Environmental behaviors of heavy metals and metal Nanoparticles
Under ocean acidification and their effects on marine organisms

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Abstract: Since the Industrial Revolution, Oceans absorb human emissions CO₂, leading to carbonate concentrations and pH continuous decline. Acidification of the global ocean. Ocean acidification (Ocean acidification, OA) In addition to directly threatening the stability of the marine ecosystem, it also indirectly changes the toxic effects of marine pollutants on marine organisms by changing their environmental behavior. In this paper, heavy metal and metal Nanoparticles (Metallic nanoparticles, MNPs) Environmental Pollutants as the main research object., Through OA in-depth analysis of the causes, Key Research OA Change the speciation of heavy metals and influence the dissolution of metal Nanoparticles, Suspension, The main mechanism of a series of processes such as migration, These heavy metals and MNPs Impact of changes in key environmental processes on individual marine organisms, And on the cause of toxicity differences the Key Analysis. Finally, OA And co-existing pollutants toxicity effect further need to carry out the research work the key prospect.

Keywords: Ocean acidification Heavy metal Metal nano-particles Environment Behavior Toxicity Effect

1. Introduction

Sea Water PH, Will change the marine environment, directly affect the survival of Marine Life. Also, The ocean is the home of the earth's material cycle and energy flow. Heavy metal and metal nanoparticles. (Metallic nanoparticles, MNPs) (Such as metal, metal oxide nanoparticles) Important pollutants such "Hui". Under acidic conditions, Heavy metals in the ocean and MNPs A series of changes will take place in the form and behavior. Also makes OA become a regulator of heavy metals and MNPs Indirect inducement of Biological Effect. Therefore, Under the condition of strengthening acidification MNPs It is very important to study the influence of biological community and ecosystem. According to OA The current research progress briefly summarizes the role of marine OA Response, The detailed analysis of Heavy metals and MNPs Chemical Processes and morphological changes, And its biological effects., The current research problems and future research directions are also discussed and prospected..

2. Ecological Effects of ocean acidification

2.1 OA Impact on the marine environment

As the atmosphere gradually increases CO₂ Will break the balance of gas exchange between ocean surface water and the atmosphere, Making sea water P(CO₂) To 21. From the end of the century 390 Mu ATM (1 atm = 1.01x10⁵ Pa) Rise 700 ~ 1000 Mu ATM[7].
Acidification of ocean surface water, OA will gradually go deeper over time. Layer penetration[5], Acidification of the whole ocean to varying degrees. Also, Other human or natural activities, such as carbon capture and storage technology (CCS), occurrence, CO₂ Leakage[6,9], Ocean sports[10], (Such as currents, upwelling) Eutrophication[11], Organic matter re-mineralization[12] can lead to seawater pH drop.

Solubility in Seawater CO₂ Including 3. Seed inorganic form: Free CO₂ (CO₂(Aq)) % Bicarbonate (HCO₃⁻) 91% And Carbonate (CO₃²⁻)

8% Among them HCO₃⁻ is the main form of existence. The equilibrium of different forms of carbonate in water(I). Along with the sea CO₂ concentration rise and pH the decline. In the sea CO₃²⁻ Concentration ([CO₃²⁻]) will gradually decline, but HCO₃⁻ concentration ([HCO₃⁻]) will rise[13].

Seawater CO₂: Rise in concentration [CO₃²⁻] will inevitably lead CACO₃. Reduced saturation, CA²⁻ Dissolution increase; [CO₃²⁻] drop on CACO₃. Stable impact, Eventually leading to the dissolution of calcareous skeletons and shells in marine life, And reduce the amount of minerals used to build marine shells and skeletons.

2.2 OA Impact on marine life

Currently OA, the study of the impact of marine life has been extensive. Table 1. Summarized the current OA Study on the toxic effects of different biological groups.

Yin double and: Ocean acidification conditions under heavy metal and metal nano-particles of Environment Behavior and its the marine biological of influence

Research. From table in summary we can approximately be the following 4 Point conclusion:

OA Will cause marine biological individual Acid-Base imbalance Change its osmotic pressure
To make its life activities by suppression. OA Also can by Influence Growth Ocean biological adverse influence.

OA The in different growth stage of individual of influence also is not the same. Not mature of no spine animals, fish and Due to its osmotic adjustment and physiological function is not perfect. OKAY OA More Sensitive. PH Reduce will cause its blood carbonate too much of and acidosis To lead to distortion and death. When individual to physiological function perfect stage By OA Stress When CA can by compensation metabolism to ease OA Cause of Acid-Base imbalance and part function damaged But growth development still will delay.

OA For different species biological same there difference response. For example Non-calcification biological competition ability to higher than that of calcium biological[27,28]. This and biological individual of morphology, cell structure, energy use and nutrient get Mechanism

Closely related. (4) Slight OA For some marine biological of growth also have promote effect. OA Makes some Diatom[16] Such as phytoplankton plant photosynthetic role enhanced Growth increased.

All in all Different of biological individual on acidification present different of Physiological Response Long-term past it will result in the marine biological population Especially the change and succession of Dominant Species, So as to influence the composition and function of marine ecosystem. Currently about OA The Study on the Influence of biological individual, community process, Food Chain and food web has become increasingly perfect. But yes OA Mechanisms that generate different response outcomes still need to be more systematic and comprehensive Cognition.

3. Effects of ocean acidification on environmental processes and toxic effects of heavy metal and metal Nanoparticles

3.1 Heavy metal

Heavy metals are common and non-biodegradable pollutants in the marine environment. High Concentration. The Ways heavy metals enter the marine environment include river runoff, atmospheric deposition, sewage sludge, industrial wastewater pouring and dredging waste, etc.[29], And accumulate in coastal, estuarine and sediment. Heavy metals
CAUSE oxidative stress on marine organisms, cause DNA injury, protein modification, lipid peroxidation, even causing biological deaths.\(^{[30]}\). OA can directly affect and harm marine life; Meanwhile, OA create seawater pH the change of chemical process of carbonate will change the speciation of Heavy Metals in seawater, and then lead to the differences in biological effects of heavy metals.

### 3.1.1 OA Change of heavy metal speciation

OA The effect of Heavy Metal Speciation in the ocean can be attributed to the following 4 points (Figure 1, Process 4):

- **OA Influence of inorganic chemical speciation of Heavy Metals in Seawater**\(^{[31,32]}\) (Figure 1, Middle Process). According to the major inorganic complexes of Heavy Metals in seawater

  **Ligand** can be divided 5. Class, Hydroxides, carbonates, chlorides, free ions, and mixed states\(^{[33]}\). Yi Yu Oh And CO\(_3\), The change of inorganic metal complexes will directly affect the composition\(^{[30]}\). In contrast, Chloride forms dominate metals and metal pairs mainly exist in free ions OA insensitive.

- **OA Changing the proportion of Heavy Metals in organic and inorganic chemical forms in Seawater**\(^{[34]}\) (Figure 1, process 2). Gledhill Such\(^{[35]}\) OA Influence Cu and Fe in the mouth of the organic form found when PH decreased when Heavy metal organic state content decreased and inorganic concentration increased. Due to organic matter usually with negative. When PH decreased when Organic particles surface adsorption site reduce Adsorption heavy metal ability decreased.

- **OA Change of Metal Elements of oxidation reduction reaction**\(^{[37]}\) (Figure 1, in the process). Sea gas Interface CO\(_2\) Exchange increased Seawater P (CO\(_2\)) Increased Often with P (O\(_2\)) Decreased The seawater in oxidation reduction environment change\(^{[38]}\) To influence heavy metal of oxidation reduction balance Such Fe (III)\(^{[39]}\) And a Cu\(^{[40,41]}\) The oxidation reaction.

### 3.1.2 OA The heavy metal biological toxicity of influence

Table 2 List. OA The heavy metal in different type marine biological toxic effect of influence. From the current research results to see OA conditions under Heavy metal biological toxicity of change there the following 4 point mechanism (Figure 2), Summed up as follows:

- **OA Change heavy metal toxicity And heavy metal of Environment concentration dense**
  - Cut related.

- **OA Will promote Heavy Metal free ion (M\(^{N+}\)) of release**
  - For itself environment concentration low Biological use limited of Heavy Metal OA can increase
  - Its Biological Utilization. For example OACauseFe (II) Concentration increased Fe (II) Can Reach the total iron 80%\(^{[59]}\) For Fe (II) Limited of sea area of primary productivity is useful; Zn Is carbonic anhydrase synthesis of coenzyme factor In
  - Mild acidification when Zn (II) The addition of can promote carbonic anhydrase of Synthesis To biological growth\(^{[42,43]}\) (Figure 2, in the process).

  **However**
  - Due to metal in acid environment are more likely to be biological uptake For
  - Some background concentration high metal or don't participate in life activities of metal OA will increase its toxicity\(^{[60]}\) (Figure 2, Process 2). OAE Enhance Cu (II)

- The nereis sperm DNA injury The larvae survival rate restrained collaborative role\(^{[59]}\). Same of is High P (CO\(_2\)) And CD (II) Common exposure will reduce dual-core shellfish of Immune Function OAI Increased CD (II) Immune-related functions
  - Adverse Effects, Making organisms sensitive to pathogens and Pathogens Sex Enhancement\(^{[49]}\).

OA The change of toxicity to heavy metals is related to the species of heavy metals. This is related to the speciation of heavy metals in the environment. (Figure 2, Middle Process). Research suggests, Hg The form of receiving OA little
impact, Chloride forms exist mainly in water bodies. At low PH, Hg Exposure 28 d Empress, Discovery OAA And Hg No additive effect on the damage caused by common exposure to the trichomus[51]. But Cu, CD Speciation of other heavy metals OAGreat Impact, So its toxicity is OADifferences under conditions[49,50].

OADifferences in accumulation and toxicity of Heavy Metals

Biological species, OADegree correlation. Moderate acidification (1000 Mu ATM) Will ease Cu (II) (2 µm) Toxicity[44], This is mainly because Hand Cu2 Extracellular Competition[54,61] OAAntagonizing the toxicity of Heavy Metals (Figure 2. Process (4)). And highly acidified (1400 Mu ATM) Will intensify Cu2 Release, OA Ambassador

Ulva itself is more sensitive and vulnerable, Aggravating Cu Toxicity, Make Ulva branch, atrophy, Causing physiological and morphological changes[44](Figure 2. In the process). And invertebrates, Such as shellfish, water fleas, etc., Generally, the increase in energy consumption can alleviate the toxicity of heavy metals[48,62].

For the same species, Same Heavy Metal, OA The toxicity difference is related to the exposure period. OACD And Cu Replacing other intracellular metals from intracellular Storage Sites, Cd (II) And Cu (II) Leading to separate shellfish tours

Leave Zn And Fe Increase, Short-term acute exposure mitigates toxicity through metal exchange mechanisms[45] (Figure 2. Middle Process). Long-term exposure, In OA Up-regulation of metallothionein and Ferritin, Enhances the metal binding capacity of blood cells[47], Alleviating toxicity through protein-metal chelate[46,32, 53](Figure 2. In the process).

3.2 Metal Nanoparticles

With the rapid development of nano technology and the popularization of nano Products, MNPs Widely used in medicine, construction, cosmetics, energy, environmental protection and other fields. It is estimated that, To 2019 Year, Global consumption of nano products will exceed 58Ten thousand tons[63]. Therefore, in the production and use of nano materials, More and more MNPs Inevitably into the ocean[64], Potentially harmful to the entire Marine Environment[65]. On typical MNPs The different marine biological species of toxicity effect has been literature summary[66,67] This paper key summary OAOA MNPs Of Environment Behavior and biological toxicity of influence and regulation.

3.2.1 OAOay MNPs Form of change

MNPs Into water environment inWill physical (Such as reunion), Chemical (Such as dissolved) And Biological Transformation. In water medium in In addition to less part MNPs Can dissolve in water Most MNPs In water will happen reunion And final settlement in the bottom sediment in. MNPs In water in Dispersion Chinese Science: Chemistry 2018 Year No. 48 Volume, And reunion and environment medium parameters including PH, Ion strength and natural organic matter (Natural organic matter NOM) Closely related. On the one hand PH The decreased will promote MNPs Of Ion Release.

On the other hand, PH Will affect MNPs Electronegativity and Transformation. Although in the sea MNPs Reunion occurs due to high ionic strength, But In offshore estuaries or waters with low ionic strength, For Isoelectric Point (ZPC)

In OA Within the scope of change MNPs, Such Fe2 O3 (~ 8.4)[70], Al2 O3 (~ 7.9)[71], CuO (~ 7.4)[72], Its electronegativity may be affected OA The impact changes, So as to affect its suspension stability and toxicity. But OAChange Variable redox environment, Okay MNPs Research on the valence state and Morphological Transformation.

3.2.2 OAOay MNPs Effects of biological toxicity

Into the ocean MNPs Influences on marine life and its physical and chemical properties, Such as size, shape, concentration, charge, etc.[73]. Currently about OA Under Conditions MNPs Very few articles on toxicity studies.

With CO2 Concentration rise, water PH Drop. In the seawater Supermatant Zn Content rise (4.72% Rise 6.47%), Zn2+ Elevated concentration (0.17% To 0.32%) , Crustian Carp in silver (C. auratus) Accumulation of different tissues increased, And ZnO MNPs Increased Oxidative Damage. OAWill improve ZnO MNPs Bioavailability and increase its toxicity.[55], Ka-dar Wait.[56] Studied Fe2 O3, MNPs And OAY es mussels (MytilusCoruscus) Toxicity, Show OAWill cause serious injury and death (50% Death Rate) Mussel Larvae, Delay its development, In PH 6 And 7. Time Fe2 O3, MNPs Exposure eases damage to shellfish, This could be in OA Under Conditions Fe2 O3, MNPs Reunion to remove toxic
substances. Huang Wait.\textsuperscript{[57]} Show low PH And TiO$_2$ MNPs Simultaneous exposure makes mussels (M. Cor-uscus) Impaired Blood Cell Function, Blood Cell Death and Reactive Oxygen Species (Reac-Oxygen Species, Ros) Accumulation increase, And as the exposure time grows, Increased toxicity, For high doses TiO$_2$ (10 mg/L) There is synergy; Also, Through settings 7 d The recovery experiment found that the immune function of mussels did not recover significantly. Note OA And TiO$_2$ MNPs The damage to the mussel's immune system is irreversible. But the mechanism is not clear. Hu Wait.\textsuperscript{[58]} Studied different PH And TiO$_2$ MNPs Yu Yi Bay (M. coruscus) Effects of Physiological Function, Mussels them selves OA Insensitive, TiO$_2$ MNPs Adsorption to gills resulted in a decrease in filtration rate, affecting eating and respiratory rate, In the absence of food O A Be sensitive, Further reduces energy intake, Intensified OA And MNPs Negative effects on mussels, Slow the growth of mussels.

Currently, About MNPs The biological toxicity research mainly concentrated in the freshwater environment. The difference between freshwater and marine water is ionic composition and content. (Especially chloride ion) The difference. Formo Wait.\textsuperscript{[74]} Research suggests, Square in the water Ag MNPs Will Receive Cl$^-$/O$_2$. Oxidation erosion, Form on the surface Ag-oKenghe Ag-Cljian, So that it presents a good dispersion in the sea. But ocean acidification could damage the surface to form a stable layer. Further promotion Ag MNPs Dissolution, Change its suspension stability, Making more AG And ions in seawater(CL). Precipitate Fixation, Increased toxicity to benthic organisms. Although the current O A Okay. MNPs Little research on Toxicity Effect, And about Nom Okay. MNPs The effects of suspension stability and bioavailability on, As well as the Toxicity Effect\textsuperscript{[75]} So we can speculate that in the natural environment, O A Will be influenced MNPs With Nom Interact to influence MNPs Reunion and Its Bioavailability. Some articles indicate that, Extracellular secretions (EPS) Will promote MNPs Dissolution\textsuperscript{[76,77]} And the sea CO$_2$. Rise, Plankton EPS Release will increase\textsuperscript{[18]}. Therefore O A Under Conditions MNPs Toxicity to organisms may increase (Figure 3. Middle Process). In addition, CO$_2$. Increase in concentration makes the water PH Lower, On the one hand promote MNPs Ion Release increases ion toxicity (Figure 3. Nakaon Cheng II), On the other hand, it may affect the redox potential and MNPs Electronegativity\textsuperscript{[78]} (Figure 3. Middle process (3) and (4)). Tortiglione Wait.\textsuperscript{[79]} Research suggests, Only positively charged MNPs Can be internalized by an organism, And negatively charged MNPs Can't be ingested. Also MNPs Affected by the change of redox environment, The change of its existence form (Such CuOTurn Cu$^2$) May also cause toxicity differences. Based on the above research and speculation, Figure 3. Summed up the regulation of ocean acidification MNPs Major potential mechanisms of Marine toxicity.

4. Outlook

21. Since the Century, O A Some progress has been made in the study of the impacts on the marine environment and marine life, O A Environmental Pollutants (Especially heavy metals) Research on the impact of environmental behavior has also begun to take shape. But O A Okay. MNPs Regulation of environmental behavior is not clear. O A The joint toxicity effect with coexisting pollutants is unknown. Therefore, We look forward to further research in this area: (1) About O A The relationship between heavy metals and their interaction is not clear enough. The current research is mainly about synergy or antagonism between the two. The mechanism needs further clarification. (2) The Earth's environment is very complicated. We have O A Prediction of ecological effects caused by limited and one-sided, And for a variety of environmental pressures (Such as temperature, hypoxia, Heavy Will appear very instead of results\textsuperscript{[80,81]}). Therefore need to more system to research of fate and toxicity of research is not comprehensive. This increase the understanding O A Conditions Research many kinds of environment factor between the contact and feedback mechanism And different sewage under MNPs The marine biological of Toxicity Effect of difficulty. Therefore need to input Dyeing of between the combined with toxicity difference and Its Mechanism To O A Of response more of attention and energy to the its in-depth study. (4) At present the research mechanism which more comprehensive of understand. (3) MNPs As an a kind of new sewage research main is in laboratory simulation conditions under the And concentrated in a single dye And traditional pollutants of physical chemical properties have obvious difference. Nearly Natural 20 Biological Species of Toxicity Study So we need more attention in natural ring years On nano-material biological
toxicity of article quantity surgeBut the main environment in real situationThe more close to the actual biological community, ecosystem to concentrated in fresh water environment of Toxicity Study[82]. MNPsIn ocean environment in system of research methodsAndOACause of long-term effect be attention.

References

1. Waters JF miller0 FJ Sabine CL.Glob biogeochem Cycle2011 25: GB4011