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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 emissionsCO_2,Leading to carbonate concentrations andPHContinuous decline,Acidification of the global ocean.Ocean acidification(Ocean audification, 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(Metalic nanoparticles, MNPs)Environmental Pollutants as the main research object.,ThroughOAIn-depth analysis of the causes,Key ResearchOAChange 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 andMNPsImpact of changes in key environmental processes on individual marine organisms,And on the cause of toxicity differences the Key Analysis.Finally,OAAnd co-existing pollutants toxicity effect further need to carry out the research work the key prospect.

Keywords: Ocean acidificationHeavy metalMetal nano-particlesEnvironment BehaviorToxicity Effect

1. Introduction

Sea WaterPH,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 andMNPsA series of changes will take place in the form and behavior,Also makesOABecome a regulator of heavy metals andMNPsIndirect inducement of Biological Effect.Therefore,Under the condition of strengthening acidificationMNPsIt is very important to study the influence of biological community and ecosystem..AccordingOAThe current research progress briefly summarizes the role of marineOAResponse,The detailed analysis of,Heavy metals andMNPsChemical 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 OAImpact on the marine environment

As the atmosphere gradually increasesCO_2,Will break the balance of gas exchange between ocean surface water and the atmosphere,Making sea water$P(Co_2)$To21.From the end of the century390 Mu ATM (1 atm = $1.01x10^5$ Pa) Rise 700 ~ 1000 Mu ATM[7].

Acidification of ocean surface water, OAWill 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)OccurrenceCO_2.Leakage[8,9]Ocean sports[10](Such as currents, upwelling)Eutrophication[11]Organic matter re-Mineralization[12]Can lead to seawaterPHDrop.

Solubility in SeawaterCO_2.Including3.Seed inorganic form:FreeCO_2.(Co_2.(Aq) 1%Bicarbonate(HCO_3^-) 91%And Carbonate(Co_3^{2-})

8%,Among themHCO_3^-Is the main form of existence. 3The equilibrium of different forms of carbonate in Water(1).Along with the seaCO_2.Concentration rise andPHThe decline,In the seaCO_3^{2-}Concentration([Co_3^{2-}])Will gradually decline,ButHCO_3^-Concentration([HCO_3^-])Will Rise[13].

SeawaterCO_2.Rise in concentration[Co_3^{2-}]Drop,Will inevitably lead$CACO_3$.Reduced saturation, CA^{2+}Dissolution increase; [Co_3^{2-}]Drop on$CACO_3$.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 OAImpact on marine life

CurrentlyOAThe study of the impact of marine life has been extensive..Table1.Summarized the currentOAStudy 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 following4Point conclusion:

OAWill cause marine biological individual Acid-Base imbalanceChange its osmotic pressure

To make its life activities by suppression. OAAlso can by Influence Growth

Ocean biological adverse influence.

OAThe in different growth stage of individual of influence also is not the same.Not mature of no spine animals, fish andDue to its osmotic adjustment and physiological function is not perfectOkayOAMore Sensitive. PHReduce will cause its blood carbonate too much of and acidosisTo lead to distortion and death.When individual to physiological function perfect stageByOAStress WhenCan by compensation metabolism to easeOACause of Acid-Base imbalance and part function damagedBut growth development still will delay.

OAFor different species biological same there difference response.For exampleNon-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)SlightOAFor some marine biological of growth also have promote effect. OAMakes some Diatom[16]Such as phytoplankton plant photosynthetic role enhancedGrowth increased.

All in allDifferent of biological individual on acidification present different of Physiological ResponseLong-term past it will result in the marine biological populationEspecially the change and succession of Dominant Species,So as to influence the composition and function of marine ecosystem..Currently aboutOAThe Study on the Influence of biological individual, community process, Food Chain and food web has become increasingly perfect.,But yesOAMechanisms 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,CauseDNAInjury, protein modification, lipid peroxidation,Even causing biological deaths.[30]. OACan directly affect and harm marine life;Meanwhile, OACreate seawaterPHThe 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 OAChange of heavy metal speciation

OAThe effect of Heavy Metal Speciation in the ocean can be attributed to the following4.Point(Figure1.Process~④):

OAInfluence of inorganic chemical speciation of Heavy Metals in Seawater[31,32] (Figure1.Middle Process). According to the major inorganic complexes of Heavy Metals in seawater

Ligand can be divided5. 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 ionsOAInsensitive.

OAChanging the proportion of Heavy Metals in organic and inorganic chemical forms in Seawater[34](Figure1In process ②). GledhillSuch.[35]StudyOAInfluenceCu

AndFeIn the mouth of the organic formFound whenPHDecreased whenHeavy metal organic state content decreasedAnd inorganic concentration increased.Due to organic matter usually with negativeWhenPHDecreased whenOrganic particles surface adsorption site reduceAdsorption heavy metal ability decreased.

OAChange different elements between the competition adsorption ability(Figure1In the process). OACaused by mineral dissolvedSuchCA^{2+}Concentration of increasedHelp sediment heavy metal of desorptionThis main is dueH^+And releaseCA^{2+}Competition adsorption sites increased the heavy metal of release[36].

OAInfluence of Metal Elements of oxidation reduction reaction[37](Figure1In the process).Sea gas Interface CO_2 Exchange increasedSeawaterP (Co_2) Increased Often with P (O_2) DecreasedThe seawater in oxidation reduction environment change[38]To influence heavy metal of oxidation reduction balanceSuchFe (III)[39]And aCu[40,41]The oxidation reduction reaction.

3.1.2 OAThe heavy metal biological toxicity of influence

Table2List.OAThe heavy metal in Different Type Marine Biological Toxic Effect of influence.From the current research results to seeOAConditions underHeavy metal biological toxicity of change there the following4Point mechanism(Figure2),Summed up as follows:

OAChange heavy metal toxicityAnd heavy metal of Environment concentration dense

Cut related.

OAWill promote Heavy Metal free ion(M^{N+})Of releaseFor Itself environment concentration lowBiological use limited of Heavy MetalOACan increase

Its Biological Utilization.For exampleOACauseFe (II)Concentration increasedFe (II)Can

Reach the total iron80%[59]ForFe (II)Limited of sea area of primary productivity is useful; ZnIs carbonic anhydrase synthesis of coenzyme factorIn

Mild acidification whenZn (II)The addition of can promote carbonic anhydrase of SynthesisTo biological growth[42,43](Figure2In the process).

HoweverDue to metal in acid environment are more likely to be biological uptakeFor

Some background concentration high metal or don't participate in life activities of metalOAWill increase its toxicity[60](Figure2In process ②). OAEnhanceCu (II)

The nereis spermDNAInjuryThe larvae survival rate restrained collaborative role[50].Same of isHighP(Co_2)AndCD (II)Common exposure will reduce dual-core shellfish of Immune FunctionOAIncreasedCD (II)Immune-related functions

Adverse Effects,Making organisms sensitive to pathogens and Pathogens Sex Enhancement[49].

OAThe 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.(Figure2.Middle Process).Research suggests, HgThe form of receivingOALittle

impact,Chloride forms exist mainly in water bodies..At lowPH,HgExposure28 dEmpress,DiscoveryOAAndHgNo additive effect on the damage caused by common exposure to the trichomus[51].ButCu,CDSpeciation of other heavy metalsOAGreat Impact,So its toxicity isOADifferences 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 becauseHAndCu^{2}Extracellular Competition[54,61]OAAntagonizing the toxicity of Heavy Metals(Figure2.Process (4));And highly acidified(1400 Mu ATM)Will intensifyCu^{2}Release, OAAmbassador

Ulva itself is more sensitive and vulnerable,AggravatingCuToxicity,Make ulva branch, atrophy,Causing physiological and morphological changes[44](Figure2.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, OAThe toxicity difference is related to the exposure period.. OACDAndCuReplacing other intracellular metals from intracellular Storage Sites, Cd (II)AndCu (II)Leading to separate shellfish tours

Leave Zn And FeIncrease,Short-term acute exposure mitigates toxicity through metal exchange mechanisms[45] (Figure2.Middle Process). Long-term exposure,InOAUp-regulation of metallothionein and Ferritin,Enhances the metal binding capacity of blood cells[47], Alleviating toxicity through protein-metal chelate[46,52, 53](Figure2.In the process).

3.2 Metal Nanoparticles

With the rapid development of nano technology and the popularization of nano Products, MNPsWidely used in medicine, construction, cosmetics, energy, environmental protection and other fields..It is estimated that,To 2019 Year, Global consumption of nano products will exceed58Ten thousand tons[63].Therefore, in the production and use of nano materials,More and moreMNPsInevitably into the ocean[64],Potentially harmful to the entire Marine Environment[65].On typicalMNPsThe different marine biological species of toxicity effect has been literature summary[66,67]This paper key summaryOAOkayMNPsOf Environment Behavior and biological toxicity of influence and regulation.

3.2.1 OAOkayMNPsForm of change

MNPsInto water environment inWill physical(Such as reunion), Chemical(Such as dissolved)And Biological Transformation.In water medium inIn addition to less partMNPsCan dissolved in waterMostMNPsIn water will happen reunionAnd final settlement in the bottom sediment in. MNPsIn water in Dispersion Chinese Science: Chemistry 2018 Year No. 48Volume, And reunion and environment medium parameters includingPH, Ion strength and natural organic matter(Natural organic matter NOM)Closely related.On the one handPHThe decreased will promoteMNPsOf Ion Release.

On the other hand, PHWill affectMNPsElectronegativity and Transformation.Although in the seaMNPsReunion occurs due to high ionic strength,But In offshore estuaries or waters with low ionic strength,For Isoelectric Point(ZPC)

InOAWithin the scope of changeMNPs,SuchFe_2O_3(~ 8.4)[70],Al_2O_3(~ 7.9)[71],CuO (~ 7.4)[72],Its electronegativity may be affectedOAThe impact changes,So as to affect its suspension stability and toxicity..ButOAChange Variable redox environment,Okay.MNPsResearch on the valence state and Morphological Transformation.

3.2.2 OAOkay.MNPsEffects of biological toxicity

Into the oceanMNPsInfluence on marine life and its physical and chemical properties,Such as size, shape, concentration, charge, etc.[73].Currently aboutOAUnder ConditionsMNPsVery few articles on toxicity studies.

WithCO_2Concentration rise, waterPHDrop,In the seawater SupernatantZnContent rise(4.72%Rise6.47%), Zn^{2+}Elevated concentration(0.17%To0.32%),Crucian Carp in silver(C. auratus)Accumulation of different tissues increased,AndZnO MNPsIncreased Oxidative Damage. OAWill improveZnO MNPsBioavailability and increase its toxicity.[55]. Ka-darWait.[56]StudiedFe_2O_3MNPsAndOAYes mussels(MytilusCoruscus)Toxicity,ShowOAWill cause serious injury and death(50%Death Rate)Mussel Larvae,Delay its development,InPH 6And7. Time Fe_2O_3 MNPs Exposure eases damage to shellfish,This could be in OA Under ConditionsFe_2O_3MNPs Reunion to remove toxic

substances. Huang Wait.[57] Show lowPHAndTio_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 doseTio_2.(10 mg/L)There is synergy;Also,Through settings7 dThe recovery experiment found that the immune function of mussels did not recover significantly.,NoteOAAndTio_2.MNPsThe damage to the mussel's immune system is irreversible.,But the mechanism is not clear.. HuWait.[58]Studied differentPHAndTio_2.MNPsYu Yi Bay(M. coruscus)Effects of Physiological Function,Mussels them selves OA Insensitive, TiO_2.MNPsAdsorption to gills resulted in a decrease in filtration rate, affecting eating and respiratory rate,In the absence of food OABe come sensitive,Further reduces energy intake,Intensified OA And MNPs Negative effects on mussels,Slow the growth of mussels.

Currently,About MNPsThe biological toxicity research mainly concentrated in the freshwater environment.,The difference between freshwater and marine water is ion composition and content.(Especially chloride ion)The difference. FormoWait.[74]Research suggests,Square in the waterAg MNPsWill ReceiveCl^-/O_2.Oxidation erosion,Form on the surfaceAg-oKeng$he$$Ag$-$Cl$Jian,So that it presents a good dispersion in the sea.But ocean acidification could damage the surface to form a stable layer.,Further promotionAg MNPsDissolution,Change its suspension stability,Making moreAGAnd ions in Seawater(CL^-)Precipitate Fixation,Increased toxicity to benthic organisms.Although the currentOAOkay.MNPsLittle research on Toxicity Effect,And aboutNomOkay.MNPsThe effects of suspension stability and bioavailability on,As well as the Toxicity Effect[75],So we can speculate that in the natural environment, OAWill be influencedMNPsWithNomInteract to influenceMNPsReunion and Its Bioavailability.Some articles indicate that,Extracellular secretions(EPS)Will promoteMNPsDissolution[76,77],And the seaCO_2.Rise,PlanktonEPSRelease will increase[18].ThereforeOAUnder ConditionsMNPsToxicity to organisms may increase(Figure3.Middle Process).In addition, Co_2.Increase in concentration makes the waterPHLower,On the one hand promoteMNPsIon Release increases ion toxicity(Figure3.Nakaon Cheng II),On the other hand, it may affect the redox potential andMNPsElectronegativity[78](Figure3.Middle process (3) and (4)). TortiglioneWait.[79]Research suggests,Only positively chargedMNPsCan be internalized by an organism,And negatively chargedMNPsCan't be ingested.Also MNPs Affected by the change of redox environment,The change of its existence form(SuchCuOTurnCu_2.S)May also cause toxicity differences.Based on the above research and speculation,Figure3.Summed up the regulation of ocean acidification$MNPs$Major potential mechanisms of Marine toxicity.

4. Outlook

21.Since the Century, OASome progress has been made in the study of the impacts on the marine environment and marine life., OAEnvironmental Pollutants(Especially heavy metals)Research on the impact of environmental behavior has also begun to take shape.,ButOAOkay.MNPsRegulation of environmental behavior is not clear. OAThe joint toxicity effect with coexisting pollutants is unknown..Therefore,We look forward to further research in this area.: (1)AboutOAThe 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 haveOAPrediction 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[80,81].Therefore need to more system to research of fate and toxicity of research is not comprehensiveThis increase the understandingOAConditions Research many kinds of environment factor between the contact and feedback mechanismAnd 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$$OA$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) MNPsAs an a kind of new sewage research main is in laboratory simulation conditions under theAnd concentrated in a single dyeAnd traditional pollutants of physical chemical properties have obvious difference.NearlyNatural 20Biological Species of Toxicity StudySo we need more attention in natural ring yearsOn 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.

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