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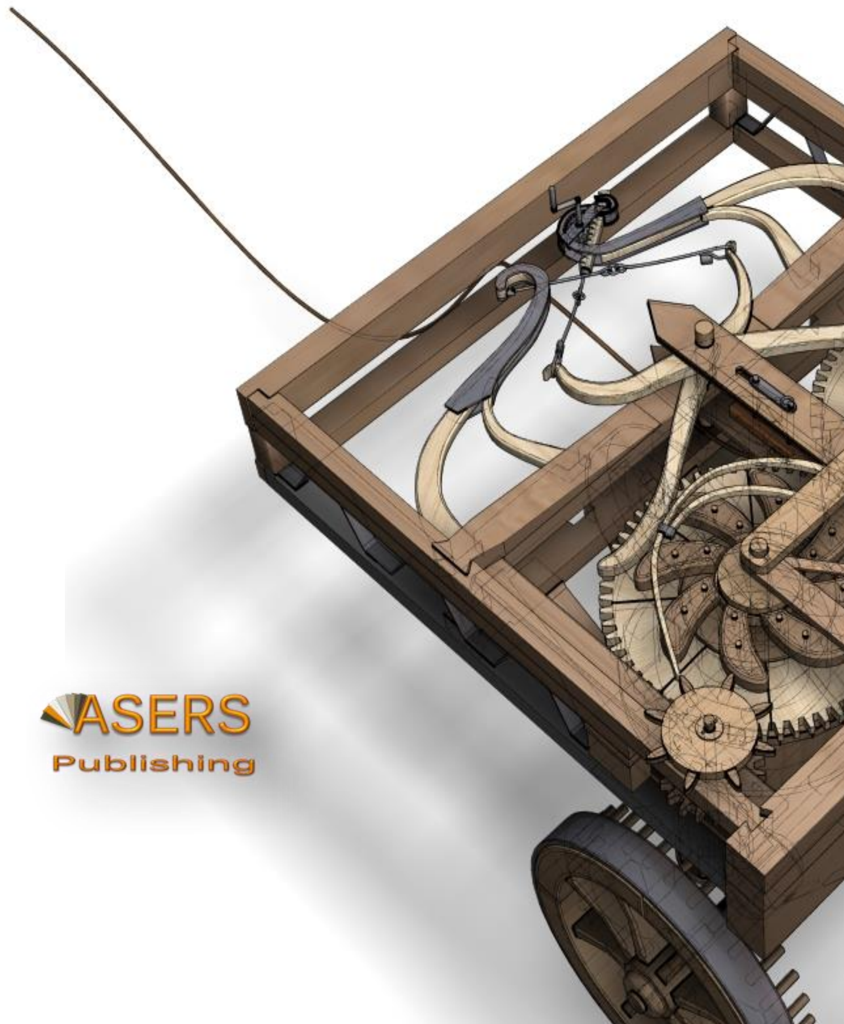

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Journal of Environmental Management and Tourism

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Accumulation of Heavy Metals in the Needles of Scots Pine of the Semipalatinsk Pre-Irtysh Region and Burabay National Park

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Abstract: Relict bogs in the northeastern area of the Republic of Kazakhstan are located in close proximity to sources of heavy metal pollution – non-ferrous metal ore mining and processing facilities, and highways. Monitoring of heavy metal transport in the air by means of a bioindicator such as Scots pine (*Pinus sylvestris* L.) is relevant for preventing the damaging effects of heavy metals on the population living in this region. The purpose of this article is to study pine needles (*Pinus sylvestris* L.) on the territory of the Semipalatinsk Irtysh region and the Burabay National Park to identify the features of the accumulation of heavy metals carried by atmospheric air flows, depending on the age of its formation. To determine the content of chemical elements in needles of the first, second and third year of formation from six experimental plots mass spectrometry method ISO 17294-2:2003 was used. Its results made it possible to conduct a primary analysis of the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris* L.) depending on the year of its formation. General scientific methods were also used in the analytical selection of the scientific literature to formulate the objectives of the experiments and to compare the results obtained with those of other authors. Experimental studies revealed a direct correlation between the increase in concentrations of individual metals and the age of the needles. Furthermore, an increase in concentrations of individual chemical elements has been detected in the conifers of the second year of formation. The findings can be used for further scientific research on the use of pine needles (*Pinus sylvestris* L.) as a bioindicator, the impact of the heavy metal composition of the north-east of Kazakhstan on plant organisms, but also used in practice to monitor the state of the environment and the management of forests.

Keywords: heavy metal pollution; bioindicators; bioaccumulation; biomonitoring; air pollution; anthropogenic pollution.

JEL Classification: Q53; L65; R11.

Introduction

This article is devoted to the study of the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris* L.) to monitor air pollution in the East Kazakhstan and Akmola regions of the Republic of Kazakhstan with heavy metals. This makes it possible to identify the role of the anthropogenic factor in the accumulation of heavy metals transported by air in living organisms. This is especially important since there are proven deposits of gold, molybdenum, uranium, lead, copper, titanium, zinc, nickel, magnesium, and iron in these areas, their extraction and processing is carried out. Furthermore, the six-lane Astana-Shchuchinsk autobahn leads to the Burabay National Park. The study of the transport of heavy metal particles by air shows the degree of accumulation of heavy metals released into the atmosphere as a result of human activity in living organisms (plants) and allows it to be separated from the accumulation obtained through root nutrition in the territories of heavy metal ores. Such a study makes it possible to reveal the features of the combination of heavy metals in the atmosphere of a given region as a result of human activity, which also affects the change in the general state of the atmosphere of the entire planet.

Such research helps to determine the most effective approach to combat air pollution, which adversely affects the health of mankind on all planets. The dangers of air pollution are highlighted by H. Cometen *et al.* (2019) and M. Cetin *et al.* (2021). As they point out, 30 million people die each year from causes related to air pollution, and according to the World Health Organisation, 92% of the world's population lives in regions with polluted air. The main sources of heavy metal pollution are non-ferrous and ferrous metallurgy, quarries and mines for polymetallic ores, road transport, oil, and waste incineration. Thus, 94-97% of lead accumulated by woody vegetation, 84-89% of cadmium, 56-87% of copper, 66-75% of nickel, 58% of mercury are of technogenic origin. The remaining part is extracted by plants from natural sources, notes N.M. Baiseitova (2014). The level of contamination with heavy metals can be determined by direct methods using special equipment or indirectly using bioindicators. According to Juranovic Cindric *et al.* (2018), the use of bioindicators to detect air pollution gives more reliable results on changes in heavy metal concentrations. The sophisticated equipment used to measure air pollution requires special laboratories to maintain and analyse the results and does not always capture the nuances of the effects of heavy metals on living organisms at different levels of accumulation. Bioindicators, according to V. Voronin and S. Soboleva (2019), is a simpler, more accessible method that allows measuring the accumulation of heavy metals even in the field. Furthermore, bioindicators are often more sensitive to changes in heavy metal concentrations than devices.

All studies of plants as bioindicators conducted by scientists from various countries focus on various factors affecting their accumulation of heavy metals. Thus, objects of investigation include the accumulation of heavy metals in different plant parts, dependence of heavy metal concentration in plants on distance from pollution sources, emission intensity, the age of plants or plant parts (*e.g.*, wood, needles), on wind direction in the studied areas, on the combination of heavy metals in these areas. These studies always give characteristics of the accumulation of heavy metals by bioindicator plants in a specific area on a specific site. Nevertheless, they also allowed for the identification of certain regularities between the accumulation of heavy metals by plants and the distance from the pollution source, the age of the plant or its parts, the integration of heavy metals in the phytocoenosis process, and the tracing of a pattern of heavy metal accumulation in homogeneous plant parts (from the most accumulating heavy metals to the least accumulating ones).

The study found that the content of Al, Mn, Sr, Zn in the needles of Scots pine (Pinus sylvestris L.) increases with age, *i.e.*, the process of bio-accumulation. Accumulation of heavy metals in pine needles has a definite pattern: Mn, Fe, Zn, Sr, Cu, Cr, Co, which are biogenic trace elements, accumulate in higher amounts than highly toxic elements – Tl, Cd, As. The elemental composition of Scots pine needles is significantly impacted by the place of growth, which is reflected in the intensity of the biogeochemical metal cycle.

1. Materials and Methods

To study the degree of heavy metal pollution in the Semipalatinsk Pre-Irtysh area and the Burabay National Park, the Scots pine (*Pinus sylvestris* L.) was selected as a bioindicator, as it is a widely distributed species of woody vegetation, very sensitive to changes in the chemical background of growing conditions (Parzych *et al.* 2017). Pine is actively studied and used in various countries as a bioindicator and bio-accumulator of heavy metals. To study the degree of atmospheric air pollution by heavy metals in Semipalatinsk Pre-Irtysh and Burabay National Park, the needles of Scots pine (*Pinus sylvestris* L.) of the first, second and third years of formation were examined. This investigation also included a comparative analysis of the content of heavy metals in coniferous needles collected from two trial plots (six test plots), including control plots. The first trial site included areas of pine forests located in the Semipalatinsk Pre-Irtysh:

1. Pilot site No. 1 was located within the city of Semey (pilot site – Semey, Silicate Plant district; 50.468442, 80.212024). This site is considered the most polluted.

2. Pilot plot No. 2 (control plot) is established at a distance of 16 km to the north of Semey (control plot – Semey, Staraya Krepost village; 50.498466, 80.090461).

3. Test site No. 3 (control area) is established 18 km eastward from Semey along Semey – Borodulikha highway (control area – Semey, Novopokrovka village; 50.571381, 80.345089).

The second test site included the territories of pine forests of the Burabay National Park:

1. Pilot site No. 4 was located within the Borovoye village, 1.5 km from its center along the main highway (pilot site – Borovoye, along the highway; 53.074672, 70.276040).

2. Pilot site No.5 (control site) is established on a mountaintop near the Abylaykhan stone throne (pilot site – Borovoye, mountain top; 53.088812, 70.233952).

3. Pilot plot No.6 (control plot) is located 120 km from the village of Borovoye, near the village of Zerenda (pilot plot – Borovoye, Zerenda; 52.887228, 69.142328).

Trees 25-30 years old, 6-9 meters in height and 24-36 cm in diameter were selected for the study. Samples of needles were sorted by age fractions (1-3 years). Chemical elements were determined by inductively coupled plasma mass spectrometry using an iCAP Q quadrupole mass spectrometer from "Thermo Scientific". The multi-element standard solutions listed in the State system for ensuring the uniformity of measurements of the Republic of Kazakhstan under KZ.03.02.00901-2010 and KZ.03.02.00902-2010 were used to construct the calibration curves. The quality of the measurements was monitored by measuring the calibration solution every 10 samples. If the calibration chart deviated by 8-10% (unsatisfactory calibration result), the instrument was recalibrated with the new background parameters. The analysis was carried out according to ISO 17294-2:2003 "Water Quality. Application of inductively coupled plasma mass spectrometry (ICP-MS). Part 2: Determination of 62 elements" (ISO 17294-2:2003) (state registration number 022/10505 of 27.12.2005).

Dry samples of plant raw materials for suitability for analysis for the content of heavy metals were previously subjected to autoclave decomposition. A 0.4±0.0001 g sample dry weight of the plant material was placed in a fluoroplastic autoclave liner and 6 cm³ of concentrate was added. HNO_3 and 2 cm³ 30% N_2O_2. After 40 minutes, the PTFE liner was closed with a lid and inserted into the "BERGHOF" Speedwave Xpert microwave sample decomposition system, clamping it tightly to ensure sealing. The cover of the external casing of the autoclave was clamped with a screw. The system was heated to 190±5°C at 80% capacity and sustained. The total heating and exposure time was 50 minutes. Upon completion of the process, the cooled sample was transferred to a measuring tube and diluted with a 1% solution of nitric acid to a volume of 15 cm^3. This solution was diluted at a ratio of 1:10 and analysed for the content of the elements of interest.

The article presents comparative data on the composition of heavy metals (Cu, Ni, Cd, Pb, Fe, Zn, Mn) in Scots pine needles in each experimental plot and on the accumulation of heavy metals in needles of different ages of their formation.

The research carried out using the above methodology and its results are to a large extent unique, as the chemical background of the tree growth areas under study is unique, being influenced both by their geographical location, the wind direction, and the specifics of anthropogenic activity. At the same time, the results of the primary analysis of pine needles (*Pinus sylvestris* L.) samples allow for comparison with the similar unique results obtained from the primary analysis by other authors. To compare the results, the authors made a brief analytical review of the scientific literature on the results of studies of pine needles (*Pinus sylvestris* L.) carried out by scientists from different countries. Particular attention was paid to studies carried out under similar conditions - in national parks and natural forests in mountainous areas, near highways and near non-ferrous metallurgical plants. Such a comparison makes it possible to identify certain trends and features of accumulation of heavy metals transported by atmospheric masses, *e.g.*, correlation with distance from pollution sources (highways, industrial plants).

2. Results

Pine trees are very sensitive to pollution. It is particularly sensitive to aerial pollution of atmospheric air by both toxic gases and chemical elements of the heavy metal group (Alaqouri 2020; Wegiel, Bielini and Polowy 2018). It is therefore used as a bioindicator in environmental pollution assessments. The experimental data indicate that there is a definite pattern of redistribution of elements in the coniferous pine needles as the plants grow. Moreover, the accumulation of some elements occurs in close correlation with each other, as previously noted by other authors (Figas, Siwik-Ziomek and Kobierski 2021; Liu, Wang, Zou and Jiang 2006; Zhang *et al.* 2010). Indicators of the content of heavy metals in the coniferous pine (*Pinus sylvestris* L.) of different years of formation, obtained during the experimental study at six sites of Semipalatinsk Pre-Irtysh and the Burabay National Park, are shown in Table 1, 2.

Table 1. The content of heavy metals (Fe, Be, Al, Cr, Mn, Ni, Cu, Zn, Sr, As) in pine needles (*Pinus sylvestris* L.)

No.	Age of needles, year	Elements content, mg/kg									
		Fe	Be	Al	Cr	Mn	Ni	Cu	Zn	Sr	As
Semey, Silicate Plant district (50.468442, 80.212024)											
1	3	92±8	<0.0004	110±1	2.3±0.1	130±1	3.6±0.02	1.3±0.1	27±1	11±0.1	<0.0015
2	2	55±4	<0.0004	76±1	1.8±0.1	120±1	1.6±0.03	1.5±0.1	25±1	9.7±0.1	<0.0015
3	1	110±8	<0.0004	140±1	1.8±0.1	150±1	5.5±0.1	1.9±0.1	29±1	13±0.1	<0.0015
Semey, Staraya Krepost village (50.498466, 80.090461)											
4	3	78±4	<0.0004	100±1	2.2±0.1	140±1	0.83±0.06	1.3±0.1	22±1	10±0.2	<0.0015
5	2	47±4	<0.0004	71±1	1.2±0.1	100±1	0.34±0.04	1.2±0.1	20±1	9.1±0.1	<0.0015
6	1	53±6	<0.0004	72±1	1.2±0.1	84±1	0.7±0.06	1.2±0.1	19±1	9.1±0.1	<0.0015
Semey, Novopokrovka village (50.571381, 80.345089)											
7	3	100±15	<0.0004	350±1	2.4±0.1	750±1	0.96±0.03	2.4±0.1	63±1	27±0.2	<0.0015
8	2	76±3	<0.0004	180±1	1.3±0.1	330±1	1.2±0.04	1.5±0.1	37±1	12±0.1	<0.0015
9	1	65±6	<0.0004	160±1	1.5±0.1	330±1	0.48±0.02	1.4±0.1	31±1	11±0.1	<0.0015
Borovoye, along the highway (53.074672, 70.276040)											
10	3	190±4	<0.0004	220±1	0.9±0.1	410±1	0.59±0.01	1.7±0.1	45±1	12±0.1	<0.0015
11	2	160±8	<0.0004	230±1	0.9±0.1	380±1	0.66±0.02	2.2±0.1	43±1	12±0.1	<0.0015
12	1	190±11	<0.0004	210±1	0.6±0.1	200±1	1±0.02	2.4±0.1	39±1	9.1±0.1	<0.0015
Borovoye, mountain top (53.088812, 70.233952)											
13	3	69±4	<0.0004	450±1	1.6±0.1	590±1	0.5±0.07	1.7±0.1	42±1	21±0.1	<0.0015
14	2	59±3	<0.0004	370±1	0.6±0.1	350±1	0.17±0.01	1.2±0.1	27±1	15±0.3	<0.0015
15	1	59±3	<0.0004	260±1	1±0.1	280±1	0.22±0.03	1.8±0.1	30±1	11±0.1	<0.0015
Borovoye, Zerenda (52.887228, 69.142328)											
16	3	74±3	<0.0004	86±1	1.7±0.1	150±1	0.74±0.04	3.5±0.1	39±1	13±0.1	<0.0015
17	2	65±9	<0.0004	63±1	1±0.1	110±1	0.57±0.05	2.8±0.1	32±1	8.5±0.1	<0.0015
18	1	54±4	<0.0004	44±1	0.7±0.1	95±1	0.95±0.01	2.7±0.1	31±1	6.7±0.1	<0.0015

Table 2. The content of heavy metals (Cd, Cs, Ba, Tl, Pb, U, Co) in the needles of Scots pine (*Pinus sylvestris* L.)

No.	Age of needles, year	Elements content, mg/kg						
		Cd	Cs	Ba	Tl	Pb	U	Co
Semey, Silicate Plant district (50.468442, 80.212024)								
1	3	<0.003	0.028±0.003	5.8±0.2	0.015±0.003	3.1±0.01	0.021±0.002	0.056±0.003
2	2	<0.003	0.018±0.001	5±0.1	0.009±0.002	2±0.01	0.028±0.002	0.041±0.003
3	1	0.051±0.009	0.034±0.004	6.6±0.2	0.01±0.001	3.1±0.04	0.022±0.002	0.1±0.004
Semey, Staraya Krepost village (50.498466, 80.090461)								
4	3	0.058±0.009	0.045±0.004	4.5±0.1	0.02±0.003	3.2±0.08	0.014±0.002	0.071±0.005
5	2	0.037±0.004	0.026±0.002	4.3±0.1	0.01±0.001	1.9±0.02	0.013±0.002	0.045±0.002
6	1	<0.003	0.022±0.002	4.8±0.1	<0.0004	1.6±0.04	0.013±0.002	0.053±0.002
Semey, Novopokrovka village (50.571381, 80.345089)								
7	3	0.066±0.013	0.027±0.001	17±0.1	0.013±0.003	1.7±0.03	0.034±0.005	0.086±0.004
8	2	0.045±0.003	0.011±0.001	8.5±0.1	0.01±0.001	0.9±0.02	0.011±0.002	0.042±0.002
9	1	0.038±0.007	0.013±0.002	7.7±0.1	<0.0004	0.94±0.03	0.015±0.001	0.044±0.008
Borovoye, along the highway (53.074672, 70.276040)								
10	3	0.033±0.005	0.023±0.002	5.2±0.1	0.01±0.002	0.99±0.03	0.019±0.002	0.075±0.002
11	2	<0.003	0.021±0.003	5.2±0.1	0.01±0.002	1.2±0.02	0.02±0.004	0.07±0.005
12	1	<0.003	0.037±0.004	6±0.1	0.009±0.001	0.63±0.01	0.033±0.002	0.082±0.006
Borovoye, mountain top (53.088812, 70.233952)								
13	3	0.1±0.028	0.014±0.003	6.3±0.1	0.025±0.004	0.52±0.01	0.015±0.001	0.094±0.01
14	2	0.071±0.012	0.017±0.004	4±0.1	0.012±0.001	0.63±0.03	0.011±0.001	0.11±0.007
15	1	0.19±0.027	0.015±0.003	3.5±0.2	0.01±0.002	0.32±0.02	0.013±0.001	0.043±0.001
Borovoye, Zerenda (52.887228, 69.142328)								
16	3	0.04±0.008	0.012±0.002	6.5±0.1	0.011±0.002	0.73±0.01	0.013±0.001	0.05±0.007
17	2	0.041±0.003	0.008±0.001	4.5±0.1	0.008±0.002	0.62±0.01	0.014±0.002	0.042±0.004
18	1	0.035±0.009	0.008±0.002	3.8±0.1	<0.0004	0.46±0.01	0.008±0.002	0.052±0.006

Summarised results of the study on the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris* L.) at the six experimental plots are shown in Figures 1-6. The figures contain data on the composition of heavy metals in Scots pine needles at each trial site and on the accumulation of heavy metals in the needles of different ages of their formation. The figures represent the results of an initial analysis and synthesis of the data obtained from the study of the needle samples at each of the sites. The identified features of the accumulation of heavy metals in Scots pine needles can be a starting point for further research, both empirical and scientific analysis, and for the comprehensive compilation of the primary results obtained. The results of analyses of Scots pine needles across the Semipalatinsk Pre-Irtysh are presented below (Figure 1-3).

Figure 1. Accumulation of heavy metals in pine needles by years of their formation at experimental plot No.1 (Semey, Silicate Plant district; 50.468442, 80.212024)

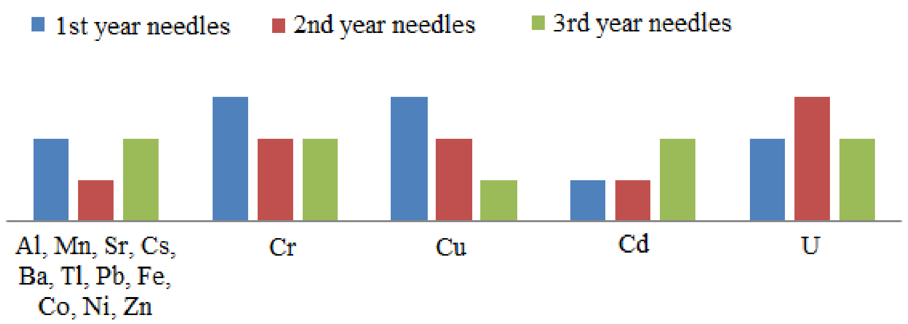


Figure 2. Accumulation of heavy metals in pine needles by years of their formation at experimental plot No.2 (Semey, Staraya Krepost village; 50.498466, 80.090461)

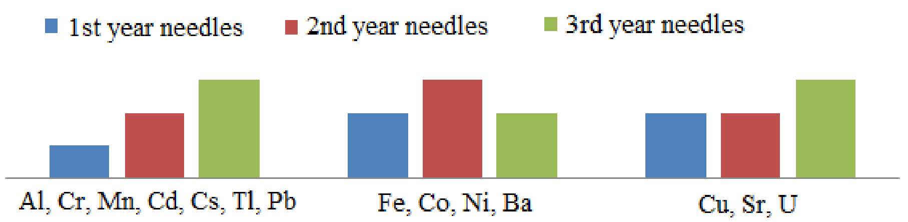
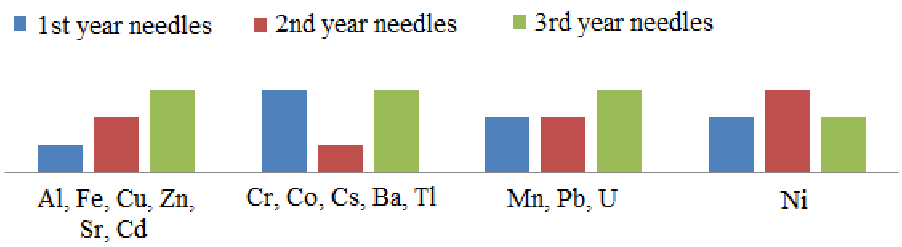


Figure 3. Accumulation of heavy metals in pine needles by years of their formation at experimental plot No.3 (Semey, Novopokrovka village; 50.571381, 80.345089)



Regarding the Burabay National Nature Park, the results of analyses of pine needles were as follows (Figure 4-6).

Figure 4. Accumulation of heavy metals in pine needles by years of their formation at experimental site No. 4 (Borovoye, along the highway; 53.074672, 70.276040)

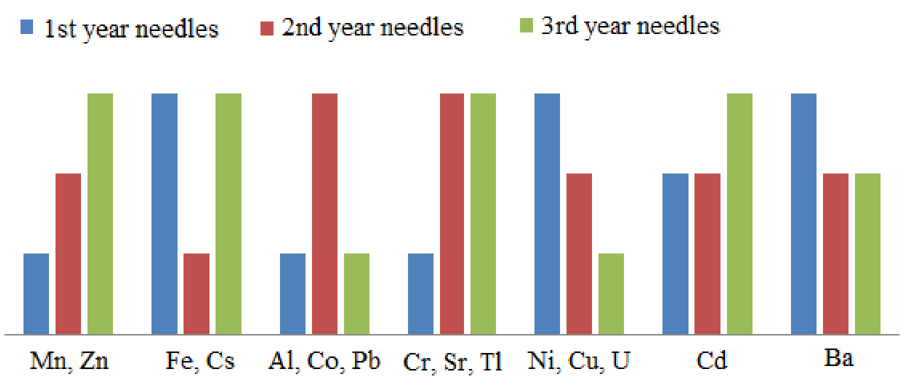


Figure 5. Accumulation of heavy metals in pine needles by years of their formation at experimental site No. 5 (Borovoye, mountain top; 53.088812, 70.233952)

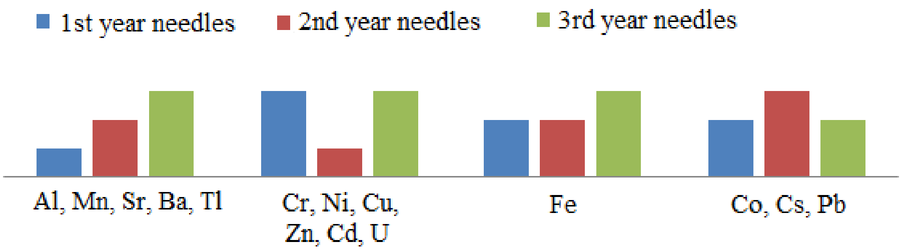
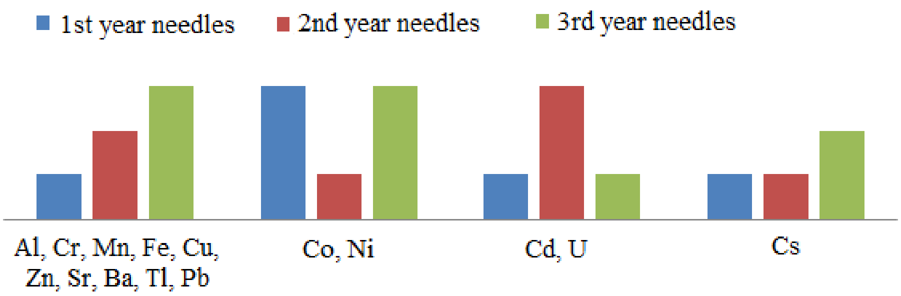


Figure 6. Accumulation of heavy metals in pine needles by years of their formation at experimental site No.6 (Borovoye, Zerenda; 52.887228, 69.142328)



The trees in the control and experimental plots exhibited a direct correlation between the increase in concentrations of individual metals and the age of the needles. The study found that in the needles of Scots pine (*Pinus sylvestris* L.), regardless of the environmental conditions of the study area, the accumulation of metals such as Al, Mn, Fe, Cr, Zn increases with age. Mn, Cr, Fe and Zn are biogenic trace elements, while aluminium is one of the elements likely to have some effect on plant metabolism, but the role of this element (along with Ba, Cu, U, Cs) in plants and its biogenic significance require further study.

It has also been determined that the needles in the second year of formation exhibit an increase in the concentration of certain chemical elements, and then either the needles die off or the concentration decreases. This pattern can be explained by the leaching of these elements as the cuticle of the needles breaks down. Such variations in the deviations of values indicate the adaptability of pine to pollution. It is also possible that under the influence of environmental factors or the protective mechanisms of the plant itself, little-studied mechanisms of blocking the toxic effect of absorbed metals are activated. When studying the content of heavy metals in Scots pine needles (*Pinus sylvestris* L.) in the territory of Semipalatinsk Pre-Irtysh and Burabay State National Nature Park, the following pattern in their accumulation (bioaccumulation) was noted, which can be represented by the following series of elements:

$$Mn>Al>Fe>Zn>Sr>Ba>Ni\geq Pb\geq Cu\geq Cr>Co>Cs=U>Tl>Cd>As>Be \quad 2.1$$

The heavy metal accumulation series obtained in this study consists of more chemical elements (17) than the accumulation series presented in the scientific literature by other authors. This may be indicative of the wide variety of minerals that are extracted and processed in the region by human industrial activity. The established pattern (1) agrees well with the data of various authors on the physiological role of individual elements. Thus, Mn, Fe, Zn, Sr, which are at the beginning of this row, are biogenic trace elements, without which the organism cannot grow, develop, and complete its natural life cycle. The same applies to elements such as Cu, Cr, Co. The elements Al and Ba in this series are very close to the biogenic elements, but their biogenic value has not been proven. The final elements in this series are Tl, Cd, As, which are highly toxic (Hassan and Aarts, 2011). The degree of toxicity of heavy metals can be represented by the following sequence:

$$Cu>Ni>Cd>Zn> Pb>Hg>Fe>Mo>Mn \quad 2.2$$

Studies of various plant species with different ability to accumulate heavy metals have allowed heavy metals to be divided into four groups depending on the degree of bioaccumulation: elements of intensive absorption (Cd, Cs, Rb), elements of medium absorption (Zn, Mo, Cu, Pb, As), elements of weak absorption (Mn, Ni) and elements that are difficult for plants to access (Se, Fe, Va). It was found that in Scots pine (*Pinus sylvestris* L.) elements of intensive absorption (*e.g.*, Cd, Cs) are less accumulated in the needles, and those difficult to access for plants (Fe, Ba) and elements of low absorption (Mn, Ni) have a high degree of accumulation in this organ.

Other researchers describe a similar but slightly different composition of these groups: elements of intense absorption (Cd, Cs, Rb); elements of medium absorption (Zn, Mo, Cu, Pb, Co, As); elements of low absorption (Mn, Ni, Cr); elements difficult for plants to access (Se, Fe, Ba, Te). One of the indicators of heavy metal pollution in the atmosphere is the age of the needles, as the accumulation of heavy metals in them, exceeding the critical limit, leads to diseases and the complete dying off of the needles. This critical limit for the concentration of base metals is 50-100 times higher than the reference value. As evidenced by I. Juranovic Cindric *et al.* (2018), the average age of the needles of the Scots pine (*Pinus sylvestris* L.) in the background areas is usually 5-9 years. Studies conducted at six trial plots in the Semipalatinsk Pre-Irtysh and the Burabay National Nature Park did not find pine plants with needles older than five years. This indicates significant cross-border transport of air pollutants and their dispersion over large areas.

3. Discussion

Scots pine (*Pinus sylvestris* L.) has proved to be a good indicator of airborne pollution, with high sensitivity, and is used in many countries for biomonitoring of atmospheric air pollution. An example is more than half a century of biomonitoring of changes in air and forest soil chemistry in two mature stands of Scots pine (*Pinus sylvestris* L.) as described by J. Pritzel *et al.* (2020), which allowed conclusions to be drawn about the dependence of forest ecosystem condition on changes in the chemical composition of anthropogenic emissions. However, the mechanisms of heavy metal uptake and accumulation through the surface of the needles are still largely understudied.

It is worthwhile to make a brief review of studies on the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris* L.), made by other authors in conditions similar to those of Semipalatinsk Pre-Irtysh and the Burabay National Park in order to direct further comparative analysis of the obtained research results presented in this article. The main sources of heavy metal pollution are mining and their industrial processing, as well as highways. All of these sources are in the vicinity of the sites investigated by the authors and polluted by their emissions. Therefore, when analysing such investigations, attention was paid to the distance of pine forests from the source of pollution, the combination of heavy metals depending on the dominant sources, and the accumulation of heavy metals in the needles depending on the age of their formation. The authors investigating the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris* L.), depending on the proximity to non-ferrous metallurgy enterprises, state that, in general, their accumulation decreases along the distance from the source of pollution. Although there are deviations for individual metals. There is also a difference in the degree of absorption between different types of trees, even of the same species.

Atmospheric emissions from ferrous and non-ferrous metallurgy plants consist mainly of sulphur dioxide and heavy metal particles (Cu, Pb, Cd, Zn, Fe, Ni, Co, etc.). Thus, H.A.A. Alaqouri *et al.* (2020) investigated the features of the accumulation of heavy metals in pine needles near the magnesium plant, focusing on the change in their concentrations depending on the age of the needles and the distance from the plant. A study of samples of scots pine needles (*Pinus sylvestris* L.) shows its efficiency as a bioindicator for monitoring the concentration of heavy metals in the air, in particular magnesium. A decrease in magnesium concentrations was noticeable with increasing distance from the pollution source. No such correlation was observed for Al, Fe, Mn and Ca. The direct correlation between the accumulation of heavy metals in conifers and the distance to industrial plants is also confirmed by the study of V. Popovic *et al.* (2022).

The second main source of heavy metal pollution is highways. This is important in the context of this study, as the Astana-Schuchinsk Autobahn is located near Burabay National Park, and the study areas of the Semipalatinsk Pre-Irtysh are close to large cities and industrial centres with intensive road infrastructure. Lead and cadmium are the main heavy metals in road emissions, and both are highly toxic. There is an inverse relation between lead and cadmium content and tree distance from the road, with roadside plants having lead concentrations 10-100 times higher than roadside plants, and cadmium concentrations 11-17 times higher than roadside plants. Also, heavy metal concentrations can increase by up to 60% in the lowlands and upwind compared to the flat landscape. This is evidenced in a study by N.M. Baiseitova (2014). Monitoring lead and cadmium in the air is very important because of the high toxicity of these metals and their long elimination period from the body. Thus, the half-life of cadmium from the human body is about 10 years. The use of Scots pine as a bioindicator is more effective than deciduous trees, as the needles have a large absorption area and waxy surface to trap metal particles. Scots pine (*Pinus sylvestris* L.) is also a good bioindicator for Mo and Ag and a bioaccumulator for K and Na.

The study by R. Kozlowski and M. Strzyz (2021) in the Świętokrzyskie National Park (Poland), where roads of different traffic levels are the main close sources of pollution, is of interest in the context of this investigation. The study confirmed the direct dependence of the concentration of Zn, Pb on the distance to the highways, as well as on the intensity of traffic. The lead content in the exhaust gases has decreased slightly due to its partial replacement in petrol by zinc. The authors note that the highest concentrations of these metals, along with Cu, Cd and Ni, were observed in the uplands, as the Świętokrzyskie Mountains, where the park is located, are elevated above the surrounding terrain. As such, strontium was detected in addition to the heavy metals' characteristic of automotive emissions. Cu, Cd, Sr, and Ni may be emissions from enterprises in the Upper Silesian industrial area, trapped by pine forests growing in the mountainous area of Świętokrzyskie National Park.

Research conducted by S. Ayan *et al.* (2021) in Kerey and Dzhanibek Khan Park in Astana, the capital of Kazakhstan, aimed to trace the dependence of heavy metal accumulation in five tree species, including Scots pine (*Pinus sylvestris* L.) on traffic density on the roads close to the park. Heavy metal pollution near highways is caused by exhaust fumes (Pb, Cd and Zn, used as fuel additives), abrasion of car tyres (Cd and Zn), and brake pads (Cu and Ni). The study confirmed that concentrations of Pb, Cd and Zn increase with higher traffic densities and decrease with greater distance from the road. There is also an increased level of concentration of these metals on curved sections of the road. In addition to the above-mentioned metals, elevated contents of Ni, Cr, Li, Co, Fe were detected in areas close to the roads. Comparison of the heavy metal accumulation capacity of different tree species makes it possible to assess the efficiency of their use as bioindicators, depending on the potential combination of chemical elements in the air at different sites, as well as to prioritise their use for the purposes of extraction, accumulation, and purification of air from toxic impurities. The ability of different tree species to accumulate heavy metals and the nature of their accumulation has been studied by authors such as J. Jonczak *et al.* (2021), in national parks, arboretums, respectively in Lisicine (Croatia) and Mlynany (Slovakia), and in nature reserves.

Some authors, such as A. Wegiel *et al.* (2018), take another step in the study of the properties of Scots pine (*Pinus sylvestris* L.) not only as a bioindicator of heavy metals in atmospheric air and soils, but also as their bioaccumulator for cleaning air and soils from elements harmful to living organisms. They investigated the dependence of accumulation levels of metals such as cadmium (Cd), nickel (Ni), chromium (Cr) and lead (Pb) on plantation density. A significant direct correlation was established between the density and mass of the stands of Scots pine (*Pinus sylvestris* L.) and the accumulation of Cd and Cr. Phytoextraction uses plants that are able to accumulate heavy metals without their toxic effects. The properties of Scots pine for phytoextraction are not widely investigated, but due to its unpretentious growth conditions and large distribution range, it can be considered as an effective phytoextractor. Research into the relationship between heavy metal accumulation and plantation density is important not only scientifically, but also practically for forest management. The purpose of the plantation as a phyto-extractor determines the decision to conduct felling. In this case, instead of thinning, the site is clear-cut and the mass of trees is disposed of, based on the nature of the contamination, which is removed by phytoextraction.

Plants that collect heavy metals from the air can thereby purify the air from heavy metals. Heavy metals accumulate in different parts of plants in different ways. Different plants also tend to have varying degrees of heavy metal accumulation, as evidenced in a study by R. Gamrat (2022). Therefore, depending on the combination of heavy metals in a particular area, it is important to choose as bioindicators the plants that are most sensitive to it or the plants that accumulate heavy metals the most for air purification. Depending on the performance of the desired function, the most effective plant species are determined. In the current study, Scots pine (*Pinus sylvestris* L.) was chosen to measure the accumulation of heavy metals. The needles of Scots pine (*Pinus sylvestris* L.) of the first, second and third years of formation were examined. Conifers, which include Scots pine, are used to measure the accumulation of heavy metals from the atmosphere, as the needles stay on the tree for several years and are covered with a layer of a waxy substance that traps the heavy metal particles. Pine forests of the Republic of Kazakhstan cover an area of 832 thousand ha, of which ribbon forests of Pre-Irtysh make up 58%, or 545 thousand ha (Belgibaev 2009). It should be noted that western, north-western, and south-western wind directions prevail in the territory of Semipalatinsk Pre-Irtysh and Burabay National Park, bringing particles of heavy metals from industrial mining and processing areas, as well as from the Astana-Shchuchinsk autobahn (Burabay National Park).

Conclusions

Pinus sylvestris L. is used as a bioindicator of heavy metals in the air in many countries because of its sensitivity to heavy metals, the nature of its needle surface and its life cycle of several years before it dies off. However, the features of the accumulation of heavy metals in various organs of pine, in conifers of different ages of formation, and the tendency to greater or lesser accumulation of various heavy metals still require extensive research. Pine needles can be used as bio-indicators for continuous monitoring of air pollution, and for extracting heavy metals from the air and neutralising them. This study is devoted to the features of accumulation of heavy metals by Scots pine needles of 1-3 years of formation in the Semipalatinsk Pre-Irtysh and the Burabay National Park, located at a relatively short distance from the main sources of pollution – iron and steel enterprises and highways, and requiring constant monitoring of air and its purification by bio-extraction. The identification of a special combination of pollutant elements will also determine the main industrial or transport pollutants. Accordingly, the Environmental Inspectorate will be able to exercise targeted control over emission reductions from one or another source of pollution.

The study found that the content of Al, Mn, Sr, Zn in the needles of Scots pine (*Pinus sylvestris* L.) increases with age, *i.e.*, the process of bio-accumulation. Accumulation of heavy metals in pine needles has a definite pattern: Mn, Fe, Zn, Sr, Cu, Cr, Co, which are biogenic trace elements, accumulate in higher amounts than highly toxic elements – Tl, Cd, As. The elemental composition of Scots pine needles is significantly impacted by the place of growth, which is reflected in the intensity of the biogeochemical metal cycle. The results of the primary analysis of pine needles (*Pinus sylvestris* L.) samples allow comparison with similar unique results obtained from primary analysis by other authors. Such a comparison makes it possible to confirm certain patterns in the accumulation of heavy metals and the specificity of their combination for a given area, which reflects the specifics of anthropogenic pressure on the ecosystem. A comparison of the series of heavy metal accumulations in the needles of Scots pine (*Pinus sylvestris* L.) requires further in-depth study. The accumulation of an array of findings from such studies will make it possible to further advance to higher levels of generalisation. This will provide a scientific basis for the management of woodlands through the use of Scots pine as a bioindicator of heavy metals, as their bioaccumulator, which purifies the air, the degree of involvement of heavy metals in the plant phytocoenosis and their neutralisation, and subsequently the degree of toxicity of the wood.

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Credit Authorship Contribution Statement

The authors contributed equally to this work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Alaqouri, H.A.A., Genc, C.O., Aricak, B., Kuzmina, N., Menshikov, S., and Cetin, M. 2020. The possibility of using scots pine needles as biomonitor in determination of heavy metal accumulation. *Environmental Science and Pollution Research* 27: 20273-20280. DOI: https://doi.org/10.1007/s11356-020-08449-1

[2] Ayan, S., Sarsekova, D., Kenesaryuly, G., Yilmaz, E., Gulseven, O., and Sahin, I. 2021. Accumulation of heavy metal pollution caused by traffic in forest trees in the park of Kerey and Janibek khans of the city of Nur-Sultan, Kazakhstan. *Journal of Forensic Sciences* 67. DOI: https://doi.org/10.17221/37/2021-JFS

[3] Baiseitova, N.M. 2014Phytotoxic effect of heavy metals in technogenic environmental pollution. *Young Scientist* 2(61): 382-384.

[4] Belgibaev, M.E. 2009. On the origin of the Irtysh relic pine forest. *Geography in Schools and Universities of Kazakhstan* 2: 2-4.

[5] Cetin *et al.* 2021. Using abies's needles as biomonitors of recent heavy metal accumulation. *Kastamonu University Journal of Engineering and Sciences* 7(1): 1-6. Available at: https://dergipark.org.tr/en/pub/kastamonujes/issue/63105/892118

[6] Cometen, H., Cetin, M., Aricak, B., Sevik, H. and Erdem, R. 2019. The change of some heavy metal concentrations in Scotch pine (Pinus Sylvestris) depending on traffic density, organelle and washing. *Applied Ecology and Environmental Research* 17(3), (Online). DOI: http://dx.doi.org/10.15666/aeer/1703_67236734

[7] Figas, A., Siwik-Ziomek, A., and Kobierski, M. 2021. Heavy metals and sulphur in needles of Pinus sylvestris L. and soil in the forests of city agglomeration. *Forests* 12(10), article number: 1310. DOI:https://doi.org/10.3390/f12101310

[8] Gamrat, R. 2022. The use of scots pine needles for the assessment of pollution in the Baltic towns in Poland. *Applied Ecology and Environmental Research* 20(2): 979-994. DOI:http://doi.org/10.15666/aeer/2002_979994

[9] Hassan, Z., and Aarts M. G. M. 2011. Opportunities and feasibilities for biotechnological improvement of Zn, Cd or Ni tolerance and accumulation in plants. *Environmental and Experimental Botany*, 72(1): 53-63. DOI:https://doi.org/10.1016/j.envexpbot.2010.04.003

[10] ISO 17294-2:2003 "Water Quality. Application of inductively coupled plasma mass spectrometry (ICP-MS). Part 2: Determination of 62 elements". 2003; https://www.iso.org/standard/36127.html

[11] Jonczak J. *et al.* 2021. Bioaccumulation of Potentially Toxic Elements by the Needles of Eleven Pine Species in Low Polluted Area. *Water Air Soil Pollut* 232, 28. DOI: https://doi.org/10.1007/s11270-020-04959-3

[12] Juranovic Cindric, Zeiner M., Starcevic A., and Stingeder G. 2018. Metals in pine needles: characterisation of bio-indicators depending on species. *International Journal of Environmental Science and Technology.* DOI:https://doi.org/10.1007/s13762-018-2096-x

[13] Kozlowski, R., and Strzyz, M. 2021. Heavy metals accumulation in silver fir needles in Swietokrzyski national park. *Chemistry-Didactics-Ecology-Metrology* 26: 65-72. DOI: https://doi.org/10.2478/cdem-2021-0005

[14] Liu, D.H., Wang, M., Zou, J.H., and Jiang, W.S. 2006. Uptake and accumulation of cadmium and some nutrient ions by roots of maize (Zea mays L.). *Pakistan Journal of Botany* 38(3): 701-709. Available at: https://www.researchgate.net/publication/288428720

[15] Parzych, A., Mochnacky, S., Sobisz, Z., Kurhaluk, N. and Pollakova, N. 2017. Accumulation of heavy metals in needles and bark of Pinus species. *Folia Forestalia Polonica* 59(1): 34-44. DOI: https://doi.org/10.1515/ffp-2017-0004

[16] Popovic, V., Seslija Jovanovic, D., Miletic, Z., Milovanovic, J., Lucic, A., Rakonjac, L., and Miljkovic, D. 2022. The evaluation of hazardous element content in the needles of the Norway spruce (*Picea abies* L.) that originated from anthropogenic activities in the vicinity of the native habitats. *Environmental Monitoring and Assessment* 195, article number: 109. DOI: https://doi.org/10.1007/s10661-022-10732-2

[17] Pritzel, J., Falk, W., Reger, B., Uhl, E., Pretzsh H., and Zimmermann, L. 2020. Half a century of Scots pine forest ecosystem monitoring reveals long-term effects of atmospheric deposition and climate change. *Global Change Biology* 26(10): 5796-5815. DOI: https://doi.org/10.1111/gcb.15265

[18] Voronin, V. and Soboleva, S. 2019. The study of the bioindication ability of the pine (Pinus Sylvestris). *Danish Scientific Journal* 1(29): 16-19. Available at: http://www.danish-science.org/wp-content/uploads/2019/11/DSJ_29_1.pdf

[19] Wegiel, A., Bielini, E. and Polowy, K. 2018. Heavy metals accumulation in scots pine stands of different densities growing on not contaminated forest area (north-western Poland). *Austrian Journal of Forest Science* 135(3): 259-281. https://www.researchgate.net/publication/328749160

[20] Zhang, X., Zhang, S., Xu, X., Li, T., Gong, G., Jia, Y., Li, Y. and Deng, L. 2010. Tolerance and accumulation characteristics of cadmium in Amaranthys hybridus L. *Journal of Hazardous Materials* 180: 303-308. DOI:https://doi.org/10.1016/j.jhazmat.2010.04.031

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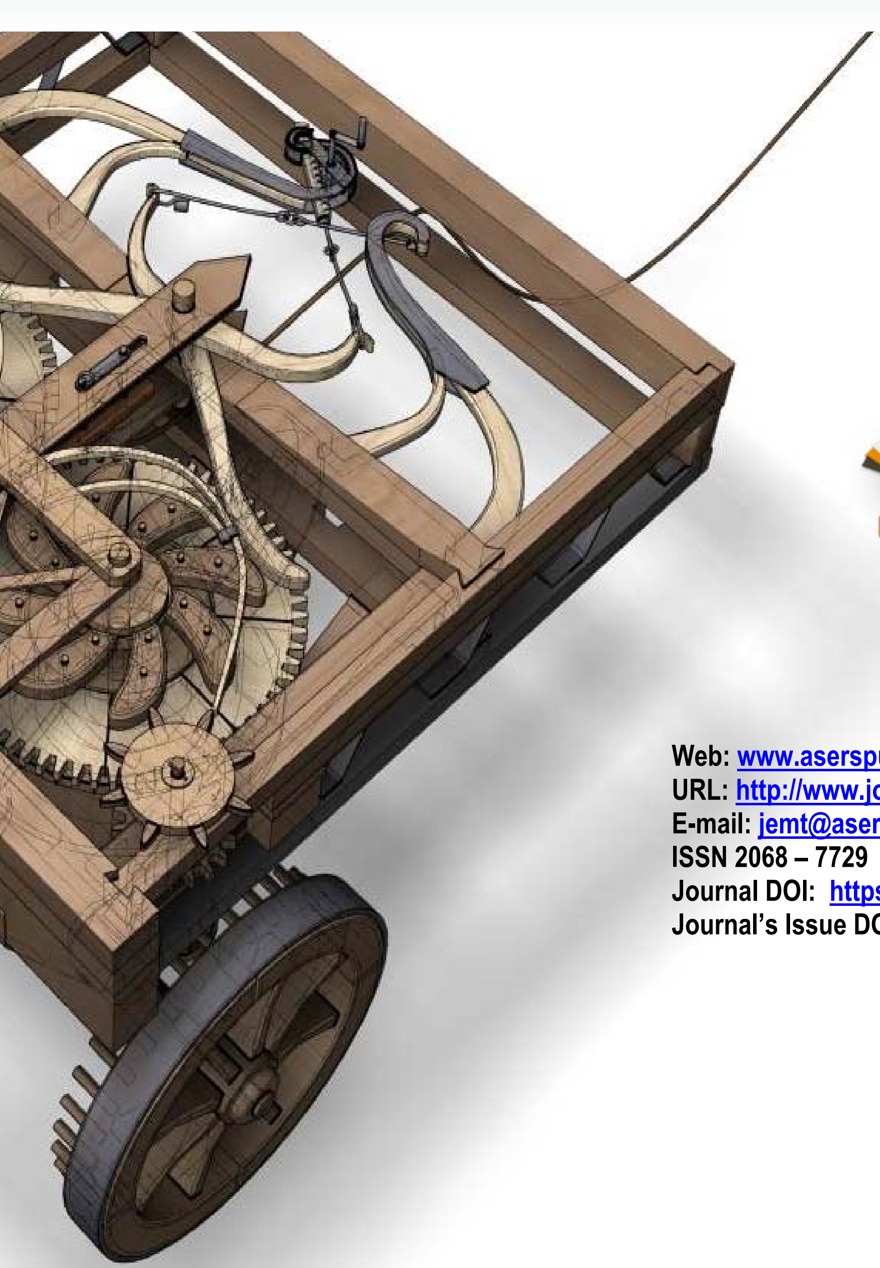

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