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THE APPLICATION OF SPENT ION EXCHANGERS AS FERTILIZER CARRIERS IN RESTORATION OF DEGRADED SOILS

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Abstact: The present studies aimed at comparing the effect of the potassium monoionic form (prepared from a model spent ion exchanger) and a conventional potassium fertilizer (KCl) on plant vegetation after addition to depleted soil. To achieve the study aim a pot experiment using orchard grass (*Dactylis glomerata* L.) as the test plant was carried out. The vegetation cycle lasted seven weeks. The plants were grown on four series of media: on untreated soil, on soil with added monoionic K form, on soil with added KCl and on soil with Biona-312 substrate added (2% v/v). Biona-312 served as the control fertilizer containing all macro- and microelements.
The application of monoionic potassium form positively influenced orchard grass vegetation. The addition of K form into soil increased stem wet and dry biomass, root dry biomass and total dry yield by 15, 10, 13 and 12%, respectively. Bearing in mind that the amount of dry plant matter as source material for humus formation is crucial in soil reclamation, the effectiveness of potassium monoionic form was found to be similar to that of the mineral fertilizer – KCl. Biona-312 was the most efficient fertilizer used in the study, resulting in the greatest yield of *Dactylis glomerata* L.
Keywords: Ion exchangers, potassium, soil restoration

INTRODUCTION

Degraded soils occupy a relatively large area in the world nowadays. Their poor production capacity is mainly caused by human activity, especially by mining, marsh draining and the construction of industrial and military objects. To restore the original properties of degraded lands, technical and biological recultivation is required. Technical recultivation includes ground forming, regulation of water conditions and sometimes technical soil reconstruction. Biological recultivation consists in scarp planting and humus layer forming, as this layer with adequate properties positively influences soil properties. Scarp planting, as well as humus layer forming, is connected with plant cultivation. Intensification of plant development on degraded soils occurs after organic and mineral fertilization. Mineral fertilizing is used to enrich soils with macro- and microelements, especially with nitrogen, phosphorus and potassium (Niewiadomski *et al.*, 1983). It can be accomplished by using different means, including ion exchangers saturated with nutrient ions. Ion exchangers seem to be successfully used in soil restoration due to their high ion exchange capacity, high chemical and mechanical stability and ability to gradually release nutrient ions, preventing their leaching by rainfall.
The possibility of using synthetic ion exchange resins as nutrient carriers for plants was confirmed in the last half century (Arnon and Grossenbacher, 1947; Zemljanuchin *et al.*, 1964, 1966).

Since that time interest in ion exchangers as nutrient carriers has been increasing, finally resulting in a preparation of ion exchange substrates by a research team from the Belarusian National Academy of Science. Ion exchange substrates, presently named Biona®, contained the whole set of macro – and microelements and enabled plant cultivation in closed ecological systems such as submarines, arctic stations and spacecraft (Soldatov *et al.*, 1968, 1969, 1978). Parallel investigations of the effect of monoionic forms prepared from synthetic resins and containing some nutrients (Ca^{2+}, K^+, NO_3^-) on the properties of sandy soils were carried out in Bohemia (Podlesakova and Bouchal, 1978; Podlesakova, 1979a, 1979b). The results of Podlesakova's experiments showed that plant yields obtained in the presence of monoionic forms were higher than those obtained on soils fertilized with mineral salts of calcium, potassium and nitrogen. The positive study results with Biona substrates initiated a new series of model experiments at Lublin University of Technology (Poland) on their applications in the restoration of degraded soil. Among a number of other findings the study recommended the use of Biona additions (1%–2% v/v) for fertilization of barren soils (Soldatov *et al.*, 1998).

In the work described here only fresh previously unused ion exchangers were studied. As the price of new resins might be a barrier to their wide utilization as fertilizers the idea of using spent ion exchangers in soil recultivation has appeared. Spent ion exchangers are periodically discharged by water purification plants because of the mechanical destruction of their granules, a decrease in their ion exchange capacity and irreversible sorption of humic compounds. As was shown in the studies, such materials could be used for preparing a complete ion exchange substrate, the addition of which to pure sand significantly increased plant yield (Chomczyńska and Pawłowski, 2003). These materials can also be used for preparation of monoionic forms containing ions of macro- or microelements. Their preparation is much easier than that of the complete substrate. The application of spent ion exchangers to prepare monoionic forms is an ecologically attractive method of their reuse as opposed to incineration, which results in emission of SO_2 and NO_x in the case of cation exchangers and anion exchangers, respectively.

The first attempts on application of monoionic forms prepared of waste resins have been made. Chomczyńska used nitrate, phosphate and potassium forms as fertilizers introduced together into sand as a model of degraded soil. The application of the mentioned forms increased plant biomass as compared to that obtained on sand alone (Chomczyńska and Pawłowski, 2003). In these experiments conventional fertilizers as controls were not used. Thus, the aim of the present study is to compare the effectiveness of fertilizing depleted soil with potassium bound to a spent resin model with potassium in a conventional fertilizer form – KCl.

MATERIALS AND METHODS

In the study, mineral soil, monoionic potassium form, potassium chloride and ion exchange substrate Biona-312 were used. The mineral soil was taken from an excavation boundary of a sand mine (in Turka near Lublin). It consisted of the following fractions: sand (1.0–0.1 mm) – 78%, dust (0.1–0.02 mm) – 11%, silt and clay (< 0.02 mm) – 11% (the texture was determined using areometric method). According to the granulometric composition, the soil was classified as light loamy sand (Polish Society of Soil Science) or sandy loam (USDA). It contained 0.05 g of available potassium per kg (0.06 g K_2O kg^{-1}), which is considered rather low for light soils (Czuba, 1980). The pH of the soil in distilled H_2O was 5.39.

The monoionic potassium form was prepared by treating the strong acid cation exchanger KU-2 in H form with KOH solution. The prepared monoionic form contained 4.29 mmol K per g. Its moisture content was 130 g kg^{-1}. This form was ground in a Retsch grinder (type S 1000) in order to produce a structure similar to that of a spent ion exchanger.

The ion exchange substrate Biona-312 was prepared at the Institute of Physical Organic Chemistry of BNAS in Minsk and served as the control fertilizer in the study. It was a mixture of 56% (mass) of ion exchange substrate Biona-111 and 44% of clinoptilolite (a zeolite of formula (K_2, Na_2, Ca)$Al_6Si_{30}O_{72}\cdot 24H_2O$). The Biona-312 substrate contained the following amounts of elements (g kg^{-1}): N – 11.206, P – 3.407, K – 17.595, Mg – 4.378, Ca – 22.244, S – 6.094, Mn – 0.220, Cu – 0.064, Zn – 0.057, Co – 0.015, Mo – 0.044, B – 0.110, Fe – 2.234, Na –1.379, Cl – 3.900.

To achieve the study aim, a pot experiment was carried out in open air conditions. The test plant was orchard grass (*Dactylis glomerata* L.) – a species recommended as a constituent of plant recultivation mixtures. For the needs of the experiment four series of media were prepared, including two control series: soil and soil with 2% (v/v) addition of ion exchange substrate Biona-312 and two test series: soil with an addition of potassium monoionic form and soil with an addition of conventional potassium fertilizer (Table 1). The additions of the monoionic form and KCl contained the same potassium amount resulting from recommendation for fertilizing meadows on mineral soils (100 kg K_2O ha^{-1}). The addition of Biona-312 resulted from previous studies which exhibited that a 1%–2% dose of ion exchange substrate was sufficient for soil recultivation purposes (Soldatov *et al.*, 1998).

The experiment started on the 3rd of April 2006. There were 10 pots (of 360 cm^3 volume) in each series. In each pot 0.05 g of *Dactylis glomerata* L. seeds were sown. After 11 days of growth the number of plants in all pots was standardized. During the experiment, plants were watered with distilled water. The temperature, as well as the relative air humidity, was monitored using a TZ-18 thermohygrograph („Zootechnika", Cracow, Poland). The day air temperature was in the range: 15°C–33°C. The night air temperature varied between 8°C and 23°C. The day air humidity ranged from 18% to 88%, the night air humidity achieved values between 21% and 77%. The experiment was terminated after 50 days from the time of seed sowing. The height of plants was measured and above-ground shoots were cut down. The plant roots were also separated. The wet and dry (105°C) biomass of stems and dry (105°C) biomass of roots were weighed. The obtained results were used for calculation of arithmetical mean values. The experimental error was assumed as 5%.

Table 1. Characteristics of series in the vegetation experiment

series	soil [ml, g/pot]	mass of fertiliser [g/pot]	amount of introduced macroelements [g/pot]
soil	**300**	-	-
(G)	514		
soil+KCl	**300**	0.1243	K - 0.0652
(G+K)	514		
soil+monoionic form	**300**	0.3887	K - 0.0652
(G+JK)	514		
soil+Biona-312	**300**	5.1384	K - 0.0904
G+B 312)	514		N - 0.0576
			P - 0.0175
			Ca - 0.1143
			Mg - 0.0225
			S - 0.0313

RESULTS AND DISCUSSION

The study results are presented in Fig. 1–5. It can be seen that the mean values of measured parameters obtained for plants growing on soil with KCl addition were higher than those for plants growing on soil alone. The plant height, wet stem biomass, dry root biomass and total dry yield on soil with added conventional potassium fertilizer were higher than those obtained in the control series by 21%, 10%, 17%, and 9%, respectively. The value for dry stem biomass in the control series was by 3% higher than that obtained on the medium with KCl addition, however, the difference was below the experimental error.

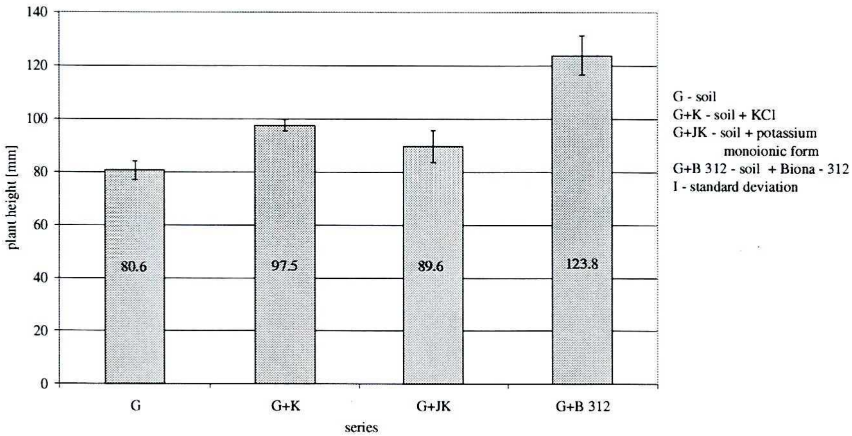

Fig. 1. Mean plant height in experimental series

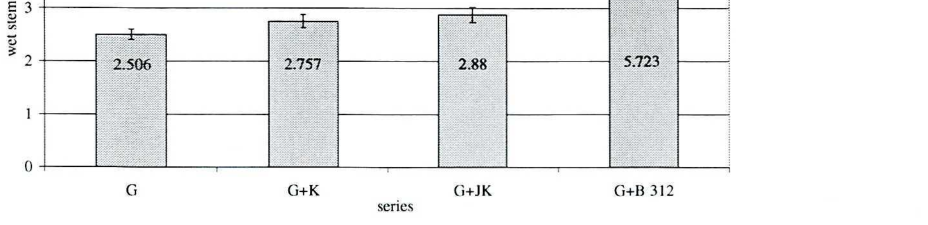

Fig. 2. Mean wet stem biomass in experimental series

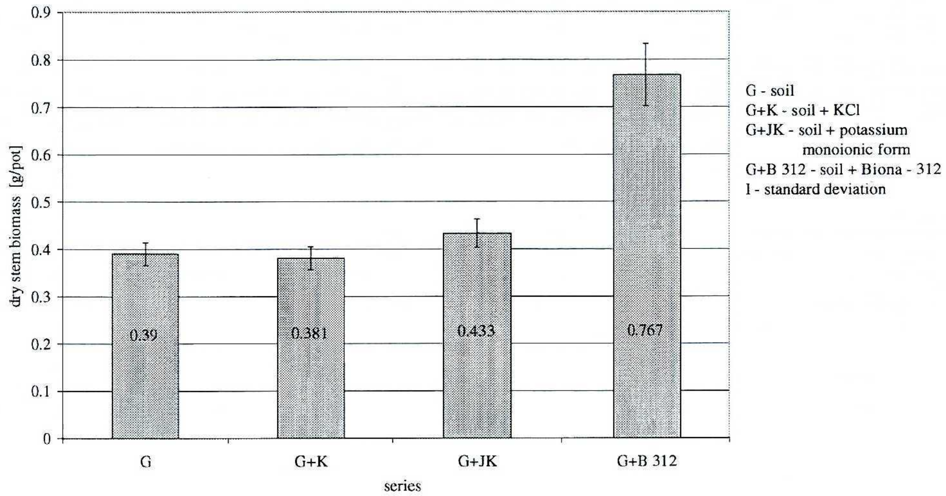

Fig. 3. Mean dry stem biomass in experimental series

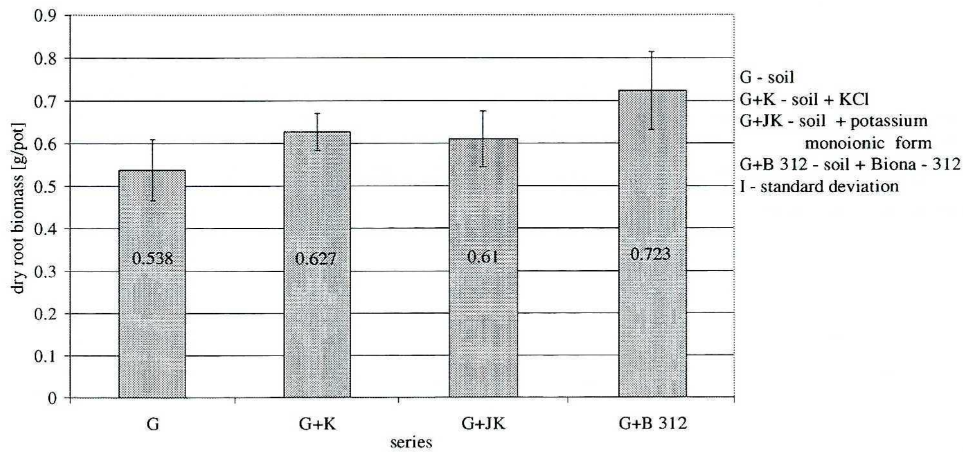

Fig. 4. Mean dry root biomass in experimental series

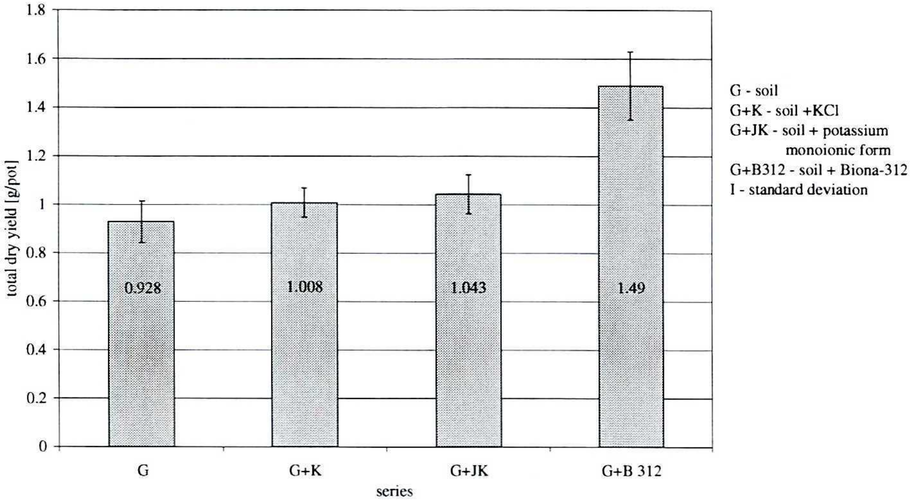

Fig. 5. Mean total dry yield in experimental series

The application of monoionic potassium form had a positive influence on orchard grass vegetation. In this case, the mean values for the height of the plants, wet and dry stem biomass, dry root biomass and total dry yield were higher than those obtained in the control series by 11%, 15%, 10%, 13% and 12%, respectively (Fig. 1–5).

The results obtained for Biona-312 addition showed that application of this control fertilizer had the greatest influence on test plant vegetation (Fig.1–5). Mean wet and dry stem biomass in the series with Biona-312 exceeded those obtained on soil alone by more than twofold and slightly less than twofold, respectively. The mean height, mean dry root biomass and mean total dry yield of orchard grass growing on soil supplemented with Biona-312 were higher than those obtained on the soil of the control series by 54%, 33% and 60%, respectively.

At the assumed experimental error (5%) mean values of wet stem biomass and dry root biomass of orchard grass obtained in the series with the addition of potassium monoionic form and KCl did not differ (Fig. 2 and 4). However, dry stem biomass of test species growing on soil enriched with potassium bound to ion exchanger was 13% greater than that obtained on soil supplemented with KCl (Fig. 3). Additionally, the total dry yield of orchard grass in the series with monoionic form was only 3% higher than that in the series with KCl (Fig. 5). The effectiveness of potassium monoionic form was similar to that of mineral fertilizer (KCl) in dry matter production, which is important in soil reclamation as source material for humus formation.

A comparison between all the measured parameters characterizing the test species in fertilized experimental series confirmed the greatest efficiency of Biona-312. The mean height, mean dry root biomass and mean total dry yield of orchard grass growing on soil supplemented with the Biona-312 exceeded those in the series with KCl by 27%, 14% and 48%, respectively (Fig. 1, 4, 5). Mean values for the wet and dry stem biomass of plants growing on the medium with added Biona-312 were more than twofold greater than those obtained on soil plus conventional potassium fertilizer (Fig. 2, 3). The addition of Biona-312 to soil caused almost a twofold higher figure for the wet stem biomass of orchard grass (Fig. 2) as compared to that obtained on soil with monoionic potassium form. The plant height, dry biomass of stems and roots and total dry yield in the series with Biona-312 addition were higher by 38%, 79%, 18% and 43%, respectively, than those obtained on the medium with added potassium bound to ion exchanger (Fig. 1, 3–5). The highest efficiency of Biona-312 as a fertilizer resulted from its high content of potassium and other macroelements. The added Biona-312 (2% (v/v)) contained the highest amount of potassium and supplemented the soil also with nitrogen, phosphorus, sulphur, calcium and magnesium (Table 1).

The introduction of potassium monoionic form into soil had a positive effect on plant vegetation, which was also observed by Kloc and Szwed (1995), Wasąg *et al.* (2000) and Chomczyńska and Pawłowski (2003) in their studies with monoionic forms prepared on the basis of ion exchanger. These authors used different mixtures of monoionic forms, different control media, and sometimes, different test species (Table 2). Thus, direct comparison between their results and the results presented in this paper is not possible. However, as mentioned above, in almost all the cited works the application of monoionic forms saturated with ions of macroelements elevated plant biomass, and the highest increase in yield was observed in Chomczyńska's studies (2003) with orchard grass. Here the addition of three monoionic forms (NPK) into sand caused 4-fold increases in wet stem biomass and dry root biomass, and an almost 5-fold increase in dry stem biomass.

Table 2. The effectiveness of monoionic form mixtures described in references

mixture	control medium	test species	mean biomass on control medium [g/pot]	mean biomass on fertilized medium [g/pot]	effect [%]	reference
potassium, calcium, and magnesium forms	garden soil	maize (*Zea mays* L.)	1.70*[1] 0.79*[2] 0.628*[3]	3.66 1.813 0.764	129 115 22	Kloc and Szwed, 1995
nitrate, phosphate and sulphate forms	garden soil	maize (*Zea mays* L.)	1.70*[1] 0.79*[2] 0.628*[3]	2.77 1.377 0.484	63 74 30	Kloc and Szwed, 1995
nitrate, phosphate and potassium forms	mineral soil	orchard grass (*Dactylis glomerata* L.)	0.770*[1] 0.145*[2]	0.909 0.127	18 -	Wasąg *et al.*, 2000
potassium, calcium, sulphate and phosphate forms	mineral soil	orchard grass (*Dactylis glomerata* L.)	0.685*[1] 0.132*[2]	0.906 0.144	32 9	Wasąg *et al.*, 2000
nitrate, phosphate and potassium forms	sand	orchard grass (*Dactylis glomerata* L.)	0.258*[1] 0.048*[2] 0.072*[3]	1.051 0.231 0.286	307 381 297	Chomczyńska and Pawłowski, 2003
nitrate, phosphate and potassium forms	sand	birds-foot trefoil (*Lotus corniculatus* L.)	0.291*[1] 0.065*[2] 0.057*[3]	0.541 0.115 0.088	86 77 54	Chomczyńska and Pawłowski, 2003

Explanations: *[1] - wet stem biomass, *[2] - dry stem biomass, *[3] - dry root biomass,

The application of potassium bound to ion exchanger to soil gave a similar orchard grass yield (total dry biomass) to that observed in the presence of potassium dosed in the form of KCl. Different results were obtained by Podlesakova, who studied the effectiveness of monoionic forms (potassium-, calcium- and nitrate forms) as compared to mineral fertilizers (KCl, $CaCO_3$, and $NaNO_3$) in maize (*Zea mays* L.) cultivation on sandy soil during pot experiments (Podlesakova and Bouchal, 1978; Podlesakova, 1979a). In the case of calcium fertilization, Podlesakova observed that the above-ground dry biomass of maize on soil with an addition of Ca monoionic form was 13%

higher than that obtained on soil fertilized with $CaCO_3$ (Podlesakova, 1979a). The maize yield on soil fertilized with different nitrogen doses applied as nitrate monoionic form was from 23% to 127% higher than that obtained where parallel N doses were introduced in $NaNO_3$ form (Podlesakova and Bouchal, 1978; Podlesakova, 1979a). In the experiments on potassium fertilization, Podlesakova found that maize dry biomass on soil enriched with different potassium doses introduced as K monoionic form was from 7% to 22% higher than that obtained on soil fertilized with parallel K doses applied as KCl (Podlesakova and Bouchal, 1978; Podlesakova, 1979a). The cited results of Podlesakova's studies concerned the first vegetation period of the test species. The observed increases in maize yield after application of particular monoionic forms corresponded to dry above-ground shoot biomass. Perhaps taking into account the total dry matter of maize (unfortunately data not shown in Podlesakova's papers) would show similar findings as for orchard grass, particularly in the case of application of potassium monoionic form and KCl.

CONCLUSIONS

The results obtained allowed the following conclusions to be formulated:

1. Potassium in the conventional fertilizer form (KCl) positively influences orchard grass vegetation – after introducing into sandy soil it causes an increase in wet stem biomass, dry root biomass and total dry plant yield.
2. The monoionic potassium form seems to be an effective fertilizer, increasing degraded soil productivity – mean values for all measured parameters on the medium with an addition of monoionic potassium form are higher than those obtained on soil alone.
3. Regarding total dry plant yield, it can be said that the efficiency of monoionic potassium form, as compared to a conventional fertilizer, is similar. However, the evident advantage of using ion exchanger as a potassium source is that the resin has an ability for mild release of K cations without introducing chlorine, which is undesirable in a soil environment, especially in high concentrations.
4. Biona-312, as a standard ion exchange substrate, turns out to be the most efficient fertilizer used in the study, resulting in the greatest yield of *Dactylis glomerata* L.

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