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Distribution of manganese in the Soil-Water-Plant in the zone of Burshtyn Thermal Power Station

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Abstract
Thermal power stations have a multifaced and scale impact on natural biogeocenosis. This problem is of great actuality in the Precarpathia, where such most powerful enterprise as Burshtyn Thermal Power Station (BTPS) is the main polluter in all western region.
When researching technogenic impact of BTPS on local environment, there studied the amount of manganese in soil, water and celandine in the territory of its direct impact by atomic absorption spectrometry with inductively coupled argon plasma on analytic system "Plasmaquant 110" and by methods of mathematical statistics.
This study deals with the impact of BTPS on the amount of manganese in soil, water and celandine tissue. It was proved that emissions of BPTS change not only gross manganese amount, but also significantly break correlation between different manganese fractions in water and soil. Gross and changeable manganese amount in soil, water and celandine tissue are changeably interrelated and depend on the season, the distance from the polluter. Manganese distribution in celsndine tissues is organically specified, which is determined when a particular tissue is a part of the plant powering process and depends on the environmental possibilities where celandine grows.

Keywords: celandine (*Chelidonium majus L.*), Burshtyn thermal power station (BTPS), gross and changeable manganese amount, industrial areas (IA).

1. Introduction

A significant factor of techno genic transformation of overland and water biogeocenosis is the introduction of a wide spectrum of pollutants into natural ecotypes. In the zone of BTPS influence some of the priority environmental polluters are heavy metals that are introduced in natural biogeochemical course and are capable to disrupt structural and functional organization of biogenesis [1, 4].

Within Ivano-Frankivsk region one of the most active polluters is electricity production enterprise, it means BTPS. In the Precarpathia emission of this station is more than 85% of the total number of stationary pollution sources. Sulfur dioxide and such heavy metals as iron, copper, manganese and zinc are some of the substances vented by BTPS. Manganese takes the third prize due to the mass fraction in the earth's crust in comparison with heavy metals and it is naturally very well-spread [2, 5].

Manganese (Mn) is necessary to preserve a reproductive function of a living organism, metabolism of glucose and lipids. It is a part of enzyme systems that perform redox reactions of intracellular metabolism. With human and mammals deficiency phosphor and calceous metabolism is disturbed that can cause rickets development. Mn accelerates the formation of antibodies, increases the synthesis of thyroid hormones, affects positively the absorption of iodine [3, 4].

Therefore in the research of migration the peculiarities of migration, accumulation and manganese toxicity are actual in technogenesis process. This occurs especially in the zone of BTPS.

Celandine (*Chelidonium majus L.*) as a synanthropic everseen species can be a sample in biological monitoring studies. The fact that it is capable to survive in a wide range of ecological factors' impact of natural and anthropogenic origin attracts interest to the plant in order to clarify the mechanisms of adaptation in the process of technogenic changes of existance and evaluation of promising [5]. The impact of complex anthropological technological factors caused by BTPS's activity can make some changes in pharmacological activity and can also cause some significant side effects to appear when celandine is used in medical practice. As stated above, it has been assessed a metal accumulating ability and reactions in enzyme system of *Chelidonium majus L.* in the process of technogenic impact of

BTPS [8, 9].

The objectives are to investigate spatial features and seasonal dynamics of accumulating gross and changeable manganese forms in ecotypes, to assess a metal accumulating ability of celandine (*Chelidonium majus* L.) vegetative organs.

2. Materials and Methods

The research facilities are chosen as International raster grid required. In the process of researching techno genic impact of BTPS on environment, the amount of manganese in soil, water and celandine was searched in the area of its direct impact. Selection of soil, water and celandine samples, and also their storing and analytical preparation were taken in accordance with the requirements of State Standard of Ukraine (State Ecological Testing System 4388-72).

The amount and form of gross and changeable manganese in soil, water are determined by atomic absorption spectrometry with inductively coupled argon plasma on the analytic system "Plasmaquant 110" [9].

Processing the results of research carried out by the methods of mathematical statistics [10].

3. Results and Discussion

The amount of gross manganese Mn in local edafotopies is under significant fluctuation and is seasonably dependent on ecotypical peculiarities and the distance from the enterprise (Table 1).

Table 1: The total amount of manganese in local edafotopies in the zone of BTPS influence (n=8, mg/kg)

Season / Research area	Spring	Summer	Autumn	Averages
Background biogeocenosis	565,6±12,2 6,10	515,5±12,6 6,92	501,6±6,84 3,86	527,6±19,5 6,40
IA BTPS	953,3±17,7* 5,24	840,8±18,7* 6,28	874,4±8,9* 2,87	889,5±33,3# 6,49
8 km from enterprise	846,5±15,0* 5,02	717,7±13,3* 5,22	843,7±10,3* 3,45	802,6±42,5& 1,93
16 km from enterprise	648,9±9,7# 4,24	558,5±13,1 6,65	514,1±8,1 4,26	573,90±39,7 11,97

Note: probable changes compared with the control parameter: * – P < 0,001; # – P < 0,01; & – P < 0,05.

The highest amount of gross manganese in soils were found in the industrial areas (IA) of BTPS, where according to seasonal research they vary within 840,8 mg/kg in summer time and 953,3 mg/kg in spring time accounting appropriate target values 515,5 – 565,62 mg/kg. At the distance from BTPS the amount of gross manganese decreases, but radically differs from target values even at the distance of 16 km from the enterprise in spring time (648,9 mg/kg).

Spatial dynamics changeable manganese amount and forms is similar to gross fraction (Table 2).

The average amount of trace elements in target area soils is equal 24, 22 mg/kg with a coefficient of variation 8,58%. In the IA of BTPS and at the distance of 8 km from the location of enterprise exceeding of target values was found relatively 1,8 and 1,4 times more, and also an increase of its degree of variability. At the distance of 16 km the amount of changeable manganese in soils shows a tendency to norms and doesn't radically differ from target during a year.

Table 2: The total amount of changeable manganese in local edafotopies in the zone of BTPS influence (n=8, mg/kg)

Season / Research area	Spring	Summer	Autumn	Averages
Background biogeocenosis	26,24±1,95 21,03	22,09±0,97 12,41	24,39±1,22 8,67	24,22±1,20 8,58
IA BTPS	50,49±2,06* 11,55	42,14±1,24* 8,30	39,99±1,12* 7,92	44,20±3,20& 12,55
8 km from enterprise	32,84±1,24& 10,65	32,74±1,08* 9,30	39,51±0,97# 6,98	35,02±2,24& 11,08
16 km from enterprise	26,71±1,25 13,19	29,55±1,14 10,87	28,75±1,51 14,85	28,31±0,85 5,17

Note: probable changes compared with the control parameter: * – P < 0,001; # – P < 0,01; & – P < 0,05.

Amount of changeable Mn fractions is more variable in comparison with gross forms of trace element. In the majority of analyzed soil samples the coefficient of variation rate exceeds 10%.

Amount of gross Mn in the surface water is significantly lower in the comparison with groundwater, and they have well-defined seasonal and spatial dynamics (Table 3).

Table 3: The total amount of gross manganese in water lotional biogeocenosis in the zone of BTPS influence (n=8, mkg/dm^3)

Season / Research wing	Spring	Summer	Autumn	Averages
Control	66,3±3,60 15,36	76,4±1,72 6,38	66,0±2,74 11,73	69,6±3,42 8,51
0 km from BTPS	177,9±5,37* 13,26	184,3±3,26* 5,01	103,3±2,87* 7,86	155,2±26,0# 9,83
8 km	81,4±2,91# 10,12	77,7±2,65 9,66	78,7±3,07& 11,02	79,3±1,14 2,48
16 km	69,3±2,84 11,59	82,0±3,31 11,41	68,8±2,50 10,26	73,4±4,32 10,20

Note: probable changes compared with the control parameter: * – P < 0,001; # – P < 0,01; & – P < 0,05.

Within the sanitary protection zone (SPZ) of BTPS the gross manganese amount in surface water exceeds target values almost three times more, and depending on the season reaches 103,3 – 184,3 mg/kg at 66,0 – 76,4 in the target area. As moving away from BTPS, these figures are reduced to target values.

Seasonal figure dynamics was the most clearly observed in the top polluted areas of the Hnyla Lypa River that is the place of technical reservoir outfall. According to amount of increasing gross Mn (p < 0,01) can be shown in a sequential series: autumn time (103,3 mkg/dm^3) > spring time (177,9 mkg/dm^3) > summer time (184,3 mkg/dm^3). The average annual coefficiency was 29, 02%. Spatial amount changes were mostly revealed in summer when surface water contained the greatest amount of trace elements in the majority of research wings.

Amount of changeable manganese contain a small proportion of its gross amount around all target area of the Hnyla Lypa River. (Table 4.).

Table 4: The total amount of changeable manganese fractions in water lotional biogeocenosis in the zone of BTPS influence (n=8, мкг/дм^3)

Season / Research wing	Spring	Summer	Autumn	Averages
Control	4,56±0,20 12,63	7,13±0,27 10,90	7,42±0,22 8,42	6,37±0,91 24,71
0 km from BTPS	9,79±0,32* 9,35	10,87±0,40* 10,34	7,22±0,17 6,82	9,29±1,08$^{\&}$ 20,18
8 km	7,78±0,16* 5,80	8,27±0,29 9,94	7,00±0,18 7,35	7,68±0,37$^{\&}$ 8,34
16 km	6,31±0,18$^{\#}$ 8,06	6,79±0,11 4,61	6,05±0,23 10,79	6,38±0,22 5,88

Note: probable changes compared with the control parameter: * – P < 0,001; # – P < 0,01; & – P < 0,05.

Average annual amount of trace element in the control area is 6,37 mkg/dm^3, but significant excess (p < 0,05) of the specified value is observed in the place of technical river reservoir outfall in the territory of BTPS and at the distance of 8 km from it (relatively 1.5 and 1.2 times more).

The amount of changeable manganese in water has a clear seasonal dependence. Within SPZ of BTPS in spring and in summer the amount of changeable manganese significantly (p < 0,001) increases in comparison with control figures (relatively 4.56 and 7.13 mkg/dm^3) and is 9.79 and 10.87 mkg/dm^3. In autumn the amount of changeable Mn significantly differs from control figures and keeps the rate of 7.22 mkg/dm^3.

In the direct impact zone of BTPS (8 and 16 km) the changes in amount of changeable manganese are significantly (p < 0,01) higher than control figures in spring (relatively 7.78 and 6.31 mkg/dm^3), when in other seasons the amount of changeable metal fractions rang between control values.

The amount of manganese in vegetative organs *Chelidonium majus* L. varies considerably depending on the season and location of the research area and has a clear organic specificity (Table 5).

Root plant's receipt of manganese in the target area and within SPZ of BTPS. The greater amount of trace element in root tissues is the demonstration of it, comparing with above-ground parts of plants. At the distance of 8 i 16 km from the enterprise the amount of manganese in leaves is higher than in other vegetative organs. The specified sample is best seen in spring time.

Table 5: The amount of manganese in vegetative organs *Chelidonium majus* L. within technogenic impact of BTPS (n=6, mkg/1000 mg of ash)

Season	Organ	Research area localization			
		Target	IA of BTPS	8 km from BTPS	16 km from BTPS
Spring	Leaves	400,67±9,55	628,00±16,44*	1389,50±55,17*	5081,33±50,34*
	Stem	32,33±2,42	67,50±6,72*	385,17±14,03*	742,00±18,81*
	Root	690,00±10,45	996,50±43,47*	724,33±17,80*	385,67±17,90*
Summer	Leaves	398,17±13,05	215,00±15,04*	464,83±16,54*	3138,20±64,02*
	Stem	137,67±9,50	155,67±5,89$^{\&}$	296,50±14,29*	1002,67±23,58*
	Root	413,67±18,79*	560,33±14,20*	519,83±24,69*	956,67±18,16*
Autumn	Leaves	232,33±19,81	414,67±11,76*	605,88±21,40*	1146,33±42,54*
	Stem	90,50±8,94	284,83±13,92*	340,20±13,22*	775,67±16,51*
	Root	311,17±22,36	178,50±46,00*	624,75±11,40*	869,00±13,96*

Note: probable changes compared with the control parameter: * – P < 0,001; # – P < 0,01; & – P < 0,05.

The maximum amount of Mn in phytomass (full mass) of *Chelidonium majus* significantly (p < 0,001) increases in equal distance proportion to BTPS. Maximum increases of a target manganese amount were observed in spring time at the distance of 16 km from BTPS: for leaves – 12.7 times more, for stem – 23.0 times more. In the roots internal tissue amount of manganese reaches its top at summer-autumn time exceeding target value 2.8 times more.

Thus, vegetative organs of *Chelidonium majus* are characterized by different metal accumulating abilities and selectivity when accumulating trace elements that show rates of biological absorption.

4. Conclusions

1. The impact of BTPS on environment is implemented by the action of emissions into atmosphere when burning of energy-resource materials.
2. Under the influence of emissions from BTPS not only gross amount of manganese changes but also the correlation between different manganese fractions in water and soil is disturbed. Changes have seasonal and spatial dependence. In surface water the greatest amount of Mn is found in spring and in summer time. The changeable amount of Mn in water has no seasonal dependence. In micro edafotopies maximum amount of Mn is determined in spring and summer time.
3. Celadine (*Chelidonium majus L.*) is characterized by differential metal accumulating possibility which has clear seasonal and organic specificity and depends on the distance from the source of pollution. Maximum amount of manganese was found in leaves and stems in spring time at the distance of 16 km from BTPS, but in roots – in summer time in the industrial areas of BTPS. No direct dependence between the distance from BTPS and organic specificity of metal accumulation indicates a mixed flow of pollutants into the plant.

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