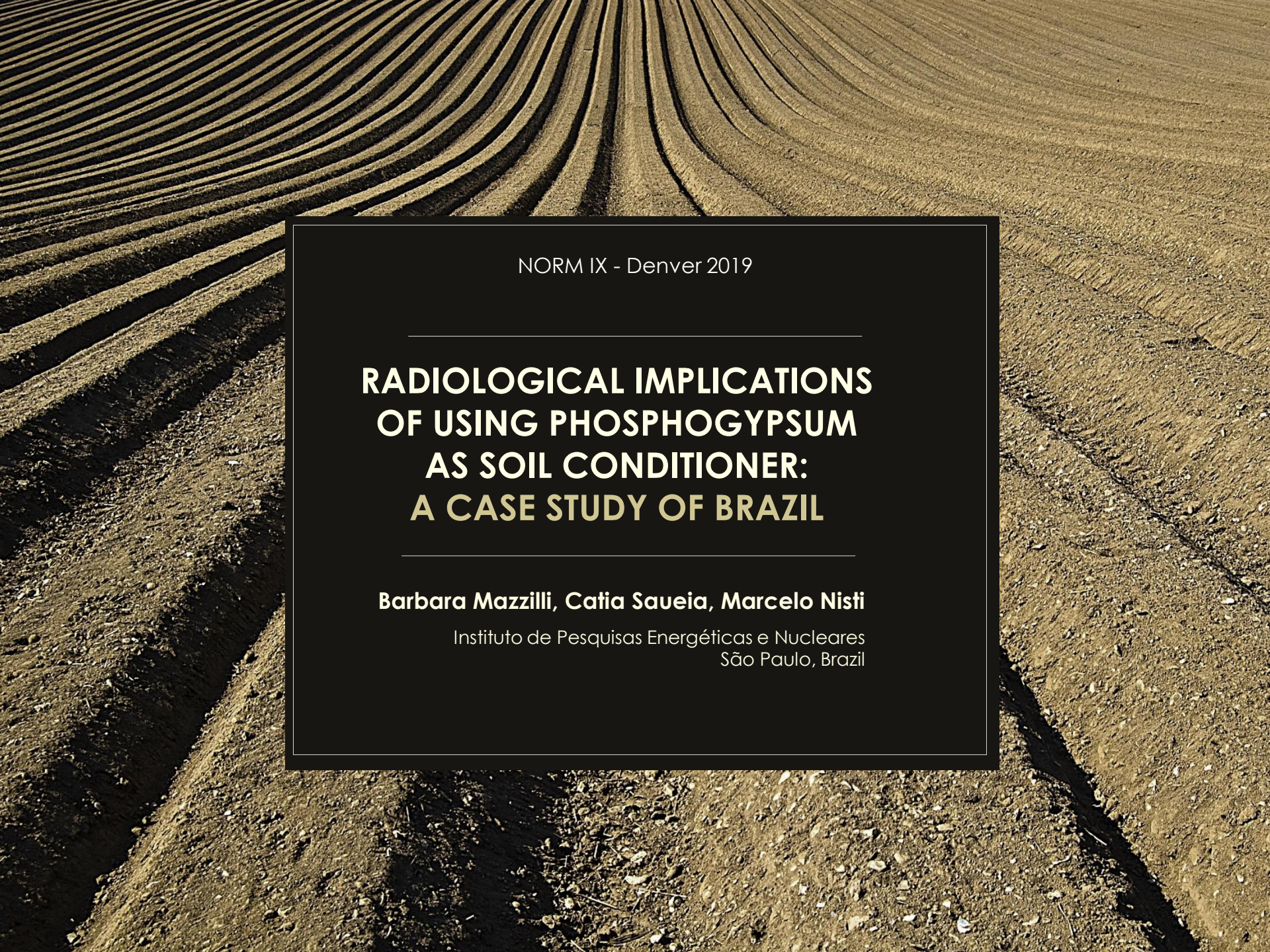

NORM IX - Denver 2019

# RADIOLOGICAL IMPLICATIONS OF USING PHOSPHOGYPSUM AS SOIL CONDITIONER: A CASE STUDY OF BRAZIL

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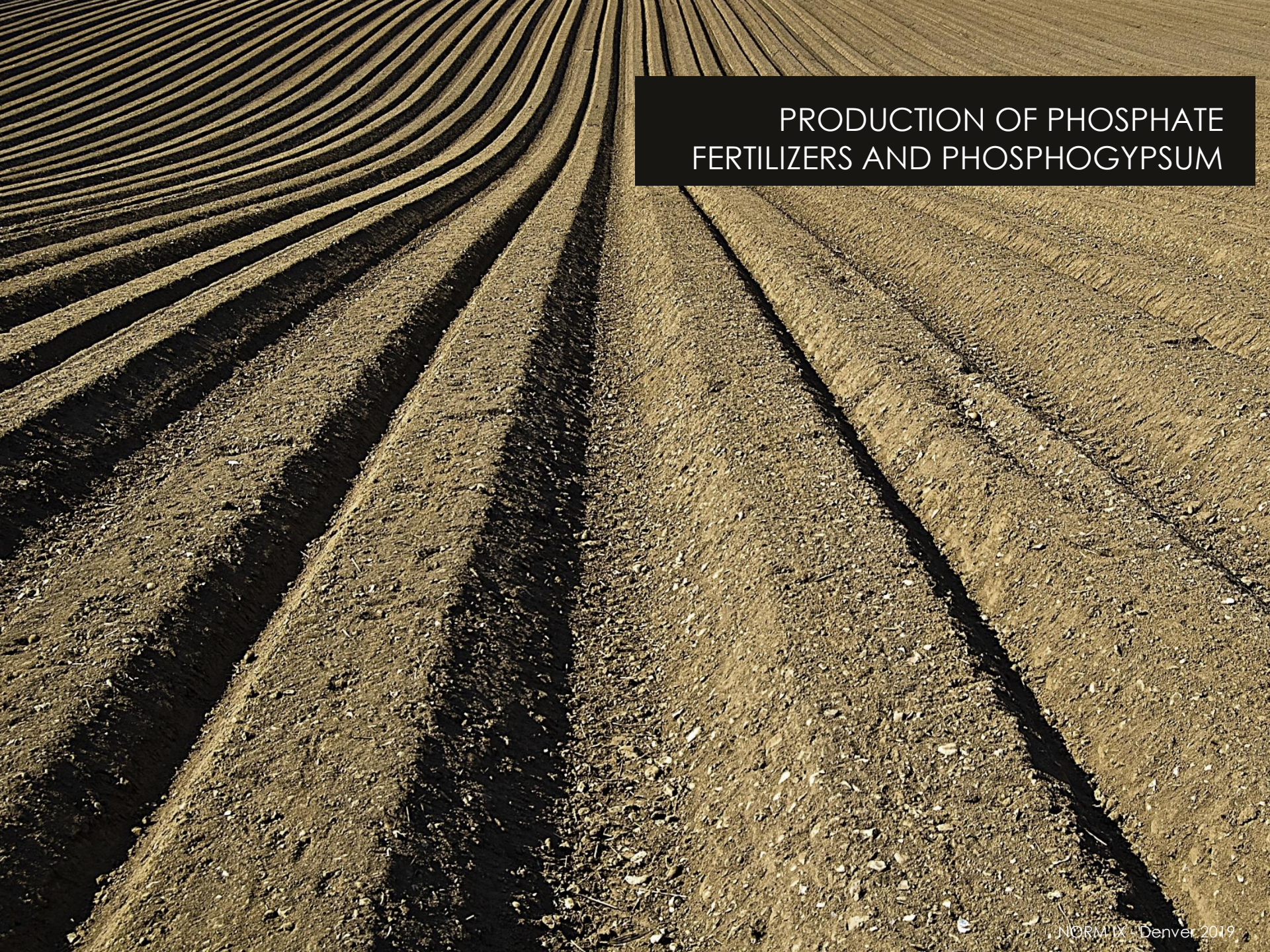
# AGENDA

- ✓ PRODUCTION OF PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM
- ✓ USE OF FERTILIZERS AND PHOSPHOGYPSUM IN AGRICULTURE
- ✓ RADIONUCLIDES CONTENT IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM
- ✓ METALS CONTENT IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM
- ✓ CASE STUDIES
- ✓ CONCLUSION



# PRODUCTION OF PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM

# PRODUCTION OF PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM

PG is a by-product of the chemical reaction, in which sulfuric acid is reacted with phosphate rock to produce phosphoric acid needed for fertilizer production.

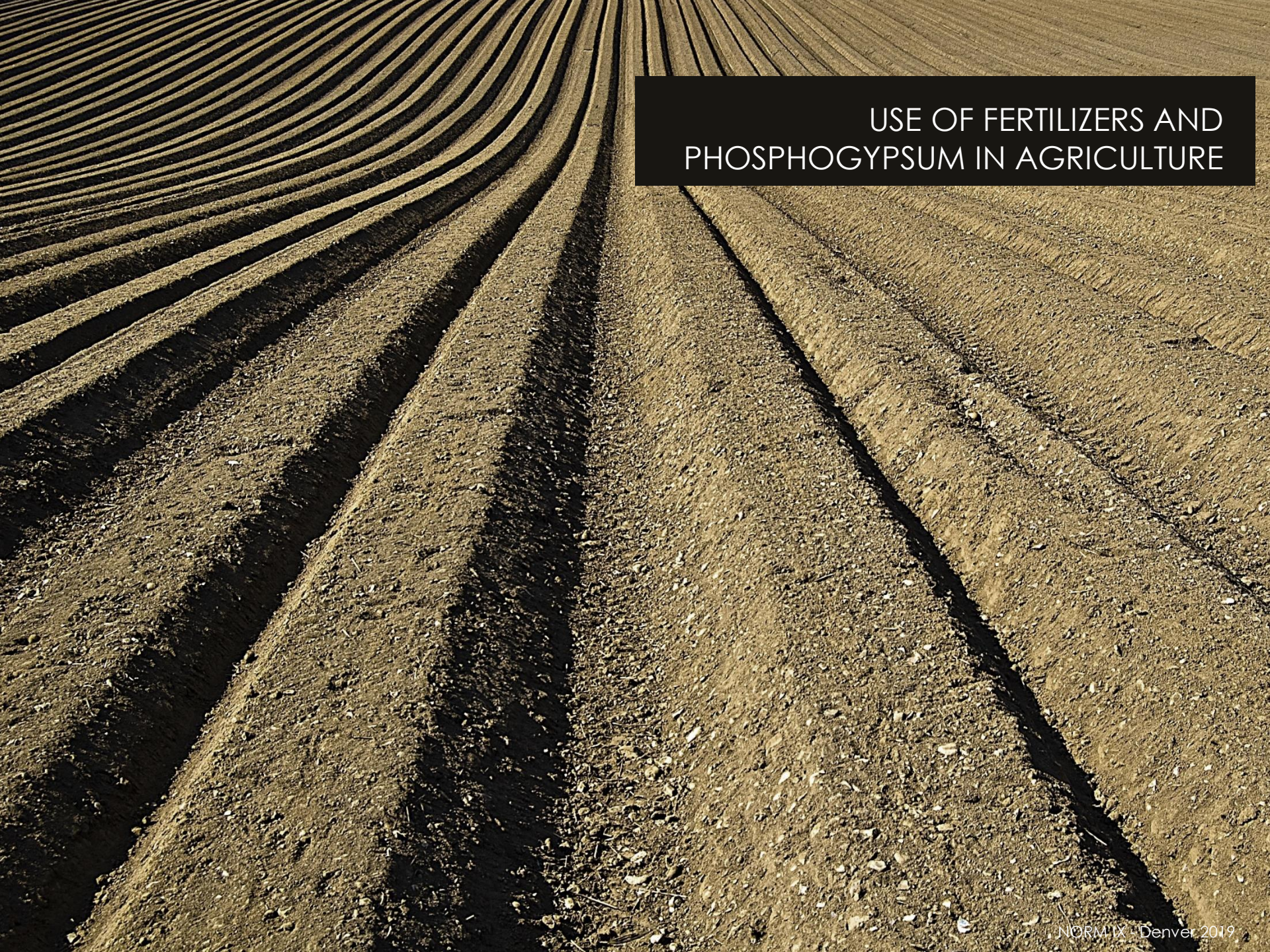
Phosphoric acid is the starting material for the most utilized fertilizers: triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP).

The conversion of apatite takes place according to the following general equation:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4nH_2O + 6H_3PO_4 + 2HF$$

In the phosphate rock, the radionuclides of the U and Th series are in equilibrium.

During the chemical process, this equilibrium is disrupted, and the radionuclides migrate in the products, by-products and residue according to their chemical properties and solubility.



# USE OF FERTILIZERS AND PHOSPHOGYPSUM IN AGRICULTURE

# USE OF FERTILIZERS AND PHOSPHOGYPSUM IN AGRICULTURE

In terms of rounded figures, the production of 1 ton of phosphate results in the generation of 4-5 ton of PG.

PG is produced at a rate of 12.5 million tons per year. The level of impurities (metals and radionuclides, among others) present in PG makes its disposal or reutilization an environmental concern.

PG has been used as soil conditioner in Brazil well before the establishment of applicable standards by the Brazilian Regulatory Agency.

The application of PG as soil amendment is mainly due to the characteristics of $CaSO_4$, which improves the root penetration in soil. It provides calcium in the soil depth, reduces the aluminium saturation and favours the absorption of water and nutrients.

Therefore, it is a common practice in the Brazilian agriculture to use the phosphate fertilizers mixed with PG.

# RADIONUCLIDES CONTENT IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM

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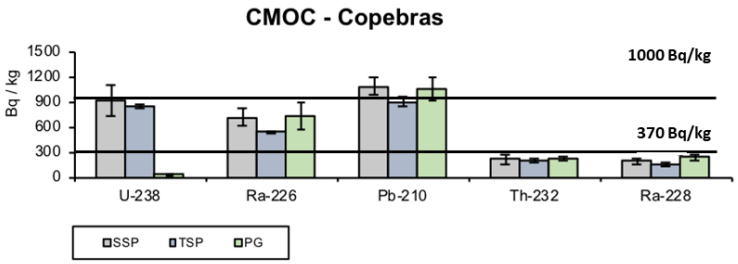
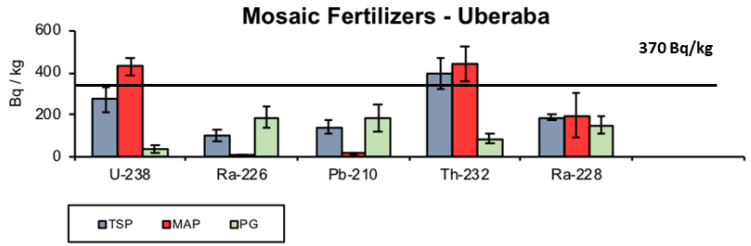
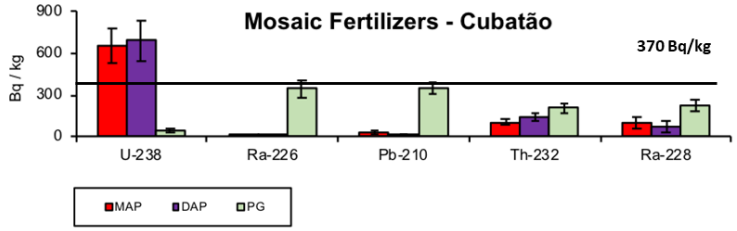



PG below clearance levels recommended by BSS, except for the industry CMOC-Copebras.

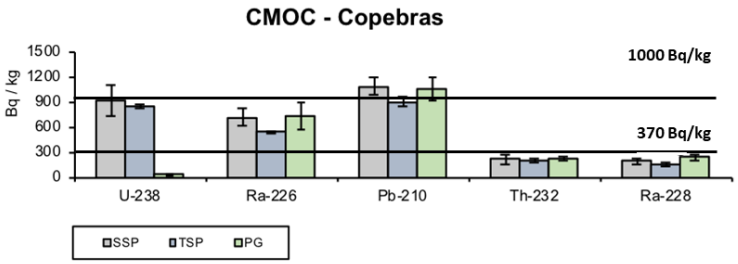
During the chemical attack of the phosphate rock, different compounds can be formed, depending upon the experimental conditions and the stoichiometry of the reaction. In the production of triple superphosphate (TSP), phosphoric acid reacts with apatite according to the reaction:

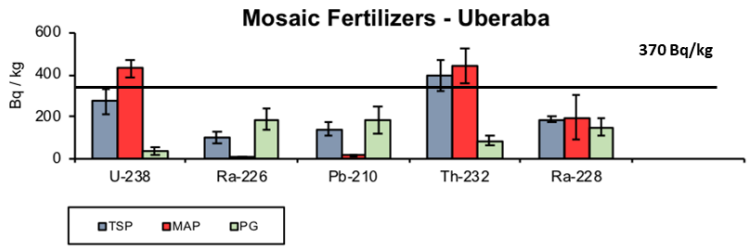
$$Ca_{10}(PO_4)_6F_2 + 14\ H_3PO_4 + 10\ H_2O \rightarrow 10\ Ca(H_2PO_4)_2.H_2O + 2\ HF$$

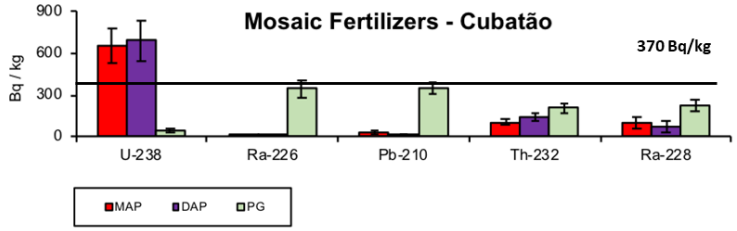
There is almost no formation of PG; therefore, in these cases all the radionuclides originally present in the phosphate rock (U, Th, Ra and Pb) migrate preferentially to the fertilizers.

At the end of the process, PG, TSP and SSP will present the same content of natural radionuclides.

# RADIONUCLIDES CONTENT IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM



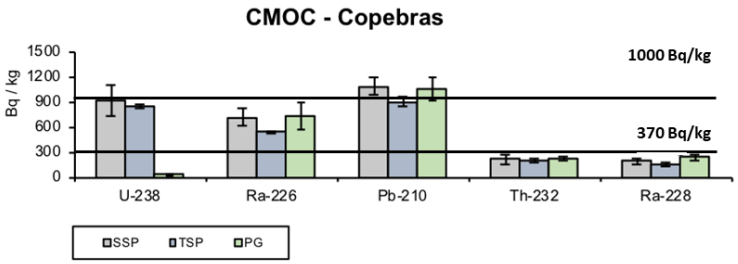

TSP, SSP and PG from industry CMOC-Copebras and Mosaic Fertilizers-Uberaba present Ra activity above EPA limit of 370 Bq $kg^{-1}$.

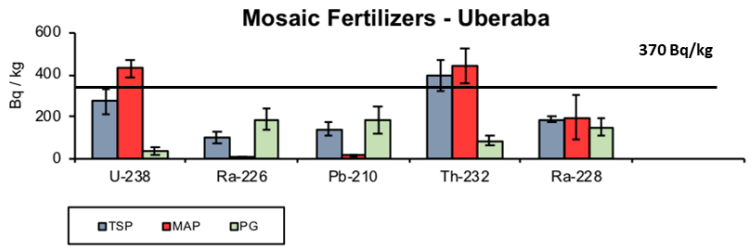
MAP and DAP are obtained by reacting phosphoric acid with different amounts of $NH_3$.

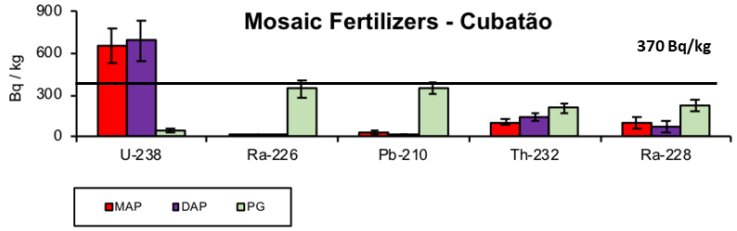
MAP and DAP present in their composition only the radionuclides U-238 and U-234, since uranium has chemical affinity with phosphates.

All the Brazilian PG samples present Ra-226 and Ra-228 concentrations below 1000 Bq $kg^{-1}$, established by the Brazilian Regulatory Agency.

# RADIONUCLIDES CONTENT IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM



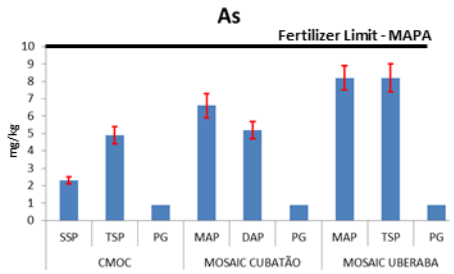



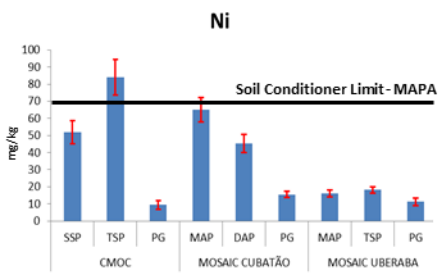

There is an **urgent need for harmonization of the limits adopted** by different countries for the utilization of PG as soil amendment.

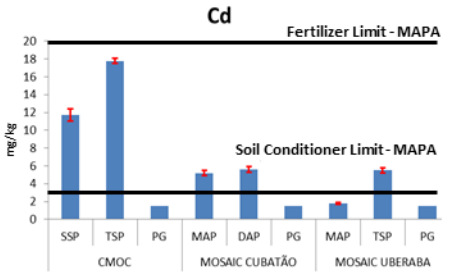
These limits should keep in mind that if **they are too restrictive, they will eventually make it impossible to use also the fertilizers** SSP and TSP.

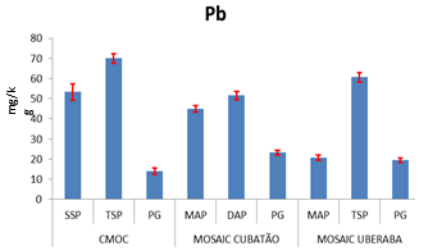
# METALS CONTENT IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM

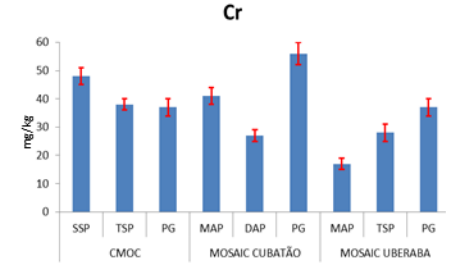
# METALS CONTENT IN BRAZILIAN PHOSPHATE FERTILIZERS AND PHOSPHOGYPSUM



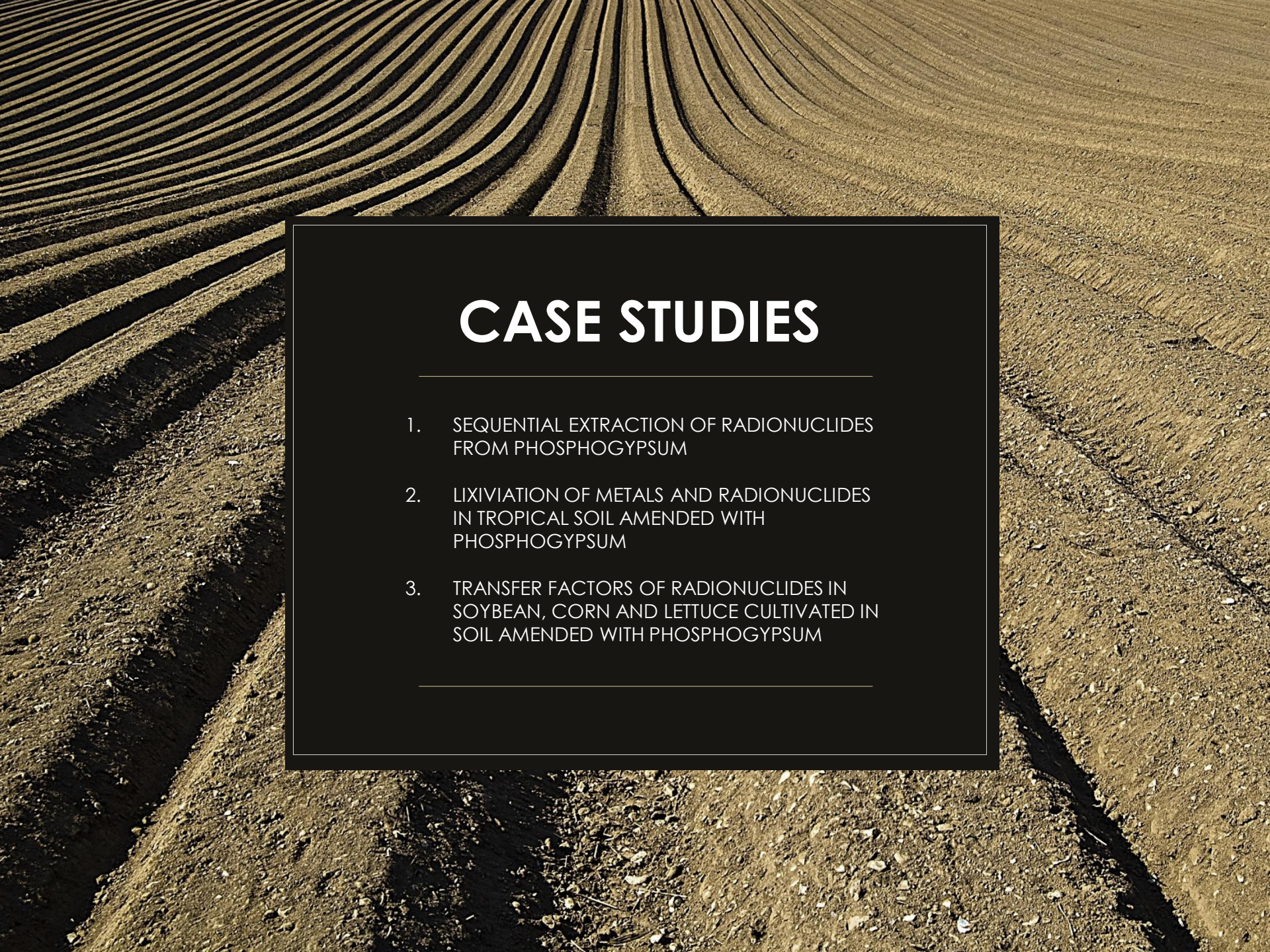




All the results obtained for the metals concentration are lower than the threshold values adopted for the heavy metals in fertilizers and soil conditioner in Brazil.

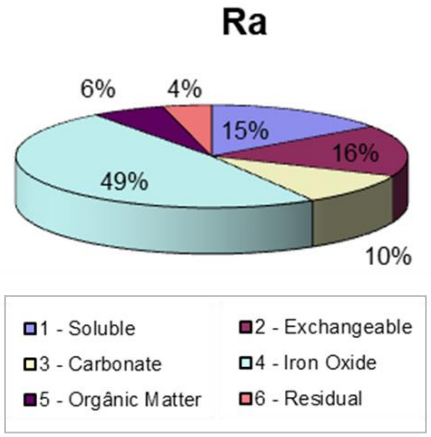
The concentration of Hg and Se were below the detection limits of the methodologies used, 0.2 mg $kg^{-1}$ and 0.3 mg $kg^{-1}$, respectively.

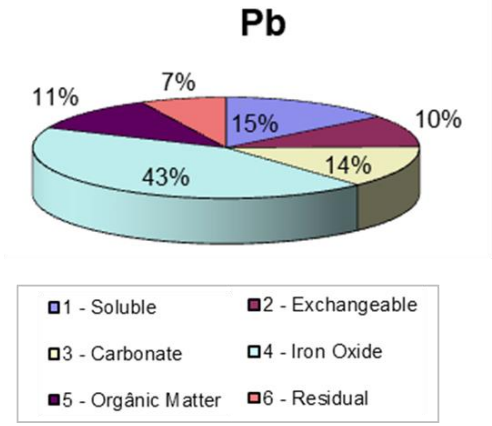


# CASE STUDIES

1. SEQUENTIAL EXTRACTION OF RADIONUCLIDES FROM PHOSPHOGYPSUM
2. LIXIVIATION OF METALS AND RADIONUCLIDES IN TROPICAL SOIL AMENDED WITH PHOSPHOGYPSUM
3. TRANSFER FACTORS OF RADIONUCLIDES IN SOYBEAN, CORN AND LETTUCE CULTIVATED IN SOIL AMENDED WITH PHOSPHOGYPSUM

# 1. SEQUENTIAL EXTRACTION OF RADIONUCLIDES FROM PHOSPHOGYPSUM



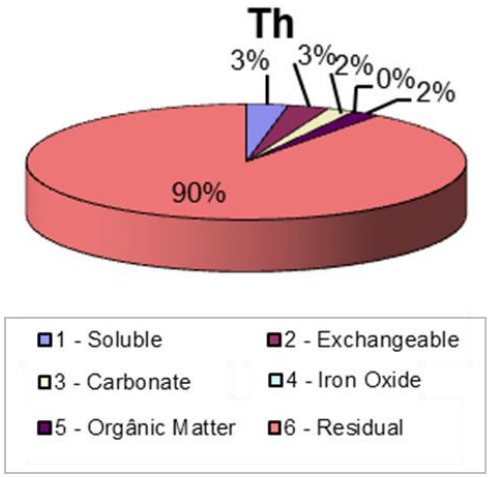




To assure a safe long-term application of PG in the agriculture, it is important to determine not only the total concentration levels of the impurities but also to evaluate their fraction which is available to the environment. The content of the labile elements was determined by the application of the sequential leaching defined by Tessier.

Since PG is in a water-soluble phase, a deionized water extraction was added as an initial step in addition to the five extractions.

Most of Ra and Pb are found in the iron oxide fraction. It can be concluded that the availability of Ra and Pb is not predominant in the soluble fraction that corresponds to the environmental conditions such as water percolation as rain.

# 1. SEQUENTIAL EXTRACTION OF RADIONUCLIDES FROM PHOSPHOGYPSUM

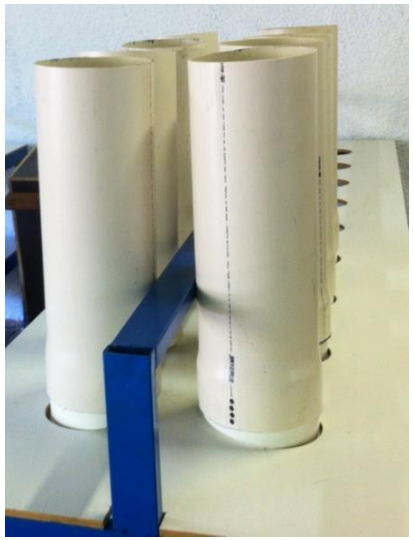



It should be noted that in the first step added to the sequential extraction, the PG/H2O mass ratio was sufficient to reach the solubility of PG in water.

In this phase the weight loss of PG was about 85%, showing that most of the Ra and Pb present in PG was not associated with the soluble calcium sulphate.

Th was found predominantly in the residual phase.

# 2. LIXIVIATION OF METALS AND RADIONUCLIDES IN TROPICAL SOIL AMENDED WITH PHOSPHOGYPSUM



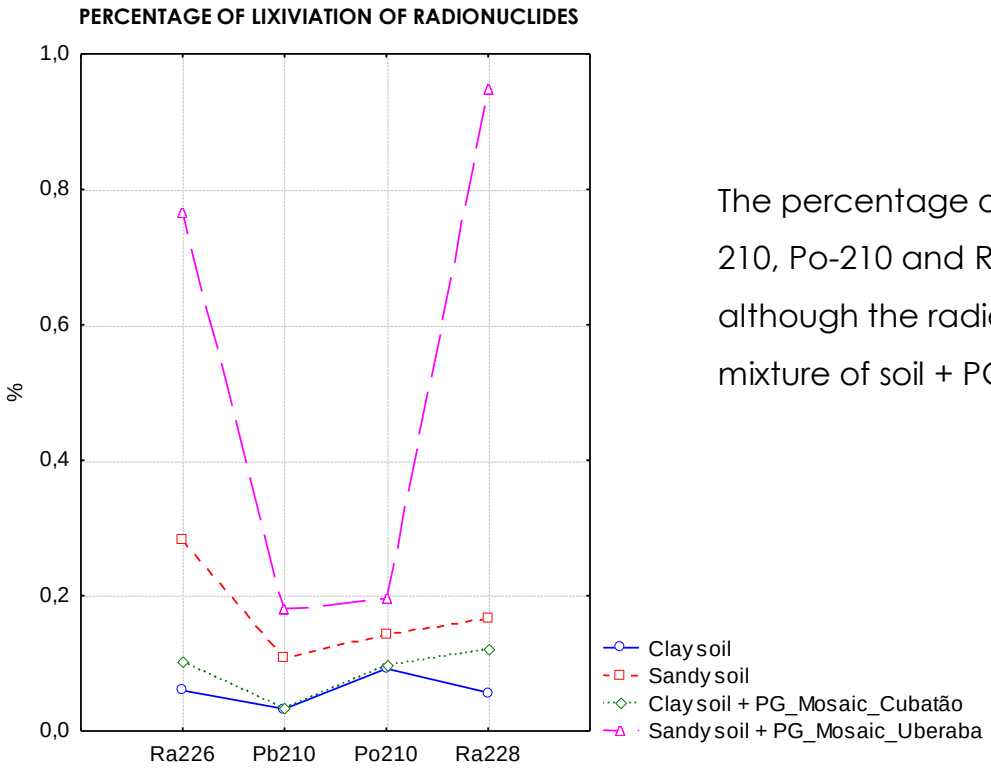
An experiment was conducted in laboratory, in which columns were filled with Brazilian typical sandy soil and clay soil amended with PG and percolated with water, in order to achieve a mild extraction of these elements.

The amount of PG added to the soils exceeded 10 times the amount of PG necessary to achieve 50% of the soil base saturation.

The volume of water to be percolated was based in the average rainfall of the study area.

The availability of the radionuclides and metals was evaluated by measuring the total concentration in the soil, soil + PG and the concentration in the leachates, in order to establish the ratio between the available fraction and the total one.

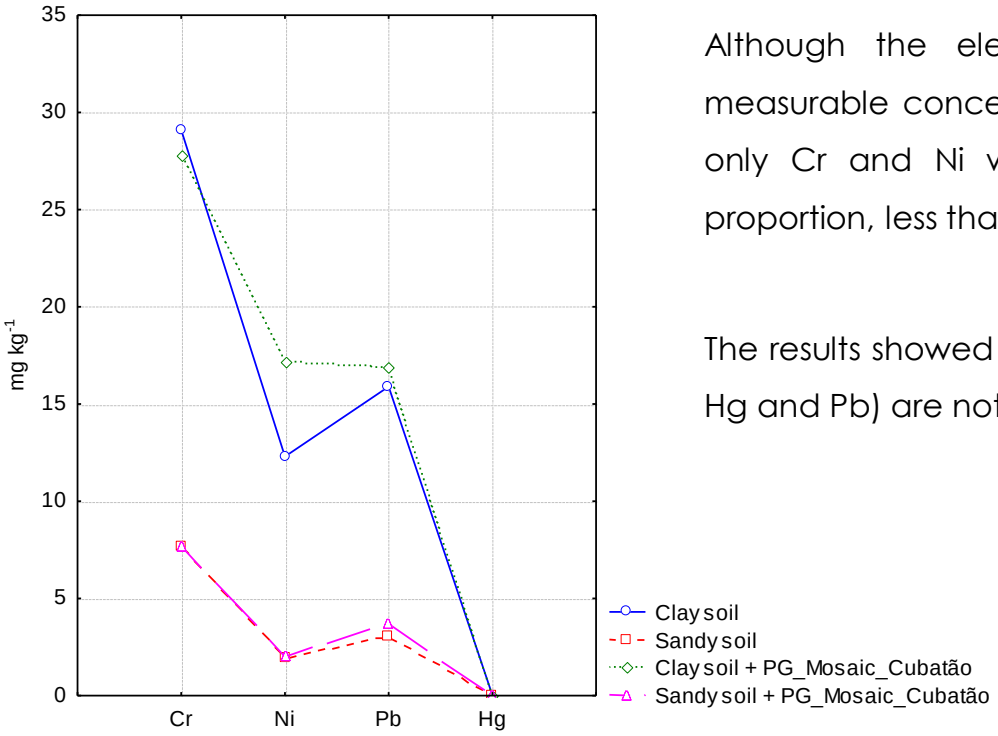
# 2. LIXIVIATION OF METALS AND RADIONUCLIDES IN TROPICAL SOIL AMENDED WITH PHOSPHOGYPSUM




The percentage of lixiviation of the radionuclides Ra-226, Pb-210, Po-210 and Ra-228 are below 1%, giving evidence that although the radionuclides are initially present in the soil and mixture of soil + PG they are not available to the water system.

# 2. LIXIVIATION OF METALS AND RADIONUCLIDES IN TROPICAL SOIL AMENDED WITH PHOSPHOGYPSUM

**CONCENTRATION OF METALS IN SANDY SOIL, CLAY SOIL AND THE MIXTURE SOIL PLUS PG**




Although the elements Cr, Ni, Pb and Hg presented measurable concentration in the soil and soil + PG samples, only Cr and Ni were found in the leachate at a small proportion, less than 0.1%.

The results showed that the metals studied (As, Cd, Cr, Ni, Se, Hg and Pb) are not available to the water system.

# 3. TRANSFER FACTORS OF RADIONUCLIDES IN SOYBEAN, CORN AND LETTUCE CULTIVATED IN SOIL AMENDED WITH PHOSPHOGYPSUM

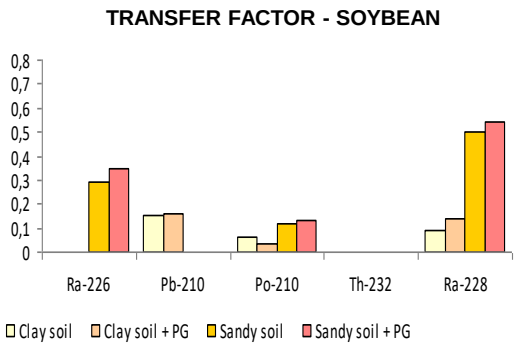


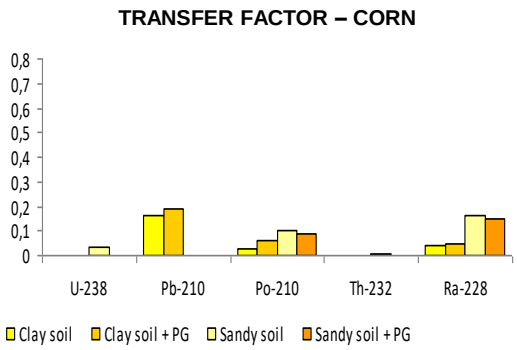
This study aimed to evaluate the environmental impact of the use of PG in agriculture, as soil amendment, by evaluating the radionuclides transfer in the soil/plant system.

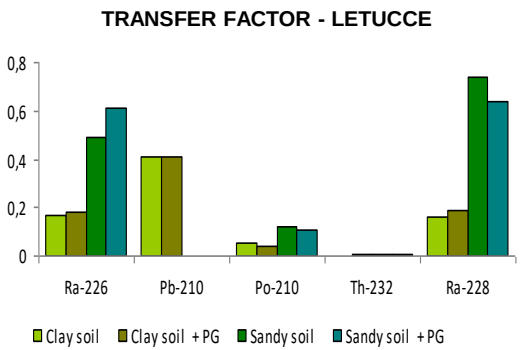
The experiment was carried out in greenhouse.

Soybean, corn and lettuce were grown in clay (red-yellow dystrophic latosol) and sandy soil (yellow dystrophic latosol) amended with PG.

# 3. TRANSFER FACTORS OF RADIONUCLIDES IN SOYBEAN, CORN AND LETTUCE CULTIVATED IN SOIL AMENDED WITH PHOSPHOGYPSUM




The addition of PG to the soils did not alter significantly the levels of radioactivity for all the radionuclides studied; consequently, the soil-to-plant transfer factors for U, Th, Ra, Pb and Po did not present significant variations due to the addition of PG.

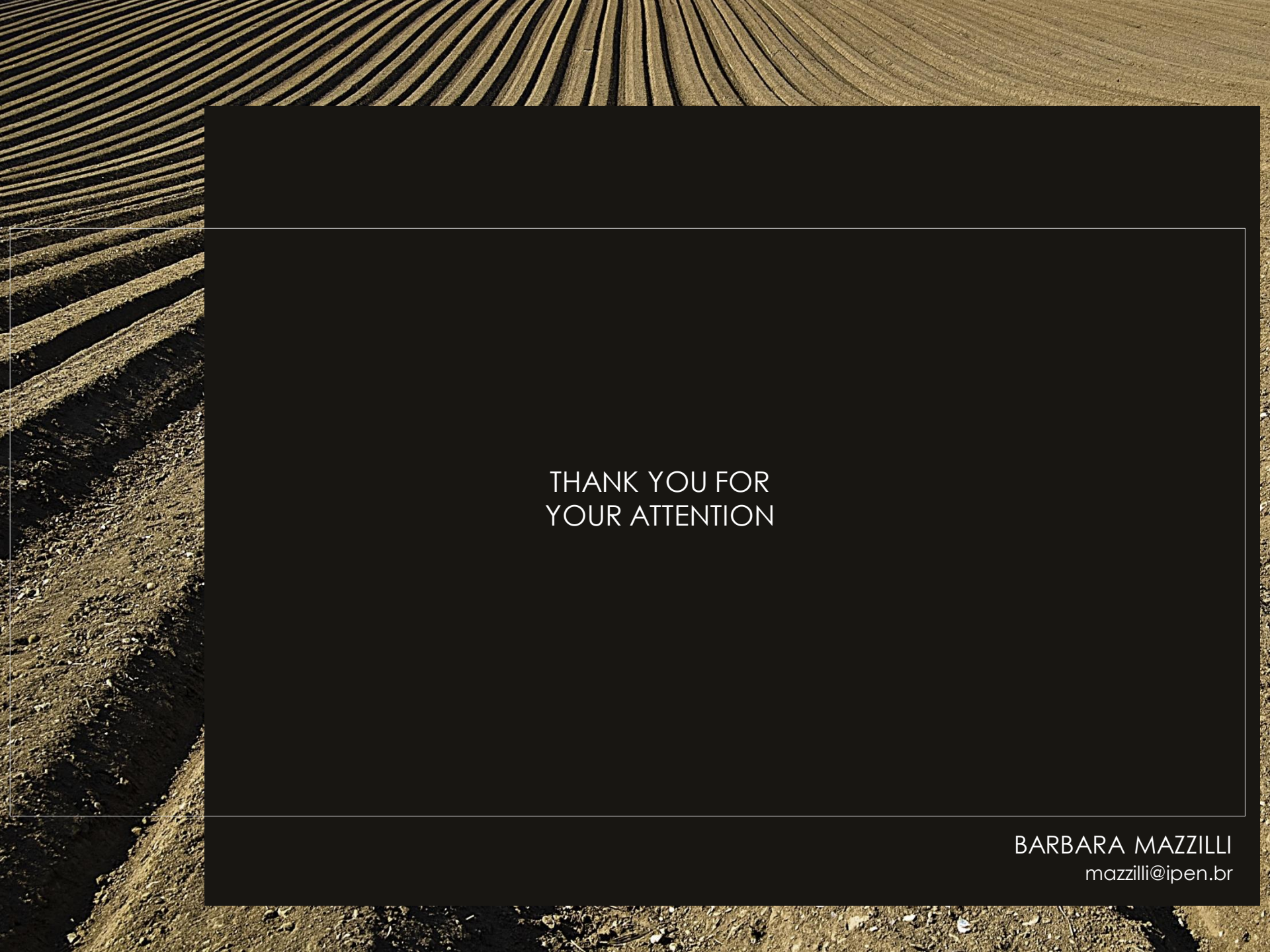
Therefore, the impact of a single application of Brazilian PG as a corrective soil does not imply in any additional risk due to the transfer of radionuclides.

# CONCLUSION

In conclusion, the results obtained for the lixiviation of radionuclides and metals and their transfer factors in the soil/plant system gave evidence that the use of PG as agricultural amendment does not imply in any additional health risk to the final consumers.

Furthermore, the re-use of PG meets the principles of sustainability preserving natural sources of $CaSO_4$ and reducing the amount of residue stockpiled and its consequent environmental impact. Therefore, the use of PG instead of natural gypsum as soil amendment should be encouraged, following the recommendations of IAEA, TECDOC 1712 "Management of NORM Residues" (2013).

As a final conclusion, it is emphasized that the research carried out over the last 2 decades has shown that the application of PG as soil conditioner is safe from the point of view of radiation protection and is economically feasible, **provided that adequate regulation is implemented and harmonized worldwide**.



THANK YOU FOR
YOUR ATTENTION

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