9th International Conference on Sustainable Solid Waste Management

Politechnika Krakowska im. Tadeusza Kościuszki

Wydział Inżynierii i Technologii Chemicznej

Physicochemical characterization of sewage sludge ashes in terms of phosphorus recovery



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Corfu, 15-18 June 2022

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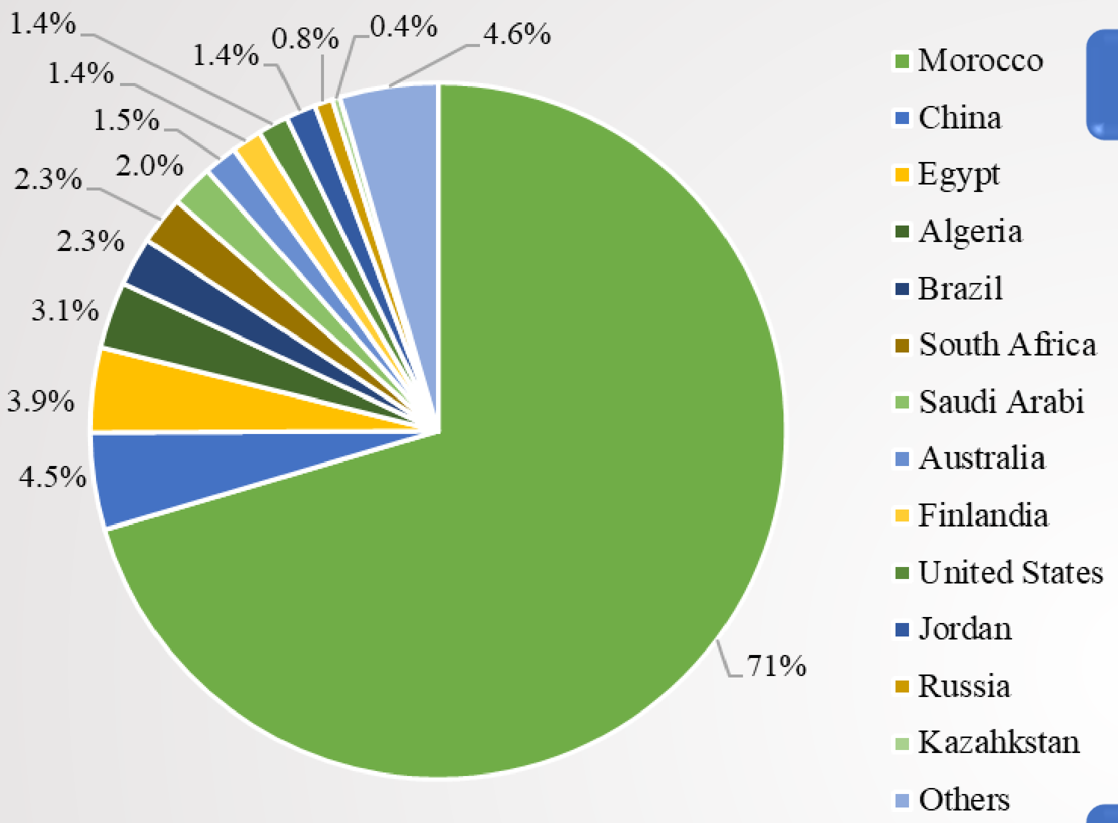

Figure 1. *Global reserves of phosphate rocks [1]*

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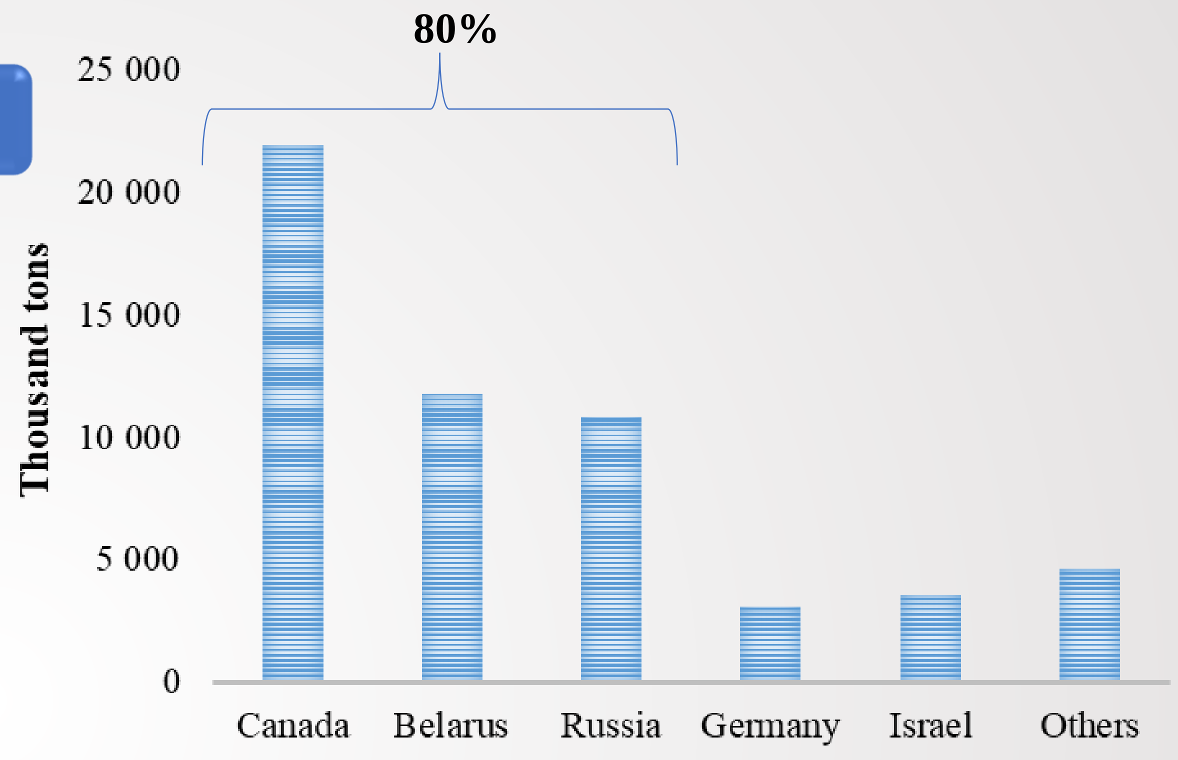

Figure 2. *Global potash export [2]*

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It is estimated that the world's reserves of phosphorus ores will be exhausted **in 320 years**.

However, if, according to the forecasts, the demand for phosphorus fertilizers grows by 1.2% annually, the world's reserves will be exhausted not in 320 but **in 190 years**.

2/3 of the ammonia is produced from natural gas, the rest from the coal gasification process.

The largest reserves of natural gas are in Russia (19.9%), Iran (17.1%), Qatar (13.1%) and the United States (6.7%) [3].

The largest reserves of coal are in the United States (23.2%), Russia (15.1%), Australia (14.0%), China (13.3%) and India (10.3%) [4].

The resource availability has been decreased due to the COVID-19 pandemic, mainly because of:

- global restriction of transport activities and disruptions in supply chains and logistics;
- delays in the exploration of new mine sites;
- investment reduction.

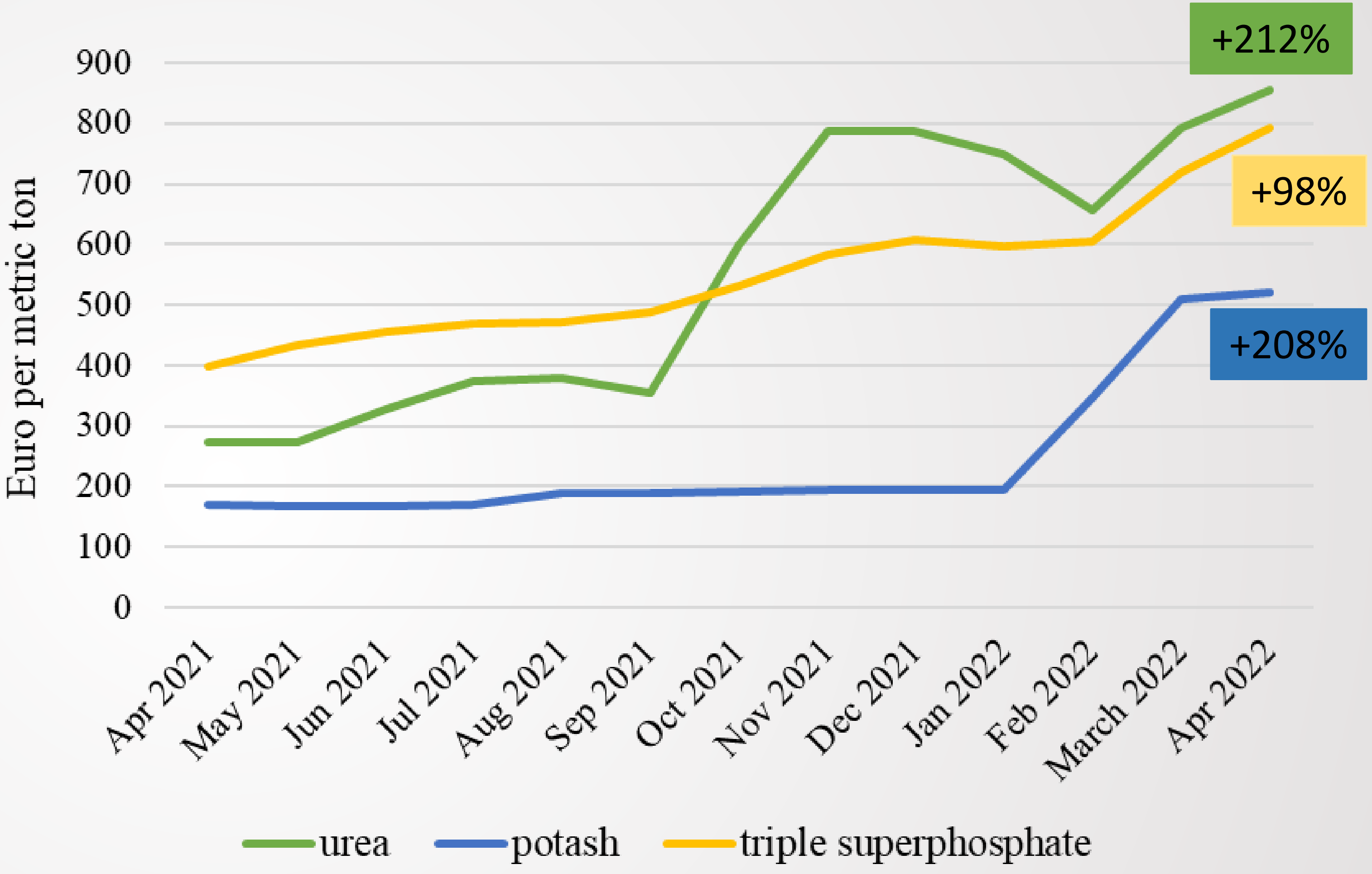


Figure 3. *Fertilizer prices [5]*

The fertilizer prices will continue to grow because of Russian war in Ukraine and sanctions imposed on Russia and Belarus in connection with this.

"A circular economy means **rejecting the linear take-make-waste economy and adopting a regenerative model**: using processes that restore, renew or revitalise their own sources of energy and materials and wasting as little as possible." [6]

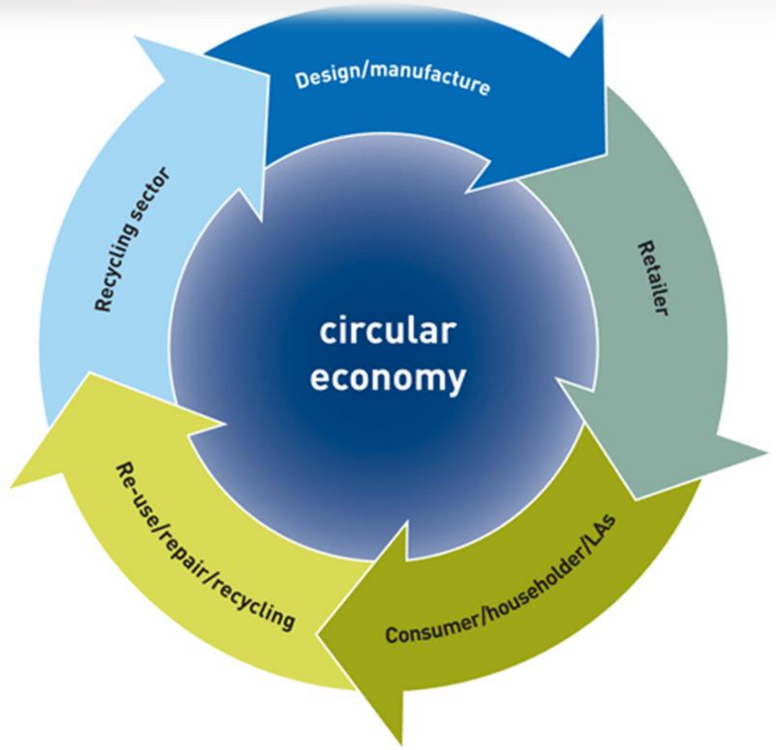


Figure 4. *Circular economy model [7]*

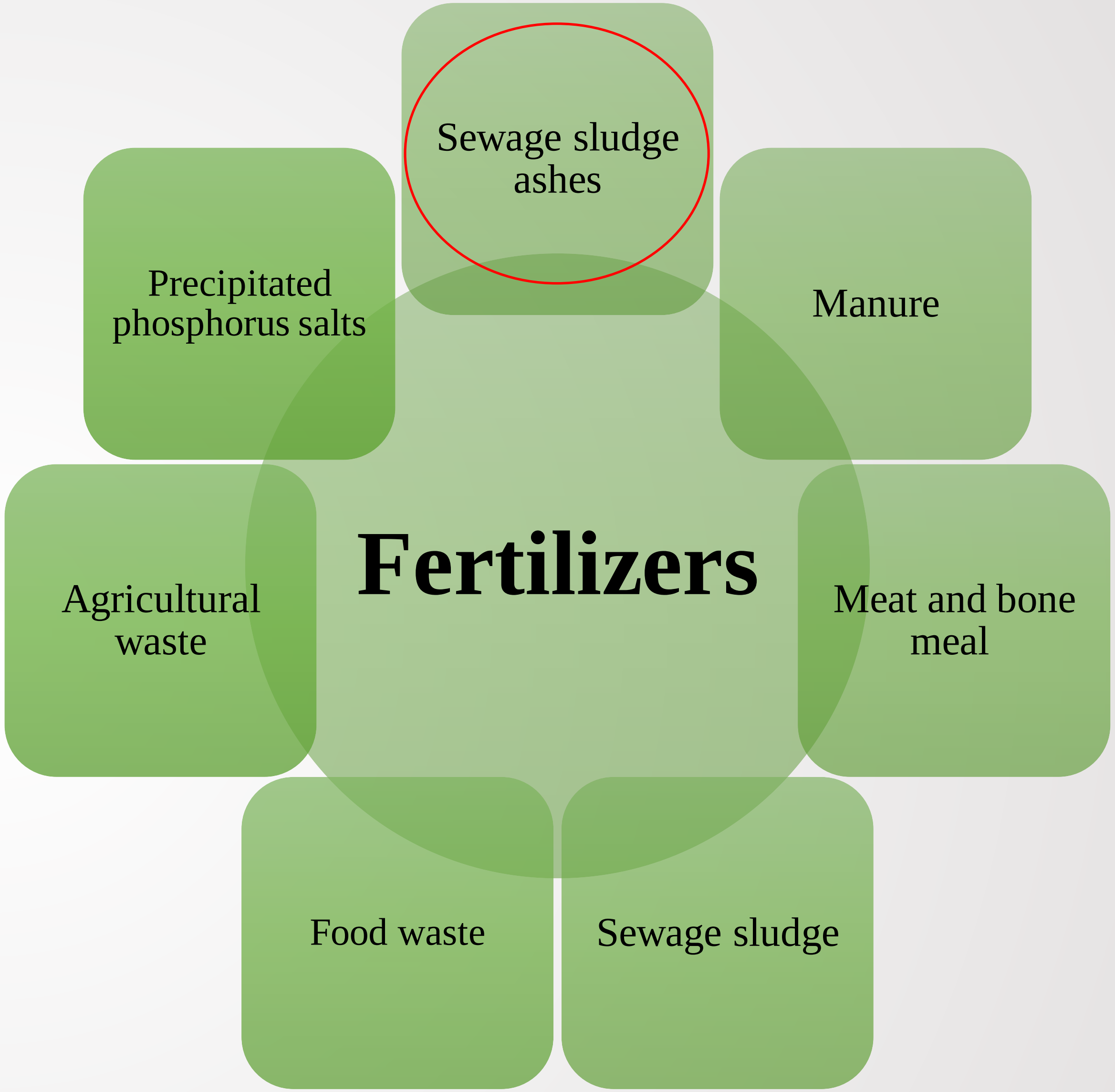


Figure 5. *Waste raw materials for the production of fertilizers [8]*

COMPONENT MATERIAL CATEGORIES (CMC) according to EU 2019/1009

- CMC 1: Virgin materials substances and mixtures
- CMC 2: Plants, plant parts or plant extracts
- CMC 3: Compost
- CMC 4: Fresh crop digestate
- CMC 5: Digestate other than fresh crop digestate
- CMC 6: Food industry by-products
- CMC 7: Microorganisms
- CMC 8: Nutrient polimers
- CMC 9: Polimers others than nutrient polimers
- CMC 10: Derived products within the meaning of Regulation (EC) No 1069/2009
- CMC 11: By-products within the meaning of Directive 2008/98/EC

REGULATION (EU) 2019/1009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/200

DISCUSSED but not included

- CMC 12: Determined industrial by-products
- CMC 13: Precipitated phosphate salts & derivates
- CMC 14: Thermal oxidation materials & derivates
- CMC 15: Pyrolysis & gasification materials

Table 1. Short characterization of the thermal sewage sludge treatment station in Poland

	Incineration technology	Amount of SSA, Mg/year	SSA management
Kraków	fluidized bed	8 200	Handing over to an external company
Kielce		800	Handing over to an external company
Gdynia		1 700	Landfilling
Gdańsk		4 100	Landfilling and partly recovery by external company
Szczecin		1 000	Handing over to an external co mpany
Łódź		2 200	Landfilling
Warszawa		10 147	Handing over to an external co mpany, recovery and disposal
Bygdoszcz	grate furnace	1 557.3	Handing over to an external company
Łomża		388.5	A sand-ash-slag mixture is used as a ballast for commercial and ind ustrial facilities, except for use u nder roadways and pavements

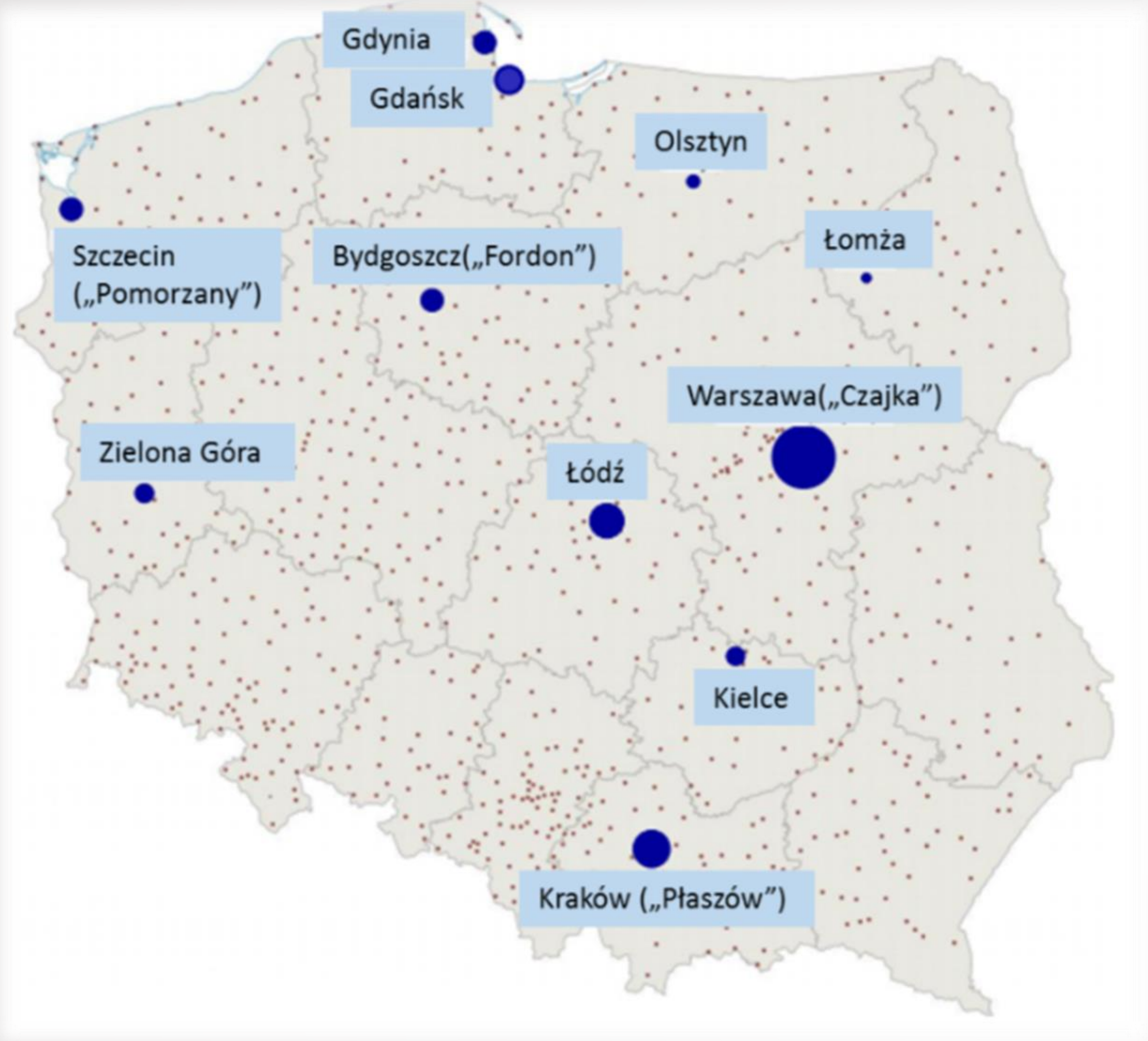
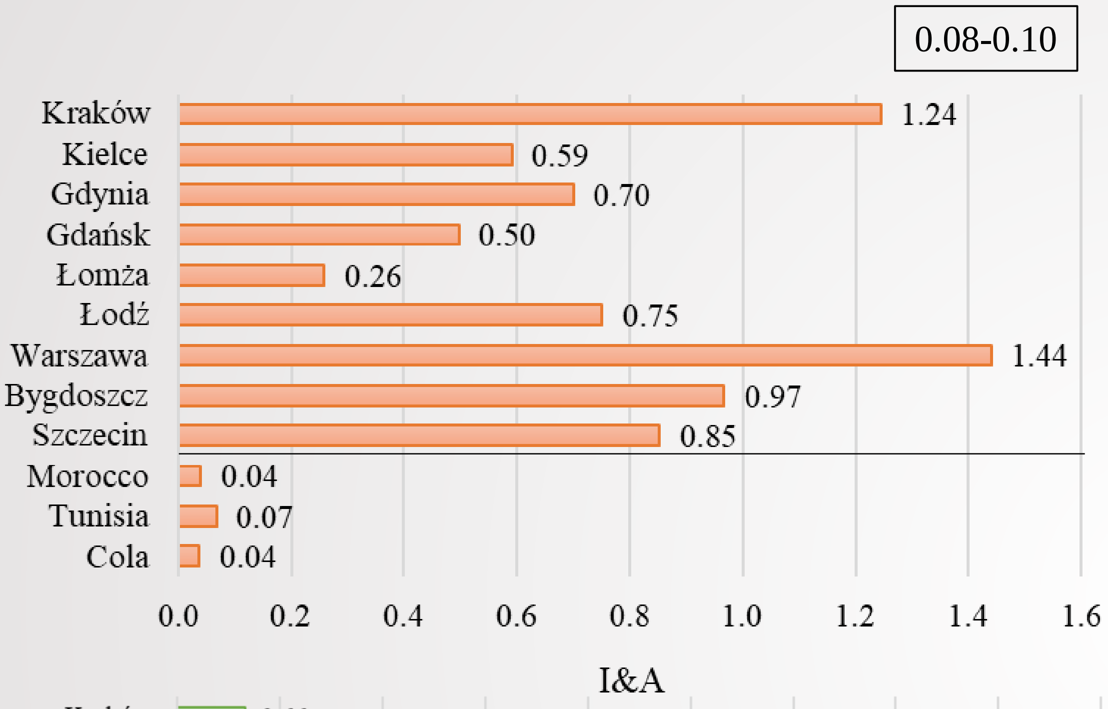


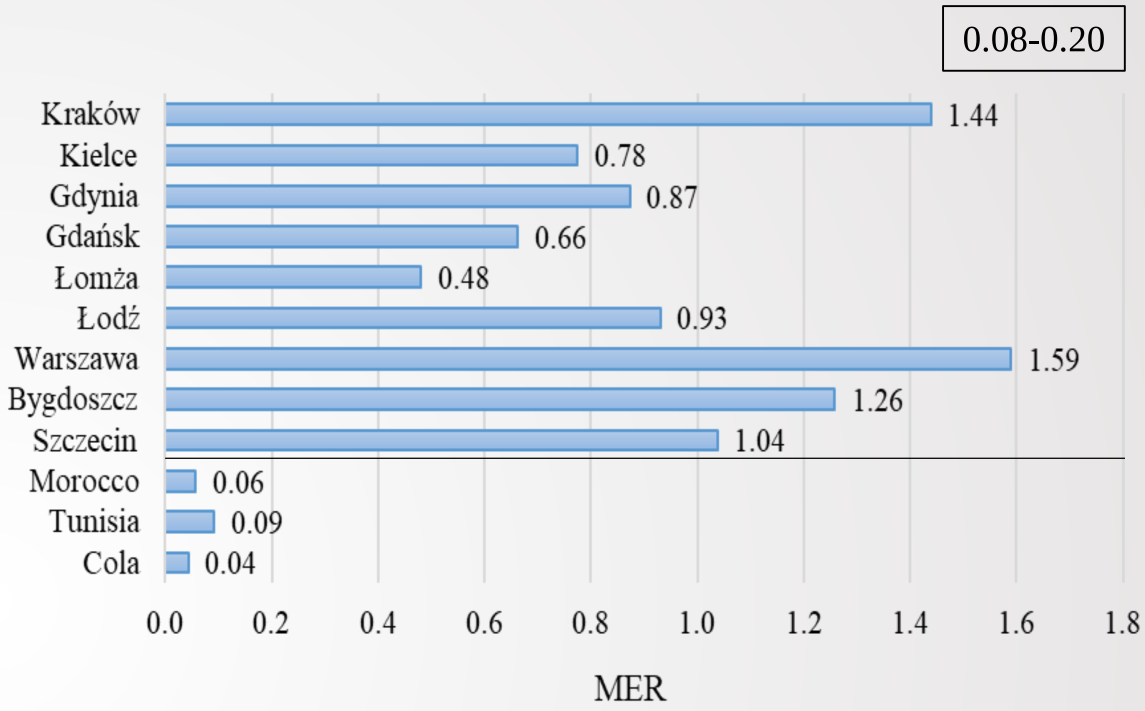
Figure 6. *Locations of the thermal sewage sludge treatment station in Poland*

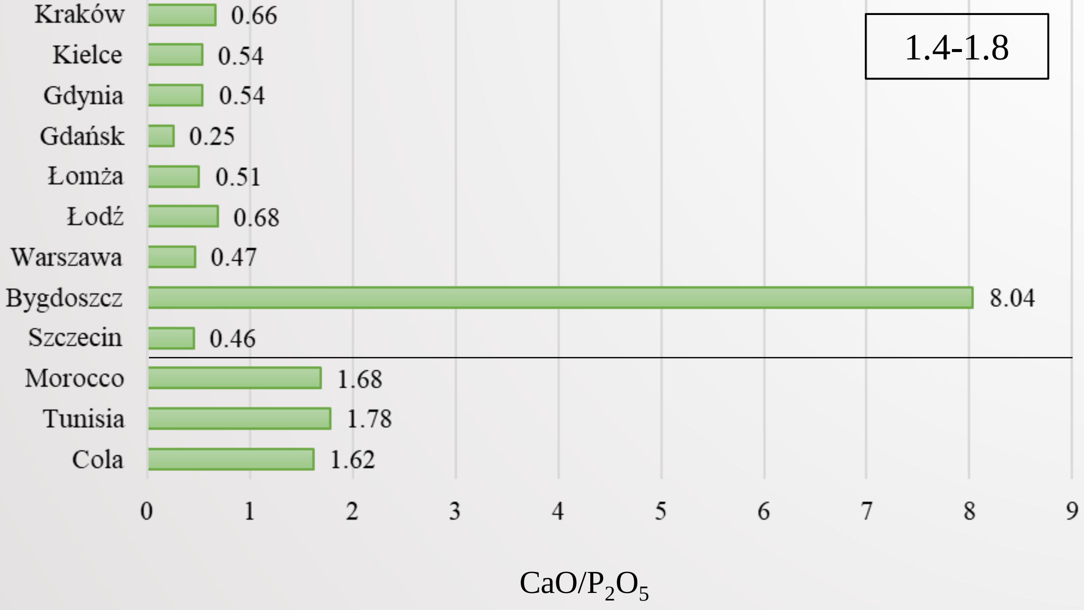
Table 2. Characterization of sewage sludge ashes and phosphate ores

	P_2O_5	K_2O	CaO	MgO	Fe	Al
	% d.m.					
Sewage sludge ashes						
Kraków	17.5±0.2	0.605±0.011	11.5±0.1	3.31±0.02	10.8±0.16	3.52±0.31
Kielce	25.6±0.1	1.10±0.09	13.7±0.03	4.71±0.07	7.40±0.23	2.53±0.11
Gdynia	29.0±0.6	0.748±0.005	15.7±0.4	5.00±0.07	7.620.08	5.11±0.10
Gdańsk	28.0±0.4	1.03±0.01	7.14±0.18	4.62±0.05	6.53±0.04	2.54±0.01
Łomża	22.8±0.5	0.743±0.091	11.5±0.03	5.04±0.12	2.15±0.05	1.56±0.05
Łódź	20.9±0.1	0.755±0.002	14.2±1.1	3.75±0.02	7.17±0.04	2.98±0.02
Szczecin	23.1±0.1	0.965±0.009	10.6±0.2	4.26±0.56	5.21±0.76	6.57±0.13
Bygdoszcz	8.37±0.03	0.181±0.002	67.3±4.9	2.42±0.02	1.91±0.03	2.87±0.07
Warszawa	16.9±0.2	0.549±0.019	7.94±0.07	2.53±0.05	3.94±0.05	10.0±08
Phosphate rocks						
Morocco	35.6±0.1	0.0777±0.0040	59.9±0.7	0.608±0.030	0.201±0.007	0.601±0.016
Tunisia	33.3±0.2	0.119±0.01	59.3±0.1	0.836±0.003	0.401±0.08	0.876±0.009
Cola	35.1±0.6	0.111±0.02	56.8±0.1	0.200±0.012	0.620±0.020	0.243±0.010

Technological parameters



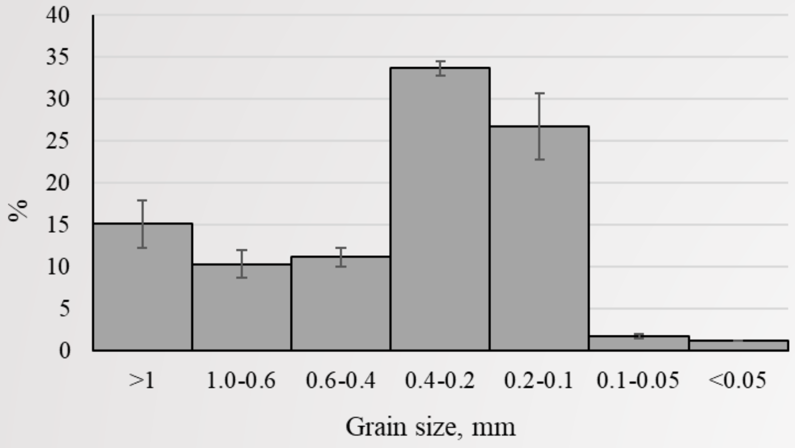




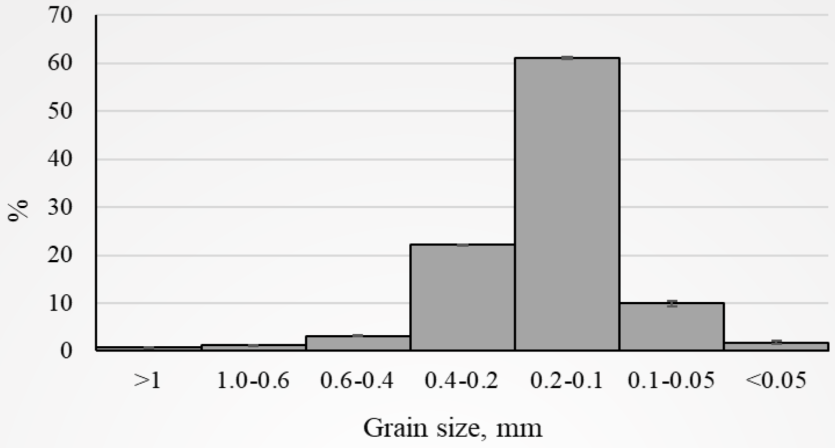
$$I\&A = \frac{Fe_2O_3 + Al_2O_3}{P_2O_5}$$

$$MER = \frac{Fe_2O_3 + Al_2O_3 + MgO}{P_2O5}$$

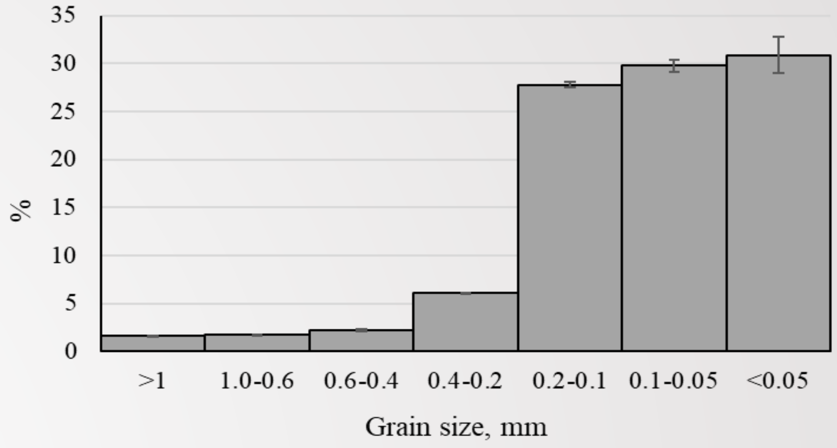
Particle size distribution



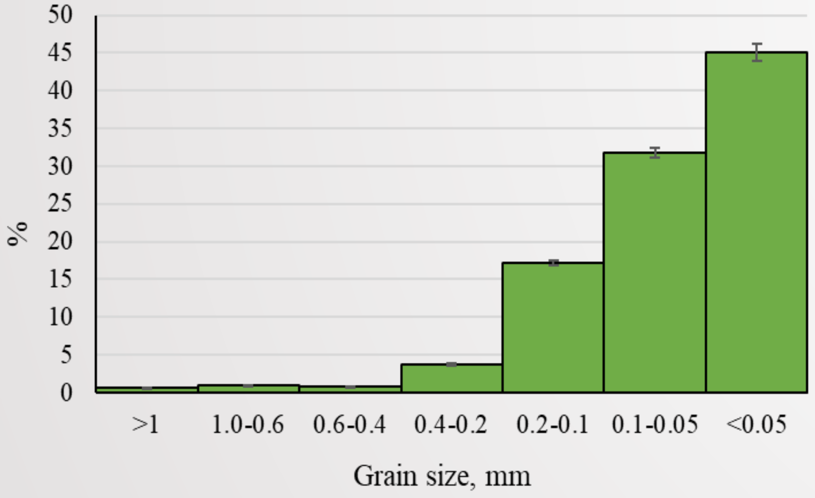
Morocco



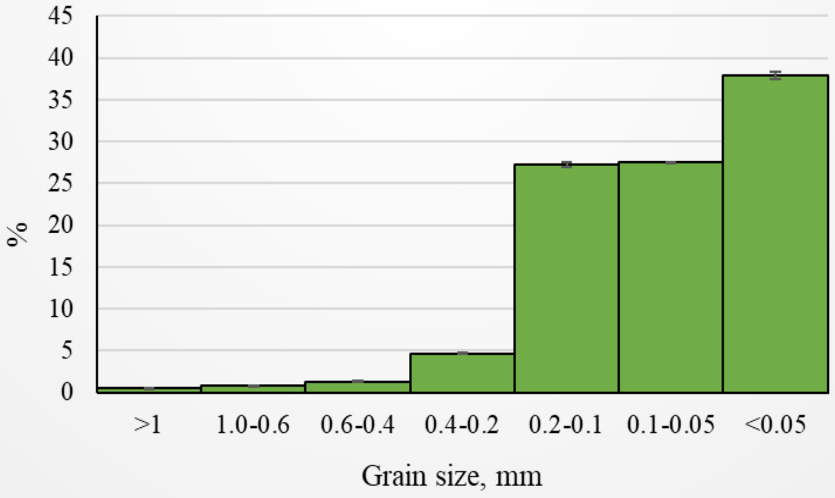
Tunisia



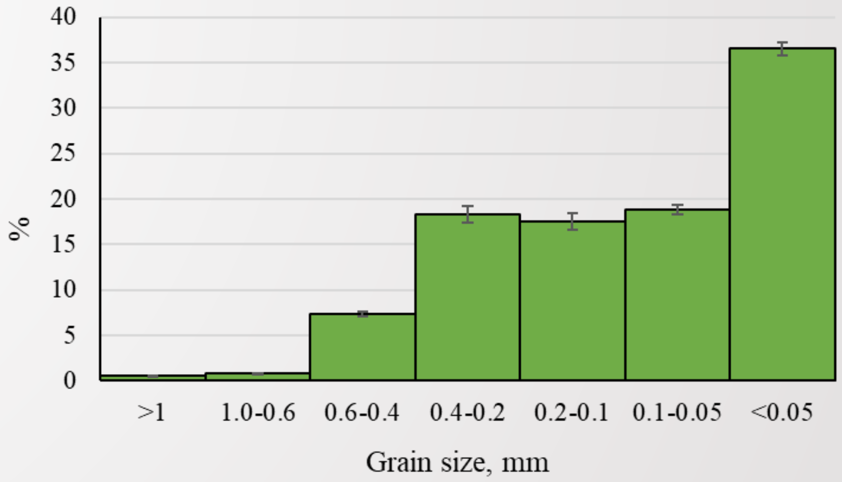
Cola



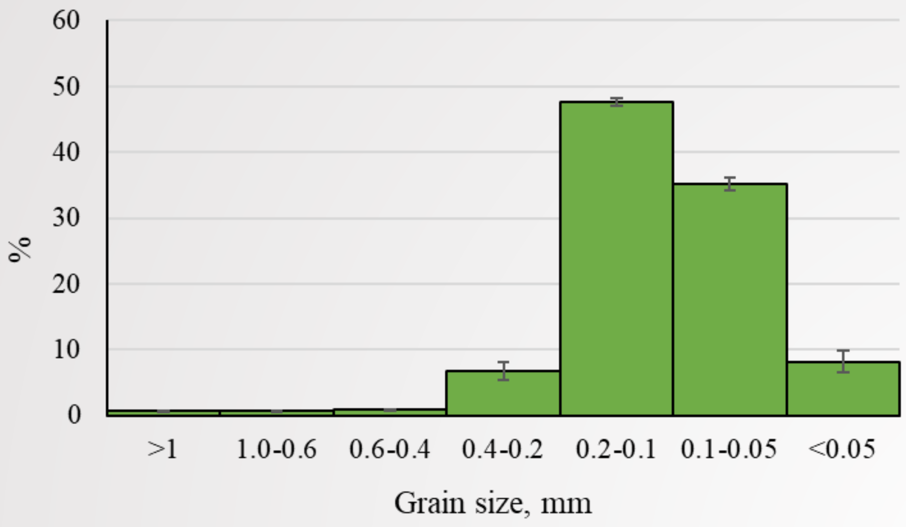
Kraków



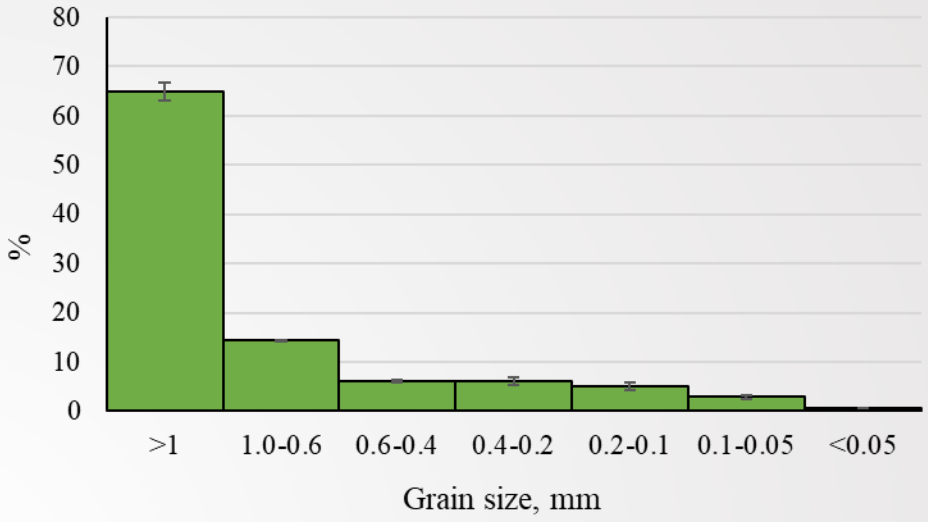
Kielce



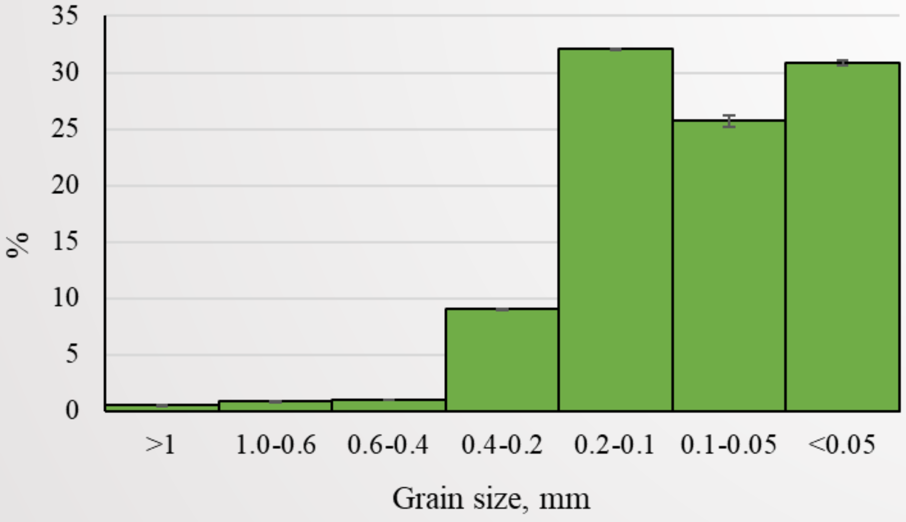
Gdynia



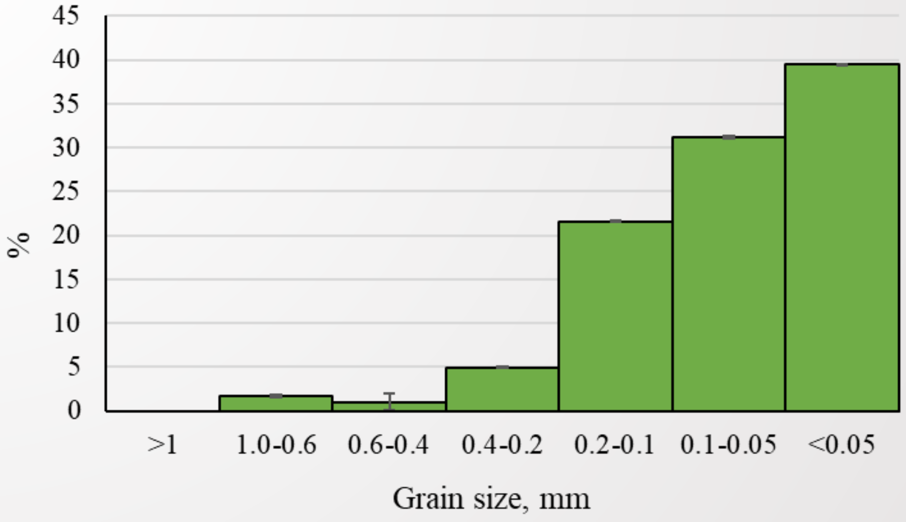
Gdańsk



Łomża



Łódź



Warszawa

Table 3. Heavy metal content in sewage sludge ashes and phosphate rocks

	Zn	Cu	Cr	Ni	Pb	As	Cd	Cd
	mg/kg d.m.							mg/kg P_2O_5
Sewage sludge ashes								
Kraków	6481±62	745±6	1347±16	247±2	177±8	430±1	9.88±0.06	56.6
Kielce	3965±41	703±9	201±5	74.4±0.04	117±5	12.7±0.5	6.78±0.21	26.8
Gdynia	4930±60	1024±6	219±8	76.8±2.3	101±3	9.77±0.55	5.54±0.35	19.1
Gdańsk	2716±3	945±4	197±3	89.4±1.9	107±1	12.4±0.3	5.33±0.06	19.0
Łomża	868±10	536±25	122±3	49.9±0.7	36±4	3.80±0.17	1.41±0.01	6.20
Łodź	3590±43	863±8	1700±43	115±3	120±11	8.83±0.17	6.44±0.18	30.8
Warszawa	657±15	924±9	332±3	109±2	133±5	16.6±0.1	5.30±0.1	31.2
Bygdoszcz	1918±1	313±10	379±26	187±5	52.9±0.05	14.2±0.6	1.74±0.03	20.8
Szczecin	2589±15	705±3	194±24	97.2±2.3	31.7±0.4	1.44±0.10	1.80±0.37	7.77
Phosphate rocks								
Morocco	252±8	39.9±0.7	203±1	31.8±4	30.1±0.1	18.0±0.2	19.7±0.2	55.5
Tunisia	404±14	20.8±1.6	295±2	16.3±0.1	37.4±0.5	43.3±0.3	47.1±2.5	141
Cola	411±12	36.3±0.3	11.3±0.2	6.74±1.45	35.6±0.7	47.0±0.3	0.571±0.029	1.63

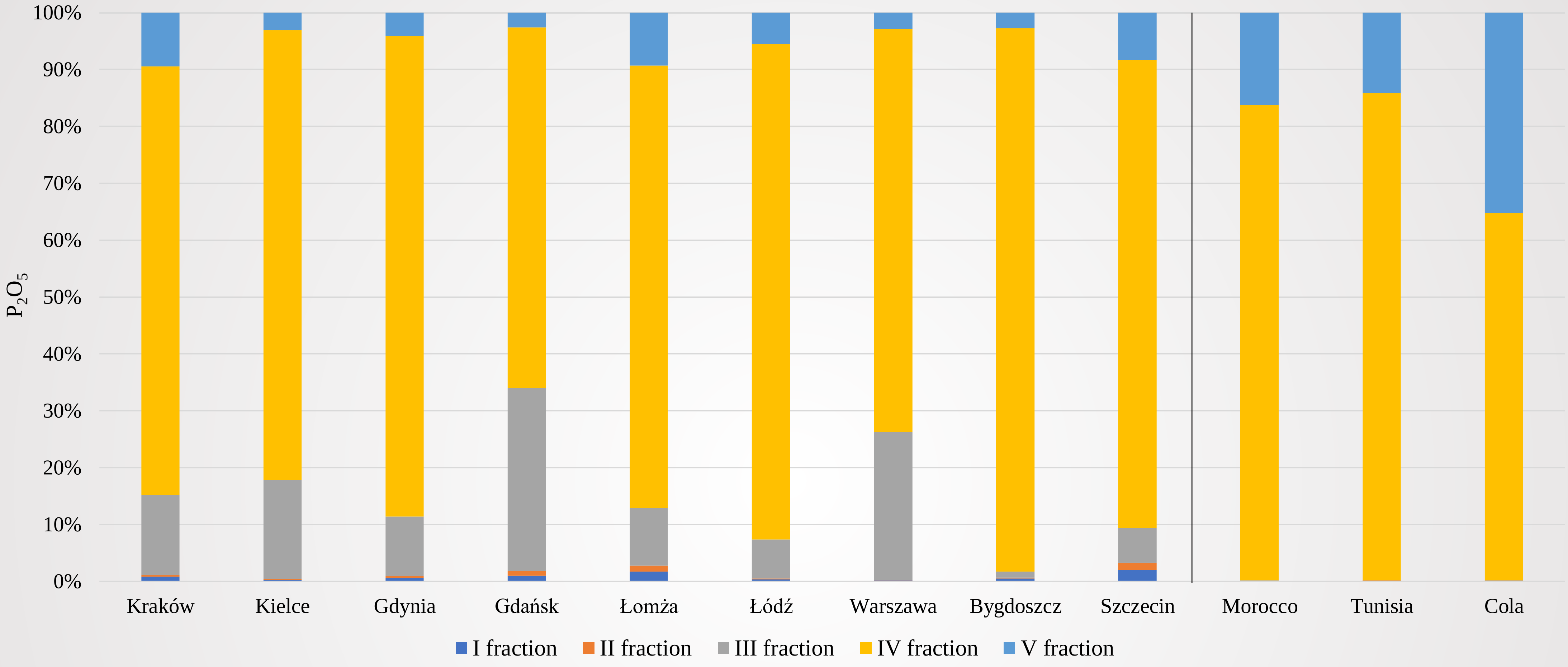


Figure 7. *Results of fractionation analysis*

I fraction	Labile or loosely bound phosphorus
II fraction	Redox sensitive iron bound
III fraction	Hydrated ions of Al-bound phosphorus
IV fraction	Calcium bound
V fraction	Residual phosphorus

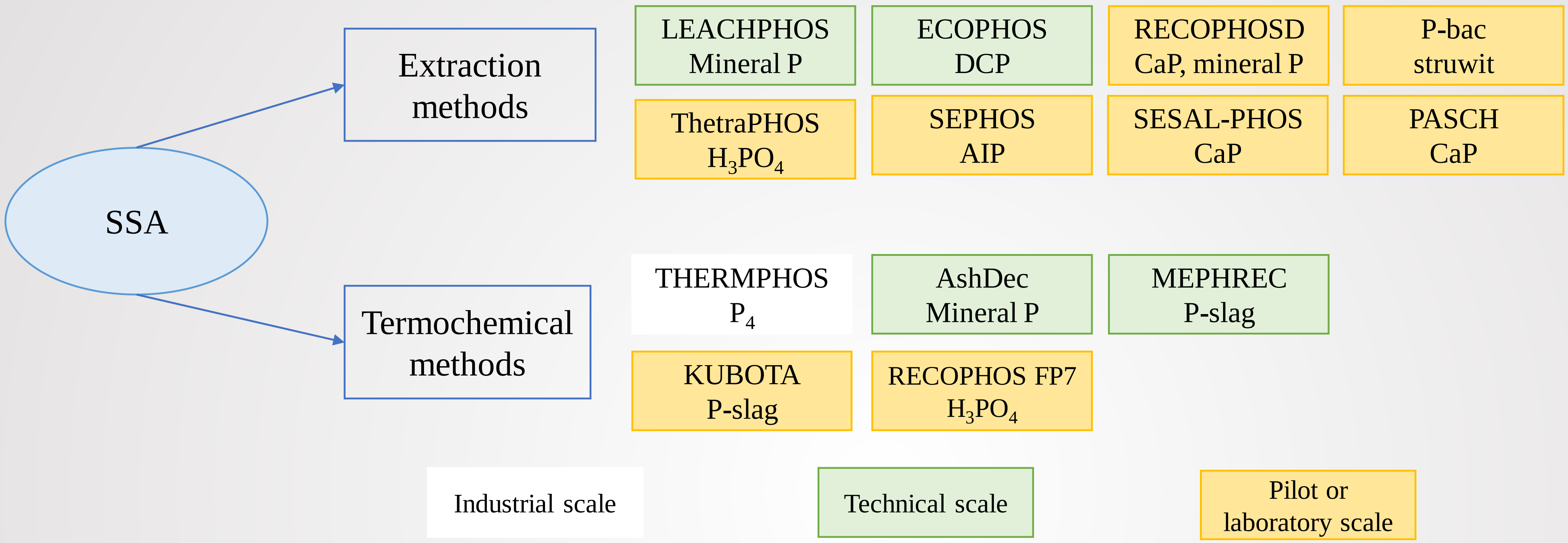


Figure 8. *Methods of phosphorus recovery from sewage sludge ashes*

Technological challenges

- High recovery efficiency and selectivity
- Process flexibility
- In thermochemical methods low iron content is required
- Extraction of ash using hydrochloric and sulphuric(VI) acid involves the generation of additional wastes in the form of calcium chloride and phosphogypsum

Conclusions

1. Due to the high phosphorus content sewage sludge ash is a potential substitute for phosphorus ores.
2. Technological parameters for SSA differ significantly from phosphorus raw materials, showing on average: a half lower CaO/P_2O_5 ratio, 14 times higher MER, 14 times higher I&A, which can limit their use for production of phosphoric acid and fertilizers.
3. Due to the high heavy metal content (Ni, Cr, Pb) in sewage sludge ashes purification techniques should be used for acid/extract.
4. It is recommended to partly substitute phosphorus rocks in production of phosphoric acid/fertilizers. Due to the large variation in the composition of ashes from different installations, the selection of the substitution level should be made for each of the ashes or their averaged mixtures.
5. A detailed analysis of the impact of ash composition and quality on the recovery processes should be carried out. This will help to choose an appropriate phosphorus recovery method.

References

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