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APPROACHES TO LIMITING THE CONTENT OF ENVIRONMENTALLY HARMFUL IMPURITIES IN PHOSPHATE FERTILIZERS (a)

Nadya Dylevskaia, Phosagro, Russia

This paper deals upon contents of harmful impurities in phosphate fertilizer and raw materials. In particular, it examines their effects on human health and environment and ways and challenges the fertilizer industry faces to reduce the levels of hazardous impurities in fertilizer and their negative environmental impact.

Mankind and environment are constantly affected in many ways: mechanically, radiologically, toxicologically, climatically and so on. Now, the modern eco-oriented and humane society makes stricter demands to major human contacts – atmosphere, drinking water and foodstuffs. Thus, some countries with higher social standards and ever stronger market competition have already adopted regulations on a national level and have created conditions to reduce impact of hazardous impurities on environment and, as a result, on human health:

- Atmosphere control

There are standard and individual technical means for industrial exhaust purification and preliminary purification of transport exhaust. New power sewage and water treatment universal technologies are applied to each type of impurity to meet sanitary requirements.

- Water quality control

Is implemented through corresponding legal documents: in EU countries though EU Directive 76/464 on the discharge of dangerous substances into the aquatic environment, in USA – through National Primary Drinking Water Regulations, Standards of the Use of Disposal of Sewage Sludge and etc.

- Foodstuff quality control

Foodstuffs control involves many factors. These factors make up a chain through which hazardous impurities migrate into foodstuffs. The chain includes fertilizer raw materials - mineral fertilizer → soil → crop→ raw materials for food processing.

Mineral fertilizers are the major source which transmits inorganic elements to foodstuffs. Concentrations of inorganic elements in fertilizer largely depend on the raw materials used to produce them. Phosphate rock accounts for a larger proportion of hazardous impurities as compared to sulphur, nitrogen and potassium containing raw materials (Table 1). Unlike organic contaminants, metals do not have an environmental half-life. They persist indefinitely in biosphere. Hence, special precaution and effective control are required to prevent metal accumulation in the environment. As compared to other contaminants, metals have an elimination half-life (in the human body) of approximately 20 years. Consequently, their removal from the human body is low.

Email : Dylevskaya@agrofinprom.ru

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Table 1. Concentration of Hazardous Impurities in Sulphur-, Nitrogen-, Potassium containing raw materials.

No	Element	Concentration, mg/kg				
		Pyrites	Potassium sulphate	Potassium chloride	Ammonium sulphate	Ammonium nitrate
1	Cu	3000 – 5000	9-22	20-25	3-30	2-20
2	Pb	100 – 2000	5-20	3-7	1-2	<1
3	Ni	-	10-15	10-12	5-50	5-20
4	Zn	5000 - 6000	5-10	30-40	20-70	10-30
5	Cr	-	40-80	15-35	20-50	2-20
6	Mn	-	15-80	150-170	40-150	10-75
7	As	700 - 900	1-5	~2	2-20	<1
8	Cd	5,5 - 8,1	<1	2-3	1-2	<1
9	Co	50 - 200	5,0	<0,6	1-2	~1
10	Se	30 - 60	-	-	-	-
11	Tl	25 - 40	-	-	-	-

There is no universally recognized approach to regulate the contents of harmful impurities in fertilizer. Separate attempts have been made by individual countries to restrict the levels of some elements. So, in 1999 three European countries - Austria, Finland, Sweden – took their own steps to set maximum limits for cadmium in fertilizers at the national level. These measures had immediate and noticeable results. For example, the average cadmium content of fertilizers in Sweden fell from 80 mg/kg P to less than 20 mg/kg P (approximately 8 mg/kg P_2O_5). The growing scientific research into, and increasing public disquiet regarding, the threat posed both to human health and the environment by cadmium, led to the adoption of the 1991 Cadmium Directive which tackles the threat posed by cadmium in the industrial arena by placing tight controls, and in some cases prohibiting outright, the use of cadmium in the production of a range of products. The willingness of the EU to address the dangers inherent in the industrial use of cadmium makes its failure to regulate properly the values of cadmium in fertilizers at an EU-wide level all the more surprising, particularly given the increased likelihood of cadmium entering the human diet via this route.

The scientific community became aware during the late 1960s, the threat posed by the presence of significant levels of cadmium in agricultural soil following the outbreak, in Japan, of the infamous "itai itai" disease which turned out to be caused by chronic cadmium poisoning resulting from the absorption of the toxin through the roots of the rice plant. Yet still no concerted action has been taken to ensure that the very real threat to human health created by the presence of excessive levels of cadmium in agricultural soil is, as a minimum, controlled but, ideally, is eliminated.

There are two types of phosphate rock – sedimentary (which accounts for 88% of total phosphate rock production and is mainly found in North Africa, such as in Morocco, Tunisia) and igneous rock (as produced in Russia and South Africa). Sedimentary phosphate rocks in general contain a much higher concentration of potentially hazardous elements (mainly cadmium, chromium, mercury, uranium, vanadium) than igneous rock (Table 2).

Table 2. Concentrations of Hazardous Elements in Phosphate Rocks, ppm

No	Element	Morocco		Togo	Senegal	Jordan		Tunisia	Algeria	USA	Israel	Syria	Russia		South Africa
		Bu Cra	Khouribga	Benin	Taiba	Eshidia	ElHassa	Gafsa	DjebelOnk	Florida	Nahal Zin	Kneifiss	Kola	Kovdor	Phalaborva
1	Cadmium	25-42	3,0-27	53-65	53-110	3,0-9,6	2,7-34,7	15-63	11-22,5	6,8-11,2	20-30	5-15	0,05-0,12	0,5-0,9	0,04-5,0
2	Hg	0,1	0,03-0,1	-	0,1-0,5	0,03	0,01-0,5	0,05-0,2	0,3-5,0	0,08	0,4-0,6	0,01-0,1	<0,01	0,1	0,15-0,2
3	As	3-9	6-13	-	0,1-3,6	5-7	2,6-27,5	1,5-31,9	10-22,6	8,0-9,0	3-10	15-30	0,2-1,0	2-4	3-15
4	Pb	1	1-3,3	-	4-5	3,4	1-16,2	4-11,4	6-20	18	2-7	2-10	0,6-2,0	2-14,3	2-19
5	Cr	130	300	30	6-200	60-100	72-100	81	200	91	50-70	-	2,1-3,0	1-69	7-10
6	Sb	-	-	-	-	-	-	-	10-15	-	-	-	1,0-2,0	1,0-4,0	-
7	Ba	-	-	-	100	-	-	-	-	-	-	-	700-1000	70-690	-
8	F*	3,9-4,5	3,9-4,1	3,8	3,7-3,9	3,6-4	3,7-3,8	3,54-4,9	3,3-3,7	3,8	3,3-4,0	3,6-4,0	2,65-3,3	0,96-1,01	0,22-2,25
9	Cu	14	39-47	-	50-70	21	9-27	19-28	15-24	9,0	20-40	5-29	29-70	4-40	105-130
10	Ni	40	41	-	28-53	11	15-71	28	16-20	30	35	53-61	5-11	14-28	14-40
11	Zn	66-120	200-255	-	-	135-164	85-420	151-370	185	95	300-500	320-340	20-30	23-64	6-20
12	Co	-	-	-	1	6	9-26	17-20	17	-	-	8	2,5-5,3	5	-
13	Mn	200	-	200	20	11,6	30-77	35-37	14-35	290	5,0-10	6-7	200-500	300-1100	200
14	Sr	-	150	30	120-800	-	1100-2500	1925	2022	-	2000-4000	1900	22500-36300	1600-2830	4650-5500
15	V	122	21	-	140	50-70	32-70	62	45	70	100-160	-	81-150	3-90	8-15

* concentration in %

Concentrations of harmful impurities in fertilizers, including cadmium, depend on the type of phosphate rock, production technologies employed, and type of fertilizer produced. Higher cadmium concentrations are found in superphosphates (SSP, TSP) as these are straight rock products. In NP fertilizer production (MAP, DAP, AP's), the cadmium values depend on the production technologies used (thermal or wet-process technology). Though the use of the thermal process results in a low cadmium concentration in the final product, this method is not normally used in the production of phosphate fertilizers as the costs of the process are excessively high. As for phosphate fertilizers of Russian origin, the amount of cadmium does not normally exceed 0.1 mg/kg P_2O_5, as their production is based on igneous rocks with a low cadmium content. Cadmium values in fertilizers produced from other sources are usually considerably higher. The same is true of content of other harmful impurities.

To comply with the principles of lower values of hazardous elements in fertilizers, the producers face two options: either to employ impurities removal technologies (in case of cadmium – decadmiation technology) or to use contaminant-free phosphate rock and phosphate fertilizers. For instance, it has been estimated that the application of cadmium removal technologies would entail a fertilizer price increase to farmers in EU of $6-$32 pt depending on the type of the technology used, plus a 30% rise in the installation of the given technique. However, the switch towards low cadmium fertilizers manufactured using low cadmium rock would entail a 5-10% rise in fertilizer prices, a much lower cost rise of $3-$6 (assuming an average phosphate rock price of $44) (Table 3). As fertilizers are an important agricultural input, the costs of agricultural production would also rise, reducing the competitiveness of EU agriculture. That is why, it seems strange that despite all the benefits of eco-friendly fertilizers from Russia, EU countries effectively block the flow of such high quality products by imposing a 6.5% import duty.

Table 3.

Indicator	Unit	Phosphate rock		
		Morocco	Togo	Senegal
1. Major impurities to be removed.		Cadmium, As, Cr		
2. Capital costs to purify by-products to bring in line with recognized standards, processing of 50 000 t/P2O5 per year.	1000 $	2300-3800		
3. Operating costs to process phosphate rock.	$/тP2O5	10-15	15-20	15-25
4. Expenses including 15- year depreciation of basic equipment.	$/тP2O5	13-20	18-25	18-30

Concentration of harmful impurities in fertilizers has direct implications for soil, ground and surface water.

Application of mineral fertilizers involve 2 pollution cycles:
soil → agricultural products → foodstuffs
soil → ground water → surface water → drinking water

Highly hazardous toxic elements, which pose threats to soil and crops are realized through their mobility of these elements in soil. High mobility of the elements means their high absorption by plant and lower deposit capacity in soil. By contrast, lower mobility means higher accumulation in soil. However, soil prevents some part of the elements from transmission to the plant. Irrational application of fertilizers with high levels of impurities resulted in soil overloading with these elements. At present, the protection capacity of soil is almost completely exhausted. To reduce soil pollution, the maximum concentration levels (MCL) for individual elements have been introduced in different countries. If we compare MCLs observed in Russia, Germany and the Netherlands, we will come across different treatment of elements which is mainly determined by the difference in chemical inputs used, cultivation technologies, application rates, etc. (Table 4)

Table 4. Maximum Admissible Concentration Levels (MCL) of Chemicals in Soil, mg/kg.

No	Element	MCL, Russia (Sanitary standards No6229-91)	MCL, Germany [2]	Concentration standards, the Netherlands [3]		Form
				Level not recommended to exceed	Penalty for concentration above recommended levels	
1	F	10,0	500			Water
2	Cu	3,0				Mobile
3	Ni	4,0				
4	Zn	23,0				
5	Co	5,0				
6	F	2,8				
7	Cr	6,0				
8	Cu	55,0	100	100	500	Total content
9	Ni	85,0	50	100	500	
10	Zn	100,0	300	500	3000	
11	Co		50	50	300	
12	Cr		100	250	800	
13	Cd		3	5	20	
14	Sr		10			
15	Sn		50	50	300	
16	Mo		10	40	200	
17	Pb	30,0	10	150	600	
18	As	2,0	20	30	50	
19	Hg	2,1	2	2	10	
20	Ba			400	2000	
21	Sb	4,5	5			
22	Mn	1500,0				
23	V	150,0	50			
24	(V) +	100,0+1000				
25	(Pb)	20,0+1,0				

Negative implications of toxic elements in fertilizers for ground and surface waters are even higher. The quality of drinking water is strictly regulated. Availability of toxic impurities, such as arsenic, cadmium, mercury, lead, thallium, in primary water above a maximum admissible level requires a multi-stage expensive drinking water production.

Higher toxic impact on ground waters than on soil by hazardous elements can be illustrated by cadmium pollution analysis. This analysis defines the pollution scale for soil, ground and surface waters when 100 kg P_2O_5/ ha are applied. Cadmium in apatite concentrate of Russian origin has the smallest impact both on soil and ground waters (Table 5).

Table 5. Cadmium Pollution of Soil and Surface Waters. Phosrock application rate -100 kg P_2O_5/ ha

Phosphate rock	Pollution cycle for soil and foodstuffs		Pollution cycle for soil and surface waters
	Background content, mg/kg	Pollution level for soil, t	Pollution level for waters, м3
Morocco, Bu Craa	0,5	3,00	7500
Morocco, Khouribga		1,30	3200
Togo, Benin		5,20	13000
Senegal, Taiba		5,60	14000
Jordan, Eshidia		0,30	800
Jordan, El Hassa		0,55	1400
Tunisia, Gafsa		3,30	8150
Algeria, Djebel Onk		1,50	3700
USA, Florida		0,70	1850
Israel, Nahal Zin		1,90	4750
Syria, Kneifiss		1,20	2950
Russia, Kola		0,03	90
Russia, Kovdor		0,05	120
South Africa, Phalaborva		0,11	270

Despite vast information available on contents of inorganic elements in phosphate rock, their distribution at various processing phases, to date, no single approach to phosphate fertilizer and rock control has been worked out.

The following principles can be the basis for such an approach:

- to single out a group of hazardous trace elements which determine high integral level of toxicity in phosphate fertilizer,
- to summarize research information on by-products and fertilizer to define a distribution index for the elements in processing,
- to choose a toxicity index for inorganic elements individually to define their toxicity level in phosphate raw materials,
- to determine an integral toxicity index to classify phosphate raw materials and phosphate fertilizer from the point of view of their environmental and health risks.

Hazardous elements occurring in phosphate rock make up the following 3 groups:

- Elements with high toxicity: cadmium, mercury, arsenic, thallium, selenium, lead, chromium, barium, antimony, fluoride. These elements oppress metabolism processes, have a complex destructive impact and accumulate in organs and tissues.
- Elements with moderate toxicity: manganese, copper, nickel, molybdenum, cobalt, strontium. Low concentrations of the elements stimulate metabolism processes and transfer energy and mass on the cellular level.
- Elements with low toxicity: tin, iron, vanadium. These elements stimulate metabolism, do not, as a rule, accummulate in organs and tissues. Their concentration in organism can vary within a wide interval without any harm to functional systems.

Table 6. Classification of Toxic Elements

	Groupings	Element	Targeted impact on human health	MCL		Level of Toxicity*
				In water ,mg/l	In foodstuffs	
	With high toxicity	Cd	Cardiovascular system, lungs, bony tissue, pancreas	0,001	0,01-0,1	2
		Hg	Nervous system, blockade of biologically active protein molecules	0,0005	0,005-0,5	1
		As	Metabolic disturbance, blood system, nervous system, liver, kidneys	0,05	0,05-1,0	2
		Tl	Nervous system, gastro enteric tractт, kidneys	0,0001	-	1
		Se			0,5-1,0	
		Pb	Nervous system blood, vessels, bone marrow, protein synthesis, cells, chronic intoxication	0,03	0,1-1,0	2
		Cr	Kidneys, liver, pancreas, mutagenic effect	0,05	0,1-0,3	3
		Ba	Nervous system, bony tissue, vessels, bone marrow, liver	0,1	-	2
		Sb	Cardiovascular system, respiratory system	0,05	0,05-0,5	2
		F	Metabolic disturbance, bony tissue	1,5	2,5-10	2
	With moderate toxicity	Mn			-	
		Cu	General toxic effect	1,0	0,5-10,0	3
		Ni			0,1-0,5	
		Zn	Imbalance of metals in tissues and organs	1,0	5-40	
		Mo	General toxic effect	0,25	-	2
					-	
	With low toxicity	Sr	Bony tissue, liver, blood	7,0	-	2
		Sn	Cardiovascular system, respiratory system, nervous system	-	100-200	3
		Fe		-	3-50	
		Cl		350	-	

Level of Toxicity*: Highly toxic 1 - Moderate toxic 2 – Low toxicity 3

Cd – Cadmium mobility in soil is largely determined by soil acidity. Its mobility is highest in soil with low acidity within pH 4,5-5,5. Cadmium does not bind well to organic part of soil. The major point of accumulation in plants is the rooting system.

Hg – Its mobility is highest with soil acidity of pH 4-5. Inorganic mercury compounds are absorbed by humus. Organic mercury compounds and vapour from soil solutions pose a higher danger to the plant. Mercury compounds absorbed by the plant transmit easily to all systems.

As – Arsenic most frequently occurs in AsO_4^{2-} compound which is absorbed by humus and argillaceous minerals. Higher phosphorus and sulphur soil concentrations reduce arsenic impact on plant. Mushrooms and green leaf vegetables have a higher arsenic absorbing capacity than fruits.

Pb – Lead mobility depends largely on soil acidity as that of cadmium. As lead inorganic compounds have a low solubility, it is least mobile and binds to the organic soil substance and argillaceous minerals. The major accumulation point in plants is the rooting system. Though lead is passively absorbed by plants, its organic compounds retain a high toxicity level and depress physiological processes (photosynthesis, growth)

Se – Its mobility is also determined by soil acidity. The higher is the soil acidity the higher is the plant absorption capacity of the element. Its low concentrations stimulate metabolism. Though with rising concentration it becomes a toxic element, deters absorption of micro-components by plant and blocks major physiological processes. On the positive side, selenium reduces cadmium uptake by the plant.

The breakdown of elements contained in phosphate rocks and indication of their content in rocks give a clear picture of the quality of phosphate rocks and their downstream products.

To give an general description of various phosphate rocks from the point of view of their environmental toxicity (integral criterion of biological toxicity) a modified index (I) worked out by Russian scientists A.N. Angelov and V.G. Kozak can be applied.

1. Pollution cycle: soil – agricultural products – foodstuffs.

$$I = \frac{\Sigma C_i/MCL_{i\ soil}}{C\ P_2O_5}$$

C_i – concentration of i-element in phosphate rock, mg/kg;

MCL – maximum concentration level of i-element in soil, mg/kg;

$C\ P_2O_5$ – concentration of the P_2O_5 component in phosphate rock

2. Pollution cycle: soil – ground water – surface water – drinking water.

$$I = \frac{\Sigma C_i/MCL_{i\ water}}{C\ P_2O_5}$$

C_i – concentration of i-element in phosphate rock, mg/kg;

MCL – maximum concentration level of i-element in water, mg/kg;

$C\ P_2O_5$ – concentration of the P_2O_5 component in phosphate rock

This approach takes into consideration the basic concentration of hazardous impurities in phosphate rocks, processing technologies, distribution of the elements in the by-products and finished products.

Table 7. Toxicity Index (I). Pollution Cycle 1.

No	Phosphate rock	BPL Grade	I (for elements with high toxicity)	I (for elements with moderate toxicity)	I (for elements with low toxicity)	Integral I
1	South Africa,Phalaborva	88	1,5	2,0	0,3	3,9
	Russia, Kovdor	83	2,6	1,8	0,6	5,1
	Russia, Kola	85	1,5	1,3	2,5	5,2
2	Jordan, Eshidia	73/75	6,7	2,1	3,5	12,3
	USA, Florida	75	9,4	1,6	4,1	15,1
	Jordan, El Hassa	72/74	9,1	3,8	3,4	16,3
	Syria, Kneifiss	63/65	14,3	3,9	2,8	20,9
3	Morocco, Khouribga	70/71	20,6	3,3	1,3	25,3
	Israel, Nahal Zin	71	19,9	3,5	8,1	31,5
	Algeria, Djebel Onk	63	29,0	3,7	3,2	36,0
	Morocco, Bu Craa	80	28,4	1,8	6,7	36,9
	Tunisia, Gafsa	63	30,9	4,7	4,3	39,9
	Togo, Benin	80	43,6	0,4	0,0	43,9
	Sensgal, Taiba	80	48,9	1,6	7,7	58,2

Table 8:Toxicity Index (I). Pollution Cycle 2.

No	Phosphate rock	BPL Grade	I I*10-3 (for elements with high toxicity)	I*10-3 (for elements with moderate toxicity)	I*10-3 (for elements with low toxicity)	I*10-3 (integral)
1	Russia, Kola	85	16	0,2	0,8	2,7
	Russia, Kovdor	83	2,9	0,5	0,3	3,7
	South Africa, Phalaborva	88	3,8	0,6	0,1	4,5
2	Jordan, Eshidia	73/75	12,2	0,6	1,7	14,6
	Jordan, El Hassa	72/74	18,9	1,2	1,6	21,7
	USA, Florida	75	24,4	0,6	2,0	27,0
	Syria, Kneifiss	63/65	33,9	1,6	1,4	36,8
3	Morocco, Khouribga	70/71	51,3	1,3	0,7	53,3
	Algeria, Djebel Onk	63	54,5	0,9	1,6	57,0
	Israel, Nahal Zin	71	51,9	1,2	4	57,1
	Morocco, Bu Craa	80	81,3	0,8	3,3	85,4
	Tunisia, Gafsa	63	88,1	1,3	2,1	91,5
	Togo, Benin	80	130,4	0,0	0,0	130,4
	Senegal, Taiba	80	144,3	0,7	3,8	148,8

The calculation of the integral index of biological toxicity helps make up 3 groups of phosphate rocks:

1. <u>Phosphate rocks with a low level of toxicity.</u> They include apatite concentrates from Russia (JSC Apatit, Kovdor beneficiation plant), South Africa (Phalaborwa). This group is regarded as an elite one. To process these rocks various well-known technologies and equipment can be used without any restrictions and additional removal technologies for harmful impurities. The value of the rocks is increasing today with tighter environmental control.

2. <u>Phosphate rocks with a moderate toxicity level</u>. They include phosphorites of medium grade from Jordan, Morocco, USA, China, Israel and others. To meet environmental requirements in countries with strict regulations these rocks should be treated additionally to reduce concentration of contaminants. Application of removal technologies involves a rise in operating costs.

3. <u>Phosphate rocks with a high level of toxicity.</u> These are low-grade phosphates from Tunisia, Algeria and high-grade rocks from Togo, Senegal and Morocco. Fertilizers traditionally produced fall short of the safety requirements in economically advanced countries. To meet these environmental standards extensive purification of finished products is needed with expensive technologies employed (ion exchange, ion flotation, etc.)

Radioactivity is an additional factor which helps distinguish the 1st group from the other two. All types of apatite concentrates have a low radioactivity level, by far lower than the levels required by radiological safety standards. By contrast, phosphorite concentrates are enriched with radioactive isotopes and have a high radioactivity level.

Table 9. Radioactivity level of phosphate rocks.

				Radiation standard		
No	*Phosphate rock*	*BPL Grade*	*Total radioactivity* bq/kg*	*Russia*	*Ukraine*	*Europe***
1	Morocco, OCP, Bu Craa	80	2200 - 3500			
2	Morocco, OCP, Khuribga	70/71	2200 - 3500			
3	Togo, OTP, Benin	80	1000 - 2000			
4	Senegal, ICS, Taiba	80	1200 - 2500			
5	Jordan, JPMC, Eshidia	73/75	600 - 800			
6	Jordan, JPMC, El Hassa	72/74	600 - 800			
7	Tunisia, GCT, Gafsa	63	800 - 1200	2800	1860	
8	Algeria, Djebel Onk	63	700 - 900			
9	USA Florida	75	2000 - 5000			
10	Russia, Kola	85	< 200			
11	Russia, Kovdor	83	< 150			
12	South Africa, Foskor, Phalaborva	88	< 250			

* - total activity of natural isotopes U^{238}, Th^{232}, K^{40}.
* - standards are established by a different method.

Russia has enough reserves of high-quality contaminant-free apatite concentrates to provide the regions with high environmental requirements with eco-friendly phosphate rocks and apatite concentrate-based finished products.

Apatite concentrates from Russia and South Africa have the lowest integral toxicity and radioactivity levels of all phosphate raw materials. Phosphate fertilizers produced on their basis meet the strictest environmental and sanitary demands without any additional purification phases and operating costs involved.

The value of apatite concentrates and their fertilizer derivatives becomes far more evident with their small share in world production and trade – about 13%. Another option for the use of apatite concentrates and environmentally pure phosphate fertilizer is an increase in capital costs to equip operating plants with additional phases for contaminant removal and a consequent rise in operating costs.