



Volume 7

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# CHEMISTRY

## JOURNAL OF MOLDOVA

General, Industrial and Ecological Chemistry

Editor-in-chief: Gheorghe DUCA

Academy of Sciences of Moldova  
Institute of Chemistry  
State University of Moldova

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CHISINAU, MARCH 2-3, 2012

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Tamara Leah

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**SOIL DEGRADATION PROCESSES FROM POLLUTION**

Popov Leonid, Ciudin Gheorghe, Rotaru Serghei

Investigations found HCH and DDT residuals in bottom sediments from several reservoirs and lakes as well as the main rivers, Nistru and Prut (concentrations ranged between 0.2 and 15.8 ppb). The concentration of PCBs in the topsoil collected beneath the capacitors battery at the Vulcănești substation reached a level of 7100 ppm which is exceeding the MAC by five orders of magnitude (!). With no exception, allowable concentrations of PCBs in soil were exceeded also on the territory of other investigated substations, with peaks registered at the Briceni substation (2545 ppm) and the Orhei substation (1959 ppm).

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**ADVANCED TECHNOLOGY WASTEWATER TREATMENT OF NITRITE IONS**

E.G. Morozov, V.M. Nikol'skii, T.V. Saprunova, A.A. Yakovlev

The main reason for high concentration of nitrite ions in water is the existence of sources of industrial and agricultural pollution. Contamination of drinking water, juices, wine and other liquids of nitrite ions as a result of improper use of nitrogen fertilizers has an adverse effect on living organism, because under the influence of enzymes nitrite ions in living organisms form high carcinogenic nitrosamines, and the interaction of nitrite ions from blood hemoglobin causes such toxicity that leads to disease cyanosis [1]. Therefore removal of nitrite ions from water has received increased attention. The paper discusses an innovative wastewater treatment technology from the nitrite ion with hypochlorite produced during electrolysis.

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A.B. Yankauskas, S.N. Lukashenko, A.A. Amirov, P.V. Govenko

The ecological situation in the former Semipalatinsk test site is characterized by a combination of both radiative and "nonradiative" factors. There were investigated near-portal areas of the tunnels with water seepage at "Degelen" site. All the tunnel waters are characterized by higher concentrations of uranium, beryllium, and molybdenum. The watercourse of the tunnel # 504 is unique for its elemental composition, in particular, the content of rare earth elements, whose concentration in the water is in the range  $n \cdot 10^{-5} - n \cdot 10^{-7}$  %. Of all the rare earth elements in the samples were found 13, the concentrations of aluminum, manganese, zinc are comparable to the concentrations of macro-components. Concentration of  $^{238}\text{U}$  in the studied waters lie in the range of  $n \cdot 10^{-4} - n \cdot 10^{-6}$  %, which suggests the influence of uranium, not only as a toxic element, but its significance as the radiation factor.

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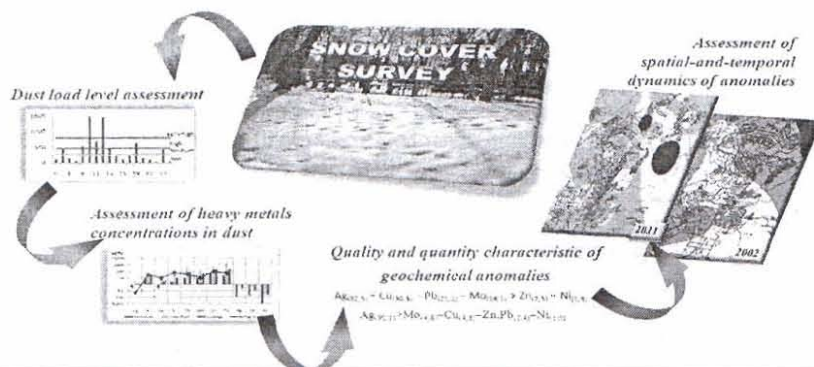
**ENVIRONMENTALLY FRIENDLY COMPLEXONES. THE THERMODYNAMIC CHARACTERISTICS OF THE FORMATION OF  $\text{Al}^{3+}$  ION COMPLEXES WITH ETHYLENEDIAMINEDISUCCINIC ACID IN AQUEOUS SOLUTIONS**

L.N. Tolkacheva, T.V. Saprunova and V.M. Nikol'skii, A.A. Yakovlev

Complex formation between  $\text{Al}^{3+}$  and ethylenediamine - N,N'-disuccinic acid ( $\text{H}_4\text{L}$ ) was studied at 25°C against the background of 0.1, 0.5, 1.0 N solutions of  $\text{KNO}_3$  by potentiometry and mathematical modeling. The extrapolation of concentration constants to zero ionic strength was used to calculate the thermodynamic constants of the formation of the  $\text{AlL}^-$ ,  $\text{AlHL}$  complexes using an equation with one individual parameter ( $\log \beta^0 = 16.27 \pm 0.07, 9.19 \pm 0.2$  respectively).

**GEOCHEMISTRY OF ATMOSPHERIC DUST ON THE TERRITORY OF THE CITY OF YEREVAN**

Armen Saghatelyan, Lilit Sahakyan, Olga Belyaeva



**STUDY OF DESTRUCTION PROCESSES OF SYNTHETIC SURFACE-ACTIVE SUBSTANCES (SURFACTANTS) IN BARRIER DISCHARGE**

V.I. Grinevich, A.A. Gushchin, T.V. Izvekova, V.Y. Shulyk

Kinetic data of degradation on aqueous solutions of surfactants in the plasma of barrier discharge are presented. The possible mechanism of proceeding processes is offered and considered. It is shown that the treatment in a barrier discharge results in decomposition efficiency of 95%. It is established that the main product of degradation are carboxylic acids.

**WASTE DUMPS IN LATVIA: FORMER LANDFILLING, CONSEQUENCES AND POSSIBLE RE-CULTIVATION**

Burlakovs Juris, Vircaivs Magnuss

Particular attention in this article is paid to the research of two waste dumps in the capital city of Latvia – Riga, which are planned to be re-cultivated in the nearest future and one site, which is former toxic hazardous soil dump site, where the remediation of site is of priority need. The present study is giving a general overview of contamination level in two waste dumps in Riga, which were made in the period from 50-ties to 70-ties of the 20<sup>th</sup> century, also the case of hazardous soil dump site formed in a period of more than 100 years is described. Planned actions as well as direct remediation technologies to reduce the poisonous impact to the urban environment and the role of re-cultivation in the urban planning in general are proposed.

**ENVIRONMENTAL ASSESSMENT OF HEAVY METALS CONTENT IN SOIL-PLANT SYSTEM**

Gr. Stasiev, I. Eni, T. Leah

The content of heavy metals (Ag, Cd, Sn, Cs, Ba, La, Rb, Sr, Mn, Fe, Cu, Zn) has been determined in the soil-plant system: cambic chernozem - winter wheat. It was found that the amount of Ag, Sb, Sn and Ba are accumulating in soil, exceeds the admissible concentration limit. In winter wheat, the content of Cd, Fe and Zn exceed the maximum admissible concentrations. The Rb, Mn, Zn accumulate in the winter wheat grains, and Fe and Cu – in the vegetal organs of wheat.

**ENVIRONMENTAL REGULATION OF TRACE ELEMENTS IN SOILS OF MOLDOVA**

Vladimir Kiriliuc

The scale of environmental regulation (content and pollution levels) of trace element in soils of Moldova was proposed. Contamination levels are justified, depending on the adverse effects that have trace elements in soils, plants, groundwater and more - per person. Proposed scale has 6 content and 4 pollution levels. Together with equalized MPC may help to consider a number of deficiencies that are available in this area and improve the practical application of the assessment of soil contamination. Scale Indicators are flexible values, taking the large variability content of trace elements.

**ADEQUATE UV EXPOSURES FOR HEALTHY LIFE: *IN SITU* MONITORING AND MODEL CALCULATION OF THE VITAMIN-D-SYNTHETIC CAPACITY OF SUNLIGHT**

Irina Terenetskaya, Tetiana Orlova, Pavel Kapinos

Vitamin D which is formed upon UV solar radiation in human skin is essential in many physiological functions. To estimate beneficial vitamin-D-synthetic capacity of sunlight a bio-equivalent UV dosimeter that is based on the same molecular photochemistry from which vitamin D is photosynthesized in human skin has been developed. The examples of an *in situ* monitoring of the vitamin-D-synthetic capacity of sunlight using an *in vitro* model of vitamin D synthesis are presented, and various operational principles of the UV biosimulator are discussed. In addition, reliable algorithm is presented for direct calculation of previtamin D<sub>3</sub> accumulation using the photoreaction mathematical model with solar UV spectra as input data. Critical dependence of previtamin D<sub>3</sub> accumulation on cloudiness and aerosols is demonstrated.

**INCREASE OF CROP YIELDS ON SEED TREATMENT BY ENVIRONMENTALLY SAFE COMPLEXONES IN SOLUTIONS**

V.M. Nikolskiy, L.N. Tolkacheva, Ya.M. Khalyapina, T.I. Smirnova, A.A. Yakovlev

In the laboratory and plot experiments the effect of ethylenediaminedisuccinic acid (EDDS) and iminodisuccinic acid (IDS) on chlorophyll content in wheat germ leaves and adult plants was investigated. It was estimated that both complexones increased chlorophyll content in leaves and crop yield.

**BLACK SOILS DEGRADATION IN THE SOUTH-WESTERN BLACK SEA REGION AT IRRIGATION AND IN THE POST-IRRIGATION PERIOD**

Bilanchyn Yaroslav, Rezvaya Svetlana, Medinets Volodymyr

Many years' studies of process of changes in composition, properties and fertility of the black soils of the North-Western Black Sea area in Ukraine with irrigation have revealed mobility of carbonates and humus in them, decrease of capacity of cationic consumption and content of consumed calcium, increase of share of consumed magnesium and sodium. Indicators of agro-physical state of soils under irrigation conditions are worsening significantly.

**BIOCHEMICAL PROCESSES IN CHERNOZEM SOIL UNDER DIFFERENT FERTILIZATION SYSTEMS**

Ecaterina Emnova

The paper deals with the evaluation of the intensity of certain soil biochemical processes (e.g. soil organic C mineralization) at Organic and mixed Mineral+Organic fertilization of typical chernozem in crop rotation dynamics (for 6 years) by use of eco-physiological indicators of biological soil quality: microbial biomass carbon, basal soil respiration, as well as, microbial and metabolic quotients. Soil sampling was performed from a long-term field crop experiment, which has been established in 1971 at the Balti steppe (Northern Moldova). The crop types had a more considerable impact on the soil microbial biomass accumulation and community biochemical activity compared to long-term Organic or mixed Mineral + Organic fertilizers amendments. The Org fertilization system doesn't make it possible to avoid the loss of organic C in arable typical chernozem. The organic fertilizer (cattle manure) is able to mitigate the negative consequences of long-term mineral fertilization.

**RESEARCH ON DETOXICATION OF SOILS POLLUTED WITH ARSENIUM AND DEVELOPMENT OF NEW SORBING MATERIALS**

L.V. Kireycheva, L.I. Moskovkina

Arsenium being a hazardous substance is harmful for plants, animals and people. Having been applied to the soil arsenium is partly transformed as the result of interaction with the soil minerals. It may enter plants, animals as well as human body through the feed circuit. Nowadays issue of the anthropogenic impact diminishing as well as environmentally friendly farm production obtaining in the polluted soils becomes more and more urgent. Therefore development of soil detoxication techniques using natural sorbing materials is challenging and timely.

**INFLUENCE OF CLIMATE CHANGES ON WATER RESOURCES IN MOLDOVA**

Violeta Ivanov

The paper aims to analyze the current state of affairs with water resources in Moldova, the challenges it faces for its national human and economic development, having in mind that the water resources are quite limited in Moldova, which encounters pollution, degradation influenced by climate change and unwise human activity to their biodiversity and ecosystems, availability and accessibility. It also attempts to highlight the relationship between climate change and water resources in Moldova, which has adverse effects on both environment and people's health, and raise significant hurdles to the international, regional and sectoral development.

**SILVER LOADED CLAY AND INVESTIGATION OF THEIR ANTIMICROBIAL ACTIVITY**

Violeta Elena Copcia, Ion Sandu, Nicolae Bilba, Simona Dunca

To guarantee the microbiological quality of the water, which is been affected by the pollution of the bacterium, is necessary to implement a tertiary drinking system in the resident houses. A possible complementary system is the utilization of clay for treatment of drinking water.

**THE POLLUTION SPECTRUM OF OLD PESTICIDES STORAGES IN MOLDOVA**

Duca Gh., Bogdevich O., Cadocinicov O., Porubin D.

The inventory of old pesticide storages in Moldova executed by Ministry of Environment and World Bank showed a large quantity of polluted sites (near 1500) remains after the repacking and evacuation project. This work was made first of all for Persistent Organic Pollutants (POPs). More that 15 % sites were determined as extra high polluted territory with the POPs concentration in soil more 50,0 mg/kg. They include some of the world's most harmful chemicals including highly toxic pesticides such as HCH, DDT; industrial chemicals such as PCBs. The management of domestic and hazardous wastes is considered as one of the most urgent environmental problems in Moldova.

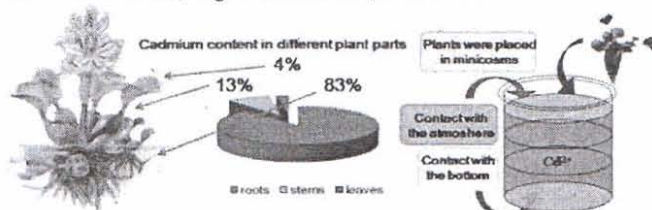
**TRENDS OF CURRENT DYNAMICS OF CHEMICAL PROCESSES IN THE SOILS OF ODESSA REGION**

Bilanchyn Yaroslav, Rezvaya Svetlana, Medinets Sergiy, Pitsyk Vasiliy

Results of chemical processes' dynamic studies of many years (1971-2011) in the soils of Odessa Region have been described. The most significant in the last 15-20 years have been changes of humus content and ecological & agrochemical status of black soils. In spite of some increase in the norm of fertilizers input for the last 5 years the negative balance of plant nutrition elements in soils is preserved. Ways of optimization of humus and ecological & agrochemical status of soils in the region and increase of their fertility have been proposed.

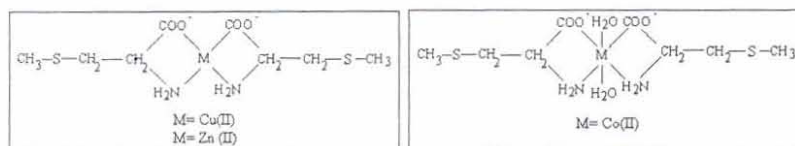
**THE STUDY OF CADMIUM UPTAKE BY WATER HYACINTH (*EICHHORNIA CRASSIPES*) USING A NATURAL MODELLING APPROACH**

Tamara E. Romanova, Ludmila A. Belchenko, Olga V. Shuvaeva, Maria V. Kurbatova



**SPECTROSCOPIC STUDIES OF AMINOACIDS COMPLEXES WITH BIOMETALS**

Andreea Stanila, Sorin Stanila



## **BLACK SOILS DEGRADATION IN THE SOUTH-WESTERN BLACK SEA REGION AT IRRIGATION AND IN THE POST-IRRIGATION PERIOD**

Bilanchyn Yaroslav<sup>a</sup>, Rezvaya Svetlana<sup>a\*</sup>, Medinets Volodymyr<sup>a</sup>

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**Abstract:** many years' studies of process of changes in composition, properties and fertility of the black soils of the North-Western Black Sea area in Ukraine with irrigation have revealed mobility of carbonates and humus in them, decrease of capacity of cationic consumption and content of consumed calcium, increase of share of consumed magnesium and sodium. Indicators of agro-physical state of soils under irrigation conditions are worsening significantly. In the last 15-20 years, due to sharp decrease in area of irrigated fields an extensification of agriculture the display of agro-physical solonetzicity of previously irrigated lands is strengthening, as well as processes of their dehumification; indicators of ecological&agrochemical state are degrading. Substantiated is the system or agro-amelioration measures aimed to prevent from degradation processes of irrigated black soil missives and increase their fertility.

**Key words:** black soils, irrigation, post-irrigation period, degradation processes.

### **Introduction**

South-Western Black Sea region with high resources of sun warmth and potentially highly fertile black soils suffers insufficiency and non-stability of atmospheric precipitation and in the last decades – growth of weather aridness and increase of temperature in summer and autumn months. Only irrigation could be a reliable means of agriculture intensification in the region and decrease of its dependence upon unfavourable weather conditions. In 1960-1990 here were the periods of wide-scale irrigational development and regular irrigation of lands, both black soils southern and black soils common. In the last 15-20 years area of regular irrigation in the region decreased sharply (5-8 times). At that, significantly decreased input into the fields of irrigated massive of organic and mineral fertilizers, chemical ameliorants, pesticides and herbicides. As the black soils are very sensitive to the influence of irrigative water and differ with increased selectivity to Na-ions consumption, significant change is stated in changes of composition and property of these soils both during irrigation and during current post-irrigation period of their evolution on the background of decrease of agro-amelioration culture and extensification of agriculture [1-3]. More often the changes of degradation direction taking place, and measures must be grounded and elaborated for protection and sustainable use of those highly fertile soils.

The objective of the paper is to reveal the essence and ecological & soil consequences of degradation processes of South-Western Black Sea Black soils during irrigation and in the current post-irrigation period of their evolution, development of measures to prevent degradation processes in irrigated massive and to increase their fertility.

### **Organization and Performance of Work and Researches**

Studies of essence, spatial regularities and ecological & soil consequences of processes of North-Western Black Sea black soils' changes at irrigation and in the current post-irrigation period of their evolution, beginning from 1971, are carried out on the stationary plots for soil monitoring and irrigated massive monitoring in Odessa Region. The plots differ in their landscape & geochemical and soil & agro-amelioration conditions, duration and intensity of irrigation, quality of irrigation waters, duration of the period of post-irrigation landscape and black soils' evolution in the last 15-20 years. In parallel similar soil monitoring studies were carried out on the adjacent bogharic (non-irrigated) lands. Every year density of consistence is determined, and in the selected samples – pH, grain size, structural & aggregate and micro-aggregate composition, salinization and carbonate content, content and composition of absorbed bases, total and active fluorine, as well as NPK forms available for plants. In the samples of irrigation and drainage waters pH, ions composition, mineralization, content of different NPK forms and fluorine were determined. Stock of yields' sizes is taken. Since 2010, in experimental & production conditions, agro-ameliorative efficiency of measures developed by us to prevent black soils degradation in irrigated massive, liquidate unfavourable soil conditions-soil & ecological consequences of irrigation and increase of fertility are studied.

### **Main Results of Studies and their Discussion**

With the beginning of irrigation in the region, mainly on plain watersheds and high river terraces, conditions of functioning of all components of nature-geographic environment changed, as well as the established in centuries scheme of landscape and geochemical junction. Our studies of many years (1971-2011) have established that under the influence of irrigation main characteristics and indicators of source state of natural- and soil-ameliorative environment change



significantly, direction and intensity of landscape & geochemical and soil-forming processes. As the result, landscape & ecological situation change in general – composition, properties of soils, often structure of soil cover of the territory of irrigated massive. At that landscape & geochemical and soil-forming processes could have reversible, partially reversible or irreversible character (usually of *degradation* direction) [1-3]. Among negative events and processes are; rising of under-soil waters to the surface, activation on local and regional levels of galo-geochemical processes. Practically everywhere the consequences of irrigation are increase in soils of mobility of carbonates and humus substances, decrease of capacity of cationic exchange and content of consumed calcium. The share of consumed magnesium and sodium grow which evidences of alkalization and salinization processes of black soils with irrigation. At that, significantly degrade indications of their agro-physical state as the result of processes of aggregates destroying – incrustation, increase of density and hardness, decrease of permeability, increase of hydrophilicity of irrigated soils. More intensive degradation in initially non-carbonate black soils at irrigation with low-quality waters with high mineralization (1-3, sometimes 4-5 g/dm<sup>3</sup>) of sodium & magnesium chemical properties. Significantly less change at irrigation parameters of black soils in case if they are carbonate, with no-deficit balance of humus and calcium, at careful regimes of irrigation with good quality waters, as well as at observance of corresponding culture of irrigated agriculture.

In conditions of significant decrease in the last 15-20 years of area and intensity of irrigation in the region there is evident tendency to eventual re-naturalization of landscape & ecological and soil & amelioration situation on massive of irrigation, re-gradation soils changed by irrigation in the previous years, black soils first of all. Eventual change of agricultural & amelioration conditions on irrigation massive entail changes and certain difficulties with existing nature & economic and agro-amelioration and soil situation. On this background it is stated that new landscape & geochemical and soil-formation processes of previous period of large-scale irrigation develop, or their essence transform. Correspondingly, characteristics of soils state eventually change. First of all, those are salt characteristics of black soils of irrigation massive, composition of soil solution and soil adsorption complex (SAC), and largely – parameters of humus and agro-physical state. In particular, in soil massive on watersheds elution of salts from upper horizons of profile grow. At the same time the soil depth of geochemically subordinated landscapes differ with higher content of easily-soluble salts. In upper horizons of black soils after irrigation had stopped content of soluble and absorbed sodium decreased. At that the share of calcium in SAC grows. In lower horizons of black soils, especially those which were irrigated in past years with highly mineralized water of sodium chemical properties, ratio  $Ca^{2+}:Na^{+}$  stays narrow (0,3-0,6) and content of exchangeable sodium is quite high (up to 3-6% of capacity of cationic exchange). At the background of desalination – dealkalinisation of black soil irrigated massive in post-irrigation period of their evolution the indicators of agro-physical state eventually improve. Tendency to decompactization is observed, quantity of blocky aggregates decreases, share of agronomic valuable aggregates and coefficient of soil pedality. Speed of agro-physical properties degradation is significantly higher in soils, which were previously irrigated with good quality (fresh) water.

In the last 20 years under both under bogharic conditions and in irrigated massive of the region humusness of soils eventually go down. I.e. process of dehumification of studied soils take place. The reason of this very unfavourable degradation process is domination of grain and sunflower in crop structure without application of necessary quantities of organic and mineral fertilizers. Only under perennial grasses, starting with 2<sup>nd</sup> year of cultivation, content and amount of humus grow, which enables us to recommend increase of grasses share up to 25-35% of area in the structure of crop rotation.

Thus, based on experimental & research materials, both our and other authors' it is revealed that irrigation of the South-Western Black Sea black soils cause significant changes (most often negative) in soil natural regimes and processes, and connected with them morphological indicators, soil composition and properties. Tendency of degradation of many soil parameters is preserved in current post-irrigation period of evolution of landscapes and soils of irrigated massive. Most often, as it was pointed out above, processes of decarbonization and irrigation salinization take place, and locally – salting of soils, degradation of their humus and agro-physical state, supply of nutrients for plants. Usually these degradation changes of the indicators of state and properties of soils reveal simultaneously [1-3]. Taking into account size of values of salinization, salting of soils and alkalization of black soils of irrigated massive, their humus and agro-physical state, pollution with heavy metals and water-soluble fluorine, recently an integral classification of soils according to the level of their degradation had been proposed [2, 3]. At that, it had been established that at low level of soil degradation in irrigated massive crop yields decrease 15-20%, at medium level – 20-30%, at high level – 30-50% and over.

On the basis of results from researches and work of many years' system of agro-ameliorative measures had been substantiated and developed to prevent from the processes of degradation of black soil irrigated massive in the region and to increase their fertility. At present the system of measures proposed by us is being introduced in two farms of Odessa Region as a pilot-experimental activity.

## Conclusions

1. Studies of the processes of composition, properties and fertility changes in the Ukrainian South-Western Black Sea black soils have been carried out both under irrigation conditions and during current 15-20 years long post-irrigation period of their evolution. Essence and ecological & soil consequences of processes of degradation of black soil massive of irrigation in the region have been studied.

2. In the black soils studied most often revealed are the processes of decarbonization, irrigational salinization and local salting of soils, degradation of humus state, ecological & agrochemical state and agro-physical state indicators.

3. System of agro-ameliorative measures has been substantiated and is being introduced as a pilot experiment to prevent processes of degradation of the black soils of irrigated massive and to increase their fertility.

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