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Part 3: PHAs in "The Circular Economy": Denitrification

Part of the series: Preventing pollution with PHA

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In Part 1 of this **GO!**PHA White Paper Series we touched upon the size and scope of Plastics Pollution and how PHA plays a role in reducing it $_1$. In Part 2 we outlined GHG emissions, plastics' share of that emission and how PHA plays a major role in reducing them $_2$. In this third paper we speak about excess and toxic nitrogen compounds, like nitrates, nitrites and ammonia, that pollute our water and soil, and generate nitrous oxide (N_2O) gas and a little about GHG that significantly affects global warming. PHAs play a role in mitigating these types of pollution.

Sources of Nitrogen Compounds and resulting Nitrous Oxide

Nitrogen is the most abundant element on our planet and is a critical component of all life 3. Plants require nitrogen to grow, proteins and our DNA contains nitrogen. Most nitrogen exists in the form of gas in our atmosphere and nitrogen fixation in nature happens three in different ways:

- a) Biological: Diffusing nitrogen gas into the soil is fixed by microorganisms into ammonium ions, which can be used by plants as nutrients,
- b) Lightening: Conversion of nitrogen into ammonia and nitrates, and
- c) Humans and animals: Human and animal waste contain high levels of nitrogen compounds which prior to the Industrial Revolution was the only form of fertilizer used in agriculture.

Humans started to industrialize the conversion of nitrogen gas into ammonia and other nitrogen rich fertilizers to supplement the naturally available nitrogen compounds for agriculture. Fertilizers being soluble in water, run off with rainwater after application in fields and in order to ensure high yields, farmers add excess fertilizers to offset the fertilizer run off. Today it is estimated that the world uses over 50% more fertilizer, than is necessary for agriculture 4,5.

Excess fertilizer usage and burning fossil fuels for energy and transportation are the major causes of N_2O emission, however, agriculture is by far the most



important source of N_2O at 72% $_{6,7}$. 6% of all GHG emissions are N_2O , and N_2O is 265-298 times more potent in trapping heat over a 100-year scale compared to CO_2 . Therefore, reducing N_2O must also be a priority to combat climate change. A large portion of this N_2O emission can be controlled if fertilizer usage is optimized through controlled release methods and by denitrification of the soil prior to these excess nitrogen compounds entering our waterways.

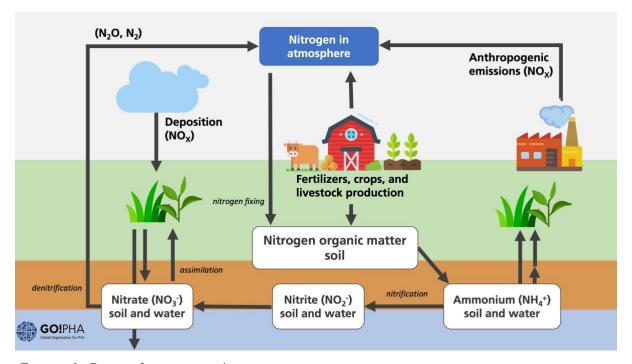


Figure 1: Denitrification cycle

Denitrification

Denitrification is the process of converting nitrogen compounds into free nitrogen gas by chemical or biological treatment, which then is released into the environment. This process removes toxic nitrogen compounds which when present in soil, freshwater and marine environments also adversely affect aquatic flora and fauna. Nitrogen containing compounds, are restricted from release after wastewater treatment in most countries $_8$. Wastewater treatment plants are the only place where nitrogen compounds along with other toxic effluents are treated before the effluent water is discharged. There are no organized methods for treating agricultural field runoffs, including nitrogen compounds even though they help create 72% of all N_2O gas, and are primarily responsible for algae blooms and dead zones in deltas. Therefore, reducing excess nitrogen fertilizer usage or treating them *in situ* in soil to release N_2 gas are the only ways to eliminate these toxic and harmful nitrogen compounds.

Wastewater treatment facilities often use a carbon source, chemicals such as methanol, ethanol or acetic acid to oxidize the nitrogen compounds into nitrogen



gas 9,10. Addition of these compounds are monitored closely using sophisticated and expensive feedback control systems in order to ensure that excess amounts of these chemical compounds themselves do not leach out with the effluent water. Wastewater treatment plants also use mixed microbial cultures (MMCs) to treat accumulated waste and many of these microbes produce PHA 11.

PHA's role in denitrification

PHAs are known to denitrify in two different ways:

- a. Wastewater treatment plants couple nitrification/denitrification reactions along with the enrichment of activated sludge using mixed microbial cultures (MMCs), and
- b. As a degradable polymer PHAs act as a solid-state carbon source in converting nitrogen compounds into nitrogen gas.

Many of the microorganisms in the MMCs produce/accumulate PHA as part of the denitrifying process. This is feasible by implementing anoxic – aerobic conditions whereby nitrate (NO_{3-}) is used as the electron acceptor during PHA accumulation enabling the removal of nitrate from various types of wastewater via PHA-based denitrification, which also accumulates PHA $_{12}$. In this type of system denitrification results in the accumulation of PHA, which could also act as a means of large-scale industrial production of PHA. Efforts in this direction are already underway $_{13}$. This approach can be integrated within the normal operation of a wastewater treatment plant (WWTP). This strategy has been studied recently for the treatment of condensate and wash water originating from a sugar factory. According to the results, carbon removal (in terms of chemical oxygen demand-COD) reached 94-96%, while soluble nitrogen removal was up to 80% with the PHA intracellular content being at 60% g PHA/g of dry biomass in terms of Volatile Suspended Solids (VSS) $_{14}$.

The action of PHA as a solid-state carbon source has far reaching implications in reducing N_2O . PHAs being biodegradable via a wide variety of microorganisms, clear metabolic and regulatory relationship between PHA degradation and denitrification have already been established. In this case PHAs are used as a solid substrate, replacing many of the volatile organic compounds which themselves can be a problem when left in effluent water. PHAs being completely benign and nontoxic do not require expensive feedback controls in such processes. This type of denitrification of water and wastewater is termed 'solid-phase denitrification' 9.15.

Such an approach can have a major beneficial effect in treating excess nitrogen compounds left in agricultural fields. First off, a controlled release coating would



slow down the release of excess nitrogen compounds in agricultural fields. Biodegradable coatings such as with PHAs would eliminate microplastics, a growing environmental epidemic. The biodegradable PHA coating would release carbon during biodegradation, which in the presence of excess nitrogen compounds and moisture in the soil would help convert the nitrogen compounds into nitrogen gas, thereby reducing nitrogen compound runoffs with rain or irrigation water.

Closing the loop on Denitrification naturally with PHA

PHAs or Polyhydroxyalkanoates are a versatile class of natural materials, they are renewable, biodegradable in soil, fresh water & marine environment and are home compostable. They can also be recycled, incinerated to generate energy when these materials become available during waste collection. PHAs can be tailored for use as controlled release fertilizer coatings, that would have the added benefit of denitrifying agricultural fields and without generating microplastics. PHAs are already used to denitrify wastewater in treatment facilities, thereby reducing nitrous oxide emission. In addition PHAs are being used in small and large aquariums as degradable solid state carbon source to mitigate nitrogen compounds. Studies have already shown that they can used successfully used to mitigate nitrogen compounds in large aquaculture farms 9. PHAs can be manufactured using all renewable carbon sources, so also carbon dioxide and methane, and due to its role in mitigating N₂O, PHAs can help mitigate, all three major GHGs – carbon dioxide, methane and nitrous oxide.

Case in point: PHA based denitrification of municipal sewage systems, wetlands and closed fisheries

PHBV, produced by Tianan Biologic Material, is used as a insoluble denitrification agent in aquatic systems, such as sewage systems, fisheries. wetlands and closed Depending on the nitrogen content, the enzymatic activity to biodegrade the PBHV increases, allowing the controlled release of carbon sources. denitrification that enables the process.



Municipal water test site, China (image courtesy: Tianan Biologic Material)



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The Global Organization for PHA is a member-driven, non-profit initiative to accelerate the development of the PHA-platform industry. Polyhydroxyalkanoate polymers (PHAs) provide a unique opportunity as a solution for reducing greenhouse gases and environmental plastics pollution, and establishing a circular economy, by offering a range of sustainable, high-quality and natural products and materials based on renewable feedstocks and offering diverse end-of-life options.

GO!PHA provides a platform for creating and sharing experiences and knowledge and to facilitate joint development initiatives.

Become a member or sponsor to start sharing, contributing and collaborating to accelerate the PHA-platform industry.

If you are interested in denitrification of water or soil, please contact us to find out how we can be of help to you

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