RESEARCH ARTICLE

Soil phosphorus fractionation as a tool for monitoring dust phosphorus signature underneath a Blue Pine (*Pinus wallichiana*) canopy in a Temperate Forest

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Abstract

Aim of the study: This study aims (i) to monitor the amount of dust deposition during dry season in the moist temperate forest; (ii) to study nature of P fractions in the dust samples falling on the trees in the region; (iii) to study soil P fractions as influenced by the processes of throughfall and stemflow of a Blue Pine (Pinus wallichiana) canopy and to finger print the contribution of dust towards P input in the temperate forest ecosystem.

Area of study: The site used for the collection of soil samples was situated at an elevation of 6900 feet above sea level (temperate forest in Himalaya region) in the Thandani area national forest located in the north west of Pakistan.

Material and methods: For soil sampling and processing, three forest sites with three old tree plants per site were selected at approximately leveled plain for surface soil sampling. Two dust samples were collected and analyzed for different physicochemical properties along with different P fractions. First dust sample was collected from a site situated at an elevation of 4000 feet and second one was collected from an elevation of 6500 feet above sea levels. Modified Hedley procedure for the fractionation of P in the dust and soil samples were used.

Main results: The input of dust was 43 and 20 kg ha^{-1} during drier months of the year (September-June) at lower and higher elevation sites respectively, and the dust from lower elevation site had relative more all P fractions than the other dust sample. However, HCl-P_i fraction was dominant in both samples. Both labile (water plus NaHCO$_3$) and non-labile (NaOH plus HCl) inorganic P (P_i) fractions were significantly increased in the surface soil by both stemflow and throughfall compared to the open field soil. The buildup of NaOH and HCl-P_i pools in soils underneath the canopy might prove useful in fingerprinting the contribution of atmospheric dust towards P cycling in this temperate forest.

Research highlights: The role of dust in the cycling of P in temperate forest in Himalaya region.

Keywords: soil phosphorus fractions; atmospheric dust; stemflow, throughfall; temperate forest.

Introduction

Atmospheric dust plays an important role in the cycling of many nutrients especially phosphorus (P) in both terrestrial and aquatic ecosystems (Mills *et al.*, 2004; Schlesinger, 1997; Wang *et al.*, 2015). Dust particles suspended in the air intercepted by tree canopies uses two pathways to enter into the soil. Firstly, washed with rain water and fall onto the soil surface known as throughfall and secondly, with rain water running on the surface of shoots and stems and enter the soil at the base of stem known as stemflow (Smith & Smith, 2001). Moreover, open field surface present beyond the influence of tree canopies receives atmospheric dust in the form of dry fall (Whitford, 2002; Wang *et al.*, 2015).

Forest trees generally influence the soil fertility underneath the tree canopies especially if situated in

nutrient poor environment. Researchers have found enhanced soil fertility in the forms of island of fertility in the immediate surroundings of plants (Schlesinger & Pilmanis 1998). Under most circumstances, canopy serves as nutrient trap whereby nutrients present in the fine dust particles slowly get deposited onto the leave surfaces which eventually get into soil by throughfall or by stemflow. Additionally, more litter fall likely accumulate underneath the tree canopy which during decomposition liberate organically tied up nutrients in the forms that can be utilized by tree in soil limited by nutrients (Smith & Smith, 2001; Mcgowan & Ledgard, 2005).

The major forms of P in soil-derived atmospheric dust are minerals from the apatite group and, to a lesser extent, P bound to iron /aluminium oxides/hydroxide minerals (Singer *et al.*, 2004; Eijsink *et al.*, 2000). These minerals are highly insoluble under alkaline and oxygenated conditions. The apatite minerals are calcium (Ca) bearing P minerals (Lindsay, 2001). Most of these are sedimentary in origin and are sparingly soluble in the soil solution. During the course of weathering, the P resealed from these minerals can be used by living organisms besides its reactions with soil constituents. The interactions include adsorption on to the soil surfaces, and precipitation into secondary P bearing minerals that can be stable under changing soil environment (Schlesinger, 1997). Acidification of atmospheric aerosols is a prime mechanism producing soluble P from soil-derived minerals and deposition of aerosols provides the major external source of P to marine surface waters (Nenes *et al.*, 2011).

Phosphorus fractionation procedure developed by Hedley *et al.* (1982) consisted of using various extracting solutions of increasing strength in sequential order to extract various forms of P that were held with various strength of bioavailability in the soil. The most labile forms of P are extracted with anion exchange resin and 0.5 M $NaHCO_3$ solution adjusted to pH 8.5. These extractants help dissolving and releasing P from soil surfaces which are held with weak forces. The next solutions used in the sequential order are 0.1M NaOH and 1M HCl, where NaOH solution will bring P into the solution that is held with aluminum (Al) and iron (Fe) with more strength. However, 1M HCl will cause dissolution of apatite (primary minerals of P). Both of these forms are sparingly soluble and represent P fractions of limited bioavailability to plants. Organic forms of P are also determined in extracts obtained from $NaHCO_3$ and NaOH solutions and represent labile and resistant forms of organic P respectively. Finally, left over residue is digested with H_2SO_4 and H_2O_2 at high temperature to determine residual P. This form of P has only limited significance in plant nutrition. Since, atmospheric dust is intercepted by forest canopy; therefore we can see its signature in the form of changes in some P fractions using aforementioned procedure underneath a tree canopy on top few mm of the forest soil.

Most P requirement for either increased productivity or for the sustainable growth of the forest in the tropics is controlled by inputs of dust which originate thousands of miles away from the source of interception. Entire growth of Amazon forest in the tropics was depended on huge annual interception of dust containing apatite like minerals originated from the Saharan desert in North Africa (Swap *et al.*, 1992). Similarly, dust originated from Asia also contributed a significant amount of P in maintaining productivity of forests in highly weathered Oxisols located in Hawaii islands in USA (Pett-Ridge, 2009; Chadwick *et al.*, 1999). Moreover, human induced increased eolian (wind transported) dust deposition was monitored in throughout the western United States (Neff *et al.*, 2008).

Little work has been done on the role of dust in the cycling of P in temperate forest in Himalaya region. Temperate forest chosen for present study is a unique habitat that supports huge biodiversity. In fact it is one of the biodiversity hot spots in Pakistan. Forest growth on high altitude mountains receiving high rainfall are generally limited by both nitrogen (N) and P. However, internal recycling of litter and native surface and subsurface organic matter plus free-living and symbiotic nitrogen fixation, along with wet deposition of NH_4^+ and NO_3^- in the rainfall generally alleviate the N deficiency (Schlesinger, 1997). Therefore, P deficiency is recognized as the major constraint that may lead to reduced net primary productivities in both temperate and in tropical forests (Schlesinger, 2005). The soils of moist temperate forest resemble much with tropical regions. These are generally acidic in nature, rich in oxides of Al and Fe which generally cause precipitation of P and also offer their surfaces for irreversible adsorption of P and thus may cause reduced P bioavailability in the forest ecosystems. Since, P does not have any gaseous component and rely on mineral weathering, mineralization of organic matter and annual input of dust for the provision of bioavailable P. Therefore; this study aims (i) to monitor the amount of dust deposition during dry season in the moist temperate forest; (ii) to study nature of P fractions in the dust samples falling on the trees in the region; (iii) to study soil P fractions as influenced by the processes of throughfall and stemflow of a Blue Pine (*Pinus wallichiana*) canopy and to finger print the contribution of dust towards P input in the temperate forest ecosystem.

Material and methods

Site description

The site used for the collection of soil samples was situated at an elevation of 6900 feet above sea levels in the Thandani area national forest located in the north west of Pakistan. The average annual rainfall of the area is about 2200 mm per year and more than 80% of the total is received during the monsoon months of July and August. Winter precipitation does include snow which generally covers the area from the month of December till March. Month of June is warmest with an average noon time temperature of 24.6 °C and temperature dips below freezing during the month of January. Soils are shallow on the slopes and relatively deep in the depression areas and classified as Ultisols. These soils are developed from underlying bed rock which is mostly in calcite ($CaCO_3$) and dolomite ($CaMgCO_3$) in composition (Hasan, 2005). Warm and moist conditions especially during summer months would have caused weathering of these rocks at moderate rate which is evident in the loss of base forming cations and development of acidity on the surface soil horizons. Since it is protected national forest, therefore, land clearing for agriculture is strongly prohibited and only few old scattered farms are present in the area. Both slopes and depressions areas were occupied by Blue Pine (*Pinus wallichiana*) and Silver Fir (*Abies pindrow*) with under story shrubs and grasses were also common. The effective growing period (frost free days) for the vegetation begins in April and last till November and growth becomes stunted owing to the prevalence of frost during winter months.

Soil sampling and processing

Three forest sites with three old tree plants per site were selected at approximately leveled plain for surface soil sampling. Blue pine tree was chosen because of its dominance presence in this forest and had greater than 90% coverage at these sampling sites. All sites were situated in close proximity to the site from where forest dust sample (6500 feet above sea level) was collected. Since dust deposition effects can only be monitored on the top soil surface, therefore only 0-5 cm soil depth was sampled using steel augur. Three sampling areas under each tree were demarcated which were also regarded as the three treatments in this study. The areas consisted of along the stem, under the canopy and open space to represent the influences of stemflow, throughfall, and just precipi-

tation / dry fall respectively. The radius of surface soil area that might be influenced by stemflow was 15 cm while the horizontal spread of the canopy around each tree allowed us to demarcate area that would receive throughfall and that varied slightly for each tree ranging from 300 cm to 400 cm. At a given site, soil samples were collected from 8 to 10 different places under each tree for each treatment and made into a bulk soil sample and stored at cool environments. Prior to collection of soil samples, loose surface organic material was removed from each soil sampling site. The soil samples were air dried under the sun and ground to pass less than 2mm sieve and stored at room temperature prior to their use in the chemical analysis in laboratory.

Dust collection

Two dust samples were collected and analyzed for different physicochemical properties along with different P fractions. First dust sample was collected from a site situated at an elevation of 4000 feet and second one was collected from an elevation of 6500 feet above sea levels. The forest site at lower elevation was located close to urban areas. The major activities responsible for generating dust at this site were blasting for mining rock phosphate, stone crushing industry, erosion of P rich surface soil particles from agriculture fields and last but not the least heavy traffic, while the second sample was collected from the site that was 20 to 30 km away from the aforementioned activities and was situated well into the deep forest. We used smooth mirror surface of tables for the collection of dust samples which had dimensions of 119 cm x 61 cm and 60 cm x 60 cm for the lower and higher elevation sites respectively. These tables were placed inside the center of rooms which had dimensions of 487.7 cm x 365.7 cm and 365.7 cm x 365.7 cm at lower and higher elevation sites respectively. The height of both rooms was 10 feet (304.8 cm). The second site was situated near the forest trees from where the surface soil sample were collected and height of room windows were ~ 2 to 3 meter higher than the tree canopies intercepting the dust. It was insured that both rooms had four ways crossing through windows of nearly uniform size. As the air passed through the room, the finer particle of the dust would start to deposit on the surface of the table which will also simulate conditions analogous to the dust deposition on the surface of forest leaves. Dust was allowed to deposit from April 1st and continued through May 31st and finally, was scrubbed off from the smooth surface by using fine brush and

brought to the laboratory where initial weight was recorded. The quantity of dust was 630 and 144 mg per unit table surface area at lower and higher elevation forest sites respectively. Finally, calculations were done regarding the amount of dust received by the area in the units of gram or kg dust per hectare during the dry months of the year. The dust collection during these months represented the amount of dust falling in the region during dry months which start from September and last till end of June. The amount of dust supposed to be minimal in the months of July and August owing to the onset of monsoon season. The dust samples after collection were stored at room temperature prior to their use in chemical analysis in the laboratory.

Chemical analysis

Phosphorous fractionation

We used modified Hedley procedure (Hedley *et al.*, 1982) for the fractionation of P in the dust and soil samples. The soil and dust samples were weighed to the nearest of one gram and placed into 50 ml centrifuge tube. The samples were sequentially extracted first with 25 mL of de-ionized water and subsequently with 25 mL of 0.5 M $NaHCO_3$ solution (adjusted to pH 8.5), 0.1M NaOH, and with 1 M HCl after 16 hours of shaking on end-over-end shaker run at 125-135 excursions per minutes for all extractions. Lastly, the residues of the soil and dust samples after the aforementioned sequential extractions were transferred to the digestion tube and were subsequently digested with 5 mL of H_2SO_4 and with 15 mL of H_2O_2 in three steps (5 mL each) at high temperature (275 ºC) and residual P were determined. The P extracted and measured from all aforementioned extracts was inorganic P (Pi). The extracts from de-ionized water, $NaHCO_3$ and NaOH were digested with H_2SO_4 and potassium per sulfate ($K_2S_2O_8$) at 120 ºC for the determination of total P; and organic P (Po) was subsequently determined by difference of total P and Pi determined previously by the procedure of Bowman, (1989). The Po present in the de-ionized water and in $NaHCO_3$ extracts are considered as labile forms which can easily be hydrolyzed in the soil environment. The exact nature of Po present in NaOH are still un-known but largely consisted of humic P which are thought to be resistant in nature and have long persistence time in the soil environment. The inorganic P in all soil and dust extracts was determined by molybdenum blue method (Murphy & Riley, 1962) and blue color intensity was read at 880 nm using visible spectrophotometer.

Other physico-chemical analysis of soil and dust samples

The amount of organic matter present in the soil (SOM) and in the dust samples was determined by loss in weight after ignition at 500 ºC in high temperature furnace (Storer, 1984). The soil pH and electrical conductivity were determined in 1:5 soil and de ionized water suspension using calibrated pH and conductivity meters respectively. Owing to relatively small quantity of dust samples, we used 1:10 and 1:20 ratio for the dust samples collected from lower and higher elevation respectively.

Statistical analysis

We have chosen randomized complete block design (RCBD) for the statistical analysis of data and have been shown on the top of each figure. Bulk soil samples collected from the stemflow, throughfall, and open field were three treatments and site to site variations were removed by blocking technique where each site served as a block. General Linear model (Proc-GLM) in statistical analysis system software (SAS) was used to carry out analysis of variance (SAS, 2009). The means of the treatments were separated using least significant difference (LSD) value calculated by using appropriate error mean square and α value at 0.05. Thus any two means of a given P fraction as influenced by the aforementioned treatments followed by different letter / letters would be significantly different at 95% of the probability for the comparative purposes. Since we collected one sample each for the dust samples from both sites, therefore means were not presented with measure of internal variation. Therefore, comparison between both dust samples in terms of P fractions would be interpreted on the relative scale in this study.

Results and discussion

P fractions of dust samples

The results regarding various P fractions of dust samples for both locations are presented in the Fig. 1A. The distribution of P fractions for lower elevation dust sample was HCl-Pi> $NaHCO_3$-Pi> NaOH-Po> water soluble-Po> $NaHCO_3$-Po> NaOH-Pi >water soluble-Pi, while at higher elevation site was HCl-Pi> $NaHCO_3$-Po> NaOH-Po> $NaHCO_3$-Pi> NaOH-Pi > water soluble-Po> water soluble-Pi in decreasing order respectively. The concentration of HCl-Pi fraction was 810 and 440 mg P kg^{-1} dust samples collected from lower
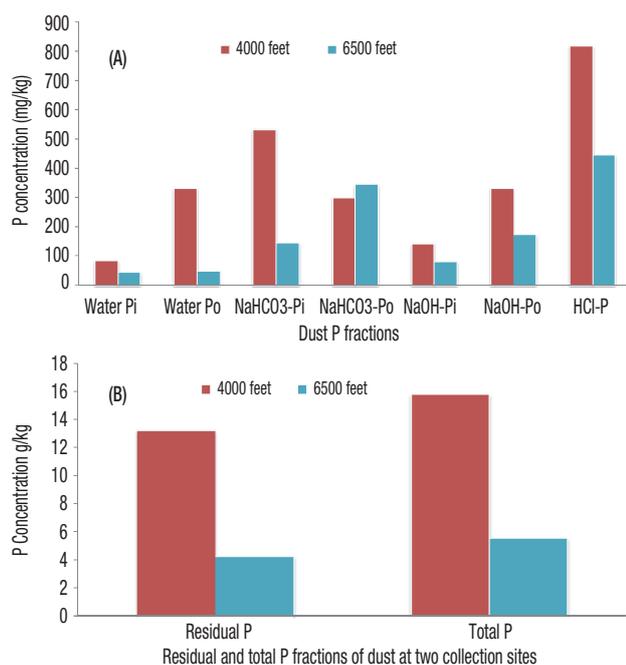
Figure 1(A): Phosphorus **(P)** fractionation of dust samples collected from lower Himalaya, Pakistan; (B); Residual and Total-P fractions of dust samples and amount of dust deposition in the region (Pi=inorganic; Po=organic).

and higher elevation sites respectively, and was the largest P fraction and stood next only to residual P (Fig. 1B), while the respective values for the water soluble-Pi fraction were 90 and 50 mg P kg^{-1} which were the lowest among all the P fractions monitored in this study. Since, atmospheric dust mostly originates from top soil surface and consists of finer earth particles and travels to the far flung areas in air suspension before interception by plant canopies in the forest ecosystem. Therefore, the composition of the top soils will find its signature in the dust samples as well. The probability that arid soils with low organic matter (OM) content will contribute more towards load of finer dust particles in the air than soils of tropical region where top surface contains a lot of OM which binds primary soil particles into stable structure and will least allow finer particles to enter into the air and secondly, tropical soils might not had large pools of HCl-Pi, as apatites might disappear at extreme stage of weathering (Walker & Syers, 1976).

Previously, researchers (Schlesinger, 1997; Pett-Ridge, 2009; Chadwick *et al.*, 1999) concluded that finer dust particles originated in desert storms from the Gobi desert in China were rich in apatites (HCl – Pi fraction) and found their way into the tropical forest in Hawaii where intercepted by tree canopies practically fulfilled all P requirements of the forests. However, the amount of deposition was 10000 times more in this study owing to higher levels of anthropogenic distur-

bances which were responsible for dust emission in the region. The prevalence of large amounts of HCl–Pi fraction in our samples also supported that these might have originated from parent material / soils containing apatite like minerals (Fig. 1).

Dust samples collected from the lower elevation also had relative more water soluble, NaHCO$_3$, and NaOH extractable Pi fractions compared to the dust samples collected from higher elevation (6500 feet). However, labile Po fraction extracted with NaHCO$_3$ solution was relatively more in the dust sample collected from the higher elevation compared to dust samples collected from lower elevation site. These differences in dust composition at both sites can be attributed to the prevalence of more P rich particles in the urban dust (lower elevation) than the dust samples collected from higher elevation. There were huge pockets of loose soil in and around the city used for growing specialty crops with heavy inputs of P sources in the form of fertilizer and manures which might have caused more relative P concentrations in various P fractions in the dust from lower elevation compared to the dust collected from the higher elevation site. As dust travels distance, only finer fraction will eventually end up for long-distance transport and heavy fraction might settle along the way to its journey. This was also depicted in both lesser total amounts of each P fraction as well as in total P content of dust collected from higher elevation site as shown in Fig. 1B. Other than HCl-Pi fraction, high elevation dust also had relative large amount of labile form of Po extracted with NaHCO$_3$ solution suggesting some role of organic P in the cycling P in the forest ecosystem. Although it would be hard to find its fingerprint on the ground surface soil underneath the canopy owing to its rapid turnover rate and contribution of litter fall towards this labile pool of Po. The input of dust was 43 and 20 kg ha^{-1} during drier months of the year (September-June) at lower and higher elevation sites respectively. The possible reason for large quantities of dust deposition in this region can be ascribed to the prevalence of larger number of stone crusher units along with blasting for mining rock phosphate in the perimeter of about 100 km. Previously, large dust flux resulted in a more than fivefold increase in inputs of nutrients including phosphorus to the alpine ecosystem, with implications for surface-water alkalinity, aquatic productivity and terrestrial nutrient cycling (Neff *et al.*, 2008). Keeping in view relatively large deposit of dust in this study plus higher total P content suggests large contribution of dust towards P inputs in this temperate forest.

The concentrations of residual-P were 13.0 and 3.0 g P kg^{-1} at lower and higher elevation dust samples respectively (Fig. 1B). Residual P includes more

chemically stable Po forms and relatively unknown insoluble Pi forms of low bioavailability. The total P content was 16 g P kg^{-1} and 5 g P kg^{-1} for the aforementioned sites respectively (Fig. 1B). High relative content of total P at lower elevation site compared to higher elevation could be attributed to various natural and anthropogenic factors such as fertilizer and manure inputs in agricultural land, land excavation for construction of roads and buildings plus the use of waste water rich in P for irrigation purposes which were operative in urban areas located next to lower elevation site. Excess deposition of nutrients in dust is important for the nutrient budgets of forests in near urban areas (Lovett *et al.*, 2000).

Soil organic matter (SOM) levels, and soil pH underneath Blue Pine canopy

The results regarding the amount of SOM and pH of the soil samples from various treatments underneath a Blue pine canopy are presented in Table 1. The amount of SOM was not influenced by canopy related treatments used in this study. However, on the relative basis, we found higher content of SOM in soil samples influenced by the processes of throughfall and stemflow compared to open field soil possibly due to large inputs of decomposed bark and litterfall in former two treatments. Higher amount of SOM are generally associated in forest soils all over the world and can impart benefit to the forest ecosystems (Brady & Weil, 2007).

The soil pH is considered as master variable and is very important in controlling nutrient availability, especially P and effecting many biochemical interactions taking place in soil (Stevenson, 1999). The pH was significantly highest in soil samples collected from the area influenced by throughfall compared with all other treatments (Table 1). The lowest pH was < 6 and was found in soil samples influenced by stemflow and was also significantly different from all treatments. The possible reasons could be addition of acidity from different organic acids generated during decomposition

of intact bark, from where subsequently acidity entered in the stemflow and ended up in the soils. Previously, Cantú & González (2001) studied the pH of solution material running along the stemflow and found extremely acidic in reaction (<4.0) while they also monitored higher pH in water samples collected from throughfall and attributed this to the additions of basic cations leached from leaf cells. The same reason can be true in this study plus addition of alkaline dust (pH was 6.2 and 7.5 for lower and high elevation dust respectively) can also be contributing factor in our study especially when the amount of dust currently deposited in the region was huge.

Water Soluble P Fractions underneath Blue Pine canopy

The results regarding the influence of various canopy related treatments of a Blue Pine on water soluble P fractions are presented in the Fig. 2. The amount of water soluble Pi was 3.8 and 2.4 mg P kg^{-1} soil for the stemflow and throughfall respectively, and were statistically at par with each other but significantly different from water soluble Pi concentration in the soil samples collected from open field (0.5 mg P kg^{-1}). These findings suggest that canopy related processes (stemflow and throughfall) are influencing water soluble Pi fraction in the soil samples collected from underneath Blue Pine canopy. We can partly ascribe this significant variation to the dust deposited on to the stems and branches as well as on the leaves which become soluble in rain water and run along stem and branches (stemflow) and leaches from the leaves (throughfall) and subsequently enters the soil surface underneath the canopy. The composition of the dust samples collected from both sites also supported this observation as it had relative small amounts of water soluble Pi fraction (Fig. 1A). However, we cannot say for surety that dust is the only available mode of this Pi fraction as it can also be contributed by the mineralization of easily decomposable fraction of organic material which is constantly in the mode of flux

Table 1. Influence of Blue pine canopy on soil EC[a], pH, and organic matter content in a temperate forest soil

Canopy Treatments	Soil EC$_{1:5}$ (µS m^{-1})	Soil pH$_{1:5}$	Soil organic matter (%)
Stemflow	220 B[b]	5.9 C	15.2 A
Throughfall	251 A	7.1 A	15.0 A
Open field soil	173 C	6.6 B	12.0 A
P value	<0.0001	<0.0001	0.22
LSD value	3.70	0.09	4.63

[a] Electrical conductivity; [b] Means followed by different letter in a given column are statistically different from each other.
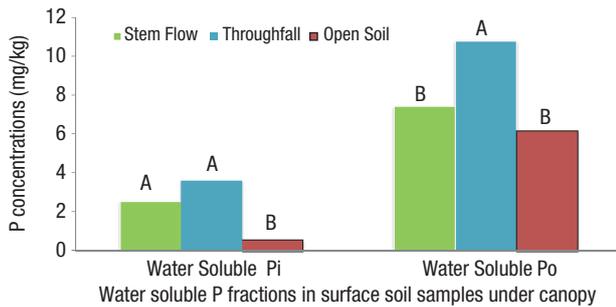
Figure 2. Influence of Blue Pine canopy on Water Soluble phosphorus (P) fractions (Pi=inorganic; Po=organic). Mean followed by different letter / letter are significantly different from each other at p<0.05.

in the form litter fall underneath the canopy. This observation was also supported by the data on water soluble Po fraction presented in the same figure (Fig. 2) where we found the highest concentrations of 10.8 mg P kg^{-1} in the soil samples for the throughfall and was significantly different from stemflow (7.5 mg P kg^{-1}) and from open field soil (6.05 mg P kg^{-1}). However, the means of last two treatments viz. stemflow and open field soil were statistical at par with each other. Since, water soluble P fractions including both Pi and Po are considered as labile forms P which can be taken up by microbes as well as plants and thus have rapid turnover rate. This is also the P form which is more susceptible to loss in the runoff generated by the rainfall event especially in a watershed dominated by forest and thus has relevance to the environment. Relatively large amount of water soluble Po was present in all the treatments compared to the Pi fraction which reflected increasing role of Po in surface P dynamics in the forest ecosystem where surface soil always had regular additions of litter fall from the main tree along with understory shrubs. The results regarding the increased water soluble P level in stemflow as compared to open soil are in conformity with (Døckersmith *et al*., 1999) who establish that concentration of plant-available P is higher in soils near stems than in soils from beyond the canopy. In another study (Dezzeo, & Chacon, 2006), they found significant higher nutrient concentrations in stemflow than in throughfall, but stemflow inputs were much lower compared to throughfall which was related to the large differences in the water amount between both flows and also to the adsorption of nutrients by epiphytic organisms and lichens present on the bark of stem.

NaHCO$_3$ extractable P fractions underneath Blue Pine canopy

The results regarding the effects of throughfall and stemflow of a Blue Pine canopy on the NaHCO$_3$ ex-

tractable Pi fraction are presented in Fig. 3. The amount of Pi in the soil samples was ~ 20 mg P kg^{-1} for both stemflow and throughfall and was significantly different from the open field soil which had 8.0 mg P kg^{-1} soil. Concentration of Pi in the open field soil was significantly lower than soil samples collected from the areas influenced by stemflow and throughfall which suggest the same reasons as described under water soluble Pi fractions. Since, this fraction consisted of P forms which are loosely or weakly held on to the surfaces of soil constituents and / or more soluble P bearing secondary minerals which can furnish / maintain high concentrations of bioavailable P in the soil system. However, the concentrations of Pi in soils underneath stemflow and throughfall were significantly higher than open field soil would result unique niches that will support more biodiversity on the forest floor. Bioavailable P concentrations in the soils have been implicated in controlling the biodiversity in natural ecosystems (Ceulemans *et al*., 2014).

As for as Po fraction was concerned, soils receiving throughfall had significant less amount of Po (30 mg P kg^{-1}) than in soil samples from open field (36 mg P kg^{-1}) and stemflow (37 mg P kg^{-1}) respectively. Since, bark / wood of twigs and stems are composed of organic material that might contain P and would also likely offer space for different microbial communities to reside which might be involved in mineralization / decomposition of easily soluble organic materials. Moreover, turnover of microbial communities themselves would likely provide Po which eventually passes and enrich the soils just next to the stem (stemflow). These conditions might not be conducive for the leaves (throughfall) where water will evaporate quickly through air turbulence and sunshine (certainly higher temperature than stem) and thus only litterfall and subsequent decomposition on the soil surface will contribute towards Po. Like water soluble P fractions, we found relative larger amounts of Po compared to Pi in NaHCO$_3$ extracts suggesting more importance of Po in the cycling P in the temperate forest soils. Previously, Schlesinger, (1997) also suggested the importance of labile pools of Po in the nutrition of tropical forest where most inorganic P stocks were depleted due to intense weathering or changed to the forms which could not be taken up by the plants.

Since both P fractions (Pi and Po) extracted with NaHCO$_3$ solution are considered highly bioavailable and thus has rapid turnover time. Therefore, despite their presence in dust samples it was very difficult to assess whether the observed difference of different canopy related treatments on Pi and Po concentrations were entirely related to dust inputs or inputs of litter fall and subsequently decomposition might be a respon-
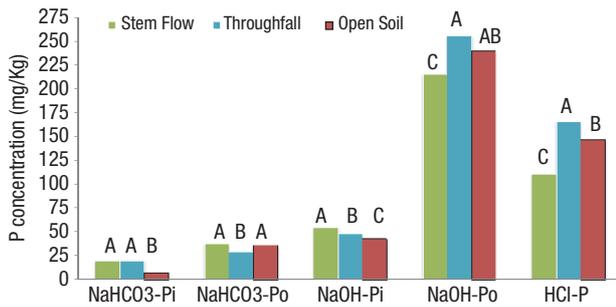
Figure 3. Influence of Blue Pine canopy on $NaHCO_3$, NaOH, and HCl extractable phosphorus (P) fractions (Pi=inorganic; Po=organic). Mean followed by different letter/letter are significantly different from each other at $p < 0.05$.

sible factor. We believe a combination of both dust and litter fall was responsible for the changes monitored on water soluble P fractions.

NaOH extractable P fractions underneath Blue Pine canopy

After the first two fractions which were extracted with mild extracting solutions (distilled water and 0.5M $NaHCO_3$), left over soil residue was extracted first with NaOH and subsequently with HCl solution. The increased strength of these solutions would extract those pools of P which were held with greater tenacity with the soil components or had limited solubility and thus would probably have limited bioavailability and more residence time in the soil environment. Thus, these fractions might enable us to find any fingerprint if present regarding the contribution of dust towards P pools in the current study. The data regarding the influence of canopy related treatments on NaOH extractable Pi and Po are also presented in Fig. 3. The results showed that soil samples collected from area influenced by stemflow had the highest amount of 60 mg P kg^{-1} Pi followed by 50 mg P kg^{-1} in the throughfall and 40 mg P kg^{-1} in the soil samples collected from open field. All three treatments were significantly different from each other. Since, Pi extracted with NaOH solution consisted of forms which were precipitated with Al and Fe or adsorbed to the surface of their oxides and hydroxides. These forms of P are generally having poor solubility in the soil environment (Lindsay, 2001). Hence these forms can persist longer period of time in the soil system. Since, dust samples also had large amount of this P fraction (Fig. 1B), therefore its deposition on the trees and its subsequent transfer by rain water will enrich surface soils with this P fraction in respective zone of the canopy related treatments. Significant higher Pi was detected in both canopy related

treatments than in control soil. We could again possibly ascribe this variation in P fraction to the contribution of dust as well as to relative higher intensity of weathering rate underneath the canopy due to better temperature and moisture regimes. The possible explanation might be significant more acid environment resulted from better moisture regimes in the soil samples under the canopy (Fig. 4) which might resulted in increased soluble Fe and Al concentrations which eventually had reacted with other soluble forms of P and precipitated it as secondary minerals of Al and Fe phosphates and thus contributed extra amount of P than what dust might have contributed especially in zones influenced by stemflow.

The Po fractions extracted with NaOH solution are generally referred to as humic P which has low decomposition potential in the natural soil environment. The litter fall and its cycling resulted in significant higher levels of Po in soil samples collected from the throughfall compared to other treatments (Fig. 3). The amount of Po also followed the same pattern as were seen under previous two extracting solutions (distilled water and $NaHCO_3$). It suggested that top forest soil regularly received huge inputs of litter fall from the main Blue pine trees and from other vegetation on the forest floor and resulted in buildup of higher levels of Po on the top surface soils. Although both Pi and Po fractions extracted with NaOH are resistant forms of P, but can serve as important pools of bioavailability as decomposition and pedogenesis might liberate this P over time for the forest trees in this temperate forest (Cross & Schlesinger, 1995; Schlesinger, 1997).

HCl-extractable Pi fraction underneath Blue Pine canopy

The results regarding the influence of stem flow and throughfall on HCl-extractable Pi fraction underneath a Blue Pine canopy are presented in Fig. 3. The highest amount of HCl- Pi fraction was 165 mg P kg^{-1} and was monitored in the soil samples influenced by throughfall, followed by 148 mg P kg^{-1} and 125 mg P kg^{-1} in the open field soil and stemflow in decreasing order respectively. The mean values of all treatments were significantly different from each other. The P bearing minerals extracted with 1M HCl are generally Ca –phosphates which are extremely low in solubility and not extracted with previous solutions used in the study (water, $NaHCO_3$ and NaOH). The most prominent minerals belong to this group are known as apatites which are further classified as chlorapatite, fluorapatite, hydroxyl–apatite which based on the presence of Cl, F or OH$^-$ in the mineral structure and are present in huge quantities in soils of
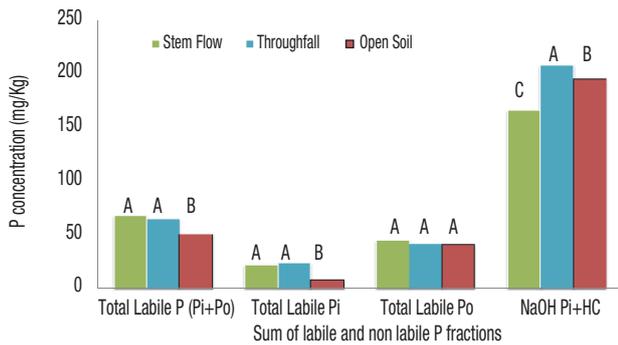
Figure 4. Influence of Blue Pine canopy on labile and non-labile soil phosphorus (P) fractions (Pi=inorganic; Po=organic). Mean followed by different letter/letter are significantly different from each other at p<0.05.

arid region which are developed under least or at moderate rate of weathering intensity (Sposito, 2008). Therefore, their content can decline in the soil environment conducive for weathering (Walker & Syers, 1976). Significant higher quantities of HCl-Pi fraction was observed in our soil samples influenced by throughfall than in soil samples collected from open field which suggested input of these P- bearing minerals from some external sources. The external sources could be in the form of leaching of P compounds from the leaves, through litter fall or dust intercepted by the leaves and leached on the ground surface through rain water. The probability of leaching of P compounds from the leaves would be minimal as P inside cells is tied up in various forms of organic compounds. The role of litter without doubt is important in the cycling of P in most ecosystems especially in tropical forests which grow on P deficient acid soil. In this study, the result of $NaOH-P_o$ fraction partly correlates with the same fraction in the dust sample. Since the temperate forest was present on soils which were rich in apatite (HCl-P) and at intermediate stage of weathering and had above optimum levels of bioavailable-P (water + $NaHCO_3-P_i$ and P_o) which support the growth of these forest trees and thus might result in litter with narrow C:P ratios. Two scenarios might happen, firstly microorganisms will decompose the litter but the Po would not mineralized due to adequately present in the soil system and thus will conserve in the organic form as depicted partly in $NaOH-P_o$ fraction as well as supported by statistical similar levels of soil organic matter for all canopy related treatments in this study. Secondly, the release of Pi during decomposition might undergo reactions with Ca, Mg, Al, Fe etc and results in the formation of secondary minerals of phosphates. But the tendency of such formation in carbon rich surface horizons are less because decomposition by microbial activities will results in various organic acids and other chelating agents which might interact with

aforementioned cations and keep this P in soluble forms. This is supported by the findings of Pierzynski et al., (1990) which suggest the P generally present in amorphous / poorly crystallized forms in organically amended soils. These phases could easily be extracted by distilled water or mild extracting solution of $NaHCO_3$. Therefore, the only viable explanation left at our disposal to support increased levels of HCl-Pi fraction is the atmospheric dust which is intercepted by the canopy. This was also supported by the fact that both dust samples collected in the area also had large amount of HCl-Pi fraction (Fig. 1A). It has been reported that entire growth of Amazon forest in the tropics is depended on huge annual interception of dust containing apatites like minerals originated from the Saharan desert in North Africa (Swap et al., 1992). Similarly, dust originated from Asia can also contribute a significant amount of P in maintaining productivity of forests in highly weathered Oxisols located in Hawaii islands in USA (Pett-Ridge, 2009; Chadwick et al., 1999). Our findings suggest that not only the contribution of dust towards P inputs in the temperate forest is large but HCl-Pi fraction of surface soils can also be influenced by throughfall which can be used to asses dust P input into forest ecosystem. Significant less amount of HCl-Pi fraction in soils collected from the area influenced by stemflow suggest more dissolution of apatites like minerals. This was also supported by data on soil pH (Fig. 4) which was most acidic of all treatments in vicinity of stemflow which could favor increased solubility of sparingly soluble apatites. The results of our study are in conformity with the findings of Singer et al. (2004) and Eijsink et al. (2000) who suggest that the major forms of phosphorus in soil-derived dust are minerals from apatite group and, to a lesser extent, P bound to iron oxide and hydroxide minerals.

Blue Pine canopy and soil electrical conductivity (EC1:5)

The highest value of soil EC was 250 μS cm⁻¹ in canopy related treatments and found in soil samples influenced by throughfall, followed by 220 and 170 μS cm⁻¹ for the stemflow, and open field soil in decreasing order respectively (Table 1). The means of all treatments were significantly different from each other. We can offer three explanations responsible for variations reflected in soil EC values. Firstly, some cations and anions such as K, Ca, Cl and NO_3 are highly mobile inside cell which may leak out from the cells when immerse in rain water and become part of water running along stemflow and throughfall and thus enter the soils underneath plant canopy. Secondly, dust depos-

ited on the surface of leaves and bark can also have soluble concentrations of anions and cations (EC values were 3775 µS /cm and 3941 µS /cm for lower and high elevation dust samples respectively). Thirdly, decomposition / mineralization of litter on the soil surface might also release soluble salts into the soil. Each of these processes has its share in increasing soluble salts underneath the plant canopy.

All canopy related treatments were statistically similar but we had relatively more residual and total P in the soil samples collected from soils influenced by stemflow and throughfall compared with open field soils (data not shown). We can partly ascribe all these variations to the buildup of levels of humus in soil as the end product of decomposition from annual litterfall and input of recalcitrant fraction of P associated in dust.

Labile and non-labile soil P fractions underneath Blue Pine canopy

The total labile fractions of Pi and Po consisted of sum of water and $NaHCO_3$ extractable fractions and their grand total in the form of Pi+Po fractions while non labile fractions consisted of NaOH and HCl extractable Pi forms and data on these fractions are presented in Fig. 4. The results suggested that total labile Po concentrations were not influenced by any treatments owing to heavy contribution of surface litter on the forest floor. As for as the total labile Pi was concerned, significant more Pi was contributed by both throughfall and stemflow than in the open field soil. The grand labile P fractions (sum of labile Pi+Po) followed trend similar to what was seen in total labile Pi and differences were only attributed to the variations detected in Pi fractions. The amount of these labile P fractions (grand total) were in the range of 50 to 60 mg P kg^{-1} depending upon the treatments under study which further suggest that top soil in this temperate forest has more than adequate amounts of P in the labile pool for the growth of surface lower plants.

As for as non-labile or less available P pools were concerned, significant difference in means were detected in the soil samples collected from the aforementioned treatments underneath the Blue pine canopy. Presence of significant higher amounts of P in the soils samples influenced by throughfall than open field treatment suggests the role of some external input into the system. There can be two available sources in this system in the form of either litterfall and or dust contribution.

The P fractionation of dust samples suggest presence of relatively large amount of stable P in both extractions (NaOH and HCl; Fig. 1A) plus intercep-

tion of large amount of dust by Blue Pine canopy might be responsible for significant build up of these fractions in surface soils impacted by throughfall treatment. Significant less amount of these stable P fractions in soils impacted by stemflow than in open field soil was attributed to dissolution of some of these mineral in the acidic environment in and around the stemflow. However, we believe from our data that these two fractions or especially, HCl-Pi fraction in the surface soils impacted by throughfall can serve as good fingerprint to detect the contribution of dust towards P cycling or build up in this forest ecosystem. Other pathway that could significantly build up P in the surface soils consisted of internal cycling in the form of litter fall.

Conclusions

The amount of dust input into the temperate forest is staggering during dry months of the year and values are ranged from 43 kg at lower elevation to 20 kg ha^{-1} $year^{-1}$ at higher elevation sites respectively. The results of P fractionation of the dust samples suggest both labile and non-labile P fractions along with total P concentration are higher in dust collected from lower than from higher elevation site but both dust samples are rich in apatites suggesting that these dust particles might have originated from surface soils located in dryer region. The canopy related processes of blue pine is significantly influencing the P fractions in the surface soil with significant higher concentrations of all P fractions in the stemflow and throughfall than in the control soil. The significant higher concentration of P in pools extracted with harsh reagents such NaOH and HCl in soils samples influenced by stemflow and throughfall which reflected the contribution of dust in this forest because P fractions extracted with aforementioned reagents was not only present in the larger amounts in the dust but were also have longer residence time in the soil environment.

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