Chapter 11

The Influence of Zeolites on Quality Indicators of Soil-Plant Connection and Food Safety

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Additional information is available at the end of the chapter

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Abstract

Applying zeolites to natural environment is important from the point of view of monitoring the toxic metals' mobilization (Al(III), Mn(II), Cd(II), and Pb(II)) as well as microelements (Fe, Mn, Zn, and Cu). These elements influenced food chain and their deficiency as well as excess and determined plant quality and health of humans and animals. Furthermore, zeolites, while having particular physical, physicochemical, and chemical properties, interact with physical, physicochemical, chemical, and biological features of the soil and may lead to alterations in their properties. This exchange is dependent on many factors, i.e. pH, concentration of metal ions in solution. When natural zeolites are applied, one should bear in mind that they are ecological material and do not show any harmful action neither to humans nor to animals. Studies in this chapter will show the influence of described and tested zeolites on the properties and quality indicators of the first food chain link: soil-plant as well as on the quality of food. It would allow to understand, predict, and control the behavior of these elements in natural environment as well as evaluate their potential toxicity and bioavailability.

Keywords: heavy metals, zeolites, some soil properties, some element ratios in plants, food security

1. Introduction

The primary effect of the negative impact of acidic reaction consists in adverse changes in physical, chemical, and biological properties of soils, as well as poor growth and development of plants (lower yields). Secondary effect is the mobilization of aluminum and heavy metal ions in amounts proportional to the acidity of the soil. In acidic soils with pH below 4.2, aluminosilicates are decomposed, whereas the concentration of Al^{3+} and Mn^{2+} ions that occupy space of Mg^{2+} and Ca^{2+} in the sorption complex and contribute to increased leaching of alkaline cations is increased. These changes are a major cause of poor growth and development of crops [1–4]. At first, high concentration of aluminum ions has a destructive effect on the root system, which makes nutrient uptake difficult and results in Mg and P deficiency symptoms in plants and their poorer growth. Aluminum ions also limit the growth of shoots leading to the decay of vertices and the necrosis of leaves. Aluminum also forms the ion ratios in cereals, including enhancement of K:(Ca + Mg) ratio and affects the higher content of Mn and Fe in the above-ground parts of plants. Finally, toxic aluminum reduces the quantity and quality of cereal crops [2, 3, 5]. Considering the influence of environmental conditions on the quality of wheat grain, the health aspect of raw material cannot be overlooked, especially the content of heavy metals, including cadmium, even small amounts of which are harmful to the health of humans and animals and which is characterized by very high mobility within the environment. Cereals are the main source of cadmium for humans.

There is quite broad differentiation in the quantity of cadmium uptaken from the soil. More cadmium is absorbed by durum rather than common wheat kernels [6, 7]. Diverse cadmium levels are also found in grains depending on the cultivar [8–11]. The presence of heavy metals, such as Pb and Cd, in the soil, significantly affects the quality of grain yield, since exceeding the permissible content of these elements in the intervening purchase of cereals (>0.2 mg/kg) disqualifies the grain for further processing and consumption, which may lead to substantial economic losses. It is therefore necessary to monitor the heavy metals content in soils [12, 13].

Applying new sorbents, such as zeolites, in natural environment is important from the point of view of monitoring the toxic metals mobilization (Al, Mn, Cd, and Pb) as well as microelements (Fe, Mn, Zn, and Cu) or macroelements (Mg, Ca, and K). These elements influenced food chain and their deficiency as well as excess and determined plant quality and health of human and animals [4, 5, 14]. Furthermore, new substances, while having particular physical, physicochemical, and chemical properties, interact with physical, physicochemical, chemical, and biological features of the soil, its phases (solid, liquid, and gaseous), as well as its components (mineral-organic complex, soil solution) and may lead to alterations in their properties [14–18]. This exchange is dependent on many factors, i.e. pH, concentration of metal ions in solution, and their speciation. The transport of inns in the environment begins in the liquid phase. This pathway is not only the manner in which ions translocate but also has significant importance for metal accumulation in plants and the food chain [10, 11, 19–21]. Therefore, the knowledge of the properties and behavior of new substances in particular elements of a natural environment does not only have cognitive, but also social aspects.

Among zeolites, clinoptilolite is the most common and the best studied one, not only due to its largest abundance in nature and lowest prices, but also the widest scope of its physicochemical properties [22]. This zeolite is characterized by the following features: large sorption and ion-exchange capacity, ion-exchange selectivity, properties of molecular sieve, catalytic activity, structural thermal stability at temperatures of up to 700–750°C. The chemical composition of zeolites determines their behavior under particular conditions. In an alkaline environment, these minerals are decomposed—their fibrous crystals collapse—mordenite converts into analcites. In an acidic environment, a zeolite can be completely deprived of cations, which in consequence produces a hydrated amorphous silica skeleton that retains its initial shape of crystal. Natural clinoptilolite is characterized by Si/AI ratio >4 as well as higher contents of Na^+ and K^+ cations in relation to Ca^{2+}, Ba^{2+}, and Sr^{2+}. When natural zeolites are applied, one should bear in mind that they are ecological material and do not show any harmful action neither to humans nor to animals. Therefore, zeolites found quite wide spectrum of application as additives to feed and fertilizers [23], as well as soil conditioning agents [24–26]. Ion-exchange ability and sorption capacity of natural zeolites can be used at gradual and uniform release of nutrients into the soil, which prevents against their quick elution [27]. Applying zeolites to the production of mineral fertilizers allows a gradual and controlled introduction of such necessary nutrients as potassium ammonium or phosphates into the soil. Moreover, fertilizers containing some addition of zeolites modified with Cu(II) ions can be applied to copper-deficient soils. Thus, it is possible to reduce the soil irrigation, because water is well retained within zeolite's structure, as well as to decrease soil acidity [2–4, 8, 28] and to reduce the temperature oscillations. These sorbents can also be effectively used as pesticide and herbicide carriers [29].

The group of goals, which the author of this chapter proposed to describe are based on own research and literature and focus on the influence of zeolites on the following quality indicators: changes in the physicochemical properties of certain soils (pH, sorption capacity, bases saturation degree, and amounts of Cd and Pb in soils), certain food quality factors connected to toxic substances and elements (ratios of Fe:Mn and K:Ca + Mg) as factors in plants (wheat and rape).

2. Methodology

The experimental unit during incubation studies consisted of a pot containing 0.5 kg of air-dried soil weight of natural origin, from the acidity soil class considered as acidic soils (pH range 4.5–5.5). The soil moisture content will be maintained at the level of 60% of the field water capacity, optimum for a proper growth and development of test plants. Common wheat (*Triticum aestivum* L.) of Opatka cv. was the test plant used for the soil incubation experiments. Twelve seeds will be sown in each pot. After emergence (KD = 11, according to Zadoks), the number of plants will be reduced to six. Plants will be harvested at full ripeness. Rape biomass was harvested at the shooting stage (KD = 20), according to Zadoks—grade proposed by the European Association for Plant Breeding. Variants of Pb experiment were composed by introducing lead salts (in the form of $Pb(NO_3)_2$) in the amount of 100 mg Pb/kg soil, immobilizing agents such as zeolites—clinoptilolite (Fluka) at the following rates: zeolite-1—300 mg/kg soil, zeolite-2—600 mg/kg soil. Variants of Cd-experiment were composed by introducing cadmium salts (in the form of $CdCl_2$) in the amount of 5 mg Cd/kg soil, immobilizing agents such as zeolites—clinoptilolite (Fluka) at the following rates: zeolite-3—15 mg/kg soil, zeolite-4—30 mg/kg soil. Both plants were growing in both Pb and Cd experiments.

The soil material was subjected to the following analyses: pH in 1 mol KCl /dm^3 at soil-solution ratio equal to 1:2.5, hydrolytic acidity—Hh, contents of exchangeable metal forms (Cd, Pb) in soils was determined in 1 M HCl at soil-solution ratio equal to 1:10. The extraction was supported by intensive mixing using rotational mixer for 1 h. Measurements will be made by means of atomic absorption spectrometry using the Hitachi Z-8200 device with Zeeman's polarization. The content of exchangeable ions (K, Na, Ca, and Mg) was also determined by means of extraction in 1 M CH_3COONH_4 and AAS determination (as above).

The plants' material was collected after harvesting. After drying at 70°C, plant samples were digested in concentrated H_2SO_4 with the addition of 30% H_2O_2 to accelerate the process. In achieved mineralized solutions, determinations of Fe and Mn ions were made. In addition, the following items were calculated: the sum of exchangeable alkali ($S = Na^+ + K^+ + Ca^{2+} + Mg^{2+}$), sorption capacity ($T = Hh + S$) expressed in mmol (+)/kg of soil as well as the alkali saturation degree ($V = S/T \times 100\%$), molar ratios of Fe:Mn and K:(Ca + Mg) for investigated plants as food quality factors, the achieved numerical data were processed statistically applying variance analysis with Tukey confidence semi-intervals at the significance level of 0.05.

3. Zeolites and some soil condition

Zeolites exerted their strongest influence on the pH values increase in the soil contaminated with lead compounds, namely at higher doses (**Figures 1** and **2**). During the second experimental year (under rapeseed), soil pH values decreased and the soil reaction became acidic instead of slightly acidic with oscillations around 4.5–5.5 (**Figures 1** and **2**). Many authors observed different impact of zeolites on the change in pH values [1–3, 7, 29] and on the decrease in mobility of various heavy metals in soils. The reactions could be also dependent on cadmium and lead chemistry, which is connected with the strength of alkalization of both elements [7, 10, 17, 18].

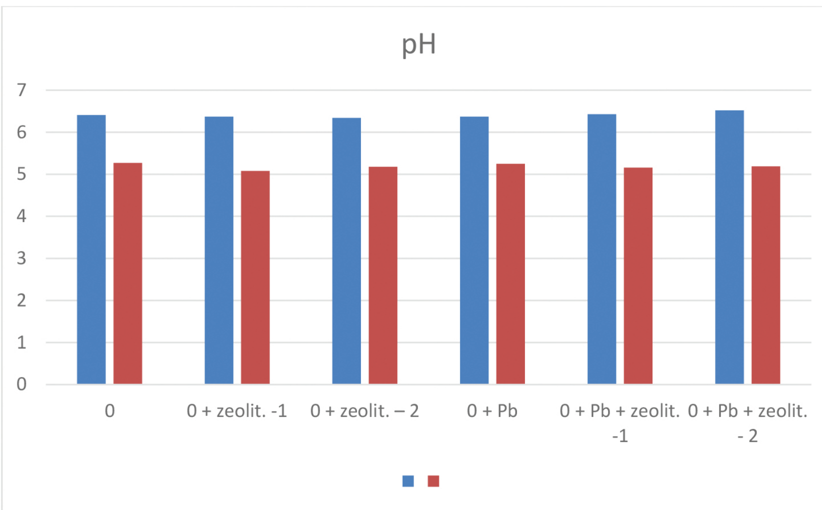

Figure 1. The pH values of soils with Pb and zeolites—own results—(blue color – under wheat, red color – under rapeseed).

Higher levels of the total sorption capacity were recorded in variants with the addition of zeolites in the presence of both heavy metals (**Tables 1** and **2**). It was found that, in comparison with the first year of experiments, the *T* value increased in the second year by over 8 mmol (+)/kg. The base saturation degree (*V*) was within the range of optimum limits and for Polish soils did not exceed 90%. The parameters of *V* were significantly differentiated between the tested plant species in both experimental years. The value of *V* indicators was found to be higher by about 10% in the first year of experiments as compared with the second year (**Tables 1** and **2**). A higher increase was also recorded for the variant with a double dose of zeolites (0 + Cd + zeolites-4) (**Table 2**).

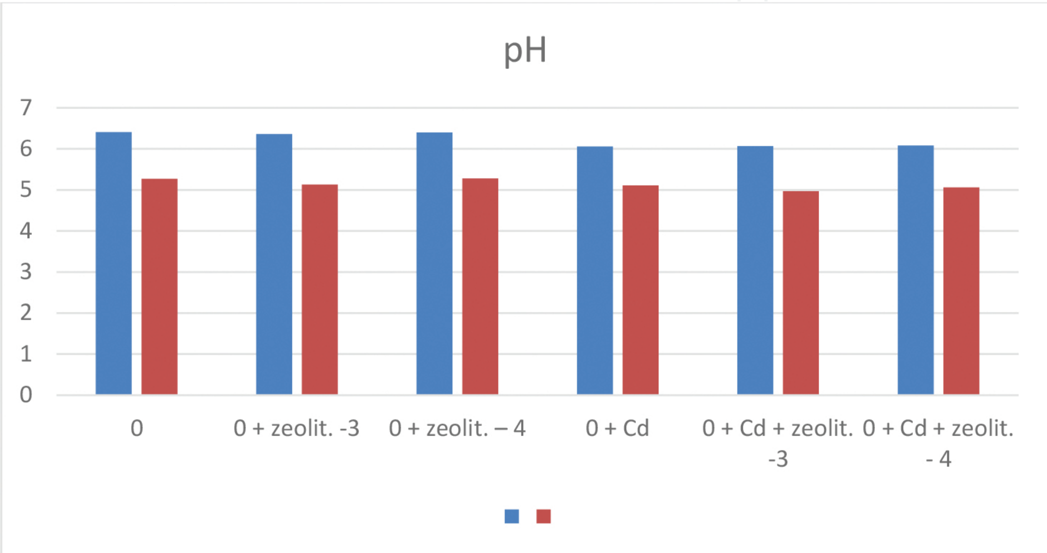

Figure 2. The pH values of soils with Cd and zeolites—own results—(blue color – under wheat, red color – under rapeseed).

No.	Variants (A)	T mmol (+)/kg		V (%)	
		Under wheat (B)	Under rapeseed (B)	Under wheat (B)	Under rapeseed (B)
1	0	57.03	71.12	80.72	70.99
2	0 + zeolites-1	59.01	73.07	81.83	68.94
3	0 + zeolites-2	57.40	76.11	81.68	70.93
4	0 + Pb	63.12	77.60	85.15	72.58
5	0 + Pb + zeolites-1	67.90	79.40	85.89	71.90
6	0 + Pb + zeolites-2	69.53	79.45	87.22	71.69
$LSD_{0.05}$	A	8.45		7.55	
	B	4.48		1.55	

Table 1. Total sorption capacity (*T*) and bases saturation degree (*V*) of investigated soils with Pb (own results).

No.	Variants (A)	T mmol (+)/kg		V (%)	
		Under wheat (B)	Under rapeseed (B)	Under wheat (B)	Under rapeseed (B)
1	0	57.03	71.12	80.72	70.99
2	0 + zeolites-3	57.98	75.21	80.79	69.35
3	0 + zeolites-4	59.29	76.61	80.81	72.33
4	0 + Cd	70.50	78.37	81.12	69.55
5	0 + Cd + zeolites-3	69.03	79.98	82.64	69.00
6	0 + Cd + zeolites-4	73.19	82.55	83.57	71.13
$LSD_{0.05}$	A	9.01		6.72	
	B	4.91		1.29	

Table 2. Total sorption capacity (*T*) and bases saturation degree (*V*) of investigated soils with Cd (own results).

Here, the presented results of the experiments revealed that the soil pH is largely determined by the presence of zeolites and also changes in toxic element contents in soil. Characteristics of the soil sorption complex indicate that applying immobilizing agents had an impact on the improvement of its properties through an increase in total sorption capacity (*T*) and bases saturation degree (*V*), both in variants with no heavy metals and lead-contaminated ones, which may be contributed to soil pH increase and, in consequence, a lower share of acidic cations. It was mainly zeolites at their double doses that affected the increase in total soil sorption capacity, which was also probably the consequence of pH changes. Those results could even be confirmed by other authors [22, 29]. Numerous authors [2, 7, 14, 16, 17] have reported that minerals in the soil contain permanent charges, while sorption capacity increases along with soil pH value, mainly due to the dissociation of H^+ and Al^{3+} ions originating from these permanent charges on mineral fragments of the sorption complex. To improve the physicochemical properties of soil is one of the basic conditions that sorbents used for the detoxication of soils contaminated with heavy metals should meet [21].

No.	Variants	Pb		Variants	Cd	
		Wheat grain	Rapeseed biomass		Wheat grain	Rapeseed biomass
1	0 + Pb	0.80	1.78	0 + Cd	2.98	32.85
2	0 + Pb + zeolites-1	0.85	3.40	0 + Cd + zeolites-3	2.82	23.70
3	0 + Pb + zeolites-2	0.70	3.00	0 + Cd + zeolites-4	2.74	27.83
	LSD 0.05	0.16	3.71	LSD 0.05	2.80	14.23

Table 3. The content of Pb and Cd in the investigated plants grown on soils with Pb and zeolites (own results).

The results revealed that applying sorbents contributed to a decrease in mobile lead ion concentrations in soil. In the soil under wheat, lead ion detoxication was observed after introducing a lower zeolite dose, whereas higher rates of the zeolite appeared to be the most efficient Pb^{2+} immobilizing agent in the soil under rapeseed. On the other hand, numerous authors [10, 17, 21] have reported the lower affinity of cadmium, as compared to lead ions, toward zeolites; here, presented results did not reveal that cadmium can be equally sufficiently bound by those minerals (**Table 3**).

It is necessary to emphasize that the reduction in cadmium concentration in both plants was observed (**Table 3**), although the pH in soil was almost at the same level in all variants with this element and zeolites—at around 6 under wheat and around 5 under rape (**Figures 1** and **2**). Such a clear effect was not observed in the Pb reduction. Many authors [4, 9, 28] have shown that zeolites can decrease cadmium toxicity more than other heavy metals. Other authors [5, 30] noted that rape and wheat showed different reactions to different heavy metal toxicity levels.

The increase in the cation sorption capacity is strongly associated with the decrease in toxic metals mobility within the soil environment. Increase in the total sorption capacity index results from the introduction of a material containing functional groups. These materials are clay minerals. Clay minerals having a larger number of pH-dependent sites (e.g. montmorillonite) are more important for heavy metals sorption, as opposed to those producing more pH-independent sites, e.g. kaolinite. Metal—solid phase in the soil bindings formed due to nonspecific sorption manifests a weaker character of bonds with the presence of water molecule between the metal and the adsorbent. Numerous studies revealed the immobilizing effect of zeolites, both natural and artificial, on toxic elements. Synthetic zeolites of the 13X and 4A types were found to reduce the availability of Pb by 70%, Cu by 57%, Ni by 53.5%, Zn by 67.5%, and Cd by 61%, as well as Pb content in tissues of certain plant species [21]. It was also reported that the addition of a natural zeolite, clinoptilolite, had positive effects on the increase in cation-exchangeable capacity (CEC) of the soil [2, 3, 21–23].

4. Zeolites and certain elements' ratios in plants as food security factors

The concept of culture (fertility) of soil means such a condition of the soil which provides growing plants with a sufficient amount of nutrients, water, and air, and is the result of many natural and soil-forming factors dependent on the climate, bedrock, and vegetation. The highest cereal yields can be usually obtained from soils abundant in high cultures (with an optimum content of available forms of plant nutrients such as Mg, K, Ca, P, N, and humus), with regulated relations between water and air and with the pH value close to neutral (pH 5.6–7.2) [13].

The present study revealed the influence of zeolites on the changing of investigated ratios such as Fe:Mn and K:Ca + Mg) (**Figures 3** and **4**). The presence of zeolites influenced positive regulation of Fe:Mn ratios in both investigated plants in the variations with Cd in soil (**Figure 4**). In the variations with Pb in soil (**Figure 3**) optimal values of Fe:Mn ratios were obtained only for wheat grain, not for rape, where lower manganese uptake was observed.

Many studies [6, 8, 9, 14] have shown that the varied concentration of heavy metals has substantial influence on other elements' uptake by plants.

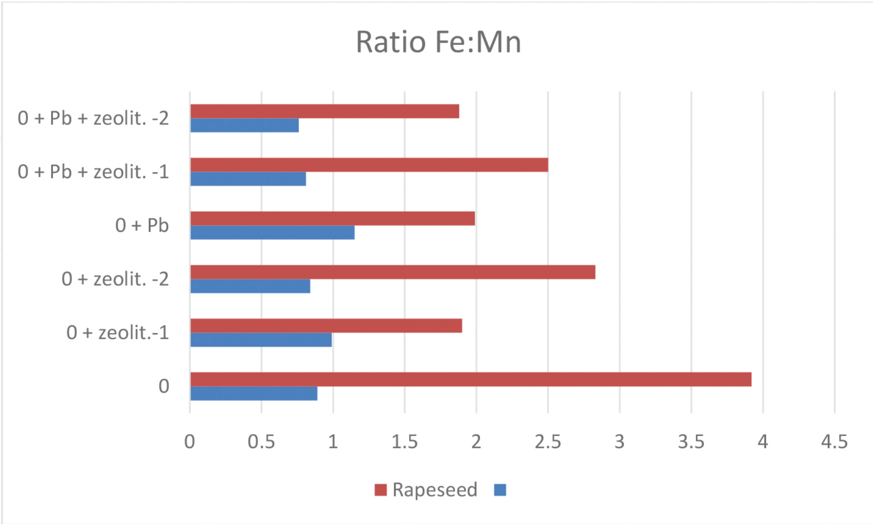

Figure 3. The influence of zeolites used for soils polluted with Pb on Fe:Mn ratio changing in wheat grain (blue color) and rapeseed biomass (red color)—own results.

The content of microelements in soils and their availability to plants depends on many factors [2–4]. Manganese deficit impairs metabolic functions of plants and reduces the sowing value of seeds. Feeding plants of winter and spring wheat with microelements has positive effects on the features of grain quality such as gluten content and sedimentation rate [4, 13, 31, 32].

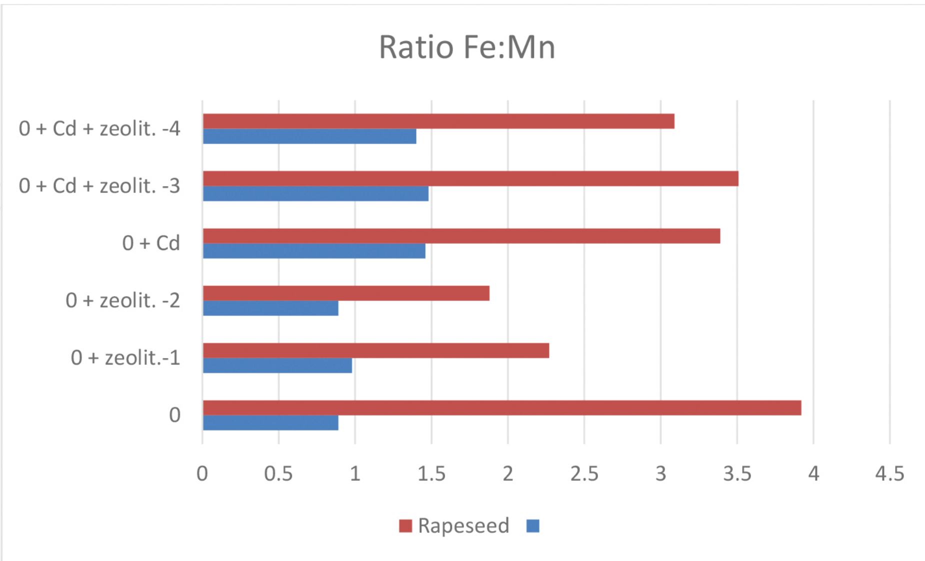

Figure 4. The influence of zeolites used for soils polluted with Cd on Fe:Mn ratio changing in wheat grain (blue color) and rapeseed biomass (red color)—own results.

In the case of K:(Ca + Mg) ratios, the presence of zeolites for the Pb and Cd immobilization, a stronger positive change was observed for wheat grain than for rape (**Figures 5** and **6**). Many authors [4, 9, 14] have shown that the optimal presence of K and Ca and Mg elements in raw materials is very important for food quality. The presence of undesirable substances in plant material entails a risk to consumer's health. The security of crop production is therefore closely linked to the status of the natural environment. Certain substances used a few dozen years ago have been interacting with the environment and the trophic chain until now, being subject to its continuous bioaccumulation [13, 20, 31]. The Polish production fields are characterized by the lack of so-called "elements of life" (Mg, Se). Magnesium deficiencies in the area of agricultural production result in deficiencies of these elements in plant material. Using zeolites for Cd and Pb immobilization in soils may also change the presence of K, Mg, and Ca in plants (**Figures 5** and **6**). The elements discussed above become parts of the food chain mainly through soils: solid surface (soil) attracts and retains the ions, atoms or the molecule layer. The sorption abilities of the soil result from the properties of the sorption complex made of soil colloids: clay minerals (smectites, vermiculite, illite, and kaolinite), crystalline and amorphous iron and aluminum oxides, amorphous minerals, humus, and clay-humus complexes [15–17, 19, 26].

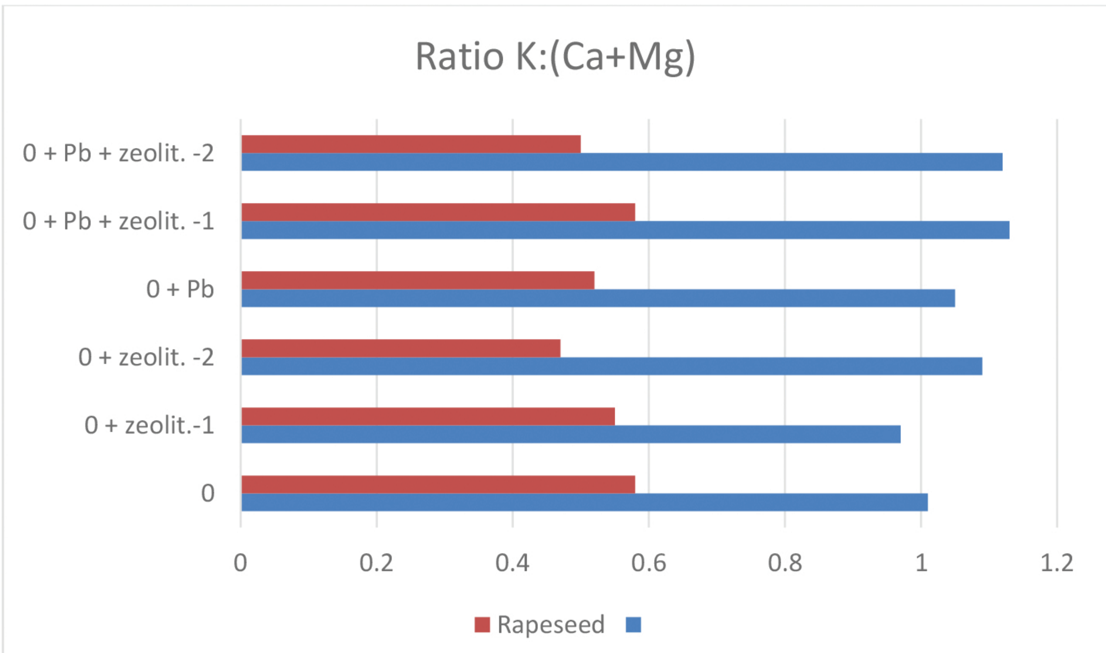

Figure 5. The influence of zeolites used for soils polluted with Pb on K:(Ca + Mg) ratio changing in wheat grain (blue color) and rapeseed biomass (red color)—own results.

Food of either plant or animal origin (sometimes also mineral) is consumed in order to provide the body with energy and nutrients. The basic unit of energy understood in this sense is kilocalorie. Such a measurement system makes it possible to estimate the amount of energy needed by the human body to regenerate itself. An insufficient amount of energy and a low intake of calories lead to hunger and subsequently to death. The daily number of calories required by a person depends on age, sex, body weight, type of work performed, and climate. The World Health Organization (WHO) has established that an adult person requires a minimum of 2200 cal/day to survive. The effects of qualitative malnutrition are not easily noticeable. People affected by it may have a normal body weight and still suffer from the effects of qualitative malnutrition. Vitamin and mineral salts deficiency can lead to serious health issues, such as significantly greater susceptibility to infectious diseases, loss of vision, anemia, coma, reduced knowledge acquisition skills, intellectual development disorder, various forms of physical deformities, and finally death. The most common deficiencies involve the following three elements: vitamin A, iron, and iodine [4, 12, 13, 20, 29, 31, 32].

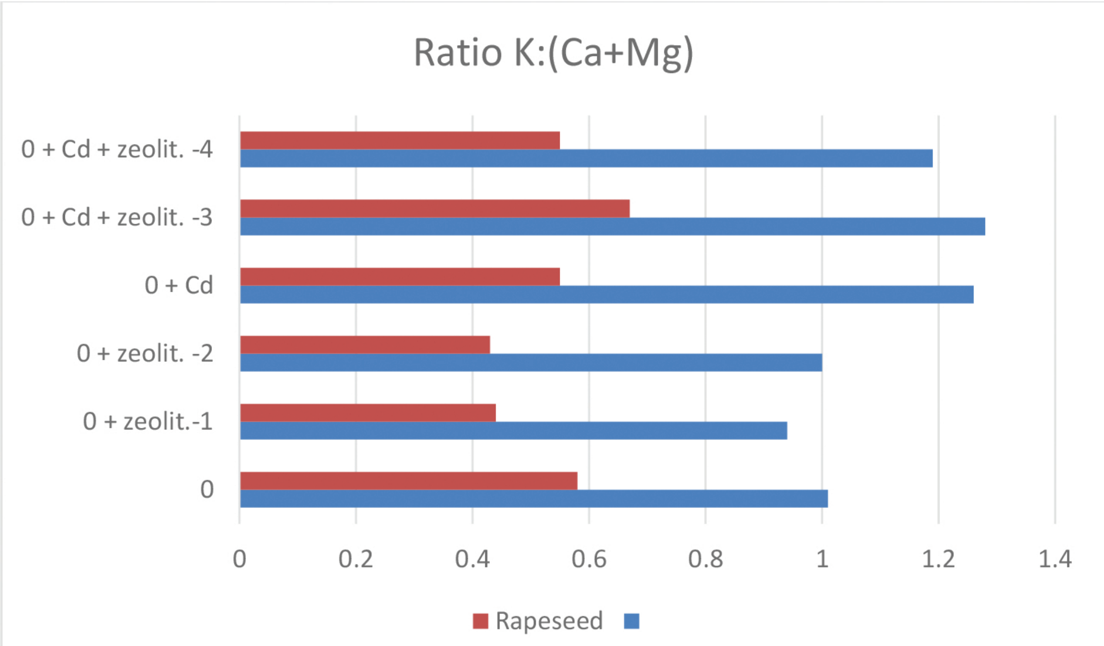

Figure 6. The influence of zeolites used for soils polluted with Cd on K:(Ca + Mg) ratio changing in wheat grain (blue color) and rapeseed biomass (red color)—own results.

5. Summary

It is important to know that half the people suffering from micronutrient deficiency are usually afflicted by cumulative deficiencies of elements, i.e. they are simultaneously lacking several vitamins and minerals in their diet. Qualitative malnutrition is a direct or indirect cause of half of deaths among children under five in the world. As a consequence of deliberate intervention in agro-ecosystems, a man can control their productivity and increase the amount of produced biomass, which can be utilized as food for humans, feed for animals, and raw material for many industry branches. Future of the agriculture should therefore be based on a variety of plants species, from which new, healthier, and less processed goods are made. Such approach promotes not only the safety, but also the nutritional sovereignty of societies.

Zeolites have appeared to be promising binding agents for lead ions mobility and for cadmium at lower doses. Also soil pH values have been changing due to applied sorbents, largely determining the forms of toxic metals in soils. Zeolites improved properties of the soil sorption complex through the increase of total sorption capacity as well as base saturation degree, which met the necessary condition of the lack of toxicity to immobilization of the heavy metals contaminated soils. Zeolites influence also the changing of Fe:Mn and K:(Ca + Mg) ratios in the investigated plants like wheat and rape. These factors can describe the quality of food products made from these plants.

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