Journal of
Earth Science & Climatic Change

Pant, J Earth Sci Clim Change 2014, 5:9
DOI: 10.4172/2157-7617.1000229

Research Article | Open Access

Phosphorus Stabilization in Constructed Wetlands under Changing Hydro-climatic Conditions

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Rec date: Aug 20, 2014, **Acc date:** Oct 21, 2014, **Pub date:** Oct 30, 2014

Abstract

Although there is a reduction in P reaching aquatic systems from point sources, non-point sources such as urban and agricultural runoffs are bringing substantial amounts of phosphorus (P) into aquatic systems as the storm events are quite common due to climatic changes in various parts of the world, and making eutrophication of surface water a global concern. Constructed wetlands could play important roles in stabilizing P; hence reduce eutrophication of natural aquatic and semi-aquatic ecosystems. However, the selection of the construction site may well determine the effectiveness of a constructed wetland. This study shows that P transformation in soils is crucial for P sequestration in a wetland rather than the amounts of native P. Using ^{31}Phosphorus Nuclear Magnetic Resonance Spectroscopy (^{31}P NMR), previously unreported an active organic P form, phosphorarginine, was identified. This study indicates that constructing wetlands on organic P-enriched sites may not solve the P loading to water bodies as the organic P compounds would not be as stable as they were thought, thus can play a crucial role in eutrophication, after all.

Keywords: Phosphorus loading; Water quality; ^{31}PNMR; Eutrophication

Introduction

Phosphorus, a component of nucleic acids and nucleoside triphosphates, the basis of enzyme synthesis and energy transfer systems at the cellular level, occupies an important position in biological systems due to its key role in biochemical reactions. Thus, P is one of the limiting nutrients, and its adequate supply to biota is crucial in regulating primary productivity in aquatic and semi-aquatic systems. Although there is a reduction in P reaching aquatic systems from point sources, non-point sources like urban and agricultural runoffs are bringing substantial amounts of P into aquatic systems as the storm events are quite common due to climatic changes in various parts of the world, and making eutrophication of surface water a global concern. Constructed wetlands could play important roles in stabilizing P, in turn, reduce eutrophication of natural aquatic and semi-aquatic ecosystems.

Constructed wetlands are considered as a low cost alternative for treating wastewater from various sources including urban and agricultural runoffs [1]. Phosphorus flux from soils to the overlying water column depends on various factors including physico-chemical characteristics of soils and the nature of the P compounds stored in soils. Although the construction of wetlands on highly fertilized agricultural lands or manure-impacted lands could help to stabilize the potential P runoff from the area to the surrounding water bodies, the construction could also result in solubilization of stored P and release to the water column. A significant portion of the water column P could be removed by biotic and abiotic processes due to dissolution of calcium (Ca)/magnesium (Mg), and iron (Fe)/aluminum (Al) bound P, and hydrolysis and mineralization of organic P during initial stabilization period. Several studies have reported on the potential use of wetlands for removal of nutrients including P from wastewater [2, 3] and runoffs, however, wetland soils could function as source or sink for P depending on the quality and quantity of native P.

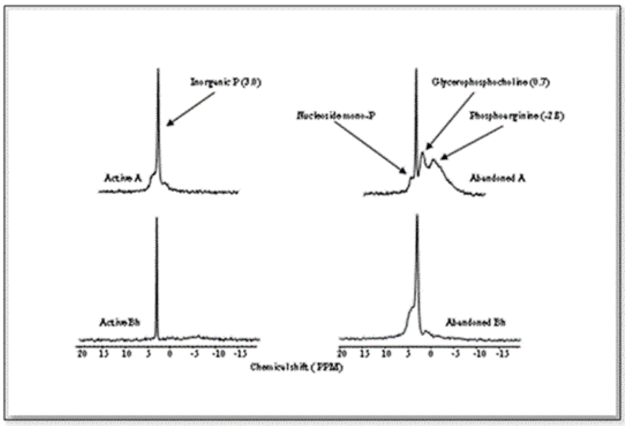

Figure 1: ^{31}P NMR spectra. Top left: topsoil from active dairy farm showing mainly inorganic P; top right: topsoil from abandoned dairy farm showing different P compounds including previously unreported phosphoarginine; lower left: subsoil from active dairy farm indicating inorganic P as a major P form; lower right: subsoil from abandoned dairy farming showing glycerol-phosphate as a major P compound

Animal waste and agricultural runoffs in the watershed are the most important sources contributing P loads to freshwater lakes [4]. Phosphorus loading from the adjacent watershed deteriorates the water quality of lakes and estuaries because of the agricultural runoffs such as Lake Okeechobee, USA, Lake Erie, USA/Canada, and Lake Winnipeg, Canada are prime examples [5]. Construction of wetland has been looked at as an alternative to curtail P influx to the lake, however, forms and amount of P stored in soil could be crucial in the selection of construction sites along with different biogeochemical processes, which occur in wetlands. The mineralization of inorganic P from organically bound P is fundamental to the maintenance of the P cycle in natural and semi-natural ecosystems [6,7]. The biological and pedological transformations of P are well recognized, but the mechanisms of organic P transformation into inorganic P are not well understood. For example, abandonment of dairies/agricultural fields after reaching critical level of P in soils is considered as preventive measures for the reduction in potential threat to the surrounding water bodies. However, study on P forms using ^{31}P NMR showed the transformation of P into different forms would increase its mobility consequently, adversely affect surface and ground water qualities.

Various operationally defined chemical fractionation schemes have been used to categorize P into different pools on the basis of their extractability. However, use of ^{31}P NMR could provide identification of individual P forms, and allow estimation of their stability pertaining to ecological consequences under changing hydro-climatic conditions.

Materials and Methods

Gel filtration and ^{31}P NMR analysis

To identify major organic P forms in Soil solutions (sodium hydroxide extracts) from active and abandoned (the area that had dairy in the past, but used as pastures or forages lately) dairy lands were subjected to ^{31}P NMR Spectroscopic analysis.

Wet soils (50 g) were extracted twice with 100 mL 0.4 M NaOH, for four hours each, by shaking in an end-over-end mechanical shaker at 20 ± 2°C. After the each extraction, the suspensions were centrifuged for 20 min at 5,000×g. The supernatants were pooled and subjected to gel filtration. The extracts were fractionated using a G-25 Sephadex column (with a fractionation range of 100-5,000 mol wt.; dry bead diameter = 20-80 µm; bed volume = 4-6 mL g^{-1}; column volume = 75 mL) as described by Pant [6] and Pant et al. [8]. The extract (20 mL) was pipetted onto the top of the column and eluted with deionized distilled water by pumping at a rate of 0.6 mL min^{-1}. Eighty, 3 mL fractions were collected using a fraction collector. The fractions containing NaOH were separated, using litmus paper test. To check for loss of any forms of P, the NaOH fractions were tested for the presence of P. No NaOH was found up to the 49thfraction and no P was found after the 49th fraction. The fractions free from NaOH were combined and concentrated (10 times) in a Vacuum Rotatory Evaporator at 35°C.

An aliquot of 4.0 mL of the concentrated extract was scanned in a 12 mm tube at 121.4688 MHz on a NT 300 ^{31}P NMR Spectrometer [9] using a 90° pulse with 5.0 sec delay and sampling interval of 0.0000622 sec. To obtain better signal to noise ratio, 8,000 scans were collected, thus, to inhibit any possible microbial activities during the scan, 0.25 mL toluene was mixed with the sample prior to scan collections. The chemical shifts were determined with respect to an external standard of 85% phosphoric acid, and the identification of peaks of various P forms in the NMR spectra were done by comparing the references reported by Pant et al. [8], Gadian [10] and Thebault et al. [11]. Moreover, since the resonances are sensitive to pH and salt concentration [10], samples were spiked with 0.1 mL (10 mg P mL^{-1}) of pyrophosphate ($Na_4HP_2O_7$), as an internal standard for the conformity in the peak identifications.

Results and Discussion

In top-soil (A horizon), active dairy site was dominated with organically bound inorganic P, and <20% of P was accounted for phosphocholine (~0.7 ppm) and nucleoside monophosphates (~4.6 ppm) (Figure 1). However, the abandoned site had a range of identifiable P compounds including nucleoside monophosphates, inorganic P (~3.0 ppm), phosphocholine and phosphoarginine (~ -2.8 ppm), indicating an active P transformation in soils, possibly closely associated with microbial activities [3]. Together with the P transformation in top-soil, signatures of phosphocholine and nucleoside monophosphates in sub-soil (Bh horizon) of abandoned dairy land is an indicative of transformation of P into different forms as the abandonment continued. Thus, the mobility and stability of P compounds in soils are highly dependent on the microbial activities [12].

This study showed transformation of P compounds over a period of time in the P-impacted soils. The transformations of highly mobile P into relatively stable P as the abandonment of the impacted land continued. As far as the control of P runoff into the aquatic systems from adjacent farmland is concerned, the transformations of inorganic P to organic P are promising. However, in the long-term, the relatively stable P would mineralize, and ultimately reaches to the adjacent water bodies. The P compounds in the soils, as revealed by ^{31}P NMR, are mainly low stability organic P compounds, and can potentially be hydrolyzed. Signature for phosphoarginine at chemical shift (~ -2.8 ppm), which is never been reported in soils/waters, was obtained. Phosphoarginine, a low stability (a high energy compound associated with eukaryotic cells) and a high adsorptive potential organic compound (due to charge associated with it, Figure 2), could maintain long-term availability of P in farmland, and alter the trophic status of the receiving water bodies.

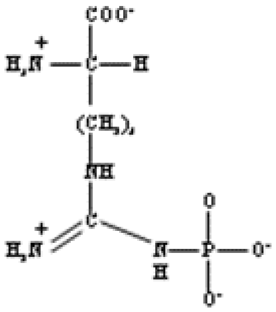

Figure 2: Structure of phosphoarginine

Thus, the constitution of different P forms, and their mobility in different soil/sediment profiles are much more important than the total P [6,13]. A substantially high composition of inorganic P in the sub-soils may suggest that manure-impacted fields could also be a potential source of P to the groundwater. Moreover, especially in Spodosols, an increase in water table could transport substantial amounts of P into the nearby slough/ditches or water bodies through the eluted E horizon.

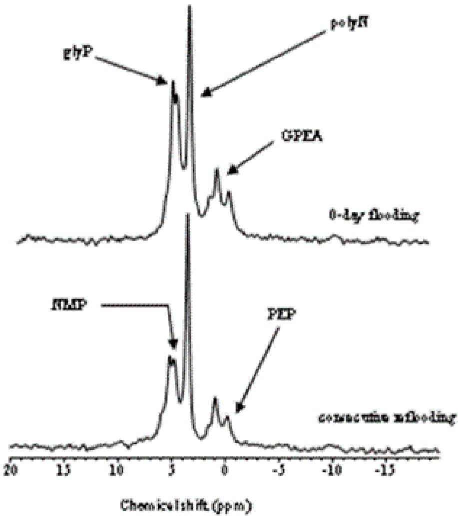

Figure 3: ^{31}P NMR spectra of wetland soils: top: showing different forms of P present in the soils; lower: the same soils showing the reduction in glycerophosphates and nucleoside monophosphates after 4 months of simulated flux, i.e., indicating relatively low stability of glycerophosphates and nucleoside monophosphates

Conclusions

The construction of several Storm Water Treatment Areas (STAs) as buffer to treat drainage water can be a major strategy to protect lakes/marshlands/estuaries as storm events could be common due to the hydro-climatic changes. The construction of wetlands in P-impacted areas could be a tempting option due to possible stabilization of P at source. However, construction of wetlands on such areas could result in solubilization of P stored in soils and release to the water columns. During stabilization period, constructed wetlands can potentially export P to the water column until the system attains equilibrium. This, as well as other studies [2,5,12,14] suggest that P flux potential of soils should be given serious consideration prior to wetland construction, otherwise massive internal P loading could reduce the effectiveness of the wetlands. In recent years, increased attention has been paid to the bioavailability estimation of the organic P to facilitate the formulation of water quality management strategies. Thus, the characterizations of P distributions (Figure 3) could help in endeavors of improving water quality with long-term parity, and play a crucial role in formulating policies for the protection and restoration of ecologically sensitive water bodies under changing hydro-climatic conditions.

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