A Survey on the History of Water Pollution Factors in Greece and the Related Impact of Nanomaterials

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Abstract: - One of the greatest challenges of this century is the access to clean and affordable water. The population worldwide is increasing day by day and as a result tackling of water pollution becomes more difficult, demanding and complex. Climate change warns of deterioration of water quality in many regions and the size of this problem is increasing rapidly. The survey herein presents the factors and categories of water pollution, as well as the related impact of the emerging nanotechnology to this phenomenon. Several studies indicate potential cellular damages from certain categories of nanomaterials and nanoparticles.

Key-Words: - Water pollution, Nanotechnology, Nanoparticles, Nanomaterials, Environment, Pollutants.

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1 Introduction

The term water pollution refers to any undesirable change in the physical, chemical and biological characteristics of the water of seas, lakes or rivers, which is or may, under certain conditions, become harmful to humans, other plant and animal organisms, as well as industrial processes and the conditions for maintaining life. Water pollution is created by the release into lakes, rivers and seas of substances that either dissolve or settle to the bottom. These pollutants are very numerous, and this is because pollutants from atmospheric and soil pollution also end up in the water horizon through rain and runoff [1].

The release of energy into water in the form of heat or radioactivity creates thermal water pollution, which causes an increase in the temperature of the water. Water pollution can be caused by microorganisms in household waste, organic substances such as oil and its products, and toxic metals. Humans require fresh drinking water to survive, which is why they lived near rivers and lakes throughout their evolution. Water as food and raw material is so closely linked to life that it can describe human cultural evolution.

Industrial development began with an ever-increasing demand for energy, a source of which was water. Industrial processes, such as cooling and washing, required ever-increasing quantities of water, while the growing population, especially in large cities, needed abundant, clean, and healthy water. The industrial use of water for cooling causes thermal water pollution. During thermal pollution, dissolved oxygen in water decreases, the toxicity of chemical pollutants increases, the rate of physiological functions in organisms accelerates and often results in death. More serious, however, was the chemical pollution of water from industrial waste, urban sewage and agricultural runoff [2].

In 2000, almost 60% of the population of Greece was connected to 270 waste treatment facilities, with a total capacity of 1.30 Mm^3/d (345 mgd). The minimum waste treatment is secondary, usually with complete or partial nitrogen removal in 80% of the cases. Quaternary treatment, in the form of filtration, is applied in some facilities, but the process of upgrading other facilities to quaternary treatment is ongoing. Considering the current situation, limited reuse is already considered as an available alternative, subject to strict standards [3].

An analysis of the distribution of treated municipal waste showed that more than 83% of the waste discharge is generated in water-scarce areas. This demonstrates that water reuse in these areas could cover a significant proportion of the water demand. Another important factor driving the reuse of reclaimed water is the fact that 88% of the waste discharge is located within five kilometres of an agricultural area requiring irrigation water. For this reason, the additional cost of irrigation with reclaimed water is estimated to be relatively low [1].

2 Sources & Categories of Pollution

The sources of water pollution can be classified in the following eight (8) categories.

2.1 Urban Wastewater – Pathogenic Contamination

Activities that enrich or pollute water recipients are discharges that mainly concern human uses. Wastewater is characterized by its high content of organic components and is usually discharged into marine, lake or river recipients or even septic tanks, thus polluting groundwater. In our country, septic tanks, which are still used to a large extent, are the worst means of disposing of wastewater, since they pollute the natural recipient, the soil and groundwater. These urban discharges with their microbial load cause various infections. Specifically, certain bacteria cause typhoid fever, dysentery, gastroenteritis and cholera. Viruses in water and certain strains of them cause poliomyelitis and hepatitis, while eggs and larvae of some parasites (roundworms, etc.) are often found in unclean waters, causing other diseases. The types of these pathogenic microorganisms are found in urban and livestock wastewater. Pathogenic microbes and viruses usually find an inhospitable environment in seawater and quickly become inactive. However, contaminations, mainly radioactive, are caused in waters by accidents or damage to nuclear power plants and by nuclear tests or explosions [4].

2.2 Agricultural Activity

One of the most polluting human activities in terms of water quality is agriculture. The widespread and most often uncontrolled use of agrochemicals, which are widely used by farmers with the main aim of increasing the yield of their agricultural production, but also to protect their products from the action of harmful organisms, results in the contamination of water with high concentrations of chemical substances, the presence of which makes them unsuitable for any use. The term "agrochemicals" includes all categories of organic and inorganic insecticides, fungicides, herbicides, plant regulators, organic and inorganic fertilizers as well as soil improvers. The term "plant protection products" was established in Greece after an amendment to the relevant legislation in 1997 and refers to agrochemical preparations other than fertilizers and soil improvers, which contribute to:

- The protection and prevention of plants and their products from the action of all kinds of harmful organisms;
- the influence of biological processes in plants, except for nutrients;
- the preservation of plant products;
- the destruction of unwanted plants;
- the destruction of part of the plants, as well as the slowing down of unwanted plant growth.

Finally, fertilizers, organic and inorganic, used in the nutrition of plant organisms, as well as soil improvers, significantly increase and improve production. The nutrients in fertilizers are mainly nitrogen (N), phosphorus (P) and potassium (K).

Surface water pollution can occur either directly, by applying plant protection products to the surface of water bodies (lakes, rivers, coastal areas), or indirectly, by drainage waters and surface flowing waters, which carry soil material with residues of plant protection products, resulting in the pollution of the natural recipients to which they end up. The reckless application of plant protection products often leads to disruption of the balance of the ecosystem of the area in which they are applied, resulting in the destruction and elimination of part of its flora and fauna.

In the case of groundwater, its contamination with organic and inorganic water-soluble substances is directly linked to the pollution of surface waters, as well as of soil material, due to the undeveloped and reckless use of agricultural fertilizers, which are applied to agricultural crops and result in the reduction of the quality of groundwater reserves. The self-cleaning process of groundwater is quite limited, compared to that found in large surface water bodies, due to the low temperature and the absence of oxygen, resulting in the complete absence of microbial decomposers (e.g., bacteria), which contribute decisively to the decomposition of organic matter [5].

2.3 Nitrate Pollution

The relevant Ministerial Decision of the Greek Government concerning the "Protection of waters from nitrate pollution of agricultural origin", defines as nitrate pollution the direct or indirect discharge into the aquatic environment of nitrogen compounds of agricultural origin, resulting in damage to human health, living organisms and aquatic ecosystems, or damage to recreational facilities or obstruction of other legitimate uses of water. The main source of nitrogen compounds is agricultural fertilizers, which are used to stimulate plant growth. According to the above decision, these include animal manure, fish farm residues and sewage sludge [1].

2.3.1 Sources of Nitrate Pollution

The main sources of nitrate pollution come mainly from anthropogenic activities. The underground disposal of domestic wastewater in septic tanks and sinks which, however, are not emptied at regular intervals, as foreseen, resulting in them functioning as absorption cesspools and in this way further burdening the soil and underground aquifers. Also, the uncontrolled disposal of solid waste in the subsoil and in illegal landfills burdens the quality of surface and groundwater, due to the leaching caused by the water passing through the mass of solid waste. The penetration of nitrate compounds into groundwater and their subsequent surface runoff into surface waters depends on local soil conditions, drainage, precipitation and surface deposition conditions. The leachate is rich in inorganic components, such as chlorides, iron, lead, copper, sodium, nitrates, ammonia and a variety of organic substances. When solid industrial waste is also contained, then the leachate may include hazardous substances, such as cyanides, cadmium and chlorinated hydrocarbons.

The most important source of nitrate pollution is all kinds of agricultural activities, both agricultural and livestock. The excessive use of nitrogenous preparations with the aim of improving and protecting production results in the presence of high concentrations of nitrate compounds in the subsoil. High concentrations of nitrogenous compounds are observed not only in areas with increased agricultural activity, but also in areas where there is a concentration of animal waste and plant residues. Organic residues remain in the soil after harvest and are subsequently mineralized and nitrified by bacteria. In many cases, plowing of cultivated soils accelerates the nitrification process of nitrogenous compounds, which are found in the subsoil, due to the influx of oxygen.

2.3.2 Environmental Impacts of Nitrate Pollution

The maximum permissible concentration of nitrate radicals (NO^{3-}) in drinking water, according to the World Health Organization (WHO) and the European Commission responsible for water quality, stipulates that it should not exceed 50mg/L, which is equivalent to 11.3mg/L (NO^3). Specific limits regarding the maximum permissible concentration values (NO^3) in fresh vegetables, from 11-700mg/kg and in meat 500mg/kg for NO^3 and 200mg/kg for NO^2, have also been established.

The most important impacts of nitrate pollution on the environment concern:

- The degradation of the quality of surface waters, lakes and rivers, due to the development of the eutrophication phenomenon;
- the pollution of underground aquifers from which quantities of drinking water are directly extracted;
- the increase in water toxicity due to nitrate pollution also has effects on the animal realm.

The presence of increased concentrations of nitrogenous and phosphate compounds in surface water recipients, such as lakes and rivers, results in the growth of aquatic vegetation and biomass in the water, resulting in a reduction in dissolved oxygen in the recipients and the creation of toxic and malodorous gases and the conversion of the water recipients into dead zones of water, since the survival of any aquatic animal organism is impossible.

In the case of groundwater, pollution by phosphate and potassium compounds is quite small, due to the limited mobility that these compounds have in the soil. On the contrary, the high solubility of nitrate compounds in water results in the transport of these compounds through underground natural flow to underground aquifers and recipients. The presence of nitrate compounds comes not only from the application of agricultural fertilizers, but also from the decomposition of animal and plant organisms, plant residues and organic matter in the soil, as well as from the underground disposal of domestic wastewater in septic tanks.

2.3.3 Effects of Nitrate Pollution on Humans

The presence of increased amounts of nitrate (>70mg/kg) and nitrite (>20mg/kg) compounds in the human body, due to the widespread use of mainly ammonium fertilizers in agriculture, can be dangerous for human health. Typical cases are methemoglobinemia or blue-baby syndrome and stomach cancer.

The nature of nitrates is not toxic, but when they enter the blood they contribute to the direct oxidation of Fe++ of hemoglobin to Fe+++, resulting in the creation of methemoglobin, which, at high levels in the blood, can lead to asphyxiation, due to its inability to transport oxygen to peripheral tissues. During this process, nitrate radicals are simultaneously reduced to nitrite compounds, which are particularly toxic. The presence of nitrite compounds in the blood can cause the formation of nitrosamine compounds that are responsible for the development of cancer in many organs of the human body. Finally, the accumulation of nitrate radicals in the human body can cause damage to the thyroid, tachycardia and other milder forms of pathological diseases.

2.4 Industrial Pollution

It comes from liquid industrial effluents (water or by-products), related to the industrial production process. The industrial pollution that may burden the waters of Greece is mainly:

- Organic, with effects on the oxygen consumption of the waters, as well as from other industries (milk pasteurization, slaughterhouses);
- nutrient pollution, with effects on the occurrence of eutrophication in the waters, such as from fertilizer industries or other industries;
- pollution with heavy metals, such as from chemical industries and tanneries;
- thermal pollution from cooling waters (this form of pollution is limited in Greece).

2.5 Eutrophication

Eutrophication occurs in lakes or closed shallow bays under certain conditions. The result is that the fauna and flora of the waters change, their appearance is particularly unsightly and, due to the green slimy surface, fishing becomes difficult. The consequence of eutrophication is the progressive deterioration of water quality, the reduction of its aesthetic value, the limited possibilities for recreation and sports. Pollution and eutrophication are not the same thing. An area can be polluted without having become eutrophic. For example, pollution can be caused by industrial toxic waste that inhibits the processes of photosynthesis. However, eutrophication can also lead to pollution, causing a lack of oxygen in the water, massive algae growth, etc.

2.6 Oil Pollution

Oil has the property of dispersing and spreading over vast areas, because it forms monomolecular layers. Thus, by covering the surface of the water, it prevents the exchange of gases between air and water and harms aquatic organisms. Furthermore, oil affects food chains, pollutes the food sources at the beginning of the food chain, prevents the reproduction of marine life and reduces the natural resistance of organisms. However, many bacteria that live in oil have the ability to break it down, thus cleaning up the polluted areas. Oil is also broken down by the movement of waves and tides.

2.7 Toxic Chemicals

Toxic chemicals for aquatic ecosystems are heavy metals, namely iron (Fe), chromium (Gr), lead (Pb), mercury (Hg), cadmium (Cd), zinc (Zn), manganese (Mn), copper (Cu), nickel (Ni), arsenic (As) etc. Furthermore, pesticides, insecticides, herbicides and acids above a certain limit cause poisoning, inhibition of growth and photosynthesis, selective accumulation and absorption in certain species. Pollution from pesticides and herbicides comes from the wastewater of their production industries, from textile mills, from food processing industries and from agricultural uses. Heavy metal pollution in Greek aquatic ecosystems is relatively low and at levels similar to those given internationally for areas with relatively low pollution.

2.8 Acid Rain

The phenomenon of acid rain occurs when rainwater has very high acidic properties, i.e., pH 5 or less. It is created when sulfur and nitrogen dioxide, which are released into the atmosphere by certain chemical preparations or processes, are oxidized into trioxides, which are then converted into sulfuric and nitric acid in the presence of atmospheric moisture. These acids can be transported by winds over long distances and fall to Earth in the form of acid rain.

This phenomenon has taken on large dimensions in Central Europe and the Scandinavian countries, where entire lakes have been killed by acid rain. Acid rain also causes serious problems for plant organisms, crops and animal organisms, especially in lakes. The effect of acid rain on plants and trees can be direct, affecting the above-ground part of the plant and causing its destruction, but it can also have an indirect effect by passing to the root system of the plant through the soil [6].

3 Water Pollution and Nanomaterials

Researchers have identified several important characteristics of nanoparticles that are thought to be important for their toxicity, including size, surface area, shape, structure, core composition, surface composition, and aggregation properties [1]. The surface area of nanoparticles is particularly important because on a bulk basis, more atoms are available on the surface of the molecule to interact with its surroundings.

Nanotoxicology is the field of science typically associated with the task of determining these particle characteristics and assessing the safety of engineered nanomaterials.

Nanomaterials have a large surface area per unit volume, which gives them novel electric properties, compared to conventional chemicals. These special properties that make nanomaterials useful can also under certain conditions convert some nanomaterials to pose risks to humans and the environment. The major toxicological concerns are the fact that some of the engineered nanomaterials are redox active and are transported across cell membranes and especially mitochondria. It has been shown that carbon nanotube products caused dose-dependent epithelioid granulomas in mice and, in some cases, interstitial inflammation in animals after seven days of exposure [7].

The author in [8] showed that nanomaterials (Fullerenes, C60) create oxidative stress in a fish species. Therefore, the emerging toxicity of nanoparticles raises questions about the sustainability and future of nanoproducts. An in-depth critical review in this context published in [9] described the main aspects, their fate, behavior, disposition and toxicity, with a special emphasis on industrialized nanomaterials.

Similarly, the authors in [10] combined different microscopic techniques to try to visualize the percentage of nanoparticles in red blood cells. The techniques they used were:

- Fluorescent particles by laser scanning microscopy, combined with digital image analysis;
- gold particles by conventional transmission electron microscopy and transmission electron energy filtering microscopically;
- titanium dioxide particles by transmission electron energy filtering.

Using these microscopic techniques, nanoparticles were detected in red blood cells. The results showed that nanoparticles can also penetrate the blood cell membrane by an unknown mechanism other than phagocytosis and endocytosis. The toxicity of nanoparticles is usually manifested by some form of inflammation.

The author in [11] discovered the effect of nanoparticles on human health for the first time. The author reports on several effects of artificial nanoparticles on human health, including effects on the colon, blood, endothelial cell function, muscle, skin, and sarcoma development. Antimony trioxide nanoparticles were found to affect human hematopoietic progenitor cells at a concentration of 5 μg/mL. Pathological examinations of the lung tissue of the patients (in this case, seven young women, 18-47 years old) demonstrated non-specific pulmonary inflammation, pulmonary fibrosis and pleural foreign body granulomas, thus confirming the chronic toxicity of nanoparticles to the lungs.

Considering the rapid development of nanotechnologies, it is essential to establish adequate criteria for assessing the risk and potential harmful effects resulting from the specific properties of substances appearing in the form of nanoparticles. The toxicity of some known metals and metal oxide nanoparticles is known and understood. However, there is still a lack of literature on many of the aquatic and especially terrestrial organisms that can provide new information on the possible interaction of these nanoparticles. Further efforts in this direction would bridge the knowledge gap, given that there is a transition from terrestrial to aquatic environments. Such information would be also proved practical for regulatory agencies to set thresholds for these nanoparticles [12].

The ecotoxicity of engineered nanomaterials (ENMs) has been the subject of many extensive reviews. These reviews highlight the importance of understanding the chemistry of the particles in the context of the bioavailability and ecotoxicity of ENMs. Some environmental factors that may alter the toxicity of ENMs, such as pH, salinity, divalent ions and the presence of natural organic matter, have also been discussed [9].

Much of the research has focused on fundamental aspects of ecotoxicity, such as estimating lethal concentrations, documenting lethal effects in organisms, identifying potential mechanisms of toxicity, and describing the fate and behavior of ENMs. Inevitably, researchers have tailored exposure protocols and the selection of biological parameters to suit their research objectives, and therefore have used a variety of methods. In addition to the scientific community's use of non-standardized, customized methods in basic research, there are a variety of standardized methods for the regulated ecotoxicity testing of chemicals. For example, in 2007 the US Committee on Testing and Materials published protocols for testing substances in a range of aquatic invertebrates and fish. Similarly, the US Environmental Protection Agency (US EPA) has issued protocols for testing aquatic, terrestrial, and microbial organisms [13].

All of these tests, however, were developed with traditional chemicals in mind, not engineered nanomaterials ENMs. Consequently, there has been debate about the usefulness of existing regulatory tests for ENMS. The consensus is that existing methods and frameworks for hazard assessment (standardized test organisms, parameters for mortality, growth, and reproduction) are generally adequate for this purpose, but the details within each test suite may require modification or optimization to work well with ENMs [1].

The Organisation for Economic Co-operation and Development (OECD) has made some preliminary suggestions on how to calculate the dose in toxicity test systems with ENMs [1]. In addition, academic researchers are continuously improving methodologies, as the scientific community gains experience working with ENMs. The Society of Nano Environmental Toxicology and Chemistry Advisory Group (SETAC) hosted a technical workshop in the summer of 2010, bringing together a group of researchers with significant experience with ENMs to document practical issues and options for conducting ecotoxicity experiments with ENMs. The toxicity of different nanomaterials has been documented in [12].

4 Conclusion

Although humans have been exposed to nanosized particles at all stages of their lives, the nature and magnitude of exposures to them have changed in recent years. With the advent of the industrial revolution, exposures to nanosized particles have increased dramatically, due to anthropogenic sources, such as internal combustion engines and power plants. The rapidly growing field of nanotechnology is likely to become another source of human exposure to nanosized particles, through the routes of inhalation, ingestion, dermal absorption and direct injection. The nature of unintentional and intentional nanoparticles is quite different, from the polydisperse and chemically complex particles found in nature to the often monodisperse and chemically produced particles manufactured in the laboratory, but it is likely that the same toxicological principles apply.

Nanoparticles often have increased surface reactivity, due to their small size and large specific surface areas, which means that they should exhibit greater biological activity per unit mass compared to larger particles and can be taken up by living organisms. Uptake by living organisms can be positive and desirable when used intentionally for medical purposes, but can be negative and undesirable when introduced unintentionally, causing oxidative stress, cellular dysfunction and damage [14], or other toxic effects. Organisms often have many defense mechanisms against exposure to certain environmental agents, but the concern with nanoparticles is that their size is so small that they make defense mechanisms ineffective.

Researchers have successfully identified four main routes of exposure of organisms to nanoparticles: deposition on the skin from air, water, and clothing, injection (for example during drug administration), inhalation of nanoparticles, and ingestion from food and water. Once in the body, nanoparticles are translocated to the lymph nodes, nervous and circulatory systems, and then to the bone marrow, kidney, spleen, heart, and liver [15].

However, most of this knowledge comes from studies in other non-human mammals that are usually highly exposed to nanoparticles. Little is known about human exposure to nanoparticles at more realistic doses, or even what the actual magnitudes of realistic doses are. Therefore, research towards this direction in imperative.

In addition, a robotic vehicle is being prepared with the aim of safely taking samples in operationally difficult and dangerous environments for humans. The vehicle is equipped with an intelligent Human-robot interface (iHRI) that allows it to receive commands in the form of dialogue and to strategically choose its movements [16].

Declaration of Generative AI and AI-assisted Technologies in the Writing Process

During the preparation of this work the authors used Google Translate services in order to improve the readability and language of their manuscript. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

C. Paschaliori assessed and validated the chemical and biological aspects of the project.
K. Koutlas carried out the initial research and wrote the initial report (in Greek).
I. Giachos carried out the optimization of the material and structured the reports.
E. Papakitsos has organized the experimental processes and prepared the English text.
T. Ganetsos validated the environmental methodology.
N. Laskaris organized and supervised the project.

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The authors have no conflicts of interest to declare that are relevant to the content of this article.