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NANOPARTICLES: DEFINITION, TOXICITY, APPROACHES TO REGULATION, MIGRATION ROUTES IN THE ENVIRONMENT

Korniyenko V. I., Khyzhnyak S. V., Voitsitskiy V. M.

INTRODUCTION

Nanotechnology is an industry for the targeted production and use of materials based on nanoparticles with a size smaller than 100 nanometers. The use of nanotechnology will become one of the most promising areas of science and technology in the 21st century, which will lead, as expected, to the improvement or emergence of new qualities and properties of products. A nanoparticle is a particle of matter with dimensions from 1 to 100 nanometers, and in nanotechnology – the name of an object that behaves as a single body in terms of transport and physical (mass, shape, volume) properties. It is believed that a nanoparticle is the result of the formation of nanoclusters of atoms or molecules as a result of their aggregation, which occupy an intermediate place between isolated atoms and molecules, on the one hand, and volumetric (massive) bodies, on the other[1].

The main methods for determining the size of nanoparticles are nanomicroscopy methods, as well as optical methods based on the phenomenon of light scattering or using labels or probes, including fluorescent[2].

Nanoparticles are widely used in a wide variety of industries, agriculture, medicine[3], in particular, for the creation of alloys, ceramics and composites with improved properties, as catalysts for the remediation of components of the polluted environment, as sensors for detecting toxicants and pathogens in environmental objects, food and drinking water, and in agriculture and veterinary medicine as nanominerals, antibiotics, etc.[4,5]. In the food industry,

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[1] Волков С.В., Ковальчук Є.П., Огенко В.М. Решетняк О.В. Нанохімія, наносистеми, наноматеріали. Київ: Наукова думка, 2008. 422 с.

[2] Мельничук Д.О., Мельничук С.Д., Войціцький В.М. та ін. Аналітичні методи досліджень. Спектроскопічні методи аналізу: теоретичні основи і методики: навчальний посібник /За ред. Д.О. Мельничука. Київ: ЦП «Компринт», 2016. 289 с.

[3] Трахтенберг І.М., Дмитруха Н.М. Наночастинки металів, методи отримання, сфери застосування, фізико-хімічні та токсикологічні властивості. *Український журнал з проблем медицини праці*. 2013. № 3. С. 5–14.

[4]Xiao L., Takada H., Gan X., Miwa N. The water-soluble fullerene derivative “radical sponge” exerts cytoprotective action against UVA irradiation but not visible-light-catalyzed cytotoxicity in human skin keratinocytes. *Bioorg. Med. Chem. Lett.* 2006. № 16. P. 1590–1595.

[5] Ситар О.В., Новицька Н.В., Таран Н.Ю. Нанотехнології в сучасному сільському господарстві. *Фізика живого*. 2010. № 8. С. 113–116.

the use of nanoparticles ensures better properties of food products, including during their storage, and in cosmetics – detergents, varnishes, paints, gels and creams, etc.[6]. In medical practice, nanodevices or nanopreparations are used for the prevention, diagnosis and treatment of various diseases with the control of the pharmacological and toxicological effects of the obtained medicines[7,8,9]. The use of nanoparticles as substances for the creation of new medications or in the development of nanopreparations by forming complexes of known therapeutic agents with nanoparticles will contribute to deeper penetration of such drugs into the focus of the pathological process[10]. Some nanoparticles have become an integral part of diagnostic procedures[11].

Such diverse use of nanoparticles will inevitably lead to the entry of significant amounts of them into the environment, accumulation in the components of biota and abiotic media with subsequent possible entry into the human body[12]. At the same time, there is no unambiguous conclusion regarding the danger of nanoparticles, since there is no complete understanding of their physicochemical properties that determine and condition their dangerous properties of the effect on the body and the long-term consequences of this effect[13]. For a significant number of nanoparticles, the mechanisms of entry into the body, the processes of biotransformation and translocation in organs and tissues, and their toxicity remain unclear. Therefore, taking into account the possibility of close human contact with nanotechnology products in production and everyday life, studying the toxicity and danger of nanoproducts for humans remains one of the most important tasks.

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[6] Войціцький В.М., Данчук В.В., Хижняк С.В. та ін. Безпека та ризики добавок в продуктах харчування, косметиці та засобах особистої гігієни: довідник. Видання друге, перероблене і допов. Київ: ЦП «Компринт», 2018. 296 с.

[7] Розенфельд Л.Г., Москаленко В.Ф., Чекман И.С., Мовчан Б.А. Нанотехнології, наномедицина: перспективи наукових досліджень та впровадження їх результатів в медичну практику. Український медичний часопис. 2008. 67(5). С. 63–68.

[8] Чекман І.С. Наночастинки: властивості та перспективи застосування. *Український біохімічний журнал*. 2009. 89(1). С. 122–129.

[9] Partha R., Conyers J.L. Biomedical applications of functionalized fullerene-based nanomaterials. *International Journal of Nanomedicine.* 2009. № 4. P. 261–275.

[10] Cai X., Hao J., Zhang X. et al. The polyhydroxylated fullerene derivative $C_{60}(OH)_{24}$ protects mice from ionizing-radiation-induced immune and mitochondrial dysfunction. *Toxicology and Applied Pharmacology*. 2010. 243(1). P. 27–34. DOI: 10.1016/j.taap.2009.11.009

[11] Черноусова С., Еппле М. Наночастинки в медицині. *Наносистеми, наноматеріали, нанотехнології.* 2012. 10 (4). С. 667–685.

[12] Леоненко Н.С., Демецька О.В., Леоненко О.Б. Особливості фізико-хімічних властивостей та токсичної дії наноматеріалів – до проблем оцінки їхнього впливу на живі організми (огляд літератури). *Сучасні проблеми токсикології, харчової та хімічної безпеки.* 2016. № 1. С. 64–76.

[13] Москаленко В.Ф., Яворський О.П. Екологічні і токсикологічно-гігієнічні аспекти біологічної безпеки нанотехнологій, наночастинок і наноматеріалів. *Науковий вісник Національного медичного університету.* 2009. № 3. С. 25–35.

Currently, there is a lack of data on the safe use of nanomaterials. Along with this, there is a need to determine the main migration routes of nanoparticles in the environment, since final ideas have not yet been formed about the migration routes of nanoparticles in the environment due to the peculiarities of their sizes and properties (in particular, characteristics that determine mobility, adsorption ability on other substances, etc.). The results of these studies can be the basis for the development of methods and means to reduce or even prevent the entry of nanoparticles into the environment and the human body, as well as to minimize the consequences of contamination of the environment, food products and drinking water with nanoparticles. Thus, taking into account the wide application of nanoparticles in various spheres of human activity, it is necessary to study their migration in the environment and ways of getting into the biota, including the human body, as well as studying the toxicity of nanoparticles.

1. Classification of nanoparticles and mechanisms of their toxicity

Nanoparticles are divided into natural and artificial by origin. Natural sources of nanoparticles are forest fires (formation of powdery residue from incomplete combustion and thermal decomposition of hydrocarbons in uncontrolled conditions with the formation of particles of various sizes, including nanoparticles). Also volcanic eruptions (formation of nanoparticles in the ejected gases); wind and water dispersion, for example, by sea tides, waves of immiscible liquids (in particular, water and oil spills) with the formation of nanoemulsions and nanofilms, etc.

There are also biogenic (associated with living organisms) sources of nanoparticles. This is, in particular, virus-mediated synthesis of metal-containing nanoparticles. For example, Fe_2O_3 by the tobacco mosaic virus, CdS and PbS using the amino acids of the protein shell (capsid) of certain viruses; synthesis by some algae and bacteria of nanoparticles containing a number of metals, etc. Natural nanoparticles include viruses of small sizes. Many biological molecules have nanoscale dimensions, for example: linear dimensions of insulin (about 2.2 nm), hemoglobin and fibronectin (from 4.5 to 7.0 nm), lipoproteins (about 20 nm), fibrinogen (from 5 to 70 nm)[14].

The main methods of artificial creation of nanoparticles are: grinding, condensation from gas, hydrothermal synthesis, precipitation, pyrolysis (splitting of substances when they are heated to high temperatures without

[14] Цехмістренко С.І., Бітюцький В.С., Цехмістренко О.С. та ін. Екологічні біотехнології "зеленого" синтезу наночастинок металів, оксидів металів, металоїдів та їх використання: наукова монографія/За ред.С.І. Цехмістренко. Біла Церква: СПДФО Пшонківський О.В., 2022. 270 с.

access to oxygen), radiolysis under the action of ionizing radiation, in particular, γ-radiation, etc.[15, 16].

Nanoparticles are characterized by complexes of physical, chemical properties and biological effects, which allows them to be classified as new types of materials and products. Substances in the nanoscale state are characterized by the following features[17]:

1) increased solubility and reactivity due to the large curvature of the nanoparticle surface;

2) high specific (per unit mass) surface area of nanomaterials, which increases their adsorption capacity, chemical reactivity and catalytic properties;

3) the ability to integrate into biomembranes, penetrate through them into cells and cell organelles, affecting their activity;

4) the ability to absorb organic and inorganic compounds, in particular toxicants, which improves their penetration into cells and cell organelles;

5) high resistance, that is, practically not subject to biotransformation, and reduced ability to excrete from the body, which leads to their accumulation in plant and animal organisms and intake through food chain to the human body;

6) given the small size of nanoparticles, they may not be recognized by the body's defense systems.

According to the generally accepted definition, in particular IUPAC, nanoparticles are characterized by a size from 1 to 100 nm. However, this value is purely conditional and is necessary only for formal classification, since the group of nanoparticles includes very heterogeneous types in terms of chemical structure and physical properties.

There are several classifications, according to which nanomaterials can be classified by many parameters[18]. In accordance with Technical Report ISO/TR 11360:2010[19], four types of classification of nanomaterials are proposed (by geometric size, structure and type, chemical nature and properties).

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[15] Волков С.В., Ковальчук Є.П., Огенко В.М. Решетняк О.В. Нанохімія, наносистеми, наноматеріали. Київ: Наукова думка, 2008. 422 с.

[16] Трахтенберг І.М., Дмитруха Н.М. Наночастинки металів, методи отримання, сфери застосування, фізико-хімічні та токсикологічні властивості. *Український журнал з проблем медицини праці*. 2013. № 3. С. 5–14.

[17] Леоненко Н.С., Демецька О.В., Леоненко О.Б. Особливості фізико-хімічних властивостей та токсичної дії наноматеріалів – до проблем оцінки їхнього впливу на живі організми (огляд літератури). *Сучасні проблеми токсикології, харчової та хімічної безпеки*. 2016. №1. С. 64–76.

[18] Чекман І.С., Костюченко Є.В. Наноканали і нанопори: будова, властивості, використання. *Вісник НАН України*. 2013. № 8. С. 34–46.

[19] ISO/TS 11360:2010 Nanotechnologies – Methodology for the classification and categorozation of nanomaterials. – Ed. 2010 – 07–15. – ISO, 2010. – 32 p.

The most difficult, but at the same time important, is the classification of nanoobjects by geometric size, since geometry significantly affects their physical, chemical and biological properties. This is a group of three-dimensional objects (all three dimensions – length, width and height are less than 100 nm), such as fullerenes, nanocrystals and nanocomposites; a group of two-dimensional objects (transverse dimensions less than 100 nm and a relatively long length), such as nanotubes, nanopores, nanocapillaries; a group of one-dimensional nanostructures (their thickness is always <100 nm) – nanorods, nanofibers, nanoribbons[20].

The following nanoparticles are distinguished by chemical origin: inorganic –ceramics, metals (Fe, Mg, Ag, Au), alloys, natural clay materials (bentonites); organic – polymers, biological nanostructures (liposomes, celosomes), carbon (fullerenes, nanotubes); inorganic-organic – metal-organic and metal-polymer structures.

According to the type of structure, nanoparticles are divided into: fullerenes (convex closed polyhedra, which are composed of coordinated carbon atoms), nanotubes (hollow cylindrical structures), nanopores and nanochannels, nanostructured films, nanocrystals and nanoclusters, quantum dots (fragments of a conductor or semiconductor, carriers of an electric charge, which are limited to the nanorange of 1–100 nm in all three dimensions), nanocapsules (nanoparticles surrounded by a lipid, polymer or some other shell).

Nanoparticles are also classified according to the shape of the crystals of which they are composed (layered, fibrous, equilibrium); chemical composition and distribution of phases in crystals (single-phase, static multiphase with identical and non-identical distribution surfaces, matrix multiphase)[21].

According to their properties, first of all, metal nanoparticles are divided into those with biocidal, electrical, catalytic and magnetic properties[22]. Silver nanoparticles with a size of 5–50 nm have antibacterial activity[23] and have a wide spectrum of antiviral activity. ZnO nanoparticles have high antibacterial properties and are able to absorb a wide range of electromagnetic radiation (ultraviolet, infrared, microwave and radiofrequency). Nanoparticles of copper and copper oxide have a pronounced antibacterial effect against gram-positive and gram-negative bacteria. Copper nanoparticles also have a cardioprotective effect, regulate fat metabolism, increase the body's resistance

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[20] Чекман І.С. Наночастинки: властивості та перспективи застосування. *Український біохімічний журнал*, 2009. 89 (1). С.122–129.

[21] Ibid.

[22] Чекман І.С., Говоруха М.О., Дорошенко А.М. Наногенотоксикологія: вплив наночастинок на клітину. *Український медичний часопис.* 2011. 1 (81). С. 30–35.

[23] Рибачук А.В., Чекман І.С. Протимікробні властивості наносрібла. Укр. науково-медичний молодіжний журнал. 2009. № 2. С. 32–36.

to hypoxia, stimulate immunity, etc.[24]. Iron oxide nanoparticles are used as magnetic resonance contrast media during magnetic resonance imaging due to their paramagnetic and superparamagnetic properties.

In studies using experimental animals and tissue cultures, as well as clinical observations of patients who were exposed to nanoparticles (for example, when they are present in the air of workplaces), it was established that they, like other toxicants, exhibit a toxic effect depending on the dose, chemical structure, mechanism of biological action, route of entry into the body, duration of action, biological characteristics of organisms, etc.

The relatively high toxicity of nanoparticles and their potential danger to human health is due to:

1) a large concentration in the environment with a relatively small amount of the substance (for example, when 20 nm nanoparticles are sprayed in the air and the concentration of the substance is 100 $\mu g/m^3$, the air contains more than 10^{-6} particles/cm^3);

2) physicochemical and structural characteristics: solubility in water and biological fluids, charge, adsorption capacity, resistance to aggregation, hydrophobicity, adhesion to surfaces, ability to generate free radicals;

3) the ability to transdermal, transneuronal and enteral penetration into any human tissues and organs, including the central nervous system;

4) high lability and bioavailability: nanoparticles smaller than 40 nm can penetrate the cell nucleus, up to 70 nm can penetrate through the capillaries of the circulatory system, and 35–120 nm can accumulate in lymph nodes.

Significant factors are the solubility of nanoparticles in water and the charge of the particle. Thus, soluble nanoparticles, as a rule, do not differ in their toxicological properties from their chemical analogues. On the contrary, the particles of substances that are insoluble in water are capable of being free for a long time in a biological environment, causing biological effects determined by their surface characteristics. In addition, the most dangerous to human health are positively charged particles with a high affinity for DNA macromolecules, and as a consequence, genotoxic and mutagenic effects.

The toxicity of nanoparticles depends on their shape and size: small spindle-shaped nanoparticles cause more destructive effects in the body, unlike spherical particles[25].

An important factor determining the toxicological properties of nanoparticles is their ability to generate free radicals. According to modern data, the main part of the processes of the damaging effect of nanoparticles both on cells in culture and on organs and tissues in the body are mediated by

[24] Петрик І.С., Г. М. Єременко, Н. П. Смірнова та ін. Синтез та стабілізація наночастинок Cu у водних розчинах та їх бактерицидна активність. *Хімія, фізика та технологія поверхні.* 2014. 5 (1). С. 74–81.

[25] Розенфельд Л.Г., Чекман І. С., Тертишна А. І. Нанотехнології в медицині, фармації та фармакології *Фармакологія та лікарська токсикологія*. 2008. № 1–3. С. 3–7.

the mechanisms of free radical peroxidation, initiated by reactive oxygen species formed on the surface of nanoparticles in the processes of heterogeneous chemical catalysis.

Nanoobjects enter the human body through the respiratory tract, gastrointestinal tract, skin and mucous membranes, with food and drinking water. At the same time, they selectively accumulate in different types of cells and in certain cellular structures. The high penetrating ability of nanoparticles increases their potential danger to human health. Little is known about the effect of nanoparticles on the human body.

Some nanoparticles are used as food additives to give the necessary color, improve the appearance, consistency of certain food products. Such a food additive, for example, is titanium dioxide (TiO_2, E171). It is used in confectionery products, in particular in sugar glaze, sweets, jams and jellies, chewing gums, as well as in cosmetics (face powder, sunscreens, powders, ointments, dyes). This food additive can cause skin irritation and cancer in excess of the recommended dose, which has been confirmed in experiments using experimental animals.

Zinc oxide (ZnO) additive in cosmetics (shaving cream, baby powder, antiperspirants, sunscreen, hair care products) in certain doses is a toxic substance that can cause a pathological condition of the respiratory organs, skin rashes and can exhibit a teratogenic effect[26] .

When inhaled, nanoparticles can be deposited in the nasopharynx, tracheobronchial area and alveoli. It has been established that the lungs are the most accessible for nanoparticles. Having reached the intercellular space in the lungs, nanoparticles enter the blood and lymphatic systems. The main mechanism of distribution of nanoparticles is diffusion. Nanoparticles of a number of substances, for example, carbon (soot), some metals, titanium dioxide, due to their small size, penetrate deeply into the lungs with air, and are fixed in the alveoli.

Another potentially important route of entry of nanoparticles into the body is through the skin. Nanoparticles that have entered the dermis are subsequently localized with the help of skin macrophages in regional lymph nodes.

Nanoparticles can enter the gastrointestinal tract with medicine, water, and food. According to numerous studies, nanoparticles are quickly excreted from the body when they enter the gastrointestinal tract. At the same time, they are able to penetrate through the mucous membrane and spread throughout the body. Regardless of the route of entry, after entering the circulatory system, nanoparticles are carried throughout the body with blood and can accumulate

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[26] Войціцький В.М., Данчук В.В., Хижняк С.В. та ін. Безпека та ризики добавок в продуктах харчування, косметиці та засобах особистої гігієни: довідник. Видання друге, перероблене і допов. Київ: ЦП «Компринт», 2018. 296 с.

in the bone marrow, central and peripheral nervous systems, lungs, liver, kidneys, and lymph nodes. In this case, they have a long half-life[27].

The influence of nanoparticles at the cellular level is mediated through direct contact with biological membranes, which depends on their surface activity. Thus, uncharged particles are absorbed by the lipid bilayer, while charged ones cause the formation of pores in the membrane. Particle size plays an important role in interaction with the biomembrane: particles less than 1.2 nm do not affect the structure of the membrane, and 1.2–-22 nm in size form pores in the bilayer. Nanomaterials are able to interact with intracellular components, in particular, to penetrate into mitochondria and block mitochondrial respiratory activity[28].

Thus, the type, size, shape, surface area and its possible coating, crystallinity, solubility, ability to agglomerate, method of production are essential for the manifestation of the toxic effect of nanoparticles. Thanks to their small size and physical and chemical properties, nanoparticles are able to overcome tissue barriers, damage biomembranes, disrupt the functions of biomolecules, penetrate into the cells of all organs and tissues, enter intracellular structures, including the nucleus, and change DNA. Accumulating in the cells of organs and tissues, nanoparticles are able to cause abnormalities in the nucleus, mitochondria and other organelles and even lead to the death of cells[29].

The mechanism of the development of the toxicity of nanoparticles is determined mainly by oxidative stress, disruption of membrane structures and their functions, followed by an increase in the permeability of biomembranes to other toxicants, and the development of the inflammatory process[30].

Nanoparticles can affect all organs and their systems, cause DNA damage, gene and chromosomal mutations, exhibit carcinogenic, teratogenic and embryotoxic effects and cause other pathologies. This is associated with the lack of mechanisms for their active detoxification. Nanoparticles with a complex configuration, such as new forms of carbon, so-called nanotubes and fullerenes, are considered the most dangerous.

Intensive production and use of nanoparticles, taking into account the results regarding their toxicity, requires solving a number of medical and

[27] Donaldson K., Stone V. Current hypotheses on the mechanisms of toxicity of ultrafine particles. *Ann Ist. Super Sanita*. 2003. 39 (3). P. 405–410.

[28] Ferrari M. Cancer nanotechnology: opportunities and challenges. *Nat. Rev. Cancer*. 2005. 5 (3). P. 161–171.

[29] Бандас І.А., Криницька І.Я., Куліцька М.І., Корда М.М. Наночастинки: важливість сьогодні, класифікація, використання в медицині, токсичність. *Медична та клінічна хімія.* 2015. 17 (3). С.123 – 129.

[30] Jiang J., Oberdrster G., Elder A. et al. Does nanoparticle activity depend upon size and crystal phase? *Nanotoxicology*. 2008. 2 (1). P. 33–42.

environmental problems[31,32]. Since nanomaterials differ in physicochemical properties and biological effects compared to traditional analogues, it is necessary to develop new approaches to assess their dangerous effects on humans. The International Organization for Standardization ISO (International Organization for Standartisation) created "Technical Committee 229 – Nanotechnology" (ISO/TS229), the purpose of which is the development of international standards for technology, nomenclature, metrology, specifications, testing methodology, preparation of instructions for the health care industry and environmental safety[33].

Today, the question remains which factors determine and influence the dangerous properties of nanoparticles. This is due to the lack of the necessary base of experimental research, agreed international protocols for assessing the impact of nanoobjects on biota, including humans, standard methods for determining the number of particles in environmental objects (atmosphere, water, soil) and living organisms[34].

There are no agreed regulations for assessing the risks of exposure to nanoparticles. However, a number of recommendations have been proposed. Thus, the British Standards Institute (BSI) in order to compare the danger of nanoparticles of different nature and characteristics for workers recommended to take into account the following safety coefficients, which determine the so-called "Benchmark exposure level" (Table 1)[35].

The National Institute for Occupational Safety and Health (NIOSH) recommended the safety ratio of insoluble nanomaterials – 0.066, and as an alternative it is proposed to use the lower limit of quantitative concentration in contaminated areas at the level of 20 000 particles/cm^3. The value of 10 000 fibers/cm^3 is recommended for fibrous nanomaterials with reference to the standards for asbestos adopted in the UK.

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[31] Трахтенберг І.М., Дмитруха Н.М. Наночастинки металів, методи отримання, сфери застосування, фізико-хімічні та токсикологічні властивості. *Укр. журнал з проблем медицини праці*. 2013. №3. С. 5 –14.

[32] Yamawaki H., Iwai N. Cytotoxicity of water-soluble fullerene in vascular endothelial cells. *Am. J. Physiol.* 2006. №290. P. C1495– C1502.

[33] ISO/TS 11360:2010 Nanotechnologies – Methodology for the classification and categorozation of nanomaterials. – Ed. 2010 – 07–15. – ISO, 2010. – 32 p.

[34] Methner M., Hodson L., Geraci C. Nanoparticle emission assessment technique (NEAT) for the identification and measurement of potential inhalation exposure to engineered nanomaterials-part A. *J Occup Environ Hyg.* 2010. 7(3). P. 127-32. doi: 10.1080/15459620903476355.

[35] BSI – British Standarts. Nanotechnologies – Part 2: Guide to Safe Handling and Disposal of Manufactured Nanomaterials. PD6699 – 2: 2007, BSI 2007.

Table 1

Safety coefficients for substances in nanoscale state

№	Information on nanoparticles	Safety coefficient
1	Fibrous substances with a high level of insolubility*	0,01
2	Substances classified as carcinogens, mutagens, teratogens, allergens	0,1
3	Insoluble or poorly soluble substances of a non-fibrous nature and those that do not belong to the substances classified according to item 2	0,066
4	Soluble substances of a non-fibrous nature and those that do not belong to the substances classified according to item 2	0,5

* – these are particles with a length-to-diameter ratio greater than 3:1 and a length > 500 nm.

The Institute for Occupational Safety and Health (Institut für Arbeitsschutz (IFA) Germany) has proposed a limit quantitative concentration in the air of the work area of 20 000 particles/cm^3 for nanoparticles of metals and their oxides with a density of 6 000 kg/m^3. A limiting concentration of 10 000 fibers/cm^3 is proposed for biologically resistant carbon nanotubes, which have a fibrous structure, based on asbestos data[36].

The Organization for Economic Cooperation and Development (OECD), based on the traditional and generally accepted presentation of the regulations for toxicants, as the mass concentration of substances in the volume of air of the working area, recommended quantitative concentrations of nanoparticles to achieve a mass concentration of 0.1 mg/m^3 with particle sizes of 20, 50, 100 and 200 nm (Table 2)[37].

Thus, despite the inconsistency in regulation of nanoparticles in environmental objects (atmosphere, soil, water, biota), attempts are being made to solve this problem.

2. Nanoparticle migration pathways in the environment

A significant number of nanoparticles that pollute the environment are created artificially (anthropogenically). These are, first of all, untreated emissions and discharges of enterprises producing nanomaterials for various spheres of human activity, especially in emergency situations; as a result of imperfect technologies for neutralization, burial and disposal of household and industrial waste, waste of a number of industries; transport emissions, etc.

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[36] Демецька О.В., Леоненко О.Б., Ткаченко Т.Ю., Леоненко Н.С. До проблеми регламентації наноматеріалів. *Український журнал сучасних проблем токсикології*. 2012. № 1 56).

[37] List of Manufactured Nanomaterials and List of Endpoints for Phase One of the Sponsorship Programme for the Testing of Manufactured Nanomaterials (2010) https://one.oecd.org/document/env/jm/mono(2010)46/en/pdf

Military actions with the use of modern explosive materials, which cause fires, are extremely dangerous. Nanoparticles act as ecotoxicants, namely, substances that pollute the environment and have a harmful effect on its objects – air, soil, water, including living organisms.

Table 2

Dependence of mass concentration on the size of nanoparticles and their concentration per unit volume of inhaled air

№	Name	Density, kg/m^3	N in cm^{-3} at d = 20 nm	N in cm^{-3} at d = 50 nm	N in cm^{-3} at d = 100 nm	N in cm^{-3} at d = 200 nm
1	Carbon nanotubes (CNT)	1350	17683883	1131768	141471	17684
2	Polysterol	1050	22736420	1455131	181891	22736
3	Fullerene	1650	14468631	925992	115749	14469
4	Common inhaled dust	2500	9549297	611155	76394	9549
5	Titanium dioxide	4240	5630481	360351	45044	5630
6	Zinc oxide	5610	4255480	272351	34044	4255
7	Cerium oxide	7300	3270307	209300	26162	3270
8	Ferum	7874	3031908	194042	24255	3032
9	Argentum	10490	2275809	145652	18206	2276
10	Aurum	19320	1235400	79083	9885	1236

Note: N – the concentration of nanoparticles of size d, which is necessary to achieve a mass concentration of 0.1 mg/m^3.

Migration processes of nanoparticles in the environment are determined, first of all, by their shape, size, physicochemical properties, as well as the state of environmental objects and the influence of abiotic factors (temperature, humidity of air and soil, wind force, etc.) on them. However, the question of modification of nanomaterials in the environment, including biomodification (i.e., changes in their properties under the influence of living organisms) and, respectively, the effect of modified nanoparticles on biota, remains open. There is also very little information on the migration of nanoparticles in the environment. There is virtually no data on the effects of nanoparticles on humans and ecosystems as a whole or on individual populations.

Nanoparticles that have entered the atmosphere move with air currents. During the movement of air masses, these ecotoxicants, depending on weather conditions, emission height, turbulent movement of flows, gravity, etc., gradually disperse and fall from the atmosphere to the surface of the earth and concentrate in environmental objects – soil, water bodies, and then enter the human body through food chains. A feature of the wind transport of nanoparticles is that they are able to be transported over long distances due to their very small size. Atmospheric precipitation can significantly accelerate and intensify its fall, which can cause local heavy pollution of the territory.

The migration of nanoparticles in the soil is a set of processes that cause their movement in the soil and determine their distribution in vertical and horizontal directions. The migration ability of nanoparticles in the soil and their inclusion in trophic chains are determined both by the properties of these ecotoxicants themselves, and by the soil and various environmental factors (primarily weather and climate conditions). The main thing is the ability to form aggregates, which leads to a decrease in mobility in the soil, or, on the contrary, an increase in biological availability for plants due to better solubility in the soil. Ecotoxicants, including nanoparticles, enter the plants of terrestrial ecosystems in two main ways: through the above-ground organs (foliar intake) and through the root system from the soil (root intake). Foliar entry of nanoparticles to plants is possible when they enter from the atmosphere, as well as when watering with rainwater polluted by them. A prerequisite for the foliar penetration of nanoparticles in a plant is the presence of moisture.

Nanoparticles due to their ability to absorb (determined by size, shape, surface properties, etc.) have a relatively high ability to be fixed on above-ground organs of plants and not be blown away by wind or washed away by rain.

Part of the absorbed nanoparticles can remain in the place of their penetration into plants, the other can be included in the transport systems of plants, migrate and accumulate in all organs, in accordance with the characteristics of both nanoparticles and plant organs. Foliar entry of nanoparticles to plants can occur during the entire vegetation period.

The root entry of nanoparticles to plants is determined, first of all, by the nature of their connection with soil particles, as well as the ability to be absorbed by plant roots. The ability of plant roots to absorb substances, in particular nanoparticles, depends on both the properties of the substances themselves and the specifics of plants, the development of their root system, the physiological state of plants, the physical and chemical properties of the soil, the presence of substances and organisms in it that can affect the absorption capacity of roots.

Nanoparticles, like other ecotoxicants, can enter the body of terrestrial animals, including humans, in three main ways: 1) by inhalation – through the respiratory system; 2) oral – through the gastrointestinal tract; 3) contact – through the skin, mucous membranes of the mouth, nose and eyes.

It is known that getting into the living organisms, nanoparticles, due to their chemical activity, are able to form complexes with various organic substances (proteins, phospholipids, DNA, vitamins). In addition, not only nanoparticles penetrate into the body, but also various organic compounds associated with them. It is assumed that nanoparticles can be concentrated in consumers of higher orders. This, in turn, affects the severity of toxic effects in organisms at different trophic levels. It is assumed that nanoparticles, entering the body of animals, can move along the alimentary tract and concentrate in consumers of higher orders. This, in turn, can affect the severity of toxic effects in organisms at different trophic levels[38].

For aquatic ecosystems, it is especially important to determine the migration paths of nanoparticles in freshwater ecosystems, which are sources of drinking and irrigation water. At the same time, in marine ecosystems, substances that have entered them with river discharges, sediments from the atmosphere, etc. are subject to dilution by significant volumes of sea water, which significantly reduces the amount of their entry into marine biota organisms. The accumulation of nanoparticles in the organisms of aquatic plants and animals causes a negative impact on their viability, contamination of food products for humans and fodder for farm animals obtained from them. In non-flowing reservoirs with bottom sediments, ecotoxicants (including nanoparticles) that have reached them are concentrated in the upper layer of bottom sediments, usually 10–20 cm thick. The high adsorption capacity of this layer of bottom sediments is due to the large amount of organic substances in it. The consequence of this is that bottom sediments in such reservoirs play the role of secondary sources (depots) of ecotoxicants.

The migration of ecotoxicants in rivers that got to them from the atmosphere, surface runoff from the soil, discharges of enterprises and institutions, groundwater (where they got from the soil), etc. is influenced by a number of factors: their number and their physical and chemical properties, as well as the speed of water flow, the relief of the bottom, the presence of floodplains and hydraulic structures, the possibility of formation of bottom sediments, etc. Thus, the migration of nanoparticles through freshwater ecosystems is subjected to complex abiotic and biotic factors. A generalized diagram of the migration of nanoparticles in the environment is shown in Figure 1[39].

To quantitatively predict the process of migration of substances (ecotoxicants) in ecosystems, taking into account its complexity, mathematical models are used. One of them are chamber models that have

[38] Леоненко Н.С., Демецька О.В., Леоненко О.Б. Особливості фізико-хімічних властивостей та токсичної дії наноматеріалів – до проблем оцінки їхнього впливу на живі організми (огляд літератури). *Сучасні проблеми токсикології, харчової та хімічної безпеки.* 2016. № 1. С. 64–76.

[39] Войціцький В.М., Корнієнко В.І., Хижняк С.В. Мідик С.В., Березовський О.В., Таран Т.М., Полтавченко Т.В. Шляхи міграції наночастинок наземними і водними екосистемами. *Екологічні науки.* 2023. 3 (48). С. 32-36. https://doi.org/10.32846/2306-9716/2023.eco.3-48.4

been proposed to assess the migration of radioisotopes[40], heavy metals[41], polycyclic aromatic hydrocarbons[42] (including nanoparticles[43]) into environmental objects.

This method is used to describe the migration of substances along ecosystem chains that are divided into chambers, and the transition between chambers is determined by the transition coefficients:

$$\boldsymbol{K_{tc} = C_1/C_2},$$

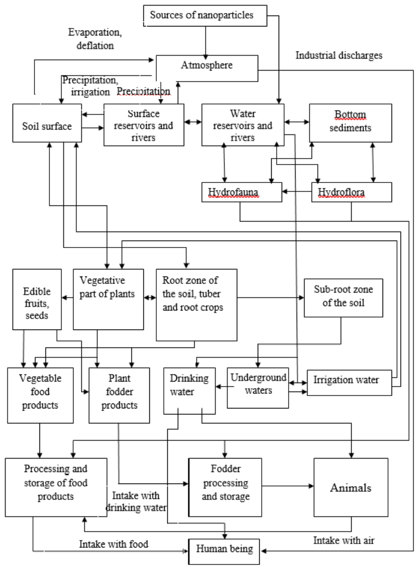

Fig. 1. The main ways of nanoparticle migration through terrestrial and freshwater ecosystems

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[42] Войціцький В.М., Хижняк С.В., Мідик С.В., Березовський О.В., Якубчак О.М., Полтавченко Т.В. Шляхи міграції поліциклічних ароматичних вуглеводнів наземними і водними екосистемами. *Екологічні науки.* 2022. 3(42). С.14–20. http://ecoj.dea.kiev.ua/3-42-2022

[43] Войціцький В.М., Корнієнко В.І., Хижняк С.В. Мідик С.В., Березовський О.В., Таран Т.М., Полтавченко Т.В. Шляхи міграції наночастинок наземними і водними екосистемами. *Екологічні науки.* 2023. 3 (48). С. 32-36. https://doi.org/10.32846/2306-9716/2023.eco.3-48.4

where $\boldsymbol{K_{tc}}$ – transition coefficient; $\boldsymbol{C_1}$ – specific content (concentration) of the substance in the previous chamber (for the first – in the environmental object); $\boldsymbol{C_2}$ – specific content (concentration) of the substance in the next chamber.

In the method of dynamic chamber models (chambers interact with each other and exchange matter), it is believed that the transfer of matter from one chamber to another occurs according to the laws of kinetics of the first order and is described by a system of differential equations. Thus, when a substance enters the environment (atmosphere, soil, water) at the beginning of its migration into the first chamber, the differential equation has the form:

$$\frac{\boldsymbol{d}\mathrm{C}_{\mathbf{0}}}{\boldsymbol{dt}} = \boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{0-1}}} \cdot \mathrm{C}_{\mathbf{0}},$$

where $\boldsymbol{C_0}$ is the concentration of the substance in the source (environmental object) at the beginning of its migration; $\boldsymbol{K}_{tc_{0-1}}$ – coefficient of transition from source to chamber 1.

Fig. 2 shows a chamber model of four chambers characterizing the trophic chain: soil – plant – animal – humans.

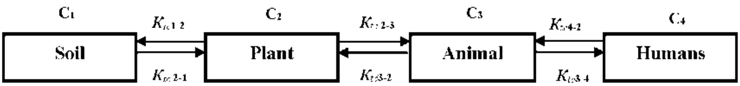

Fig. 2. The simplest dynamic chamber model of the trophic chain: soil – plant – animal – humans:

where **1, 2, 3, 4** – model camera number; $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$, $\mathbf{C_4}$ – concentration of the substance in the corresponding chambers; $\boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{1-2}}}$, $\boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{2-3}}}$, $\boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{3-4}}}$ – direct coefficients of the transition of matter between the chambers; $\boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{2-1}}}$, $\boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{3-2}}}$, $\boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{4-3}}}$ – the inverse coefficients of the transition of matter between the chambers.

For the first three chambers (1, 2 and 3), the differential equations are as follows:

$$\frac{\boldsymbol{d}\mathrm{C}_{\mathbf{1}}}{\boldsymbol{dt}} = \boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{2-3}}} \cdot \mathrm{C}_{\mathbf{2}} - \boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{1-2}}} \cdot \mathrm{C}_{\mathbf{1}};$$

$$\frac{\boldsymbol{d}\mathrm{C}_{\mathbf{2}}}{\boldsymbol{dt}} = \boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{2-1}}} \cdot \mathrm{C}_{\mathbf{1}} - \boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{2-3}}} \cdot \mathrm{C}_{\mathbf{2}} + \boldsymbol{K}_{\boldsymbol{tc}_{\mathbf{3-2}}} \cdot \mathrm{C}_{\mathbf{2}};$$

$$\frac{dC_3}{dt} = K_{tc_{2-3}} \cdot C_2 - K_{tc_{3-2}} \cdot C_3;$$

where ***d* (*dC$_0$*, *dC$_1$*, *dC$_2$*, *dC$_3$*)** – differentiation symbol; ***t*** – time; other designations see above (Fig. 2).

That is, according to the known values of the transition coefficients (K_{tc}) and the concentration of the substance under study in the previous chamber (or for the first chamber in the environmental object), when solving a system of simple differential equations, the possible concentration of this substance in subsequent chambers is calculated.

Thus, the method of chamber models is a simple and adequate mathematical way to describe the migration processes of substances in ecosystems of varying complexity. It can be used, among other things, to assess the migration of nanoparticles in ecosystems.

CONCLUSIONS

Nanoparticles are characterized by physicochemical properties and biological action, which allow them to be classified as new types of materials and products that are widely used in various industries, as well as agriculture and medicine. At the same time, nanoparticles have a toxic effect on living organisms, affecting almost all organs and systems, which requires solving a number of medical and environmental problems. In this regard, the main approaches and recommendations for assessing the risks of nanoparticles for human health and environmental safety are given.

Since the nanoparticle group includes types of particles with very different chemical structure and physical properties, several classifications are given, according to which nanoparticles can be classified according to many parameters.

Nanoparticles, which are mainly created artificially, are ecotoxicants that pollute the environment and have a harmful effect on its objects – air, soil, water and living organisms. Nanoparticle migration processes in the environment are primarily determined by their shape, size, physical and chemical properties, as well as abiotic factors. The accumulation of nanoparticles by plant and animal organisms negatively affects their viability, leads to contamination of food products and feed. Taking into account the need to reduce the load of nanoparticles on environmental objects and their content in drinking water, food for humans and fodder for domestic animals, it is relevant to predict the migration of these substances through ecosystems.

On the basis of analytical studies, a scheme of the main ways of migration of nanoparticles through terrestrial and freshwater ecosystems, the possibility of their entry into the human body is proposed. Chamber model method is proposed for quantitative forecasting of migration processes of these ecotoxicants. It is a simple and adequate mathematical method of evaluating the migration of substances in ecosystems of different complexity. Elucidation of the migration pathways of nanoparticles in environmental objects (atmosphere, soil, and water) is the basis for the development of scientific measures to prevent and minimize their negative impact on the environment and human health.

SUMMARY

The article provides a general description of nanoparticles: definition of these objects, their classification, sources of origin, methods of artificial creation, application in various industries, agriculture, medicine, toxicity. Inherent physical, chemical properties and biological action are characteristic of nanoparticles, which make it possible to attribute them to new types of materials and products. Depending on the number, size, shape, composition, properties, mechanisms of action, nanoparticles have a toxic effect on living organisms, affecting almost all organs and systems. Approaches and recommendations for assessing the risks of nanoparticles for human health and environmental safety are presented. The accumulation of nanoparticles in the organisms of plants and animals causes a negative impact on their viability, leads to the contamination of food and feed. Given the need to reduce the load of nanoparticles on environmental objects and decrease their content in drinking water, food products for humans and in feed for domestic animals, it is relevant to predict the migration of these substances through ecosystems. Based on analytical studies, a scheme of the main migration routes of nanoparticles in terrestrial and freshwater ecosystems and the possibility of their entry into the human body is proposed. For quantitative prediction of the migration processes of these ecotoxicants, the method of chamber models is recommended. Understanding the migration pathways of nanoparticles in environmental objects (atmospheric air, soil, and water) is the basis for the development of scientific measures to prevent and minimize their adverse effects on the environment and human health.

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Information about the authors:
Korniyenko Valentina Ivanivna,
Doctor of Biological Sciences, Professor,
Director of the Ukrainian Laboratory of Quality
and Safety of Agricultural Products,
National University of Life and Environmental Sciences of Ukraine,
15, Heroiv Oborony str., Kyiv, 03041, Ukraine

Khyzhnyak Svitlana Volodymyrivna,
Doctor of Biological Sciences, Professor,
Leading Researcher at the Ukrainian Laboratory of Quality
and Safety of Agricultural Products,
National University of Life and Environmental Sciences of Ukraine,
15, Heroiv Oborony str., Kyiv, 03041, Ukraine

Voitsitskiy Volodymyr Mikhaylovych,
Doctor of Biological Sciences, Professor,
Leading Researcher at the Ukrainian Laboratory of Quality
and Safety of Agricultural Products,
National University of Life and Environmental Sciences of Ukraine,
15, Heroiv Oborony str., Kyiv, 03041, Ukraine