Monitoring of radioactivity in fertilizers in Austria

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Abstract

This paper reports results of a monitoring project regarding natural radionuclides in fertilizers which are commonly used in Austria. Due to adaption of the Austrian Radiation protection rules to European legislative, fertilizers became part of products which have to be monitored by governmental authorities on their activity concentrations of natural radionuclides. In addition, the Austrian NORM ordinance lists processing of raw phosphate in chemical industry as well as in fertilizer industry as workplaces with possible elevated exposure to Uran and Thorium and their decay products and as industries, where residues could accumulate elevated concentrations of natural radionuclides. Therefore about 500 fertilizer samples were investigated by gamma spectroscopy. The fertilizers were provided by the governmental fertilizer inspection staff and preselected regarding usage in Austria and types of fertilizers with possible elevated activity concentrations (e.g. Tripelphosphate). A further distinction was made in order to compare fertilizers regarding their major components (organic-, nitrogen-, phosphate-, potassium-, multi plant nutrient- fertilizers …). The results are focused on U-238, Ra-226 and Pb-210. Using these results, input of Uranium in agricultural fields was calculated and three scenarios were discussed. These three scenarios include the total translocation of NORM nuclides into drinking water, the transfer of NORM nuclides into plants and the accumulation of Uranium in agricultural fields. The relation between Radium-226 and Uranium-238 is also discussed with focus on fertilizer processing and the probability to accumulate NORM residues in processing components.

KEYWORDS: NORM, fertilizer

Introduction

The Radiation Protection Act § 37 [1] with the amendment to the Radiation Protection EU-Adaptation Law No. 137/2004, lists animal feed and fertilizers to the explicitly listed products and materials, which in terms of their content of radioactivity, have to be monitored by the authorities. The NORM ordinance [2] lists the processing of phosphates in the chemical industry and in the fertilizer industry, both as work areas with potentially elevated exposures to uranium and thorium and their decay products, and as a work area in which residues with increased content of uranium and thorium and its decay products may incur. Next to nitrogen and potassium, phosphorus is one of three main components of fertilizer. The radioactive isotope 40K in potassium and the natural radionuclides of the uranium-radium decay series in phosphate rock are the radiological relevant radionuclides in fertilizers.

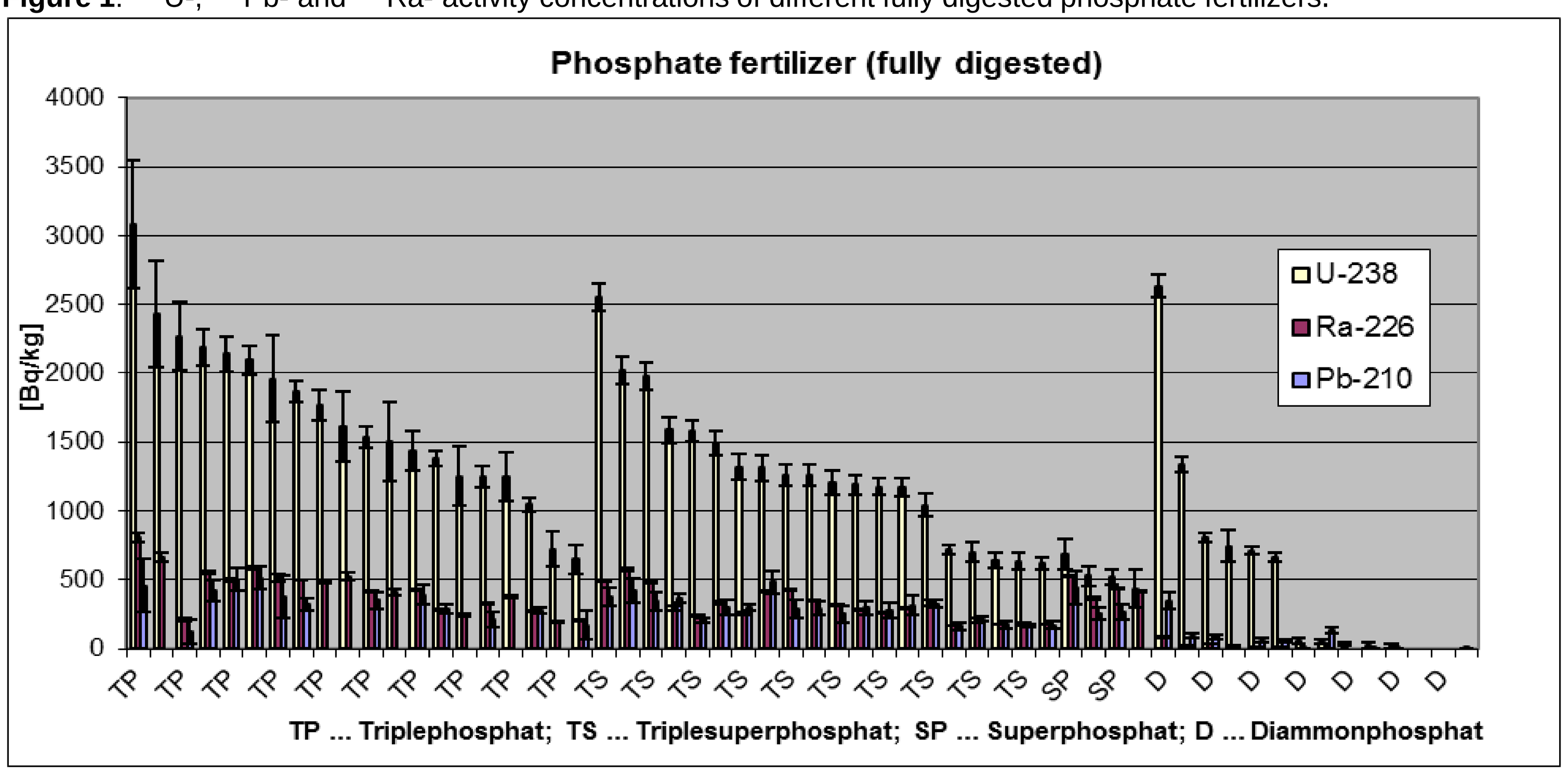
Organic fertilizer

Eleven fertilizers were assigned to the organic fertilizer. The activity concentrations of radionuclides of the natural decay series are all less than 50 Bg/kg. The mean activity concentration of ^{40}K is 188Bq/kg. The maximum activity concentration of ^{137}Cs, 40 Bq/kg, was detected. The origin of the Cs contamination is explained due to the accident of Chernobyl.

Phosphate fertilizer

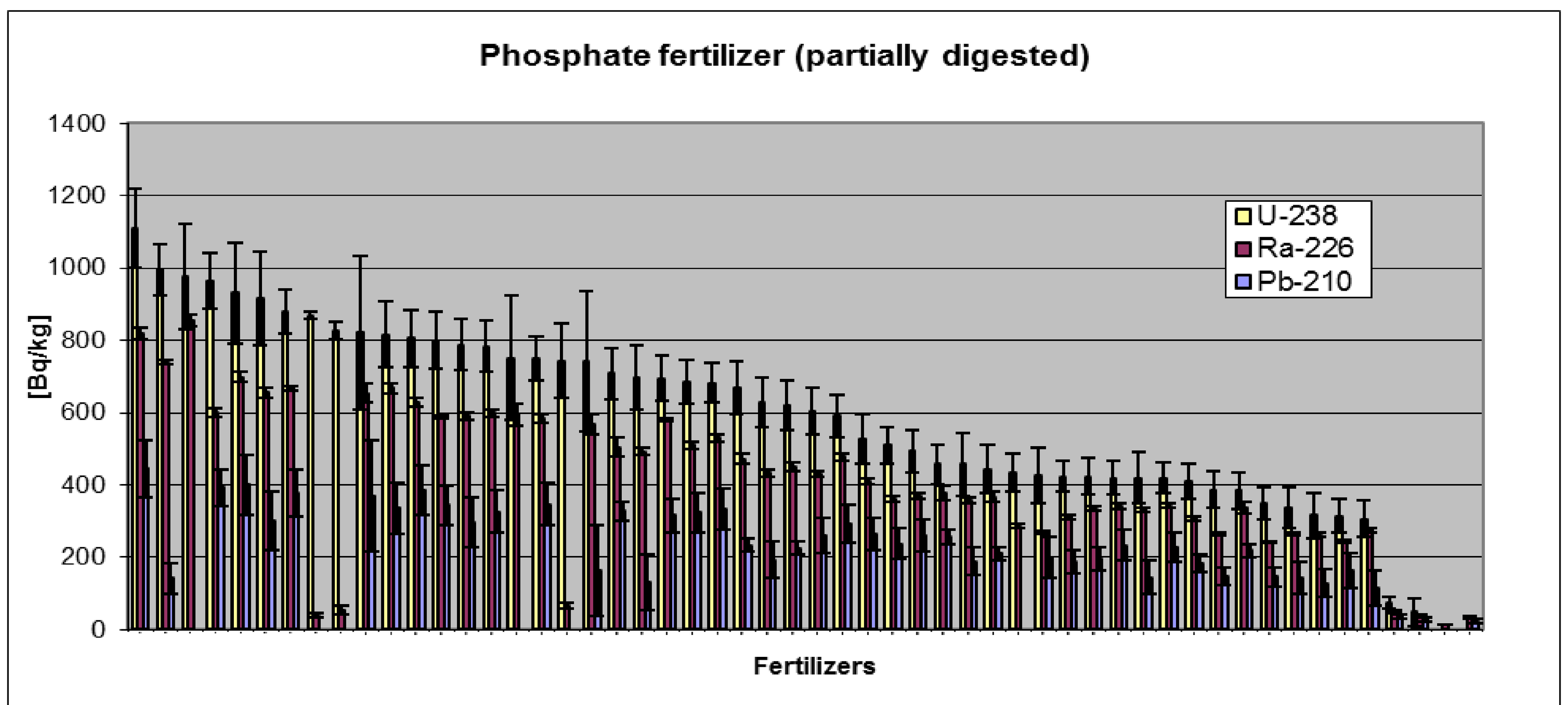
In Figure 1 different types of fully digested phosphate fertilizers (triple phosphate, triple super phosphate, di-ammonium phosphate and superphosphate, from left to right) are shown. A total of 58 fertilizers, 14 of them are assigned to di-ammonium phosphate, respectively 20 of them are assigned to triple phosphate and to triple superphosphate and 4 of them are assigned to superphosphate.
At triple phosphate fertilizers it can be seen that the rock phosphate was processed with phosphoric acid. The contribution of phosphoric acid can be identified because of the elevated ^{238}U activity concentration. Nearly no nuclides of the Thorium decay chain could be detected.
Triple super phosphate fertilizers are similar except that in the preparation in addition to phosphoric acid also sulfuric acid is used. Furthermore, the thorium series radionuclides could be measured, which, however, all with activity concentrations below 50 Bq/kg have no relevance from the viewpoint of radiation protection. The average ratio of ^{226}Ra to ^{238}U activity concentration is 0.25.
Super phosphate fertilizers are combined phosphate/sulphur fertilizer. During the processing of rock phosphate with sulphuric acid, no separation takes place between the phosphoric acid leached phosphate, uranium, thorium and the radium in the phosphogypsum. That's why the radium and uranium remains in the fertilizer [4]. The measured activity concentrations show that the radionuclides are still in equilibrium.
Di-ammonium phosphate or rather di-ammonium hydrogen phosphate is an ammonium salt of phosphoric acid. For the di-ammonium phosphate fertilizers a considerable variation in the ^{238}U activity concentrations (18 -2632 Bq/kg) was observed. Causes of these fluctuations may be the initial activity concentration in used rock phosphate and secondly the quality of the phosphoric acid.

Figure 1: ^{238}U-, ^{210}Pb- and ^{226}Ra- activity concentrations of different fully digested phosphate fertilizers.



Next to the fully digested phosphates are listed in Figure 1 also partially digested phosphates and fine ground earthy soft rock phosphates are present. A total of 54 of the partially digested fertilizer are assigned to the phosphate fertilizers. A more precise distinction as to the fully digested phosphate fertilizers is not possible. The mean activity concentration of ^{40}K is 522 Bq/kg.

Figure 2: 238U-, 210Pb- and 226Ra- activity concentrations of different partially digested and earthy soft rock phosphates.



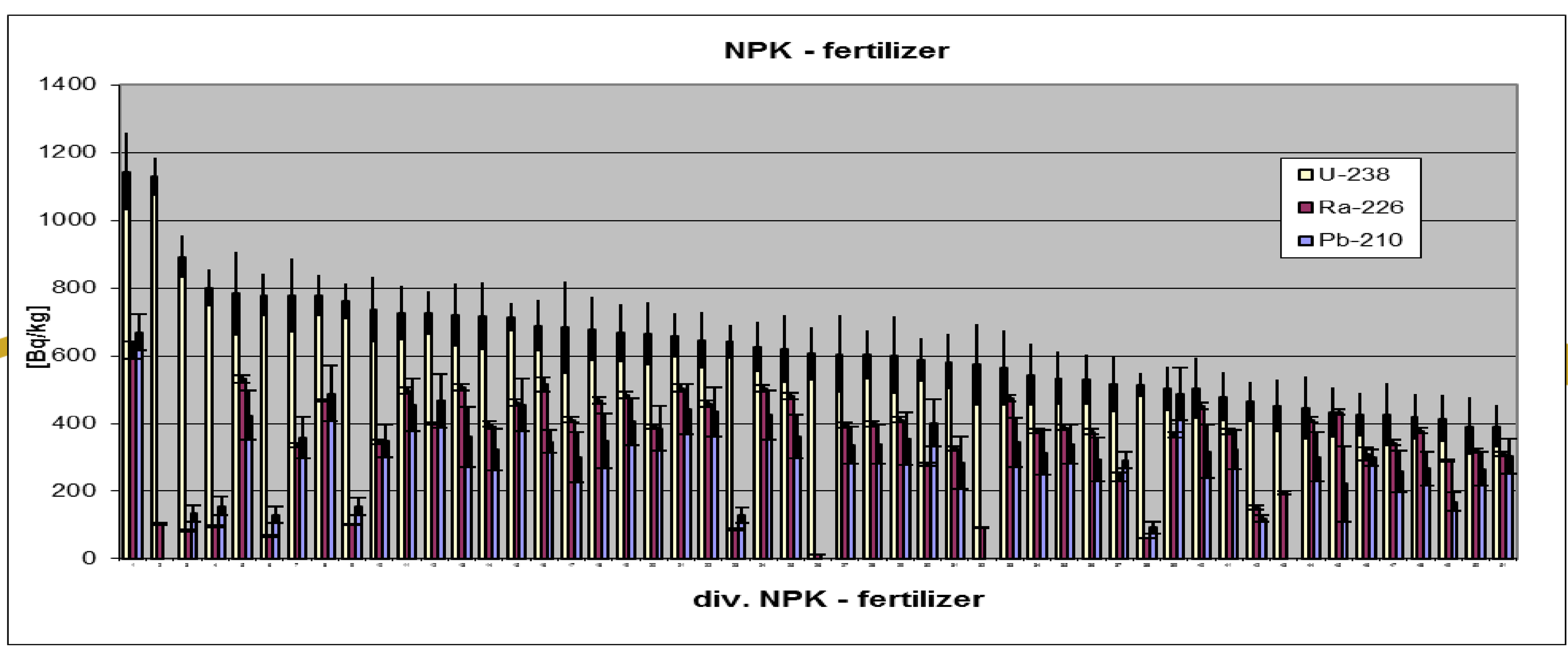
Potassium fertilizer

Potassium contains 0.012% of the radioactive isotope potassium-40 with a specific activity of 32.2 kBq/kg. The potassium content influences directly the activity concentration. Substituting the ^{40}K activity concentration of the fertilizer at the specified concentration in K_20 ratio, shows that on average, the activity concentration is 234 ± 15 Bq/kg for each per cent increase K_20. A total of 25 fertilizers are assigned to potassium fertilizers. Fertilizers designated Thomaskali, Donau Chemie 44-45 and Hyperkali are phosphor/potassium fertilizer and will be compared with the rest of PK fertilizers. Fourteen fertilizers exceeded the ^{40}K activity concentrations of 10 Bq/g. Radionuclides of the natural decay series, with more than 10 Bq/kg, were not detected.

Compound fertilizer

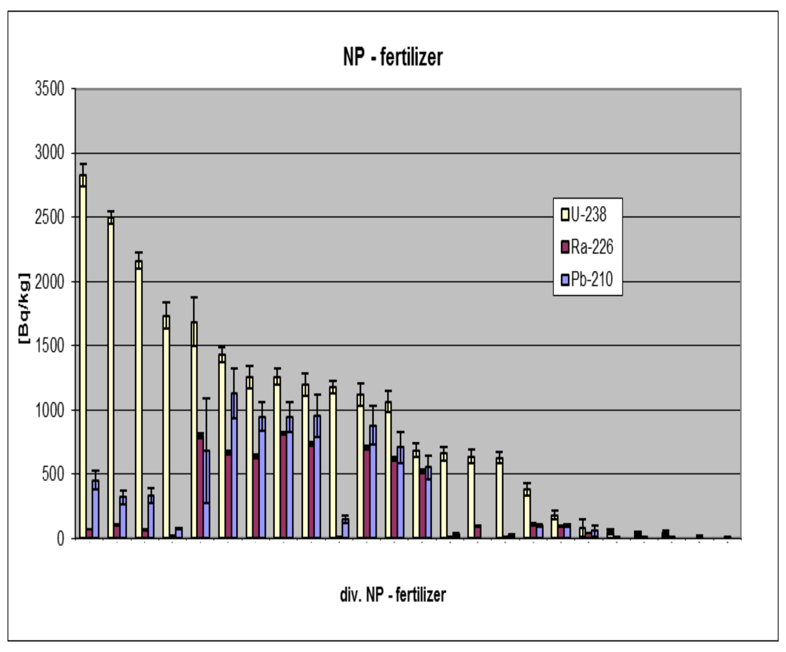
NPK fertilizers or compound fertilizer are a mixture of the three major fertilizer components (N is nitrogen, P for phosphorus and K for potassium). There are 184 fertilizers which were assigned to this group. These fertilizers are made by mixing of single-nutrient fertilizers. It is often unclear if the phosphorus is fully or partially digested. In 124 NPK-fertilizers uranium-238 could be measured. The activity concentration ratios between 226Ra and 238U show that for the manufacture of these fertilizers different sources of phosphate have been usedTwo fertilizers exceed the 238U activity concentration of 1 Bq/g. In the NPK figure are 50 NPK-fertilizers shown, which represent the highest 238U activity concentrations.

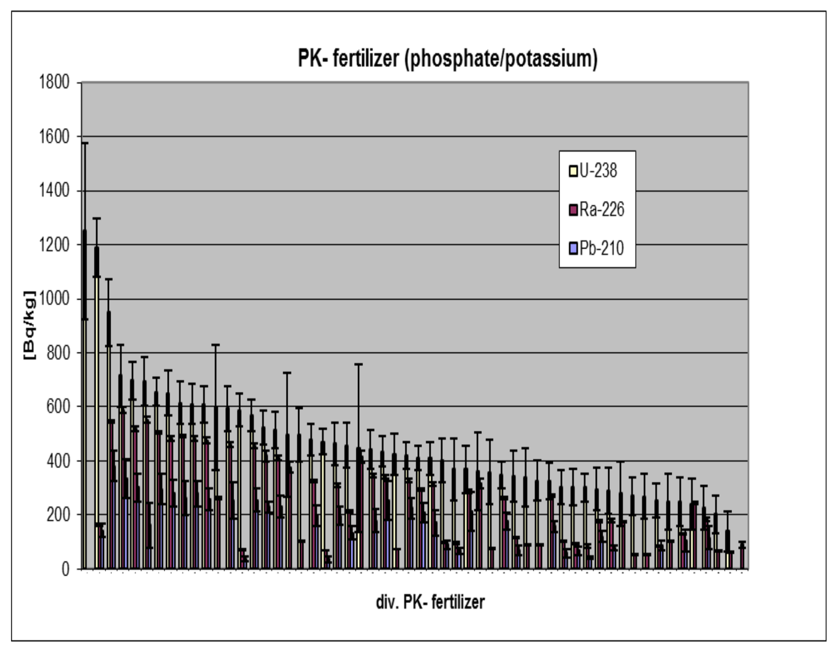
Figure 4: ^{238}U-, ^{210}Pb- and ^{226}Ra-activity concentrations of 50 compound fertilizers with the highest ^{238}U- activity concentrations.



Dual-nutrient fertilizer

Similar to the production of compound fertilizers, dual-nutrient fertilizers are made by mixing of single-nutrient fertilizers. A distinction between fully and partially digested phosphate fertilizers is not possible. Due to the large number of different dual-nutrient fertilizers, we focus only on NP (nitrogen and phosphate), PK (phosphate and potassium) and other phosphate-containing fertilizers. A total of 24 fertilizers are associated with NP-fertilizers (nitrogen, phosphorus). At 12 NP-fertilizers exceed the ^{238}U activity concentration of 1 Bq/g.





A total of 56 fertilizers are associated to PK-fertilizer (phosphorus, potassium). Two PK-fertilizers exceeded the ^{238}U activity concentration of 1 Bq/g.

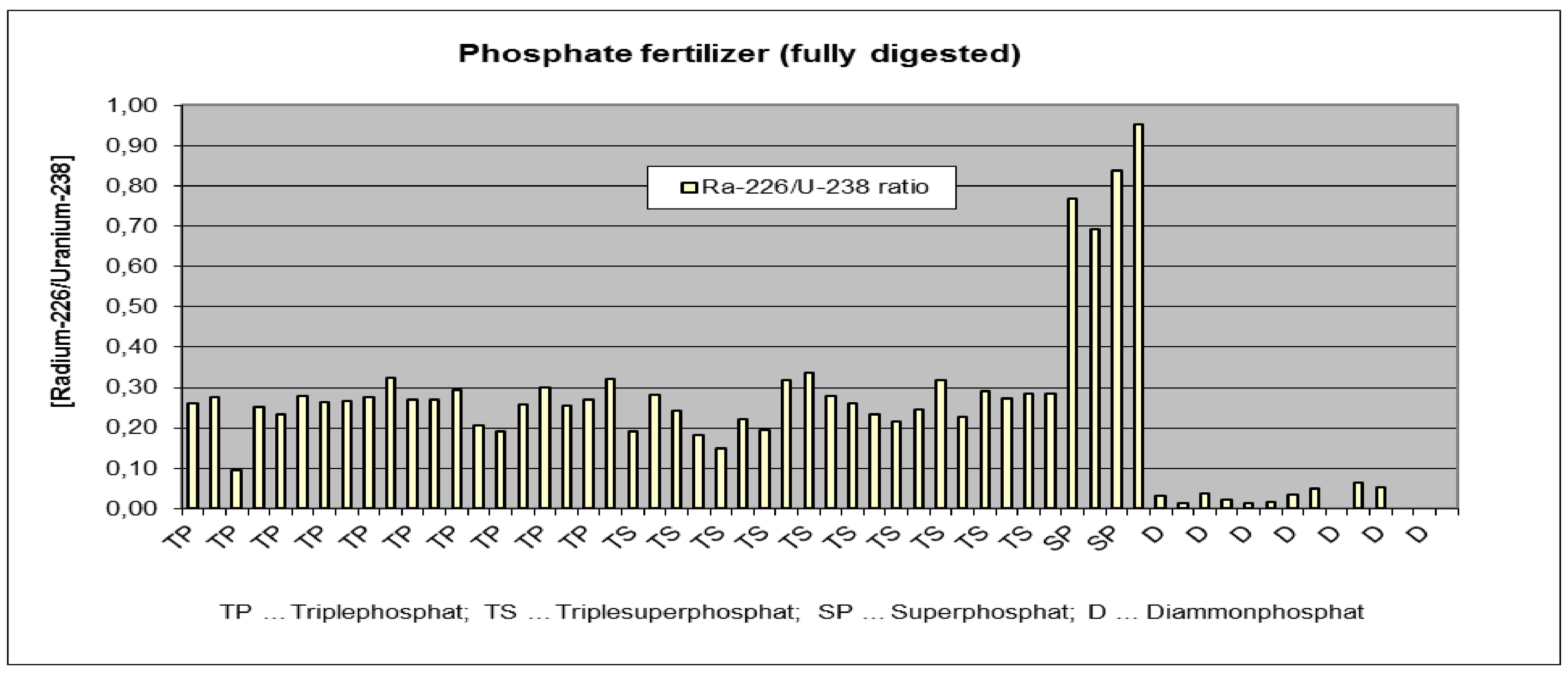
Summary of the results

An overview of the minmal, maximal and the arithmetically averaged activity concentrations of radiological relevant nuclides of all assigned fertilizers is shown in the following table.

Fertilizer Classification	^{238}U [Bq/g]			^{226}Ra [Bq/g]			^{210}Pb [Bq/g]		
	Min	Max	MW	Min	Max	MW	Min	Max	MW
Org. fertilizer (11)	-	-	-	0,001	0,014	0,007	0,010	0,010	0,010
Di-ammon phosphate (14,fully digested)	0,018	2,632	0,642	0,001	0,082	0,016	0,056	0,346	0,129
Superphosphate (4, fully digested)	0,435	0,689	0,542	0,364	0,529	0,435	0,018	0,028	0,022
Triple superphosphate (20, fully digested)	0,622	2,549	**1,272**	0,164	0,570	0,311	0,164	0,483	0,286
Triple phosphate (20, fully digested)	0,647	3,080	**1,671**	0,196	0,803	0,424	0,119	0,513	0,339
Phosphate fertilizer (54,partly digested)	0,050	1,110	0,608	0,014	0,856	0,414	0,023	0,445	0,238
PK-fertilizer (56, f/p digested)	0,139	1,250	0,460	0,054	0,587	0,254	0,036	0,381	0,178
NP-fertilizer (24, f/p digested)	0,041	2,829	**1,038**	0,02	0,817	0,259	0,029	1,130	0,471
NPK-fertilizer (190, f/p digested)	0,039	1,143	0,382	0,001	0,617	0,162	0,002	0,668	0,210
Potassium fertilizer (25)	-	-	-	-	-	-	-	-	-
Other fertilizer (93)	0,019	1,294	0,246	0,001	0,761	0,042	0,002	0,355	0,056

$^{226}Ra/^{238}U$-ratio

The $^{226}Ra/^{238}U$-ratio indicates transfers of different species of NORM nuclides within rock phosphate processing. In figure 6 is shown that triple phosphate und triple super phosphate fertilizers have similar ratios between 0.25 and 0.26. A redistribution of NORM nuclides is to assume and that the additional processing with sulphuric acid at triple superphosphate fertilizers have no significant influence. Di-ammon phosphate fertilizers have an average ratio of 0.03 which matches with former investigations [14]. Super phosphate fertilizers have a comparable average ratio, like mineralized fertilizers, of 0.81 and 0.71. That's why we conclude that during processing there is no significant redistribution of NORM nuclides. The $^{226}Ra/^{238}U$ ratio is relevant insofar as it can be concluded that in cases of small ratios a redistribution of NORM nuclides within the processing plants and elevated activity concentrations in the residues have to be taken into account. Furthermore, it allows an assignment of dual- and compound fertilizers with regard to the digestion of the phosphate.



Conclusion

At fully digested phosphate fertilizers an activity concentration with more than 1 Bq/g is likely possible. The average activity concentration is 1238 Bq/kg (99.5 mg/kg). At NP-fertilizer more than the half of them has activity concentrations higher than 1 Bq/g. The average activity concentration is 1035 Bq/kg (83.5 mg/kg). In all other investigated types of fertilizer, expect some outlier due to a possible false assignment, have significant lower activity concentrations of the uranium-radium decay chain of 1 Bq/g. Nuclides of the thorium decay chain does not matter with regard of the 1 Bq/g criteria. The assessment shows that even with conservative scenarios no real danger regarding to the NORM nuclides exists. Nevertheless we should keep in mind that phosphate fertilizing is the major large area distribution of uranium and its daughters into the environment in Europe. The potassium assessment scenario indicates that the storage of large amounts of potassium fertilizer (production, wholesale and distribution) can lead to doses above 1 mSv/year.
The $^{226}Ra/^{238}U$ ratio is a tool to identify types of fertilizer and processes within the production which can accumulate NORM nuclides in processing system and residues.

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