Distributive Characteristics of Metallic Nano-particles in China's Urban Water Bodies and their Ecological Risks

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Abstract Engineering nano-materials & their impact on human health or environmental security constitute a newly emerging R&D hot spot and a key problem now urgently waiting for its solution in supporting the sustainability of China's nano-science and related technology development. At present, water bodies in Chinese cities have been seriously polluted by metallic nano-particles (MNPs) while related monitoring data are found woefully lacking throughout the country. Based on the above understanding, this article gives a round-up explanation on distributive characteristics of MNPs in the river mouths or water bodies of Chinese cities, their ecological hazards as well as our research in this regard, providing some inspiring ideas and data for control over this scourge. In addition, our exploration probes the discharge traits of MNPs themselves and the mechanism underlying its impact on water pollution.

Keywords metallic nano-particles (MNPs), water body pollution in cities, ecological risks

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1. Key significance of the research on the water body's nano-pollution and related ecological hazards

The nano-particles are found almost everywhere in nature as they might be detected in many of natural sources such as volcanic ash, water and soil in their natural conditions. The nano-particles in nature are products derived from variegated and long-term geo-biological processes. Meanwhile, some of them in their natural states are poisonous to human health while some are not. More intriguing, some of them are existing within living beings. In the wake of the nano-technology's on-going and high-speed development worldwide, both the absolute quantity and diversity of the man-made MNPs are seen in a trend of drastic increase. In such a context, some complicated forms of their chemical integration might very likely come into being as a result of their grain's external shape, size, surface area, electric charge on the surface or due to the presence of a certain material's adsorption. In the same time, some none-biological factors, such as the pH value, the ion's intensity, the water's hardness and the chemical reaction caused by some organic matters, might be able to change an MNP's physical and/or chemical property. Contained in a certain medium, such as the atmosphere, water body and soil, they might exhibit complicated behaviors or exert an effect of potential toxicity to the surrounding ecosystem in the processes of their migration, conversion, destination, *etc* (Colvin, 2003). All of these are the essential components in an all-round appraisal of their safety and friendliness to the environment. The Figure1 shows the main pathways of transfer and destinations nano-particles might take on in an ecosystem's mass circulation (Service, 2003).

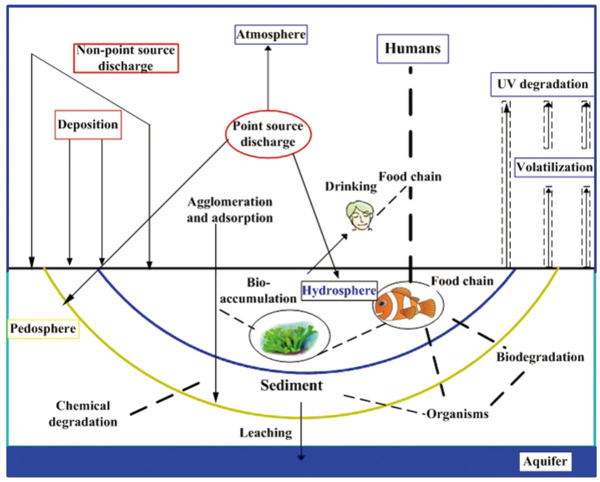

Figure1 Main pathways, the nano-particles might be taking on in an ecosystem via the processes of its migration or destination. (The none-point sources, precipitation, chemical downgrade, the atmosphere, natural and/or man-made sources of discharge, an organic substance's adsorption, a plant's adsorption, sedimentary layers, seepage, aquifers, animals or the human being, the food chain, abyssal fishes, biological down-gradation, the down-gradation caused by photo-catalysis, dust volatilization and underground water-containing layers)

2. Studies on environmental behaviors of MNPs and their ecological risks

Generally, we define that each and every of the MNPs has a grain size ranging from 1 to 100nm while its molecular weight surpasses 1,000. In the natural conditions of an environment, nano-contaminants themselves cannot be directly regarded as nano-materials even though they are within the nano-scale in terms of their grain size and sharing many characteristics in common. In most cases, the nano-pollutants in our environment are in the form of high-macromolecules or colloids. When water acts as a medium, they always form a multi-phased system of the sol with micro-interfaces with the water or the even-phased system of a real solution in the case of a high-macromolecule (Pan and Xing, 2008; Hannah and Thompson, 2008). At present, many nano-products, their derivatives or by-products are unrestrainedly released in water bodies (*via* a drainage ditch into streams, rivers, lakes, estuaries or coastal seas) without any special or effective treatment. Because of the entry of such alien materials, it is very likely that the primitive state's original material composition and related structure in an once pollution-free ecosystem are molested, exerting a negative impact in potential on the latter's normal performance. In the natural state of a hydrological system, a nano-material's behavior is influenced by many environmental factors (Fischer and Chan, 2007). In a water body, for example, we cannot neglect the water's micro-interface's influence as the nano-material might migrate or exchange something with the sediments in the water or transfer itself between the water body and the air. In addition, the water's micro-interface and its chemical components, such as lipid, hydrocarbon or protein ingredients might work as a medium to envelope the surface of an oleophilic nano-material. Without doubt, such a behavior will bring in a change in the nano-material's behavior, modifying the biological applicability of its upper-layered ecosystem. In addition, both water dynamics and morphological features in water bodies or coastal belts will be in a considerable degree to determine the nano-material's distributive layout (Aitken *et al*., 2006). To make clear a man-made nano-material's environmental behavior, it seems possible for us to predict by making reference to behavioral patterns shown by nano-particles or microscopic particles. As a matter of fact, however, research results in this respect are relatively few, if not, in quantity till now. So, this approach of drawing some analogy between the two different categories is less productive due to its methodological limitations.

The current applications of metallic nano-materials are diverse and wide in social production and daily life. Hence, their toxicity possibly brought about in the environment becomes a research focus in the global community of scientists and environmentalists. In nano-science and nano-technology of the world today, for example, TiO_2 is one of the engineering nano-materials noted for its applicable universality and therefore, it always hits the mass media's headlines in the news reportage nowadays on environmental security and nano-hazards to human health (Baun *et al*., 2009). Related scientific research has established that, the nano-particles with a size from 10 to 20nm can cause massive death of some large-size fleas such as *Daphnia magna*. It has found that, when exposed to the water solutions of TiO_2 in varied concentrations and filtered by THF (tetrahydrofuran), the fleas

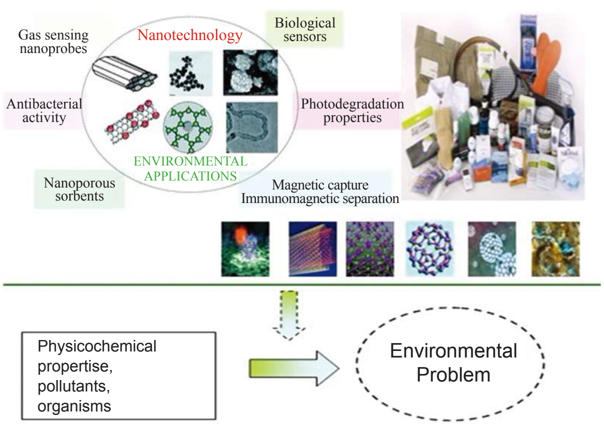

Figure 2 Effect of main nanomaterials on water environment.

were died and the mortality presents a positive correspondence with the nano-material's dosage (Lovem and Klaper, 2006). Also, it has discovered an inheritable toxicity in the bottlenose dolphin's white blood cells when the marine cetacean was put to swim in the seawater which contains a certain concentration of TiO_2 (Bernardeschi *et al*.,2010). The gold nano-particles in water solution present a colloidal state of stable and uniform distribution because their surface is covered with negative electric charges, repelling with one another in the solution. A gold nano-particle has a metallic core and a doubled ionic layer which enclose the core: the inner layer is the negative ion of the citric acid's radical and the outer layer is the positive ion H^+ which is found everywhere in water solution. The nano-clusters of Au-Au_2S have different sizes in 12, 30 and 50nm respectively. About the gold nano-particle's biological toxicity, some scientists believe that very probably, its cellular poison might not be the sole negative effect it has. What is more, it might have some influential role to play in affecting the cell's immunity (Huang, X.L., 2007). In 2005, Shukla *et al*. examined its impacts on the macrophage's proliferation, N-O compounds and products of activated oxygen In the next year, Shenoy *et al*. succeeded in the artificial culture of a naked state of gold nano-particles. Then the scientists made their functioning in company with methoxyl and coumarine's PEG mercaptan and kept them in close contact with the breast cancer cells for 24 hours. .

The naked nano-particles of iron oxides in small grain sizes might exhibit some toxic effects too. In 2008, for example, Zhu *et al*. observed some individual plants of pumpkin able to absorb, transfer or concentrate the nano-particles when they were planted in the water solution containing the nano-particles of Fe_3O_4. In the next year, Liu Hongyun *et al*. identified the influence of Fe_3O_4 or Fe_2O_3 solution on the 95-hour egg-hatching rate of the zebra fish (*Brachydanio rerio*). The rate was 100% in the solution of Fe_2O_3 when the nano-particle's grain size was 22nm in average and the concentration was 10mg/L. As soon as the concentration was changed to 50mg/L, the egg-hatching rate showed a remarkable drop in comparison with what had obtained in the corresponding group. In probing the toxicity of Al_2O_3 nano-particles on the nematode which feeds on *Escherichia coli*, it has been found the nano-particles in all grain sizes and their bulk materials are poisonous, not only in the form of inhibiting the nematode's normal growth, but also and in particular, in the disruption of the worm's reproductive competence. The most eye-catching difference was observed in the case when the nano-particle's concentration was 82mg/L and the bulk material's concentration was 153mg/L, the oxide's solubility plays a critical role in deciding the nano-particle's toxicity. But the dimensional effect seems to have a more influential say in the Al_2O_3 nano-particle than in its bulk material when poisoning the nematode. Also, it has been found in a water body, the copper nano-particle is harmful by making damages on the gill of the zebra fish, leading to fatalities in varied degrees. In a low-concentration solution and in a short duration, a copper nano-material might turn out some remarkable toxic effect on the zebra fish (Griffitt *et al*., 2007). In a water solution which contains silver ions at a low concentration of 0.4mg/L, about half of living paramecia might be found dead within an extremely short duration, showing a strong toxicity against the one-celled organism. To our surprise, if the Ag nano-particle's concentration is at 0.39mg/L, the toxicity remains being so insignificant (Navarro *et al*., 2008). The nano-particles of various metallic oxides were tested one by one to find their varied degrees of virulence against the micro-algae in a water body. Related research discovers that the toxicities shown by ZnO's nano-particles and its bulk material are alike and based on this, it has suggested that the solubility of a nano-particle might have played a critical role in the formation of its toxicity. In the same time, the nano-particles of TiO_2, SiO_2 and ZnO were found able to inhibit the normal growth of some bacteria (such as *E. coli* and *Bacillus subtilis*) and some eukaryote organisms such as large-size fleas and their anti-bacterial capabilities are to grow up in line with the increased concentration. In the order of the intensity of their anti-bacterial toxicities, they might be lined up as follows: ZnO $>TiO_2 > SiO_2$ while such a toxicity is found to be remarkable and unchanged either in a lighted condition or in dark. The optimal concentration of the ZnO nano-particle in a water solution, capable of inhibiting the normal growth of a freshwater micro-alga such as *P. subcapitata* up to half in quantity within 72 hours, or IC_{50}, is 68μg/L. The IC_{50}'s value shows nothing obvious in its numerical difference if compared with those of the counterparts obtained from similar experiments carried out on big-cluster ZnO or $ZnCl_2$ (Franklin *et al*., 2007).

3. The current state and outlook in the research of the MNPs-caused pollution

At present, nano-materials are seeing an increasingly widened expansion in their application as cosmetics, energy sources, coatings, pharmaceuticals and in other economic sections of the world today. In the same time, people become more and more aware of the reality they have to face: many potential problems might arise from the introduction of the nano-materials in social life and the public concern is now focused at their potential impact or possible risk on the environment and human health. The wider and wider scope of their application cannot but lead to their massive discharge, including substances and residues which contain them as pollutants via a variety of pathways accessible to a locality's hydrological system in the form of direct releases, deserted drags, regular or licensed emissions, etc.

As a result of their reaction with the organic matters in a water body, they might acquire a relative sound state of spatial dispersion and chemical stability. By way of the food chain in a water environment, some nano-particles might make their way to the bodies of fish or other aquatic organisms in a process of concentration and eventually get access to the human body, causing a threat to our health.

On some of the R&D journals of international renown such as *Science* or *Nature*, there are many articles exclusively dealing with the negative influences caused by nano-materials or their related technology on human health and environmental soundness. In this aspect, Chinese scientists started probing the problems on the so-called "nano-pollution" in 2003. In September of the year, for example, at a forum on Applied Progress in Nano-materials & Related Technology convened at Nanjing University of Science & Engineering, some participants had discussed the possibilities of nano-particles penetrating through a living being's cellular walls and the amassment of their variants with diverse attributes in different parts of the human body. In the November of 2003, the S&T University of Hong Kong hosted a symposium on the annual tendency for development of new materials, at which the experts once again aired their worries about the possible occurrence of the "nano-pollution."

In China today, however, the public still has insufficient understanding and awareness of the pollution caused by MNPs. An evidence of this state lies in the fact: none of related reports concerning the nano-

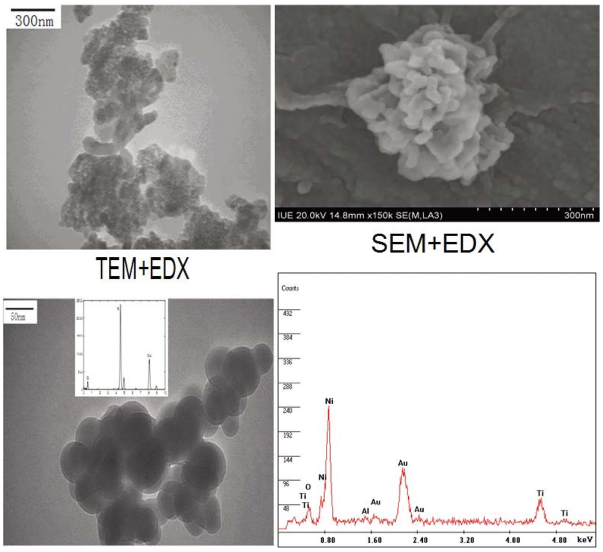

Figure 3 Nanoparticle pollutants morphology and distribution in sediment: a case study of Xiamen city in China.

pollution of Chinese water bodies is so far available on our mass media (Luo *et al*., 2011; Gao *et al*., 2010). So, it is evident that our research on the MNP pollution and its ecological risk is still very poor. Based on this, it seems both pressing and significant for us to choose some cities or river estuaries as our research targets and make preliminary studies on the MNPs' distributive pattern and ecological hazards caused by them so that some basic data might be provided for further exploration. Then, our probing focus should be aimed at the discharging characteristics and the mechanisms underlying their impact on the water environment. By furthering a trans-disciplinary fusion between nano-technology and environmental science, we might acquire the fundamental S&T grounds for control & prevention of the "nano-pollution" in coming years.

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