

Changes in the Regulating Ecosystem Service on the Contaminated Site Used for Energy Purposes

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Abstract

Soil cleaning, the ability of the soil to immobilize the risk elements, belongs to important agroecosystem services in terms of protection of the hydrosphere and plant production from contamination. Dynamic monitoring of selected indicators of soil quality was realized in a special network of site on soil used for planting fast growing willow (*Salix viminalis*). Monitoring of the study site Kuchyňa (Mollic Fluvisol) is running since 2010 year. The fast-growing willow was planted on an area of about 43 hectares. Study site Kuchyňa belonged to the degraded contaminated sites, at the time of planting (the total contents of the risk elements were as follows: Cd 1.016 mg·kg⁻¹, Zn 199.000 mg·kg⁻¹, Ni 51.500 mg·kg⁻¹) There were positive changes in the total content of cadmium, zinc and nickel (in 2018 year), the zinc content decreased by 27% compared to 2010, the nickel content was lower by 23% and the Cd content by 57% in comparison to 2010 year, these elements have a declining trend during the monitored period. The remediation ability of the willow in relation to the risk elements was manifested by the accumulation of these elements in the wood mass and by their decrease in the soil below the limit value. The regulatory ecosystem service, the potential for the immobilisation of the risk elements, was evaluated based on the sum of the assessment of the contamination potential and the sorption potential of soil. The decrease of the total content of risk elements in the soil below the limit value was manifested in the increase of the potential of the agroecosystem regulatory service, the potential of risk element immobilisation, from very low category to medium category. If willow cultivation continued in the next decade, the value of risk element Zn would most likely reach the value 73 mg·kg⁻¹, which is less than 50% of the limit value, based on the results of the predictive model. In the case of Cd, the soil would be completely cleaned and in the case of Ni, its total content in the soil would fall to 23 mg·kg⁻¹, which is less than 40% of the

limit value. The overall potential for contamination would fall into the category—very low (forecast for 2021 year). The higher potential of immobilisation reduces the risk of contaminants transport and thus prevents contamination of the other ecosystem components such as biota.

Keywords

Soil Cleaning, Willow Crops for Bioenergy, Risk Elements, Soil Quality Indicators

1. Introduction

Agroecosystems, which are key, above all, in ensuring food security, are also of their irreplaceable importance in the energy sector, in particular in the use of agricultural land for growing energy crops [1] [2] [3]. The use of biomass as a renewable energy source can be assessed not only in terms of energy, but also in synergy with other benefits of improved ecosystem services for agroecosystems [4] [5]. One of the most recent climate studies suggests that if the drastic measures will not be taken, especially in the energy sector, to significantly reduce CO₂ emissions by 2035, it will no longer be possible to reverse extreme climate change [6]. The cultivation of energy crops contributes to the reduction of greenhouse gases by carbon sequestration, which has a positive effect on the regulatory ecosystem service—climate regulation. Such cultivation has a positive effect on pollutants filtration and water regime, affects biodiversity and, above all, prevents the abandonment of less productive soils [4] [7] [8]. Ecosystem services are inherently determined by the interaction between ecological and social systems, because only those ecosystem processes that contribute to the fulfilment of human needs are defined as ecosystem services [9]. The fact that soil underlies many ecosystem services also reflects the conflict of their interaction. For example, the provision of supply services is often in conflict with the provision of regulatory or cultural services. High biomass production can often be achieved only at the expense of soil pollution by heavy metals or organic pollutants introduced into the soil by mineral fertilizers or pesticides, which negatively affect the quality of soil and water. Such interactions create increased pressure on the soil, manifested in deteriorating quality, which in turn reduces its ability to provide ecosystem services. According to MEA [10], agroecosystems are often used to the point of carrying capacity (supply services), which leads to a reduction in their multifunctionality and ability (capacity) to provide regulatory and cultural services to society. In the agroecosystem, water regime regulation (water accumulation), soil removal regulation (erosion regulation), climate regulation (soil C stocks) and pollutant filtration (soil purification) are the main regulatory services [11] [12]. Filtration of substances is the natural ability of the ecosystem to retain or immobilize risk elements in the soil profile. The ability of soil to immobilize risk elements is one of the important services of an agroecosystem in terms of pro-

tecting the hydrosphere and plant production from contamination [13]. According to Greiner, L. *et al.* [14] soil properties and soil functions are critical to ensure the provision of regulating ecosystem services. High potential for contamination reduces the potential of soil regulating service because the sorption sites are occupied and thus the free sorption capacity is reduced [15]. The distribution of the filtering potential using spatial mapping units shows that in Slovakia more than 41% of agroecosystems have very high filtering potential (for inorganic pollutants), mostly in the Bratislava, Nitra and Trnava regions. Ecosystems with low potential (more than 41% of agricultural land) are predominantly located on Fluvisols (along Váh River, Hron River and Bodrog River) with a higher content of risk elements in alluvial sediments (caused by anthropogenic deposition). The mountain soils on grassland are also strongly involved in very low category of filtering potential, predominantly in the Banská Bystrica, Žilina and Prešov regions. The greatest differences among regions were found in relation to climatic conditions, land use and the diversity of soil types [16].

Vegetation, soil bacteria and microorganisms also have the ability to accumulate risk elements from the soil and thus reduce their accessible content in the soil, reduce the degree of degradation [17]. Vegetation may be involved in soil cleaning by phytoaccumulation/phytoextraction, phytotransformation and phytostabilisation. Phytoextractors also include some energy crops. Energy crops can be successfully grown on a wide range of agricultural land [18]. Energy crops can be grown in Slovakia on areas less suitable and unsuitable for traditional agricultural activity, on contaminated soil, suitable only for production for non-food purposes and on devastated areas in industrial agglomerations.

The climatic conditions of Slovakia are most suitable for the cultivation of the following species of fast-growing trees: poplars, willows, alders, lindens, hazelnuts, rowanberries, birches, spruce trees [19]. According to the categorization of agricultural soil in Slovakia concerning the suitability of growing crops [20], 38.6% of such soils are for cultivation fast-growing willows and poplars. According to the results of the NPPC/Soil Science and Conservation Research Institute (VUPOP), the total area of soils suitable for growing energy trees and herbs, so called—the other agricultural soil fund is presented by 369,088 ha (source: VUPOP), of which almost 100,000 ha can be used for the establishment of fast-growing stands wood. The stands of fast-growing trees in Slovakia occupied an area of 120.3 ha in 2013 (VUPOP) and 2028 ha from the area of land registered in the Land parcel identification system (LPIS) in 2018. The area of fast-growing trees in the Czech Republic has increased since 2004 from 87.9 ha to 2862 ha in 2017 [21]. Fast-growing woody plants have a short time between planting and harvesting (it ranges between 2 - 5 years), they can produce a significant volume of biomass per year, for example, willows can reach up to 15 tons of dry matter per hectare per year in Slovak climatic conditions, which is excellent fertility [19]. The use of agricultural land for the cultivation of energy crops is also integrated in the processed outlooks and forecasts of further devel-

opment of agriculture and is also part of conceptual, strategic and legislative instruments of the state and the EU [3] [22] [23]. Targeted cultivation of energy crops and woody plants, in accordance with environmental standards, enables the efficient use of, mainly less productive, agricultural land as well as degraded agricultural land (contaminated with inorganic pollutants).

The binding goal of the European Union by 2030 is to achieve a 32% share of energy from renewable sources (RES) in gross final energy consumption. In 2004 this share was only 8.5%, in 2017 the share of RES in the whole European Union reached the level of 17.5% and in 2018 according to the Eurostat report it reached 18%, while the highest shares of RES are maintained by the Nordic and Baltic countries [24] [25]. From the central point of view of Slovak agriculture, biomass must be considered as an important stool of increasing the competitiveness of agricultural products, synergistically addressing important areas of the national economy, such as reducing unemployment, rural revitalization, sustainable development or improving the quality of the environment [26] [27]. Targeted cultivation of energy crops and woody plants, in accordance with environmental standards, enables efficient use of mainly less productive agricultural land as well as degraded agricultural land (contaminated with inorganic pollutants). Changes in ecosystem conditions caused by land use change (such as energy crops) may affect the ability of an ecosystem to provide services of sufficient quality and quantity [28]. The aim of this paper is to evaluate changes in soil conditions indicators and changes in one of the regulatory ecosystem service—the potential for immobilisation of risk elements at a contaminated site used for growing energy crops.

2. Material and Methods

2.1. Study Area

The study site is located in the area of Záhorská nížina (Záhorská Lowland). Soil type is Mollic Fluvisol, on non-carbonate substrates, contaminated and this site belongs according to the Methodical Guideline of the Ministry of Agriculture and Rural Development of the Slovak Republic No. 3187/2007-430 to the soils suitable for cultivation fast-growing trees (**Figure 1**).

On an area of approximately 43 ha, since 2006 there has been a stand of fast-growing willow (*Salix viminalis*) cultivated for energy purpose. Only in the first year of planting was the organomineral liquid fertilizer Darina applied. In the autumn of 2012, the growth of fast-growing willow was pruned. In 2018, the site was abandoned, and the entire area of the fast-growing willow tree had already dried up (**Figure 2**). We monitored this area from the year 2010 to 2018.

The monitoring site is circular in shape with a radius of 10 m and a total area of 314 m² in accordance with the soil monitoring system in the Slovak Republic [27] in the middle it is characterized by a pedological probe. Soil samples were taken from 5 places from the depth of 0 - 10 cm and 35 - 45 cm in the way of not to mix two different soil horizons.

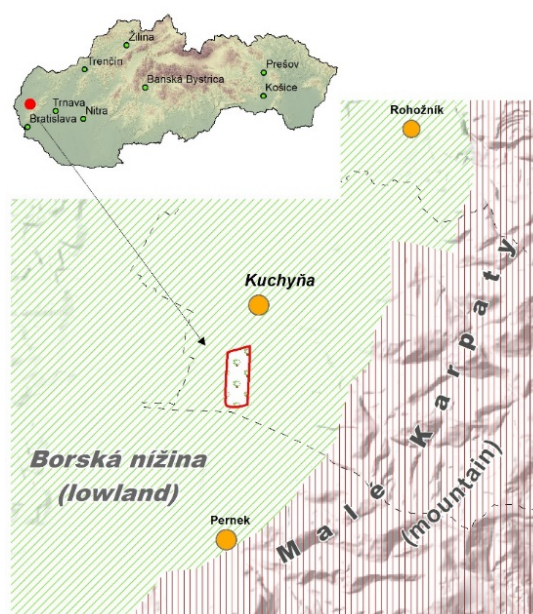


Figure 1. Study site Kuchyňa—localization.

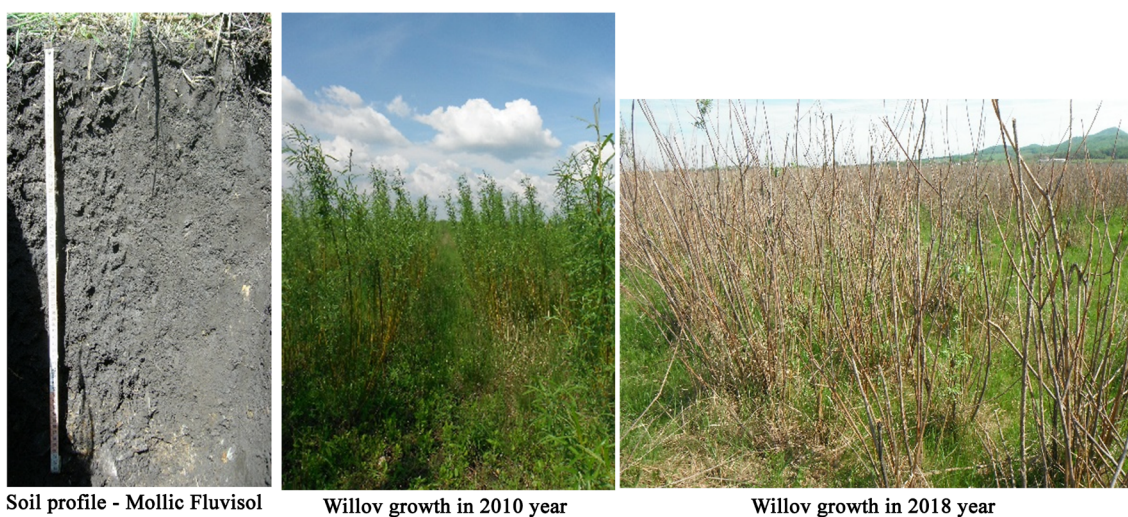


Figure 2. Study site—Kuchyňa (soil profile, willow growth in 2010 and 2018 year).

In addition to taking soil and plants samples for chemical analysis, we also took cylinders with a volume of 100 cm³ for soil physical analyses, 2 cylinders from a depth of 0 - 10 cm and 2 from a depth of 30 - 35 cm. In soil and plants samples, individual parameters (pH value, soil organic matter content, organic matter quality indicator Q_o^4 , macronutrients P, K, Mg, total content of risk elements in soil and plants) were determined according to our official laboratory methodology [29]. Methodical and analytical procedures in more details have been realized according to the work Uniform analytical procedures for soil [29]. These soil indicators are included in the soil monitoring system in Slovakia according to the recommendation of the European Commission (EC) for comprehensive soil monitoring system in Europe [30].

2.2. Methods of Regulating Agroecosystem Service Assessment—Cleaning Potential of Agricultural Land Ecosystem

The assessment method of regulating agroecosystem service—cleaning potential of agricultural land, based on natural environment parameters and land use factors is described in detail in the study by Makovníková *et al.* [16]. Cleaning potential (immobilisation of risk elements) of agricultural land was calculated as accumulative function of sum of soil sorption potential and potential of total content of inorganic contaminants evaluated according to the Act No. 220/2004 Coll. (the method is mentioned in detail in our previous article [26]. Rating evaluation of Soil sorption potential was calculated as a sum of quality factors: pH (0 - 4 points), Q_6^4 (0 - 1 points) and quantity factors: Cox (0 - 1 points), H-depth of humus horizon (0 - 2 points)) according to the equation: $PS = (pH) + (Q_6^4) + (Cox) * (H)$. A lower point value characterizes better sorption potential on the basis of better soil conditions. Potential of total content of inorganic contaminants was evaluated by the high point value and present high risk (0 - 5 points). The high Soil sorption potential (characterized by low point value) decreases the possible transport risk of harmful elements in soil. Cleaning potential of agricultural land was categorised into five groups as follows: 1—very low potential (more than 6.50 points), 2—low potential (5.51 - 6.50), 3—medium potential (4.51 - 5.50 points), 4—high potential (3.50 - 4.50 points), 5—very high potential (lower than 3.50 points). All soil indicators are part of the monitoring of soils in Slovakia [27] according to the recommendation of European Commission (EC) for comprehensive soil monitoring system in Europe [30].

2.3. Data Sources

Data sources of soil monitoring of Slovakia were used for the assessment of changes in soil conditions indicators and changes in one of the regulatory ecosystem service—the potential for immobilisation of risk elements.

3. Results and Discussion

Study site Kuchyňa is located in a warm climate area. The contaminated Mollic Fluvisol, which is in this locality, belongs to medium-heavy clay soil. The bulk density of the soil during the observed period ranged from 1.44 to 1.57 g·cm⁻³ at a depth of 0 - 10 cm and from 1.60 to 1.65 g·cm⁻³ at a depth of 35 - 45 cm. The skeletal content in the soil increases significantly with depth, from 5% at a depth of 0 - 10 cm to 60% at a depth of 35 - 45 cm. Study site Kuchyňa belongs to the weakly acidic to acidic soils, the value of the soil reaction only increases slightly with depth but also belongs to the weakly acidic area in the soil profile. Higher content of lower quality organic matter in the whole profile together with the value of soil reaction and medium content of accessible nutrients classifies this locality as moderately resistant to acidification [15].

In 2010, we assessed the total content of inorganic pollutants at a given locality in accordance with the Decree 59/2013 of the Ministry of Agriculture and Ru-

ral Development of the Slovak Republic, which amends the Soil Act 220/2004 Coll. Cadmium is not an essential element and is toxic when the metal- and organism-specific concentration is exceeded. The Cd content was highest at the depth 0 - 10 cm and decreased towards the substrate, but significantly exceeded the limit value at a depth of 0 - 10 cm and 35 - 45 cm (Cd limit value is $0.4 \text{ mg}\cdot\text{kg}^{-1}$). We observed the similar trend in the case of Ni and Zn (Ni limit value is $40.0 \text{ mg}\cdot\text{kg}^{-1}$ and Zn limit value is $100.0 \text{ mg}\cdot\text{kg}^{-1}$), which significantly exceeded the above-limit values in the whole profile. For some animals, nickel and zinc are important trace elements but only at very low concentrations they have a physiological effect. We monitored above-limit risk elements in the period 2010 to 2018 (**Table 1**).

At the depth of 0 - 10 cm as well as at the depth of 35 - 45 cm (**Table 1**) there was a slight decrease in the value of the active soil reaction in comparison between 2010 and 2018 (**Figure 3**). We did not observe a decrease in the content of organic matter in the soil at the depth of 0 - 10 cm, which McClean G. [31] reports in his work, on the contrary, when the fast-growing willow stand dried up, there was a very slight increase of soil organic carbon.

According to Anderson, the accumulation of carbon in the soil under energy crops is the same as under permanent grasses [32]. Estimates of carbon sequestered under energy crops range from 0.6 to $3.0 \text{ t}\cdot\text{ha}^{-1}\cdot\text{year}^{-1} \text{ C}$ [33].

According to Palomo-Campesino *et al.* [34], agroecosystems reflects interactions between society and nature, however, inappropriate management can have negative consequences for the agrosystem. The content of available phosphorus in the soil changed more significantly. We recorded a decrease of up to 53% at the depth of 0 - 10 cm and by 12% at the depth of 35 - 45 cm in 2017, when the willow coppice has already been partially dried. In 2018, the phosphorus content increased (it was not depleted by willow stands) and its decrease compared to 2010 was only 14% (**Figure 4**). The declining trend of available phosphorus in

Table 1. Soil quality indicators at Kuchyňa study site (state in 2010 and 2018).

Soil quality indicator		Depth 0 - 10 cm		Depth 35 - 45 cm	
		rok 2010	rok 2018	rok 2010	rok 2018
pH in H ₂ O		5.81	5.58	5.80	5.52
pH in KCl		5.21	4.91	5.21	5.05
pH in CaCl ₂		5.23	5.10	5.31	5.20
Cox in %		2.250	2.35	1.958	2.09
Q _o ⁴ (organic matter quality indicator)		4.09	4.15	3.91	4.18
Macronutrients in $\text{mg}\cdot\text{kg}^{-1}$ (Mehlich III.)	P	73.70	63.04	43.50	47.880
	K	163.00	155.80	106.00	129.30
	Mg	92.70	105.08	119.00	117.34
Total content of risk elements in soil in $\text{mg}\cdot\text{kg}^{-1}$ (in aqua regia)	Cd	1.016	0.443	0.822	0.340
	Zn	199.000	146.000	287.000	157.000
	Ni	51.500	39.600	69.600	44.400

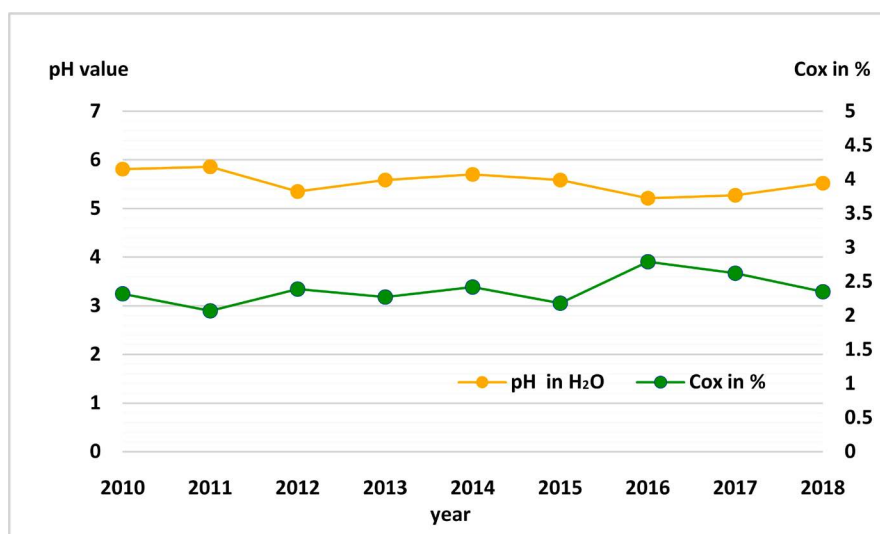


Figure 3. Changes in pH value (in H₂O) and Cox (in the depth 0 - 10 cm).

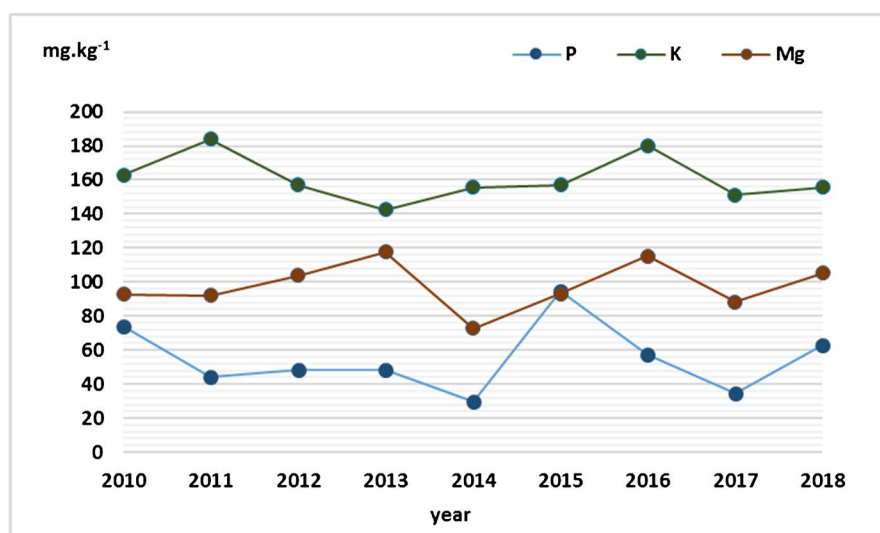


Figure 4. Changes in P, K, Mg content (in the depth 0 - 10 cm).

the use of agricultural land for the cultivation of energy crops is mentioned in the work of Šoltýsová and Danilovič [35]. When growing energy crops, there is no annual cultivation and it is uncultivated land. Therefore, in the cultivation of energy crops there is no mineralization, but there is the incorporation of phosphorus into the organic matter of the soil, which results in the fact that even with a positive balance of phosphorus, the content of its mineral component decreased. By cultivation of soil, the content of available phosphorus increases and the content of total phosphorus decreases due to the intensive mineralization of organic compounds [36]. The content of available potassium in the soil depends on the uptake of potassium by cultivated energy crops. The content of available potassium in the depth of 0 - 10 was lower in 2018 compared to 2010, while the content of magnesium increased, by 1.13%.

There were positive changes in the total content of cadmium, zinc and nickel,

the zinc content decreased by 27% compared to 2010, the nickel content was lower by 23% (**Figure 5**) and the Cd content by 57% (**Figure 6**) in comparison to 2010 year, these elements have a declining trend during the monitored period.

Willow belongs to the potentially resistant crops due to the high content of risk elements and at the same time belongs to the recordable phytoextractors used in the process of natural phytoremediation/phytoextraction [37]. Volk *et al* [14] mention in their work the bioremediation effects of willow. The Cd content in the wood mass during the monitoring ranged from 2.73 to 9.52 mg·kg⁻¹, the Zn content from 160.00 to 432.00 mg·kg⁻¹. The average value of the bioaccumulation factor of Cd (ratio of total Cd content in the plant to total Cd content in the soil) was in the observed period 9.36 (minimum 7.05 in 2010 and maximum 15.01 in the year 2015). The bioaccumulation factor of Zn was significantly lower, with an average value of 1.54 (minimum 0.41 in 2013 and maximum 2.63 in

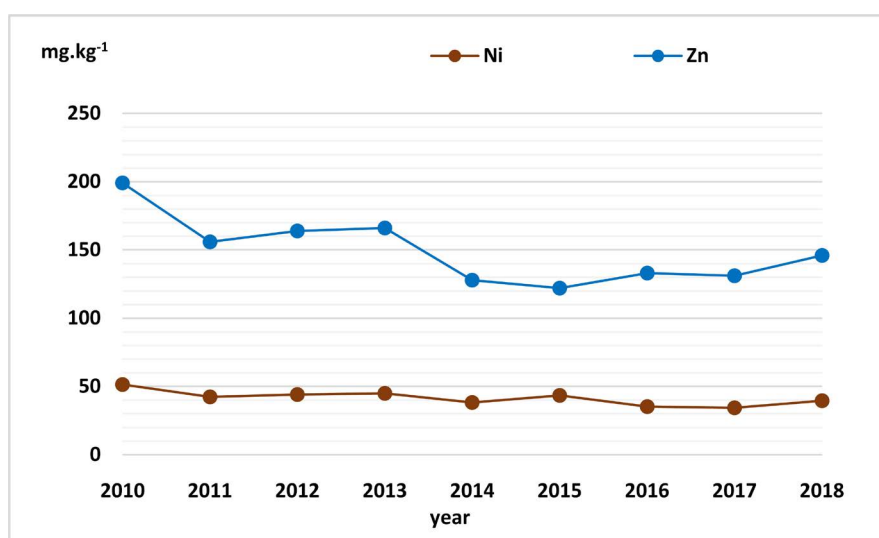


Figure 5. Changes in the total content of zinc and nickel (in the depth 0 - 10 cm).

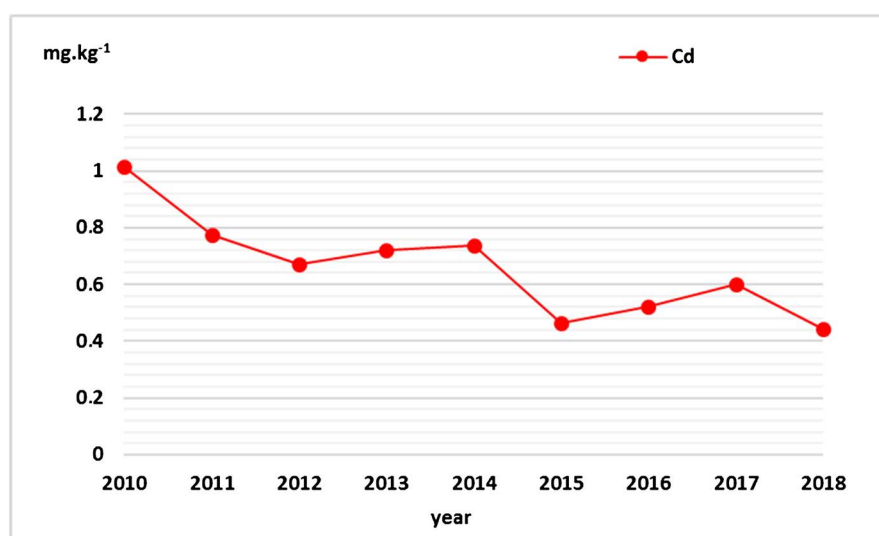


Figure 6. Changes in the total content of cadmium (in the depth 0 - 10 cm).

2012). Willow does not belong to the hyperaccumulators for Cd and Zn, but the bioremediation effect is increased by the high value of the annual increase of biomass. *Thlaspi caerulescens* is one of the best hyperaccumulators for combined contamination [38].

The total content of cadmium, nickel and zinc in the soil was below the limit value in 2018 (according to the Decree 59/2013 of the Ministry of Agriculture and Rural Development of the Slovak Republic, which amends the Soil Act 220/2004 Coll.).

We used the time series of data (content of risk elements) as input data to forecast models (Random walk method, Figures 7-9).

Table 2 summarizes the results of five tests running on the residuals to determine whether each model is adequate for the data. An OK means that the model passes test, these models are adequate for the data and can be used for prediction of total content of Zn, Cd and Ni.

If willow cultivation continued in the next decade, the value of risk element Zn would most likely reach the value $73 \text{ mg}\cdot\text{kg}^{-1}$, which is less than 50% of the limit value, based on the results of the predictive model (Figure 7, Table 2). In

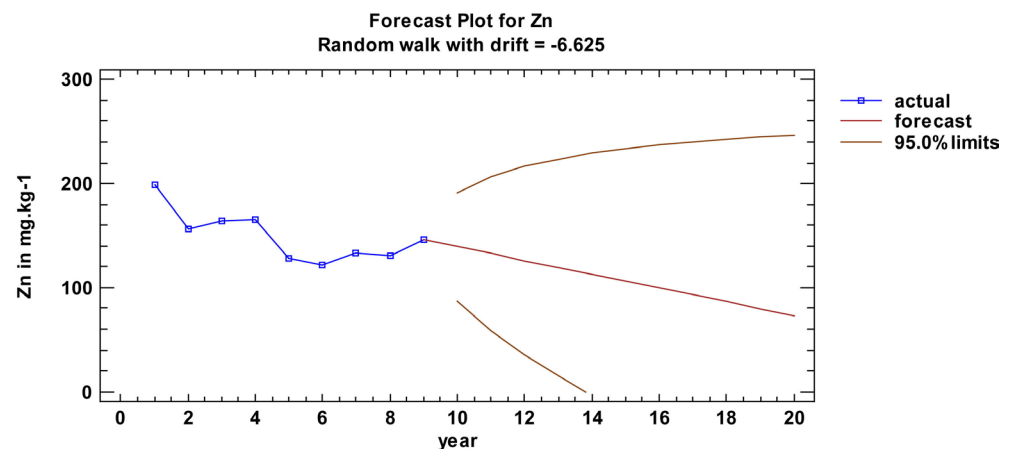


Figure 7. Forecasting Zn (Random walk method).

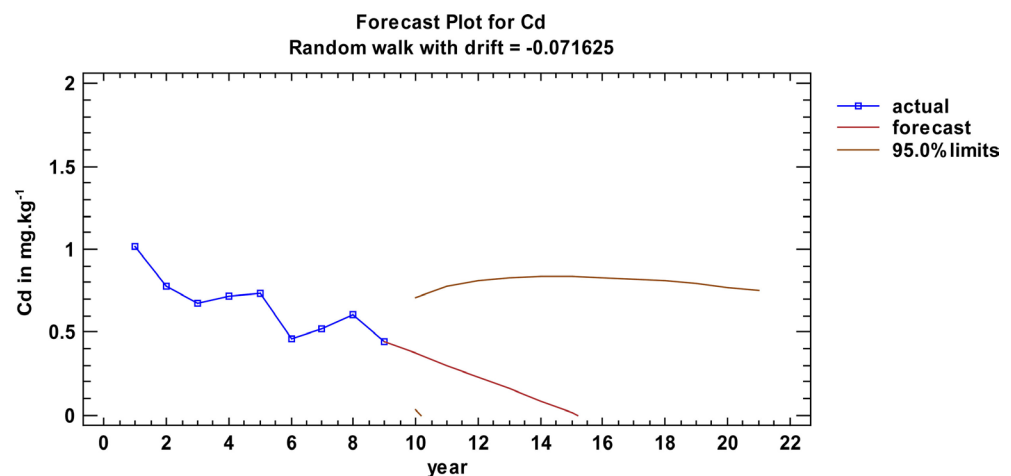


Figure 8. Forecasting Cd (Random walk method).

the case of Cd, the soil would be completely cleaned (**Figure 8**) and in the case of Ni (**Figure 9**), its total content in the soil would fall to 23 mg.kg⁻¹, which is less than 40% of the limit value. The overall potential for contamination would fall into the category—very low (forecast for 2021 year).

The monitored parameters are among the basic indicators in assessing the potential of one of the regulatory ecosystem service—the immobilization of risk elements. The potential of this regulatory agroecosystem service was assessed based on the sum of the rating assessment of the contamination potential and the sorption potential of soil [8] [25]. Positive changes in the value of the potential for immobilisation of risk elements between years 2010 and 2018 are shown in **Table 3**.

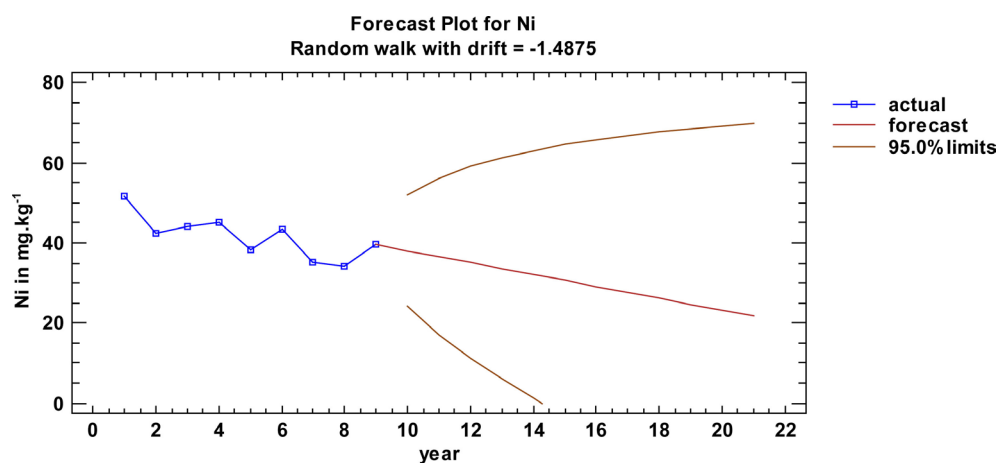


Figure 9. Forecasting Ni (Random walk method).

Table 2. Estimation period for random walk model.

Model	RMSE	RUNS	RUNM	AUTO	MEAN	VAR
Zn	22.0715	OK	OK	OK	OK	OK
Cd	0.142383	OK	OK	OK	OK	OK
Ni	5.85761	OK	OK	OK	OK	OK

RMSE = Root Mean Squared Error, RUNS = Test for excessive runs up and down, RUNM = Test for excessive runs above and below median. AUTO = Box-Pierce test for excessive autocorrelation, MEAN = Test for difference in mean 1st half to 2nd half, VAR = Test for difference in variance 1st half to 2nd half, OK = not significant ($p \geq 0.05$).

Table 3. Changes in the value of the potential for immobilisation of risk elements.

Potential	2010 year		2018 year	
	The rating assessment	Category	The rating assessment	Category
Risk contamination potential	5.0	Very high	1.0	Low
Soil sorption potential	4.50	Low	4.50	Low
Regulating ecosystem services—Potential for immobilisation of risk elements	9.50	Very low	5.50	Medium

The decrease of the total content of risk elements in the soil below the limit value according to the Decree 59/2013 of the Ministry of Agriculture and Rural Development of the Slovak Republic, which amends the Soil Act 220/2004 Coll., increased the potential of the regulatory service from very low category to medium category. Changes in the category of soil sorption potential have been not determined.

4. Conclusions

The connection of the energy sector with the economic structure of the regions is a topic of discussion due to the climate change. The scientific community is drawing attention to the need to change the energy base as soon as possible, as there is a risk of crossing the tipping point when humanity will not be able to influence climate change. One of the most recent climate studies suggests that unless drastic measures are taken, especially in the energy sector, to significantly reduce CO₂ emissions by 2035, it will no longer be possible to reverse extreme climate change [6].

The primary goal of the sustainable development combined with the efficient use of natural resources is to ensure that the use of natural resources and the associated impact on the environment, including soil quality, does not exceed the carrying capacity. During the monitoring of agricultural land used for growing energy crops, we observed a negative trend in the content of available nutrients (phosphorus and potassium) and a positive trend in the development of the total content of risk elements in the soil. The phytoremediation ability of willow with respect to the risk elements was manifested by an increase in the potential of the regulatory agroecosystem service, the potential of immobilization of risk elements, in the monitored locality

Appropriate selection of agricultural practices can result in a positive impact on ecosystem services. Agroecosystem management should always take into account the maintenance of soil multifunctionality and thus the maintenance of the agroecosystem's potential to provide ecosystem services in full. Biomass extraction for energy purposes can affect agricultural land in qualitative terms. When cultivating fast-growing woody plants, significant changes in soil properties can occur, due to the influence of growing woody plants on the nutrient potential, on the water regime of the soil. A large mass of the root system is formed underground, soil physical properties can change and soil compaction can occur. Inadequate management (non-compliance with cultivation instructions) can lead to the soil degradation and reduction of total organic matter content in the soil [28], reduction of soil nutrient potential and thus a change in soil quality. At the establishment of stands in contaminated localities, a positive trend can be observed in the reduction of the content of hazardous substances, when the phytoremediation ability of willow is manifested by the accumulation of these substances in wood mass. The allocation of agricultural land for the purpose of growing non-agricultural crops should therefore be conditional on the elaboration

tion and implementation of a project for their reclamation.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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