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A review of inorganic nitrogenous compounds toxicity to aquatic animals

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Abstract

Inorganic nitrogen compounds represented by NH_4^+, NH_3, NO_2^-, HNO_2, and NO_3 are becoming an increasingly global problem in aquatic ecosystems due to escalating human activities. These compounds are interconnected through the nitrification cycle. Excessive levels of these nitrogenous compounds cause direct toxicity to aquatic animals. The current study aimed to review the toxic effects resulting from inorganic nitrogen pollution on animals in aquatic ecosystems. Aquatic animals can absorb inorganic nitrogenous compounds directly from surrounding water, and unconsolidated ammonia is the most toxic, while ammonium and nitrate ions are the least toxic. In general, seawater animals appear to be more tolerant to the toxicity of inorganic nitrogenous compounds than freshwater perhaps due to the enhanced effect of water salinity on the carrying capacity of aquatic organisms.

Keywords: Inorganic nitrogenous compounds, toxicological effects, aquatic animals.

Introduction

Nitrogen is the most abundant chemical element in Earth's atmosphere, constituting about 80% of the total percentages of other chemical elements. Nitrogen compounds are among the main components of many biological molecules, such as amino acids and nucleotides, ranking fourth after carbon, oxygen, and hydrogen as the most common chemical elements in living tissues (Campbell, 1990, and Prakash & Khanam, 2021).

The increase in inorganic nitrogen concentrations constitutes a factor that enhances biological productivity, as it increases the abundance of primary producers in aquatic environments. However, high concentrations of inorganic nitrogen compounds that cannot be absorbed from aquatic ecosystems cause negative effects on sensitive organisms (Yu et al., 2012 and Wang et al. 2023).

Ammonia (NH_4), nitrite (NO_2), and nitrate (NO_3) ions represent the most common forms of inorganic nitrogen in aquatic ecosystems (Wetzel, 2001 and Rabalais, 2002). These ions exist naturally because of deposition in the atmosphere, surface and groundwater, surface runoff, and the dissolution of nitrogen-rich sediments, and through nitrogen fixation carried out by some prokaryotes such as blue-green algae (Cyanobacteria in particular), as well as climate change and the biodegradation of organic matter (Wetzel, 2001; Rabalais, 2002, and Garai et al., 2022).

During recent decades, humanity has contributed to major changes in the global nitrogen cycle, as well as the cycles of other chemical elements. These changes caused an increase in the transport and spread of nitrogen compounds over large areas of the Earth (Galloway and Cowling, 2002 and Wang et al. 2023). Accordingly, inorganic nitrogen can enter aquatic ecosystems through point sources and non-point sources derived from human activities. Nonpoint sources are usually more important than point sources because they are larger and more difficult to control (Howarth et al., 2000, and Prakash & Khanam, 2021).

Many studies have recorded a significant increase in the concentrations of inorganic nitrogen compounds (NH_4, NO_2, NO_3) in ground and surface waters around the world, accompanied by significant impacts on many aquatic organisms and deterioration in freshwater environments, estuaries, and coastal marine aquatic systems (Smith, 2003 and Camargo et al., 2005; Qin et al., 2017 and Schulte-Uebbing et al., 2022).

Based on the seriousness of pollution of aquatic environments with inorganic nitrogenous compounds, the current study aimed to conduct a review of the most important studies that investigated the toxic effects resulting from inorganic nitrogen pollution in aquatic ecosystems.

Ammonia toxicity

Ammonia exists in the form of ionized (ammonium ion) (NH_4) and non-ionized (NH_3) (Russo, 1985 and Zhang et al. 2018), and the relative concentration of both compounds depends mainly on the degree of acidity and temperature of the water. When the values of acidity and temperature increase, the concentrations of ammonia (NH_3) increase, but the concentration of the ammonium ion NH4 decreases (Camargo and Alonso, 2001).

Non-ionized ammonia is highly toxic to aquatic animals, especially fish, while the ammonium ion is either non-toxic or at least less toxic (Constable et al., 2003, and Prakash & Khanam, 2021). Additionally, non-ionized ammonia could be toxic to Nitrosomonas bacteria and Nitrobacter bacteria, thus inhibiting the nitrification process (Russo, 1985, and Herbert, 1999). This inhibition may lead to an increased accumulation of ammonium ions and ammonia in the aquatic environment, enhancing their toxicity to bacteria and aquatic animals (Russo, 1985).

Several studies, including Tomasso et al., 1980; Alabaster and Lloyd, 1982; Russo, 1985; Adams and Bealing, 1994; Richardson, 1997; Environment Canada, 2001, and Augspurger et al., 2003, have demonstrated the toxic effect of ammonia on animals, particularly fish. This toxicity may be attributed to one of the following reasons:

1. Damage to gill tissue, causing suffocation.
2. Inhibition of the Krebs cycle, causing high acidity and a decrease in the blood’s ability to carry oxygen.
3. Uncoupling of the phosphorus oxidation process, leading to the inhibition of ATP production and a reduction of ATP in the brain base area.
4. Disruption of blood vessels and osmotic regulation activity, impacting the liver and kidneys.

Suppression of the immune system leads to increased bacterial and parasitic infections, in addition to the contribution of ammonium to enhancing ammonia toxicity by reducing sodium content to low levels that may be fatal to aquatic organisms (Russo, 1985; Adams and Bealing, 1994; Environment Canada, 2001, and Augspurger et al., 2003). These negative physiological effects can result in reduced feeding activity, fecundity, and survival, thereby reducing the size of aquatic animal communities (Environment Canada, 2001; Constable et al., 2003; Alonso and Camargo, 2004; Alonso, 2005).

Several environmental factors affect the toxicity of ammonia to aquatic animals. In the case of fish, the most important influencing factors are acidity, temperature, dissolved oxygen, salinity, and calcium (Richardson, 1997; Environment Canada, 2001, and Augspurger et al., 2003). An increase in water acidity on the gill surface results in an increase in the concentration of de-ionized ammonia, which can be absorbed through the gill tissue. Moreover, a decrease in the concentration of dissolved oxygen in the water can increase the susceptibility of fish to ammonia toxicity, while an increase in salinity and calcium concentrations in the water leads to a decrease in the susceptibility of fish to ammonia toxicity.

The vulnerability of fish may be reduced by acclimation to high levels of ammonia (Russo, 1985; Environment Canada, 2001; Augspurger et al., 2003). On the other hand, a combination of ammonia and other chemical contaminants such as copper, cyanide, phenol, zinc, and chlorine can lead to additive toxicity or have synergistic effects (Alabaster and Lloyd, 1982; Russo, 1985; Adams and Bealing, 1994, and Environment Canada, 2001).

Many researchers have reported fish death after exposure to human waste containing high levels of total ammonia (Adams and Bealing, 1994; Environment Canada, 2001, and Constable et al., 2003). Multiple laboratory studies have recorded concentrations of non-ionized ammonia causing direct toxicity for various aquatic animals (Tomasso et al., 1980; Alabaster and Lloyd, 1982; Russo, 1985; Adams and Bealing, 1994; Richardson, 1997a; Environment Canada, 2001; Augspurger et al., 2003; Alonso and Camargo, 2004; Alonso, 2005).

Nitrite toxicity

Nitrite ion (NO_2-) and nitrous acid (HNO2) are interconnected through chemical equilibrium NO_2- + H+ = HNO_2 (Russo et al., 1981; Russo, 1985). The relative concentrations of the nitrite ion and nitrous acid mainly depend on the water's acidity. When the acidity value tends to increase, the nitrite concentration may also increase while the nitrous acid concentration decreases. The concentration of nitrous acid (HNO_2) is 4-5 times lower than the concentration of nitrite (NO_2) at a water pH of 7.5-8.5 (Russo et al., 1981; Russo, 1985).

Nitrite ions and nitrous acid contribute to the overall toxicity of nitrite to aquatic animals (Russo et al., 1981, and Russo, 1985). Like non-ionized ammonia, nitrous acid can induce toxicity in Nitrosomonas and Nitrobacter bacteria, thereby inhibiting the nitrification process (Anthonisen et al., 1976, and Russo, 1985). This inhibition may lead to an increased accumulation of nitrite ions (along with nitrous oxide) in the aquatic environment, intensifying the toxic effects of both compounds on bacteria and other aquatic animals (Russo, 1985).

Since the concentration of nitrite in aquatic ecosystems is typically much higher than that of nitrous acid, the nitrite ion is primarily responsible for nitrite toxicity to aquatic animals (Russo, 1985; Eddy and Williams, 1987; Chen and Chen, 1992, and Jensen, 2003). The main toxic effect of nitrite on aquatic animals, especially fish and lobsters, stems from the conversion of oxygen-carrying pigments into forms that are unable to transport oxygen, leading to tissue hypoxia and, consequently, death (Jensen, 2003).

Several studies by Lewis and Morris, 1986; Eddy and Williams, 1987; Harris and Coley, 1991, and Jensen, 2003, have associated toxic effects on fish and crayfish with the following reasons:

1. Depletion of chloride levels (Cl-) outside and inside the cell, causing a severe imbalance in electrolytes in the body.
2. Depletion of potassium levels inside the cell and an increase in its level outside the cell, affecting the voltage of the plasma membrane, neurotransmitter function, skeletal muscle contractions, and heart function.
3. Formation of nitrous compounds, which are mutagenic and carcinogenic.
4. Damage to mitochondria in liver cells, causing a lack of oxygen to the cells.
5. Inhibition of the immune system, reducing resistance to bacterial and parasitic diseases.

Among the various environmental factors that can affect the toxicity of nitrite to aquatic animals, chloride concentration in water appears to be the most important. This is because the entry of nitrite ions into the gills of fish and crayfish occurs through the same route as the entry of chloride ions. Therefore, a high concentration of chloride in water can inhibit nitrite absorption, thus protecting aquatic animals from nitrite toxicity (Tomasso et al., 1979; Gutzmer and Tomasso, 1985; Eddy and Williams, 1987; Harris and Coley, 1991; and Jensen, 2003 and Kroupova et al. 2018). Several studies have shown the effects of nitrite toxicity on aquatic organisms, table (1).

Table 1: Some studies have shown the effects of nitrite toxicity on aquatic organisms.

Focus	Finding	References
Nitrite toxicity adaptation	Susceptibility to nitrite toxicity decreases with adaptation to high environmental nitrite levels.	Lewis and Morris, 1986
Physiological effects of nitrite	Marine animals show greater tolerance to nitrite toxicity compared to freshwater animals, possibly due to chloride ions' mitigating effects.	Jensen, 2003
Toxicity levels in aquatic animals	Identified specific nitrite concentrations that are toxic to aquatic animals; marine species are generally more tolerant.	Tomasso et al., 1979; Russo et al., 1981; Lewis and Morris, 1986
Comparative tolerance in species	Marine animals exhibit higher tolerance to nitrite toxicity than freshwater species due to chloride ion effects.	Russo, 1985; Lewis and Morris, 1986; Jensen, 2003
Effects of nitrite exposure	Laboratory studies confirm direct toxicity of nitrite at certain concentrations in aquatic organisms.	Eddy and Williams, 1987
Toxicity assessment methods	Established methods for assessing the toxicity of nitrite in various aquatic species.	Tahon et al., 1988
Environmental impacts on tolerance	Investigated how environmental factors affect the tolerance of aquatic animals to nitrite.	Chen and Chen, 1992
Role of chloride ions	Discussed the role of chloride ions in enhancing tolerance to nitrite toxicity among marine species.	Alonso, 2005

Nitrate toxicity

Nitrate is the final oxidized form of inorganic nitrogen (Wetzel, 2001). Like nitrite, the primary toxic effect of nitrate on aquatic animals, especially fish, appears to result from the transformation of oxygen-carrying pigments (hemoglobin) into forms that are unable to transport oxygen (methemoglobin) (Scott and Crunkilton, 2000; Cheng et al., 2002). Nitrate, before becoming toxic, must be transformed into nitrite under the internal conditions of the organism's body (Cheng and Chen, 2002).

The permeability of gills to nitrate ions is low, limiting the absorption of nitrate ions in aquatic animals more than the absorption of nitrite ions. This is associated with the relatively low toxicity of nitrates (Scott and Crunkilton, 2000; Cheng and Chen, 2002; Alonso and Camargo, 2003; Camargo et al., 2005).

Freshwater animals seem to be more sensitive to nitrate toxicity than marine animals, attributed to the effect of water salinity on nitrate ion absorption (Camargo et al., 2005 and Romano & Zeng, 2013). The early developmental stages of some marine invertebrates are naturally well adapted to low nitrate concentrations and may be more sensitive, like freshwater animals, to high nitrate concentrations despite the influence of water salinity (Muir et al., 1991).

Several studies have indicated that elevated nitrate concentrations may be linked to the decline of amphibians in aquatic environments, causing poor swimming, reduced fecundity, and diminished levels of survival (Hecnar, 1995; Birge et al., 2000, and Ilha & Schiesari, 2014).

Conclusion

Aquatic ecosystem deterioration is significantly influenced by inorganic nitrogen-containing substances, such as ammonia, nitrite, and nitrate, largely due to anthropogenic environmental alterations. This overview examines the toxic effects these compounds have on aquatic organisms, focusing on their impacts at physiological, biochemical, and ecological levels. Of these substances, un-ionized ammonia poses the greatest threat, especially to fish populations, while ammonium and nitrate ions demonstrate comparatively lower levels of toxicity. The toxicity of certain compounds in aquatic environments is significantly influenced by environmental conditions such as water temperature, salinity, and acidity. Marine life often exhibits higher resistance to salinity compared to freshwater species, primarily due to salinity's buffering effects. Nevertheless, the harmful impacts of inorganic nitrogenous compounds can be intensified through synergistic interactions with other contaminants, potentially causing severe ecological imbalances in aquatic systems.

While considerable advancements have been made in comprehending the effects of nitrogen pollution, there remain notable knowledge gaps regarding its enduring ecological and evolutionary implications. Upcoming studies should concentrate on examining the interplay between nitrogenous substances and other environmental stressors, creating effective remediation techniques, and investigating the adaptive responses of aquatic life. To protect aquatic biodiversity and maintain ecosystem well-being, it is essential to enhance regulatory measures for controlling nitrogen inputs and improve monitoring systems.

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مراجعة لسمية المركبات النيتروجينية غير العضوية للحيوانات المائية

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المستخلص

أصبحت مركبات النيتروجين غير العضوية المتمثلة في الأمونيوم NH_4^+ والأمونيا NH_3 والنتريت NO_2^- وحامض النتروز HNO_2 والنترات NO_3 مشكلة عالمية متزايدة في النظم البيئية المائية بسبب تزايد الأنشطة البشرية. هدفت الدراسة الحالية إلى استعراض التأثيرات السامة الناتجة عن التلوث بالنيتروجين غير العضوي على الحيوانات في النظم البيئية المائية. المستويات المفرطة من هذه المركبات النيتروجينية تسبب سمية مباشرة للحيوانات المائية. يمكن للحيوانات المائية أن تمتص المركبات النيتروجينية غير العضوية مباشرة من المياه المحيطة بها، وتعد الأمونيا الأكثر سمية مقارنة مع بقية مركبات النيتروجين الغير عضوي، في حين أن أيونات الأمونيوم والنترات هي الأقل سمية. بشكل عام، يبدو أن الحيوانات البحرية أكثر تحملاً لسمية المركبات النيتروجينية غير العضوية من حيوانات المياه العذبة، ربما بسبب التأثير المعزز لملوحة المياه على القدرة الاستيعابية للكائنات المائية.