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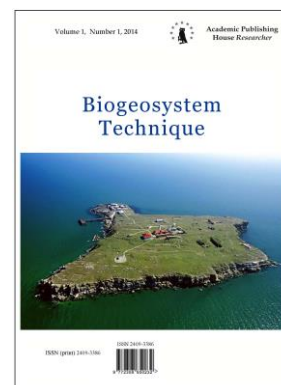
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## Articles

### Dynamics of the Red River Bed in the Hanoi Region

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#### Abstract

The article substantiates the need to study the fluctuations of the area of the Red riverbed in the area of the city of Hanoi in certain historical periods. A methodology proposed for studying the river, including methods of remote sensing of the Earth (remote sensing) and Geographic Information System (GIS). During each historical period, the Red Riverbed changes in the direction of a gradual balance of bends, erosion of the banks and growth between the two banks. The influence of climate change on spatial changes in the riverbed analyzed using a superimposed map and ceilings. Explosive fluctuations in the area of the riverbed detected during periods of peak floods and greatest droughts. The results of the research formed the basis for creating a spatial security corridor and planning operational and environmental solutions on both banks of the river.

**Keywords:** Vietnam, Hanoi, Red river, dynamics of the river, GIS, Lo river, Thao river, Da river, Red river city, historical flood, historic low water level.

#### 1. Introduction

The length of the Red River in Vietnam is about 560 km. Red River is the second largest river system (after the Mekong catchment) which flows through Vietnam to the South China Sea (Bravard et al., 2013; Bravard et al., 2014; Thi Kim Oanh Ta et al., 2012). The Red River comprises three main tributaries: Da, Lo, and Thao (Wysocka, Swierczewska, 2003; Luu Thi Nguyet Minh et al., 2010). It is also the largest river in the North of Vietnam, flowing in a natural state with a difference between two main water seasons (Dang et al., 2010; Kort, Booij, 2007). A large amount of sediment draining into the river due to alluvial deposits on the catchment (Brunier et al., 2014; Thi Kim Oanh Ta et al., 2002). Therefore, the Red River system is very complex. There are constant

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changes in water flow and erosion, which causes great difficulties in the use of the river, as well as in the use of coastal land (Phan Cao Duong et al., 2017; Thi Phuong Quynh Le et al., 2007).

Urban environmental management in the Hanoi region has attracted increasing interest in recent years, as evidenced by a large number of studies (Taylor, Wright, 2001), both in Hanoi and other cities. However, these studies focus mainly on environmental pollution. Changes in the soil cover of the Hanoi region can be studied using satellite images (Lan Pham Thi et al., 2013; Hung Vuong Pham et al., 2018). This technique is widely used for environmental monitoring of territories (Boateng, 2012; Duong Du Bui et al., 2011).

In 2006–2007, the city of Hanoi, with the assistance and support of the city of Seoul (South Korea), worked out a basic planning project for the development of the Red River through Hanoi. The study of spatial changes in the section of the Red River canal that passes through Hanoi between 1999 and 2013 conducted with the aim of creating a scientific basis for the development, implementation, evaluation and construction of the "Red River City" project.

Remote sensing and its methods were used to study fluctuations in the Red Riverbed (Nguyen Hoang Hiep et al., 2018). The remote sensing methods, as well as GIS methods, are widely used for monitoring the quality of inland waters (Haddeland et al., 2006; Prathumratana et al., 2008). Water changes can be effectively studied using Landsat images (Nektarios, Karatzas, 2011). In our study, we applied these modern powerful tools to study the process of Red River bed fluctuation.

To control the state of water bodies simultaneously with space survey, the express methods of the monitoring is used (Nguyen Hoang Hiep et al., 2018; Lan Pham Thi et al., 2013). This helps to clarify a number of important points not fully detectable by ground surveying of the territory.

## 2. Methods

### 2.1. Photo data used

Within the scope of the study, the Landsat TM and Landsat 8 images data of 1999, 2003, 2007, 2008, 2009 and 2013 were used. The data borrowed at the US Geological Department's website <http://glovis.usgs.com>. The position of the image collected Path/Row: 127/45 and are in the coordinate system WGS 84, zone 48N. The images selected in the study of changes in the riverbed were from 1999, 2003, 2007 and 2013. The images collected the days with equivalent river water level of 850 cm (according to the data of Hanoi hydrographic station). This helps easily compare the fluctuations in riverbed area over time (Thilakarathne, Sridhar, 2017; Dongnan et al., 2017). Two images collected during the historical flood (August 2008) and historical drought (November 2009) were recorded on the Red River to compare the fluctuations of the river bed due to impacts of the climate change (Table 1).

**Table 1.** List of satellite imagery

No	Date/Year	Path/Row	Sensor
1	20.09.1999	127/45	ETM+
2	05.05.2003	127/45	ETM+
3	08.11.2007	127/45	ETM+
4	30.08.2008	127/45	ETM+
5	05.11.2009	127/45	TM
6	18.12.2013	127/45	TM

The equipment with hybrid photodetectors (Boateng, 2012) and photosensitive sensors were used for the image acquisition (Lan Pham Thi et al., 2013).

Landsat TM and ETM+ images consist of component images of 7 channels, each band corresponding to a range of values of light wavelength. To represent Landsat image, use composite image of 3 channels (red, blue and blue). Here is the background information about the tapes of Landsat.

Channel 1 (0.45-0.52  $\mu\text{m}$ , Blue): This is a short wavelength band, light can penetrate water. This tape is used to study objects in water, submerged ecosystems. Use tape 1 to study alluvial flows, coral reefs, water depths.

Channel 2 (0.52-0.60  $\mu\text{m}$ , Green): This tape quality is almost the same as Band 1, and was chosen for vegetation study because the wavelength of light exhibits a green color close to that of vegetation.

Channel 3 (0.63-0.69  $\mu\text{m}$ , Red): The wavelength range of this band is absorbed by plants (this band is called chlorophyll absorption band). Band 3 is used to distinguish between plants and soil. Used to study plants (good forest, bad forest).

Channel 4 (0.76-0.90  $\mu\text{m}$ , Near Infrared): Band 4 is absorbed by water, so its image of the water surface is black, showing that the reflected light from the water surface is very weak. This tape is used to distinguish between water and land.

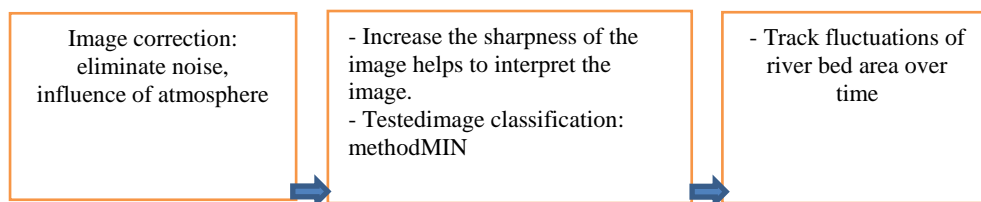
Channel 5 (1.55-1.75  $\mu\text{m}$ , Mid-Infrared): This band is very sensitive to moisture, it is used to study vegetation and soil moisture. Band 5 is also used in the study of clouds and snow.

Channel 6 (10.40-12.50  $\mu\text{m}$ , Thermal Infrared): This is Thermal Infrared tape, used to study ground temperature. Applications of this channel include studying geology, calculating the absorption of heat by plants, studying the influence of clouds on ground temperature.

Channel 7 (2.08-2.35  $\mu\text{m}$ , Far Infrared): This band is also used to study vegetation moisture like Channel 5, it is used to study geology and soil. The bands are combined according to the different ratios and color combinations to highlight research objects for image interpretation.

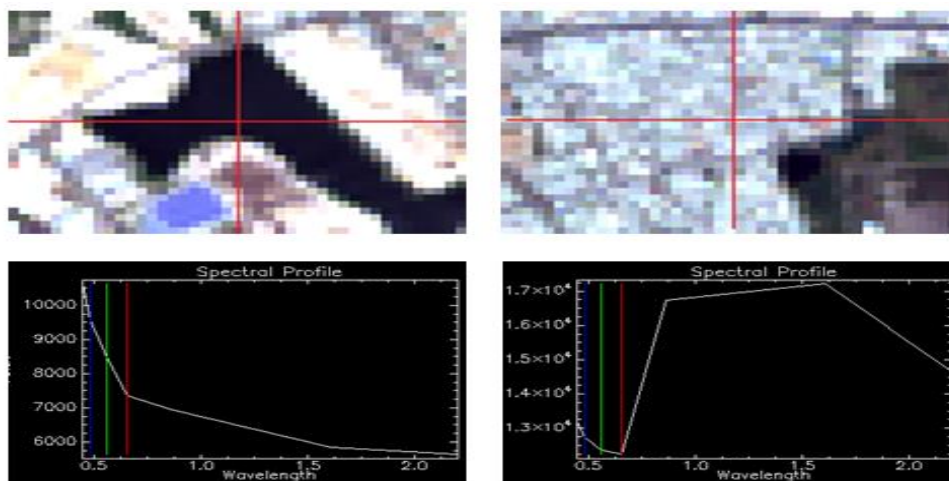
**2.2. Image processing method**

The Figure 1 shows a progress of research. After acquisition, the Landsat image was calibrated and corrected, then it was necessary to eliminate noise, sharpen the image, and adjust the spectrum. For extraction at the waterline, the image is displayed in a 5/2 channel format. An imaging helps to characterize land cover using a classification algorithm with a minimum distance test.



**Fig. 1.** Research progress

In this study, two objects need classification: river surface area and coastal area. Based on the spectral reflection characteristics of each object type (Figure 2), the keys for classification identified as follows:

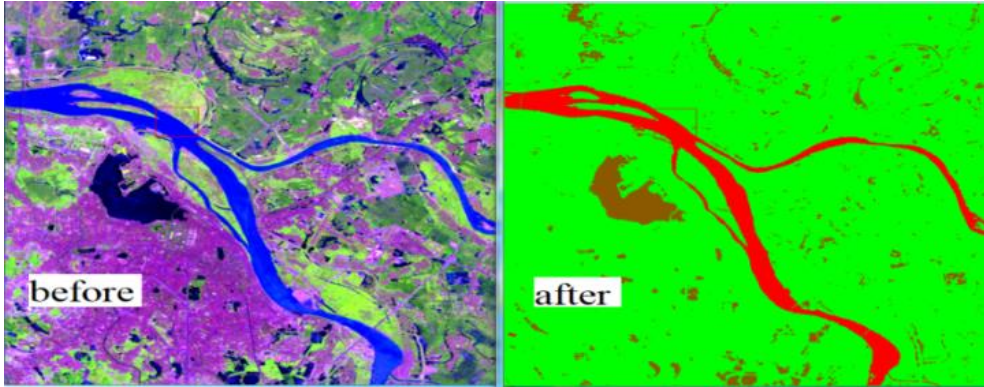


River surface area

Coastal area

**Fig. 2.** Real color composite photos of sample objects and the corresponding spectrum graph

Landsat TM images with artificial color combination are made up of three channels 4 (Red), 3 (Green) and 2 (Yellow), through basic processing and band selection to minimize the image. Clouds and silt affect the appearance of objects in the image. The color of the objects shown in the image is a fake color. The Red River bed area and the coastal area after classification presented in the Figure 3.



**Fig. 3.** Results before and after sorting using the image processing method

**2.3. Mapping volatility method**

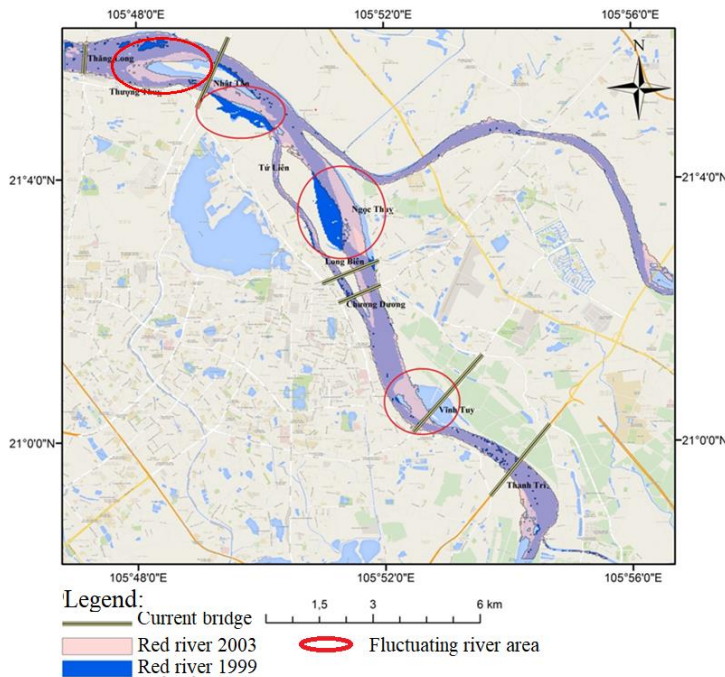
The map overlay is a convenient spatial analysis tool and an important factor behind the development of GIS technology. Overlapping is a collection of spatial data and attributes of two or more data layers, and the tool is one of the most popular and powerful data analysis in GIS.

In the project, the water information layers on the research river section from Landsat image data were transformed into the separate layers in GIS. Then the map overlay method to display and calculate volatility used.

**3. Results**

**3.1. Fluctuation of Red River bed**

Fluctuation of Red River bed space over time is shown in Figures 4-6.



**Fig. 4.** Fluctuation of Red River bed space over time: 1999–2003

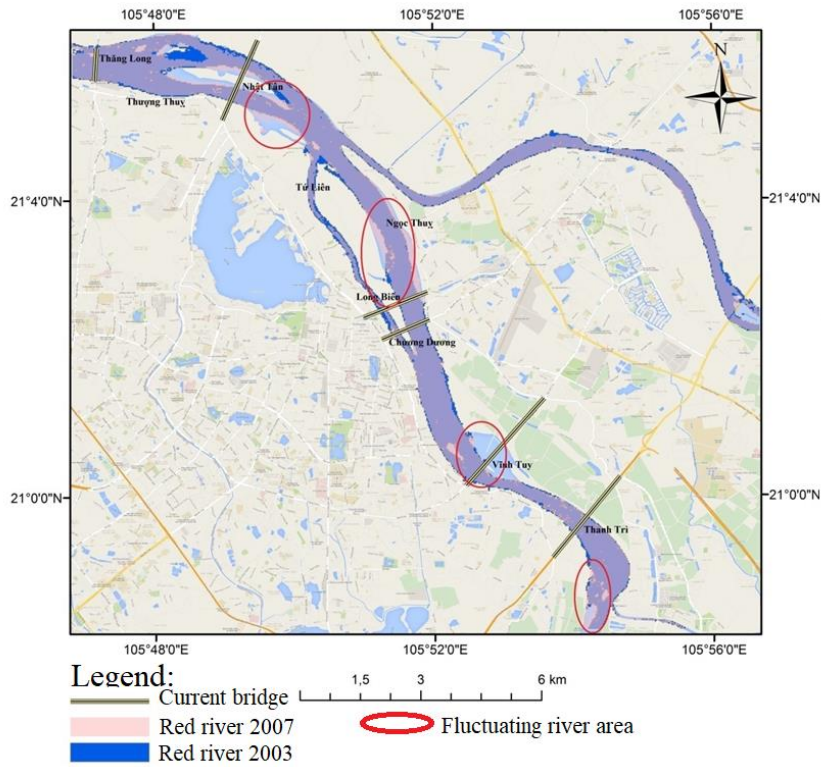


Fig. 5. Fluctuation of Red River bed space over time: 2003–2007

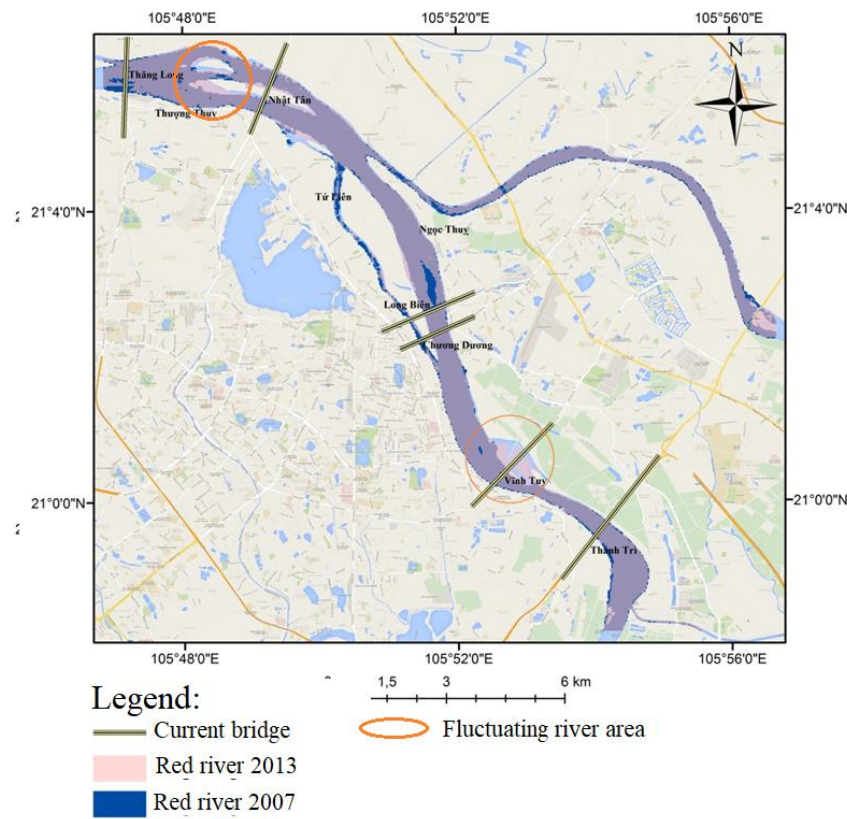


Fig. 6. Fluctuation of river bed space over time: 2007–2013

When the maps in Figures 4-6 overlap the fluctuations in 1999 and 2003, the fluctuations become more pronounced. When compared by this period, the river bed in 2003 tended to shift to the Northeast. Tu Lien area narrowed and moved to the Northeast more than 600 m. Sand dunes in Nhat Tan bridge area and Tu Lien are getting smaller and smaller.

In the 2003–2007 period, the river seemed to be more stable than the previous period. The Tu Lien alluvial area was expanded to more than 600 m compared to about 500 m in 2003.

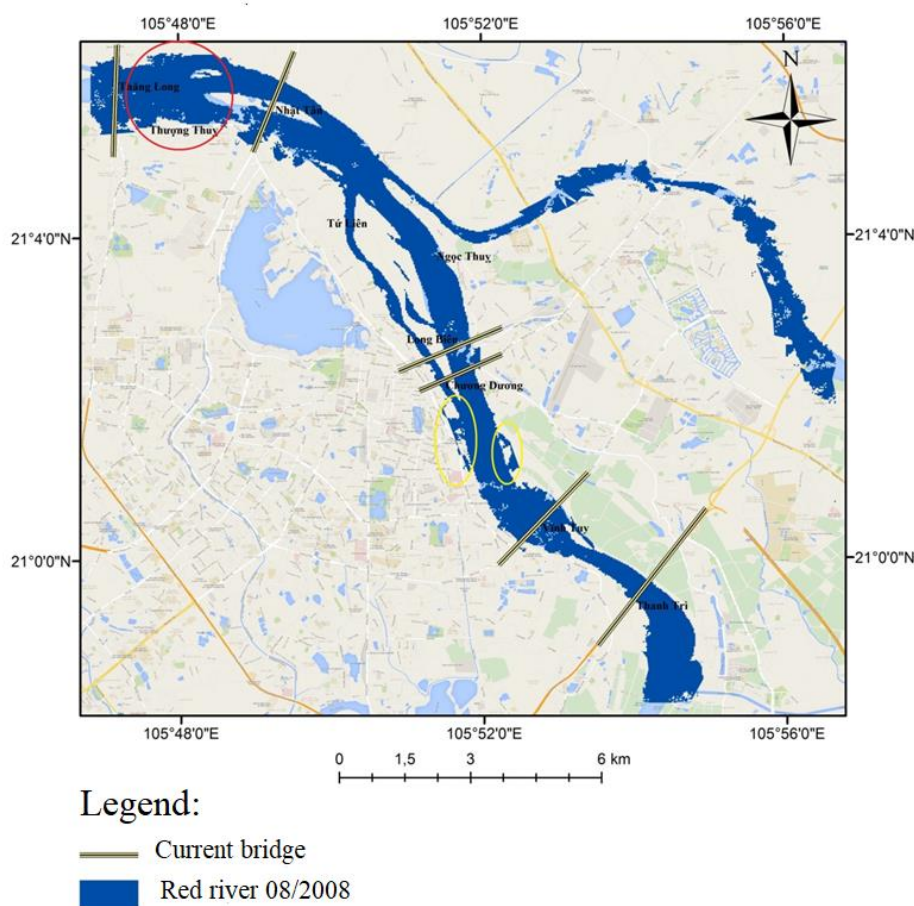
In the 2007–2013 period, most changed area was the foot of VinhTuy bridge, the river bed expanded suddenly from nearly 600 m in 2007 to more than 1100 m in 2013 to the Northeast.

### 3.2. The river bed space fluctuation due to climate change

The left part of the Figure 7 shows the space of the Red River on August 30, 2008, the end of the historical 2008 flood. Heavy rains pushed the Red River high. During this flood, the Red River bed expanded to more than 1.6 km and distributed to the southwest.

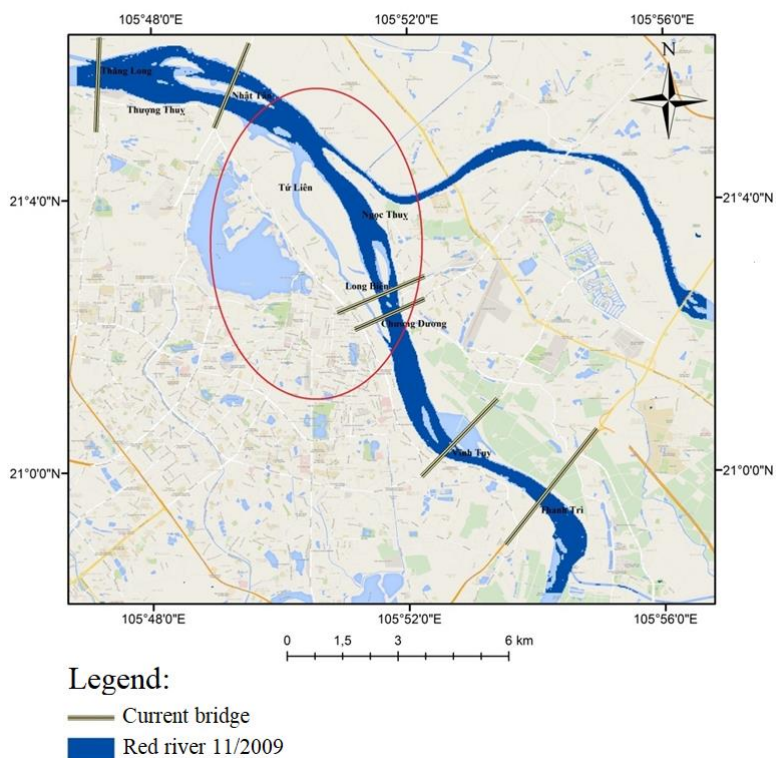
At the end of 2009, a severe drought affected the Red River. The central part of the Figure 8 shows the space of the Red River bed on November 5, 2009. The river bed seems to be narrowed to the utmost, Tu Lien beach is connected to the mainland, the branching line creating Tu Lien area disappears.

Spatial fluctuations in the section of the Red River passing through Hanoi during the historical flood (30/08/2008) and historical drought (05/11/2009) are shown in Figure 9 on the right.

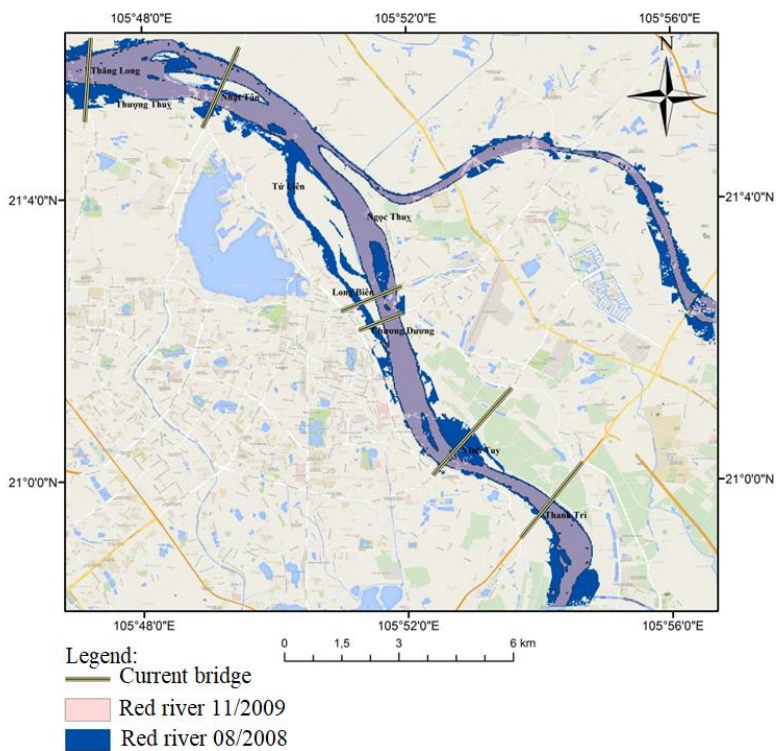


**Fig. 7.** Fluctuation of the Red River during the historical flood in 30/08/2008





**Fig. 8.** Fluctuation of the Red River during the historical drought in 05/11/2009



**Fig. 9.** Fluctuation of the Red River during the historical flood in 30/08/2008 and the historical drought in 05/11/2009

#### 4. Conclusion

The section of the Red River flowing through Hanoi plays a particularly important role in supplying and draining water to the city, adjusting the microclimate and providing a natural living environment for the people of the city. This river section also plays an important role in waterway transport in Vietnam.

In the period of 1999–2013, the Red River section flowing through Hanoi had many changes in the position and space of the river bed. For each historical period, the river bed changed in the direction of gradual balance of bends, erosion of the river banks and accretion between the two sides, especially the mudflats and sand between the rivers.

In order to build a scientific basis for the implementation of the city's planning project for the Red River bank, it is necessary to take into consideration the historical fluctuations of the river bed space to ensure that the river bed is developing normally to minimize damage to the river's natural ecosystem.

Studying the spatial changes of the Red River in times of extreme natural disasters such as historical floods, historical droughts it is necessary to have appropriate solutions to conserve riverbeds and build safety corridors in the future.

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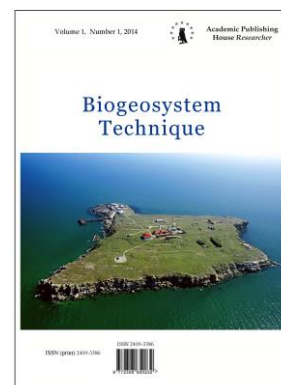
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## Nano-Priming Technology for Sustainable Agriculture

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### Abstract

Climate change affected crop growth and development which reduced crop production. Decreasing crop production can create food security-related problems. Nanotechnology is a new era of technology for the solution of climate change-related problems in agriculture we can say the "NanoTech-Agril" era that helps the farmer to produce a larger number of crops without any problem related to climate change problems like salinity, drought, flood etc. Nanoparticle-based seed priming can enhance the seed metabolism and signalling pathways, that not only enhanced seed germination but also help in the establishment of plants for the entire lifecycle. Nano-seed priming also enhanced the metabolic, biochemical, antioxidant and phytohormone pathways resulting in the promotion of abiotic and biotic stresses that cut off the need for pesticides and fertilizers. The present review provides an overview of the nanoparticle application for sustainable agriculture.

**Keywords:** Climate change, food security, nano seed priming, antioxidant, pesticides, fertilizers

### 1. Introduction

Several difficulties are being expressed by agriculture, including pest-related productivity losses, natural resources depletion, and the consequences of global climate change (De La Torre-Roche et al., 2020; Kah et al., 2019). Another issue is that conventional farming techniques depend on the constant use of fertilizers and pesticides, which pollutes the environment (Rajput et al., 2018). By 2050, the global population is predicted to reach 9-10 billion, suggesting that food production would need to expand by 25-70 % from present levels (Scott et al., 2018). As a result, new agricultural technology must be used in order to assure sustainability and boost production (Fraceto et al., 2016; Panpatte et al., 2016). Seed germination is the beginning of a plant's life, and

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good germination is critical for the survival of plant species and its conservation, especially in some ecosystems like rangeland and agricultural land (Manjaiah et al., 2018). Furthermore, in terms of drought and salt stress, the germination stage is one of the most vulnerable. If a plant can endure these challenges, it will go to the next stage of development (Akter et al., 2018). Plant development and production are determined by the rate and homogeneity of seedlings, which protect buds from damage caused by adverse environmental factors (Rajput et al., 2015). These include drought, salinity, temperature, moisture, which have significant impact on seed germination and subsequent seedling growth (Friedrichs et al., 2019; Maity et al., 2018; Zahedifar, Zohrabi, 2016).

Crop protection can benefit from nanomaterials, particularly nanoparticles (Scott et al., 2018). This is a significant area of study that has piqued the interest of a number of agricultural firms, culminating in the use of nanoparticles in formulations (Chau et al., 2019). Pest control, plant nutrition, and environmentally friendly production methods can all benefit from the use of nanopesticides and nanofertilizers (Acharya et al., 2020; Rajput et al., 2021c). Nanoparticles have been demonstrated to have varied impacts on seeds and plants in recent research (Acharya et al., 2020; Pérez-de-Luque, 2017). Some negative side effects such as phytotoxicity or germination suppression may be caused due to nanoparticles (Rajput et al., 2020a). On the other hand, some nanoparticles can function as stimulants in cellular signaling pathways, enhancing seed metabolism, seedling vigor and plant development (Abbasi Khalaki et al., 2020). The physical and chemical features of nanoparticles, such as size, zeta potential, and concentration, are the determinants that ultimately dictate biological responses (Abbasi Khalaki et al., 2020; Acharya et al., 2019; Singh et al., 2021). These features are important in the absorption and transport of nanoparticles in plants. Smaller nanoparticles, for example, are more effective at crossing biological barriers (Bombo et al., 2019; Hu et al., 2020; Palocci et al., 2017; Rajput et al., 2022; Valletta et al., 2014). The nanoparticles' surface charge is also important. The leaves may pick up both positively and negatively charged nanoparticles and transport them to roots. But only negatively charged nanoparticles are immediately absorbed by the roots. Formation of mucilage occurs due to positive charges which checks the plants from absorbing them (Avellan et al., 2017; Spielman-Sun et al., 2019). To protect seeds during storage, promote germination and its synchronization, boost crop tolerance to abiotic and biotic stress, and plant development, nanoprimering may be applied to seeds which will also assist in minimizing the amounts of pesticides and fertilizers required (Malik et al., 2020; Marina Voloshina, 2020). It has been suggested by new research that a variety of genes can be activated during germination such as those involved in plant stress tolerance by seed nanoprimering. Although studies have already demonstrated encouraging results (Hussain et al., 2019; Ye et al., 2020), the use of nanotechnology for seed priming is a new field of research. Because many nanoparticles contain antimicrobial properties and may thus load antimicrobial compounds, seed nano-priming can also be employed for seed protection (Hussain et al., 2019; Pirzada et al., 2020). Furthermore, nano-priming may be employed to target seed biofortification in order to improve food quality and production (Hussain et al., 2019; Pirzada et al., 2020).

## 2. Results and discussion

### Nanoparticles and nano-enabled products

Nanotechnology is an emerging technology that have the potential solution for most agriculture problems (Singh et al., 2022). Nanoparticles have many unique properties due to their tiny size in nanometers 1-100 nm with a large surface area which increase their physical and chemical importance (Rajput et al., 2021b; Singh et al., 2022). These favorable features of nanoparticles help to formation in various nano-enabled products e.g., nanofertilizer, nanoinsecticide, nanopesticides etc. for sustainable agriculture (Table 1). Four basic kinds of NPs are defined based on their chemical composition: Carbon-based such as nanofibers and nanotubes of carbon; Metal-oxide-based such as Ag, Cu, etc.; Bio-organic-based such as micelles and liposomes; Composite based (Lowry et al., 2019). Organic and inorganic types of NPs is another classification.

Organic NPs, such as polymeric NPs, liposomes, carbon-based nanomaterials, lipid-based nanocarriers, and solid lipid NPs, are biodegradable. Inorganic NPs are made of inorganic materials such as metals and metal oxides, such as silver oxide and zinc oxide. Silver NPs (Ag-NPs) are the most commonly used of all the synthesized NPs, with a dominance of more than 25 % in

diverse consumer items (Scott et al., 2018). Antifungal, antiviral, and antibacterial medicines are the most common uses of Ag-NPs.

**Table 1.** Nano-enabled agriculture products (Rajput et al., 2021b)

Nano-enabled products	Company	Country	Applications
AZterknot fungicide	Vive Crop Protection	Canada	Use as fungicide
Nanosulf Drenching	Alert Biotech	India	Use as antifungal
Natural Pesticide Nano-5-011	Organic Fertilizing	Taiwan	Use as pesticide
NeuDelta-2.5EC	Neufarm GmbH	Germany	Use as pesticide
Groagro 4: Super Kalium Catalyst + T. E	Bonding Technology Resources SdnBhd	Malaysia	Potassium nanofertilizer
PADI 3 (17: 3 : 25 : 2) + GROAGRO 4	Bonding Technology Resources SdnBhd	Malaysia	Use as NPK fertilizer
Nano-urea	Indian Farmers Fertilizer Cooperative Limited (IFFCO)	India	Nano-urea replacement of traditional urea fertilizer

New kinds of NPs with a wide range of applications in numerous industries are generated each year employing state of art technology. Two ways are there for synthesis of NPs: i) top-down method and ii) bottom-up method (Fraceto et al., 2016; Panpatte et al., 2016). In addition, NPs are also synthesized using three distinct methods: physical, chemical and biological. The variance in stabilizing and lowering the potential of biomolecules present in the plant results in the synthesis of green NPs for seed priming accumulated NPs. Camerel et al., 2002 reported the creation of gold NPs inside the live plant alfalfa when the plants were cultivated in an AuCl<sub>4</sub> rich environment. Bali and Harris discovered *Medicago sativa* and *Brassica juncea* plants' capacity to collect Au NPs from aqueous KAuCl<sub>4</sub> solutions in a comparable study. The majority of the NPs were found in the xylem parenchyma cells, although some were also found in the epidermis, vascular bundles, and cortex. Throughout the last several years, the majority of research has concentrated on synthesis of NPs utilizing the inactive component of the plants, either in powder form or as an extract (Mohamad et al., 2014). Metallic NPs may be made from a variety of plant components, including leaves, stems, flowers, fruits, roots, seed coats, seeds, and latex.

NPs are made at a certain temperature and pH by combining plant biomass/extract and a salt solution of metal. The colour change of the solution serves the major conformation of NPs synthesis (Mohamad et al., 2014). Plant extracts are made using a variety of techniques including Soxhlet apparatus, cold treatment, and hot treatment, which are then used to make NPs. Because of it is of scale-up and downstream processing, this technique of NP synthesis is more suited than intracellular approach. This approach is also environment friendly, non-toxic, biocompatible and renewable (Camerel et al., 2002; Dikshit et al., 2021; Mittal et al., 2013; Mohamad et al., 2014). These NPs are recognized to have a variety of biological uses due to their biocompatibility. The production of metal NPs begins with the addition of plant extract to a metal precursor solution containing metal salts. For the production of Ag, Au, Pt, Cu, Fe, Se, Ni, NPs, metal precursor solutions such as AgNO<sub>3</sub>, HAuCl<sub>4</sub>, PdCl<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, Na<sub>2</sub>SeO<sub>3</sub>, and (NiNO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O are often utilized (Dikshit et al., 2021). Metal NPs are synthesized primarily in three phases utilizing plant extract. The reduction of metal ions (M<sup>+</sup> or M<sub>2</sub><sup>+</sup>) to metal atoms (M<sup>0</sup>) and subsequent nucleation of the reduced metal atoms happens in the first step (Dikshit et al.,

2021). The convergence of tiny nearby NPs into bigger particles happens in the second stage, which is accompanied by rise in thermodynamic stability. The procedure is completed at the last stage by giving the NPs their final form (Makarov et al., 2014; Si, Mandal, 2007). Various functional biomolecules are present in the plant extract which help in reduction and stabilization of metal ions in the solutions. But, identifying the exact reducing and stabilizing molecules in NP production is challenging because the plant extract contains large variety of phytochemicals.

### **Germination and Principles of Seed Priming**

For crop quality and plant development in agriculture, germination is a critical phase (Abbasi Khalaki et al., 2020). Seedling growth is rapid, resulting in rapid expansion of the leaves and elongation of the roots, which favors nutrient intake, biomass production, and translocation through transpiration flow (Mahakham et al., 2016). Slow germination exposes the early seedling, which is one of the most sensitive phases of the plant life cycle, to a variety of environmental stress conditions or diseases, resulting in reduced vigor and crop output, as well as financial losses for farmers (Acharya et al., 2019). There are three phases of seed germination (Nonogaki et al., 2010). Phase I is imbibition which begins with quick water absorption, basal metabolism of seed, mitochondrial activity, transcription and protein synthesis in the seed. The metabolism becomes hyperactive in phase II (lag phase or activation), with the generation of enzymes essential for reserve mobilization and embryo growth, including as amylases, endoxylanase, and phytase. The seeds show rapid water intake in phase III, and embryo expansion culminates in radicle protrusion (Nonogaki, 2014). Auxins are responsible for seed germination or dormancy (Wu et al., 2020). To govern cellular activities associated to seed germination, ROS modulate gene expression and phytohormone signaling, as well as the homeostasis of abscisic acid, gibberellins, auxins, and ethylene (Wu et al., 2020). When ROS levels are too high, however, substantial oxidative damage occurs, causing seed germination to be hampered (Bailly, 2019). To be encompassed in the so-called oxidative window, which allows appropriate germination completion, ROS level must be spatiotemporally managed (Bailly, 2019).

To increase seed germination and plant development, seed priming is a classical agricultural practice based on seed preparation prior to planting (Carrillo-Reche et al., 2018). Its commonly a water-based approach in which seeds are soaked in water and then dried or physically by UV priming (Lemmens et al., 2019). To initiate pre-germination metabolic pathways (phases I and II), water absorption must be sufficient without causing radicle emergence. Seed metabolism is altered by this process at the molecular and cellular levels such as increased reverse mobilization capacity, transcriptomic reprogramming, loosening of cell wall, higher tendency for translation and post-translation modifications. It generates a specific physiological state on absorption that increases and strengthens the germination and vitality of primed seeds (Carrillo-Reche et al., 2018). Antioxidant mechanisms, heat shock proteins and other stress related responses are induced due to soaking and subsequent drying due to which cross resistance to additional stressors develops. Furthermore, rapid germination reduces the time that germinating seeds are exposed to unfavorable soil conditions. To promote seedling vigour, make plants more tolerant to stress conditions, and increase and coordinate germination, seed priming has therefore been used and thus improving quality of food and increasing yield as a result (Carrillo-Reche et al., 2018; Lemmens et al., 2019).

Seed priming can be done in a variety of ways, such as hydro-priming or hydro-thermopriming, in which water treatment is given to seeds, typically for 7-14 hours to keep them hydrated, allowing germination phase II to proceed (Carrillo-Reche et al., 2018). Temperature alteration (cold and hot) can be used with this approach (Noorhosseini et al., 2017). To manage hydration (about 10-20 %), and modify seed metabolism via an abiotic stress, low water potential solutions are utilized in osmo-priming. Other pre-sowing treatments include using microorganisms (Lemmens et al., 2019), solutions containing salts (Saddiq et al., 2019), and plant growth regulators (Syta et al., 2018) for bio-priming, halopriming and hormo-priming respectively.

For seed priming, a novel approach would be seed nano-priming in which nanomaterials, primarily nanoparticles are used (Table 2).

**Table 2.** Use of nanomaterial for seed priming and coating

Nanoparticle	Characteristics	Crops	Application	References
Fe-NPs	Particle size <50nm	<i>Sorghum bicolor</i>	Enhances germination, seeding growth and salinity tolerance of <i>S. bicolor</i>	(Maswada et al., 2018)
Biogenic Fe-NPs	Particle size of 19–30 nm	<i>Citrullus lanatus</i>	Modulate Antioxidant Potential and Defense-Linked Hormones in <i>C. lanatus</i> Seedlings	(Kasote et al., 2019)
Biogenic Ag-NPs	Particle size of 6-26 nm	<i>Oryza sativa</i>	Enhancing germination and starch metabolism of aged <i>O. sativa</i> seeds	(Mahakham et al., 2017)
ZnO-NPs and Fe <sub>2</sub> O <sub>4</sub> -NPs	ZnO-NPs 20–30 nm Fe <sub>2</sub> O <sub>4</sub> -NPs 50-100 nm	<i>Triticum aestivum</i>	Improved the plant growth and reduced the oxidative stress and cadmium concentration in <i>T.aestivum</i>	(Rizwan et al., 2019)
Si-NPs	Si-NPs 90nm	<i>T.aestivum</i>	Improved the biomass and yield while reduced the oxidative stress and cadmium concentration in <i>T.aestivum</i> grains	(Hussain et al., 2019)
Au-NPs	Au-NPs 10-30nm	<i>Zea mays L.</i>	promoting <i>Z. mays</i> seed germination	(Mahakham et al., 2016)
Nano-pyrite (FeS <sub>2</sub> )	FeS <sub>2</sub> -NPs10-30nm	<i>O. sativa</i>	Use as NPK fertilizer <i>O. sativa</i> production	(Das et al., 2018)

Seed priming and seed nano priming are not the same thing, because traditional seed priming mostly include hydropriming using water or solutions from which the chemicals are adsorbed on the seed and seed coating is formed with these nutrients, biopolymers or hormones. Suspensions and nanoformulations are utilized in seed nano-priming, and the nanoparticles may or may not be taken up by the seeds (Acharya et al., 2019). Even when nanoparticles are taken up, the majority of them remain as coating on the seed surface (Acharya et al., 2019; Montanha et al., 2020). To defend against diseases while storage or in the fields, fungicides or bactericides are combined with such seed coatings (Gross et al., 2020). Khodakovskaya et al. (2009) published one of the first studies demonstrating the ability of nanomaterials to alter seed germination. Despite the lack of seed priming, these researchers revealed that tomato seeds can absorb carbon nanotubes. The water intake was boosted by these nanotubes, leading to 2-fold more blooms on tomato plants. Carbon nanotubes have also been shown to improve the gene expression of various types of channel proteins for water and alter seed metabolism in plants like barley, soybean, and maize (Villagarcia et al., 2012). For seed nano-priming, distinct nanomaterials have been shown to have potency such as metallic, biogenic metallic, and polymeric nanoparticles (Siddaiah et al., 2018). This leads to alteration of gene expression that can change the metabolic processes like production of hormones, and cause rapid development of shoot and root. After seed priming, high resistance to pests and other biotic and biotic factors in the field develops in the plants due to rise in the antioxidant activity and enzymatic activities in the defense system (Itroutwar et al., 2019; Siddaiah et al., 2018).

### Application of different Nanoparticles in seed priming

#### Silver nanoparticles (Ag-NPs)

After carbon nanotubes, Ag-NPs are now one of the most frequently utilized nanoparticles. Antimicrobial properties of these NPs are widely employed in a variety of fields, including detergents, textiles, and polymers (Awasthi et al., 2017). For their distinct properties such as preferred optical, electrical and magnetic properties, Ag-NPs are highly prized. Thus, they can be mixed in cryogenic superconducting components, electronic materials, biosensor materials, cosmetics, composite fibers, checking the action of ethylene, and antimicrobial applications in



plants. They are also suggested to be beneficial in gardening and other agricultural operations because of Ag-NPs capacity to prevent seeds from bacterial and fungal attack (Parveen, Rao, 2015).

#### **Silica nanoparticles (Si-NPs)**

Following oxygen, Silicon (Si) is the most prevalent element on earth contributing around 31% of earth's crust (Dietz, Herth, 2011). Nanosilica is a valuable substance with applications in variety of disciplines of research and technology, biology and electronics. According to some experts, Si might help plants cope with salt stress (Wang et al., 2011). Si helps to enhance the light absorption of leaves, photosynthetic activity, plant resistance to biotic or abiotic stress, organ longevity, evapotranspiration reduction, and the mechanical strength of leaves. The epidermal tissue of the secretory organs of plant contains Si (Rastogi et al., 2019). Improvement in crop quantity and quality has been proven by using silicon fertilizers in a variety of climates and soil in different plants. Silicon NPs are able to influence plant metabolism because of their unique physiological features (Rastogi et al., 2019). Furthermore, DNA and other chemicals may also be transported into animal and plant cells by silica NPs (Wang et al., 2011). Germination characteristics like speed of germination, dry weight, and radicle height of plant are all improved by nanosilica (Rastogi et al., 2019; Wang et al., 2011).

#### **Copper nanoparticles (Cu-NPs)**

For proper growth and reaction involved in photosynthesis, copper (Cu) is a necessary component. It participates in exchange of proteins and hydrocarbons. Various oxidizing enzymes, such as ascorbic acid oxidase and polyphenol oxidase, include copper (Leng et al., 2015). For plant metabolism and development of plant, Cu is essential. Excess amount of copper can cause toxicity but its deficiency is indicated by curled leaves (Leng et al., 2015). Cu-NPs released from a variety of goods have the potential to harm individuals and ecological systems (Chen et al., 2012). Copper oxide (CuO) NPs have been found to be hazardous to aquatic creatures like crustaceans, algae, zebra fish, and protozoa in recent researches (Chen et al., 2012). On the other hand, for *Vigna radiata* (L.) R. Wicłczek seedling development, metabolism and germination, less CuO concentrations were shown to be preferable (Singh et al., 2017). However, some past findings are unclear because the impact of Cu-NPs on plants is still to be examined thoroughly (Leng et al., 2015).

#### **Iron nanoparticles (Fe-NPs)**

In the earth's crust, iron (Fe) is the fourth most abundant element and is considered non-toxic (Li et al., 2006). All organisms require iron as a micronutrient. It is essential for formation of chlorophyll, process of photosynthesis, and respiration (Najafi Disfani et al., 2017). Fe-NPs are one of the many nanoparticles employed in restoration of wastewater (Fu et al., 2014) and environmental applications (Najafi Disfani et al., 2017). In plant germination, proper development, and increased output, iron oxide (FeO) NPs play a critical role. Because iron is the most abundant component of chlorophyll, elevating FeO-NPs decreases iron insufficiency and boosts levels of chlorophyll a and chlorophyll b (Ghafariyan et al., 2013). As a result, iron oxide NPs have a significant impact on the advancement of agriculture and other disciplines due to their vital role in plants (Li et al., 2006). To improve iron availability to the plants, increase height, biomass and root length, and influence the action of hormones and antioxidant enzymes, FeO-NPs are also used as nano-fertilizers.

#### **Zinc oxide nanoparticles (ZnO-NPs)**

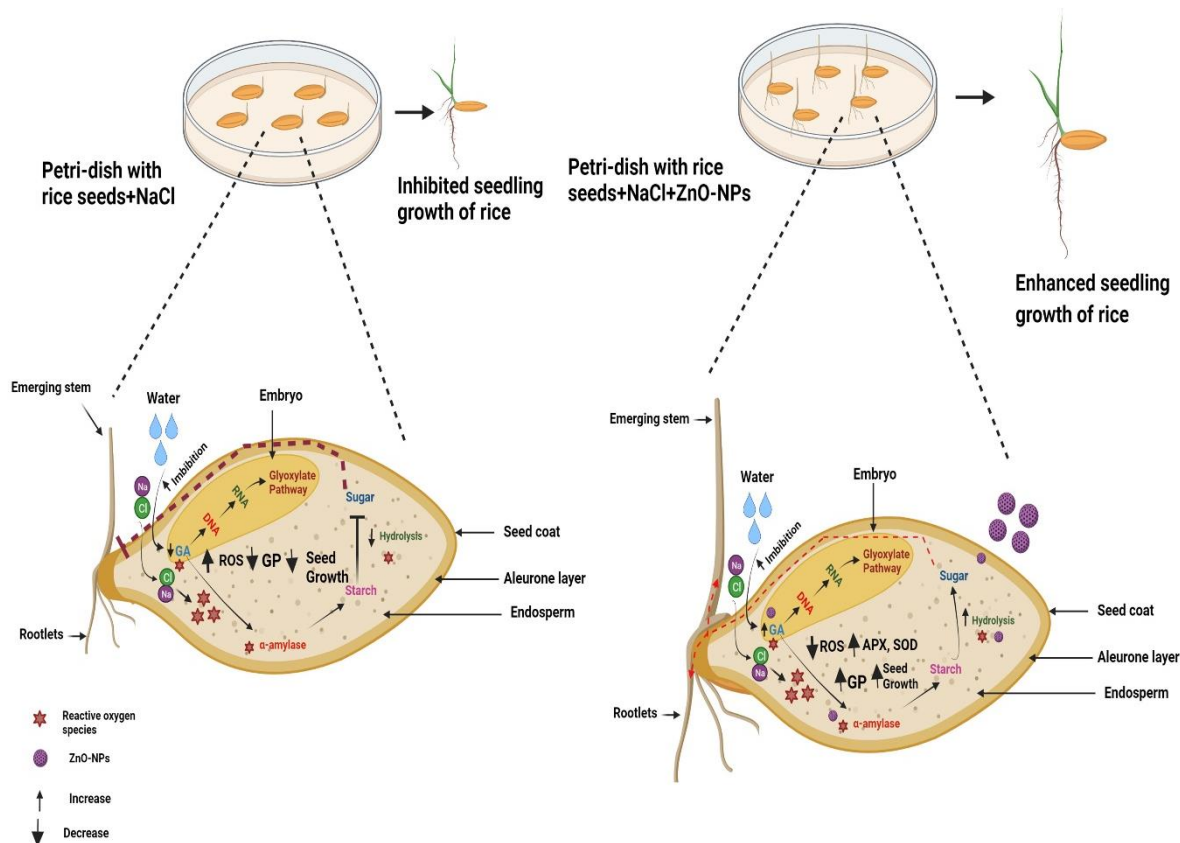
Because of its function in formation of chlorophyll and carbohydrates production, zinc is a necessary element for plant development. The absorption of harmful heavy metals is reduced when zinc levels in plants are increased and thus their toxic effects are reduced. Nanoparticles are utilized in a variety of industries including biosensors, electrodes, health and home products. While in agriculture, Zinc nanoparticles are mainly used because of their major functions in physiological responses and anatomy of plants (Awasthi et al., 2017). ZnO is required for regulating the metabolism of phytohormones and numerous enzyme functions, including superoxide dismutase and dehydrogenases (Rajput et al., 2021a). Because of their wide surface area, photodegradation, low toxicity, extended life duration, high pore volume, nanoparticles of zinc oxide can be employed as catalysts, polymer additives, chemical absorbents, and antibacterial. The effect of ZnO-NPs on seed germination in a variety of plant species has become the focus of past few researches (Awasthi et al., 2017; Gaafar et al., 2020; Sharma et al., 2021). However, due to the biological activity of metal-based NPs, the use of ZnO-NPs nano-fertilizer has been observed to have harmful impacts

on plants (Itrotwar et al., 2020). According to several studies, nano-ZnO is so poisonous that it can halt plant root development.

### Impact of nano-priming in abiotic stress

Pollution and salinity of soil can substantially reduce quantity of harvests (Maswada et al., 2018). Owing to direct ionic impacts on metabolism of plants as well as nutrient and water shortages, plant development is slowed down due to high salt content (Abdel Latef et al., 2017). Anthropogenic causes of heavy metal accumulation include waste disposal and burning, discharges from sludge and sewage, industrial operations, and use of fertilizers while natural or geogenic causes includesome local geological events or accumulation from air (Qayyum et al., 2017).

Under high salinity, roots were elongated and germination was enhanced on priming of manganese nanoparticles n jalapeno pepper seeds (*Capsicum annuum L.*). Moreover, on properly modifying sodium distribution between shoots and roots, salt stress was reduced via oxidative stress control (Ye et al., 2020). Priming of zinc NPs on lupin seeds increased their tendency to withstand the effects of salt stress along with the maintenance of pigments involved in photosynthesis and growth metrics like fresh and dry weight and root and shoot length. Because of higher amounts of organic compounds, antioxidant enzymes, phenols and photosynthetic pigments, Zn NPs primed lupin seeds showed promoted plant growth in high salt levels (Figure 1).



**Fig. 1.** Diagrammatic representation of NPs base seed priming and mitigation of abiotic stress (Salinity stress) at germination stage of rice plant

Enhanced germination, higher levels of chlorophyll, and better development in salty circumstances were demonstrated by nano-iron treated sorghum seeds (Maswada et al., 2018). Such findings suggest that not only to promote germination of seeds but also to prevent stress, this technique may be utilized. Rizwan et al. (2019) demonstrated that when wheat seeds were primed with zinc and iron nanoparticles in an instance of heavy metal accumulation, cadmium concentration was reduced in the grains due to inhibition of cadmium absorption. In shoots, roots, and grains, cadmium amounts were decreased by 38 %, 55 %, and 83 % respectively using zinc nanoparticles where as it was decreased by 54 %, 56 %, and 84 % in the shoots, roots and grains respectively by using iron nanoparticles. After priming of seeds, amount of zinc and iron was increased in plants (Rajput et al., 2020b). It was found that when seeds were primed with silicon

nanoparticles, cadmium absorption was reduced, production of carotenoids and chlorophyll a and chlorophyll b increased, photosynthetic rate and biomass of plant was increased while function of antioxidative enzymes and generation of reactive oxygen species was decreased in cadmium contaminated soil (Rajput et al., 2020a). The synthesis of phytohormones like jasmonic acid and salicylic acid which are produced during plant defense responses might be altered due to deficiencies in minerals like zinc and iron (Khan et al., 2017). Onion extracts were used to prime watermelon seeds with biogenic iron nanoparticles (Kasote et al., 2019). In the early stage of seedling, stress tolerance was boosted in the plants with higher amounts of jasmonic acid and cis-(+)-12-oxo-phytodienic acid (its precursor). Using copper nanoparticles for seed priming of maize can improve drought resilience in plants. Decreased oxidative stress with increased amounts of chlorophyll, anthocyanin, and carotenoids were maintained in the leaves (Nguyen et al., 2020). All this suggests that nano-priming of seeds might help plants cope with stress induced by contamination of heavy metals, drought, nutritional deprivation, or salty environments. Moreover, metabolism is also regulated to increase plant development and resistance to stress. For preventing the negative consequences of the climatic crisis and reducing yield losses due to man made as well as natural impacts on the globe, nano-priming of seeds can be a viable option to induce resistance to abiotic stress in plants.

### Concerns

Nanomaterials should be applied with prudence though they have the capacity to be used for coating and priming of seeds. not just in agricultural field, but also in other industrial fields, the proper use of these technologies necessitates the adoption of suitable laws based on reliable research (Kah et al., 2018). Assessment of the outcomes of nanoparticles in the ecosystem taking into account their potential of toxicity in the surroundings and lawful guidelines are necessary for the commercial production of nanoparticles, their applications in the agriculture, and disposal of the industrial discharge.

Many habitats are linked to agricultural operations, and nanoparticles can have a significant influence on them (Lowry et al., 2019). As a result, to produce nanomaterials which are safe for land as well as the larger surroundings, it is critical to comprehend their method of action. Prior to the treatment of seeds, it is important to assess the conditions for priming including size and quantity of nanoparticle, and the time span of treatment. Inhibition of germination, harmful changes in metabolism and structure of cell, alteration in interaction between microbiota and roots, and decrease in plant growth are some negative impacts which can occur due to improper priming conditions (Rahman et al., 2020). To create nanomaterials which are efficient as well as having minimum harmful consequences, it is critical to comprehend the influence of chemical and physical features of nanoparticles on seeds and related organisms (Camara et al., 2019). Polymeric, metallic, and biogenic metallic nanoparticles, all types of nanoparticles discussed above are different from one another in their physical, chemical and biological properties. Seed nano-priming can be designed for a variety of techniques including developing tolerance in plants to biotic and abiotic stressors, biofortification, protection of seeds, or a combination of all factors.

Significant benefits can be attained by using nanoparticles for seed priming. In comparison to applications in soil and foliar, seed treatments decrease the nanoparticle exposure. For seed priming, low amounts of nanoparticles are required which is another plus point. It may be delivered in a regulated manner by manufacturers, to prevent excessive material discharge into the environment. Although, research is needed to figure out how various nanoparticles like polymeric, metallic and biogenic metallic behave and interact with the growth of plant, the quantity of nanoparticles left in the plant will most likely be negligible, extremely little or perhaps zero.

### 3. Conclusion

For modulation in agriculture, nanotechnology is a potential field. One of the techniques that may be used to improve sustainability is seed nano-priming. These techniques can enhance plant growth and protect them from various stress conditions, leading to improved quality and quantity of food. Thus, seed treatment by nanotechnology has the tendency to shift conventional methods like using agrochemicals in agriculture to a highly sustainable agriculture. Such features combined can lead to a system that ensure reduced environmental damage caused by traditional methods and gives a better and secure product for farmers and consumers.

Many concerns such as priming conditions for seed, scaling up, harmful impacts on plants and associated organisms must be evaluated during the formation of these technological materials

in the industries and their field applications. But implementing such techniques of nanoparticles can change the complete management of crops with safer practices for environment, farmers and consumers by reducing pesticide application amounts and their negative impact threats.

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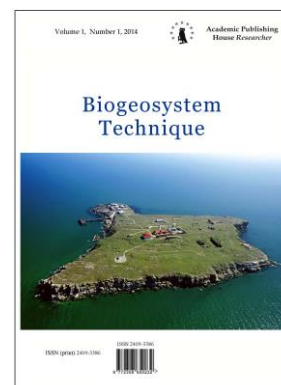
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## Geocological Aspects of Migration of Heavy Metals in Environment and Antioxidant Status of Plants

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### Abstract

The geocological assessment of the multi-component impact of technogenic pollution of natural soil zones is necessary for the comprehensive evaluation of environmental investigation of the impact of climate change on biota. The aim of a study was to use a combined assessment method of pollution in a chain soil-plant based on the values of a number of biogeochemical coefficients in the chain of soil-plant (1), and bioaccumulation of plants to assess the level of pollution for some HMs in the different regions of Armenia (2). The object of the study was the Armenian species of *Zea mays L.* and samples of soil near the river's coast. To quantitatively determine the indicators of the antioxidant system, the fifth leaf of *Zea mays L.* was used to determine the concentration of malondialdehyde in the presence of 2-thiobarbituric acid; the concentration of Ferric reducing the ability of plasma; concentration of polyphenols and flavonoids. The potential biochemical mobility of HMs from soil to plant ( $K_m$ ), index of pollution ( $I_{pol}$ ), and the value of the span of pollution (SP) were calculated in samples of soils. The excess concentration changes the  $K_m$  coefficient for Mo, Zn, and Cr for the studied samples of maize from different soil and climatic conditions are shown. It was found that, depending on the soil conditions, in almost all studied territories, Mo and Zn are strong concentrators, and the remaining HMs are deconcentrators in the range from strong (0.04-0.0025) to weak (0.4-0.25). We are inclined to assert that the antioxidant system is that sensitive component of the plant organism, which primarily reacts to changes in the environment caused by uncontrolled changes in micro and macro elements in biota.

**Keywords:** heavy metals, pollution, the chain plant-soil, biogeochemical coefficients, antioxidant system, geocological assessment.

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## 1. Introduction

The investigation of spatio-temporal changes in the environment have recently become the most urgent relevant in nature management and geocology. Changes in climatic conditions lead to the dramatic development of situations, provoking qualitative and quantitative changes in the biota. Most of the pollutants enter the environment as waste from a specific source of pollution. Heavy metals (HMs) are the main part of these pollutants or are present in trace concentrations (Seregin, Ivanov, 2001; Kasimov et al., 2016). HMs themselves are natural components of the earth's crust, determining the natural background of their content in the environment. The deposition of HMs ions in the soil in a certain way “controls” its physicochemical properties, changing such basic characteristics of the soil cover as mobilization, sorption, and adsorption (Wuana, Okieimen, 2011).

In the geochemical assessment of the state of the environment to take into account the associativity in the distribution of chemical elements is very important. This makes it possible to group HMs according to the degree of danger of environmental impact in order to comprehensively solve the problem (Hossain et al., 2012). In 1973, in the UN Global Monitoring Program, only Pb, Cd, and Hg were listed as hazardous HMs (Dobrovolsky, 1983). Later, according to the UN Environment Program, the list was expanded and consisted of both HMs (Cu, Sn, V, Cr, Mo, Co, Ni) and metalloids (Sb, As, and Se) (State of the environment, 1980). As highly hazardous HMs include As, Cd, Hg, Se, Pb, Zn, moderately hazardous ones – Ni, Mo, Cu, Sb, and low hazardous ones – Ba, V, W, Mn, Sr (GOST RF, 2008). In general, anthropogenic pollution itself is inherently multielement. That is why the content of HMs in soils, according to the study of statistical parameters of their distribution, can serve as a regional characteristic of soil contamination.

One of the important properties of the soil is its buffering capacity, which determines its resistance to anthropogenic influences. Irreversible both concentration and chemical modifications lead to the formation of complexes, the toxicity of which is detrimental to the habitat of living organisms (Pierzynski et al., 2000). Soil contamination with an increase in HMs content contributes to the stage-by-stage degradation of the environment, and the process of its restoration depends on the dynamics of HMs migration, their sorption, and accumulation in plants (Kabata-Pendias, Pendias, 2001). In this case, the predisposition of one plant species to a particular chemical element is very individual, and to a greater extent depends on the intensity of metabolic processes where it is involved (Sukiasyan, 2018). In fact, it is possible to extract positive effects from the current situation. Because of HMs accumulating and concentrating abilities of various chemical elements plants can be used in geoecological studies of the pollution of a certain territory on the basis of biomonitoring, but this will require a special understanding of the processes of soil solubilization and the mechanisms of absorption by plants (Sukiasyan, Kirakosyan, 2020).

In this study, we will use a combined assessment method based on the values of a number of biogeochemical coefficients in the chain of soil-plant and bioaccumulation of plants to assess the level of pollution for some HMs in the coastal areas of a number of rivers in Armenia in different soil-climatic regions.

## 2. Materials and methods

The object of the study was the Armenian species the of *Zea mays L.*, which was grown in Lori Marz along the Debet River (Odzun – 41°03'06"N 44°36'55"E, Shnogh – 41°08'52"N 44°50'16"E, Teghut – 41°07'05"N, 44°50'45"E), Armavir marz near the Araks river (Hushakert – 40°04'52"N, 43°55'35"E), and its genetic prototype is inbred maize (*Zea mays ssp. mays var. B73*) (González-Muñoz et al., 2004).

The ripe of *Zea mays L.* kernels were dried in a fume hood until air-dry at room temperature. For ashing, the plant material was placed in a muffle furnace using pre-calcined porcelain cups at a temperature of + 400°C for up to one hour. Then the samples of the dry residue (ash) were placed in a desiccator for further measurements.

Soil samples under dry weather conditions were taken by the envelope method from the depth of growth of the root system of the studied plant. Point sampling was carried out with non-metal instruments. A pooled sample of soil was prepared by mixing at least five incremental samples taken from the same sample site. After the samples were placed in dark glass containers and transported at a temperature of +4°C for laboratory (instrumental) measurements for 24 hours. After cleaning from the remnants of the root system, insects, and other solid

components, the soil was ground in a foot with a pestle and sifted through a sieve with a diameter of not more than 1 mm.

The prepared samples (plants and soils) were placed in special plastic tubes "XRF Sample Cups" with a diameter of 32 mm, on the bottom of which a special polypropylene film was inserted in advance. A special seal was inserted on top of the sample and the sample was pressed with a lid to the desired state. The study of the sample was carried out by directing X-rays directly onto the sample for a total of up to 210 seconds using a portable analyzer "Thermo Scientific™Niton™XRF Portable Analyzer" (USA).

The potential biochemical mobility of HMs from soil to plant ( $K_m$ ) was calculated by formula

$$K_m = \frac{C_p}{C_s} \quad (1)$$

where  $C_p$  is the content of HMs in the ash of *Zea mays L.* from a certain region of growth, mg/kg;  $C_s$  is HMs content in the corresponding growing soil, mg/kg (Perelman, Kasimov, 1999);

The index of pollution ( $I_{pol}$ ) was calculated by formula

$$I_{pol} = (K_{m1} \cdot K_{m2} \cdot \dots \cdot K_{mn})^{1/n}, \quad (2)$$

and the value of the span of pollution (SP) is defined as the ratio  $\frac{K_m}{I_{pol}}$ , and when  $SP < 0.1$  the pollution satisfy to insignificant, if  $0.11 < SP < 0.2$  is range of slight pollution,  $0.21 < SP < 4$  is range of moderate pollution,  $4.1 < SP < 8$  is range of severe pollution,  $SP > 8.1$  is range of excessive pollution; n is the number of HMs.

To quantitatively determine the indicators of the antioxidant system, the fifth leaf of *Zea mays L.* was used on the third day of its growth, up to 10 cm long from the base of the leaf according to the method (Sukiasyan, 2019). The obtained single biological material was used to determine the concentration of malondialdehyde (MDA) in the presence of 2-thiobarbituric acid (Hodges et al., 1999); the concentration of Ferric reducing ability of plasma (FRAP) (Benzie, Strain, 1999); concentration of polyphenols (Gálvez et al., 2004); concentration of flavonoids (Chang et al., 2004). Concentrations of all biochemical parameters are presented in the appropriate units and are reduced to the fresh weight of the biological material.

All experiments data had 10 biological and up to 5 technical replicates and were statistically processed. The results were processed taking into account the Student's t-criterion. The observed differences are statistically significant, since at a significance level of  $p < 0.05$ , the calculated values of the criterion were greater than the critical one (Korosov, Gorbach, 2017).

### 3. Results and discussion

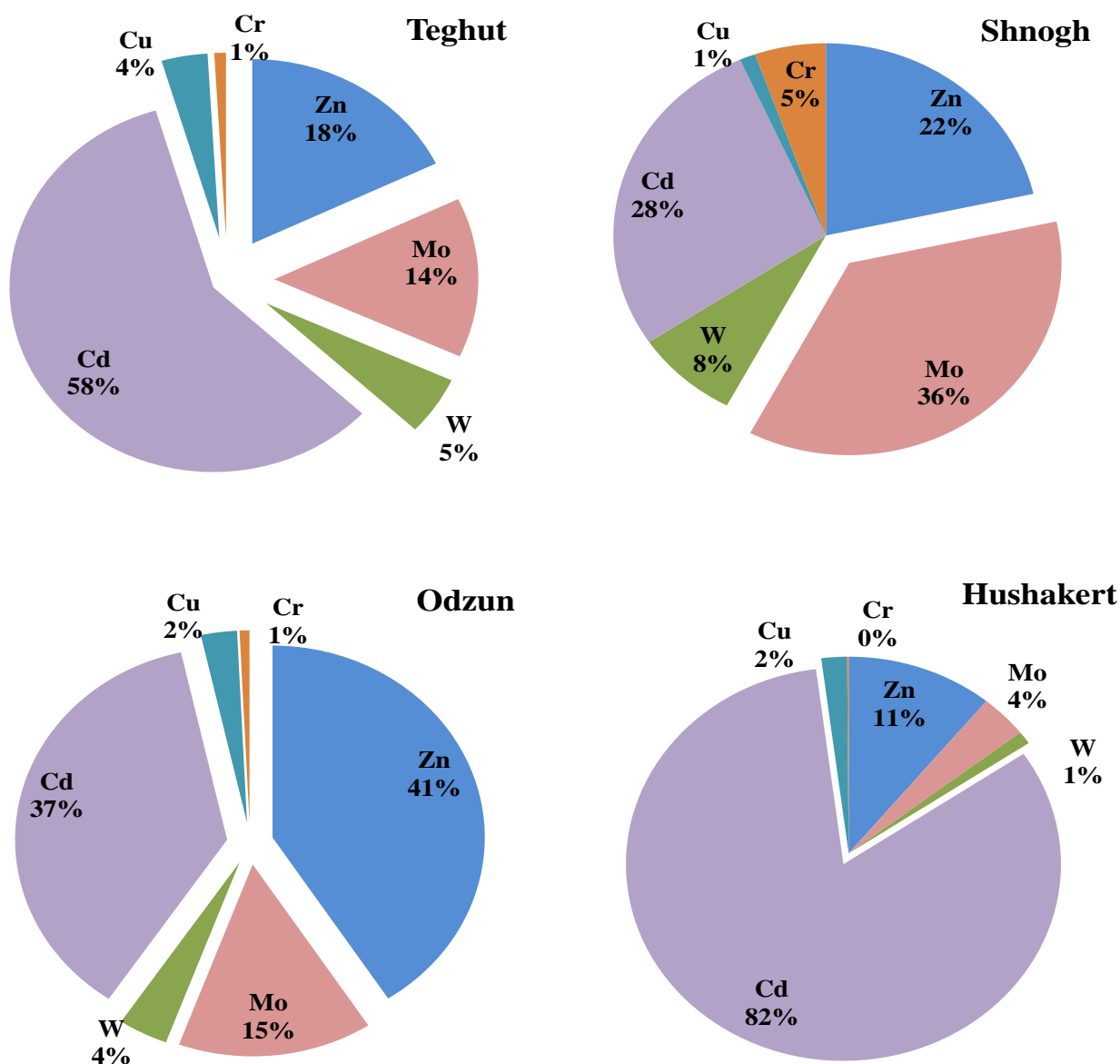
The dominance of mountainous terrain in Armenia and the presence of increased fracturing as one of the water-control criteria allow are forcing to adapt most of the coastal river territories for agricultural use (Vardanyan, 2019). That is why the level of hazardous HMs content in the soil was estimated on the basis of the ecotoxic principle, comparing the concentration effects of different chemical elements in soil and plants. In this case, the use of maximum permissible additives of chemical elements is appropriate (Vodyanskiy, 2012).

To assess the intensity of HMs migration in the chain of soil-plant, the total contamination was identified for a separate group according to the HMs hazard, which is the index of contamination. At first, the potential biochemical mobility of HMs from soil to plant ( $K_m$ ) was determined, then on the basis of which the pollution index ( $I_{pol}$ ) was calculated (Table 1). According to our results, in Hushakert the value of  $I_{pol}$  in a case of highly hazardous HMs (Se, Sb, Cd) is distinguished up to three times increased compared to other regions. For the class of moderately hazardous HMs (V, Hg, Ni, Cu, Cr, As, Ba), the value of  $I_{pol}$  was almost the same, and the value of the  $I_{pol}$  index for slightly hazardous HM (Mo, Pb, Zn, Co) had the greatest value in Teghut, and the smallest is in Shnogh.

**Table 1.** Heavy metal pollution index ( $I_{pol}$ ) in different soil-climatic regions of Armenia

Hazard class of heavy metals	Teghut	Shnogh	Odzun	Hushakert
Highly	3.89 ± 0.36	2.80 ± 0.12	3.83 ± 0.16	6.84 ± 0.37
Moderately	0.53 ± 0.04	0.45 ± 0.03	0.68 ± 0.06	0.66 ± 0.05
Low	3.09 ± 0.16	1.31 ± 0.07	2.57 ± 0.13	2.21 ± 0.09

The soil has a certain degree of dynamism, primarily due to its moisture content. At the same time, the root system of plants absorbs not only moisture from the horizons of its maximum distribution in the soil but also various pollutants dissolved in it. Plants use soil moisture due to transpiration processes, which is provided by hydration and turgor of the plant cell. This is an important factor in the migration of HMs in biota (Sukiasyan et al., 2015). *Zea mays L.* is a widespread household plant in almost all regions of Armenia. In particular, it is intensively cultivated in the coastal areas of the Debet, Shnogh, and Araks rivers. Although the growth of maize is interrelated with soil and climatic conditions, the plant itself is not demanding on the soil conditions of growth. By calculating the potential biochemical mobility of HMs from soil to plant ( $K_m$ ), received data was found that Cd, Mo, Zn dominant position when absorbed from the soil by maize samples (Figure 1).



**Fig. 1.** The potential biochemical mobility of HMs from soil to plant ( $K_m$ ) in different soil-climatic regions of Armenia

It should be noted that the activation of plant protection mechanisms with an increase in the HMs content in the environment begins already at the level of the root system (Koevoets et al., 2016). This is manifested both by the passive (non-metabolic) transfer of ions into the cell in

accordance with the gradient of their concentration and by the active (metabolic) process of absorption by the cell against the concentration gradient (Godbold, Kettner, 1991).

Further, for evaluating the state of the environment was calculating the ratio of SP (Table 2). Among the elements such as Se and Sb from the group of highly hazardous HMs, are distinguished by a wide  $K_m$  value, the value range of which ranges from 13 (Shnogh) to 164 (Hushakert).

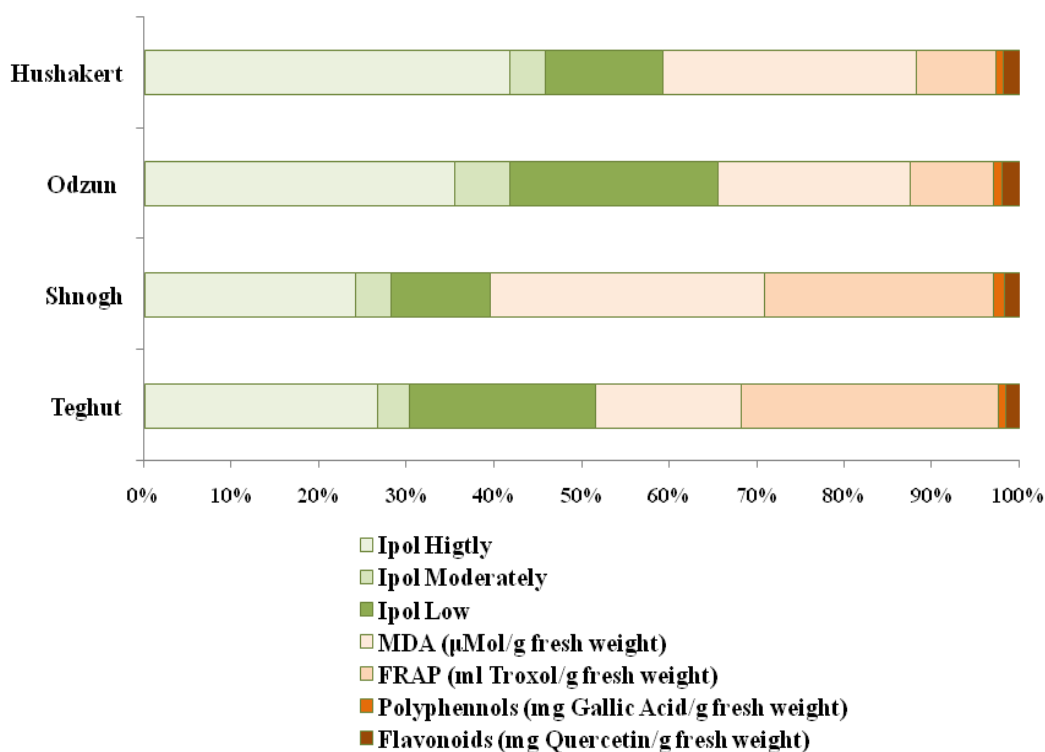
**Table 2.** The values of span pollution (SP) in different soil-climatic regions of Armenia

Hazard class of heavy metals		Teghut	Shnogh	Odzun	Hushakert
Highly	Se	0.36	0.87	0.33	0.33
	Sb	0.14	0.24	0.30	0.30
	Cd	20.14	4.74	10.27	10.27
Moderately	V	0.32	0.67	0.26	0.13
	Hg	3.25	6.10	6.59	4.62
	Ni	0.53	1.05	1.68	3.07
	Cu	9.18	1.24	4.26	5.77
	Cr	2.32	5.54	1.17	0.36
	As	0.58	0.23	0.43	0.65
	Ba	0.15	0.15	0.16	0.40
Low	Mo	6.82	6.64	3.84	2.69
	Pb	0.30	0.07	0.16	0.51
	Zn	8.69	3.95	10.58	8.26
	Co	0.08	0.07	0.04	0.05

According to the content of Se and Sb, the soil-plant system is in a state of moderate contamination. In the case of Cd, it can be stated that in all regions of the study, the chain of soil-plant is in an excessively contaminated state. In the second group as moderately hazardous HMs, according to the value of  $K_m$  plant intensively absorbs and accumulates Hg and Cr in Shnogh. A similar situation we can observe in Teghut along with strong absorption of Cu by the plant, and also a similar picture of the migration of Hg, Cu, and Ni from soil to plant we obtained in Odzun and Hushakert. To obtain a reliable picture of the degree of pollution, the SP readings were compared. The moderate pollution is observed in Teghut for Hg and Cr, in Shnogh for Cu and Ni, as well as in Odzun and Hushakert, only for Ni. At the same time, excessive pollution of the studied territories was noted in Teghut by Cu. For such as HMs like Hg and Cr in the Shnogh, also Hg and Cu in both Odzun and Hushakert severe pollution was recorded. Among the elements from the second group, Ba, As, and V are especially distinguished, for which the range of the  $K_m$  coefficient does not exceed unity. It means according to the numerical equivalent of the span of pollution ranges from slightly to moderately polluted in some cases. In the group of low-hazard HMs in the chain of soil-plant, there is weak mobility of Co and Pb, and the range of values of the SP ratio is limited from medium to moderate, but the situation is different with Mo and Zn. The values of the  $K_m$  coefficient show that *Zea mays L.* is predisposed to the absorption and accumulation of these HMs, reaching its highest Mo value in Teghut (18.80) and Zn in Odzun (43.33), and the lowest Mo value in Hushakert

(7.08) and for Zn in Shnogh (3.95). The contamination by zinc is excessive in all studied areas, except for Shnogh as in the case of the pollution by molybdenum in Teghut, is strong.

The most of results of investigations in the area of migration processes of HMs transfer, as well as their redistribution in biota, are of important methodological importance for organizing a system for monitoring the state of the environment (Mikheva et al., 2003). Environmental stresses such as drought, salinity, cooling, HMs toxicity, ultraviolet radiation, and pathogenic microorganisms inevitably provoke the generation and activate reactive oxygen species (ROS) in plants due to disruption of cellular homeostasis (Kovalchuk, Kovalchuk, 2008; Misra, Mani, 1991; Sharma, Dubey, 2005). An increased concentration of ROS is extremely dangerous for organisms. They are a group of free radicals that are derived from molecular oxygen. About 1% of the consumption of molecular oxygen by plants is directed to the production of ROS in chloroplasts and mitochondria. Moreover, if the plant organism itself cannot cope with such a situation, then the ROS level exceeds its defense mechanisms. The cell goes into a state of "oxidative stress", causing lipid peroxidation (LPO), protein oxidation, damage to nucleic acids, inhibition of enzymes, which ultimately leads to unambiguous cell death (Chen et al., 2010; Meriga et al., 2004). The use of plants as indicators for changes in the background concentrations of HMs in the soil should be considered the time-factors, which affect the solubility and forms of HMs. In conditions of a significant increase in the level of HMs, the pollutants themselves can change the properties of the soil, affecting the solubility of the metal. However, membrane transfer leads to an increase in the level of HMs in the plant in comparison with their concentrations in the soil. This, in turn, allows plants to be used to detect and identify relevant changes in the environment (Sukiasyan et al., 2016).



**Fig. 2.** Comparative analysis between antioxidant indicators of samples of *Zea mays L.* plants and pollution index ( $I_{pol}$ ) as grow soil from different soil-climatic regions of Armenia

In our studies, certain correlation patterns have been obtained that make it possible to establish the relationship between biochemical parameters (FRAP, MDA, polyphenols, and flavonoids) and the index of pollution ( $I_{pol}$ ) determined. Correlation analysis of the concentration of FRAP of plant tissue found that in a region with an increased concentration of hazardous HMs (Hushakert, Odzun), its value is much lower compared to a region with a characteristic high content of Mo, Pb, Zn, Co (Teghut and Odzun) (Figure 2). Plants differ in their ability to both accumulate individual HMs and absorb them, depending on the properties of the soil (Atoyants et al., 2009). But ROS are well known for their dual role: at high concentrations, they cause damage to biomolecules, while at low or moderate concentrations; it acts as secondary intracellular messengers in plant cells (Gichner et al., 1980).

Studies have shown that maintaining a state of high antioxidant activity during the utilization of toxic ROS is associated with increased plant tolerance to environmental stresses (Bagaeva et al., 2013). There is several mechanisms of ROS generation in which HMs are involved. Oxidative-active metals promote the formation of hydroxyl radicals (OH $\cdot$ ), which are the most aggressive type of ROS (Juknys et al., 2012). Metals with a weak redox capacity, such as cadmium, lead, zinc, nickel, etc., can contain singlet oxygen, which is capable of creating another type of ROS superoxide (O $_2^{\cdot-}$ ) (Sharma et al., 2016). Subsequently, ROS cause nonspecific oxidation of proteins and membrane lipids, DNA damage, and enzyme inhibition, leading to cell death (Schützendübel, Polle, 2016). On the other hand, ROS plays an important role in the plant protection system, because the dangerous effect of ROS is determined by their concentration, and if it exceeds the threshold level for defense mechanisms, oxidative stress will occur.

In the case of the response of the secondary product (MDA) of LPO processes an almost similar picture is observed regardless of soil and climatic conditions. The antioxidant status of the plant fully resists the effects of HMs, regardless of their hazard class. When considering the secondary metabolites of LPO processes (polyphenols and flavonoids) a weak response of these systems to environmental pollution is noted. In fact, the complex system of plant antioxidant defense, the main purpose of which is to reduce the reactivity and/or remove ROS in various organelles (chloroplasts, mitochondria, and peroxisomes) caused by the toxicity of a number of HMs, does not manifest itself in the same way. Their participation in biogeochemical processes, as well as the constant growing anthropogenic pollution of the environment, predetermined the leading place of HMs among pollutants capable of changing the metabolic processes of plant growth and development. There is a large amount of information on the scale and irreversible consequences of HMs biota pollution. Discussions of the current situation ultimately boil down to comparing the concentration changes of HMs in the environment with their accepted maximum permissible concentrations without delimiting the nature of their occurrence.

Analyzing the current situation, we have developed a quality approach for assessing environmental pollution using the example of HMs migration into the chain of soil-plant, taking into account the adaptation of plants under anthropogenic load. A change in its antioxidant status was considered as the main mechanism of adaptation of a plant organism. In response to oxidative stress provoked by anthropogenic stress, in our case, it is HMs in the plant organism that activates the work of non-enzymatic (polyphenols, flavonoids, etc.) and low molecular antioxidants (MDA), which are present in plant tissues and are capable of neutralizing ROS non-enzymatically.

## 5. Conclusion

Comprehensively analyzing the results obtained, we are inclined to assert that the antioxidant system is that sensitive component of the plant organism, which primarily reacts to changes in the environment caused by uncontrolled changes in micro and macro elements in biota. The excess concentration changes the  $K_m$  coefficient for Mo, Zn, and Cr for the studied samples of maize from different soil and climatic conditions are shown. It was found that, depending on the soil conditions, in almost all studied territories, Mo and Zn are strong concentrators, and the remaining HMs are deconcentrators in the range from strong (0.04-0.0025) to weak (0.4-0.25).

Thus, the multidirectional approaches to the study of some geoecological problems of pollutants distribution considered in the article reasonably indicate the specific features of HMs migration in the chain of soil-plant in the general concept of regional geoecology.

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