

Effects of chemical elements in the trophic levels of natural salt marshes

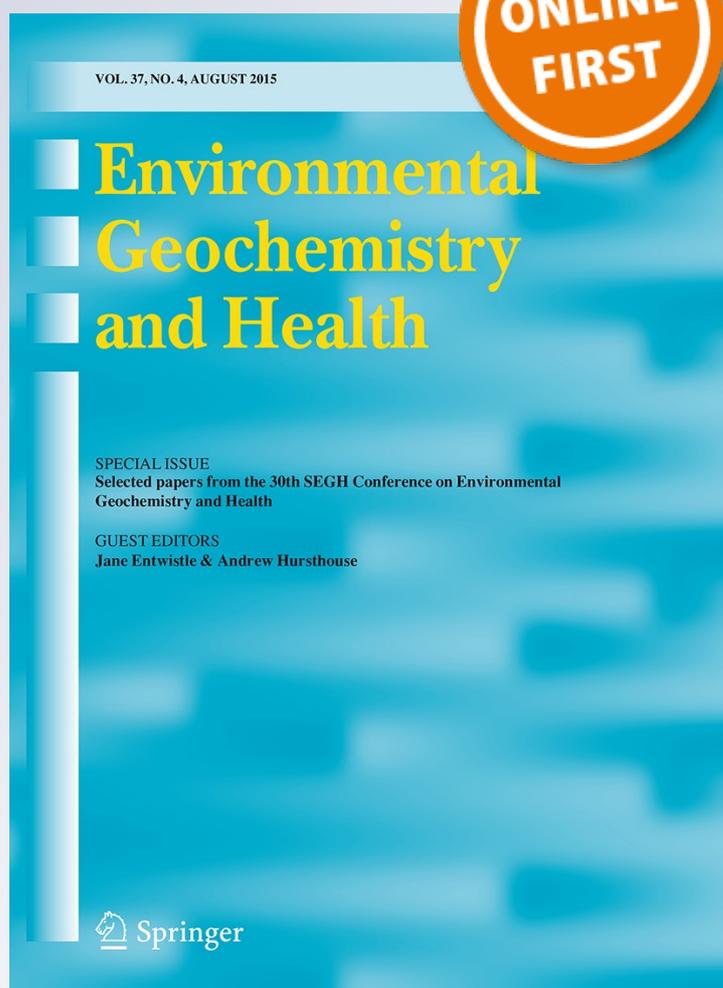
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Effects of chemical elements in the trophic levels of natural salt marshes

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Abstract The relationships between the bioaccumulation of Na, K, Ca, Mg, Fe, Zn, Cu, Mn, Co, Cd, and Pb, acidity (pH), salinity (Ec), and organic matter content within trophic levels (water–soil–plants–invertebrates) were studied in saline environments in Poland. Environments included sodium manufactures, wastes utilization areas, dumping grounds, and agriculture cultivation, where disturbed Ca, Mg, and Fe exist and the impact of Cd and Pb is high. We found Zn, Cu, Mn, Co, and Cd accumulation in the leaves of plants and in invertebrates. Our aim was to determine the selectivity exhibited by soil for nutrients and heavy metals and to estimate whether it is important in

elucidating how these metals are available for plant/animal uptake in addition to their mobility and stability within soils. We examined four ecological plant groups: trees, shrubs, minor green plants, and water macrophytes. Among invertebrates, we sampled breastplates *Malacostraca*, small arachnids *Arachnida*, diplopods *Diplopoda*, small insects *Insecta*, and snails *Gastropoda*. A higher level of chemical elements was found in saline polluted areas (sodium manufactures and anthropogenic sites). Soil acidity and salinity determined the bioaccumulation of free radicals in the trophic levels measured. A pH decrease caused Zn and Cd to increase in sodium manufactures

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and an increase in Ca, Zn, Cu, Cd, and Pb in the anthropogenic sites. pH increase also caused Na, Mg, and Fe to increase in sodium manufactures and an increase in Na, Fe, Mn, and Co in the anthropogenic sites. There was a significant correlation between these chemical elements and Ec in soils. We found significant relationships between pH and Ec, which were positive in saline areas of sodium manufactures and negative in the anthropogenic and control sites. These dependencies testify that the measurement of the selectivity of cations and their fluctuation in soils provide essential information on the affinity and binding strength in these environments. The chemical elements accumulated in soils and plants; however, further flow is selective and variable. The selectivity exhibited by soil systems for nutrients and heavy metals is important in elucidating how these metals become available for plant/animal uptake and also their mobility and stability in soils.

Keywords Trophic links · Saline environments · Ecotoxicology · Disturbed areas · Heavy metals · Acidity

Introduction

Trophic links are of great importance in understanding the processes by which chemical elements circulate in the environment and their role at various trophic levels. Most elements are released to the environment in the form of compounds as a result of human activity and biogeochemical processes. When these compounds reach the soil, they start to accumulate and thus become available to plants (Fergusson 1990;

Merian 1991; Prasad et al. 2006). The distribution of metals within these plants is the result of differences in the amount and rate of metals input, primarily by root pressure on the one hand and their release into the environment, mainly through the transpiration of the leaves on the other. Some metals accumulate in roots, probably because of some physiological barriers for the transport of toxic elements. The metals essential for metabolic needs are easily transported to the above-ground parts of the plant (Kastratović et al. 2013). The intensity and degree of circulation of these elements depend on their chemical form and therefore on the ability to pass between different components of the environment, i.e., on their bioavailability, expressed as a proportion between their concentrations at two different trophic levels. The higher this proportion is for an element, the higher is its bioavailability on a given level (Wolf et al. 1988; Prasad et al. 2006). The chemical absorption and distribution of metals in plants depend on many factors including the plant species and its characteristics, the type of metal and its physical and chemical properties and ecological environmental factors (Kastratović et al. 2013).

The bioavailability of heavy metals in salt-marsh sediments is low compared to terrestrial systems with oxidized soils. However, many pollutants are stabilized and immobilized, which can affect the availability of heavy metals in the salt-marsh sediments (Stolz and Oremland 1999) and how they perform other ecosystem services (Siddique and Aktar 2012). Banus et al. (1975) demonstrated that heavy metals can be partly retained and accumulated (Gambrell 1994; Williams et al. 1994) in the salt-marsh sediment. Interdependencies between elements at different trophic levels are dependent on the processes which take place while the elements are passing from one level to another (Richards 1979; Kabata-Pendias and Mukherjee 2007), e.g., transfer of elements from soils to plants is conditioned by physiological processes including transpiration ability and growth intensity (Richards 1979, Kabata-Pendias and Mukherjee 2007; Kabata-Pendias and Pendias 2010). Simultaneously, soils are characterized by a high activity of microorganisms, fungi, and invertebrates. They are dependent on the organic matter constantly supplied by plants. Basic food demands of soil fauna are covered by plant roots and other organic matters present in the soil. The high accumulation in the roots could be a reaction of

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the plant to the toxicity of metals, which are immobilized in the vacuoles of the roots (Kastratović et al. 2013). However, these resources can only exist due to the constant photosynthetic activity, which is dependent on the water and mineral resources absorbed by plant roots. Therefore, biological activity and the circulation of elements in soils, plants, and fauna living there are interdependent (Richards 1979; Wolf et al. 1988; Prasad et al. 2006). Soils also differ from water and air with regard to functioning, location, and physical state, so the danger of toxic metals and their constant influence on chemical elements in ecosystem are significant. As a result of the accumulation of chemical elements, soil is an important component of the environment which determines plant and animal existence in a given area (Wolf et al. 1988; Kabata-Pendias and Pendias 2010). Thus, it is important to find suitable indicators of environmental pollution, which are simultaneously linked to the trophic levels. Both plants and animals are able to absorb elements depending on their chemical form in the soil. The rate of uptake by plants additionally depends on transpiration ability, soil properties, organic and mineral compounds (Hopkin 1989) and to higher links in the trophic chains. It is dependent on the intensity of ciliary cuticle mechanisms, the efficiency of trachea-bronchial system, and intestinal absorption (Martin and Coughtrey 1982; Merian 1991; Prasad et al. 2006). Furthermore, transportation of elements from soils to plants and animals is influenced by element–element interactions (Martin and Coughtrey 1982; Kabata-Pendias and Mukherjee 2007; Kabata-Pendias and Pendias 2010). The absorption and distribution of elements depend mainly on the solubility of lipids and their compounds. This is a consequence of their ability to penetrate lipid membranes by organic compounds, which penetrate and accumulate in an organism more frequently and easily than inorganic compounds (Hapke 1991). Moreover, the inflow of chemical elements is higher than their outflow in most trophic chains which start in soils. Thus, their accumulation takes place. Further circulation of these elements is also dependent on different factors, such as water circulation, soil properties, acidity, and salinity (Ma et al. 1983; Sanders and Adams 1987). Salt marshes are one of the most productive ecosystems, and they provide a buffer zone between terrestrial and aquatic ecosystems (Rajendran et al. 1993). Physical, chemical, and biological interactions between freshwater

and saltwater systems can have a significant influence on the transportation of trace elements and heavy metals in the estuarine environment (Ip et al. 2006). Salt marshes act as protective filters and repositories for runoff of pollutants (Teal and Howes 2000), pathogens, and different types of nutrients (Weis and Weis 2003).

Most papers examining the circulation of chemical elements in the trophic chains deal with the relationships between soils and plants (Kuo et al. 1985; Sanders and Adams 1987; Alloway et al. 1990; Adams et al. 2005; Prasad et al. 2006; Kabata-Pendias and Pendias 2010). Some studies refer to the circulation of elements in the chains between soil–plants–soil fauna and epigeic fauna (Ma 1982; Ma et al. 1983). Some papers discuss the influence of heavy metals on soils with different contamination levels (Prasad et al. 2006; Kabata-Pendias and Pendias 2010) and on the reaction of plants to heavy metals (Sawicka-Kapusta 1990a, b; Sawicka-Kapusta et al. 1990; Henriques and Fernandes 1991; Kabata-Pendias and Pendias 2010). Only Andrews et al. (1989a, b) investigated the complete food chain for small rodents.

Toxic heavy metals play a very specific role in the inflow of microelements in the trophic chain. They are nonessential metals, recognized as extremely significant pollutants due to their large solubility in water and high toxicity. They are also persistent in most organisms, being most toxic to vascular plants (Ghosh and Singh 2005; Paton et al. 2005; Ayyappan et al. 2014; Chakraborty et al. 2014; Cosio et al. 2014). Total Cd levels exceeding 8 mg kg^{-1} , or soluble levels exceeding 0.001 mg kg^{-1} , are considered toxic to plants (Kabata-Pendias and Mukherjee 2007). Cadmium is currently considered a priority pollutant by the European Community (Carmen et al. 2013) and USA (USA EPA 2001; OSPAR 2004). Cadmium effects can be observed at both the organism and population levels, but it may also enter the food chain, where it becomes biomagnified posing a potential threat to community and ecosystem health (Hu et al. 2010). Numerous studies reported the accumulation of toxic metals in roots of water macrophytes. However, conclusions about the further translocation through the plant were varied (Kastratović et al. 2013). Cd and Pb are two of the most important toxic metals, and the fact that they are mostly absorbed by roots suggests that the root acts as a filter protecting the plant from undesirable effects. Mn and Cu are essential nutrients for

plants, which are functional components of nitrate assimilation and indispensable elements of many enzyme systems in plants. Zn is essential for plants, mainly as a part of several metalloenzymes. In most aquatic ecosystems, Zn^{2+} can be toxic for organisms (Kastratović et al. 2013), while Pb and Hg are potentially dangerous and toxic to most forms of life and are relatively accessible to aquatic organisms. They are present in aquatic environments in areas with heavy vehicular traffic near cities. Other papers (Burke et al. 2000; Prasad and Freitas 2003; Ayeni et al. 2010; Kastratović et al. 2013) recorded the highest concentration of toxic metals in the roots of water macrophytes, while only small amounts were transported to other parts of plants. Salinity is a major adverse environmental constraint to plant productivity, limiting the utilization of agrocenoses (Dendooven et al. 2010; Ayyappan et al. 2013). Such cultivated land is affected by soil salinity and acidity (Askaril et al. 2006). High levels of soil salinity can cause water deficits, ion toxicity, and nutrient deficiency, leading to molecular damage and plant death (Maggio et al. 2010; Teuchies 2012; Prasad and Freitas 2003). Many halophytes have a high metal tolerance, which is strongly linked to traits associated with salt tolerance. Some halophytes are also considered as hyperaccumulators of certain metals (Reboreda and Cacador 2007; Pastor and Hernandez 2012; Chakraborty et al. 2014). Halophytic plant species have been tested for their possible use in remediation of salt-affected soils exposed to toxic metals (Ravindran et al. 2007; Bonanno and Giudice 2010; Rabhi et al. 2010; Bonanno 2011; Koyro et al. 2011; de Souza et al. 2012; Ayyappan et al. 2013; Duarte et al. 2013).

There are few studies referring to the concentration of chemical elements and their circulation in the full trophic chain, i.e., starting from soil and ending with vertebrates, including humans. To date, no investigations considered these problems as toxins flow through the food chain from soils to host plants, phytophags, entomophags, and higher consumers. Only one analysis concerning the relationships between plants and invertebrates has been undertaken (Fritioff et al. 2005, Notten et al. 2005; Prasad et al. 2006; Ayeni et al. 2010; Siddique and Aktar 2012; Teuchies 2012; Batzer 2013).

The subject of numerous studies has been physiological responses of plants in the controlled conditions. However, there is also still a need for research of interdependencies of glycophytes and halophytes with

multiple biotic and abiotic factors in their natural environments. Thus, the aim of this paper was to investigate morphological and biochemical variations in plants in salted and alkaline anthropogenic environments in disturbed Kujawy region. Actually patches dominated by common glasswort *Salicornia europea* occur only in the industry area next to sodium factories (Piernik 2006) in this region. Some of species of halophytes have been settled on this saline area as a result of breakdowns of brine pipelines and sewage collectors. After removing the damage, halophytes remain there for 2–3 years and then retire as a result of natural process of salt leaching down in soil and the development of glycophytes (Piernik 2003). However, the main species expansively appearing on salty meadows, especially after cutting out of their cultivation, is common reed *Phragmites australis*. It gradually eliminates photophilous halophytes from their habitats and causes their degradation. It is thus important to estimate the impact of edaphic factors (salinity, acidity, nutrients availability (organic matter content) on the growth and changes of biochemical parameters (e.g., malondialdehyde and proline) in roots and green parts of both glycophytes and halophytes in their natural environments. We can thus evaluate the range of plant responses to differentiated environmental stressors, i.e., concentration and destabilization of chemical elements' management, which allow compare adaptation strategies to these conditions.

Thus, the objective of this study was also to investigate the effects of chemical elements and trophic relationships in saline and acidulated anthropogenic environments. We examined the dependencies and interactions of Ca and the accumulation of heavy metals and soil acidity (pH), soil salinity (electrolytic conductivity E_c) and organic matter content (OMC) of different environments. We further established the role of trophic links in the bioaccumulation and bioavailability of the macroelements Na, K, Ca, Mg, the microelements Fe, Zn, Cu, Mn, Co, and the toxic heavy metals Cd and Pb in differentiated disrupted salted environments within the full trophic chain (soils–plants–invertebrates). Four ecological groups included plants: trees, shrubs, minor green plants, and water macrophytes were analyzed. Among the invertebrates, we sampled breastplates *Malacostraca*, small arachnids *Arachnida*, diplopods *Diplopoda*, small insects *Insecta*, and snails *Gastropoda*. These enabled the

estimation of the bioindicative properties of the trophic chain and also its significance in surrounding agrocenoses, as the level of free radicals is relatively high, and specific underground and hydrological circumstances and biogeochemical properties exist there (Kabata-Pendias and Mukherjee 2007; Kabata-Pendias and Pendias 2010). We thus determine the selectivity exhibited by soil systems for nutrients and heavy metals and to estimate its importance in elucidating how these metals become available for plant/animal uptake with reference to their mobility and stability in soils.

Study area

The investigations were carried out in selected saline areas of Kujawy region (central Poland) in the Inowrocław Region of Ecological Danger IRED (an area affected by salinity, acidification, disturbed levels of Ca, Mg, and Fe and toxic heavy metals). These areas were in various degrees of degradation due to discharge from sodium manufactures in Mątwy and Janikowo (Inowrocław district) hence labeled as “sodium manufactures” (1); wastes utilization in Giebnia and surrounds which contained very polluted areas due to industrial manufacturing which hereafter are labeled as “anthropogenic environments” (2); Pakość and surrounded districts containing dumping grounds for wastes and agricultural cultivation (agrocenoses), also labeled as “anthropogenic environments” (3); and control, unpolluted areas, i.e., not contaminated by anthropopression and relatively pure environments without the impacts of industry and agriculture. These control sites included areas along the Noteć River (trough and flood water) and areas around very small towns and agrocenoses of Złotniki Kujawskie and Borkowo (about 30 km away). These areas are labeled as “control” (4); Fig. 1.

Materials and methods

Field studies were carried out from 2006 to 2010 between April and September, with samples taken from the surfaces (every 3 days). Fifty samples of water, soil, plants, and invertebrates were collected from each of the agricultural sites (according to Górny

and Grüm 1993 and Demirezen and Aksoy 2006) in IRED. Measures of acidity (acidification), electrolytic conductance (salinity), disturbed Na, Ca, Mg, and Fe, toxic heavy metals Cd and Pb were recorded where a high degree of natural and anthropogenic degradation was observed. Four ecological groups of plants: trees, shrubs, minor green plants and water macrophytes were also sampled. As for invertebrates, we sampled breastplates *Malacostraca*, small arachnids *Arachnida*, diplopods *Diplopoda*, small insects *Insecta*, and snails *Gastropoda*.

The chemical elements studied were divided into three groups based on different physiological impact on the organism as follows: macroelements Na, K, Ca, Mg (1); trace elements Fe, Zn, Cu, Mn, Co (2); and toxic heavy metals Cd and Pb (3). Salinity (electrolytic conductivity E_c) and acidity (pH) of soils were simultaneously recorded.

The soil samples were dried by using a drying Memmert laboratory (in a temperature of 65 °C to a constant mass) and then were homogenized in a porcelain mortar and sieved through a 1-mm mesh. The roots were purified from the remnants of the soil under a stream of running water and washed three times with distilled water. Similarly, ground parts of plants were washed three times with distilled water. The material was separated into two parts. The portion for biochemical analysis was homogenized and stored frozen at a temperature of –80 °C. Part of the samples intended for analysis of chemical elements content was dried similar to the samples of soil at a temperature of 65 °C using the Memmert drying system and then was homogenized in a porcelain mortar.

The pH of soils was determined by potentiometric method according to the standards of ISO 10390. The sample of the soil material (10 g of dry weight) was placed into a volumetric flask, and 25 ml of distilled water was added (the active acidity; pH (H₂O)). The potential acidity; pH (KCl) was determined in the same way, i.e., 10 g soil and 25 ml of 1 M KCl were placed into a volumetric flask. Then, they left for 24 h and pH was measured using a pH meter of CP-501 model by Elmetron Co. with using the electrode of type EPP3 (by Elmetron).

Electrolytic conductivity (E_c) of soils was determined using the method of conductivity according to the standard of ISO 11265+ AC1. In a volumetric flask, 15 g of homogenized soil and 30 ml of distilled water were mixed. The measurement of organic soils

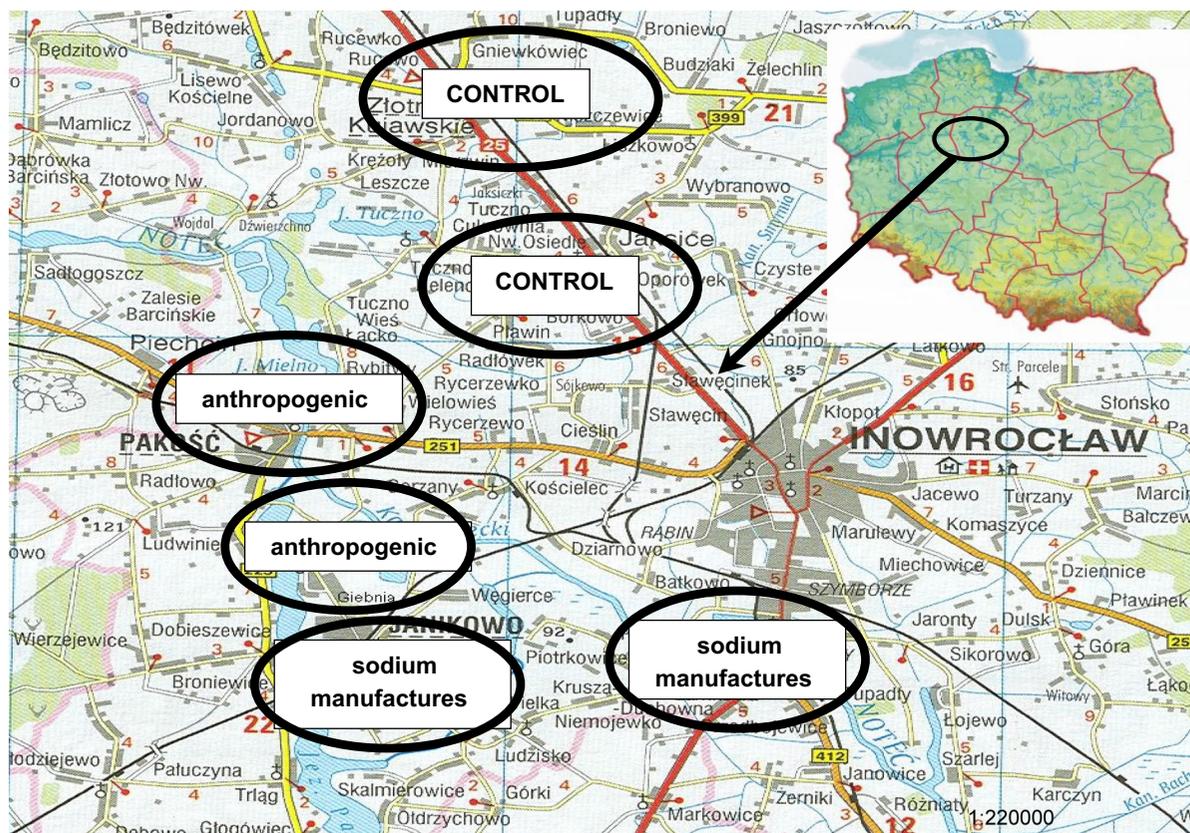


Fig. 1 Study area: the Inowrocław Region of Ecological Danger (central Poland); www.maps.google.pl, modified

salinity was determined in solutions of homogenized soil in which the ratio of dry mass of soil to H_2O was 1:5. The flask content was shaken for 1 h. The electrolytic conductivity (E_c) was measured by electrode in the upper layer solution with using a conductivity meter (conductometer of type Elmetron CC-401). The measured values of electrolytic conductivity were given in millisiemens ($mS\ cm^{-1}$).

The content of organic matter (OMC) was determined on the basis of the method for the determination of organic carbon. The percentage of organic carbon content was determined using the roasting method based on the methodology reported by Szczepaniak (1996) and Więckowska (1997). The samples of 2 g dry matter were heat treated and processed with a high temperature of $540\ ^\circ C$ in a muffle furnace. The roasting time was 6 h. Then, samples were subsequently cooled in a desiccator and weighed to the nearest 0.01 g. The reference method was a thermogravimetric analysis (thermogravimetric analysis)

performed using the thermoanalyzer, i.e., simultaneous thermal analyzer TGA–DTA by Thermal Analysis TA Instruments of SDT 2960. The types of analysis parameters were: the attempt atmosphere, the air with temperature range $20\text{--}1000\ ^\circ C$, heating rate: $10\ ^\circ C\ min^{-1}$.

Samples for chemical analyses were weighed and dried to a constant mass at a temperature of $65\ ^\circ C$ using a Memmert electronically controlled drying oven ULE-600, which is covered by the European Union Directive 93/42/UE. Dried samples were then homogenized with the aid of a porcelain pestle and mortar. Invertebrates were such that each taxonomic group in a given habitat had a total dry weight of the sample of about 50 mg. Such an amount was then used to analyze the concentration of chemical elements by the AAS method. Determinations of Ca and heavy metal concentrations in each sample was preceded by a mineralization process, which was done using Berghof Speedwave MWS-2 system (microwave

pressure digestion unit with built-in in situ temperature measurement), using 1.5 ml of nitric acid 65 % pure for analysis by Sigma-Aldrich to receive clear solution. The content of all elements ($\mu\text{g kg}^{-1}$; ppm of dry weight) was then determined according to Weltz (1985) with use of PerkinElmer AAnalyst 800-RW0683/3PYC AAS spectrophotometer. Standard curves were prepared using standardized Merck samples.

The concentration of chemical elements in the samples of water, soil surface layer, soil deeper layer, plants and invertebrates was obtained. Water samples were taken from water reservoirs adjacent to areas from which soil and invertebrate samples were taken. These samples were taken from the reservoirs at a depth of 0.5–1.0 m and sealed in 250 ml polyethylene containers. Samples of soils were taken from the surface and a deeper layer 20–40 cm below the surface, according to the methods of Górny and Grün (1993; see below) based on observations made previously that heavy metals falling to the ground are mainly accumulated in these layers (Prasad et al. 2006; Kabata-Pendias and Pendias 2010).

Invertebrates living on the soil surface were caught in 1 l containers dug directly into the soil (Barber's method). The individuals living on plants were obtained using an entomological sweep net (Górny and Grün 1993; Southwood and Henderson 2000; Schauff 2001). The pitfall traps were a plastic container (diameter 95 mm, volume 1000 ml) sunk into the soil so that the mouth is level with the soil surface. The traps were filled with approximately 150 ml of ethylene-glycol solution (1:2) with a detergent added to reduce surface tension. Pitfall traps on each unit were used from 15th of May to 15th of June, the time of main activity of invertebrates. Insects, spiders, and snails on terrestrial vegetation were collected with a sweep net (30 cm diameter). Twenty-five sweeps were made for each sample. All collected specimens were removed on two occasions during trapping and placed in 70 % alcohol and analyzed in the laboratory. Invertebrate specimens were stored as wet material either in ethanol 70 % or Hoyer's medium or Oudemans fluid (breastplates *Malacostraca*, small arachnids *Arachnida*, diplopods *Diplopoda*, small insects *Insecta*, snails *Gastropoda*) as appropriate. Snail samples were treated by tranquilizer (isoflurane) and then classified to species level according to a key (for references see below). Larger

specimens of arachnids and insects were stored as dry specimens in boxes (a collection). These were subsequently identified by external morphology using a Nikon SMZ 1000 stereo-microscope and Nikon Eclipse E 200 microscope. Specimens of insects (imagines), woodlice, and snails were identified down to species level using German keys (Freude et al. 1966, 1967, 1969, 1971, 1979, 1983, 2004) and Polish keys (Lis 2000; Radchenko et al. 2004; Wiktor 2004). A full list of all invertebrates collected from selected saline areas of Inowrocław Region of Ecological Danger (central Poland) from 2006 to 2010 is given in Table 1.

Plants were categorized into four ecological groups: (1) trees—*Acer platanoides* L., *Betula verrucosa* Roth., *Populus alba* L.; (2) shrubs—*Sambucus nigra* (L.), *Euonymus europaeus* (L.); (3) minor green plants—*Cirsium arvense* (L.), *Tanacetum vulgare* L., *Arctium tomentosum* L., *Urtica dioica* L., *Cichorium intybus* L., *Hieracium alpicola* L., *Achillea millefolium* L.; and 4) water macrophytes—*Phragmites australis* (Cav.). Plants were measured on the basis of results by Szafer et al. (1986) and Rutkowski (2011). Among the plants we analyzed roots and leaves separately, and among invertebrates we analyzed all individuals.

Statistical analysis

The analysis of the results was performed using the statistical package Statistica v. 10.0 for Windows 8 (www.Statsoft.pl). The results were expressed as arithmetic mean \pm standard deviation (SD), which are the statistical standards with collections of descriptive statistics of parametric data (arithmetic mean \pm SD). Significance of differences of levels of chemical elements in the trophic levels (water, soils, roots, green parts of plants (only leaves), invertebrates) from different environments was set at $p < 0.05$. All data were tested using the Shapiro–Wilk test for the distribution of the data set, in accordance with the requirements of the statistical methods. Data not normally distributed were log-transformed. Significant differences in element levels in the trophic links (water, soils, roots, green parts of plants (only leaves), invertebrates) from different environments (significance level at $p < 0.05$) were examined using one-way ANOVA followed by a multiple range test (significance level at $p < 0.05$) using the RIR-Tukey post hoc test (test of reasonably important difference

Table 1 Invertebrates collected from selected areas of the saline Inowrocław Region of Ecological Danger (central Poland) from 2006 to 2010 (A—sodium manufactures, B—anthropogenic environments, C—control)

Classis	Ordo	Familia	Species	Environment	<i>n</i>
Arachnida	Opiliones	Phalangidae	<i>Phalangium</i> spp.	C	32
Arachnida	Araneae	Linyphiidae	spp.	C	42
Diplopoda	Julida	Julidae	spp.	B	4
Gastropoda	Pulmonata	Helicidae	<i>Cepaea hortensis</i> (Müll., 1774)	C	1
Gastropoda	Pulmonata	Helicidae	<i>Arianta arbustorum</i> L., 1758	C	4
Gastropoda	Pulmonata	Helicidae	<i>Cepaea hortensis</i> (Müll., 1774)	B	64
Gastropoda	Pulmonata	Helicidae	<i>Arianta arbustorum</i> L., 1758	B	87
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Dyschiriodes globosus</i> Herbst, 1784	A	1
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Acalles camelus</i> (Fabricius, 1792)	A	4
Insecta	Coleoptera	Coccinellidae Latreille, 1807	<i>Subcoccinella vigintiquatuorpunctata</i> (L., 1758)	A	1
Insecta	Coleoptera	Tenebrionidae Latreille, 1802	<i>Crypticus quisquilis</i> (L., 1761)	A	1
Insecta	Coleoptera	Byturidae Thomson, 1859	<i>Byturus ochraceus</i> (Scriba, 1790)	A	11
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Phyllobius arborator</i> (Herbst, 1797)	A	1
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Strophosoma albolineatus</i> Seidlitz, 1867	A	2
Insecta	Coleoptera	Elateridae Leach, 1815	<i>Cardiophorus asellus</i> Erichson, 1840	A	1
Insecta	Coleoptera	Cholevidae Kirby, 1837	<i>Catops fuscus</i> (Panzer, 1794)	A	1
Insecta	Coleoptera	Hydrophilidae Latreille, 1802	<i>Cercyon haemorrhoidalis</i> (Fabricius, 1775)	A	2
Insecta	Coleoptera	Elateridae Leach, 1815	<i>Agrypnus murinus</i> (L., 1758)	A	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Notiophilus aquaticus</i> (L., 1758)	C	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Carabus nemoralis</i> Müll., 1764	C	8
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Pterostichus melanarius</i> (Illiger, 1798)	C	1
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Otiorhynchus ovatus</i> (L., 1758)	B	2
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Phyllobius arborator</i> (Herbst, 1797)	B	2
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Acalles echinatus</i> (Germar, 1824)	B	2
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Sitona lineatus</i> (L., 1758)	B	1
Insecta	Coleoptera	Silphidae Latreille, 1807	<i>Thanatophilus sinuatus</i> Fabricius, 1775	B	1
Insecta	Coleoptera	Silphidae Latreille, 1807	<i>Silpha carinata</i> Herbst, 1783	B	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Amara equestris</i> (Duftschmid, 1812)	B	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Harpalus affinis</i> (Schrank, 1781)	B	10
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Harpalus tardus</i> (Panzer, 1797)	B	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Panagaeus bipustulatus</i> (Fabricius, 1775)	B	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Curtonotus aulicus</i> (Panzer, 1797)	B	3
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Harpalus luteicornis</i> (Duftschmid, 1812)	B	1
Insecta	Coleoptera	Silphidae Latreille, 1807	<i>Nicrophorus vespillo</i> (L., 1758)	C	1
Insecta	Coleoptera	Cantharidae Imhoff, 1856	<i>Cantharis livida</i> L. 1758 v. <i>rufipes</i> Herbst, 1784	C	1
Insecta	Coleoptera	Staphylinidae Latreille, 1802	<i>Ocyopus fuscatus</i> (Gravenhorst, 1802)	C	4

Table 1 continued

Classis	Ordo	Familia	Species	Environment	<i>n</i>
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Carabus nemoralis</i> Müll., 1764	A	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Nebria brevicollis</i> (Fabricius, 1792)	A	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Harpalus rufipes</i> (Degeer, 1774)	C	4
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Leistus rufomarginatus</i> (Duftschmid, 1812)	C	2
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Asaphidion pallipes</i> (Duftschmid, 1812)	C	1
Insecta	Coleoptera	Carabidae Latreille, 1802	<i>Ophonus puncticollis</i> (Paykull, 1798)	C	1
Insecta	Coleoptera	Byturidae Thomson, 1859	<i>Byturus ochraceus</i> (Scriba, 1790)	C	130
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Otiorhynchus scaber</i> (L., 1758)	C	21
Insecta	Coleoptera	Curculionidae Latreille, 1802	<i>Acalles echinatus</i> (Germar, 1824)	C	4
Insecta	Coleoptera	Cholevidae Kirby, 1837	<i>Catops westi</i> Krogerus, 1931	C	1
Insecta	Coleoptera	Elateridae Leach, 1815	<i>Agriotes obscurus</i> (L., 1758)	B	7
Insecta	Hymenoptera	Formicidae	<i>Formica</i> sp.	A	1
Insecta	Hymenoptera	Formicidae	<i>Lasius fuliginosus</i> (Latreille, 1798)	A	44
Insecta	Dermaptera	Forficulidae	<i>Forficula auricularia</i> L., 1758	A	3
Insecta	Lepidoptera	Noctuidae	larvae	A	1
Insecta	Heteroptera	Pentatomidae	<i>Aelia acuminata</i> (L., 1758)	A	1
Insecta	Heteroptera	Geocoridae	<i>Geocoris ater</i> (Fabricius, 1787)	A	2
Insecta	Lepidoptera	Noctuidae	larvae	C	2
Insecta	Heteroptera	Geocoridae	<i>Geocoris ater</i> (Fabricius, 1787)	C	7
Insecta	Collembola		spp.	C	13
Insecta	Hymenoptera	Formicidae	<i>Lasius fuliginosus</i> (Latreille, 1798)	C	15
Insecta	Orthoptera	Acrididae	<i>Chorthippus</i> sp. larvae	B	4
Malacostraca	Isopoda	Oniscidae	<i>Oniscus asellus</i> L., 1758	A	6
Malacostraca	Isopoda	Oniscidae	<i>Oniscus asellus</i> L., 1758	C	10

for bumpy numerical force of attempt, i.e., test of casual differences for a varied number of trials) according to Zar (1998). Correlations between elements in studied trophic links from particular environments of different regions at determining significance level were determined by regression analysis (significance level at $p < 0.05$). Interactions were established by Pearson test for linear correlation (Zar 1998).

Results

There were no differences between years in our study (tested by ANOVA Kruskal–Wallis test; significance level at $\alpha < 0.05$) so the data were presented together. The studied trophic links and the types of

environments differed in the concentration of chemical elements in natural salted and disturbed environments. We recorded an accumulation of Zn, Cu, Mn, Co, and Cd in the green parts of plants and invertebrates in the trophic chains studied (Fig. 2a–e). However, abnormalities in Cu level in control areas with much higher copper level in soils of control areas were found (Fig. 2b). Simultaneously, there was a higher level of elements in salted polluted areas (sodium manufacture). We can thus suggest the accumulation processes of these elements in sodium manufacture and also anthropogenic environments (these elements have as a rule the higher values of their concentration there; Fig. 3a–e), except of control areas (Fig. 3b), probably by the reason of existence of unknown unfathomable factor disturbing balance there, and may be the effect of fertilizers in this area.

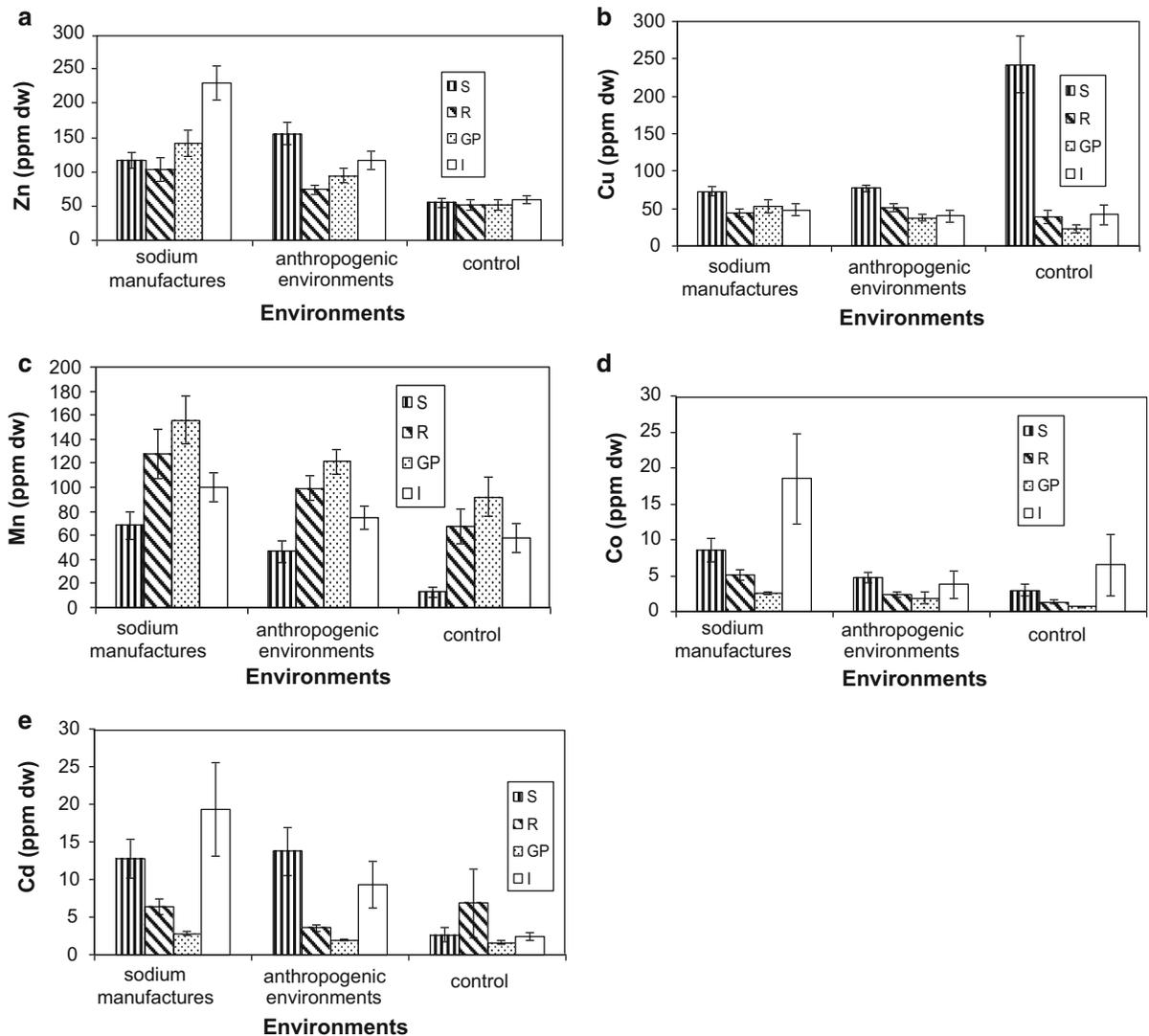


Fig. 2 Arithmetic mean \pm SD of zinc, copper, manganese, cobalt, and cadmium concentration (ppm dw) in soils (S), roots (R), the green parts of plants (GP), and invertebrates (I) collected from different environments (sodium manufactures,

anthropogenic environments, and control) of the saline Inowrocław Region of Ecological Danger (central Poland) from 2006 to 2010. **a** Zinc. **b** Copper. **c** Manganese. **d** Cobalt. **e** Cadmium

We found significant differences in the concentration of chemical elements in the trophic links between differentiated environments (sodium manufactures, anthropogenic environments, controls) of the salted Kujawy Region in the Inowrocław Region of Ecological Danger (Table 2). These levels were also correlated predominantly with high acidity (pH) and also high salinity (Ec) of investigated environments while these relations were both positive and negative (Table 3). This suggested that decreased acidity (pH) of the

environment (soil) may cause an increase in the concentration of Zn and Cd level in sodium manufactures, and the increase in Ca, Zn, Cu, Cd, and Pb level in anthropogenic environments, and also an increased level of Pb in control environments. Simultaneously, the increased acidity (pH) of the environment may cause an increase in the concentration level of Na, Mg, and Fe in sodium manufactures, an increase in the Na, Fe, Mn, and Co level in anthropogenic environments, and also an increase in Na level in control areas (Table 3).

Table 2 Significant differences in the levels of chemical elements (ppm dw) in studied trophic links between different environments (A—sodium manufactures, B—anthropogenic environments, C—control) of the saline Inowrocław Region of Ecological Danger (central Poland) from 2006 to 2010

Elements	One-way ANOVA		Tukey test	n
	F	p		
Na	3.53884	0.030367		280
K	0.42683	0.653003		280
Ca	1.84980	0.159214		279
Mg	5.23740	0.005851	B:C*	281
Fe	0.99038	0.372745		280
Zn	15.13694	0.000001	B:C*** A:C***	277
Cu	6.92639	0.001161	B:C**	280
Mn	5.98655	0.002853	A:C* A:B*	277
Co	3.78010	0.024033	A:B*	274
Cd	8.91809	0.000176	A:C*** B:C*	280
Pb	22.98579	0.000000	A:C*** B:C***	280

The differences were tested using one-way ANOVA for correlation followed by multiple range test and using RID-Tukey test (test of reasonably important difference for bumpy numerical force of attempt)

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

Chemical element correlations with salinity (Ec) were also significant in soils of the studied areas. We found negative associations with Pb in sodium manufactures and K in anthropogenic environments. These associations were negative in control areas in the case of Ec-Na and Ec-Fe. Simultaneously, we found positive associations between Ec and Na, Mg, Fe, Cu, Mn, and Cd in anthropogenic environments (Table 3). We also found significant interrelations between acidity and salinity in soils of all studied environments. So these associations were positive in saline areas (sodium manufactures) and negative in anthropogenic and control areas (Table 3). These dependencies between chemical elements and both pH and Ec (Tables 3–5) testify that cations selectivity and their fluctuated exchange in soils provides important information about the affinity and binding strength of particular cations on soil surface (Fig. 3).

We also found element–element interactions between trophic links in differentiated environments.

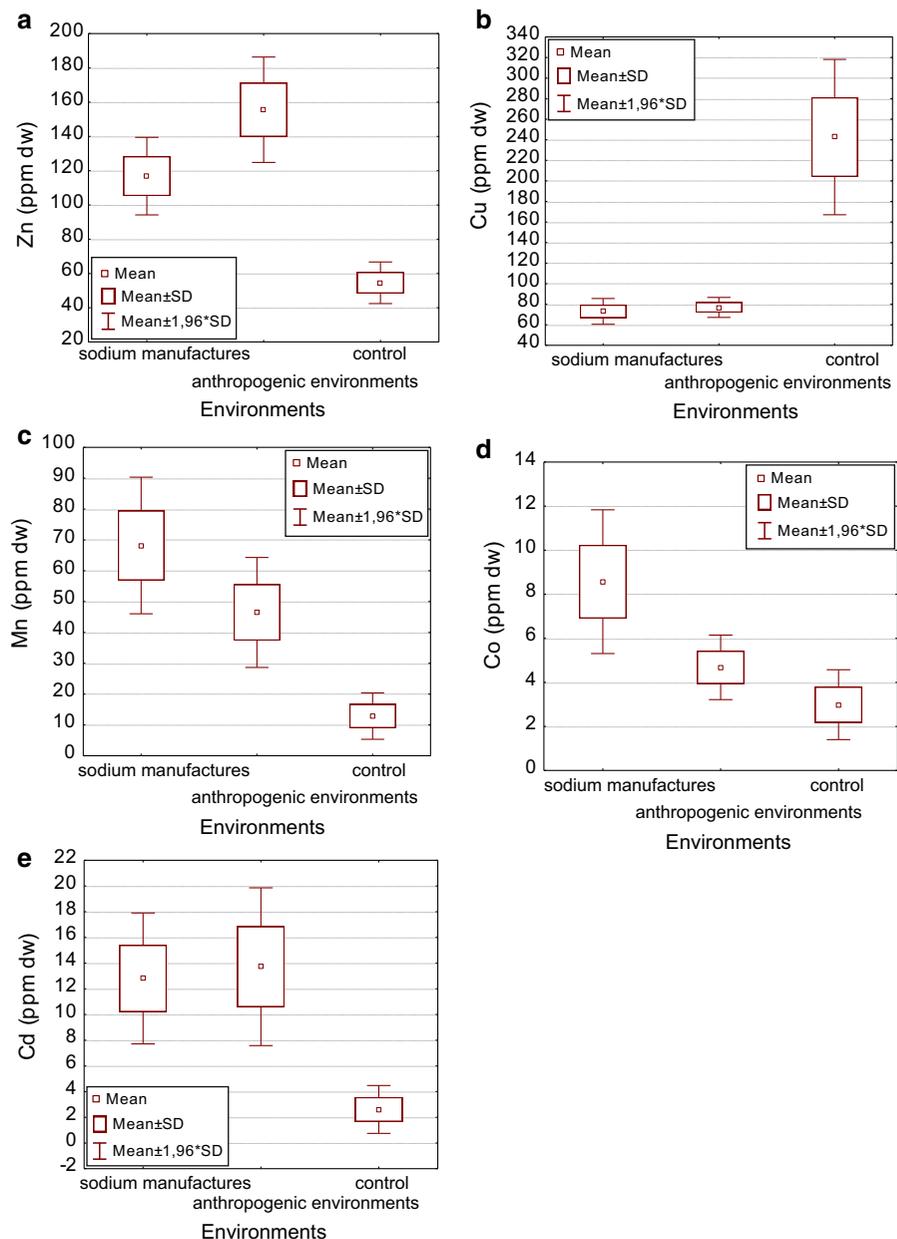
Table 3 Relationships between acidity (pH) and salinity (Ec) and the level of chemical elements' (ppm dw) in the studied trophic links from different environments of the saline Inowrocław Region of Ecological Danger (central Poland) from 2006 to 2010

Dependence	r	p	n
<i>Sodium manufactures</i>			
pH: Ec	0.33	0.004	78
pH: Na	0.40	0.000	78
pH: Mg	0.26	0.020	78
pH: Fe	0.47	0.000	78
pH: Zn	−0.34	0.003	75
pH: Cd	−0.23	0.039	78
Ec: Pb	−0.41	0.000	78
<i>Anthropogenic environments</i>			
pH: Ec	−0.38	0.000	158
pH: Na	0.18	0.021	156
pH: Ca	−0.30	0.000	156
pH: Fe	0.24	0.002	156
pH: Zn	−0.43	0.000	156
pH: Cu	−0.29	0.000	156
pH: Mn	0.17	0.039	156
pH: Co	0.17	0.039	156
pH: Cd	−0.29	0.000	157
pH: Pb	−0.16	0.046	157
Ec: Na	0.18	0.027	156
Ec: K	−0.27	0.001	156
Ec: Mg	0.22	0.006	157
Ec: Fe	0.26	0.001	156
Ec: Cu	0.33	0.000	156
Ec: Mn	0.22	0.005	154
Ec: Cd	0.19	0.018	157
<i>Control</i>			
pH: Ec	−0.45	0.002	47
pH: Na	0.32	0.029	46
pH: Pb	−0.35	0.017	45
Ec: Na	−0.37	0.010	46
Ec: Fe	−0.38	0.009	46

Correlations were conducted with regression method ($p < 0.05$). The interactions were established by the Pearson test for linear correlation

Most of these associations concerned soils, roots, and the green parts of plants and most were positive (Table 4). Thus, these results indicate that elements may be accumulated in lower links of the trophic chain, i.e., in soils and plants; however, their further flow is selective and variable.

Fig. 3 Concentration (ppm dw) of zinc, copper, manganese, cobalt, and cadmium in studied trophic chain collected from different environments (sodium manufactures, anthropogenic environments, and control area) of the saline Inowroclaw Region of Ecological Danger (central Poland) from 2006 to 2010 (arithmetic mean \pm SD). **a** Zinc. **b** Copper. **c** Manganese. **d** Cobalt. **e** Cadmium



We found the differences between $\text{pH}(\text{H}_2\text{O})$ and $\text{pH}(\text{KCl})$, i.e., soil reaction measured in distilled water (H_2O) and in potassium chloride (KCl), in studied soils in different environments (Table 5). The same was true to the organic matter content (OMC) and electrolytic conductivity (E_c) in the in soil samples taken in different environments analyzed (Table 5). Thus, we can suppose that in the case of soils from the environments studied by us a process of mutual

interdependencies between the vertical movement of chemical elements (that was exhibited predominant association with soil pH and organic matter content, and also electrolytic conductivity) takes place. The OMC in the studied soils was relatively different (Table 5), and this, in combination with other edaphic parameters of studied soils, could be the cause of a diverse bioavailability of chemical elements (see “Discussion”).

Table 4 Interrelations between the level of chemical elements (ppm dw) in different environments of the saline Inowrocław Region of Ecological Danger (central Poland) from 2006 to 2010

Dependence	Regression equation	<i>r</i>	<i>p</i>	<i>n</i>
<i>Sodium manufactures</i>				
Na ^{S:I}	$y = -0.909x + 16.597$	-0.48	0.011	27
Na ^{S:GP}	$y = 0.939x + 0.811$	0.60	0.000	71
K ^{S:R}	$y = 0.216x + 8.174$	0.61	0.000	33
Ca ^{S:I}	$y = 0.87x - 0.429$	0.45	0.008	33
Fe ^{S:I}	$y = -0.933x + 16.921$	-0.43	0.012	33
Fe ^{S:GP}	$y = 0.684x - 0.1319$	0.55	0.000	71
Cu ^{S:R}	$y = 0.572x + 1.391$	0.42	0.016	33
Zn ^{S:GP}	$y = 0.535x + 1.734$	0.29	0.016	68
Zn ^{S:I}	$y = 0.492x + 2.934$	0.35	0.047	33
Zn ^{S:R}	$y = 0.921x + 0.051$	0.59	0.000	33
Mn ^{S:R}	$y = 1.972x - 5.78$	0.62	0.000	33
Co ^{S:GP}	$y = 0.072x + 0.689$	0.32	0.007	70
Co ^{S:I}	$y = 1.075x - 1.327$	0.50	0.003	33
<i>Anthropogenic environments</i>				
Na ^{S:R}	$y = 0.346x + 7.351$	0.32	0.015	59
Na ^{S:I}	$y = -1.037x + 17.006$	-0.51	0.000	45
K ^{S:GP}	$y = -0.147x + 11.18$	-0.25	0.003	133
Mg ^{S:GP}	$y = 0.061x + 7.947$	0.19	0.029	133
Mg ^{S:R}	$y = 0.117x + 7.885$	0.21	0.046	88
Mn ^{S:GP}	$y = -0.238x + 3.785$	-0.53	0.000	133
Mn ^{S:R}	$y = 0.203x + 3.576$	0.44	0.000	88
Co ^{S:R}	$y = 0.141x + 0.178$	0.38	0.000	87
Co ^{S:GP}	$y = 0.114x - 0.302$	0.37	0.000	129
Cd ^{S:R}	$y = 0.402x + 0.02$	0.69	0.000	88
Cd ^{S:GP}	$y = -0.102x + 0.332$	-0.23	0.009	128
<i>Control</i>				
Mg ^{S:R}	$y = 0.746x + 2.062$	0.62	0.003	21
Fe ^{S:GP}	$y = -1.649x + 21.359$	-0.46	0.004	37
Cu ^{S:I}	$y = 0.372x + 0.716$	0.47	0.019	24
Mn ^{S:GP}	$y = -0.474x + 2.736$	-0.80	0.000	37
Co ^{S:GP}	$y = 0.179x + 0.112$	0.48	0.022	22
Cd ^{S:R}	$y = 0.266x + 0.821$	0.55	0.010	21
Cd ^{S:GP}	$y = -0.337x - 0.605$	-0.58	0.000	35

Correlations were conducted with regression method ($p < 0.05$). The interactions were established by the Pearson test for linear correlation

Discussion

We explored the state of studied environments of significant impact on the plant condition by analyzing soil conditions of these varied environments in terms

of anthropogenic impact (soil pH, soil electrolytic conductivity *Ec*, organic matter content OMC, concentration of chemical elements in the rhizosphere). Metals added to soil will normally be retained at the soil surface. Movement of metals into other environmental compartments, i.e., ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix. The retention mechanisms for metals added to soil include adsorption of the metal by the soil solid surfaces and precipitation. The retention of cationic metals by soil has been correlated with such soil properties as pH, redox potential, surface area, cation exchange capacity, organic matter content, clay content, iron and manganese oxide content, and carbonate content. Anion retention has been correlated with pH, iron and manganese oxide content, and redox potential. In addition to soil properties, consideration must be given to the type of metal and its concentration and to the presence of competing ions, complexing ligands, and the pH and redox potential of the soil-waste matrix. Transport of metals associated with various wastes may be enhanced due to (McLean and Bledsoe 1992): (1) facilitated transport caused by metal association with mobile colloidal size particles, (2) formation of metal organic and inorganic complexes that do not adsorb to soil solid surfaces, (3) competition with other constituents of waste, both organic and inorganic, for sorption sites, and (4) decreased availability of surface sites caused by the presence of a complex waste matrix. Because of the wide range of soil characteristics and various forms by which metals can be added to soil, evaluating the extent of metal retention by a soil is site/soil/waste specific. Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix (McLean and Bledsoe 1992).

Plants are usually subjected to combined stressors in their natural environments, and stress factors cause

Table 5 Edaphic parameters of soils (soil pH, organic matter content OMC, salinity, i.e., electrolytic conductivity Ec) of studied environments: SM—neighborhoods of soda manufactures ($n = 86$), AE—dumps ($n = 91$), WE—surroundingwatercourses ($n = 98$), AGRE—agrocenoses ($n = 83$), C—control area ($n = 95$) at a depth of 0–25 cm (roots harvesting and glycophytes and halophytes)

Environment	Arithm. mean	SD	Min	Max	<i>H</i>	<i>p</i>	Comparison
pH(H ₂ O)							
SM	8.516	1.403	7.030	11.285	41.253	***	C < SM***, AE***, WE***,
AE	8.658	0.961	7.595	10.810		***	AGRE***
WE	8.063	0.263	7.060	8.505		***	
AGRE	8.089	0.185	7.720	8.300		***	
C	6.034	1.307	4.080	7.885		***	
pH(KCl)							
SM	8.370	1.239	7.140	11.275	44.130	***	C < SM***, AE***, WE***, AGRE*
AE	8.264	0.646	7.540	10.065		***	
WE	7.802	0.283	6.675	8.115		***	
AGRE	7.760	0.139	7.470	7.900		***	
C	5.595	1.440	3.430	7.640		***	
OMC (%)							
SM	6.926	2.053	2.855	10.740	38.701	***	AGRE > AE***, WE***, C**
AE	5.702	2.736	2.820	15.970		***	SM > WE**
WE	4.584	2.224	2.160	10.560		***	
AGRE	11.952	2.915	8.760	16.400		***	
C	7.228	4.337	3.620	14.020		***	
Ec (mS)							
SM	36.269	21.832	0.938	67.369	57.719	***	SM > WE***, AGRE***, C***
AE	14.679	16.533	1.287	57.969		***	AE > WE***, C***
WE	1.656	0.940	0.399	3.651		***	
AGRE	1.554	0.517	1.143	2.977		***	
C	1.207	0.796	0.482	2.607		***	

pH(H₂O), pH(KCl), soil reaction measured in distilled water (H₂O) and in potassium chloride (KCl); OMC, organic matter content; Ec, electrolytic conductivity; arithm, mean—arithmetic mean; SD, standard deviation; min, minimum value; max, maximum value; *H*, indicator of the ANOVA test of the ranks of Kruskal–Wallis (differences between the environments); *p*, the evaluation of significance of differences at the level of $\alpha = 0.05$; comparison, rank test of multiple comparisons for all tested parameters (pH, OMC, Ec) in different environments, with the level of * $p < 0.01$; ** $p < 0.001$; *** $p < 0.0001$

many changes in plant metabolism and morphology (Çakırlar et al. 2008) and species distribution (Piernik 2006). Salinity, alkalinity, and heavy metal effects on soil biogeochemistry, adversely affects associated ecological balance, and free radicals and reactive oxygen species (ROS) are relatively high there (Kabata-Pendias and Mukherjee 2007; Kabata-Pendias and Pendias 2010; Kabata-Pendias and Szteke 2012). ROS, especially hydrogen peroxide and hydroxyl radicals, damage the membrane lipids and result in lipid peroxidation (Imlay 2003). However, oxidative stress could be caused not only by salinity, but also by multiply combination of

environmental stressors in natural conditions (Elkhoui et al. 2005).

Investigations of the impact of anthropopression on the structure and functioning of ecological systems (Dąbrowska-Prot 1996; Eens et al. 1999) highlight the interdependence of biocenoses or whole ecosystems. We emphasize the need to employ living organisms as bioindicators of environmental contamination, because of the impact of contaminants on quality and quantity changes, domination structure changes and physiological changes of insects (Ulgenturk and Toros 1993; Jurkiewicz-Karnowska 1998). However, the typical symptom of structural and functional

changes of invertebrates caused by irreversible environmental changes has been observed after the threshold of environmental damage has been exceeded (Dąbrowska-Prot 1996). We found significant differences in the concentration of chemical elements in the trophic links between differentiated environments, suggesting that decreased acidity (pH) of soils may cause changes in the concentration of important chemical elements. These dependencies between the chemical elements and both pH and E_c testify that the selectivity and their fluctuating exchange of cations in soils provide important information about the affinity and binding strength of particular cations on the soil surface. At this point, it should be noted that Bezel et al. (2001) found that plants and small animals from one trophic chain had an increase in the variation of reproductive parameters and that chemical environmental pollution favored the survival of those individuals in the populations that are better adapted to changes in climate and environmental conditions. An increased variation in reproductive parameters may promote the elimination of less fit individuals from populations, and the ensuing energy loss may be the cost of maintaining population size in chemically degraded environments. Thus, changes in the variation of major population parameters may be one of the mechanisms ensuring efficient adaptation of natural animal and plant populations to chemical pollution of the environment. This increased variation in the populations of invertebrates and dandelion (ceno-populations) in response to the deterioration in environmental conditions due to chemical pollution favors the survival of individuals that are better adapted to those environmental conditions. On the other hand, a decrease in the variation of these population parameters also indicates that the population may have partially lost its capacity to adequately respond to further fluctuations of climatic and other natural factors. These losses of further variability thus represent a cost to maintaining population size in degraded environments (Bezel et al. 2001).

The environments investigated in this study were significantly different for a number of parameters, as evidenced by the results obtained. The soils from areas under the influence of anthropogenically altered soda industry were characterized both by a high pH ($\text{pH} > 8$) and the level of salinity (Table 5), significantly exceeding 4 mS, considered to be the limit for the proper development of plants sensitive to this factor (Mane

et al. 2011). Moreover, the average Na concentration in soils collected from sodium-industry-related environments (near the soda plants, landfills) accounted for, respectively, 29 times and 17 times of average concentration of this element in soils in the control areas. The results summarized in Table 5 (this paper) also indicate a high Ca level in soils in areas used for agricultural purposes and also in related industry sodium landfills. Similarly, Mg concentration in Kujawy region was significantly higher in soils relative to these in the control; high Mg concentrations were found particularly in agrocenoses (2807 mg kg^{-1}), but also in dumps (2033 mg kg^{-1}); Koim-Puchowska (2014). The studies by Cieśla et al. (1981), Cieśla and Dąbkowska-Naskręt (1984), Rytelewski et al. (1993) and Czerwinski (1996) confirm the high saturation of soils sorbing complex of these areas by sodium cations, which is associated predominantly with close proximity to sodium manufactures of Inowrocław and Janikowo region. Sodium cations as one of the most easily leached from the soil by rain water may be present in larger amounts in the surface layers of the profile only if a continuous flow of sodium compounds into the soil from specific sources occurs (Krzyżaniak-Sitarz 2011). In turn, the high C and Mg concentration in the soil is mainly connected with natural factors, namely the outflow to the surface of salt sources and the impact of bedrock (Krzyżaniak-Sitarz 2011). The alkalization of the environment affect both water soluble and exchangeable ions of a basic nature. Rytelewski et al. (1993) also show a high pH value ($\text{pH} > 10$) in soils profiles arranged along the pipeline and saline in embankment damage settlers, while in most black earth saline pH is in the range of pH 7–8. In turn, higher average levels of potassium in soils found in the agrocenoses (2296 mg kg^{-1}) with respect to other environments (Table 5), which was related to the agricultural practices used in the area. The content of organic matter in soils from different backgrounds clearly suggests that the area, which was characterized by the highest content of humus, was agrocenoses (Table 5). Krzyżaniak-Sitarz (2011) confirms that the black earth Kujawy has large resources of organic matter, a high content of calcium carbonate, and a large cation exchange capacity associated with high Ca and Mg concentration and with a lesser extent of potassium. The abundance of black soils in an alkaline cations at the same time affects the formation of pH of soils and the small share of hydrogen sorption complex cations.

These regularities are highly correlated with soil pH; we suggested that decreased acidity (pH) of the environment (soil) may cause an increase in the concentration of Zn and Cd level in sodium manufactures, the increase in Ca, Zn, Cu, Cd, and Pb level in the anthropogenic environments, and also an increased level of Pb in control environments.

The bioavailability of chemical elements is conditioned by many environmental factors, mainly acidity, redox potential, salinity, organic matter content, soil structure, concentration of elements, and interactions taking place between them (Martin and Coughtrey 1982; O'Neill 1998; Samecka-Cymerman and Kempers 2001; Sundareshwar et al. 2003; Manahan 2006). In addition, factors other than those of soils, such as atmospheric deposition on the surface of the leaf, cyclic plant physiology, body research, translocation and compartmentalization elements, may be relevant to bioaccumulation of different chemical elements (Bargagli 1998). Additionally, test results obtained by Koim-Puchowska (2014) clearly show that environmental stress, mostly salt stress, associated with strong alkalinity of the ground, causing inhibition of shoot length of plants. Studies by Feitosa de Lacerda et al. (2003) also show that the development of the stems of two genotypes of sorghum *Sorghum* sp. was inhibited by the action of salt stress. Sorghum growth inhibition was higher in sensitive than tolerant genotypes, and the difference increased with the duration of the experiment. Also, Shi and Sheng (2005) show that the development of relatively tolerant varieties of sunflower *Helianthus* sp. to salinity is inhibited with increasing levels of salt and additionally soil pH, whereas under low salinity and pH the growth of sensitive varieties is inhibited only average or even stimulated by salt stress. However, studies by Merino et al. (2010) indicate that the increase in nutrient availability for plants is not a factor in increasing tolerance to salt stress grass *Spartina patens*. The general regularity is that the plants are forced to deploy energy for the growth of vegetative synthesis include osmoprotectants to maintain ionic homeostasis in various organs and cells, maintaining the integrity of cell membranes and activation of antioxidant system (Jain et al. 2001).

Thus, living environment largely determined the concentration of chemical elements in the studied plants (this paper), which particularly translated into condition of plant organisms. Particularly significant

increase in the concentrations of elements such as Na, Ca, Mg, and Cu demonstrated in examined plant organs in differentiated environments, which was associated with both natural factors and anthropogenic. It was not without significance also proved to be the impact of agricultural activity on plant bioaccumulation of K, Mn, Fe, and Zn. On the basis of the results of this paper, we can assume that bioaccumulation and mobility of chemical elements depend on the element and species/groups of plants, environmental factors, and even plant organ. Intensive bioaccumulation by plants primarily subject to K, Mo, and Na, in contrast to Mn, Co, Al, As, Fe, and Pb. In contrast, Na, Mg, Ca, Cu, Zn, Ni, Cr, and Cd were intensively accumulated only between species/groups of plants and the environment. It should be emphasized on a high accumulation in the bodies of glycophytes and in bodies of halophytes. The mobile elements may include Na (halophytes), K (glycophytes and halophytes), Ca, Mg (glycophytes) for the group/plant species. Similar regularities were found in the case of accumulation of Zn, Mn, Cu, Se, Cd, Cr, and Ni, depending on the state of the environment (this paper and Koim-Puchowska 2014).

Based on the test results of this study and the literature data, we can conclude that environmental factors largely determine the development not only of plants, but affect their natural range of occurrence in degraded environments. We know that halophytes (especially mandatory common glasswort *Salicornia europaea*) as a result of a decrease in salinity by leaching salts from the ground, with the lack of mowing uncultivated highly salted areas, can be eliminated by strong opponent, invasive species—common reed *Phragmites australis* (Koim-Puchowska 2014). Further studies are required under natural conditions in order to confirm the results obtained in our experiments. The results are therefore also underline the conduct of proper management in areas heavily degraded by sodium-salt industry.

We can also assume that sodium-salt industry and natural salt marshes have a significant impact on the environment of the region, generating an alkaline soils and high levels of salinity. Agricultural practices are not indifferent to the homeostasis of chemical elements in the trophic chains. The concentration of trace elements in areas impacted not exceeds the permissible standards for agricultural soils (except for Zn). Cd is an element that could pose a threat to crops in areas contaminated and those considered as environmentally clean.

Additionally, K and Mo are intensively accumulated by plants, unlike Mn, Co, Al., As, Fe and Pb, Na, Mg, Ca, Cu, Zn, Se, Ni, Cr, and Cd are also accumulated intensively, but depending on the group of plants and the environment. Fe, Co, Al., As, Cr, Ni, and Cd are elements cumulated particularly in the roots of plants. K and Mo may be included to the mobile elements in the investigated plants. Sodium is transported from the roots to the aerial parts of the plants; sodium ions are probably serving the function of the substance compatible. Thus, we can finally believe that strong environmental stress in the form of a high level of salinity and alkalization of soils stimulates the plastic protective mechanisms in plants and thus generates energy expenditure allocated in the budget of plants on their growth. Additionally, it should be noted that when the soil is suitable to high concentration of such ions as Na^+ and Cl^- , there is a very high salinity. Increasing the electrolytic conductivity of the soil limits the collection of calcium ions, among others. This results in competition between Na and Ca ions for binding at the root. Calcium is displaced by sodium (Pawłowicz 2004; Wozny and Przybyl 2007). The sodium ions displace the calcium ions from the cell membrane, leading to impair its permeability and causing a greater flow of electrolyte. Sodium ions displace calcium ions cause stiffening of the cell wall, which slows the growth of plants (Wozny and Przybyl 2007).

According to research carried out in the framework of this work, element concentrations investigated in sediments (especially in SM, AE, AGRE; this paper) reflect the higher degree of pollution than in the control sites in Tuchola Forestry. The higher total Na, Ca, Cr, Cu, Fe, Ni, and Zn sediment concentrations were found in disturbed environments (SM, AE, AGRE), because of proximity sodium factory and other branch of industry and probably because of using fertilizers in agricultural practices. Besides, the soils from sodium manufacture and agricultural environments were of high degree of salinity and alkalinity ($E_c > 4 \text{ mS cm}^{-1}$, $\text{pH} > 7$). The same results were obtained by Mane et al. (2011). We also should consider the impact of wastes from sodium industry containing mainly CaCO_3 , CaSO_4 , Ca(OH)_2 , Fe(OH)_3 , silicates, aluminosilicates, and over-sedimentary liquid (solution of KCl, NaCl, NH_4OH , Na_2SO_4 , NaOH, MgCl_2 , and CaCl_2); Piernik (2003) infiltrate into the soils and grassland irrigation and than impact on soil salinity and alkalinity, and soil

ability to maintain chemical homeostasis in ecosystems and thus bioaccumulation of elements in plants. However, average concentrations of trace metals Cu, Zn, Ni, Cr, Mo, and Fe did not exceed acceptable contents in soils used agriculturally (Kabata-Pendias and Pendias 2010).

Very important for explanation the significant differences in the concentration of chemical elements in the trophic links due to the decrease in acidity (pH) and salinity (E_c), organic matter content (OMC) and due to vertical movement of chemical elements (that commonly exhibited predominant association with soil pH and organic matter) is to introduce mechanisms and regularities of metal retention in the studied soils. We also need to know the physicochemical characterization of studied soils (pH, cation exchange capacity, organic carbon content, electrolytical conductivity), that is needed for a better evaluation of availability of chemical elements. Therefore, metals associated with the aqueous phase of soils are subject to movement with soil water and may be transported through the vadose zone to ground water. Metals, unlike the hazardous organics, cannot be degraded. Some metals, such as Cr, As, Se, and Hg, can be transformed to other oxidation states in soil, reducing their mobility and toxicity. Immobilization of metals, by mechanisms of adsorption and precipitation, will prevent movement of the metals to ground water. Metal–soil interaction is such that when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded, or metal interaction with the associated waste matrix enhances mobility. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix in question (McLean and Bledsoe 1992). It is also important that in soil metals are found in one or more of several “pools” of the soil: (1) dissolved in the soil solution; (2) occupying exchange sites on inorganic soil constituents; (3) specifically adsorbed on inorganic soil constituents; (4) associated with insoluble soil organic matter; (5) precipitated as pure or mixed solids; (6) present in the structure of

secondary minerals; and/or (7) present in the structure of primary minerals. In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fractions, and those fractions in equilibrium with this fraction, i.e., the exchange fraction, are of primary importance when considering the migration potential of metals associated with soils (McLean and Bledsoe 1992).

Moreover, metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for Hg, Se, and As. At the same time, metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation–reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions. The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated. Metals exist in the soil solution as either free (uncomplexed) metal ions (e.g., Cd^{2+} , Zn^{2+} , and Cr^{3+}), in various soluble complexes with inorganic or organic ligands (e.g., CdSO_4^0 , ZnCl^+ , and CdCl_3^-), or associated with mobile inorganic and organic colloidal material. A complex is defined as an unit in which a central metal ion is bonded by a number of associated atoms or molecules in a defined geometric pattern, e.g., ZnSO_4^0 , CdHCO_3^+ , and $\text{Cr}(\text{OH})_4^-$. The associated atoms or molecules are termed ligands. In the above examples, SO_4^{2-} , HCO_3^- , and OH^- are ligand. The total concentration of a metal in the soil solution is the sum of the free ion concentration, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material (McLean and Bledsoe 1992). Metals will form soluble complexes with inorganic and organic ligands. Common inorganic ligands are SO_4^{2-} , Cl^- , OH^- , PO_4^{3-} , NO_3^- , and CO_3^{2-} . Soil organic ligands include low molecular weight aliphatic, aromatic, and amino acids and soluble constituents of fulvic acids. Organic complexation of metals in soil is not as well defined as inorganic complexation because of the difficulty of identifying the large

number of organic ligands that may be present in soils. Most of the metal–organic complex species identified in the literature were generated from metal interaction with fulvic acids extracted from sewage sludges. The soluble metal organic complexes that may form in other waste systems, however, have not been identified (McLean and Bledsoe 1992).

The presence of complex species in the soil solution can significantly affect the transport of metals through the soil matrix relative to the free metal ion. With complexation, the resulting metal species may be positively or negatively charged or be electrically neutral (e.g., CdCl_3^+ , CdCl^- , and CdCl_2^0). The metal complex may be only weakly or more strongly adsorbed to soil surfaces relative to the free metal ion. A more detailed discussion on the effect complex formation has on metal mobility is given in the section: Effect of anions on adsorption and precipitation. Speciation not only affects mobility of metals but also the bioavailability and toxicity of the metal. The free metal ion is, in general, the most bioavailable and toxic form of the metal. The formation of a solid phase may not be an important mechanism compared to adsorption in native soils because of the low concentration of trace metals in these systems. Precipitation reactions may be of much greater importance in waste systems where the concentration of metals may be exceedingly high. Calcite (CaCO_3) serves as a site for adsorption of Cd^{2+} at low concentrations of Cd, while CdCO_3 precipitation, possibly as a coating on the calcite, occurs only at higher Cd concentrations (McLean and Bledsoe 1992). Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Adsorption differs from precipitation in that the metal does not form a new three-dimensional solid phase but is instead associated with the surfaces of existing soil particles. The soil matrix often includes organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates. Soil organic matter consists of (1) living organisms, (2) soluble biochemicals (amino acids, proteins, carbohydrates, organic acids, polysaccharides, lignin), and (3) insoluble humic substances. The biochemicals and humic substances provide sites (acid functional groups, such as such as carboxylic, phenolics, alcoholic, enolic-OH and amino groups) for metal sorption. The biochemicals form water soluble complexes with metals, increasing metal mobility, as discussed in

a previous section. The humic substances consist of insoluble polymers of aliphatic and aromatic substances produced through microbial action. Humic substances contain a highly complex mixture of functional groups. Binding of metals to organic matter involves a continuum of reactive sites, ranging from weak forces of attraction to formation of strong chemical bonds. Soil organic matter can be the main source of soil cation exchange capacity, contributing >200 meq/100 g of organic matter in surface mineral soils. Organic matter content, however, decreases with depth, so that the mineral constituents of soil will become a more important surface for sorption as the organic matter content of the soil diminishes. Fe and Mn oxides are the principal soil surface that controls the mobility of metals in soils and natural water. In arid soils, carbonate minerals may immobilize metals by providing an adsorbing and nucleating surface (McLean and Bledsoe 1992).

Soil surfaces carry either a net negative or positive charge depending on the nature of the surface and the soil pH. The permanent net negative charge on surfaces is due to charge imbalance resulting from the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layers and/or substitution of Mg^{2+} , Fe^{2+} , etc. for Al^{3+} in the octahedral layers of aluminosilicate clays. The charge on the surface is not affected by changes in soil pH, and hence, it is termed a permanent charged surface. pH-dependent charged surfaces are associated with the edges of clay minerals, with the surfaces of oxides, hydroxides and carbonates, and with organic matter (acid functional groups). The charge arises from the association and dissociation of protons from surface functional groups. Using an iron oxide surface functional group as an example, the association of protons with the functional group results in a positive charge [$-\text{Fe}-\text{OH}^{2+}$] and dissociation of protons, under more alkaline conditions, results in a negative charge [$-\text{Fe}-\text{O}^-$]. The structural charge developed on either a permanent charged surface or a pH-dependent charged surface must be balanced by ions of opposite charge at or near the surface. The cation exchange capacity is a measure of negatively charged sites for cation adsorption, and anion exchange capacity is a measure of the positively charged sites for anion adsorption. The anion capacity is, however, very small relative to cation adsorption capacity of soils (McLean and Bledsoe 1992).

The relative affinity of a soil surface for a free metal cation increases with the tendency of the cation to form strong bonds, i.e., inner sphere complexes, with the surface. The general order of preference for monovalent cations by montmorillonite is $\text{Cs} > \text{Rb} > \text{K} = \text{NH}_4 > \text{Na} > \text{Li}$. For the alkaline earth metals, the order is $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$. The preference series indicates a greater attraction of the surface for the less hydrated cations that can fit closer to the clay surface. For transition metals, the size of hydrated cation cannot be used as the only predictor of adsorption affinity since electron configuration of a metal plays an important role in adsorption. On the basis of relative sorption affinity of metals onto a variety of soils and soil constituents, it can be concluded that although there is consistently a higher affinity of these surfaces for Pb and Cu compared with Zn or Cd, the specific order of sorption affinity depends on the properties of the metals, surface type, and other factors, i.e., redox potential, electrolytic conductivity, pH (McLean and Bledsoe 1992).

Common anionic contaminants include arsenic (AsO_4^{3-} , AsO_2^-), selenium (SeO_3^{2-} , SeO_4^{2-}), and chromium forms in one of its oxidation states (CrO_4^{2-}). Soil particles, though predominantly negatively charged, also may carry some positive charges. The oxide surfaces, notably iron, manganese, and aluminum oxides, carbonate surfaces, and insoluble organic matter can generate a significant number of positive charges as the pH decreases. The edges of clay minerals also carry pH-dependent charge. Clay minerals, oxides, and organic matter exert a strong preference for some anions in comparison with other anions, indicating the existence of chemical bonds between the surface and the specific anion. Phosphate has been the most extensively studied anion that exhibits this specific adsorption (inner sphere complex) phenomenon (McLean and Bledsoe 1992). The adsorption capacity (both exchange and specific adsorption) of a soil is determined by the number and kind of sites available. Adsorption of metal cations is correlated with such soil properties as pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content. Anion adsorption has been correlated with Fe and Mn oxide content, pH, and redox potential. Adsorption processes are affected by these various soil factors, by the form of the metal added to the soil, and by the solvent introduced along with the metal. The results of these

interactions may increase or decrease the movement of metals in the soil water (McLean and Bledsoe 1992). For specific adsorption sites, trace cationic metals are preferentially adsorbed over the major cations (Na, Ca, Mg) and trace anionic metals are preferentially adsorbed over major anions (SO_4^{4-} , NO_3^{3-} , soluble ionized organic acids). However, when the specific adsorption sites become saturated, exchange reactions dominate and competition for these sites with soil major ions becomes important. Metal cations form complexes with inorganic and organic ligands. The resulting association has a lower positive charge than the free metal ion and may be uncharged or carry a net negative charge. For example, the association of Cd with chloride results in the series of charged and uncharged cadmium species: Cd^{2+} , CdCl^+ , CdCl_2^0 , CdCl_3^- . The interaction between metal ions and complexing ligands may result in either a complex that is weakly adsorbed to the soil surface or in a complex that is more strongly adsorbed relative to the free metal ion. In general, the decrease in positive charge on the complexed metal reduces adsorption to a negatively charged surface. The actual effect of complex formation on sorption depends on the properties of metal of interest, type and amount of ligands present, soil surface properties, soil solution composition, pH and redox conditions (McLean and Bledsoe 1992).

Complex formation between metals and organic ligands affects metal adsorption and hence mobility. The extent of complexation between a metal and soluble organic matter depends on the competition between the metal-binding surface sites and the soluble organic ligand for the metal. Metals that readily form stable complexes with soluble organic matter are likely to be mobile in soils. The order of metal–organic complex stabilities: $\text{Hg} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Cd}$. The mobility of metals through soil followed the order: $\text{Cu} > \text{Ni} > \text{Pb} > \text{Ag} > \text{Cd}$. The high mobility of Cu and Ni was attributed to their high complexing nature with soluble soil organic matter (the increased mobility of Cu, Ni, and Pb in the presence of dissolved organic matter). Cd leached from the columns is not associated with dissolved organic carbon but is associated with Cl or acetate anions. Metals such as Cd and Zn that do not form highly stable complexes with organic matter are not as greatly affected by the presence of dissolved organic matter in the soil solution as metals that do

form stable complexes, such as Cu, Pb, or Hg. The effect of complexation formation on sorption is dependent on the type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH, and redox. The presence of complexing ligands may increase metal retention or greatly increase metal mobility (McLean and Bledsoe 1992). The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. The impact of soil pH on the adsorption of Pb, Ni, Zn, and Cu by two soils adjusted to various pH ranging between 4 and 8. As is true for all cationic metals, adsorption increased with pH. However, as a rule, the retention of metals did not significantly increase until pH was greater than 7. As is true with all oxyanions, i.e., As, Se and hexavalent Cr, sorption decreases with pH. The pH dependence of adsorption reactions of cationic metals is due, in part, to the preferential adsorption of the hydrolyzed metal species in comparison with the free metal ion. The proportion of hydrolyzed metal species increases with pH. Many adsorption sites in soils are pH-dependent, i.e., Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals. As the pH decreases, the number of negative sites for cation adsorption diminishes while the number of sites for anion adsorption increases. Also, as the pH becomes more acidic, metal cations also face competition for available permanent charged sites by Al^{3+} and H^+ . All trace metal hydroxide, oxide, carbonate, and phosphate precipitates form only under alkaline conditions. The dissolution of these metal precipitates is strongly dependent on the pH of the system. Most functional groups of complexing ligands are weak acids; thus, the stability of the metal complex is pH-dependent with little association in acid media. In soils with significant levels of dissolved organic matter, increasing soil pH may actually mobilize metal due to complex formation (McLean and Bledsoe 1992).

The pH of the soil system is a very important parameter, directly influencing sorption/desorption, precipitation/dissolution, complex formation, and oxidation–reduction reactions. In general, maximum retention of cationic metals occurs at $\text{pH} > 7$ and maximum retention of anionic metals occurs at $\text{pH} < 7$. Because of the complexity of the soil-waste system, with its myriad of surface types and solution composition, such a generalization may not hold true. Almost half of the metals have more than one

oxidation state in the soil and are directly affected by changes in the oxidation–reduction (redox) potential of the soil. The redox potential of a soil system is the measure of the electrochemical potential or availability of electrons within a system. A chemical reaction in which an electron transfer takes place is called an oxidation–reduction process. Metals or elements which gain electrons and lose in valence are undergoing reduction, while those losing electrons and gaining in valence are becoming oxidized. A measure of the redox potential (electron availability) indicates whether the metals are in oxidized or reduced state in soils; reducing conditions are brought about by the absence of oxygen (anaerobic). This is caused by the oxygen being utilized or consumed at a greater rate that it can be transported into the soil system. This can be caused by water-logged soils or soils contaminated with oxygen-consuming compounds. The consumption could either be chemical or biological. The biological consumption of oxygen is the results of microbes utilizing the organic contaminant, which have entered the soil system. Oxidizing conditions are normally found in well-drained soils as well as soils that have not been subjected to contamination by spills or leaks (McLean and Bledsoe 1992). Redox reactions can greatly affect contaminant transport, in slightly acidic to alkaline environments; Fe(III) precipitates as a highly adsorptive solid phase (ferric hydroxide), while Fe(II) is very soluble and does not retain other metals. The reduction of Fe(III) to Fe(II) will bring about the release of ferrous iron to the pore waters and also any metals that were adsorbed to the ferric hydroxide surfaces. Metal mobility in soil-waste systems is determined by the type and quantity of soil surfaces present, the concentration of metal of interest, the concentration and type of competing ions and complexing ligands, both organic and inorganic, pH, and redox status. As organic constituents of the waste matrix degrade, or as pH or redox conditions change, either through natural processes of weathering or human manipulation, the potential mobility of the metal will change as soil conditions change (McLean and Bledsoe 1992).

The results of our studies indicate that different environments displayed different responses to chemical elements pollution at the level of their trophic links. The abnormally high level of Cu in control areas (Fig. 2b) and simultaneously, the higher level of chemical elements in saline polluted areas (sodium

manufactures) relate to the accumulation processes of these elements in sodium manufactures and anthropogenic environments. The reason for this is probably the existence of unknown factors disturbing the balance of free radicals there (e.g., fertilizers). On the other hand, according to research by Ye et al. (2001), the capacity of the roots of the common bulrush *Typha latifolia* to absorb Cu increased with increasing levels of Fe or Mn on the root surface and with increased concentration of Cu in natural conditions. Thus, root plaque can act as a Cu reservoir, depending on the amount of Fe or Mn on the roots and the amount of Cu in the environment. However, Barnabas et al. (1999) examined chemical elements levels and their distributions in various parts (leaves, upright stems, rhizomes, roots) of seagrass *Thalassodendron ciliatum*, found that Cl was the most abundant element present in all parts, occurring in all tissues, but present in relatively low level in epidermal cells of the leaves and roots. They also found that Na, K, S and Mg were also abundant and occurred in all parts of plants, while Ca concentration was highest in the leaves.

We found significant differences in the concentration of chemical elements in trophic links between differentiated environments (sodium manufactures, anthropogenic and control areas) of saline regions (Table 2). These levels were predominantly correlated with acidity (pH) and salinity (Ec); Table 3. This suggested that decreased soil acidity may cause an increase in Zn and Cd level in sodium manufactures, an increase in Ca, Zn, Cu, Cd, and Pb in the anthropogenic areas, and an increase in Pb levels in control environments. Simultaneously, an increased acidity of the environment may cause an increase in Na, Mg, and Fe levels in sodium manufactures, an increase in Na, Fe, Mn, and Co level in anthropogenic areas, and an increase in Na in the control areas. Chemical element correlations with salinity were also significant in soils (Table 3). These different relationships between chemical elements and both pH and Ec signify that selectivity and fluctuations in exchange of cations in soils provide important information about the affinity and binding strength of particular cation on soil surfaces. Additionally, variations in the selectivity of nutrients and heavy metals exhibited by soil systems are important in elucidating how available these metals will be for plant/animal uptake and sheds light on their mobility and stability in soils (Appel et al. 2003). Thus, conditions affecting elements

transfer and the movements of radicals between trophic links are important for clarifying the role of metal transfer in the trophic chain. For example, McBride (2005) found that wastes applied to agricultural land contained significant concentrations of bioavailable Mo. The bioavailability of important trace elements remained elevated in soil several decades after sewage sludge application (McBride 2005). Similar investigations in agricultural landscape were conducted by Wu et al. (2005), who evaluated the use of weeds to remove pollutants from agroecosystems. The biomass production of weed species was not affected by Pb in the polluted soil compared with growth in unpolluted. Lead is accumulated primarily in the roots of weed species. Independently, Tretyakova and Noskova (2004) found that environmental conditions causing stress had a significant effect on the generative parts of Scotch pine trees *Pinus silvestris*. They found that the parameters characterizing pine pollen experienced significant interannual variations, which were closely connected with climatic conditions in the period of pollen formation. On the other hand, Lefe'vre et al. (2005) found that the perennial shrub *Zygophyllum fabago* L. was an invasive weed able to proliferate in coarse mineral substrates contaminated with heavy metals. Most of the absorbed Cd remained in the roots, but the shoots accumulated much of the Cd. These plants were able to regulate Cd translocation from roots to shoots, where it accumulated preferentially in older leaves. Cd accumulation reduced water content and water potential in shoots and osmotic potential and leaf stomatal conductance in young leaves, although plants were able to partly adapt to reestablish normal water balance after stress exposure. The plant population displayed considerable individual heterogeneity; thus, it may be possible to select individual plants combining high biomass production and high rates of Cd accumulation (Lefe'vre et al. 2005).

We found variations between chemical elements levels from the trophic links in differentiated environments. Most of these relationships were observed in soils, roots, and the green parts of plants, and most were positive (Table 4). Our results indicate that chemical elements may be accumulated in the lower links of the trophic chain, i.e., in soils and plants; however, their further flow within the trophic links is selective and variable. Simultaneously, higher levels of chemical elements were recorded in saline polluted

areas. Also, studies by Möller et al. (2005) found that the extent and severity of heavy metals contamination of arable soils and areas with intensive agricultural production are affected by various environmental factors. Pb, Cu, and Zn concentrations in the top soils exhibited anthropogenically induced increased values. The major sources for heavy metal contamination were emissions from vehicles. Similar studies in saline environments were conducted by Barrett-Lennard (2002), who studied restoration of saline land through re-vegetation. She found that the replacement of deep-rooted perennial native vegetation with shallow-rooted annual crops resulted in raising the water table and the subsequent development of major secondary salinity problem. It is now acknowledged that the restoration of landscapes requires the reintegration of perennial plants (trees, shrubs, fodders) into farming systems. Notwithstanding this, in many regions, salinization processes will continue because the alternative available perennial options are less profitable than continued annual cropping. One of the consequences of the use of groundwater by salt tolerant perennial plants is the accumulation of salt in the root zone. This has the potential to be highly damaging to plant growth and their survival in the longer term. Thus, there is a need to enhance community awareness of the long-term prospects for saline agricultures (Barrett-Lennard 2002). Similarly, Ajmal Khan et al. (2002) analyzed the effects of salinity on plant growth, water utilization, and ion accumulation of the subtropical perennial halophyte *Atriplex griffithii*. The effects of salinity on growth, water utilization, glycinebetaine content, and ion accumulation on water potential and osmotic potential of shoots became more negative with increasing salinity and growth in this perennial halophyte. Na^+ and Cl^- contents in both shoots and roots increased with increasing salinity, and increased levels of NaCl induced decreases in Ca^+ , K^+ , and Mg^{2+} in plants. *A. griffithii* accumulated a large quantity of ions under these circumstances. Inorganic ion accumulation was significant in contributing to osmotic adjustment and facilitated water uptake along the soil–plant gradient (Ajmal Khan et al. 2002).

Generally, environmental conditions determine growth and productivity of plants and hence their distribution. The differences among soil Ec from roots of plants we investigated in the same type of environment (anthropogenic environments, sodium

manufactures) and relation with extend of growth changes and biochemical parameters in tissues of plants (this paper) suggest that salinity is the most important factor, among other (pH, organic matter content) affecting the performances and distributions of investigated plants. As it is also concluded from the results of our present studies and from other researches (e.g., Silvestri et al. 2005), physiological responses of plants to Ec, pH, and organic matter are heavily species dependent. Moreover, we can suppose that halophytes show adaptation to development only in extremely salinity conditions, in opposite to glyco-phytes. However, the changes of soil conditions (especially the rinse of salt) and lack of control of expansion of strong competitors (common reed) by cutting or grazing (Piernik 2006) may probably influence the distribution of halophytes at anthropogenic disturbed environments. We can also assigned that changes in biochemical parameters (antioxidant defense, lipoperoxidation, stress proteins) found in studies by Koim-Puchowska (2014) were relatively different, as compared to those reported from tissues subjected to artificial stress treatments in experimental laboratory conditions (Aghaleh et al. 2009). We thus finally suggest that results of experiments carried in these conditions are very important to explain plants' physiological responses upon the action of pollutants in the environment. Simultaneously, these factors are of limited ecological relevance, because many simultaneously acting and effecting factors are active in plants in natural environments (Shi and Sheng 2005; Zhu et al. 2003). Thus, further environmental studies at broader scale are needed for compare the results in experimental conditions to effective landscape management in the industrial saline areas.

On the basis of the results obtained in our study, we conclude that dependencies between chemical elements and both pH and Ec signify that the selectivity of cations and their fluctuation exchange in soils provide important information about the affinity and binding strength of these cations on soil surface. The results of whole element–element environment interactions indicate that chemical elements may be accumulated in lower links of the trophic chain, i.e., in soils and plants, and that their further flow is selective and variable. However, the results obtained by Prokop et al. (2003) emphasized the effect of contaminated sediments on the bioavailability and mobility of metals. The physical and chemical

characteristics and ecotoxicity of sediments, pore waters, and leachates were evaluated after heavy metals contamination. The mobility and leaching of Cd and Zn in sediments increased with decreasing pH and with decreasing organic matter content. An increase in sediment toxicity to plants and an increase in eluate toxicity to invertebrates were observed (Prokop et al. 2003). They suggest that water flow through sediment reduces the actual toxicity of the upper layer of the deposited sediment but at the same time intensifies the risk of groundwater contamination. Thus, retardation and leaching potential calculations are good predictors of the mobility of Cd and Zn in land-deposited sediments. The mobility and leaching of Cd and Zn in sediments depended mainly on sediment pH and organic matter content. Water flow through sediment can thus reduce the actual toxicity of the upper layer of the deposited sediment but at the same time can intensify the risk of groundwater contamination (Prokop et al. 2003). Our present results (this paper) also indicate that the level of chemical elements in the trophic chains is correlated with soil acidity and salinity, and these positive and negative relations signify that any changes in soil acidity and salinity may cause significant fluctuations in element transfer between trophic links. At the same time, it should be noted that, according to research by Kidd et al. (2007), the augmentation of agricultural soils with municipal sewage sludge provides a valuable source of plant nutrients and organic matter. Nevertheless, the addition of heavy metals and the risks of eutrophication by this activity continue to be of concern.

Summarizing, the results of our investigations are supported by other studies (Appel et al. 2003; Florea and Büsselberg 2006; Prasad et al. 2006), and we can assume that chemical elements and compounds are natural constituents of the soil fractions and soil environment, which depend on natural biogeochemical processes and a variety of human activities. They are transformed naturally by living species that influence their mobility and accumulation in the environment. They are further influenced by acidification, salinity, and redox potential. In consequence, free radicals are released into the environment where they influence plant, animal, and human health. Due to their widespread use in human activities such as industry, agriculture, and medicine, numerous wild diseases and health risks may be associated with

exposure to these various substances. Many reports on metal intoxication have been documented, and studies especially on neurotoxicity, genotoxicity, and carcinogenicity have been conducted. These studies highlight the importance of chemical elements' in bioaccumulation and bioavailability. These dependencies signify that measurements of the selectivity of cations and their fluctuating exchange in soils provide important information about the affinity and binding strength of particular cation on soil surface. These results indicate that elements may be accumulated in soils and plants; however, their further flow is selective and variable. In addition, the mobility of chemical elements depends on their chemical form; they may be accumulated in lower links of trophic chain; however, their further flow is selective and affected by their chemical reactivity, redox potential, and binding properties. These processes may cause further ecophysiological reactions in plants and invertebrates inhabiting contaminated environments.

Conclusions

1. Soil acidity and salinity affect the bioaccumulation of free radicals in the trophic levels. Decreased soil acidity causes Zn and Cd to increase in sodium manufactures and Ca, Zn, Cu, Cd, and Pb to increase in the anthropogenic sites. Increase soil acidity causes Na, Mg, and Fe to increase in sodium manufactures sites and Na, Fe, Mn, and Co to increase in the anthropogenic sites.
2. Significant acidity–salinity relationships occur in natural salt marshes (positive in saline areas of sodium manufactures and negative in the anthropogenic and control sites).
3. The concentration of chemical elements' differed in trophic links in natural saline environments, while the selectivity of cations and their fluctuation exchange in soils provided important information about their affinity and binding strength.
4. Element–element interactions occur between trophic links in soils, roots, and the green parts of plants. Chemical elements are accumulated in lower trophic links (soils, plants); however, their further flow is selective and variable.
5. Selectivity exhibited by soil systems for nutrients and heavy metals is important in elucidating how available these metals are for plant/animal uptake as well as their mobility and stability in soils.
6. Essential for explanation the significant differences in the concentration of chemical elements in the trophic links due to the changes of acidity (pH), salinity, organic matter content and due to vertical movement of chemical elements (that commonly exhibited predominant association with soil pH and organic matter) is to introduce mechanisms and regularities of metal retention in soils.

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