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Mansour Ghorbanpour
Manika Khanuja
Ajit Varma *Editors*

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Ajit Varma, Amity Institute of Microbial Technology,
Amity University Uttar Pradesh, Noida, UP, India

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Mansour Ghorbanpour • Manika Khanuja •
Ajit Varma
Editors

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Editors
Mansour Ghorbanpour
Department of Medicinal Plants,
Faculty of Agriculture and Natural Resources
Arak University
Arak, Iran

Manika Khanuja
Centre for Nanoscience and
Nanotechnology
Jamia Millia Islamia
New Delhi
India

Ajit Varma
Amity University Uttar Pradesh,
Amity Inst of Microbial Technology
Noida, Uttar Pradesh
India

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Foreword

Nanoscience coupled with nanotechnology is one of the most important emerging tools which can complement modern agriculture by providing new agrochemical agents and new delivery mechanisms to improve crop productivity. Nanoscience has found ways to control the release of nitrogen in agriculture fields, micromorphology of soil and characterization of soil minerals, rhizospheric nature, nutrient ion transport in soil–plant system, precision water farming, etc. In the era of climate change, it is a challenge to feed the rapidly increasing world population, with agricultural productivity facing various challenges. Thus, it is now very important to improve the crop productivity to cope with this upcoming problem of food security. Nanoscience (nanotechnology) promises to accelerate the development of biomass-to-fuel production technologies. Experts feel that the potential benefits of nanotechnology for agriculture, food, fisheries, and aquaculture need to be balanced against concerns for the soil, water, and environment and the occupational health of workers. Nanoparticles (size range from 1 to 100 nm) have unique physicochemical properties, i.e., high surface area, high reactivity, tunable pore size, and particle morphology; therefore, they have novel applications in diverse fields of science including medicine, physics, chemistry, materials science, and agriculture. The appropriate elucidation of physiological, biochemical, and molecular mechanism of nanoparticles in plant leads to better plant growth and development. Several countries have recognized the potential impression of nanotechnology could have on their economies and spending profoundly in research direction.

This book "Nanoscience and Plant–Soil Systems" edited by Drs Mansour Ghorbanpour, Manika Khanuja, and Ajit Varma is an enthusiastic celebration of a new paradigm "nanoscience in agricultural research." It is important to assemble the ever-improving methods based on nanotechnology and its role in plant soil system in a book under these new guidelines, i.e., practical aspects and immediate use in the laboratory and beyond. The chapters of this book are indeed an excellent and outstanding contribution. This book succeeds in presenting many concepts, methods, etc., which can broaden our understanding of the role of nanotechnology in plant–soil system. This comprehensiveness should make this book equally valuable to students, teachers, and researchers entering this field of nanoscience. I am sure readers in the fields of biotechnology, microbiology, agriculture, and nanotechnology would find this book very useful.

Overall, I am glad to see good coverage in this book. Congratulations and my best compliments to editors of the book who performed an outstanding work in getting valuable contributions from the team of global experts on the subject which has major implications not only for food security worldwide but also for the socioeconomic condition of communities affected by climate change at the basic grassroots level. The contributors are to be congratulated on their efforts, and readers are recommended to use this volume for a long time to come. The publisher also deserves for publishing this useful book.

Department of Science and Technology, Ashutosh Sharma
Government of India
New Delhi, India
June 23, 2016

Preface

There is general belief and admission that important, innovative, and novel ideas emerge over a cup of tea or a glass of beer and the weather must be congenial and most suitable for materializations of original ideas. The genesis of this book underlines the concept developed in 2015.

Technological advances and sociological changes are such that Science demands evolution. We believe that one reason for publishing of ideas is broadening one's view, through the examination of a text of wide and extensive coverage, nurtures one's capacity for learning and reflection. The study of microorganisms has become a valuable science in the last 100 years as it has provided the means to control a number of infectious diseases. In this direction, nanotechnology has emerged as a potential candidate. The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled "There's Plenty of Room at the Bottom" by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used. Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. Nanoparticles are gaining attention due to their low cost, simplicity, and eco-friendly nature.

In this volume entitled "Nanoscience and Plant–Soil Systems," the editors have accumulated various advanced approaches for studying the different soil microorganisms for the benefit of humankind. Currently, world agriculture scientists face a wide spectrum of challenges including climate change, urbanization, and environmental issues: accumulation of insecticides and pesticides, decay in soil organic matter, and sustainable use of natural resources. These challenges are going to be further intensified due to increase in food demand. Nanotechnology has significant benefits on food and agriculture system. Through nanotechnology, optimization of agriculture inputs (viz. nanopesticides, nanoherbicides) to enhance the effectiveness of the active ingredients including targeted delivery and release and less dosage per application and to reduce bi-products that otherwise degrade ecosystem can be achieved. This book is divided into three parts. In the first part which includes Chaps. 1–3, the authors give introduction to nanoscience and nanotechnology, how nanoparticles are being synthesized with their origin and activity, and also the application of these nanoparticles. The second part of the book which includes Chaps. 4–11 describes nanomaterials in soil environment with their applications as antimicrobial and bioremediating agents and also their effect on soil properties and soil microorganisms and how they act as a fertilizer. The last part of the book which includes Chaps. 12–19 describes the interaction of nanomaterials with plants and their effect on seed germination. Chapter 14 describes the role of nanoparticles on plant growth after interacting with a novel root endophyte *Piriformospora indica*. In Chaps. 15–21, the application of nanoparticles as a biofertilizer and pesticide and in plant disease control with the challenges faced and threats involved with the use of nanoscience plant soil system is elaborated.

We are grateful to the many people who helped to bring this volume to light. We wish to thank Jutta Lindenborn and Hanna Hensler-Fritton from Springer Heidelberg for generous assistance and patience in initializing the volume. Finally, specific thanks go to our families, immediate and extended, not forgetting those who have passed away, for their support or their incentives in putting everything together. Ajit Varma in particular is very thankful to Dr. Ashok K. Chauhan, Founder President of the Ritnand Balved Education Foundation (an umbrella organization of Amity Institutions), New Delhi, for the kind support and constant encouragement received. Special thanks are due to his esteemed friend and well-wisher Professor Dr. Sunil Saran, Director General, Amity Institute of Biotechnology, and Adviser to Founder President, Amity Universe; all faculty colleagues; and his Ph.D. students, research fellows (Uma Singhal and Manpreet Kaur Attri), and other technical staff.

This book will be useful to microbiologists, nanotechnologists, and ecologists if interpreted with caution. I am honored that the leading scientists who have extensive, in-depth experience and expertise in soil biology and nanotechnology took the time and effort to develop these excellent chapters. This select group of scientists is uniquely suited to write these chapters and have firsthand knowledge of the methods and techniques they have presented. This ensures that the methods presented are current, relevant, and readily applicable. I want to thank all contributing authors for their diligence and patience in bringing this book to fruition with such collegiality.

Arak, Iran — Mansour Ghorbanpour
New Delhi, India — Manika Khanuja
Noida, UP, India — Ajit Varma

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Chapter 4
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Vera Terekhova, Marina Gladkova, Eugeny Milanovskiy, and Kamila Kydralieva

4.1 Sources of Entry and Migration Pathways of Engineered Nanomaterials in Soil

4.1.1 Introduction

The latest achievements in the field of nanotechnologies and the corresponding growth in the use of nanomaterials (NMs) in many industries as well as in the production of consumer goods inevitably have led to their dispersion into the environment. It is evident that such a wide introduction of nanoparticles (NPs) in our life and their expansion and accumulation in natural habitats gives grounds to consider them as a particular type of pollutants. Specialists have come to the conclusion that the processes of nanoparticle transfer with air and water flows

V. Terekhova (✉)
Soil Science Faculty, Lomonosov Moscow State University (MSU), 1-16, Leninskiye Gory, 119234 Moscow, Russia

Severtsov Institute of Ecology and Evolution (IPEE), Russian Academy of Sciences, Moscow, Russia

Pirogov Russian National Research Medical University (RNRMU), Moscow, Russia
e-mail: vterekhova@gmail.com

M. Gladkova • E. Milanovskiy
Soil Science Faculty, Lomonosov Moscow State University (MSU), 1-16, Leninskiye Gory, 119234 Moscow, Russia
e-mail: marika230489@gmail.com; milanovskiy@gmail.com

K. Kydralieva
Moscow Aviation Institute, Volokolamskoe shosse 4, 125993 Moscow, Russia
e-mail: k_kamila@mail.ru

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and their accumulation in soil, water, and bottom sediment differ significantly from the behavior of larger particles. The active development of works on analyzing engineered nanomaterials in natural habitats helps in clarifying the following questions: What are their distribution pathways? Do artificial NMs retain their properties (size, original structure, and reactivity) in water, air, soil, and sedimentation objects? What are the consequences of nanoparticle expansion in a liquid medium? What are the distinctions in the effects of NPs and molecular and atomic forms of the same material on biota under water and soil conditions? Several definitions of nanomaterials and different variants of their classification occur in the publications (Klaine et al. 2008). The generally accepted sign that characterizes the relation of objects to nanomaterials is the dimension of constituent particles at an interval of 1–100 nm, in at least one dimension. This definition is right for natural colloids (superdispersed particles in the air, biological objects such as viruses, etc.), like water and soil colloids, as well as materials constructed using nanomaterials.

Soil colloids have been studied for many decades. These are primary nanoparticles in the structure of clay and organic substances, iron oxides, and other minerals, which play an important role in biogeochemical processes. Particular attention has been devoted to analyzing their effect on soil formation and change in the structure of soils (Fedotov and Shalaev 2012).

4.1.2 Sources of Nanoparticle Entry into the Environment

The sources of nanoparticle entry into the environment can be divided into natural and anthropogenic. Natural processes have been sources of nanomaterial entry into the environment for thousands of years. They include forest fires, sandstorms, dust, muddled waters, formation of aerosols, clustering in gases, volcanic bursts, and salt evaporation, as well as biological objects (viruses, products of vital functions, films, colloids, etc.) (Krichevskiy 2010).

Many anthropogenic objects and processes are sources of the so-called unintentional nanoparticle entry into the environment. They include the following: the combustion of waste and fuel with combustion catalysts in transport vehicle engines and at power plants, domestic waste, and mining operations, open pits and mines, industrial production and emissions, construction, welding, soldering, preparation of food, etc. Environmental objects are contaminated during the production, transportation, and use of different hygiene products and household chemical goods (sun shielding instruments, detergents), motor tire resin, typographic dyes, textile products, etc.

The development of some industries and nanotechnologies has led to abrupt growth in the quantity of engineered nanoparticles in the environment. Today, nanotechnologies have become a source for the intentional expansion of a significant amount of nanomaterials in different natural habitats. They include purification and processing using NMs from polluted groundwater, land reclamation, and application for agricultural needs. Nanoparticles may get into soils due to using NMs in soil and water purification systems for agricultural needs (as nanofertilizers, pesticides, seed treatment preparations, materials for agro-films, preparation of hydroponic solutions, etc.). Such materials include fullerenes, nanotubes, inorganic nanocrystals, quantum points, nanofilms, micelles, colloids, specific-action drugs, etc.

Many natural sources of nanoparticles can create local ecological problems, but they are included in the evolutional respect among the factors that affect the environment only periodically, without breaking the general laws of the development of cyclical successions in natural systems. Engineered materials are becoming constantly acting factors, which can give birth to global problems in the environment.

4.1.3 Pathways of Nanoparticle Entry into Soil

The pathways of nanoparticle entry into soil characterize their entry, accumulation (content), and migration. NPs can enter soil with atmospheric precipitation, sedimentation in the form of dust and aerosols, direct soil absorption of gaseous compounds, abscission of leaves or as a result of anthropogenic activity, etc. After NMs get into a water system through sewage or industrial emissions, nanoparticles can accumulate in plant organisms (e.g., in algae), as well as in organisms of invertebrates (plankton, benthos, crustaceous) that are the primary links of a food chain, and then they can pass into organisms of water vertebrates taking part in the human food chain. In a land ecosystem, NPs can accumulate in soil, surface water, sewage, and groundwater. The results of studies in this field are generalized in Table 4.1.

Coming from different sources, pollutants ultimately get on the surface of soil, and their further fate depends on its chemical and physical properties. Pollutant components stay in soils much longer than in other biospheric objects. Many examples of direct anthropogenic and man-caused environmental effects on soil are known; therefore, soil is as sort of an object depositing anthropogenic pollutants and a source of the secondary pollution of water and other environmental objects. The pollution of soils with nanomaterials presents a serious risk of getting into the human organism and tissues of land plants and animals. The entry of NPs into any biocenosis component can lead to their introduction into other objects of this system and transfer through the food chain. With allowance for the ecological functions of soil and its role in substance turnover, the following migration pathways of nanoparticle entry into this object (Fig. 4.1) are marked out: (1) the translocation pathway that characterizes the transition of a substance from land plants and NP waste; (2) the water migration pathway that characterizes the capability of a substance to migrate from groundwater, sewage, and water sources; and (3) the air migration pathway that characterizes the transition of a substance from the atmospheric air (Venitsianov et al. 2003).

Table 4.1 Environmental objects in which nanoparticles of different types can accumulate

Branch, application	Type of a nanomaterial	Environmental object					
Cosmetic products, personal hygiene products	TiO_2, ZnO, fullerene C60, Fe_2O_3, Ag	Soil	Surface water	Groundwater	Sewage	Waste	Air
Catalytic agents, lubricants, combustion catalysts	CeO_2, Pt, MoS_3	–	+	–	+	–	–
Dyes and covers	TiO_2, SiO_2, Ag, quantum points	–	+	–	+	–	+
Water treatment, recovery of the environment	Fe, Fe–Pd	–	+	–	+	–	+
Agrochemical preparations	SiO_2 (porous) as a carrier	+	+	+	+	–	–
Food package	Ag, nanoclay, TiO_2	+	+	–	–	–	+
Pharmaceutical preparations	Nanopreparations, filling agents	+	–	–	–	+	–

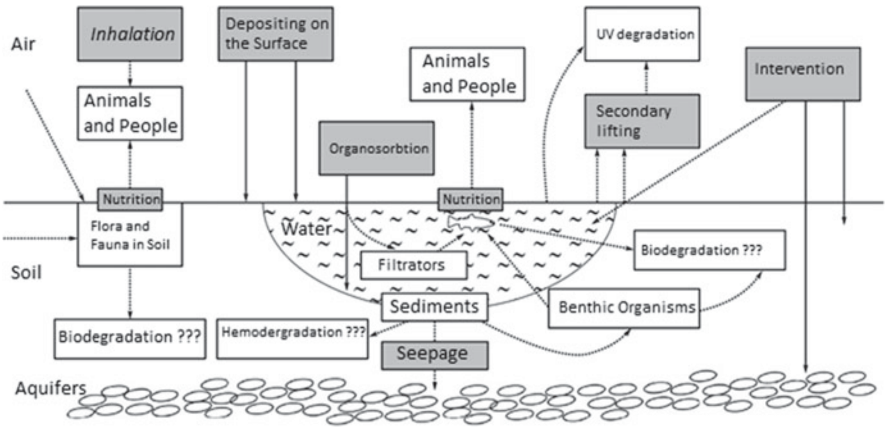

Fig. 4.1 Possible entry and migration pathways of nanoparticles proved experimentally (*a solid line*) and supposed pathways (*a dotted line*) (Krichevskiy 2010)

At present, there are few studies on revealing the nanoparticle migration processes in soil. Nevertheless, pollutants absorbed or included in colloids are known to be transported, when favorable conditions are formed for this, for example, if natural soil colloids are carriers of metals through soil profiles (Cornelis et al. 2010; Darlington et al. 2009; Fang et al. 2009; Klaine et al. 2008). A model has been developed for the migration of metal-containing nanoparticles in the NP waste–soil system (Fedotov and Shalaev 2012). Distribution along a soil profile has been ascertained to take place as follows: at the initial stages of NP introduction, the humus layer accounts for their maximum concentration; subsequently, the maximum concentration moves to the underlying layers, usually being affected by acid filtration water. The capability of metal-containing NPs to migrate in a solution has been shown to represent a high danger. This fact agrees with the experimental evidences of their having a much greater bioavailability in liquid media in comparison with natural soil (Handy et al. 2012). The depth to which waste components migrate along a soil profile and the level of their content in a filtrate are indicators of the water migration danger.

Study of the biological activity of nanomaterials in connection with different conditions of their entry into soil is very significant to understand the effect of nanoparticles on the environment. Engineered NPs can get into soil in the dissolved state (*A*), which can entail the following: (a) bioaccumulation by roots of land plants; (b) accumulation by invertebrates and, correspondingly, toxicity; and (c) microbial toxicity. The direct absorption of solid particles (*B*) can cause the toxicity of the following: (a) roots of land plants, (b) invertebrates, and (c) microbes. The direct entry of NPs (*C*) into soil can result in their sorption/ aggregation or in migration along the profile. Nanoparticles of engineered nanomaterials differ in bioavailability depending on their aggregative state. They have a greater bioavailability in the dissolved form and consequently are more toxic, since they are not included in the structure of soil. One of the suggested

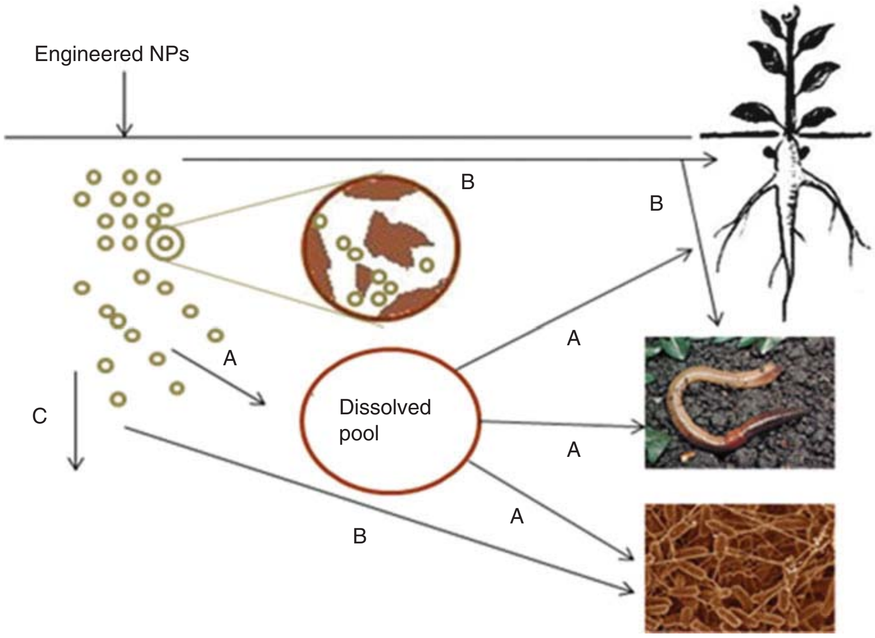

Fig. 4.2 Bioavailability of nanoparticles under different conditions of their entry into the soil environment: *A* is the dissolved pool of NPs; *B* is the direct absorption of solid NPs; *C* is the direct entry of NPs, migration along the profile

methods for detecting NPs according to accumulation and solution in soil can be used when estimating their bioavailability for plants. However, in such experiments root exudates can affect the distribution of NPs in the rhizosphere, thus changing their relative bioavailability. Nonetheless, test methods clearly should take into account the diversity of natural soils such as their pH, clay content, cation exchange capacity, texture, amount/type of organic matter, and mineralogy, as well as include a standard soil in the test (Handy et al. 2012) (Fig. 4.2).

Our research has shown that humic substances, which are known to be used to detoxify different pollutants of organic and inorganic origin (Perminova 2008), can affect the biological activity of nanomaterials. The toxic effect of some concentrations of detonation nanodiamonds (DNDs-U) and titanium nanodioxide (nano-TiO_2) has been ascertained to be removed in the presence of an industrial humic preparation potassium humate from leonardite of the POW HUMUS mark (Le-PhK) produced by the Humintech company (Germany). The detoxification properties of Le-PhK (5 mg/L) manifest themselves in biological tests with higher plants (*Brassica juncea*) in case of its being applied jointly with DNDs-U and nano-TiO_2 at the same concentration; at other concentrations of nanoparticles (50 and 100 mg/L), the effect is ambiguous (Gladkova and Terekhova 2013). The discovered difference in the direction of the action speaks for the complex interactions between humic substances and nanomaterials. At this stage, it is evidently necessary to carry out further research and to accumulate significant information on the factors affecting the detoxification capability of both natural and industrial humic substances.

There is relatively little information on the entry and expansion pathways of engineered nanomaterials and their subsequent fate in water and land ecosystems currently. The difficulty in detecting engineered nanoparticles in the presence of natural colloids is one of the obstacles in studying NMs. It is rather difficult to detect the behavior of engineered nanoparticles. Second, the interaction of nanoparticles and natural colloids will affect the behavior of NPs depending on their concentration (Boxall et al. 2007). In soil, natural colloids have much lower concentrations, but NP concentrations would likely be much lower also because of increased aggregation and sedimentation at higher ionic strengths (Klaine et al. 2008). With allowance for the difficulties in detecting NPs in soil, studies on soil organisms have become an alternative method for proving this interaction, which analytic methods have shown that they accumulate here. Thus, the experiments using ^{14}C-labeled single-layer nanotubes (SLNTs) have fixed their absorption by *Eisenia fetida* worms and then the purification of animal organisms. An attempt has been made to investigate the absorption of silver nanoparticles by nematode tissues (Meyer et al. 2010) and gold and copper nanoparticles by rainworms (Unrine et al. 2008, 2010).

However, complex methods, which will hardly be applied in normative testing, were used for this to isolate and characterize natural NPs in soil (the so-called soil colloids) (Gimbert et al. 2006, 2007). Reliable detection requires that particles be isolated from the solid soil phase (desorption) and dispersed in a water suspension, which is a significant analytical problem. At present, works aimed at its solution are very few in number (Klaine et al. 2008). Thus, the opinion has been advanced that the major theses of colloid chemistry can help in studying the behavior of nanoparticles. Relying upon the research on natural water colloids with a dimension of several nanometers, foreign specialists have drawn the conclusion that they can behave analogously to industrial NPs (Gustafsson and Gschwemd 1997; Lead and Wilkinson 2007; Madden et al. 2006). This comparison is possible first because colloids are given to aggregation and ultimately aggregated into particles > 1 mkm, which are sufficiently large, and sedimentation is dominant in their transfer (Honeyman and Santschi 1992).

The results of analyzing the literature indicate that the problem of the expansion of nanomaterials in the environment is becoming ever more acute. Soil seems to be the most useful for the development of reliable methods for analyzing and revealing the content of nanoparticles. Being a very specific part of the biosphere, it not only geochemically accumulates pollution components but also plays the role of a natural buffer that controls the transfer of chemical elements and compounds into the atmosphere, hydrosphere, and living matter. Coming from different sources, pollutants ultimately get on the surface of soil, and their subsequent fate depends on its chemical and physical properties.

The problems of detecting nanoparticles in soil are related not so much to the well-known technical difficulties, which require expensive special equipment and a high level of technical qualification of specialists, as to the fact that soil, which is a complex multiphase system, contains a great number of mineral and organic macro- and micro-components as well as natural nanoparticles. The modern methods do not permit the bioavailability of engineered nanoparticles to be investigated in detail. However, judging from indirect indicators (the change in standard test functions in biotests), the bioavailability of nanoparticles in natural habitats can be asserted to depend primarily on their sizes and degree of aggregation, and, when they are found in soil, the diversity of natural soil properties (acidity, presence of cations, organic substances, etc.) acquires paramount significance.

4.2 Problem of Bioassay Engineered Nanomaterials in Soil

Because of the recent development and rapid advent of nanotechnologies, great attention is paid to the effect of engineered nanomaterials (NMs) on living organisms. Both Russian and foreign researchers pay emphasis to the search for potential methods of assessing the effect of synthetic products of nanotechnologies on natural complexes and on the functioning of the main links of the trophic chain and separate organisms. The complexity of the soil organo-mineral composition and the unpredictable dynamics of soil properties in time and space create problems in the structural and functional analysis of the biotic complex of soil under the impact of conventional pollutants, whose chemical transformations are well understood. Available data indicate that, to assess the impact of nanoparticles on soil components, the existing methods should be adapted and new methods have to be developed. This work is devoted to the analysis of the behavior of engineered NMs in soil and the description of the methods for their ecotoxicological assessment. It is known that the behavior of nanoparticles in natural media differs from that of coarser particles of the same material. As a rule, NMs more easily enter into chemical reactions with other environmental components compared to coarser objects of the same composition; they are capable of forming complexes with previously unknown properties. An important factor for assessing NMs' impact on living organisms is the effect of the NMs' interactions. The inverted dose–response ratio, or the U-shaped curve describing this relationship in ecotoxicological studies of dispersed systems, is largely due to the formation of aggregates at high concentrations and the increase in the content of free nanoparticles under dilution. The biotic and abiotic transformations of any chemical compounds, including NMs, during bioassays can give different results: (1) the formation of more toxic products, including those with delayed action or new properties; (2) the formation of products with higher hazard indices compared to the original substance; (3) the formation of products whose toxicity is similar to that of the original substance; and (4) the formation of less toxic products. Therefore, the revelation and investigation of the adaptation of living organisms and their resistance to the action of engineered nanoparticles in the soil, which is a depositing medium for pollutants from different sources, are of special importance under the increasing technogenic impact.

4.2.1 *Problems and Advances in the Studies of the Impact of Nanoparticles on the Environment*

One of the problems in the study of nanoparticles is related to the revelation of engineered nanoparticles in the soil in the presence of natural colloids. Natural nanoparticles in the soil (referred to as soil colloids) are difficult to separate and characterize (Noack et al. 2000; Gimbert et al. 2006, 2007). Their reliable detection includes the separation of particles from the soil solid phase (desorption) and their dispersion in a water suspension, which represents a serious analytical problem. Works aimed at its solution are extremely scarce now (Klaine et al. 2008). An alternative method for confirming the presence of nanoparticles in soil is the study of the responses of soil organisms. In some cases, analytical methods proved the accumulation of nanoparticles in tissues of living organisms. Thus, the uptake of ^{14}C-labeled monolayer carbon nanotubes by *Eisenia fetida* earthworms was experimentally confirmed (Petersen et al. 2008). Gold and copper nanoparticles were found in the earthworm tissues (Unrine et al. 2008; Yang and Watts 2005). Attempts were made to analyze the adsorption of silver nanoparticles by nematode tissues (Meyer et al. 2010). Complicated analytical methods and sophisticated equipment were used for this purpose, which are hardly suitable for the wide distribution of these methods in conservation practice. In the resolution of the 2005 seminar of the European Centre for Ecotoxicology and Toxicology of Chemicals (ECOTOC) devoted to the biosafety of NMs, it was specially emphasized that the nature, surface area (including the state of aggregates and agglomerates), and shape of nanoparticles should be taken into consideration in the study of the toxic effect of NMs. It is inadvisable to use a single dimension (e.g., mass, surface area, or particle size) to characterize nanoparticles (Masycheva et al. 2008). The conventional assessment of the toxicity is more informative than the physicochemical methods of analysis. Therefore, along with analytical methods, bioassay procedures find increasing use in the assessment of the environmental effect of nanoparticles. Bioassays provide advanced information about problems before the appearance of obvious changes in natural ecosystems It is advisable to include representatives of the main trophic levels in the system of bioassays (Terekhova 2011).

4.2.1.1 Effects of Nanoparticles on the Environments

There are opposite opinions about the safety of nanoparticles for living objects: some authors declare the complete harmlessness of NMs; other authors, on the contrary, express extreme concern over the distribution of products of new technologies and are at an alarm. This again emphasizes the poor knowledge and complexity of the identification of NMs and their effects not only in soil but also in aerial and aqueous environments and organisms.

Under real conditions almost all nanoparticles in water environments form conglomerates, which undergo sedimentation and elimination from active processes. One relates these processes to the peculiar self-purification of water environments, which would erase the problem of assessing the effect of high concentrations of nanoparticles. However, the hazard of such concentrated precipitates for soil-inhabiting and benthic organisms cannot be excluded. At this stage, there is neither a clear idea of the hazard of NMs nor any general concepts of the possible mechanisms or theory explaining the effect of NMs on living cells. It is essential that, although authors hold significantly different views on the environmental hazard of nanoparticles, most of them recognize the existence of this hazard. Daniel Watts wrote “as far as the use of nanoparticles increases, their risk also increases.” At the same time, “we should attentively examine this domain and probably undertake some serious measures.” Let us consider some studies on the toxicity of NMs widely used in the production area.

4.2.1.2 Carbon Nanoparticles

Fullerenes and/or carbon nanotubes are most widely used in different areas. For example, the annual production of single-wall carbon nanotubes carbon nanotubes stronger than steel by 460 times reached 1000t in 2011. Studies of the toxic effects of fullerenes give contradictory results. Some authors express concern that these particles can damage microorganisms, “whose disappearance can cause a real ecological catastrophe” (Klaine et al. 2008). However, evidence of the harmlessness of fullerenes for soil is more abundant. A recent study performed at Purdue University showed that fullerenes are harmless for microorganisms and are adsorbed by soil without damaging it. No effect on soil organisms was recorded in the analysis of fullerenes (nC_{60}) by Tong et al., who supposed that the interaction of nC_{60} with soil organic matter ensures the neutralization of the potential toxic effect of fullerenes (Unrine et al. 2008). It was shown that fullerenes modified by amino groups have toxic effects. In particular, the inhibition of test functions in the assays with *Escherichia coli* reached 60 % compared to the control (coliform bacteria untreated with NMs). Toxic and other unfavorable effects of NMs can be manifested in different forms. Carbon nanotubes show varying degrees of toxicity depending upon their arrival into animal organisms (Allsopp et al. 2007; Donaldson et al. 2006).

However, the data obtained on their harmfulness for living organisms are also contradictory. Some authors showed that ultra dispersed diamonds from detonation synthesis have no carcinogenic or mutagenic properties. Due to their high adsorption capacity and other specific properties, hyperactive sorbents act as immobilizers of biologically active substances (Schrand et al. 2007). Our studies showed that, in spite of the carbon nature of nanodiamonds, which imparts them a specific affinity for organic elements of the environment, they have a toxic effect when present in specific concentrations. This was in particular revealed in the study of the effect of synthetic nanodiamonds (PL-D-G02, PlasmaChem GmbH) on the growth and fluorescence of a standardized algal culture of *Chlorella vulgaris*. Studies performed according to the standardized procedure recommended for ecological control, where the assessment is based on the changes in two different test functions (an increase in the cell population of the microalgae and fluorescence), showed that the revelation of nanodiamond toxicity largely depends on the selected method of the toxic effect's registration, as well as on some other factors. The direct counting of cells under a microscope, rather than fluorescence indices, is obviously a more reliable method of studying the biosafety of nanodiamonds, which inevitably form aggregates of different sizes in suspensions. It is interesting that a lower concentration of synthetic nanodiamonds (0.0005 %) had a higher damaging effect than a higher concentration of 0.005 %. This conclusion is based on the analysis of changes in the cell number and the fluorescence study of algae. This perfectly agrees with observations of other authors and our data obtained for other test species. Finer particles and aggregates of nanodiamonds were also found to be more toxic for other test organisms, including *Paramecium caudatum*. This can be related to the higher aggregation of nanodiamond particles in the incubation medium and, hence, the lower ability of coarse aggregates to penetrate into the cells of living organisms (Karateeva et al. 2009).We have performed thorough studies of the biological activity of Russian industrial detonation nanodiamonds (DNDs-U produced by OOO SKN, Snezhinsk, Chelyabinsk Oblast) differing in the size of the free particles in water suspensions. In experiments on three nanodiamond samples with mean particle sizes of 15, 30, and 100 nm (at 5, 50, and 500 mg/L), we studied the responses of standardized test organisms of the main trophic levels: (1) producers, higher plants (the leaf mustard *Brassica juncea*); (2) consumers, infusoria (the slipper animalcule *Paramecium caudatum*); and (3) reducers, bacteria (a luminescent strain of *Escherichia coli*). A relationship between the toxicity of the DNDs-U samples and the size of the particles was revealed. An increase in toxicity with the decrease in particle size (100–30–15 nm) was observed, as in some other known cases (Gladkova 2011).

4.2.1.3 Metal-Containing Nanoparticles

The safety of metal-containing NMs attracts no less attention than that of carbon NMs. Nanotitanium dioxide is a material widely distributed in consumption products and the nanoindustry. The studies of the uptake and accumulation of titanium dioxide nanoparticles in test cultures (chlorella and daphnia) showed their high accumulation rate and concentration in phyto- and zooplanktons. Thus, the content of titanium in algal cells exceeded that in the environment by more than 200 times. In daphnia organisms, the content of titanium was half as high as in chlorella but 100 times higher than in the environment. The study of the effect of titanium dioxide nanoparticles (nano-TiO_2) with a mean particle size <75 nm in a water suspension (a mixture of two crystalline TiO_2 modifications, anatase and rutile, Sigma-Aldrich, USA) in three bioassay systems revealed uncertain effects, although toxicity was more frequently detected at the studied concentrations of

5, 50, and 500 mg/L. For example, a phytotest with mustard seedlings showed that the impact of nano-TiO_2 suspension (5, 50, and 500 mg/L) inhibited the development of leaf mustard roots. In an experiment with paramecia, it was found that nano-TiO_2 at concentration of 5 mg/L had a low stimulating effect on the development of a protozoan culture, while an acute toxic effect was manifested data concentration of 50 mg/L. In a bioassay with luminescent bacteria, a low concentration of nano-TiO_2 (5 mg/L) suppressed the fluorescence of bacteria (evidence of a toxic effect), but a stimulation of fluorescence was observed at concentrations of 50 and 500 mg/L with the higher stimulation being observed at 50 mg/L (Gladkova 2011). Thus, no linear dose–effect relationship was revealed in most of our experiments on the analysis of biotic responses to the concentrations of nanoparticles in water suspensions, as was observed by many authors for other NMs. This can be due to the peculiar interaction mechanism of nanoparticles and the relationship between the aggregation of nanoparticles and the degree of dilution, i.e., the minimum distance between nanoparticles in the dispersed system. This relationship can also be explained by different impacts of NMs on living organisms. In a series of experiments on studying the responses of soil microorganisms to the antibacterial properties of silver nanoparticles (Benjamin Colman, Duke University), the almost complete suppression of the development of nitrogen-fixing bacteria was observed a month after the treatment. This group of microorganisms was more susceptible to silver nanoparticles by a million times compared to other microorganisms. Another experiment showed that the activity of bacterial enzymes degrading organic substances in soil treated with silver nanoparticles decreased by 34 % compared to the untreated soil. These data indicate that a profound study of the interaction between nanoparticles and soil components is necessary.

4.2.1.4 Effect of Soil Properties on the Manifestation of NMs Toxicity

Data on the behavior of nanoparticles in different soil environments are gradually being accumulated in the literature. It was experimentally shown that soil is a reliable filter for the migration of nanoparticles if it contains an increased amount of clay or has a high ionic strength. In a series of experiments performed at the Georgia Institute of Technology, water-containing fullerenes was passed through vessels filled with sand, sediment, glass microgranules, and other materials; it was revealed that even sand retains up to 80 % of the nanoparticles. It was also shown that the filtration of nanoparticles depends on the water's composition. It is interesting that the presence of humic acids or surfactants allowed nanoparticles to freely pass through sand. Under hydroponic conditions, toxic effects of engineered NMs on higher plants were frequently observed (Meyer et al. 2010). In soil, the phytotoxicity of NMs for the grown test plants is minimum if any (Baun et al. 2008; Fernandes et al. 2007).

4.2.2 *Possible Mechanisms of the Impact of Nanoparticles on Living Organisms*

Most mechanisms of the toxic action of NMs are unclear; however, relatively well-defined concepts are reported in the literature for some of them.

Studies of the quantitative uptake and accumulation of NMs by whole organisms showed that nanoparticles mainly arrive into multicellular animals by ingestion and absorption through intestinal walls (Donaldson et al. 2006; Fountain and Hopkin 2001; Stampoulis et al. 2009). Most works on assessing the possible migration of nanoparticles in animal tissues were performed with model test organisms. The first works dealt with well-studied species widely used in ecotoxicology, in which species these processes could be observed in an optical microscope. The absorption of fluorescent carboxylated nanoparticles by daphnia (*Daphnia magna*) and their translocation from the intestinal tract to fat deposits were demonstrated. The mechanism of this absorption remains in the focus of the attention of researchers (Lin et al. 2007).Varied mechanisms for the development of the toxic effect of nanoparticles are determined by their specific physicochemical properties, which depend not only on their size but also on the adhesive, catalytic, optical, electrical, and quantum-mechanical properties, as well as their geometry, size distribution, and organization in the nano object.

Many NMs are capable of inducing active oxygen species due to their physical nature (Roberts et al. 2007; Lyon et al. 2005; Klaine et al. 2008). The mechanism of the impact of nano objects on living structures is related to both the formation of free radicals in their presence and the appearance of complexes with nucleic acids. The induction of active oxygen is considered as the main mechanism of the toxic effect of TiO_2 nanoparticles; the reactivity depends not only on the size of the nanoparticles but also on the structure of the TiO_2 (a crystalline or amorphous one) (Kai et al. 2003). Some NMs are capable of penetrating through tissue barriers into cells and interact with intracellular components (Kapustka et al. 2006). Some types of NMs (dendrimers of different degrees of generation) can disturb membrane structures and make them permeable.

It has been shown that nanoparticles can penetrate into cells in different ways. Some authors observed simple diffusion through the cell membrane (Reevesa et al. 2008), and other authors reported endocytosis (Klaine et al. 2008) or adhesion (Terekhova and Gladkova 2013; Lin et al. 2007). Nanoparticles arriving into an organism can act as catalysts for the formation of toxic compounds, even if they themselves are harmless. Similar phenomena are typical for TiO_2 and ZnO nanoparticles catalyzing photooxidation and oxide nanoparticles of iron and some other metals causing metal (most frequently, zinc) fever. As for higher plants, it is believed that the sensitivity of plants to NMs is based on the capacity to filter and accumulate nanoparticles. The revealed toxicity mechanisms of nanotechnological products are difficult to classify, because they differ even within a class of materials. For example, fullerol (hydroxylated fullerene $C_{60}(O)_x$) generates single oxygen and can behave as a powerful oxidant in biological systems, but it reveals no cytotoxicity (Reevesa et al. 2008). The covering of fullerene with polyvinyl pyrrolidone is accompanied by the formation of nanoparticles also generating singlet oxygen, which can cause the peroxidation of lipids and the damage of cell DNA (Kang 2008). Other studies of water suspensions of fullerene showed their antibacterial activity in the absence of light and oxygen and thus denied the exceptional effect of singlet oxygen at the manifestation of toxicity. Different mechanisms are reported for explaining the toxicity of silver nanoparticles. Some of them relate the toxicity of these particles to changes in the penetrability of cell covers, because the adhesion of nanoparticles to the surface of cells affects the properties of membranes. It is not excluded that the silver nanoparticles penetrating within bacteria damage their DNA and can release toxic Ag^{+} ions during the interaction with the cell. Some authors disagree even concerning the interpretation of the toxicity mechanisms for the same nanoparticles. Several authors relate the suppression of growth of five different plant species (cabbage, carrot, corn, cucumber, and soybean) by aluminum nanoparticles (Al, 13 nm, 2 mg/ml) to the presence of free hydroxyl groups on the surface of particles, while other authors suppose that the phytotoxicity is due only to the increased solubility of aluminum nanoparticles (Noack et al. 2000). A special problem is related to the assessment of NM toxicity in soil and the effect of soil properties on the biological activity of nanoparticles. This involves the complicated development of methodological approaches and the formation of a system for estimating the ecological toxicity of nanoparticles in terrestrial cenoses. The aging and changes of nanoparticles during long-term experiments with soil organisms significantly hamper the studies of their toxicity. The studied material can be transformed in the soil within several weeks or months. It is known that this problem is also typical for conventional chemical pollutants. However, the interaction of nanoparticles with the soil also involves specific features of NMs. For example, unstable nanoparticles can be completely eliminated during an experiment on the revelation of acute and chronic toxicity with the use of test plants. This was observed in experiments with silver nanoparticles. Assays with a short exposure of test organisms are necessary to minimize the effect of aging. Nematode bioassays (e.g., ASTME2172, ISO/DIS10872) are promising (Asli and Neumann 2009; Jiang et al. 2008). The determination of test functions susceptible to nanoparticles in soils was repeatedly discussed in ecotoxicological works. It is considered difficult to reveal the biological activity of nanoparticles from the test parameters used for detecting the effect of conventional chemical pollutants (the survival and propagation of pedobionts). Some authors are sure that such common test functions as seed germination and seedling root growth have a limited sensitivity to NMs In separate cases, the behavior of soil-inhabiting animals can be considered as a sensitive test function. However, the correct interpretation of behavioral changes is very important in soil bioassays. For example, earthworms can cease to feed and move in the contaminated soil. This protecting mechanism prevents the negative effect. A conclusion about the absence of acute toxicity can be drawn in this case, which will be a false negative result. In this context, it is recommended to select more sensitive test species and not focus efforts on searching for more sensitive test parameters in the standard test organisms. For example, springtails, which showed good results in the study of metal toxicities in soils (Geiser et al. 2005), can be also very sensitive to metal-containing NMs (Hong et al. 2004). Some authors focus attention on the sensitivity to NMs of such plant species as the adzuki bean (*Phaseolus radiatus*), tomatoes (*Lycopersicon esculentum*), and *Arabidopsis thaliana*. Biochemical or metabolic measurements are recommended in this case, e.g., for the content of chlorophyll (Meyer et al. 2010), the respiration rate, or the nitrogen fixation by legumes.

The diversity of the developed engineered NMs, the absence of common priorities for assessing their safety, and the unsuitability of the conventional toxicological (hygienic) characteristics for nanosized structures result in the necessity for searching for and using new approaches in econanotoxicology. The preparation of natural samples and the composition of the incubation medium for standard test cultures require special attention. The range of bioassay procedures designed for the ecotoxicological assessment of soils should obviously be based on the responses of soil-inhabiting organisms (pedobionts). Contact methods, rather than eluate methods, are more reliable for determining the effects of NMs in soil, including from the responses of microorganisms. However, authors rarely set themselves the task to develop procedures suitable for legitimate decision making and practical use. The natural diversity of soils, the pH variations, the clay content, the cation exchange capacity, the texture, the mineralogy, and the organic matter should obviously be taken into consideration in the creation of standardized assays for the determination of the effects of nanoparticles in soils. The effect of the organic matrix on the toxicity of NMs was repeatedly manifested, including in our works with nanodiamonds from detonation synthesis and nanotitanium dioxide (Gladkova and Terekhova 2014; Gimbert et al. 2006, 2007). Animated discussions still accompany proposals for the creation and use of model soil samples (Hong et al. 2004) for comparing the toxicity of different preparations and concentration effects of NMs in different countries.

The analysis of the literature data showed that the assessment of the implications of the NM distribution in the environment remains an open problem. This is largely due to the insufficient methodological supply of their identification in natural environments, especially in soils. There is no universally accepted theory explaining the mechanism of the effects of any nanosized structures with consideration for the structural features of their surface and reactivity. There are no reasons for hampering the development of nanotechnologies and the propagation of NMs in soils taking into account the imperfection of the methodological approaches to the analysis of their toxicity. To overcome nanophobia and extreme views on the problem considered, we should extend ecotoxicological studies to all produced NMs, accumulate experimental data, and gradually select the sets of test systems the most adequate for the analysis of the biological safety of NMs in soils.

4.3 The Biological Activity Modulation of Engineered Nanomaterials in Soils Under the Humic Substances' Influence

In our experiments test responses of three trophic level organisms (producers, consumers, and reducers) on nanomaterials of different natures: carbon containing (nanodiamonds) and metal containing (nanodioxide titanium and nanomagnetite) adding humate in water were analyzed. Water extracts from natural and artificial soils were used durring experiments. The objective of this research is to study engineering carbon- and metal-containing nanomaterials' toxicity change under humic substances' influence.

Widespread engineered nanomaterials and their accumulation in environments give grounds to consider them as a special kind of pollutants. Currently the most effective areas of humic substances' (HS) application are known. Their use as detoxicants of organic and inorganic pollutants is one of the most important (Kaniskin et al. 2011; Tan 2003). Nanomaterials' biological activity in soils and HS influence on nanomaterials remain poorly understood despite of considerable attention given to the nanomaterials' study in environments.

In our work following materials were investigated: (1) humate "POW HUMUS" (Le-PhK, K-humate originated from leonardite, "Humintech", Germany); (2) carbon-containing nanomaterials—nanodiamonds produced by industrial detonation synthesis of high explosives (DNDs, different size free particles in aqueous suspensions up to 15, 30, and 100 nm, "SNK", Snezhinsk, Chelyabinsk region, Russia); (3) metal-containing NMs—nanodioxide titanium (nano-TiO2, <25 nm, "Sigma-Aldrich", US); (4) metal-containing NMs—nanomagnetite (nano-Fe3O4, 30 nm, MAI, Russia). Nanomaterials' concentration varied in range of 5–500 mg/L; humate concentration was 5 mg/L in water.

The research is based on standard environmental soil control methods recommended for industrial and state issues. The bioassay of standardized test cultures represented by different trophic levels such as producers (higher plants *Brassica juncea* L.), consumers (infusorium *Paramecium caudatum* Ehrenberg), and reducers (bacterial biosensor—genetically modified strain of *Escherichia coli*) was carried out.

In one set of experiments, the test responses of organisms on nanomaterials in water (0.5–500 mg/L) and humic preparation's response reactions to them were analyzed. In another set of experiments, the nanoparticles' toxicity and humate's response reactions to it in water extracts of podzolic soil (Chashnikovo, Moscow region, A horizon) and artificial soil, model soil prepared in accordance with ISO 11268-1, were investigated.

Bioassay showed that soil contaminated with nanomaterials exhibit inhibiting and stimulating biological activity. Biotic response level fluctuations in nanoparticles' presence in water and in soil sample extracts were noticed. Depending on the type of medium and nanomaterials, humate's detoxication effect on test cultures varies.

In addition, nanomaterials' bioassay in water on test cultures of different trophic levels with and without HS was performed.

Nanodioxide titanium inhibited producers' test functions (higher plants–root length) in all range of concentrations (0.5–500 mg/L). At the same time, humate in all concentrations, except 50 mg/L, relieves inhibition, stimulating root growth and seed germination. Nano-TiO_2 has a stimulating effect on infusorium and bacteria test cultures, and the HS presence increased twice more stimulating effect compared to higher plants.

Nanomagnetite except of nanodioxide titanium stimulated the development of higher plants at all concentrations, except 50 and 100 mg/L, which showed an inhibitory effect. HS effect on the nano-Fe_3O_4 bioactivity at different test cultures appeared ambiguous: at high concentrations (100 and 500 mg/L), inhibition of higher plants' roots and bacterial luminescence stimulation was observed, and at low concentrations, on the contrary, inhibition of bacterial luminescence and stimulation of the plant roots and infusorium's survival.

Adding humate to nanodiamonds (particle size 15–100 nm) mitigated toxic effects. These effects are more evident in concentration of 500 mg/L in nanodiamond water suspension.

Thus, research has shown that the toxic effect of nanomaterials in water was nearly removed in the presence of humate Le-PhK (5 mg/L). In some cases, HS combined with nanomaterials increases toxic effects in concentrations 50 and 500 mg/L.

Bioassays of nanomaterials with and without HS on test cultures of different trophic levels in soil extracts from natural and artificial soils revealed the followings.

Nanodioxide titanium in the extract of podzolic soil is almost neutral for higher plants. Humate addition caused stimulating effect at all concentrations (0.5–500 mg/L) from 8 to 35 %. Phytotesting on model soil extract showed stimulatory effect in all concentrations. Humate stimulates further growth of *Brassica juncea* roots for 3–14 %. Bioassay on infusoria showed that nano-TiO_2 has mostly inhibitory effect except of 0.5 mg/L, in which stimulation was showed. Adding HS eliminates this inhibition with the exception of 0.5 mg/L, in which it certainly inhibited survival of infusoria not only in the extract of podzolic soil but also in artificial soil. Nano-TiO_2 significantly increased the bacteria luminescence in both media, and the addition of humate further enhanced this effect.

Nanomagnetite phytotesting mainly shows little stimulatory effect in podzolic soil extract, excepting of 500 mg/L. Adding humate doesn't affect nanomagnetite's nature of impact. Nano-Fe_3O_4 impact is neutral in the artificial soil medium. Adding humate at low concentrations depresses higher plant root development. Natural soil extract with 100 mg/L nanomagnetite concentration showed acute toxic effect on infusorium's survival, but humate completely eliminated this effect. However, in the range of lower concentrations (5–10 mg/L), nanomagnetite toxicity increases. Nano-Fe_3O_4 reduces infusorium's survival in the range 100–500 mg/L in the model soil medium. HS further enhances toxicity at 500 mg/L. Bacteria luminescence inhibited in the whole range of concentrations (0.5–100 mg/L) in podzolic soil media and in the range of 100–500 mg/L in artificial soil medium. Humate exhibits inhibitory effect in both mediums.

Nanomagnetite's exposure stepwise nature has been established. Equal inhibitory activity is typical for 0.5 mg/L concentration and ten times bigger concentrations (e.g., 5 mg/L). Equal stimulating activity is typical for 1 mg/L concentrations and ten times bigger concentrations (e.g.. 10 mg/L). Such dependence is difficult to explain by the basic of different soil matrixes. This can be attributed to different mechanisms of impact in each concentration range (Gladkova and Terekhova 2014).

Determined by a number of peculiarities, concentrations of nanomaterials differed by an order or two have a similar effect; the bioactivity sign changes from concentration to the concentration "stimulation-inhibition." Average zone concentration effect in some cases is lower than in small concentration; it was also noticed in other researches (Terekhova and Gladkova 2013).

We may also conclude that the bioactivity of engineering nanomaterials entering environments (water or soil, enriched with natural organic matter) can be modified by the presence of humic substances. Generalizing humate (5 mg/L) impact data positive effect is clearly evident in conjunction (1) with nanomagnetite on infusoria in water (10 mg/L), bacteria (500 mg/L), extraction from podzolic soil on infusoria (0.5 and 100 mg/L), and from artificial soil (100 mg/L) and (2) with nanodioxide titanium on infusorium (1 mg/L), bacteria (10 mg/l), extraction from podzolic soil on higher plants (10 mg/L), and infusorium (1 and 50 mg/L). This confirms the universality of detoxication properties of humates (Yakimenko and Terekhova 2011) and expressed in neutralizing nanoparticles toxic effect.

The obtained bioassay data of the three nanomaterial types (nano-TiO_2, nano-Fe_3O_4, and DNDs-U) showed that toxicity depends on the physical nature of the nanoparticles (metal or carbon containing), size, and ability to form aggregates.

4.4 Influence of Nanomaterials on Soil Structure and Mechanical Properties: Effect with and Without Humic Substances

Research in the field of environmental behavior of nanomaterials has been increasing over the past decade due to their unique physical and chemical properties and to an expected rise in their production in the future.

The question of their fate and impact on soils has become a major concern since poorly understood interactions of nanomaterials with the soil particles. Impact of nanomaterials on the fate of other pollutants in soil remains controversial. There is almost no data on the effects of nanomaterials on soil structure and physical and chemical properties with different humus status.

In experimental research (Gladkova et al. 2015) we applied metal-containing nanomaterials, nanomagnetite (nano-Fe_3O_4), which are characterized 30 nm in size

(MAI, Russia). Concentration of nano-Fe_3O_4 was 500 mg/kg in soil. Among HS we have chosen "POW HUMUS" (Le-PhK) (K-humate, originated from leonardite) manufactured by German company "Humintech." Concentration of humate Le-PhK was 100 mg/kg in soil.

This experimental study aimed to reveal the rheological properties of structural bonds between gray-humus soil (Botanical garden, MSU, Moscow, Russia) particles in samples treatment by nanomagnetite with addition of humate potassium and without it.

Determination of rheological parameters was carried out by amplitude sweep test on a modular rheometer of MCR-302 (Anton Paar, Austria) (Markgraf et al. 2006; Khaydapova and Milanovskiy 2013; Khaydapova et al. 2013). The following parameters were determined: elastic modulus, viscosity modulus, and point of destruction of structure at which the elastic modulus becomes equal to the viscosity modulus ($G' = G''$-crossover).

The results of rheological studies using a MCR 302 modular research rheometer of soil samples are shown in Fig. 4.3. It was found out that the soil with nanomagnetite has more elastic properties ($G' - 3.95 \times 10^5$ Pa) than the original (control) samples ($G' - 1.48 \times 10^5$ Pa).

Adding humate to the soil with nanomagnetite enhances the strength of the structure.

The destruction of the structure (the point of equality models $G' = G''$) for the original soil deformation occurs at 13.7 % and with nano-Fe_3O_4 and humate is much less (1.88 %).

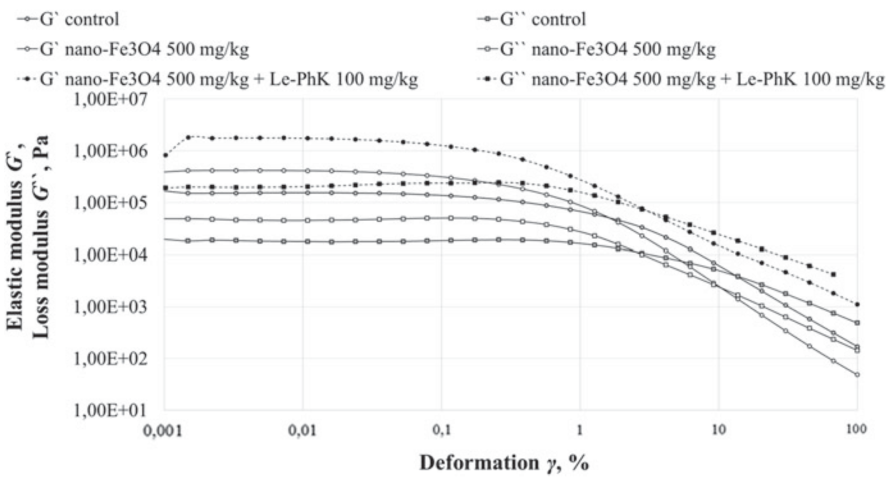

Fig. 4.3 Depending on the loss modulus and elastic modulus from the deformation

4.5 Conclusion

It can be concluded that the previously identified differences in toxicity effect nanomagnetite in soils by adding humates associated not only with the expected change in the specific surface of the particles (our preliminary results) but also with the physical and chemical characteristics of the rheological interaction between soil particles and engineered nanoparticles in the presence of humate.

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