

# Analysis of Phytoremediation Potential of Crop Plants in Industrial Heavy Metal Contaminated Soil in the Upper Mures River Basin

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Received 23 September 2014; revised 20 October 2016; accepted 3 December 2016; published online 15 February 2018

**ABSTRACT.** Phytoremediation represents an efficient ecological solution for treating the polluted soils through the use of plants. This is a passive process, with low costs, appropriate for the limitation of the risk of hazardous wastes in the case of in-depth contaminated soil. This paper presents a research with a novel result on soil remediation through phytoremediation in the upper Mures river basin, situated in the east-central Romania. The research focuses on the experiments performed using the following three crops: spring wheat, spring rape and soybean for the phytoremediation of polluted soil by the following combination of heavy metals: As, Cd, Cr, Cu, Pb, Zn and Ni. The main objective was to determine the ability of the studied crop plants cultures in the climate region of Mures County to reduce the heavy metals concentration in soils contaminated by industrial activities. The proposed phytoremediation solution enables efficient remediation of soils polluted by the activities of chemical platforms located in the upper Mures river basin, giving to the treated soil the potential of natural preservation of its physical, chemical and biological properties. The obtained research results show that the phytoremediation potential of the heavy metals, except the nickel, for the three plants, is similar (it is not statistically different) in the neighbourhood regions of the two studied chemical platforms. The choice of one of the three plants for phytoremediation should be made based on other considerations than the phytoremediation potential, like the financial investment, etc.

**Keywords:** anthropic risk, environmental management, environmental statistics, industrial pollution, outlier detection, phytoremediation, relational database

## 1. Introduction

In recent years, types of research were made related to air, water and different types of soil pollution identification and solving, using different techniques (Forsythe et al., 2010; Wang et al., 2014). The main motivation consists in the fact that these are major global problems that should be identified as soon as possible and solved efficiently.

Soil pollution has constituted an increasingly important environmental problem in many regions from Romania in particular, and in the world in general. This fact can be seen especially in industrial areas where different wastes deposited on the soil can contain significant concentrations of metals, but also significant amounts of synthetic organic products (Apostol and Marculescu, 2006; Chira et al., 2014).

There are several methods for the remediation of contaminated soil which are described in Micle and Neag (2009), and Volf (2007). We will refer only to phytoremediation, which

represented the objective of this study.

Raskin et al. (1997) outline that phytoremediation is an innovative and cost-effective method, which uses plants whose properties allow them to concentrate, to degrade or to transform pollutants. Compared to other methods such as extraction under vacuum of the pollutants, bioventing and bioslurping, in situ biodegradation, etc., phytoremediation does not involve the use of equipment and installations to be installed at the place of decontamination, which would require increased investments. The remediation time may be shorter than the phytoremediation, but such methods do not have an increased accessibility.

An important reason for choosing the phytoremediation method is the fact that local farmers can apply it, in order to avoid leaving the land fallow and furthermore, the plants may be used in biofuel production, considered as waste or incinerated.

In this paper, the results of a novel research on soil remediation are presented, by using phytoremediation in the upper Mures river basin located in the east-central Romania. The region where the research was fulfilled has a temperate continental climate. The winters are relatively cold; the summers are warm and dry.

Experiments were carried out using the following three

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crop plants: spring wheat (*Triticumaestivum*), spring rape (*Brassica napus ssp. oleifera*) and soybean (*Glycine hispida*) for the phytoremediation of soils polluted by the following combination of heavy metals: As, Cd, Cr, Cu, Pb, Zn, and Ni. These plants were never used for phytoremediation in this climatic region of the world for soils polluted with this combination of heavy metals.

Years before this research, other researches and studies were performed, related to: contaminated potable water (Morar, 2014); rape, like: oil production from rape (Chirila and Morar, 2007), ecological function of the rape (Morar, 2008); biofuel obtained from rape (Morar and Peterlicean, 2014), etc. Alongside with other studies that were undertaken for this climate region, observations on the behaviour of these plants and discussions with experienced farmers from the region were carried out.

The objective of the research was to determine the ability of the studied crop plant cultures in the climate region of Mures County to reduce the heavy metals concentration in soils contaminated by industrial activities. The study focuses on areas under the influence of two industrial chemical platforms, which represent major pollutants in Mures County.

The obtained results prove that the studied plants offer an efficient remediation of soils polluted by the activities of chemical platforms located in the upper Mures river basin. Treated soil naturally preserves its physical, chemical and biological properties.

The rest of the paper is organized as follows: Section 2 presents advances on phytoremediation of soil polluted by heavy metals. The research is presented in Section 3, treating aspects such as: 3.1 presents the applied materials and methods, in 3.2 the observations during the experimental research are treated; Section 3.3 presents the performed statistical analysis, Section 3.4 contains discussions related to the fulfilled research, in 3.5 future research directions are presented, which will be based on current results. Section 4 presents the conclusions of the research.

## 2. Advances on Phytoremediation of Heavy Metal Polluted Soil by Industrial Activities

Phytoremediation consists in the treatment of soil pollution problems through the use of plants. Such solutions eliminate the need to excavate the contaminant material that should be disposed elsewhere.

Plants are used in phytoremediation to degrade pollutants “in vivo”, or within the limits of the penetration of the root system, pollutants being accumulated by the plant roots or leaves (Raskin et al., 1997; Fuentes et al., 2004). In this case, the remediation process consists in growing plants on the polluted lands and in consequently removing pollutants by plant harvesting.

Phytoremediation allows for in-situ soil remediation without disturbing the environment. On the other hand, the treated soil naturally preserves its natural physical, chemical and biological properties (Micle and Neag, 2009).

The presence of heavy metals such as arsenic, cadmium, copper, nickel, lead, and zinc, is of particular concern, due to their toxicity at low concentration. The effects of heavy metals on the microbiological processes from soil were observed in the early years of the last century (Giller et al., 1998; An, 2004), but it was only in the 1960s ~ 1970s when researchers discovered that some soil microorganisms might be affected and some microbiological processes could be interrupted, causing serious disturbances in the ecosystem (Nwachukwu and Pulford, 2009).

Ebbs and Kochian (1997) prove that a concentration above the normal value of the heavy metals in the soil, such as the zinc, affects the growth and development of plants. Therefore, the remediation of the contaminated areas is highly required, especially by using procedures which are likely to restore some properties of these soils.

Cadmium is a very toxic widespread pollutant for micro and macro-organisms from the soil. It has a negative effect on roots and limits the growth of the plants (it affects homeostasis and nutrient up-take). In the remediation of Cd polluted soils, the Indian mustard (*Sinapisalba*) and Chuanyou II-10, a type of canola obtained in China, are often used. Wang et al. (2003) proves that Chuanyou II-10-presents a good potential for the absorption and accumulation of cadmium from the soil. Chuanyou II has even higher hyper-accumulating ability than Indian mustard.

The application of some substances for increasing the plant extractability of heavy metals from the soil is a promising research direction. In the paper (Quartacci et al., 2006) the effects of citric acid and nitrilotriacetate applications on metal extractability from a multiple heavy metal contaminated (Cd, Cr, Cu, Pb and Zn) sandy soil are studied. The considered plant for the study of accumulation was the Indian mustard (*Brassica juncea*). Desorption of metals from the soil increased with chelate concentration. Control pots were not treated with any chelate. The results prove that nitrilotriacetate is more effective than citric acid.

However, the shortcoming that arises in the case of the phytoremediation methods is the next step: further use of the resulted plants.

The harvested plants can be used to recover the pollutants by using adequate technologies; it is worth mentioning that the high costs of these solutions must be taken into account. Alternatively, when it is possible, plants can be destroyed, therefore destroying the accumulated pollutants.

In a previous research (Morar, 2014), the negative effect of the heavy metals on the environment was studied, for example through the contaminated potable water, like the uptake via the food chain. Heavy metals are dangerous because they tend to bioaccumulate. Compounds accumulate in living organisms when they are assimilated and stored with a higher speed than when they are destroyed or removed.

A research in order to examine the hydrological factor affecting the situation and transport of the pollutants in soils is presented in the paper (Tallon and Si, 2004). Tallon and Si (2004) proved that there is a spatial variability in field soil wa-

ter. The main purpose of the research was to examine whether there are temporally stable soil moisture patterns in a field.

An important research direction consists in the evaluation of pollutants propagations in water, particularly in rivers using statistical approaches (Ping et al., 2010). A case study was conducted in two urban rivers in eastern Canada. The aim of the presented research was to support water management decisions and practices.

On the same topic of water management can be considered the studies regarding the proliferation of some bacteria, that could be dangerous to human health, but also some of the species can be used as a biosorption solution. Urquhart et al. (2015) present an important study related to human infections caused by *Vibrio* spp. The study was realized for Virginia and Maryland waters of Chesapeake Bay. The authors propose a novel algorithm for predicting the probability of *Vibrio parahaemolyticus* and *Vibrio vulnificus* likelihood and abundance. For the purpose of operational potential in the Chesapeake Bay, the authors developed a novel two-step classification hybrid approach. This was used to generate estimates of abundance in the absence of bacteriological data on presence of *Vibrio* spp. In the presented study, the risk of human infection as a function of *Vibrio* spp. was considered.

Another aspect related to the water and soil pollution concerns the sludges obtained from different industrial activities. An important usage of the sludges consists in the soil fertilization. However, it is necessary to determine the concentration of different pollutants from the sludges obtained as a result of different technological processes and at the wastewater treatment. Fuentes et al. (2004) analyse the heavy metals that are presented in sludges produced in wastewater treatment. This study presents a comparative study of different types of sludges related to the distribution of some heavy metals (Cd, Cr, Cu, Ca, K, Fe, Mg, Ni, Na, Pb, and Zn) that they contain. The distribution of heavy metals is according to the treatment that they have to undergo. The analysed sewage sludges were subjected to phytotoxicity testing. The conclusion of the research was that the stabilisation treatment undergone by the sludges influenced the heavy metal distribution. The sludge extracts did not exert any significant adverse effect on the relative seed germination of cress (*Lepidium sativum*) and barley (*Hordeum vulgare*).

Akram et al., (2016) present a study on management practices in controlling sediment loss to different surface water bodies. The authors consider the grass strips as an effective management practice in controlling sediment loss. They have formulated the research problem to predict the amount of sediment retention in grass strips. For the prediction of the efficiency of grass strips in trapping sediments, a nonparametric supervised learning statistical model was proposed. From the model outputs, it was concluded that very long strips are needed in severe conditions such as wet soil and steep slopes in order to trap sediments effectively.

The research presented above is relevant due to the fact that in Mures county, in some towns like Ludus for example,

there are farmers that use on their land sludges produced in wastewater treatment. When the sludges do not contain pollutants that could affect the soil or the plant culture medium, the usage with the purpose of fertilization, for the soil-PH correction, and as a soil remediation, is welcomed.

Some researches are focused on finding plants that can be cultivated by farmers in polluted soil with different heavy metals based on the fact that they absorb the heavy metals in very small (admitted) amounts. In the paper (Pavel et al., 2010) a sterile hybrid plant between *Miscanthussinensis* and *Miscanthussacchariflorus* called *Miscanthussinensis* "giganteus" is experimented. The plant was cultivated on a land polluted with the following two heavy metals: Pb and Cd. The tests were performed for the use of the stems cropped after two years in obtaining biodiesel. The conclusions of the research where that *Miscanthussinensis* can be successfully cultivated, even on soils heavily polluted with Pb and Cd. The amount of Pb and Cd in the upper parts of the plants is very small, this allowing its unrestricted use.

In order to apply the phytoremediation method, several crops may be used, such as: maize (*Zea mays*), rape (*Brassica napus ssp. oleifera*), wheat (*Triticumaestivum*), cucumber (*Cucumissativum*), etc., plants which are able to reduce soil ecotoxicity for certain metals (Qing et al., 2003; Oros, 2012; Park et al., 2012).

The results obtained by the previously mentioned authors are relevant to the studied area soils, but the absorption capacity of heavy metals may vary depending on the geographic area and the specific combination and concentration of the heavy metals.

Fuentes et al. (2004) demonstrated that the presence of the metals in the biological material is manifested differently, depending on the origin of the soil sample and therefore on its characteristics, but also depending on the plant capacity to accumulate metals taken up from the soil solution.

### 3. The Performed Research on Polluted Soil Phytoremediation

#### 3.1. Materials and Methods

The areas from which soil samples were taken for this study are part of Mures County, a district that includes a number of areas where environmental quality indicators are exceeded systematically compared to standardized norms, affecting: air, surface waters and groundwater, soil. Damages caused by environmental factors have negative consequences (sometimes serious) on human health, economy and natural capital.

The main stationary sources of pollution are identified in the current and former industrial units located in Tirgu Mures and Tirnaveni settlements assigned to S.C. Azomures S.A. Tirgu Mures and former chemical plant Tirnaveni which was subsequently divided in 1990 into S.C. CarbidFox S.A. Tirnaveni and S.C. Bicapa S.A. Tirnaveni respectively.

In Tirgu Mures area, a significant negative impact on the atmosphere is related to the emission of ammonia, nitrogen

oxides and dust. The monitoring records of the pollutants emissions from the atmosphere, not infrequently, show the exceeding of the permitted values in the impact zone of the chemical fertilizer activity.

In Tirnaveni area, a significant source of contamination is linked to S.C. Bicapa S.A. Tirnaveni, a company with the specific activity on the chromium based products that ceased its main operations half a decade ago, but rather high remnant pollution persists due to the waste landfills (B1, B2 and B3 sludge pits) located along the Tirnava Mica River, which continues to pollute in a certain degree through groundwater.

As there has not been established an agreement on the choice of decontamination pathway in these areas (with the mention that S.C. Azomures S.A. Tirgu-Mures carries out re-technologization activities and has also started greening activities of the waste landfill) and taking into account the agricultural activity taking place in the area, it is appropriate to conduct a study on the possibility of depolluting, in time, the land in the area by phytoremediation.

In the frame of a project entitled "Updating the Arrangement Plan of the Mures County Territory" (Benedek, 2012), a documented characterization of the soil samples type in Mures County was realized. The studied soil types in our research are based on the official report (Benedek, 2012) and the Mures County Development Programme (DPMC) which are described in accordance with the first edition of Romanian Soil Taxonomy System - SRTS 2003 (Blaga et al., 2005) as:

- In Tirgu-Mures, Azomures-Cristesti area, brown illuviated clay luvisols are prevalent (Luvisol inclass soils) and podzolic soil (Podzol).
- In Tirnaveni area, the presence of the neighbour Tarnava Mica River influences the relief and in the same time the soil; however, there are present eubazic brown soils (Dystric Cambisols class), brown acid, brown podzolic, prevailing soils from Dystric Cambisols and podzolit classes. The phreatic level is near to the surface, mostly in the neighbour region of the Bicapa plant, manifested in sliding processes, but also as sloughing. All these influence the presence/migration of the elements from soil and subsoil.

Azomures S.A. is one of the leading fertilizer producers in Romania. The company produces ammonium nitrate  $\text{-NH}_4\text{NO}_3$ , ammonium nitrate  $\text{N:CaCO}_3\text{-27:20}$ , urea  $\text{CO(NH}_2)_2$ , complex fertilizer (N:P:K), melamine.

In the impact area of Azomures, in its immediate vicinity respectively, there are not listed protected species or habitats, or sensitive areas. One must note that the residents cultivate vegetable species, as well as maize (*Zea mays*), sugar beet (*Beta vulgaris*), etc, plants that generally have a developed vegetative mass.

The activity of Bicapa platform consisted in the production of chromium products such as: sodium dichromate, potassium dichromate, chromic anhydride, sulphur-based anti-pests, fluorine products, various inorganic chemicals such as aluminium sulphate and zinc oxide.

In order to study the ability of the crop plants such as spring wheat (*Triticumaestivum*), spring rape (*Brassica napus*

*ssp. oleifera*) and soybean (*Glycine hispida*) to accumulate the following combination of heavy metals: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn) and nickel (Ni), an experiment was conducted based on vegetation pots. The material of the experiment consisted of soil samples obtained from locations situated at different distances from the two areas affected by the pollution sources.

The experimental factors which were used are:

- the plant species used in the experiment, which actually represent the biological material: spring rape, spring wheat and soybean.
- the soil (collected from the previously mentioned areas directly affected by chemical industry). Soil sampling was performed at depths ranging from 10 to 30 cm. After harvesting, the plants were taken from each container soil samples of vegetation, which were subjected to some specific laboratory determinations.

The general objectives of the research were: to identify the possibility of using crops to reduce the heavy metal concentration in industrial contaminated soils, and to compare the absorption capability of the crop plants spring wheat, spring rape and soybean. For the data analysis stored in a database we have used a robust statistical data analysis.

Consequently, the steps followed in the research were:

- a pre-analysis (before the beginning of the research) in order to establish the research settings, like the most appropriate crop plants chosen for the phytoremediation of the soil polluted by the specific combination of heavy metals, in a temperate continental climate.
- monitoring the growth and development of plants under study;
- determining the concentration of heavy metals in the soil (before sowing and after the plants' harvesting) and from the harvested plants;
- statistical analysis, by analysing the presence of outliers and interpretation of the experiment data.

Soil samples were collected from a depth of 10 to 30 cm, based on the main penetration depth of the heavy metals in the soil. Thus, four variants for a soil sample collected from a single sampling point were established: (control sample - uncultivated - further denoted as Mt), seeded with spring rape-1, seeded with spring wheat-2, seeded with soy-3, resulting a total of 36 variants of samples.

Soil samples that represent the material used in the experiment, obtained from different distances from the points of the two areas affected by industrial pollution sources were collected (Table 1).

The sowing in vegetation vessels was performed depending on the specificity/requirements of the plant; thus, the spring wheat and the spring rape were sown in the first half of March, while soybean (plant with requirements for higher temperatures compared to the other two species used as biological material under study) was planted in April.

During the study, the main activities consisted in monitoring the growth and development of plants under study (syn-

**Table 1.** Samples of the Plants from the Area of the Former Plant Bicapa- Tarnaveni

Polluted area/pollution source	Soil samples			
	Name of the sample	Resulted sample	Distance from the pollution source (m)	Land usage/prior plant
Azomures-Cristesti Area	Sample A – PA	PA0, PA1, PA2, PA3	150	Agricultural / vegetable garden
	Sample B – PB	PB0, PB1, PB2, PB3	500	Agricultural / maize, potatoes
	Sample C – PC	PC0, PC1, PC2, PC3	1100	Agricultural / vegetables
	Sample D – PD	PD0, PD1, PD2, PD3	900	Agricultural / maize
BICAPA-Tirnaveni area	Sample F – PF	PF0, PF1, PF2, PF3	150	Uncultivated
	Sample G – PG	PG0, PG1, PG2, PG3	250	Uncultivated
	Sample H – PH	PH0, PH1, PH2, PH3	350	Uncultivated
	Sample I – PI	PI0, PI1, PI2, PI3	500	Agricultural / sugar beet
	Sample J – PJ	PJ0, PJ1, PJ2, PJ3	1500	Agricultural / vegetable garden

**Table 2.** Observations on Plant Samples from Azomures Area during the Vegetation Period

Sample/ Variant	Appearance of the plant
PA1	Plants of 5 ~ 8 cm in height, weak development, 10% of them with slightly yellowed appearance;
PA2	Plants of 20 ~ 30 cm in height, two tillers appeared, the first leaves withered;
PA3	Plants of 8 ~ 12 cm in height, normal appearance;
PB1	Plants of 15 ~ 20 cm in height, normal appearance;
PB2	Plants of 25 ~ 38 cm in height, yellowed leaves at the base;
PB3	Plants of 10 ~ 12 cm in height, normal appearance;
PC1	Plants of 11 ~ 12 cm in height, uniform plants developed;
PC2	Plants of 30 ~ 35 cm in height, first leaves yellowed;
PC3	Plants of 14 ~ 15 cm in height, slightly yellowed;
PD1	Plants of 10 ~ 12 cm in height, normal appearance;
PD2	Plants of 35 cm in height, well-developed;
PD3	Plants of 14 cm in height, normal appearance.

thesized in Tables 2 and 3), the determination of the heavy metals concentration in the soil (before planting and after harvesting) and that contained in harvested plants, finally followed by the interpretation of results.

After harvesting, plants and soil samples were taken from each vegetation pot, which were subject to determinations at the environmental analysis laboratory Wessling Tirgu-Mures that belongs to Wessling SRL, member of a well-known laboratory network in Europe, with the central headquarters in Altenberge, Germany. The heavy metals content in our research was determined: from the soil - before sowing and after harvesting the plants, from the harvested plants. The determination of the heavy metals from the samples was performed using the following methods: atomic absorption spectrometry (AAS) and atomic emission spectroscopy with inductively-coupled plasma (OES - Optical Emission Spectroscopy) according to the EPA Method 3051A:2007 standards (acidic mineralization of the soil and sludge samples using the microwave oven), EPA Method 6010C:2000/Inductively Coupled Plasma– Atomic Emission Spectrometry; SR EN ISO 11885:2009 (Water Quality. Determination of the 33 elements with atomic emission spectroscopy with inductive coupled plasma), EPA Method 6010C:2000, SR EN ISO 11885:2009 (Water Quality. Determination of the 33 elements with atomic emission spectroscopy with inductive coupled plasma) SR EN 1483:2007.

**Table 3.** Observations on Plant Samples from Bicapa-Tirnaveni Area during the Vegetation Period

Sample/Variant	Appearance of the plant
PF1	The plants did not sprout, the seeds remained in the soil without rotting, the embryo was destroyed;
PF2	Idem;
PF3	Idem;
PG1	Idem;
PG2	Idem;
PG3	Idem;
PH1	Idem;
PH2	Idem;
PH3	Idem;
PI1	Plants of 2.5 ~ 3 cm in height, about 20% of the plants withered;
PI2	Plants of 15 ~ 17 cm in height, about 30% of the plants yellowed;
PI3	Plants of 11 cm in height, slightly yellowed, root about 11 cm long;
PJ1	Plants of 5.5 ~ 6.5cm in height, plants look puny, slightly yellowed;
PJ2	Plants of 18 ~ 22cm in height, slightly yellowed;
PJ3	Plants of 10 ~ 13 cm in height, normal appearance.

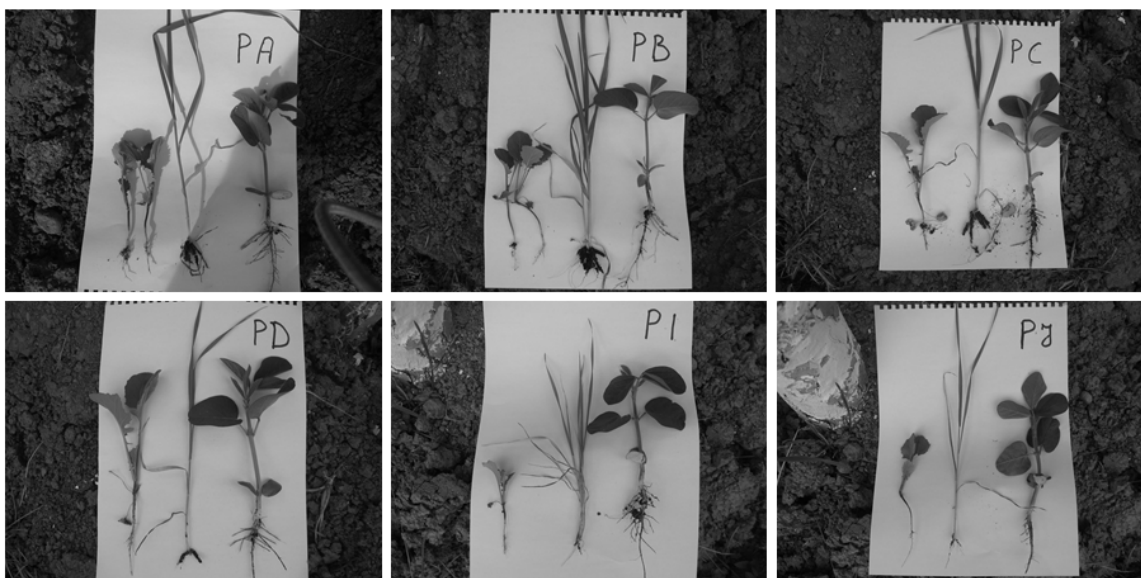


Figure 1. Phases of the plant growth and development.

### 3.2. Observations during the Vegetation Period

Seeding was performed considering the specificity of the plants, thus the spring wheat and the spring rape were seeded in the first half of March, and the soybean, a plant with higher temperature needs, was seeded in April. The behaviour of the plants in terms of growth and development was observed since seeding until harvesting. One month after seeding, the plants registered different growths, according to plant species and especially depending on the soil used (Tables 2 and 3; Figure 1).

It has to be noted that weeds such as: the amaranth (*Amaranthusretroflexus*), the ryegrass (*Loliumperenne*) and the henbane (*Hyoscyamusniger*) grew in the following control variants: PA0, PB0, PC0, PD0. Similarly; in the control variants PJ0 and PI0 grew weeds such as *Dactylisglomerata* and *Festucapratensis*.

In the case of the soil samples from the Bicapa-Tirnaveni area, neither the soybean nor the spring rape formed flowering strain, while the ear of the spring wheat was small - about 2 ~ 3 cm, presenting small and shrivelled wheat grain.

In case of the samples from the Azomures-Cristesti region soil, the plants grew better than those in the Bicapa Tirnaveni area. Spring rape formed flowering strain but had only 1 ~ 2 branches without forming flowers and the soy did flourish. Moreover, the agricultural land areas from Azomures-Cristesti are not currently designed for the crops of soy and spring rape. Years ago, before the construction of the chemical plant, crops such as maize and sugar beet had predominated. The residents from the area currently cultivate corn and vegetables in their vegetable gardens. It is well known that the Nitrogen is an essential nutrient for crop plant growth and development. Certainly, the nitrogen from atmospheric emissions (the ammonia - NH<sub>3</sub> in the present case) has a positive influence on the growth of our plant in the collected soil samples. The fact that the plants in some pots did not flourish is certainly influenced by the pre-

sence in the soil of the heavy metals above the normal/admitted value.

### 3.3. Statistical Analysis

For demonstration that the studied crop plants: spring wheat, spring rape and soybean, are appropriate as an efficient phytoremediation solution in the considered two places Bicapa-Tarnaveni and Azomures-Cristesti; geographical location: upper Mures river basin located in the east-central Romania, with a temperate continental climate, a statistical analysis of the obtained experiment data was performed. The main objective of the research was to compare the phytoremediation potential of the considered three crop plants, in case of the soil contaminated with the following heavy metals As, Cd, Cr, Cu, Pb, Zn and Ni, and also to analyse behaviour of the plants phytoremediation potential based on the distance from the most polluted soil (nearest to the pollution source).

The data obtained during the experiments was retained in a relational database, database model proposed by Codd in 1970 (Codd, 1970; 1990), normalized to the third normal form (3NF). Codd proposed the third normal form in 1971 (Codd, 1972). Our consideration from applicative point of view is that it is enough for a relational database to be in the third normal form (3NF) even if there are higher normal forms, proposed based on just theoretical considerations. In almost all the practical applications they do not offer a viable solution. The proposal is motivated based on the fact that obtaining a higher normal form supposes the decomposing of some database tables (relations); however, the tables number increases according to higher normal forms (obtaining a higher normal form from a previous one supposes the decomposition of some of the relations in more relations). This has as increasing effect to the time until the queries collect data from more tables (there are made joins between the database tables). Based on the

**Table 4.** Reference Values for Traces of Heavy Metals in Soil (mg/kg dry weight), in Accordance with the 756/11.03.1997 Regulation (ANPM 1997a, b)

Metal traces	Normal values	Alert thresholds/Types of uses		Action levels/ types of uses	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Arsenic	5	15	25	25	50
Cadmium	1	3	5	5	10
Total chromium	30	100	300	300	600
Hexavalent chromium	1	4	10	10	20
Copper	20	100	250	250	500
Nickel	20	75	200	150	500
Lead	20	50	250	100	1000
Zinc	100	300	700	600	1500

**Table 5.** Concentration of Heavy Metals (As, Cd, Cr, Cu) in Soil and Plants of the Samples Analyzed from the Azomures Area

Sample	Arsenic (mg/kg dry weight)			Cadmium (mg/kg dry weight)			Chromium (mg/kg dry weight)			Copper (mg/kg dry weight)		
	From soil sample		From harvested plants	From soil sample		From harvested plants	From soil sample		From harvested plants	From soil sample		From harvested plants
	Before sowing	After harvesting		Before sowing	After harvesting		Before sowing	After harvesting		Before sowing	After harvesting	
0	1	2	3	4	5	6	7	8	9	10	11	12
PA-0	5.46 <sup>&amp;</sup>	4.3	Mt	1	1	Mt	31.96 <sup>&amp;</sup>	30.1 <sup>&amp;</sup>	Mt	41.16 <sup>&amp;</sup>	38.5 <sup>&amp;</sup>	Mt
PA-1	5.46 <sup>&amp;</sup>	3.1	0.4	1	0.6	0.3	31.96 <sup>&amp;</sup>	29.4	1.19	41.16 <sup>&amp;</sup>	36 <sup>&amp;</sup>	4.47
PA-2	5.46 <sup>&amp;</sup>	2.95	1.8	1	0.25	0.1	31.96 <sup>&amp;</sup>	27.7	2.75	41.16 <sup>&amp;</sup>	33.9 <sup>&amp;</sup>	6.3
PA-3	5.46 <sup>&amp;</sup>	3.7	0.7	1	0.9	0.1	31.96 <sup>&amp;</sup>	30.4 <sup>&amp;</sup>	1.8	41.16 <sup>&amp;</sup>	32.7 <sup>&amp;</sup>	7.16
PB-0	4.6	4.1	Mt	1	1	Mt	26	25.1	Mt	32.03 <sup>&amp;</sup>	31.2 <sup>&amp;</sup>	Mt
PB-1	4.6	4.1	0.2	1	0.4	0.1	26	23.2	2.91	32.03 <sup>&amp;</sup>	26.2 <sup>&amp;</sup>	5.36
PB-2	4.6	3.3	0.9	1	0.9	0.1	26	23.9	0.85	32.03 <sup>&amp;</sup>	28.4 <sup>&amp;</sup>	3.17
PB-3	4.6	3.9	0.3	1	0.8	0.1	26	23.5	1.1	32.03 <sup>&amp;</sup>	27.9 <sup>&amp;</sup>	4.8
PC-0	4	2.9	Mt	1	1	Mt	17.33	15.9	Mt	23.5 <sup>&amp;</sup>	23 <sup>&amp;</sup>	Mt
PC-1*	4	3.2	0.2	1	0.6	0.09	17.33	17.1	0.9	23.5 <sup>&amp;</sup>	22.8 <sup>&amp;</sup>	0.9
PC-2	4	3.8	0.1	1	0.9	0.1	17.33	16.5	0.2	23.5 <sup>&amp;</sup>	18.3	4.3
PC-3	4	3.6	0.1	1	0.9	0.1	17.33	16.2	0.7	23.5 <sup>&amp;</sup>	17.7	5.07
PD-0	4.2	3.7	Mt	1	1	Mt	23.63	23.3	Mt	25.4 <sup>&amp;</sup>	24.9 <sup>&amp;</sup>	Mt
PD-1	4.2	2.8	1.1	1	0.5	0.09	23.63	21.9	1.25	25.4 <sup>&amp;</sup>	19.9	5.02
PD-2	4.2	3.1	0.5	1	0.2	0.1	23.63	22.1	1.15	25.4 <sup>&amp;</sup>	22.3 <sup>&amp;</sup>	2.67
PD-3	4.2	3.6	0.2	1	0.2	0.1	23.63	20.6	2.62	25.4 <sup>&amp;</sup>	18.2	5.85
MAL			5			0.1			30			10

Note: & denotes the exceedance of normal value; Mt denotes uncultivated control sample.

fact that the designed database does not contain a large quantity of data we concluded that indexing is not necessary.

As a future research direction, the phytoremediation potential of some other crop plants will be considered, in order to obtain alternative efficient phytoremediation solutions. These novel results will be retained also in the relational database and their phytoremediation potential will be compared using statistical methods with the actual results.

Interesting discussions and considerations related to statistical analysis and interpretation of experimental data are presented in (Sokal and Rohlf, 1995; Marusteri and Bacarea, 2010).

The interpretation of the values obtained from the determination of heavy metals in the soil samples is performed according to the reference values provided by the national regula-

tions (Table 4).

After harvesting plants from the vegetation vessels, on the one side, the heavy metal content decreased due to their accumulation in plants and due to the transition of the metals in the rainwater that leaked out from the vessel or evaporated, on the other side. Sometimes normal values were exceeded, but this was below the alert value, except for the PA sample case for example.

Tables 5 and 6 present the As, Cd, Cr, Cu, Pb, Zn, and Ni content of the analysed soil (before sowing and after harvesting) and plant samples originating from the Azomures area. Tables 7 and 8 present the As, Cd, Cr, Cu, Pb, Zn, and Ni content of the analysed soil (before sowing and after harvesting) and plant samples originating from the Bicapa-Tarnaveni area.

**Table 6.** Concentration of Heavy Metals (Ni, Pb, Zn) in Soil and Plants of the Samples Analyzed from the Azomures Area

Sample	Nickel (mg/kg dry weight)			Lead (mg/kg dry weight)			Zinc (mg/kg dry weight)		
	From soil sample		From harvested plants	From soil sample		From harvested plants	From soil sample		From harvested plants
	Before sowing	After harvesting		Before sowing	After harvesting		Before sowing	After harvesting	
0	1	2	3	4	5	6	7	8	9
PA-0	24.76 <sup>&amp;</sup>	24.1 <sup>&amp;</sup>	Mt	25.56 <sup>&amp;</sup>	23.1 <sup>&amp;</sup>	Mt	120.6 <sup>&amp;</sup>	112.8 <sup>&amp;</sup>	Mt
PA-1	24.76 <sup>&amp;</sup>	23.2 <sup>&amp;</sup>	5.1	25.56 <sup>&amp;</sup>	20.8 <sup>&amp;</sup>	0.5	120.6 <sup>&amp;</sup>	73.1	45.6
PA-2	24.76 <sup>&amp;</sup>	23.7	5	25.56 <sup>&amp;</sup>	21.6 <sup>&amp;</sup>	0.5	120.6	92.3	28.2
PA-3	24.76 <sup>&amp;</sup>	23.0 <sup>&amp;</sup>	4.0	25.56 <sup>&amp;</sup>	21.0 <sup>&amp;</sup>	0.1	120.6 <sup>&amp;</sup>	87.1	32.5
PB-0	28.70 <sup>&amp;</sup>	27.0 <sup>&amp;</sup>	Mt	20.20 <sup>&amp;</sup>	19.6	Mt	112.6 <sup>&amp;</sup>	101.0	Mt
PB-1	28.70 <sup>&amp;</sup>	27.6 <sup>&amp;</sup>	5.3	20.20 <sup>&amp;</sup>	19.3	0.3	112.6 <sup>&amp;</sup>	63.0	49.2
PB-2	28.70 <sup>&amp;</sup>	28.5 <sup>&amp;</sup>	5.1	20.20 <sup>&amp;</sup>	18.6	0.3	112.6 <sup>&amp;</sup>	82.7	23.2
PB-3	28.70 <sup>&amp;</sup>	24.8 <sup>&amp;</sup>	4.3	20.20 <sup>&amp;</sup>	19.4	0.3	112.6 <sup>&amp;</sup>	62.4	48.3
PC-0	18.93	17.9	Mt	19.90	17.6	Mt	157.2 <sup>&amp;</sup>	90.8	Mt
PC-1*	18.93	18.6	0.2	19.90	17.5	0.5	157.2 <sup>&amp;</sup>	91.8	21.3
PC-2	18.93	18.5	0.2	19.90	19.4	0.5	157.2 <sup>&amp;</sup>	97.3	37.1
PC-3	18.93	17.2	1	19.90	18.0	0.5	157.2 <sup>&amp;</sup>	97.9	54.1
PD-0	17.90	16.6	Mt	17.10	14.9	Mt	102.7 <sup>&amp;</sup>	62.8	Mt
PD-1	17.90	17.4	0.3	17.10	17.0	0.5	102.7 <sup>&amp;</sup>	63.2	33.4
PD-2	17.90	17.8	0.1	17.10	15.7	0.6	102.7 <sup>&amp;</sup>	64.6	25.8
PD-3	17.90	12.8	0.9	17.10	12.9	0.5	102.7 <sup>&amp;</sup>	48.5	29.7
MAL			6			0.5			50

Note: & denotes the exceedance of normal value; Mt denotes uncultivated control sample.

**Table 7.** Concentration of Heavy Metals (As, Cd, Cr, Cu) in Soil and Plants Corresponding to Bicapa-Tarnaveni Area

Sample	Arsenic (mg/kg dry weight)			Cadmium (mg/kg dry weight)			Chrome (mg/kg dry weight)			Copper (mg/kg dry weight)		
	From soil sample		From harvested plants	From soil sample		From harvested plants	From soil sample		From harvested plants	From soil sample		From harvested plants
	Before sowing	After harvesting		Before sowing	After harvesting		Before sowing	After harvesting		Before sowing	After harvesting	
0	1	2	3	4	5	6	7	8	9	10	11	12
PF-0	40**	18.6 <sup>!</sup>	Mt	4.56 <sup>!</sup>	1.02 <sup>&amp;</sup>	Mt	7257**	5833**	Mt	177 <sup>!</sup>	59.9 <sup>&amp;</sup>	Mt
PF-1	40**	19.8 <sup>!</sup>	-	4.56 <sup>!</sup>	1.16 <sup>&amp;</sup>	-	7257**	5856**	-	177 <sup>!</sup>	68.4 <sup>&amp;</sup>	-
PF-2	40**	20.6 <sup>!</sup>	-	4.56 <sup>!</sup>	1.04 <sup>&amp;</sup>	-	7257**	5239**	-	177 <sup>!</sup>	57.3 <sup>&amp;</sup>	-
PF-3	40**	20.6 <sup>!</sup>	-	4.56 <sup>!</sup>	1.1 <sup>&amp;</sup>	-	7257**	6756**	-	177 <sup>!</sup>	61.1 <sup>&amp;</sup>	-
PG-0	14.3 <sup>&amp;</sup>	9.88 <sup>&amp;</sup>	Mt	1.0	0.90	Mt	8709**	4775**	Mt	47.1 <sup>&amp;</sup>	46.2 <sup>&amp;</sup>	Mt
PG-1	14.3 <sup>&amp;</sup>	8.67 <sup>&amp;</sup>	-	1.0	1.0	-	8709**	7684**	-	47.1 <sup>&amp;</sup>	39.3 <sup>&amp;</sup>	-
PG-2	14.3 <sup>&amp;</sup>	6.83 <sup>&amp;</sup>	-	1.0	1.0	-	8709**	8211**	-	47.1 <sup>&amp;</sup>	30.0 <sup>&amp;</sup>	-
PG-3	14.3 <sup>&amp;</sup>	7.74 <sup>&amp;</sup>	-	1.0	0.85	-	8709**	8393**	-	47.1 <sup>&amp;</sup>	31.7 <sup>&amp;</sup>	-
PH-0	19.9 <sup>!</sup>	19.4 <sup>!</sup>	Mt	3.24 <sup>!</sup>	2.46 <sup>&amp;</sup>	Mt	2516**	2048**	Mt	97.9 <sup>&amp;</sup>	92.6 <sup>&amp;</sup>	Mt
PH-1	19.9 <sup>!</sup>	16.8 <sup>!</sup>	-	3.24 <sup>!</sup>	2.25 <sup>&amp;</sup>	-	2516**	1761**	-	97.9 <sup>&amp;</sup>	86.4 <sup>&amp;</sup>	-
PH-2	19.9 <sup>!</sup>	15.7 <sup>!</sup>	-	3.24 <sup>!</sup>	2.09 <sup>&amp;</sup>	-	2516**	2162**	-	97.9 <sup>&amp;</sup>	71.5 <sup>&amp;</sup>	-
PH-3	19.9 <sup>!</sup>	17.1 <sup>!</sup>	-	3.24 <sup>!</sup>	2.33 <sup>&amp;</sup>	-	2516**	1988**	-	97.9 <sup>&amp;</sup>	79.7 <sup>&amp;</sup>	-
PI-0	9.8 <sup>&amp;</sup>	8.61 <sup>&amp;</sup>	Mt	1.0	1	Mt	112 <sup>!</sup>	49.7 <sup>&amp;</sup>	Mt	42.9 <sup>&amp;</sup>	35.3 <sup>&amp;</sup>	Mt
PI-1	9.8 <sup>&amp;</sup>	7.56 <sup>&amp;</sup>	2.2	1.0	0.7	0.1	112 <sup>!</sup>	48.4 <sup>&amp;</sup>	6.58	42.9 <sup>&amp;</sup>	34.9 <sup>&amp;</sup>	8.31
PI-2	9.8 <sup>&amp;</sup>	8.38 <sup>&amp;</sup>	0.9	1.0	0.65	0.08	112 <sup>!</sup>	59.4 <sup>&amp;</sup>	1.68	42.9 <sup>&amp;</sup>	36.1 <sup>&amp;</sup>	5.08
PI-3	9.8 <sup>&amp;</sup>	6.12 <sup>&amp;</sup>	1.4	1.0	0.9	0.05	112 <sup>!</sup>	57.2 <sup>&amp;</sup>	1.11	42.9 <sup>&amp;</sup>	35.4 <sup>&amp;</sup>	6.99
PJ-0	6.34 <sup>&amp;</sup>	5.07 <sup>&amp;</sup>	Mt	0.8	0.7	Mt	52.3 <sup>&amp;</sup>	34.4 <sup>&amp;</sup>	Mt	49.3 <sup>&amp;</sup>	41.7 <sup>&amp;</sup>	Mt
PJ-1	6.34 <sup>&amp;</sup>	3.9	1.1	0.8	0.3	0.02	52.3 <sup>&amp;</sup>	29.4	2.17	49.3 <sup>&amp;</sup>	41.8 <sup>&amp;</sup>	3.69
PJ-2	6.34 <sup>&amp;</sup>	5.13 <sup>&amp;</sup>	0.5	0.8	0.3	0.01	52.3 <sup>&amp;</sup>	34.1 <sup>&amp;</sup>	1.01	49.3 <sup>&amp;</sup>	43.1 <sup>&amp;</sup>	5.86
PJ-3	6.34 <sup>&amp;</sup>	4.58	1	0.8	0.6	0.03	52.3 <sup>&amp;</sup>	32.1 <sup>&amp;</sup>	1.16	49.3 <sup>&amp;</sup>	41.7 <sup>&amp;</sup>	6.59
MAL			5			0.1			30			10

Note: & denotes the exceedance of normal value; ! denotes the exceedance of alert threshold; \*\* denotes the excess of intervention value; Mt denotes uncultivated control sample.



**Table 8.** Concentration of Heavy Metals (Ni, Pb, Zi) in Soil and Plants Corresponding to Bicapa-Tarnaveni Area

Sample	Nickel (mg/kg dry weight)			Lead (mg/kg dry weight)			Zinc (mg/kg dry weight)		
	From soil sample		From harvested plants	From soil sample		From harvested plants	From soil sample		From harvested plants
	Before sowing	After harvesting		Before sowing	After harvesting		Before sowing	After harvesting	
0	1	2	3	4	5	6	7	8	9
PF-0	561**	392**	Mt	134.2**	72.9!	Mt	1301**	190 <sup>&amp;</sup>	Mt
PF-1	561**	398**	-	134.2**	79.5!	-	1301**	190 <sup>&amp;</sup>	-
PF-2	561**	347**	-	134.2**	73.3!	-	1301**	193 <sup>&amp;</sup>	-
PF-3	561**	377**	-	134.2**	79.7!	-	1301**	198 <sup>&amp;</sup>	-
PG-0	450**	100.3!	Mt	44.8 <sup>&amp;</sup>	42.0 <sup>&amp;</sup>	Mt	175 <sup>&amp;</sup>	151 <sup>&amp;</sup>	Mt
PG-1	450**	236**	-	44.8 <sup>&amp;</sup>	33.3 <sup>&amp;</sup>	-	175 <sup>&amp;</sup>	155 <sup>&amp;</sup>	-
PG-2	450**	244**	-	44.8 <sup>&amp;</sup>	30.9 <sup>&amp;</sup>	-	175 <sup>&amp;</sup>	152 <sup>&amp;</sup>	-
PG-3	450**	287**	-	44.8 <sup>&amp;</sup>	33.7 <sup>&amp;</sup>	-	175 <sup>&amp;</sup>	173 <sup>&amp;</sup>	-
PH-0	51.5 <sup>&amp;</sup>	48.5 <sup>&amp;</sup>	Mt	78.5!	60.4!	Mt	208 <sup>&amp;</sup>	175 <sup>&amp;</sup>	Mt
PH-1	51.5 <sup>&amp;</sup>	45.3 <sup>&amp;</sup>	-	78.5!	60.3!	-	208 <sup>&amp;</sup>	175 <sup>&amp;</sup>	-
PH-2	51.5 <sup>&amp;</sup>	45.2 <sup>&amp;</sup>	-	78.5!	68.4!	-	208 <sup>&amp;</sup>	192 <sup>&amp;</sup>	-
PH-3	51.5 <sup>&amp;</sup>	50 <sup>&amp;</sup>	-	78.5!	68!	-	208 <sup>&amp;</sup>	193 <sup>&amp;</sup>	-
PI-0	53.9 <sup>&amp;</sup>	41.6 <sup>&amp;</sup>	Mt	27.5 <sup>&amp;</sup>	24.8 <sup>&amp;</sup>	Mt	114 <sup>&amp;</sup>	90.4	Mt
PI-1	53.9 <sup>&amp;</sup>	40.5 <sup>&amp;</sup>	5.55	27.5 <sup>&amp;</sup>	25.1 <sup>&amp;</sup>	0.5	114 <sup>&amp;</sup>	88	44.5
PI-2	53.9 <sup>&amp;</sup>	42.6 <sup>&amp;</sup>	5.45	27.5 <sup>&amp;</sup>	25.3 <sup>&amp;</sup>	0.45	114 <sup>&amp;</sup>	92.1	30.5
PI-3	53.9 <sup>&amp;</sup>	42.9 <sup>&amp;</sup>	5.32	27.5 <sup>&amp;</sup>	24.7 <sup>&amp;</sup>	0.51	114 <sup>&amp;</sup>	90.5	41.3
PJ-0	34.7 <sup>&amp;</sup>	28.3 <sup>&amp;</sup>	Mt	29 <sup>&amp;</sup>	26 <sup>&amp;</sup>	Mt	153 <sup>&amp;</sup>	118 <sup>&amp;</sup>	Mt
PJ-1	34.7 <sup>&amp;</sup>	27.5 <sup>&amp;</sup>	5.2	29 <sup>&amp;</sup>	25.5 <sup>&amp;</sup>	0.6	153 <sup>&amp;</sup>	110 <sup>&amp;</sup>	41.8
PJ-2	34.7 <sup>&amp;</sup>	29.2 <sup>&amp;</sup>	5.1	29 <sup>&amp;</sup>	26.3 <sup>&amp;</sup>	0.4	153 <sup>&amp;</sup>	122 <sup>&amp;</sup>	38.4
PJ-3	34.7 <sup>&amp;</sup>	27.9 <sup>&amp;</sup>	4.9	29 <sup>&amp;</sup>	26.7 <sup>&amp;</sup>	0.7	153 <sup>&amp;</sup>	112 <sup>&amp;</sup>	41.3
MAL			6			0.5			50

Note: & denotes the exceedance of normal value; ! denotes the exceedance of alert threshold; \*\* denotes the excess of intervention value; uncultivated control sample denoted as Mt.

**Table 9.** Checking for Outliers in Soil Samples before Sowing from Azomures Area

	Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
	5.46; 4.6; 4; 4.2	1; 1; 1; 1	31.96; 26; 17.33; 23.63	41.16; 32.03; 23.5; 25.4	24.76; 28.7; 18.93; 17.9	25.56; 20.2; 19.9; 17.1	120.6; 112.6; 157.2; 102.7
Mean	4.57	1	24.73	30.52	22.57	20.69	123.28
Standard deviation	0.65	0	6.05	7.98	5.08	3.53	23.77
CV	14.17	0	24.47	26.14	22.5	17.08	19.28
Outliers / Grubbs test	No	*	No	No	No	No	No

\*No outliers were detected; all the values are the same, resulting in a standard deviation = 0 and CV = 0. Grubbs test cannot be applied based on this consideration.

**Table 10.** Checking for Outliers in Soil Samples before Sowing from Bicapa Area

	Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
	40; 14.3; 19.9; 9.8; 6.34	4.56; 1; 3.24; 1; 0.8	7257; 8709; 2516; 112; 52.3	177; 47.1; 97.9; 42.9; 49.3	561; 450; 51.5; 53.9; 34.7	134.2; 44.8; 78.5; 27.5; 29	**1301. 175; 208; 114; 153
Mean	18.07	2.12	3729.26	82.84	230.22	62.8	390.2
Standard Deviation	13.27	1.69	4041.02	57.21	254.45	44.88	510.30
CV	73.45	79.84	108.36	69.06	110.52	71.47	130.78
Outliers / Grubbs test	No	No	No	No	No	No	*Yes

\*\* At the first application of the Grubbs test the value 1301 was detected as a single outlier (soil sample denoted PF, where no crop plant germinated). After repeating the Grubbs test with this eliminated value, no other outliers were detected.

By analysing the data shown in Tables 7 and 8 it can be observed that the soil samples from the Bicapa-Tarnaveni area contain heavy metals whose values reach the intervention threshold value, which is considered a dangerous situation for

plants, humans and animals health

It is important to note that in the soil samples PF, PG, PH, which were taken near the three pits of the former Bicapa plant (the place for storing the waste resulted following the indus-

trial activities fulfilled at the Bicapa plant), the seeds did not germinate, because the soils contain a larger quantity of heavy metals.

In the case of samples in which the seeds did not germinate, there is a decrease of cadmium, certainly because of the passage into the atmosphere of the element (this process is favoured by the texture and compaction of the soil from vegetation vessels), but also because of the water leaking from rainfall, that was collected to avoid contamination of the land on which the vegetation pots were placed.

The chromium reaches high levels of 1,761 mg/kg (PH1) and 8,393 mg/kg (PG3), compared to 600 mg/kg value of the intervention threshold for sensitive areas.

This is explainable if one takes into account the activity profile that the company had, having consisted in manufacturing and marketing of chromium-based products (potassium dichromate, chromic anhydride, sodium dichromate). The chromium content in the analysed plants exceeded the MAL (Maximum Acceptable Limit).

The soil analysis before sowing the samples PF and PG shows content in nickel two times higher than the intervention threshold for sensitive areas, while other samples show values of nickel content which are between the normal and the alert value.

In the first pit wastes with an appreciable quantity of zinc were stored, which influenced the adjacent area; this resulted in the double zinc content compared to the value of intervention (600 mg/kg) in the PF sample. However, a sharp decline for this metal is registered between March / April to July / August, which can be explained by the reduced presence of iron and manganese oxides in the analysed soil, which is known to have the capability of immobilizing the zinc.

For a robust statistical analysis, as a first step, a descriptive statistics and analysis of the presence of outliers in the soil samples “before sowing” were carried out. This was done for the soil samples from the Azomures-Cristesti area, with the results presented in Table 9 and the Bicapa-Tarnaveni area results presented in Table 10. The analysis included the verification of outliers in the quantity of following heavy metals present in the soils: As, Cd, Cr, Cu, Pb, Zn, and Ni. A descriptive statistics was made to obtain the coefficient of variation (CV) for the estimation of homogeneity/heterogeneity of data sets and after that the Grubbs test for outliers detection (Barnett and Lewis, 1994) with significance level  $\alpha = 0.05$  was used.

The Grubbs test was proposed by Frank Grubbs in 1950 (Grubbs, 1950). The Grubbs test for a data set means that if an outlier is detected the test is repeated. Applying the Grubbs test in case of our data, a single outlier was detected (see Table 10).

The obtained results show that the soil samples from Bicapa-Tarnaveni are more heterogeneous (the value of CV is higher) than those from Azomures area. For the data normality testing, we applied the Kolmogorov-Smirnov Goodness-of-Fit Test (Chakravarti et al., 1967). The Kolmogorov-Smirnov Goodness-of-Fit Test was chosen based on the relatively small degrees of freedom of the data set.

**Observation:** During the interpretation of scientific data/ results, the data graphical visualization is often very important as a first step, followed, as a second step, by a descriptive statistics and sometimes the outliers’ detection. After these steps, based on the previous results and observations, different statistical analyses are performed, like: verification of data normality (if the data is sampled from a Gaussian population) and statistical tests for equality of means, equality of variances, etc.

Adequate handling of the outliers provides robustness, allowing a correct conclusion formulation, even if there are values that can lead to wrong conclusions if they are not eliminated. There are many tests for the outliers’ detection, like: Grubbs, Chauvenet’s criterion (Ross, 2003; Zerbet and Nikulin, 2003), Peirce’s criterion (Stigler, 1978), Dixon’s Q test (Dean and Dixon, 1951), etc. These outliers detection tests effectiveness could be increased if, in a particular type of research fulfilled in a specific domain, there is taken into consideration a domain specific knowledge that should be constructed in time. For example, in Table 10 the Grubbs test was able to detect only 1301 as an outlier. At the corresponding soil sample denoted PF the seeds did not germinate, but at the soil samples PG and PH the seeds did not germinate either, even if the heavy metals quantity in the soil samples was not identified as outlier. This suggests that these soil samples are also outliers for the studied crop plants, even if these values are not detected as outliers by the selected statistical test for outliers’ detection.

Analysis of variance (ANOVA) proposed by Ronald Fisher is used in order to analyse the differences among group means

**Table 11.** Azomures Area: Results of Two-Factor without Replication ANOVA

		SS	MS	F-value	P-value
<b>Arsenic</b>	SV/Distance	1.0692	0.3564	1.6793 (FR)	0.2694
	SV/Plant	0.5267	0.2633	1.2408 (FC)	0.3540
	SV/Error	1.2733	0.2122		
<b>Cadmium</b>	SV/Distance	0.0107	0.0036	1 (FR)	0.4547
	SV/Plant	0.0054	0.0027	0.7570 (FC)	0.5091
	SV/Error	0.0214	0.0036		
<b>Chromium</b>	SV/Distance	3.0478	1.0159	1.1958 (FR)	0.3882
	SV/Plant	0.2753	0.1377	0.1620 (FC)	0.8540
	SV/Error	5.0974	0.8496		
<b>Cooper</b>	SV/ Distance	9.9340	3.3113	1.4273 (FR)	0.3244
	SV/Plant	7.7322	3.8661	1.6664 (FC)	0.2657
	SV/Error	13.920	2.3200		
<b>Nickel</b>	SV/Distance	56.829	18.943	56.593 (FR)	8.59E-05
	SV/Plant	0.065	0.0325	0.0971 (FC)	0.9089
	SV/Error	2.0083	0.3347		
<b>Lead</b>	SV/Distance	0.1092	0.0364	2.7872 (FR)	0.132
	SV/Plant	0.035	0.0175	1.3404 (FC)	0.3302
	SV/Error	0.0783	0.0131		
<b>Zinc</b>	SV/Distance	182	60.667	0.4365 (FR)	0.734
	SV/Plant	333.095	166.55	1.1984 (FC)	0.3648
	SV/Error	833.845	138.97		

**Table 12.** Azomures Area: Statistical Data for the Plants

Crt.		Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
1	<b>S. Rape:</b>	0.475/	0.145/	1.563/	3.938/	2.725/	0.45/	37.375/
	Mean/variance/ {max; min}	0.1825/ {1.1; 0.2}	0.0107/ {0.3; 0.09}	0.8304/ {2.91; 0.9}	4.2351/ {5.36; 0.9}	8.1758/ {5.3; 0.2}	0.01/ {0.5; 0.3}	160.5625/ {49.2; 21.3}
	<b>S. Wheat:</b>	0.825/	0.1/0/	1.238/	4.11/	2.6/ 8.0067/	0.475/	28.575/
2	Mean/variance/ {max; min}	0.5292/ {1.8; 0.1}	{0.1; 0.1}	1.1740/ {2.75; 0.2}	2.5965/ {6.3; 2.67}	{5.1; 0.1}	0.0158/ {0.6; 0.3}	36.4692/ {37.1; 23.2}
	<b>Soybean:</b>	0.325/	0.1/0/	1.555/	5.72/	2.55/ 3.43/	0.35/	41.15/
3	Mean/variance/ {max; min}	0.0692/ {0.7; 0.1}	{0.1; 0.1}	0.7108/ {2.62; 0.7}	1.1198/ {7.16; 4.8}	{4.3; 0.9}	0.0367/ {0.5; 0.1}	141.5833/ {54.1; 29.7}

**Table 13.** Bicapa Area: Results of Two-Factor without Replication ANOVA.

		SS	MS	F-value	P-value
Arsenic	SV/Distance	0.6017	0.6017	7.3673 (FR)	0.1132
	SV/Plant	0.9033	0.4517	5.5306 (FC)	0.1531
	SV/Error	0.1633	0.0817		
Cadmium	SV/Distance	0.0048	0.0048	9.3226 (FR)	0.0926
	SV/Plant	0.0004	0.0002	0.4194 (FC)	0.7046
	SV/Error	0.001	0.0005		
Chromium	SV/Distance	4.2168	4.2168	1.4711 (FR)	0.349
	SV/Plant	13.1484	6.5742	2.2935 (FC)	0.3036
	SV/Error	5.7329	2.8665		
Cooper	SV/Distance	2.9963	2.9963	0.7435 (FR)	0.4795
	SV/Plant	1.7649	0.8825	0.219 (FC)	0.8204
	SV/Error	8.0601	4.0301		
Nickel	SV/Distance	0.2091	0.2091	256 (FR)	0.0039
	SV/Plant	0.0716	0.0358	43.857 (FC)	0.0223
	SV/Error	0.0016	0.0008		
Lead	SV/Distance	0.0096	0.0096	1.3061 (FR)	0.3715
	SV/Plant	0.034	0.017	2.3152 (FC)	0.3016
	SV/Error	0.0147	0.0074		
Zinc	SV/Distance	4.5067	4.5067	0.297 (FR)	0.6404
	SV/Plant	84.023	42.0117	2.7691 (FC)	0.2653
	SV/Error	30.343	15.1717		

(two or more groups, usually more than two groups) and their associated variation among and between groups. ANOVA is used worldwide in a large number of researches including the agricultural sciences (Littell, 2002; Gertheiss, 2014). In an ANOVA test the most important calculated values are: *SS*, *MS*, *F*-value, *Fcrit*, *P*-value. *SS* is the abbreviation for Sum of Squares (deviations of the values from the mean of those values). There is no variation only if the values are the same. *MS* is the abbreviation for Mean of the Squares (average squared deviation from the mean). *MS* should be calculated by using the formula  $MS = SS/df$ , where *df* denotes the degrees of freedom.

*F* (*F*-value) denotes the result of *F* test statistic. *F* is the ratio of two sample variances. *Fcrit* denotes the critical value extracted from a statistical table. The identification of the critical value is made based on degrees of freedom and the chosen significance level. *P*-value is the result of the *F* statistics, allowing the decision taking by accepting or rejecting the Null Hypothesis denoted  $H_0$ . If  $F < Fcrit$  (similar interpretation with the  $P$ -value  $> 0.05$ ) then, we accept  $H_0$ .  $F \geq Fcrit$  ( $P$ -value  $\leq 0.05$ ) indicates the failure to accept  $H_0$ .

For analysing the experimental data, a statistical Two-Factor without Replication - ANOVA analysis were realized separately for the Azomures area (Table 11) and Bicapa area (Table 13), in order to conclude if there are differences between the absorption of the considered heavy metals (As, Cd, Cr, Cu, Pb, Zn, and Ni) by the studied three crop plants, plant 1-spring rape, plant 2-spring wheat and plant 3-soybean (the absorption of the plants is statistically equal or different) and the dependency of phytoremediation on distance (if a change in distance led to a change in the absorption of the plants was checked). The changing/decreasing tendency of the heavy metals quantity based on distance from the polluted source can be demonstrated also by regression analysis (Armstrong, 2012).

It was considered as most appropriate significance level denoted  $\alpha = 0.05$ , the probability of rejecting the null hypothesis when this is true (to make a type one error). This value for  $\alpha$  was chosen based on the type I and type II errors (incorrect failure to reject a false null hypothesis). A type I error is detecting an effect that is not present, while a type II error is failing to detect an effect that is present.

The obtained results of the Two-Factorial ANOVA were presented in Table 11 for Azomures and Table 13 for Bicapa below, where *SV* denotes *Source of Variation*. Table 12 for Azomures and Table 14 for Bicapa present the results of descriptive statistics of the data from Azomures and Bicapa.

The following notations are used for Tables 11 and 13:

- for the planting distance: *FR* -the calculated *F*-value, *FRc* -the critical value selected from a statistical table based on the  $\alpha$  and the degrees of freedom;  $FRc = 4.757$  at Azomures;  $FRc = 18.513$  at Bicapa; *PR* is the calculated *P*-value;
- for the plants: *FC* -the calculated *F*-value, *FCc* -the critical value selected from a statistical table based on the  $\alpha$  and the degrees of freedom;  $FCc = 5.143$  at Azomures;  $FCc = 19.000$  at Bicapa; *PC* is the calculated *P*-value.

Conclusions of the ANOVA test in the Azomures area include:

- There is no statistical difference between the absorption of the heavy metals by the three studied plants: As, Cd, Cr, Cu, Pb, Zn, and Ni (concluded by comparing the values *FR* and *FRc*; in case of each considered heavy metal  $FR < FRc$  and  $PR > 0.05$ ).
- The absorption of the heavy metals by the plants (As, Cd, Cr, Cu, Pb, and Zn), except the Ni, does not differ with changing the distance (concluded by comparing the values *FC*

**Table 14.** Bicapa Area: Statistical Data for the Plants

Crt.		Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
1	<b>S. Rape:</b>	1.65/	0.06/	4.375/	6/	5.375/	0.55/	43.15/
	Mean/variance/	0.605/	0.0032/	9.7241/	10.6722/	0.0613/	0.005/	3.645/
	{max; min}	{2.2; 1.1}	{0.1; 0.02}	{6.58; 2.17}	{8.31; 3.69}	{5.55; 5.2}	{0.6; 0.5}	{44.5; 41.8}
2	<b>S. Wheat:</b>	0.7/	0.045/	1.345/	5.47/	5.275/	0.425/	34.45/
	Mean/variance/	0.08/	0.0025/	0.2245/	0.304/	0.0613/	0.0013/	31.205/
	{max; min}	{0.9; 0.5}	{0.08; 0.01}	{1.68; 1.01}	{5.86; 5.08}	{5.45; 5.1}	{0.45; 0.4}	{38.4; 30.5}
3	<b>Soybean:</b>	1.2/	0.04/	1.135/	6.79/	5.11/	0.605/	41.3/0/
	Mean/variance/	0.08/	0.0002/	0.0013/	0.08/	0.0882/	0.0180/	{41.3; 41.3}
	{max; min}	{1.4; 1}	{0.05; 0.03}	{1.16; 1.11}	{6.99; 6.59}	{5.32; 4.9}	{0.7; 0.51}	

and  $FCc$ ; in case of each considered heavy metal, except the Ni,  $FC < FCc$  and  $PC > 0.05$ ).

- There is no statistical difference between the absorption of the three plants of the Ni (concluded based on  $FR < FRc$  and  $PR > 0.05$ ), but there is a difference between their absorption of Ni at different distances (concluded based on  $FC > FCc$  and  $PC < 0.05$ ).

Conclusions of the ANOVA test in the Bicapa area are as follows:

- There is no statistical difference between the absorption of the heavy metals by the three studied plants, of the heavy metals: As, Cd, Cr, Cu, Pb and Zn (concluded by comparing the values  $FR$  and  $FRc$ ; in case of each considered heavy metal  $FR < FRc$  and  $PR > 0.05$ ).
- The absorption of the heavy metals by the plants: As, Cd, Cr, Cu, Pb and Zn, does not differ during the distance changing (concluded by comparing the values  $FC$  and  $FCc$ ; in case of each considered heavy metal: As, Cd, Cr, Cu, Pb and Zn,  $FC < FCc$  and  $PC > 0.05$ ).
- There is a statistical difference between the absorption of the three studied plants of the Ni (concluded by comparing the values  $FR$  and  $FRc$ ;  $FR > FRc$  and  $PR < 0.05$ ). Also, there is a difference between the absorption at different distances ( $FC > FCc$  and  $PC < 0.05$ ).

The statistical analysis proves that the absorption of nickel was different versus that of the other studied heavy metals. The differences related with the nickel absorption, between Azomures and Bicapa, have as explanation the difference between the soil types and the quantity of accumulated heavy metals that influence the crops growth, and the default physiological processes taking place in the plant, respectively.

### 3.4. Discussions

The obtained results related with the experiments realized for the three crop plants: spring rape, spring wheat and soybean absorption of the heavy metals As, Cd, Cr, Cu, Pb, Zn, and Ni were presented in the Table 11 (Azomures-Cristesti area) and Table 13 (Bicapa-Tirnaveni area). In Tables 12 and 14 there were included results, like: mean absorption per plant, statistical variance, minimum value, and maximum value in case of each considered heavy metal. The results of statistical analysis prove that the absorption of As, Cd, Cr, Cu, Pb, and Zn by the studied crop plants were not statistically different in the considered Azomures area and in the Bicapa-Tirnaveni area. There were statistical differences only in the Ni absorption, as presented

in the previous section.

In the case of samples PF, PG, PH (150, 250 and 350 meters distance from the polluted source) collected from Bicapa-Tirnaveni area, the embryo of the seeds did not germinate in the presence of the heavy metals contaminants in the soil. In the case of the spring wheat plants from the samples PI, PJ, there a normal growth was not registered, mainly due to the sensitivity to copper. Some studies prove that the plants embryo is more sensitive to copper than to some other heavy metals. This study and other investigations carried out in 1995 by IPM Tirgu-Mures show that the main source of risk to the Bicapa-Tirnaveni is the exfiltration of the waste from the disposal pits containing chromium.

The obtained experimental data was retained in a relational database. It can be concluded that the third normal form (3NF) adoption in case of a relational database implementation is the necessary and sufficient condition. Even if there are defined higher normal forms than 3NF, proposals based on pure theoretical considerations, they are not appropriate in many situations based on practical reasons.

There are several statistical tests for outliers detection presented in the scientific literature that offer robustness to the statistical analysis. Some of the most known and frequently used are the Grubbs test (Grubbs, 1950; Barnett and Lewis, 1994), Chauvenet's criterion (Ross, 2003; Zerbet and Nikulin, 2003), Peirce's criterion (Stigler, 1978), Dixon's Q test (Dean and Dixon, 1951). Consequently all these tests were analysed, and if a synthesis should be made, it can be seen that each of them has advantages and disadvantages. They perform very well under normal conditions, but in some cases, like under the influencing factors of biological systems (with an inherent complexity and variability) like plants for example (our research considers the influence of heavy metals on the growth of the plants), they are not always able to accurately detect outliers. It is necessary in such cases to elaborate some adapted tests for the outliers' detection. Such adapted tests for outliers' detection could decrease the research costs by eliminating, for example, useless costly experiments where the phytoremediation does not offer a viable solution.

### 3.5. Future Research Directions

#### 3.5.1. Research on Biofuel Production from Crops

The main ecological function of the rape is the improvement, conservation and soil protection (Morar, 2008). Rapeseed

oil is considered a source of alternative energy -biofuel for diesel engines, either alone or methyl ester, in global efforts to reduce the consumption of fossil fuels that are on a depletion process, and of the "greenhouse" effect intensified by burning thereof. It is biodegradable, non-toxic to aquatic organisms, emits less smoke by burning, it does not emit sulphur oxides responsible for acid rains, it does not contain aromatic hydrocarbons, but it is still responsible for nitrogen oxides emissions. This aspect is analysed by a previous research performed on oil production from rape (Chirila and Morar, 2007).

Based on the fact that biofuels may reduce the greenhouse gases, their production became very tempting. Recently, numerous researches are undertaken worldwide trying to identify sources that would allow the production of biofuel and corresponding efficient technologies of production. A previous research of one of the authors of this paper includes the study of growing rape in Mures County as an alternative in obtaining biofuel (Morar and Peterlicean, 2014).

It has to be noted that in case of decontaminating plants usage for obtaining biofuel, or even in case of incineration (for disposal as waste in small quantities) it is compulsory to use installations equipped with filters for the gases or units for the treatment prior to discharge the vapours in the atmosphere. As a future research direction, the production of biodiesel from plants used for phytoremediation will be considered. These three selected plants presented in the paper will be further used, based on their phytoremediation capacity established in the present research.

### 3.5.2. Research on Intelligent Decision Support Systems

Another future research direction will consist in the development of an intelligent agent-based decision support system that may help in deciding the most appropriate plant as a phytoremediation solution for different kinds of polluted soils. In previous researches different aspects related with artificial intelligence have been analysed, which include: computational intelligence and intelligent systems (many times intelligent agent-based systems). In the scientific literature it is considered that the computational intelligence includes artificial neural networks (Rumelhart and McClelland, 1986), evolutionary computation (Fogel et al., 1966) and fuzzy logic (Zadeh, 1965). Even if an artificial computing system (a mobile robotic agent for example) has computational intelligence (it uses a neural network for the recognition of some simple images for example), it does not mean that it could be considered intelligent. It is considered that computational intelligence and intelligence of a system do not have the same meaning. In previous researches, Iantovics (Iantovics, 2008; Iantovics 2013) proved that the most appropriate solution for decision support is many times represented by the intelligent agent-based decision support systems. Intelligence may often offer advantages to a system versus a system that does not have intelligence (Iantovics and Zamfirescu 2013).

## 4. Conclusions

This paper presents a solution on polluted soil remediation

through phytoremediation realized in the east-central Romania. The region where the research was fulfilled has a temperate continental climate, with relatively cold winters, and warm and dry summers. The following three crops were proposed: spring wheat, spring rape and soybean for the efficient phytoremediation of soil polluted by the following combination of heavy metals: As, Cd, Cr, Cu, Pb, Zn and Ni.

The obtained results show that the phytoremediation potential of the heavy metals, except the nickel, for the three plants, is statistically similar in the neighbourhood regions of the two studied chemical platforms Azomures and Bicapa. Treated soil naturally preserves its physical, chemical and biological properties. The decision related to the choice of one of the considered plants for phytoremediation should be made based on considerations such as the financial investment and agricultural aspects like: harvesting time, long time weather forecast favourable for the plant growth.

**Acknowledgements.** The authors would like to thank Wessling laboratory from Tirgu-Mures for the valuable help in offering the infrastructure support for the experimental determinations.

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