

Biogeochemical Aspect of Atmospheric Methane and Impact of Nanoparticles on Methanotrophs

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Abstract

Increasing concentration of atmospheric greenhouse gas and its implications to the global climate change is a major concern. Methane (CH₄) emitted from terrestrial ecosystem by human activities and or by natural processes gets oxidized by certain group of soil microbes. Any imbalance or negative impact on these microbial groups may lead to ecosystem collapse. Due to rapid industrialization there is increasing threat of various environmental pollutants on the soil microbes. One of the recently identified pollutants is nanoparticles. This paper reviews the impact of nanoparticles on the global climate regulating methanotrophs and potential negative or positive impact of nanoparticles on the soil microbes. Here we assessed the effects of metal nanoparticles on the microorganisms and also the physiology and phylogeny of methanotrophs. Altogether, the study suggests that metal nanoparticle could significantly produce ecotoxicity and killing of phytostimulatory soil bacteria. Thus, the engineered nanoparticle (ENPs) should be further tested as a possible ecofriendly agent.

Keywords: Methanotrophs; Nanoparticles; Methane; Oxidation

Introduction

Microbial mediated methane (CH₄) oxidation play a major role in reducing global atmospheric CH₄ and annually about 10-40 Tg atmospheric CH₄ is consumed by methane oxidizing microbes [1-4]. Microbial CH₄ oxidation has been reported to occur at significant rates in many natural ecosystems and soils can act as sinks for CH₄ from atmosphere [5-10]. Therefore the biological CH₄ oxidation process is important process to minimize global climate change and there is need of extensive research to characterize methanotrophic activity in various ecosystems for possible application to reduce atmospheric greenhouse gas. CH₄ is produced anaerobically from flooded rice field while its oxidation takes place under aerobic condition. So far most of the studies characterizing methane oxidation rate are restricted to upland aerobic soil ecosystem and limited information are there to support our understanding in flooded soil ecosystem [7,11-13]. Soil moisture is important to regulate soil CH₄ oxidation [14] either by affecting diffusion of gas phase [15] or affect soil methanotrophs metabolism by osmotic stress [16] In increased moisture containing wetter soils, CH₄ oxidation decreases with higher soil moisture [17-20], but at lower soil moistures CH₄ oxidation is not highly correlated with soil moisture [21-23]. Typically in very dry soils such as in deserts, CH₄ oxidation is higher after precipitation [24]. In such soils osmotic stress may limit activity of CH₄-oxidizing bacteria more than diffusion of gases through the soil [16]. Few studies have revealed that water addition to soil can stimulate CH₄ oxidation and methanotrophic activity maxima can be attained at intermediate soil moistures [25,26]. It has been projected that climate change will affect the water distribution globally and increasing temperature will lead to more wet lands [27,28]. Many upland soils will remain flooded and this may influence the green house gas (GHG) foot print by affecting both methanogenic and methanotrophic bacteria.

In a flooded rice soil, CH₄ oxidation activity varies with cropping period [29]. Under flooded condition anaerobic microbes are predominantly active and reduces aerobic microbial metabolism. However flooded soil does not necessarily result in the development of uniformly reduced profile. A thin, oxidized surface horizon overlying a deep, reduced horizon is formed due to the dissolved oxygen from the overlying floodwater diffusing across the surface water-soil interface

and in soils planted with rice, the rhizosphere is oxidized because of the delivery of oxygen (O₂) into roots [30-32]. In periodically submerged soil, anaerobic microbial redox metabolism takes place by sequential reduction of inorganic electron acceptors such as oxygen, nitrate, manganese (IV), iron (III), sulphate and carbon dioxide (CO₂). The sequence of reduction processes is best described by the thermodynamic theory, which predicts preferential reduction of available electron acceptors with the most positive redox potential [33,34] Many studies have investigated on the impact of oxidized electron acceptors on methanogenic microbes in flooded rice field soil [35,36]. In anaerobic layer anaerobic microbes like denitrifiers, dissimilatory iron reducers, sulphate reducers, and methanogenic bacteria are active in presence of high input of labile organic material. These microbial groups are often competing for common reduced carbon sources [37-39]. In the flooded soil ecosystem CH₄ oxidation activity is affected due to O₂ limitation and along with predominance of reduced species [40,41]. Under such anaerobic condition i.e absence of O₂, CH₄ oxidation has been reported at the less reduced site through NO₃⁻, Fe³⁺ and SO₄²⁻ reduction [42,43] Anaerobic CH₄ oxidation is poorly understood process because the microorganisms capable of performing this process have not been characterized from soil. The significance of increasing concentration of greenhouse gas, CH₄ in the atmosphere and its role in the global warming has been reviewed earlier [44-47]. Flooded soil ecosystems are considered as one of the major sources of CH₄ to the atmosphere and this process is governed by many factors like moisture regime, temperature, organic matter (added or native), sulphate, pH,

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aquatic plant related factors [48,49]. CH₄ oxidation acts as sink to the atmospheric CH₄. This activity is carried out by specific microbial groups known as methanotrophs. The following literature review is concerned with the significance of CH₄ as the greenhouse gas, its role in global warming, the sources, and sinks of CH₄ i.e. CH₄ oxidation and factors affecting the processes.

Nanoparticles released from products and applications can get directly or indirectly to the soil. Direct soil contamination occurs from purposefully applying products like biocides, compost, fertilizer, and nanoparticles for remediation, and products which contaminate soil unintentionally like abraded material, some coating materials, contaminated soils, and water for irrigation. Product ingredients reaching soils indirectly on the other hand are released to other environmental compartments e.g. air, water, or groundwater. Thus nanoparticles get exchanged between the environmental compartments.

Methanotrophs physiology

Methanotroph bacteria consume methane for energy and carbon [50]. All known methanotrophs under α- and γ-proteobacteria phyla oxidize methane ultimately to carbon dioxide. Basically 3 types of pathways are followed by methanotrophs. In the general methanotrophic pathway, methane is initially hydroxylated to methanol by pMMO (particulate methane monooxygenase) or sMMO (soluble methane monooxygenase), which is further oxidized to formaldehyde by periplasmic methanol dehydrogenase (MDH) [51]. In the catabolic pathway, formaldehyde is oxidized to CO₂ via formate by formaldehyde dehydrogenase (FaldH) and formate dehydrogenase (FDH), yielding reducing equivalents as either quinol or NADH. In the anabolic pathway, formaldehyde is incorporated into cell biomass via incorporation into either ribulose monophosphate (RuMP) or serine pathway, depending on the type of methanotroph.

Phylogeny

Methanotrophic bacteria are classified into one of two major groups, type I and type II. The major distinction between the two types is the pathway via which formaldehyde is incorporated into cell biomass. Type I methanotrophs assimilate biomass via ribulose monophosphate (RuMP) pathway, while type II methanotrophs use serine pathway for the same operation. Also, there are other notable differences that are used to distinguish these groups of methanotrophs other than biomass assimilation pathway such as cell morphology, composition of phospholipid fatty acids, and membrane arrangements as listed in Table 1.

Atmospheric Methane and Global Warming

In stratosphere, CH₄ influences ozone (O₃) by secluding O₃ by

Characteristic	Type 1	Type 2
Cell morphology	Short rods, usually occur singly; some cocci or ellipsoids	Crescent-shaped rods, rods, pear-shaped cells, sometimes occur in rosettes
G+C content of DNA (mol%)	49-60	62-67
Nitrogen fixation	No	Yes
RuMP pathway present	Yes	No
Serine pathway	No	Yes

Table 1: Differential biochemical and physiological characteristics of type I and II methanotrophic bacteria [51].

destroying Cl-atoms into HCl molecules which on reaction with-OH radicals releases O₃ depleting Cl-and ClO-radicals. It also undergoes photochemical oxidation and produces water vapour that reacts with O₃ destroying NO and NO₂ to less reactive HNO₃ [52,53]. CH₄ contributes about 15-20% of the current increase in global warming [49]. In addition to general climatologically effects, global warming may affect the global carbon cycle by greatly reducing the soil organic carbon content, which may be released as CO₂ and is likely to add to the current burden of CO₂ in the atmosphere [54].

Sources and Sinks of Atmospheric Methane

CH₄ production can be from biological and abiological sources. The abiological sources such as mining, transport, fossil fuels, and biomass burning contribute about 20-30% to the total atmospheric CH₄ (Figure 1). The main sink of atmospheric CH₄ is its reaction with-OH radicals [55]. The build up in the global atmospheric CH₄ concentration is attributed to many activities including the bacteria mediated methanogenesis (microbial CH₄) occurring in the anoxic ecosystems and the thermocatalytic reactions (thermogenic CH₄) during petroleum formation [56].

Biogeochemical Cycling of Methane

The primary producer i.e plants fix carbon atoms photosynthetically into a myriad of organic molecules, varying in size and complexity, but all being intermediate in redox potential between CO₂ and CH₄. In anoxic (anaerobic) conditions, organic materials are converted into organic acids, alcohols, methylated amines and H₂ by microbial communities [57,58]. Under highly reducing conditions and in the absence of other potential electron acceptors such as NO³⁻, SO₄²⁻, or Fe³⁺, these substrates can be converted to CH₄ by strict anaerobic methanogenic bacteria [59]. CH₄ thus formed enters the atmosphere at or near earth's surface after escape from methanogenic habitats including wetland, rice paddies and other sources. A high redox potential equals to well-aerated environmental conditions and a low redox potential equals to saturated environmental conditions. Saturated soils become depleted of oxygen, because this is rapidly consumed by aerobic organisms and cannot be replenished by diffusion quickly. Then, anaerobic and facultative organisms continue the decomposition process. In the absence of oxygen, other electron acceptors begin to function, depending on their tendency to accept electrons. When flooding occurs the reduction of the remaining oxygen will take place first, followed by the reduction of nitrate, then manganese, iron, sulphate, and carbon dioxide. The reduction of oxygen occurs by the O₂ consumption of aerobic organisms, NO₃ serves as a biochemical electron acceptor involving N-organisms that ultimately excrete reduced N, the reduction of Mn can be initiated

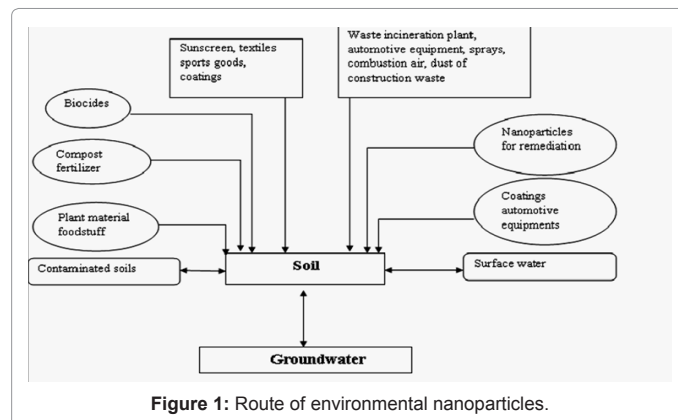


Figure 1: Route of environmental nanoparticles.

in presence of NO_3^- , whereas the reduction of Fe cannot be initiated in presence of NO_3^- , and sulphate reducing bacteria are involved to reduce SO_4^{2-} . The sequential reduction of the different electron acceptors in soil is assumed to be due to different types of microorganisms that compete for common electron donors with greater efficiency according to the redox potential of the electron acceptors [60]. For example, the two most important immediate precursors for CH_4 formation are acetate and H_2 for which, however, SO_4^{2-} -reducing and Fe^{3+} -reducing bacteria compete successfully, if SO_4^{2-} and Fe^{3+} are available, respectively. CH_4 production in anoxic rice paddies begins only if all the other redox processes, i.e. reduction of NO_3^- , Fe^{3+} and SO_4^{2-} are finished. Methanogenesis is inhibited by competition for H_2 , if SO_4^{2-} reduction and Fe^{3+} reduction was made possible by addition of SO_4^{2-} and Fe^{3+} , respectively. About 85% of the total CH_4 input flux is consumed by tropospheric OH, producing CO_2 , H_2O , CO, H_2 and various intermediate products. The remaining flux enters the stratosphere. Reaction with stratospheric OH is the dominant sink, followed by reaction with O and Cl atoms. Under anoxic conditions CH_4 is oxidized in the presence of electron acceptors with sugar as the end product [42]. Sugar thus formed is oxidized by other microorganisms with ultimate CO_2 formation. In the presence of oxygen, CH_4 is oxidized to CO_2 by methanotrophic bacteria. The oxidation of CH_4 to CO_2 completes the carbon cycle.

Oxidation of Methane by Methanotrophs

The capability of methanotrophs to degrade a wide variety of potential pollutants, including methane and halogenated hydrocarbons, has been studied for applications in climate change control and bioremediation [61-71]. Methane is an important greenhouse gas contributing to global climate change. Although present in relatively small concentrations in the atmosphere, ~1.7 ppmv, methane is approximately 25 times as efficient as carbon dioxide at absorbing infrared radiation [72,73] and the atmospheric methane concentration has risen rapidly since the industrial revolution. The increase in atmospheric methane concentration is attributed to increased anthropogenic methane emissions, which have led to a disruption of global methane cycling [72]. A significant portion of natural and anthropogenic methane generation occurs via biological methanogenesis. Strictly anaerobic environments such as wetlands and landfills promote microbial methanogenesis and thus, are major sources of the atmospheric methane. It is known, however, that significant amounts of methane are also emitted from upland forest soils, ruminant animals, and fossil fuel combustion [74].

Degradation of atmospheric methane occurs via two general pathways: (1) photochemical elimination and (2) microbial oxidation [75]. In photochemical elimination processes, atmospheric methane is primarily degraded through reactions in the stratosphere with either the hydroxyl radical ($\text{OH}\cdot$) or electronically excited singlet oxygen (O^1D) [76]. It is estimated that methanotrophic consumption of methane accounts for 1-15% of the combined amount of biotic and abiotic methane removal [77]. In natural environments, e.g., wetlands, methanotrophs are known to oxidize a significant portion of methane generated in anaerobic zones with reported methane oxidation potentials of up to $0.29 \mu\text{mol CH}_4/\text{g wet peat-h}$ [78]. It is also known that methanotrophs in landfill cover soils significantly reduce the amount of methane released from landfills. Methane oxidation potentials up to $10.8 \mu\text{mol CH}_4/\text{g dry weight of soil-h}$ were reported in *in vitro* experiments performed with landfill cover soils [79].

Nanoparticles Flow between Soil and Its Environment

Nanoparticles come to the soil and leave it through various processes. Out of information on nanoparticles applications found in

web and literature studies, a chart of nanoparticles fluxes to and from soil could be drawn (see Figure 1). Included are only fluxes within the system boundary.

Of major relevance for soil contamination are the directly applied products and nanoparticle applications with indirect flows to the soil, either because of mass production or high concentrations of nanoparticles in the products. These are especially automotive equipments, biocides, fertilizers, soil remediation, irrigation, coatings, and air deposition.

Effects of Nanoparticles on Soil Microbes

Several researches revealed that nanoparticles impact terrestrial organisms. Mostly the aquatic organisms are exposed to nanoparticles primarily through gut intake followed by translocation within the body [80,81]. Terrestrial animals are exposed through the lung (inhalation) and gut (diet), while plants are most likely to be exposed via root uptake. Nanoparticles can diffuse through the cell membrane or can be taken up by adhesion and endocytosis. A consistent body of evidence shows that nano-sized particles are taken up by a wide variety of mammalian cell types, are able to cross the cell membrane and become internalized [82-84]. The uptake on NP is size-dependent [85,86]. The uptake occurs via endocytosis or by phagocytosis in specialized cells. They are not dependent upon the circulatory system but can move through the body via cell-to-cell contact. This is a very important consideration in understanding nanoparticle distribution and metabolism within organisms. Potential mechanisms of toxic action within an organism include: disruption of membranes or membrane potential, formation of reactive oxygen species, oxidation of proteins, interruption of energy transduction, release of toxic constituents, and genotoxicity [87]. Antibacterial activity occurs as a direct contact between a positively charged nanoparticle and the bacterial cell surface. This changes the surface phosphorylation and membrane permeability, causes oxidative stress and formation of highly reactive epoxides resulting in DNA damage, and affects the integrity of the bacterial cell membrane.

Conclusion

There is currently a lot of attention being paid to the behaviour and effects of engineered NP, but there is still only limited solid information. However, the mechanisms underlying the nanotoxicity potential of ENPs are still not clear enough. Nanotechnology applications in food and agriculture are in its nascent stage. Moreover, some guidance is needed as to which precautionary measures are warranted in order to encourage the development of "green nanotechnologies" and other future innovative technologies, while at the same time minimizing the potential for adverse effects on human health and/or the environment. Thus there is urgent need for a systematic evaluation of the potential adverse effect of nanotechnology. It is therefore recommended that the ecotoxicological effect of nanomaterial be clarified before their application.

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