Chapter 7

Potassium in Soils of Glacial Origin

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/52005

1. Introduction

1.1. Soils in Poland

Poland occupies a territory of 312,7 km2 with 99,7% of its area lying in the Baltic Sea catchment. The average altitude is 173 m and about 90% of the territory is situated below 300m above sea level, hence there is the predominance of lowlands. The majority of the country's territory is drained by two big rivers Vistula (55,7%) and Oder (33,9%) and few small Coastal rivers discharging directly to the Sea (9,3%). Vistula is exclusively the Polish river with springs in Carpathian Mountains in the South, flowing across the middle of the country and discharging the water to Baltic Proper, while river Oder borders the territories of Poland and Germany (Figure 1).

Considering the area and the population, Poland constitute an average sized (38 million inhabitants) country according to European standards. The rural area comprise around 190 km2 i.e. about 60% of the country's territory. From those area around 160 km2 is dedicated to agricultural activities and the rest to rural infrastructure. Poland is a country with the highest ratio of agricultural land compared to other European countries. According to European standards the country is quite densely afforested, with about 30% of forests land. A substantial territory is submerged under the lakes and rivers, including world well known Mazurian and Pomeranian regions. The majority of soils in the country are of glacial origin. The first so-called Narwian glaciation, covering the small area only occurred already in early Pleistocene. The main glaciation, South Poland and Middle Poland occurred in proper Pleistocene era and were split into five sub-periods (named after rivers: Nidian, Sanian 1, Sanian 2, Odranian and Wartanian). The youngest so-called Vistulian glaciation followed in late Pleistocene, dated back to 100 thousands of years (Figures 2, 3).

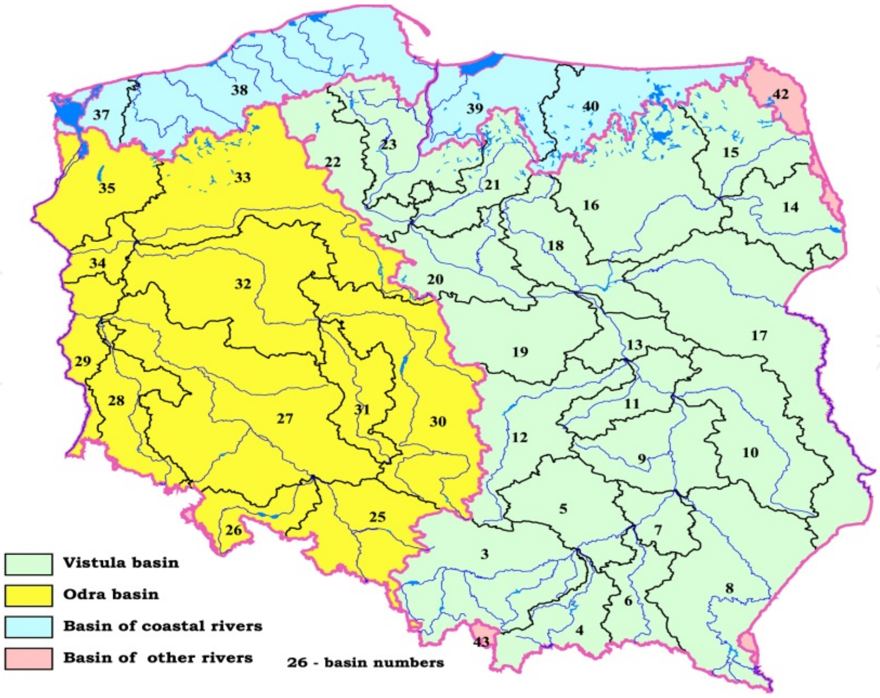

Figure 1. Drainage areas of the Vistula, Oder and Coastal rivers

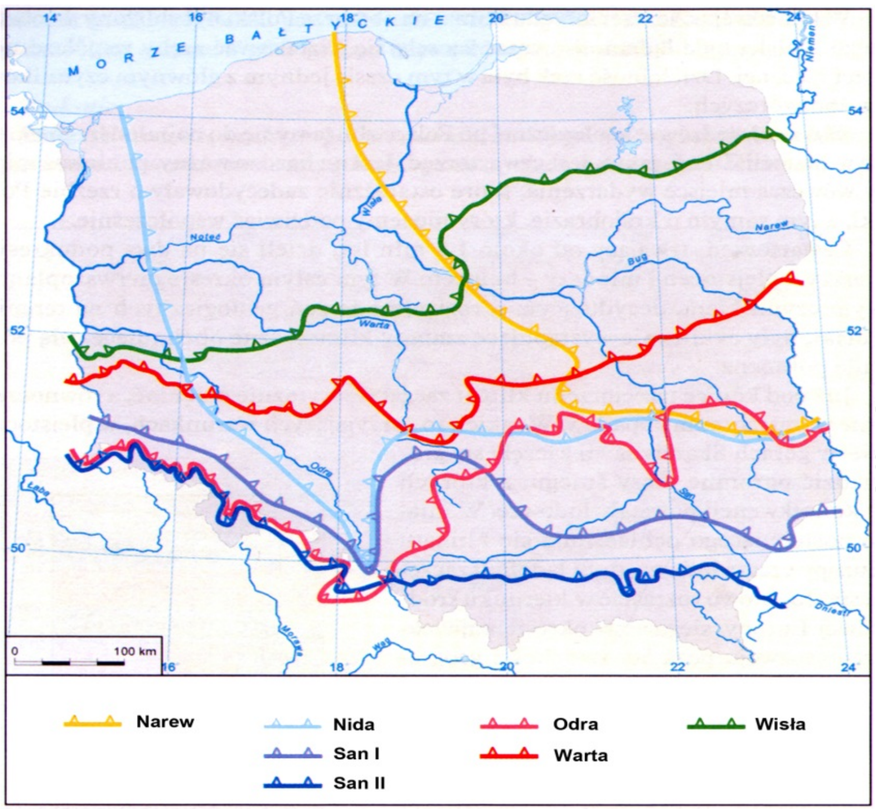

Figure 2. The borders of sequential glaciations in Poland [1]

Crossing the country from the north (Baltic Sea) to the south (Carpathian and Sudety Mountains) the following zones of the soils can be distinguished [2]:

- poorly sorted clays and sands of moraines (Cambisols, Stagno-gleyic Luvisols, Cambic Arenosols)
- fluvi-glacial sands (Podzols)
- broad, flat periglacial zone (Luvisols, Podzols, Arenosols, Fluvisols, Gleysols,Histosols)
- old eroded mountains and hills covered by loess and glacial deposits (Luvisols, Phaezems,Rendzinas)
- mountaineous zone

Pleistocene era												
Narew glaciation	Early interglaciation	South Poland glaciation					Great intergalaciation	Middle Poland glaciation			Late interglaciation	Vistula glaciation
		Nida glaciation	Interglaciation 1	San 1 glaciation	Interglaciation 2	San 2 glaciation		Oder glaciation	Interglaciation 3	Warta glaciation		
Thousands of years B.C.												
1000	850	760	660	630	560	530	430	330	230	210	130	110

Table 1. Sequence of glaciations in Poland [1]

According to geological history above 70% of Polish mineral soils have been formed from Pleistocene boulder clay and sand, strongly bathed and sorted by glacial waters. About 28% of soils are formed from loose and slightly loamy sand as well as from gravel. Soils of loess and alluvial origin cover a very small area of agricultural land (Table 1). It is not surprising that the ratio of soils of low fertility and productivity is estimated at 40% of the area.

For agricultural purposes, the soils in Poland are classified according to their productivity into soil suitability complexes and according to their buffer capacity (with respect to water and nutrients) into soil categories. Both classifications partly overlap. Productivity complexes, altogether thirteen on arable soils and three on grassland, are distinguished on the base of the soil parent's rocks, climate, soil water properties and the position in relief. This classification focuses on the possibility of growing different crops and on potential crop yield. On the very high quality complexes, numbered 1, 2 and 10, all crops can be grown satisfactorily, on the high ones, numbered 3, 4, 8 and 11 practically all crops can be grown as well but yields are significantly lower. On medium quality soil complex numbered 5 triticale, rye, and maize may be grown. Low quality soil complexes, numbered 6, 9 and 12 are suitable for rye, oats and potato and the very low quality ones, numbered 7 and 13 for rye and lupine only. The very high quality and high quality soil suitability complexes cover roughly 50% of arable soils, medium quality complex about 16% and the low and very low quality ones about 34% of arable land. Soil classification into categories is based on the content of fine fraction, i.e. soil particles below 0,02 in diameter. In this study four soil categories have been distinguished: very light up to 10% fine fraction, light 11-20% fine fraction, medium 21-35% fine fraction and heavy above 35% fine fraction. The very light soils cover 23,4% of arable area, light soils 36,1% of area, medium 29,4% and the heavy ones 11,1% of area only. For the purposes of this paper soil classification into such categories will be used extensively. Other factors limiting the fertility and productivity of Polish soils are the low content of soil organic matter SOM and strong acidification of most of the soils. According to the newest survey 7,6% of arable soils show low content of SOM (below 1%), 47,1% soils, medium content (1,1-2,0% SOM), 29,3% high content (2,1-3% SOM) and only 3% of soils, very high content of organic matter (above 3,0%) [3]. The summary of the last four-years period of agrochemical soils monitoring program reveals that 20,2% of soils are very acid (pH_{KCl} below 4,5), 29,4% acid (pH 4,5-5,5), 28% slightly acid (pH5,5-6,5), 14,7% neutral (pH 6,5-7,2) and 7,7% alkaline (pH above 7,2) [4]. There is a strong relationship between soil pH and soil's category. Very light and light soils are simultaneously very acid and acid while medium and heavy soils are much less acidified.

Parent rocks of soils	Total area thousands ha	% share in relation to	
		Total area	Agricultural land
Light loam	2562	15,8	18,8
Medium and heavy loam	2062	10,4	14,2
Loess	1396	3,3	4,8
Alluvial	788	4,7	5,8
Medium sand	2476	10,2	12,4
Sand and slightly loamy sand	4262	34,6	24,8
Very fine sandy soil	739	4,2	4,6
Rendzina	235	1,1	1,6
Massive rocks	599	6,1	3,9
Peat and muck	1414	8,5	9,6
Gravel	88,4	0,9	0,5

Table 2. Parent rocks of soils in Poland [3]

2. Soil potassium–conceptual–functional approach

Potassium is the seventh most abundant element in the Earth's crust representing on average 2,8% of total elemental composition. The average concentration of potassium in mineral soil is 1,4%, ranging between 0,01-3,7% [5] and, hence it is the fourth or fifth the most abundant element. The enrichment ratio, i.e. the relation between K in soil and K in Earth's crust, for potassium is 0,67 and is similar to the one for another important plant nutrient, phosphorus. In plant nutrition potassium is the second, after nitrogen element appearing in the highest concentration. The most important, potassium bearing minerals are primary aluminosilicates (feldspars, biotite and micas-muscovite) and secondary aluminosilicates called phyllosilicates. The last group of minerals is formed either through weathering the primary minerals or through the precipitation of secondary silicates [5]. Phyllosilicates and associated clay minerals play the most important role in the soil processes governing the availability of potassium for plants. Secondary clay minerals make up the greatest part of clay fraction of the soil characterized by particle less then 0,002 mm and, hence soils rich in clay fraction are generally abundant in potassium.

Researches on potassium in agriculture, concerning soil are as a rule based on conceptual-functional approach [6, 7, 8]. In this approach, four forms or pools of potassium have been distinguished (Figure 3). The potassium in soil solution plays the pivotal role in plant nutrition. This pool represents only up to 5% of the average plant demand for this element and not more than 0,1–0,2% of the total content of potassium in the upper soil horizon. The exchangeable or readily available potassium refers to the form of this element reversibly adsorbed on the edges of soil secondary minerals making up about 1-2% of the total potassium. Non-exchangeable or fixed potassium pool is slowly available for plants but represents a considerable 1–10% share of the total amount of this element. This form of potassium is adsorbed on wedge sites of secondary clay minerals, showing selectivity for potassium ions. The remaining pool called structural or lattice potassium is held in the structure of the primary soil minerals, feldspars and micas and becomes available for plants throughout very slowly running weathering processes. A conceptual – functional approach is based on the recognition of soil mineralogy and potassium transformation processes occurring in the soil. The availability of potassium for plants is, in this approach recognized as well.

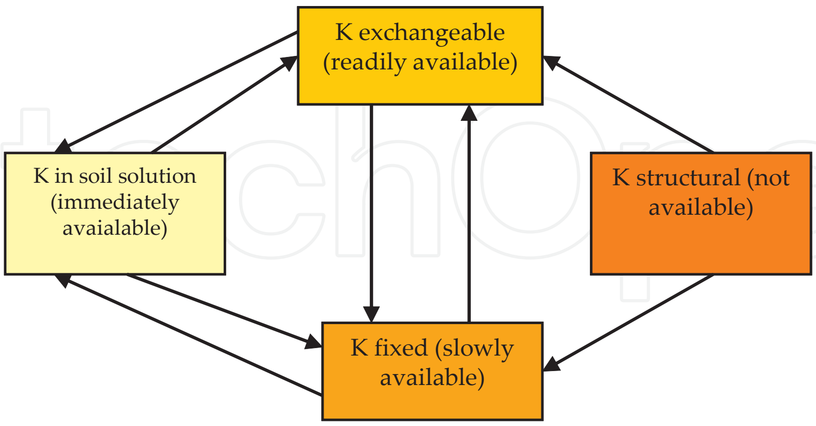

Figure 3. Conceptual–functional approach, forms (pools) of potassium in soil [8]

In the soil's solution, potassium occurs as a monovalent cation K^+ in the hydrated form. The diameter of this cation, 0,66 nm is smaller than the diameter of sodium Na^+, 0,72 nm. The hydration number of potassium ion, i.e. the number of water particles surrounding K^+, being

10,5 is smaller as this number for sodium ion, 16,6. The K+ charge density, as the relation of its charge to the radius, is 0,0075 C•pm-1. Potassium does not form any chelates, ion pairs and/or ion complexes in soil solution. The concentration of potassium in the soil solution is in the range 0,1–1 mmol•L-1 K+ i.e. up to 40 mg K•dm-3. In Poland, in the previous research not referred in this paper, the average concentration of potassium in 136 soil samples of glacial origin was 30 mg K·L-1 and in 80% of samples it did not exceed 50 mg K·L-1 [10]. Due to very high solubility of potassium compounds applied in fertilizers, potassium ions are almost instantly removed from the soils solution by adsorption and plant uptake processes and the solution is very rarely saturated with potassium ions. In the upper 30 cm soil layer, saturated to field water capacity the content of potassium in soil solution is in the range 5–25 kg K·ha-1. This content is far below the potassium requirements of high-yielding crops. However, this pool is rather quickly replenished from the other pools, mainly from the exchangeable potassium pool.

The exchangeable potassium is held at the non-specific adsorption sites of clay minerals and at the phenolic and carboxylic groups of soil, organic matter. Potassium ion is adsorbed non-specifically in the hydrated form. These non-specific adsorption sites occur in planar "p" and edge "e" position of clay minerals and amorphous iron and aluminum hydroxides (Figure 4) [11,13,14].

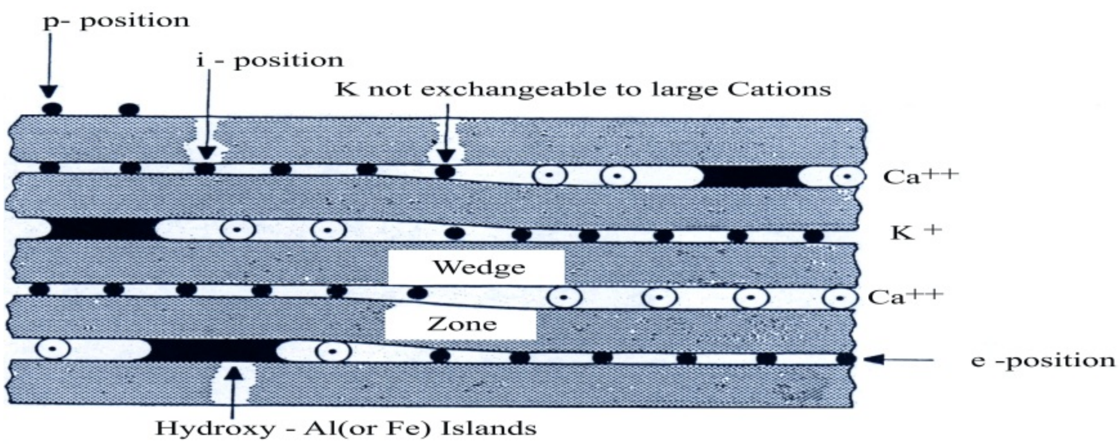

Figure 4. Model of 1:2 type clay mineral (illite) showing the positions of K^+ adsorption [11].

Clay minerals have a sheet-like structure and are built of Si tetrahedral layer and Al octahedral layer(s) in either 1:1 or 1:2 arrangement. Clay minerals are charged negatively due to the isomorphous substitution of ions pairs having the same size and coordination number, but differing in valences, i.e. Al3+ - Si4+ in tetrahedral layer and/or Mg2+-Al3+ in tetrahedral layer. The arising negative charges of clay minerals are balanced by exchangeable cations, e.g. potassium held at planar or edge positions. The 1:1 clays have very little isomorphous substitution and hence low negative charge and cation exchange capacity. Negative charges occur also at broken edges of mineral's crystals at the surfaces of amorphous and oxide minerals and soil organic matter [5,16]. The structure and properties of clay minerals and soil organic matter SOM are presented in Table 3. In Poland the prevailing soil – layered minerals are hydrated micas and illite [Długosz et al. 2005], non-expanding minerals of low cation exchange capacity.

Clay mineral	Isomorphous substitution	Cation exchange capacity cmol(+) kg^{-1}
Kaolinite 1: 1	None	1 – 15
Montmorillonite 1: 2 (expanding)	Mg for Al, Al for Si	80 – 150
Vermiculite (limited expanding)	Al for Si	140 – 200
Hydrous mica (illite) (non expanding)	Al for Si, Mg for Al	40 – 70
Amorphous oxides		2 – 4
Soil organic matter		200

Table 3. Structure and properties of clay minerals and SOM [12, 13].

The soil solution as well as the soil adsorption complex contains not only potassium but other cations as well. The total amount of cations for a certain element is partitioned amongst the soil solution and the fraction of the element adsorbed as a complex. The prevailing cation in well managed agricultural soils is calcium. To describe the relations between potassium and calcium several kinetic equations of cation exchange have been developed [5, 14]. The best-known and the most often used is Gapon equation [13]:

$$K_G = [\text{K-soil}]n(Ca^{2+})^{1/2}/[Ca_{1/2}\text{soil}]n(K^+)$$

Where: K_G is equilibrium constant often called selectivity coefficient, [K-soil] and [$Ca_{1/2}$ soil] are expressed in $mol{\cdot}kg^{-1}$ and $(Ca^{2+})^{1/2}$ and (K^+) in $mol{\cdot}L^{-1}$

The value of K_G varies between the pair of exchanging cations and on the binding site at the clay mineral. As lower the value of K_G as easier is potassium exchanged for calcium cation. According to [11] the K_G for p-position is 2,21 $(mM{\cdot}L^{-1})^{-1/2}$, for e-position is 102 $(mM{\cdot}L^{-1})^{-1/2}$ and for i-position is infinite (Figure 4). The binding selectivity of kaolinite type 1:1 minerals and for the organic matter are close to this at p-position. Potassium adsorbed in p-position and e-position at clay minerals and on the soil organic matter is, therefore, easily exchangeable and available for plants and adsorbed in i-position is practically fixed and hence slowly available only.

Non-exchangeable or fixed potassium is held between tetrahedral layers of clay minerals like hydrous micas and vermiculite (Figure 4). Potassium ion in non-hydrated form has almost the same size as oxygen ion and fits perfectly into the spaces between sheets of 2:1 types of clay minerals [15].The binding forces between K+ and mineral's surfaces are greater than between these cations themselves. It results in the partial collapse of clay structure and "entrapping" potassium ions at wedge position between tetrahedral layers. The ions of the similar size as NH_4^+, but not much larger Ca^{2+} and Mg^{2+}, fit into these positions and can replace (exchange) entrapped K^+.

Structural or lattice potassium is covalently bonded with crystal structure of potassium rich primary silicates minerals like micas (biotite, muscovite) showing layered structure and feldspars (orthoclase, microcline) showing framework structure. Micas contain 8,7–9,8% of potassium. These minerals are found in coarser fractions of soils, silt, sand and here included potassium is freed in the long-term weathering processes (Figure 5). This pool of potassium is practically unavailable for plants, at least in the perspective of crop rotation. The typical weathering process runs from muscovite through hydro muscovite to illite and mixed clay minerals kaolinite-illit or illit-montmorollinite. In these processes potassium ion is substituted by hydroksyanion H_3O^+ and, hence each next product contains less potassium [16]. Clay minerals can be formed as well as a secondary ones as a result of synthesis from the end-products of weathering the feldspars.

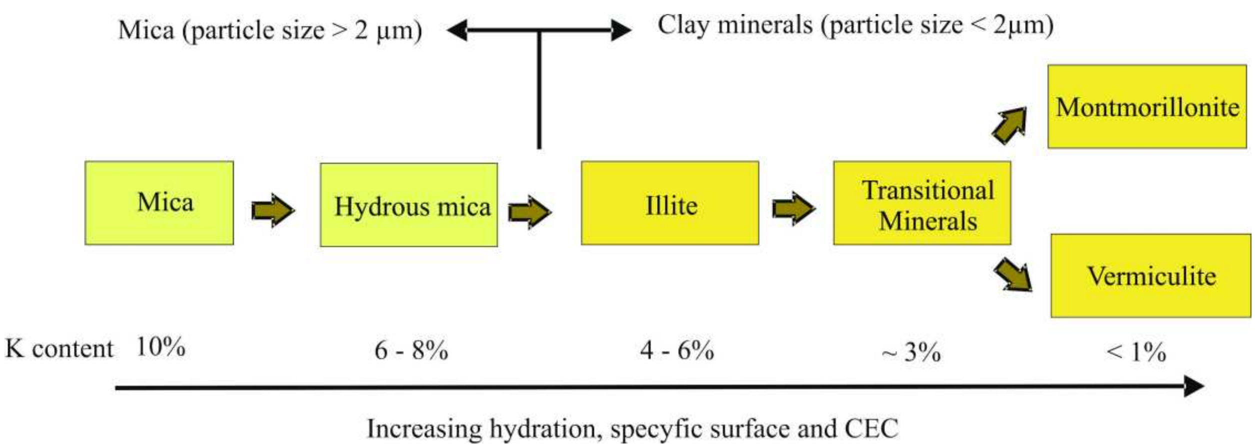

Figure 5. Model of freeing potassium in the sequence of weathering processes the primary soil minerals [17].

3. Methods and materials

3.1. Operational–analytical approach

Conceptual – functional approach is theoretically oriented, and its focus is on the chemistry of soil potassium and principles of potassium availability for crops. From agricultural point of view more interesting is, however analytical approach focused on distinguishing by laboratory methods the potassium forms and linking these forms with crop's potassium requirements. In

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this approach, five analytical forms of potassium have been distinguished : water soluble, available, reserve, nominal total and total (Table 4).

Potassium form	Brief description of method	Remarks
Water soluble K_{H2O}	Extraction with water at soil/water ratio 1: 5	Close to soil solution, form immediately available for plants
Available (exchangeable) K_{ex}	Extraction with ammonium acetate buffered to pH 7,0	Classical method of estimation , form recognized as available
Available K_{DL}	Extraction with calcium lactate buffered with HCl to pH 3,5	Official method in Poland and Latvia
Available K_{CAL}	Extraction with calcium acetate and calcium lactate, buffered with acetate acid to pH 3,7	Official method in Austria and Germany
Available K_{AL}	Ammonium lactate, buffered with acetate acid to pH 3,7	Official method in Lithuania, Slovenia and Hungary
Available K_{Meh}	CH_3COOH,0,25NH_4NO_3, NH_4F, HNO_3, EDTA	Mehlih-3 method, official in Estonia, Czech Rebublic, Slovakia
Reserve K_{res}	Extraction with boiling mol·dm^{-3} HNO_3	Close to fixed, form slowly available for plants
Nominal total K_{sem}	Extraction with hot HCl and HNO_3 (Aqua Regia)	Very slowly available for crops
Total K_{tot}	Fluorescence atomic spectrometry	Total content of potassium, unavailable for crops
Soil texture	Except the soils from KALIFERT project soil texture was evaluated by the "finger" method directly in the field. In Kalifert, the full particle composition of soil was analyzed quantitatively by laser method.	

Table 4. Analytical form of potassium in the soils of glacial origin, mg K·kg^{-1} soil [18, 19]

Analytical forms of potassium, however, based on the conceptual pools differ from them quite substantially. The amount of potassium extracted with water is higher than the amount in soil solution. For this reason, it is expressed in mg K·kg^{-1} soil and not in mg K·L^{-1}. Available potassium includes the water soluble one and a part of exchangeable form of this element. Otherwise the relations between exchangeable and available forms are statistically very close. Reserve potassium has an analytical meaning only, although conceptually reflects the potassium pool entrapped in layers of non-expanding clay minerals. In the analytical approach two forms of "total" potassium is distinguished. Nominal total K_{sem} is extracted with boiling Aqua Regia and, apart from previously mentioned three forms includes a part of structural potassium of soil's primary and secondary minerals. Total potassium can be measured either by fusion with alkali or by roentgen spectrometry, and includes all, already distinguished forms of this element and the whole potassium in soil minerals and organic substance. The analysis for nominal potassium is much easier than for the total one and, therefore it is often applied in research on soil potassium, which sometimes is a source of misunderstanding. Operational - analytical approach was applied in the own investigation on potassium in soils of Poland, executed in three research projects funded by Polish Ministry of Science and Higher Education. These projects have been running in the years 2002-2005 (1^{st} project), 2006 – 2008 (2^{ed} project) and 2009-2012 (3^{rd} project). The 1^{st} project was focused on so called available forms of potassium and the relation between water soluble potassium K_{H2O} and available one K_{DL} and the 2^{ed} on different forms of potassium in Polish soils. The 3^{rd} project is still running in scope of international collaboration with 10 countries belonging to MOEL group (Mttelosteuropaische Lander). This collaboration was established already in 1998 for exchanging information and standardizing methods of soil fertility investigation and fertilizer recommendations [23]. The main aim of this project including not only the soils of glacial origin from Estonia, partly Germany, Latvia, Lithuania and Poland but also soils from Austria, Czech Republic, Hungary, Slovakia and Slovenia was to follow long-term changes in the soil's potassium forms depending on fertilization. Another aim was to compare the methods of estimation the content of so called available potassium in the soils (see table 4) in different countries.

The results of all three projects have been partly published [8,18,19,21] but rather in a reports-like way. In this paper the cross-synthesis of all projects, subordinated to the specific problems is presented. In operational-analytical approach, the content of potassium forms is linked with the soil texture and not with the mineralogical composition of soil. Mineralogical soil analysis is very cumbersome, and depends considerably on the method of extraction the clay minerals. Otherwise it is well known that the content of potassium increases from the coarse sand to the clay soil's fractions. According to Brogowski et al. [20] in soil composed of 38% of sand, 52% silt and 10% of clay the share of total potassium in the fraction of sand was merely 13% in the fraction of silt 64% and in the fraction of clay 23%. The conclusion is that total potassium is under-proportionally located in sand fraction, almost proportionally in silt and over-proportionally in clay fraction.

4. Results

4.1. Water soluble K_{H2O}–versus available K_{DL} potassium

In the years 2006 and 2007 each of the 17 Agrochemical Laboratories operating in Poland collected about 1.600 representative soil samples and analyzed them for soil texture, soil pH and the content of available potassium K_{DL}. In the same soil samples, the content of water soluble K_{H2O} potassium was estimated in the laboratory of the Institute of Soil Science and Plant Cultivation at Puławy using method described in Table 4. In the population of almost 24.000 soil samples the content of both potassium forms was significantly differentiated depending on soil texture (soil category) and soil pH. The mean values of the K_{H2O} and K_{DL} contents in the classes of soil texture and soil reaction are presented in tables 5 and 6. Due to the far from normal distribution of the data, medians were presented along with average values.

Soil category	No of samples	K_{DL} mg K·kg^{-1} soil		K_{H2O} mg K·kg^{-1} soil		% K_{H2O} in K_{DL}	
		average	median	average	median	average	median
very light	2044	86,3	78,0	27,5	24,2	33,3	32,1
light	10290	115,2	108,7	32,1	28,6	28,7	27,4
medium	9492	130,7	124,5	28,2	24,5	21,9	20,8
heavy	1832	135,2	120,8	25,2	21,1	19,2	17,8
all soils	23658	120,4	112,0	29,6	26,1	25,6	24,2

Table 5. The content of potassium forms depending on the soil category [19]

Soil reaction,pH	No of samples	K_{DL} mg K·kg^{-1} soil		K_{H2O} mg K·kg^{-1} soil		% K_{H2O} in K_{DL}	
		average	median	average	median	average	median
very acid	4012	87,9	75,5	21,2	18,4	26,9	25,4
acid	6934	117,8	111,2	27,9	25,2	25,0	23,5
slightly acid	6488	132,7	126,2	32,2	29,8	25,0	23,9
neutral	3668	137,3	128,2	34,7	31,1	25,4	24,4
alkaline	2554	123,6	115,4	33,0	29,1	26,9	25,5

Table 6. The content of potassium forms depending on soil pH [19]

The content of available potassium increases in the direction from the very light and light soils to the medium and heavy soils and from the very acid soils to the neutral ones. Alkaline soils contain less available potassium than the slightly acid and neutral ones. The content of water soluble potassium is admittedly the lowest in the very light soils, but soils of remaining categories show rather similar content of this potassium form. The content of water soluble potassium depends more on the soil's acidity and increases significantly in the direction from the very acid to alkaline soils. In the whole population of soil samples, the mean share of water soluble potassium makes about a quarter of the available form of this element. This share decreases significantly in the direction from the very light to heavy soils. Due to the opposing tendency in changing the content of available (increase) and water soluble (decrease) content of potassium in conformity with soil pH, the share of K_{H2O} in K_{DL} is practically independent of this soil characteristic. Generally, the heavier soils are more abundant in available forms of potassium, but this element is less accessible for the crops in comparison with the coarse-textured soils. Increasing soil pH influences, however, positively both the content of available and water-soluble forms of potassium. The latter is easily accessible for the crops. These statements are very important in Poland due to the prevalence the very light and light soils and the high soil acidity. Between the content of available potassium and potassium soluble in water exists a significant correlation and this relation was quantified by linear regression models. Two approaches were applied here: multiplicative regression analysis for each soil category separately and model of comparison the linear regressions including four soils categories jointly. The calculations were performed using two adequate procedures, a multiplicative regression model and comparison of regression lines model, offered by statistical package Statgraphic 5+. The regression equations for multiplicative model are presented below in frame.

Very light soils: $K_{DL} = 4{,}7689 \cdot K_{H2O}$^0,8698 $R^2 = 0{,}74$

Light soils : $K_{DL} = 6{,}9677 \cdot K_{H2O}$^0,8068 $R^2 = 0{,}71$

Medium soils: $K_{DL} = 12.5141 \cdot K_{H2O}$^0,7023 $R^2 = 0{,}65$

Heavy soils: $K_{DL} = 10{,}8869 \cdot K_{H2O}$^0,7788 $R^2 = 0{,}70$

On the base of these equations the content of available potassium K_{DL} can be calculated for a given range of potassium soluble in water K_{H2O} contents, separately for soil categories. Such calculation has been performed in a new approach to calibrate the content of available potassium K_{DL} in soils of glacial origin in Poland (Table 7). For a better visualization of the dependence on the relation $K_{DL}K_{H2O}$ the comparison of regression lines model offered by Statgraphic 5+ package has been applied (Figure 6) as well.

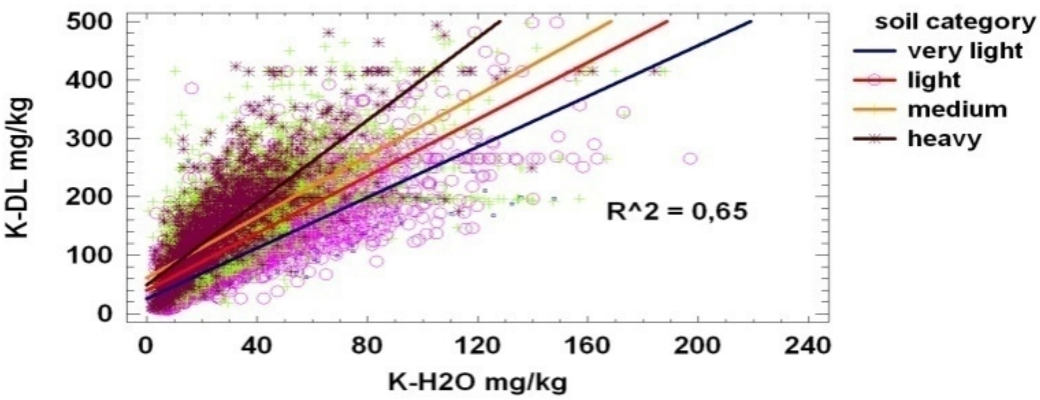

Figure 6. Relation between available K_{DL} and water soluble K_{H2O} potassium depending on soil category (comparison of regression lines)

From this model the conclusion is easily drown, that as heavier is a soil as steeper is the slope of the regression line corresponding to this relation. In practice it means that by the same content of available potassium K_{DL} the concentration of potassium ions, hence its accessibility for plants is much higher in the very light against the heavy soils. This model, however gives a transparent picture, is limited to straight regression lines only and therefore its predictability (one correlation coefficient only) is lower than the already presented multiplicative regression model (in frame). By interpretation the already presented data, one must remember that the number of soil's samples and therefore its representation was the highest for light and medium soils as well as for soils characterized by acid and slightly acid reaction. Data for the very light and very acid soils (Tables 5, 6) were less representative.

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Since 1985, the five classes of available potassium content K_{DL} (along with phosphorus) are implemented in Poland. The ranges of potassium content in such classes are originating from the previous partition into three classes and have not been changed ever since. Grounding on the large number of soil samples (24.000) in which the content of water soluble and available soil potassium has been measured simultaneously the modification of official classes has been suggested. The idea underlying this suggestion was to link the content of available potassium K_{DL} with the content of water soluble K_{H2O} one, which is directly accessible to plant roots, according to the following procedure. The whole range of data concerning K_{H2O},for each soil category separately, was split into pentiles, around the median value. For the lower and upper limits of each pentile the corresponding K_{DL} have been calculated using the regression equations included above in the frame. Such calculated ranges of K_{DL} values are proposed as the new classes of available potassium content in soils of glacial origin in Poland. The details of this idea have been presented in separate publication [19]. For the sake of further consideration the official and proposed critical values of available potassium content are, however, presented in Table 7.

Soil category	K_{DL}mgK·kg^{-1} soil, official classes					K_{DL}mgK·kg^{-1} soil, proposed classes				
	Very low	Low	Medium*	High	Very high	Very low	Low	Medium	High	Very high
very light	< 20	21-62	63-103	104-145	>146	< 50	51-70	71-90	91-120	> 121
light	< 41	41-83	84-124	125-166	> 167	< 65	66-90	91-115	92-140	>141
medium	< 62	63-104	105-166	167-207	>208	<85	86-110	87-140	141-170	>171
heavy	<83	84-124	125-207	208-249	>250	< 90	91-120	92-155	156-200	>201

*threshold range focused on in the fertilizer recommendation system in Poland

Table 7. The official and proposed [19] classes of available potassium in soils of Poland

From the comparison of the official and proposed classes of available potassium content appears that official system undervalues potassium contents in very light and light soils as well as in the very low and low classes of K_{DL}. Overvalued are, indeed values for high and very high values of potassium content, independently of the soil texture. There is resemblance of both classifications in the range of medium potassium content and, with the exception of heavy soils quite similar are medians for proposed and the official systems. The author's proposition is focused on improving the officially accepted and being in use for over 25 years system of soil classification for available potassium content. In this proposition, the special position has the medium class for K_{DL}. Medium class is proposed as the threshold range for potassium content, which should be accomplished and kept on in the sustainable system of fertilization. However this proposition needs the further development, particularly in the very light and heavy soils categories for which the number of samples was not fully representative.

4.2. The content of available potassium K_{DL} in soils of Poland

In Poland, 17 Agrochemical Laboratories subjected to Ministry of Agriculture and Rural Development and covering with their activity the whole country's territory, are operating. The main task of these Laboratories is soil and plant testing and launching fertilizer recommendations. Every year several thousand soil samples are being analyzed for the soil pH and the content of available forms of potassium, phosphorus and magnesium. The results are making available for farmers, but they are collected in the data bank as well. Every fourth year the data are subjected to statistical analysis and published with the aim to monitoring the soil fertility status in Poland. The synthesis of the data concerning the content of available potassium, including the results of over 950.000 soil samples analyzed over the years 2004–2008 is presented in the following tables [4]. The synthesis reveals that the content of available potassium K_{DL} depends on the soil category and soil pH (Table 8) which is in accordance with the data already presented for 24.000 soils samples.

Soil category	mg K·kg^{-1} soil		Soil acidity	mg K·kg^{-1} soil	
	average	median		average	median
very light (37.170)*	91,2	76,0	very acid	88,9	74,7
light (376.602)	126	112	acid	118	105
medium (413.098)	159	143	slightly acid	138	126
heavy (130.681)	195	183	neutral	144	129
total (957.551)	148	130	alkaline	134	120

*number of soil samples

Table 8. The content of available potassium in soils of Poland [4]

The numeric data have been categorized and presented in the tables of contingency (Tables 9 and 10), which better visualize the link between potassium content and soil categories, and/or soil pH. Categorization of samples is based on the official classes of potassium content (Table 7)

Soil category	% samples in the classes of available potassium content				
	very low	low	medium	high	very high
very light	7,06	42,97	28,84	12,29	8,84
light	12,20	31,19	27,66	15,78	13,18
medium	17,25	24,45	31,53	12,86	13,91
heavy	15,88	20,02	41,46	9,67	12,97
total	14,68	27,21	31,26	13,55	13,30

Table 9. The ratio of soils samples in different classes of potassium content depending on soil category [4]

As follows from Table 9 one-half of the area of the very light soils is very poor in available potassium, while 20% of these soils show high and very high content of this element. Most of the medium and heavy soils contains medium to very high content of potassium.

Soil acidity	% samples in the classes of available potassium content					total
	very low	low	medium	high	very high	
very acid	25,85	37,08	24,37	7,49	5,21	20,21
acid	13,97	28,76	32,47	13,47	11,33	29,39
slightly acid	9,96	22,35	34,30	16,56	16,83	28,00
neutral	10,48	21,69	32,52	15,83	19,48	14,74
alkaline	13,30	23,66	31,22	14,44	17,38	7,66

Table 10. The ratio of soils samples in different classes of potassium content depending on soil acidity [4]

The data in Table 10 prove that very acid and acid soils are simultaneously poor in available potassium, while over 60 % of neutral and alkaline soils contain medium to very high K content. In the whole Poland around 42 % of soils shows the very low and low content of available potassium. On this area the recommended rates of potassium fertilizers exceed the of-take of this element with the crop yields. The surplus of potassium would contribute to increase the content of available nutrient and should bring the soil in the future to the medium class. The content of available potassium is substantially differentiated among the country's regions (Figure 7). In eight regions (administrative units), the ratio of soils poor in potassium is over 40% and only in three regions it does not exceed 30%. These differences are partly grounded on pedological soil origin but also on different management practices in agriculture. It concerns, mainly, different among regions consumption of potassium fertilizers and limestone, which influence the soil acidity and indirectly the content of available potassium forms. This problem lays, however outside the scope of the paper.

4.3. Comparison different method for estimation the available form of potassium

In the Central-Eastern European countries (see MOEL group in Materials) different methods are applied for estimation the available potassium in soil. In scope of the MOEL co-operation, the research project has been launched on comparison the methods used in ten countries (see last chapter). Altogether, 132 soil samples have been collected from long-term field experiments in the treatments without and with potassium fertilization and two soil layers, 0-25 and 25-50 cm. The samples were analyzed for the content of exchangeable potassium K_{ex}, which was included as a reference method, and available potassium by methods presented in Table 4. Considering very different texture of individual soils the variability of data was big enough for making the reliable comparison of the applied methods (Table 11).

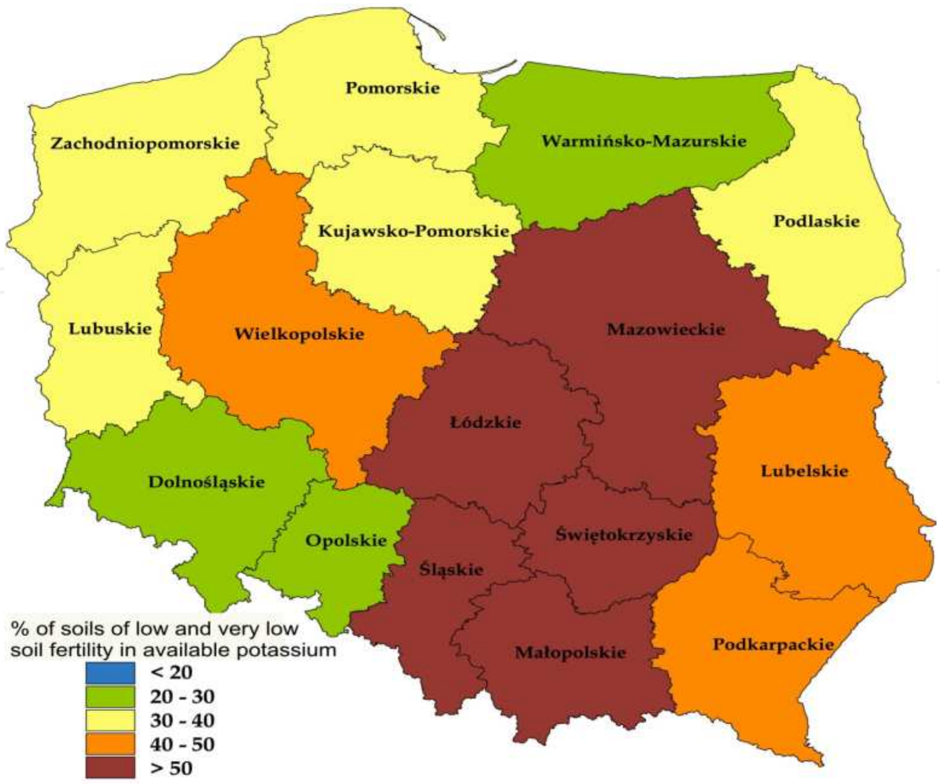

Figure 7. The percent of soils poor in potassium in regions of Poland [4]

Potassium form mg K•kg^{-1}soil	light soils(46)*		medium soil(26)		heavy soils(24)		very heavy soils(36)		total (132)	
	average	std**	average	std**	average	std**	average	std**	average	Std^{2}
K_{ex}	72,2	37,1	122	75,0	135	72,5	168	91,1	120	78,6
K_{DL}	75,5	35,4	119	83,9	112	69,1	116	78,2	102	66,7
K_{CAL}	54,6	32,9	90,0	61,8	83,3	47,9	93,3	60,0	77,3	52,5
K_{AL}	128	55,6	186	111	197	95,6	238	127	182	106
K_{Meh}	88,6	40,1	137	74,2	144	64,9	176	88,6	132	75,3

*number of samples, **standard deviation

Table 11. The content of available potassium by different methods [21]

The average amounts of potassium extracted by different methods were in the following decreasing order: K_{AL} > K_{ex} >K_{Meh}>K_{DL}>K_{CAL}. Exchangeable potassium K_{ex} is a form (pool) defined conceptually. Therefore, it may be presumed that the method of available potassium determination is as better as its results correlate closer with this theoretically grounded pool (Table 12).

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Test	K_{ex}	K_{DL} (X)	K_{CAL} (X)	K_{AL} (X)	K_{Meh} (X)
K_{Meh}	0,98	0,92	0,93	0,97	-
K_{AL}	0,97	0,94	0,95	-	K_{AL}=-0,69+1,38X
K_{CAL}	0,91	0,97	-	K_{CAL}=-8,14+0,47X	K_{CAL}=-8,64+0,65X
K_{DL}	0,90	-	K_{DL}=5,96+1,24X	K_{DL}=-6,32+0,59X	K_{DL}=-6,36+0,82X
K_{ex}	-	K_{ex}=11,27+1,07X	K_{exm}=14,17+1,36X	K_{ex}=-10,2+0,71X	K_{ex}=-15,9+1,03X

Table 12. Relationships between pairs of examined soil tests of available potassium

The closest correlation has been found between exchangeable potassium K_{ex} and the Mehlich 3 method K_{Meh}. Besides, the slope of the regression line between these two methods is close to one, which means that both lines run parallel. However, using Mehlich 3 method somewhat higher amounts of potassium are extracted. Similar proportionality has been also found between K_{ex} and K_{DL}, although the correlation coefficient between these two potassium forms is weaker than between K_{ex} and K_{Meh}. The highest amounts of potassium are extracted using K_{AL} method, and it seems that with this method, not only exchangeable potassium but a part of reserve form K_{res} is estimated.

4.4. The content and proportion of different potassium forms in Polish soils

In the years 2002–2004, in the areas of the oldest glaciation periods (Sanian I and Sanian II, see Figure 2) seven hundreds soils samples representing medium and heavy soils have been collected. The samples, from the soil layers 0-25 cm and 25-50 cm were analyzed for soil pH, and the content of different forms of potassium by methods described in Table 3. Factor which the most influence the content of all potassium forms was soil categories, i.e. the content of soil's particles less then 0,02 mm (Table 13).

Soil category	No of samples	K_{H2O}		K_{ex}		K_{res}		K_{sem}	
		0-25 cm	25-50 cm	0-25 cm	25-50 cm	0-25 cm	25-50 cm	0-25 cm	25-50 cm
v.light	32	17	8,87	59,1	31,1	156	97	234	226
light	177	24,3	14,9	91,3	56,0	254	195	503	440
medium	253	22,0	13,8	112	72,6	382	204	872	789
heavy	238	21,6	10,1	166	104	655	470	2372	2256

Table 13. The content of potassium forms in two soil layers (medians) mg $K \cdot kg^{-1}$ soil [18,19,22].

The content of all forms of potassium, except the water soluble one increased significantly from the very light to the heavy soils. The water-soluble potassium K_{H2O} makes 0,7-5%, exchangeable potassium K_{ex} 7-18% and reserve potassium K_{res} 23-45% of the nominal total potassium. In these ranges, the ratio of available or slowly available potassium forms in the nominal total potassium was the highest in the very light and the lowest in heavy soils.Therefore the coarse-textured soils although contain considerably less potassium, the greater part of it appears in the form immediately available and readily available for crops.The relative content of potassium in the subsoil against the plow soil layer was 56%, 60%, 66% and 87% for water soluble, exchangeable, reserve and nominal total potassium forms respectively. It means that the plow soil's layer (0-25 cm) is enriched, particularly in the potassium forms available for crops.

4.5. Long–term changes in potassium forms

In 2010 in 10 countries belonging to MOEL group (see Materials) at least one or more long-term fertilizers experiments, including treatments with NPK and without NP potassium fertilization has been selected. In 2010 soil samples from these treatments and from two soil layers 0-25(30) cm and 25(30)-50(60cm) were collected and prepared for analysis. All soils from Estonia,Latvia, Lithuania and Poland were of glacial origin and have been characterized by coarse texture as light ones. These soils fall in the topic of the paper and other soils, of much heavier structure make a frame of reference. Soil analysis has been performed by methods presented in Table 4. It is worth to emphasize that in this particular project, the soil texture was analyzed by laser method and the total content (not only seemingly total) of potassium has been estimated by the fluorescence atomic spectrometry. The content of all potassium forms are included in Table 14.

Potassium pool mgK•kg^{-1} soil	Soil category*				Soil level cm		Fertilization	
	light**	medium	heavy	v.heavy	0-25	25-50	NP	NPK
samples	46	26	24	36	66	66	61	71
K_{H2O}	14,6	17,0	14,8	12,3	16,8	12,0	11,8	17,0
K_{ex}	72,2	122	135	168	135	104	100	137
K_{res}	339	525	762	964	651	595	618	628
K_{sem}	1624	2903	4719	5892	3513	3692	3552	3640
K_{total}	14051	14675	15360	15877	14852	14968	14798	15009

* light < 20% of silt, medium 20-35% silt, heavy 35-50% silt, very heavy > 50% silt, silt particles less then 0,02 mm. ** soils of glacial origin friom Estonia, Latvia, Lithuania and Poland

Table 14. The content of potassium forms depending on soil texture (category) [8]

The factor which most strongly determinates the content of all pools of potassium, except the immediately available $K_{H2O,}$ is a soil category, i.e. the percent of silt. The differences in the content of K_{ex}, K_{res} and K_{sem} between the light and very heavy soils are two and three-folds and in the content of total potassium K_{tot} reaches almost 15%. The content of immediately available potassium K_{H2O} is practically independent of soil category and is generally higher in light and medium, than in heavy and very heavy soils. The content of two pools of potassium (K_{H2O} and K_{ex}), accessible for plants was higher in the upper soil layer in comparison to the subsoil while slowly available K_{res} and structural pools (K_{sem} and K_{tot}) seem to be more uniformly distributed in the soil profile 0-50 cm. Long term application of potassium fertilizers showed a positive effect on the content of K_{H2O} and K_{ex} pools of this element. However, the reserve K_{res} and total potassium K_{tot} contents in the soil have hardly changed in spite of long-term soil mining from this element in the control treatment. There is a strong correlation between immediately available K_{H2O} and readily available K_{ex} potassium and the weaker between K_{H2O} and K_{res}. No correlation exists between immediately available and total (K_{sem}, K_{tot}) potassium. Readily available potassium K_{ex} correlated the strongest with slowly available one K_{res} and significantly with the pools of total potassium. The strongest estimated correlation was between the slowly available and total potassium and, between both operationally distinguished pools of total potassium. The ratio of potassium forms has been calculated against the pool of total potassium K_{tot} (Figure 8) and/or the pool of nominal total potassium K_{sem} (Figure 9). Both approaches provide inconsistent results, when related to the soil texture.

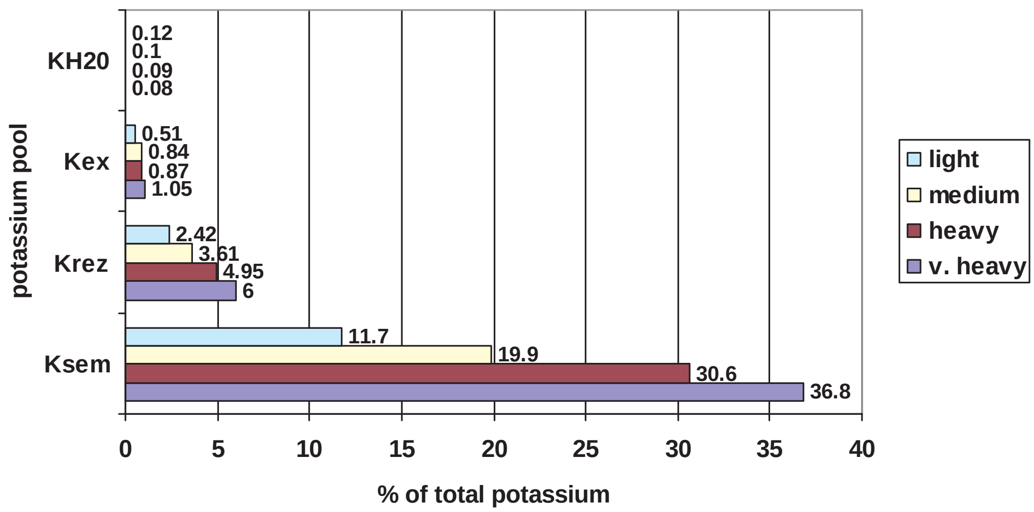

Figure 8. The ratio of potassium pools in the content of total potassium K_{tot}.

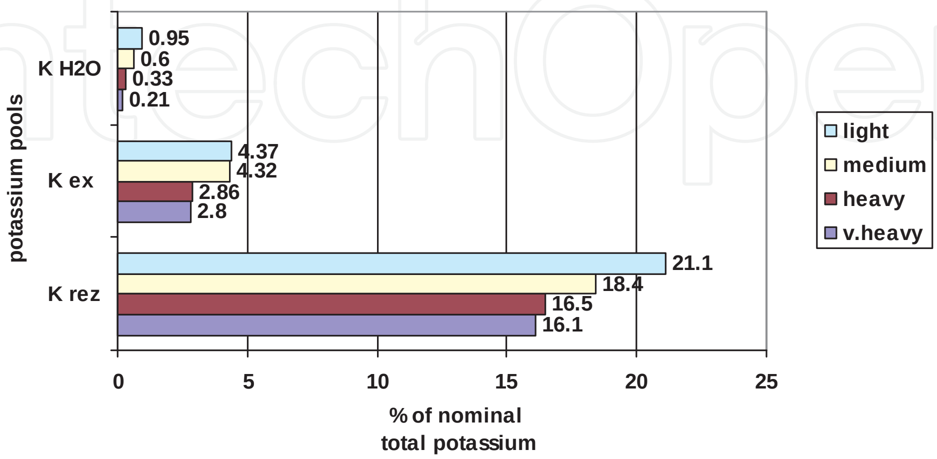

Figure 9. The ratio of potassium pools in the content of nominal total potassium K_{sem}

The relative content of all potassium forms (except the water soluble one) calculated against the total potassium K_{tot} increased systematically from the very light to very heavy soils. However, the ratio of all potassium forms calculated against the nominal total potassium, decreased in the same direction. This discrepancy has not yet deserve special attention in the available literature and needs further research. The relative content of potassium forms in light soils (mainly of glacial origin), against the nominal total potassium is very close to those found in the research conducted in scope of the 1st project in the years 2002-2005 [18]. From this finding, it can be concluded and recommended that by relating the content of different potassium forms to the total potassium a clear distinction should be made between the nominal total K_{sem} and total K_{tot} forms. Such differentiation is particularly relevant, due to analytical problems in many research conducted on soil potassium, for which only nominal total form of this element is estimated.

It has been already mentioned that in this research, the content of clay (soil particles less than 0,002 mm) and silt (soil particles less than 0,02 mm) was quantitatively estimated by a diffraction laser method. It was therefore, possible to calculate the degree of clay and silt saturation by different forms of potassium (Table 15).

Potassium pool	mg K per 1% of clay		mg K per 1% of fine fraction**	
	without potassium NP	with potassium NPK	without potassium NP	with potassium NPK
Exchangeable K_{ex}	1,15 (0,69)*	2,03 (1,53)	0,30 (0,15)	0,50 (0,30)
Reserve K_{rez}	7,25 (3,45)	9,01 (4,88)	1,88 (0,74)	2,06 (0,76)
nominal total K_{sem}	37,7 (12,3)	47,1 (23)	10,1 (2,98)	11,6 (3,79)
Total K_{tot}	208 (123)	253 (163)	56 (30)	60,0 (32,6)

*In parenthesis the standard deviation, ** particles <0,02 mm

Table 15. Saturation of clay and fine fraction with different potassium forms, depending on the long-term fertilization with this element [8]

Results from Table 15 indicate, that the arable soils in Central-Eastern Europe, properly fertilized contain about 2 mg of readily available K_{ex} and about 9 mg of slowly available K_{res} potassium per 1% of clay and respectively 0,5 mg of readily available and about 2 mg slowly available potassium per 1% of fine fraction. Long–term soil mining from potassium resulted in diminishing the saturation of clay and silt with readily available potassium K_{ex} by about 70% and the saturation with slowly available potassium K_{rez} by about 20%.

According to the results achieved in this project, comparison of potassium content in different forms at the beginning of experiments, with the amount taken up by crops in this period of time was also preliminary considered (Table 16). This problem is beyond the scope of this paper and, besides might deserve the further research.

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K pool	Light soils			Medium soils			Heavy soils			Very heavy soils		
	0-25	25-50	off*take	0-25	25-50	off take	0-25	25-50	off take	0-25	25-50	off take
K_{H2O}	75	57		86	66		79	44		69	37	
Kex	390	259		653	483		694	464		797	614	
Krez	1368	1236	2476	2152	1938	2871	3150	2580	3193	3999	3445	3374
Ksem	6253	7115		10992	11126		17973	18404		22742	22512	
Ktot	53028	53470		55064	55560		58120	58184		60220	59910	

*sum of the potassium removed from the soil by all crops grown in experiments

Table 16. The amount of potassium at the beginning of experiments, in the soil layers 0-25 cm and 25-50 cm, against its off take with crop yields in the NP treatment, kg K•ha^{-1}.[8]

Independently, of soil texture the amount of exchangeable potassium K_{ex} in the first 0-50 cm of the soils profile 0-50 cm does not meet the long-term plant's requirements for this element. Therefore, this pool needs to be constantly replenished from the pool of slowly available potassium K_{rez}. In the light soil even this pool in the soil profile 0-50 cm hardly matches the long-term plant requirements and had to be supplemented from the structural pool of potassium K_{sem}. In the medium soil, the amount of slowly available potassium K_{rez} in the upper soil level is too small against the plant requirements and only the amount in the soil profile 0-50 cm suffices to fulfill these requirements. In the heavy and very heavy soils, the upper soil level, 0-25 cm contains enough slowly available potassium to cover the long-term plant's requirements for this element. The amount of available and slowly available potassium was higher in the upper soil level in comparison to the subsoil. This regularity does not concern the nominal total K_{sem} and total K_{tot} potassium pools, which practically do not differ between the soil levels. It leads to the conclusion that upper level of arable soils is enriched with plant accessible potassium

5. Summary and conclusions

Most of the soils in Poland are of glacial origin and are formed from poorly sorted clays and sands of moraines and fluvial-glacial sands. These soils are deeply leached down, poor in bases and, therefore, acid. Almost 60% of the soils belong to very light and light categories, i.e. contain less than 20% of fine fraction and over 50% of soils are very acid and acid. The content of organic matter is generally low and very low even at the limit established in Poland, which is below 2,0% of SOM. In the paper, two approaches to potassium in the soil are presented. The first approach, conceptual – functional, is based upon the literature data, and it focuses on the defined potassium pools and physicochemical processes governing the potassium dislocation between these pools. The second approach, operational-analytical, concerns the potassium forms isolated from the soil samples using chemical methods. The second approach has been applied in the own research carried on in scope of three scientific projects in the years 2002 – 2012. The soils of glacial origin in Poland have been characterized as regards the content of water soluble K_{H2O}, available (in different extracts, mainly calcium lactate $K_{DL)}$, reserve (in boiling nitrate acid K_{res}), nominal total (in Aqua Regia) and total (Roentgen spectrometer) K_{tot} potassium forms. The content of all forms of potassium, except water soluble one depended significantly on soil granulometric composition and soils pH and increases from the very light to heavy, and from very acid to neutral soils. Properly managed soils contain 2 mg K_{ex} and 9 mg of K_{res} per 1 % of clay fraction (<0,002 mm). The new calibration figures for available potassium K_{DL} by linking the K_{DL} content to water soluble potassium K_{H2O} is proposed. Applying these figures would promote more sustainable potassium fertilizer's management. The soils of glacial origin in Poland are generally poor in available potassium and the ratio of soils showing very low and low potassium (K_{DL}) content exceeds 40 %. The water-soluble potassium (K_{H2O}) makes 0,7-5%, exchangeable potassium (K_{ex}) 7-18% and reserve potassium (K_{res}) 23-45% of the nominal total potassium. In the light soils, the ratio of nominal total to total potassium is slightly over 10 %. In long-term experiments with potassium fertilization, the amounts of potassium in different forms were compared with the uptake of this element by crops grown in control (without K fertilization)treatments. Independently, of soil texture the amount of exchangeable potassium in the soil profile 0-50 cm does not suffice to cover the crop's requirements for this element. Therefore, this pool needs to be constantly replenished from the pool of slowly available potassium K_{rez} and even from the pool of nominal total potassium. The problem of potassium fertilization and its influence on the forms of potassium in the soil is beyond the scope of this paper and, besides might deserve the further research.

Acknowledgements

The experimental part of this paper is a summary of three research projects funded by the Ministry of Science and Higher Education in Poland : Nr 3 PO6R 087 23 “Nawkal 2002 – 2005, No 2 PO6R 48 30 “Kalpol” 2006-2008 and NN 310 204437 “Kalifert” 2009 – 2012. Author expresses sincere thanks to all colleagues from the MOEL group for providing the soil samples in scope of the last project.

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