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Land Use Impact on Bioavailable Phosphorus in the Bronx River, New York

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ABSTRACT

Various forms of phosphorus (P) could become bioavailable such as from desorption, dissolution and enzymatic hydrolysis. Potential bioavailable P estimation is critical to minimize eutrophication in freshwater systems. Thus, this study was conducted to predict potential bioavailable P in the water columns and sediments and their relations with enzymatic hydrolysis, and estimate impacts of land use and anthropogenic activities on P bioavailability, P transport and water quality in the Bronx River, New York, USA. In sediment samples collected in 2006, total P (TP), total inorganic P (IP), total organic P (OP) and bioavailable P (BAP) were in highest concentrations in sites located at Bronx River Valley upstream in Westchester (site 2), Troublesome Brook (TB, site 4), Sprain Brook (SB, site 7b) and Bronx River estuary near Sound View Park (site 14) respectively. Also, phosphodiesterase and native phosphatases (PDEase and NPase) hydrolyzed distinguishingly high amounts of OP or enzymatically hydrolysable P (EHP) in samples from sites 4, 7b, 10 (New York Botanical Garden) and 14. Microbial P was in negative values (caused by different bacteria and microorganisms could not be paralyzed by chloroform), and the most negative concentrations were appeared at sties 4 and 14. Spatial comparisons among different locations showed distinguished characteristics in tributaries and estuary. In sediments collected in 2007, TP, BAP and IP were in highest concentrations at sites 7-SB, 11-Bronx Zoo, 12-East Tremont Ave Bridge where fresh and saline water meets, 13-estuary facing Hunts Point Waste Water Treatment Plant (HP WWTP) and 14-estuary along Sound View Park. Besides, PDEase-P highest concentrations appeared at sties 7, 13 and 11, NPase-P concentrations were highest at 7 and 11. Microbial P was highest at sties 11 and 14. Spatial variations showed that higher P content and more intense enzymatic hydrolysis in silty clay finer sediments at site 7, 11 and 13. Temporal variations between the two years' data showed land use and other anthropogenic factors' impacts on P transport in river and deposit in sediments. Analysis of the river water samples showed that average soluble reactive P (SRP, 67 $\mu g \cdot l^{-1}$) in 2006 and SRP (68$\mu g \cdot l^{-1}$) in 2007 both were greater than background P concentration in most natural water (42 $\mu g \cdot l^{-1}$). Water TP (TP_{water}) peaks showed at sites 7 and 13 in 2006; TP_{water} were highest at sites 6 and 13 in 2007; showing high P content in water columns at TB and estuary downstream in both years. Similarly, native phosphatases hydrolyzed substantial amounts of OP in the water samples at optimal temperature in both years, indicating potential threats to river water quality as the rise in water temperature may be imminent due to global climate change. Overall, incidental sewer overflows at Yonkers, oil spill at East Tremont Avenue Bridge, urban constructions at Woodlawn Metro-North train station, fertilizer application at WC lawns and gardens, animal manure from the zoo, combined sewer overflows (CSOs), storm water runoff from Bronx River parkway, and potential pollutants from East River all appeared to be influencing spatial and temporal variations on P transport in the river. Research data from this study could be shared among United States Environmental Protection Agency (USEPA), New York City Department of Environmental Protection (NYCDEP), New York State Department of Environmental Conservation (NYSDEC) and Bronx River Alliance to help make effective environmental policies on P application, in turn, improve water quality of the Bronx River and restore its ecology.

Keywords: *Potential Bioavailable P, Enzymatic Hydrolysis, Microbial P, Enzymatically Hydrolysable P, Spatial and Temporal Variations*

1. Introduction

Streams-nutrients occur naturally in water refereed to 'background' concentration. Anthropogenic discharges such as artificial fertilizers, manure, and septic systems effluent elevated concentrations. In U.S., five studied nutrients including nitrate, ammonia, total nitrogen, orthophosphate, and total phosphorus exceeded back concentrations at 90% of sampled streams draining agriculture and urban watersheds [1]. The highest total phosphorus concentrations were in streams in urban and agricultural areas, and the median concentration (250 $\mu g \cdot l^{-1}$) was around 6 times greater than background concentrations (42 $\mu g \cdot l^{-1}$). In urban area, P sources were runoff from urban storm water runoff, golf courses, residential lawns, construction sites, sewage overflow (treated wastewater effluent), and septic-system drainage. In agricultural area, P sources were associated with fertilizers and manure intensive applications [1-3]. Phosphorus from different natural and anthropogenic sources discharged to river has temporal and spatial variations [4].

Bioavailable P (BAP) is the total available P that could be transformed into an available form from naturally occurring processes [2]. Bioavailable P could be defined as the total of readily available P ($NaHCO_3$-P) and moderately available P (NaOH-P) [2,5]. Different P sources have different potential ecological impact on river systems [5]. Input of P to surface waters should be reduced in order to control eutrophication and algal growth [5]. Phosphorus bioavailablility is dependent on P input source; reducing P inputs could reduce algal biomass in river systems [5]. The BAP analysis could help to minimize eutrophication in rivers [5].

Orthophosphate ($H_2PO_4^{2-}$, HPO_4^{2-} , or PO_4^{3-}) is the major available P source for plant uptake [2]. Total dissolved phosphorus (TDP) includes dissolved reactive P (DRP) and dissolved unreactive P (DUP) is filterable through a 0.45 µm membrane filter [2]. The soluble P is retained, transformed and assimilated within the river channel, resulting in the spatial variations along the river [4]. Particulate P (PP) could be mobilized to orthophosphate from physical, chemical and biochemical processes, such as desorption, dissolution and enzyme hydrolysis; these processes are affected by pH, temp, and redox et al. [2,6]. Potential bioavailable PP may have higher bioavailability than immediately available P or DRP (<10 $\mu g \cdot l^{-1}$) [2]. Enzymatic hydrolysis is a powerful technique to characterize hydrolysable OP in waters and sediments [7-12]; and enzymatic hydrolysis estimates hydrolysable (bioavailable) OP in sediments and water [7,12-14].

Enzymatically hydrolysable phosphorus (EHP) was composed of labile monoester phosphates, diester phosphoates and a phytase-hydrolysable fraction that includes myo-inositol hexakisphosphate (phytic acid); EHP is an important portion of DOP, represented a significant and potential BAP fraction [15]. Dissolved organic phosphorus (DOP) plays an important role in natural water ecosystems [16]. Hydrolyzable OP could be classified by using phosphatase enzymes to simple monoester P, polynucleotide P, phytate-like P, and non-hydrolyzable P [7]. Quantifying BAP can predict EHP and potential BAP, which could be achieved by enzyme hydrolysis, sequential extraction, ^{31}P-NMR (Nuclear Magnetic Resonance) and other methods [7]. Enzymatically hyrolyzable P (EHP), the monoesters of orthophosphoric acid, is the major organo-P in natural waters. It is important to know that EHP portion in DOP, to predict the bioavailability of P in water systems [16-17]. Kobori and Taga [18] found that EHP proportation relative to DOP was between 18% - 50% in water systems where biological activity was high.

Effective regulation of P supply could help management ecosystem and achieve good water quality [4]. Phosphorus retention in rivers includes biogeochemical and physical processes associated with biotic and abiotic assimilation, which remove or transport P downstream; P retention in rivers is varied temporally and spatially [4]. Anthropogenic P inputs impact downstream communities [4]. Phosphorus cycling and transport in the river were controlled by physico-chemical factors (such as sorption/desorption, mineral precipitation and dissolution, advection and diffusion) and biological factors (such as microorganism activities) [4]. P cycling in the Bronx River was controlled by these physico-chemical and biological factors (**Figure 1**).

This study was conducted to predict potential BAP in the water columns and sediments and their relations to enzymatic hydrolysis; as well as estimate impacts of land use and anthropogenic activities on P bioavailability, P transport and water quality in the Bronx River, NY. Spatial variations along the river and the temporal variations between the two years were studied, which showed that sediment texture, land use changes, oil spill, raw sewer discharge, fertilizer application and management, animal manure management, constructions, WWTP sewer overflows, pollutants from the East River resulted in spatial

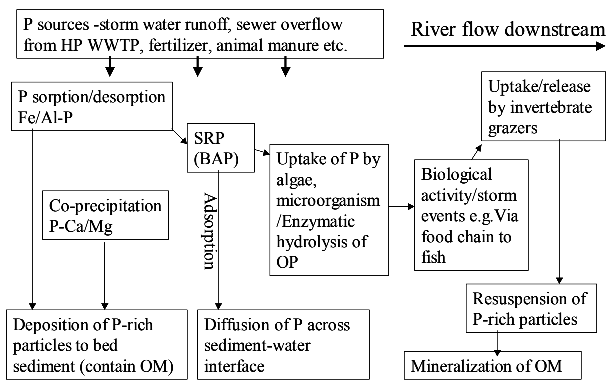

Figure 1. P cycling process in the Bronx River (modified from Withers and Jarvie, 2008).

and temporal variations.

2. Material and Methods

2.1. Study Area

The Bronx River, approximately 20 miles (32 km) long from its headwaters at Davis Brook and Kinsico Dam in Westchester County (WC) though the Bronx, flows into East River [19]. Davis Brook became the new headwater of the Bronx River after the construction of Kensico Dam. Kensico Dam was built in 1915 reduced a quarter of the water flowing into the Bronx river, and the reservoir covers 13 square miles (33.67 km^2) and holds 30 billion gallons of water for several Westchester townships and New York City (NYC) [20]. Watershed of the Bronx River in WC is 23,020 acres (93 km^2), and in NYC is 5110 acres. There are over 100 stormwater and CSOs and other discharges to the river from WC to East River; Hunts Point Wastewater Treatment Plant (HP WWTP) services this area [19]. Fresh and saline water in the Bronx River does not meet dissolved oxygen and coliform standards [19]. The pollutants in the tidal portion are floatables, pathogens and oxygen demand, and this portion was affected uses as being aesthetics, aquatic life and reaction. The main pollutants sources in freshwater section of the Bronx River are floatables, debris, oxygen demand and pathogens [19]. Pathogen was the main pollutant in the Bronx River, with urban storm runoff and CSO as the main pollution source [21]. NYCDEP constructed a four million gallon triple barrel CSO storage conduit with downstream outfall relocation in 2005 [19]. New York City Department of City Planning (DCP) designed the old industrial area such as western river bank at the mouth and the mouth including Sound View Park as a Special Natural Waterfront area [19].

2.2. Water and Sediment Sample Collection

Representative sediment samples were collected in the Bronx River from the origin at Davis Brook to the Sound View Park estuary at 15 sites (**Figure 1-2**) in July/August 2006 and 2007. Each site was located with a Global Position System (GPS) unit, and the coordinates are provided (**Table 1**). A Core Sampler (diameter 8 cm; length 17 cm) was used to obtain the bed sediments. The sediment samples were sealed in gallon zipper bags. Water samples were also collected in the Bronx River from Davis Brook to estuary at 14 sites (not including 7B Paxton Ave Southwest because the water is at site 7B was considered the same as site 7 Paxton Ave South) using 1-gallon DDI pre-washed water bottles. Both the sediment and water samples were transported to Environmental Laboratory of Department of Environmental, Geographic and Geological Sciences at Lehman College of The City University of New York at the end of each sampling day, and stored at 4ºC in a Fisher Scientific Isotemp Laboratory Refrigerator until further experimentation. The sediment samples were immediately homogenized and

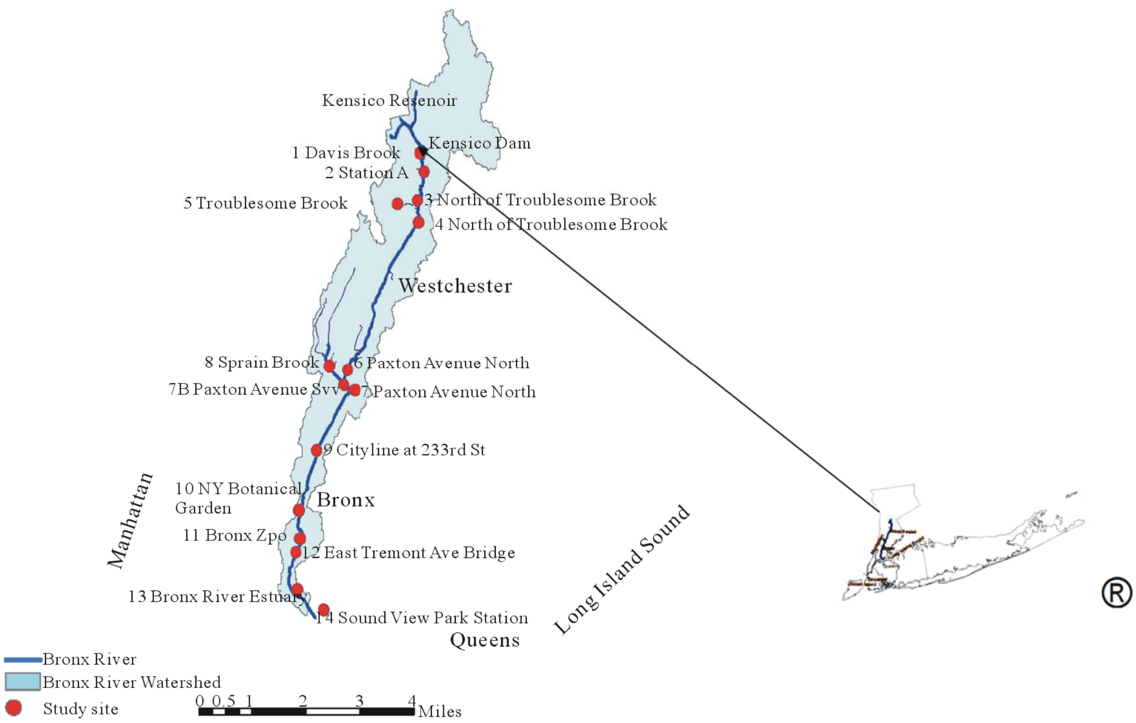

Figure 2. The Bronx River study area and 14 sampling sites along the river.

Table 1. Bronx River sampling sites locations and geographic coordinates.

Site#	Location	Latitude(North)	Longitude(West)
1	Davis Brook, Valhalla	41º04'23.63"N	73º46'20.04"W
2	Station A (Virginia Rd)	41º03'43.40"N	73º46'24.80"W
3	North of Troublesome Brook	41º02'15.58"N	73º46'37.99"W
4	South of Troublesome Brook	41º02'15.40"N	73º46'38.39"W
5	Troublesome Brook	41º02'16.24"N	73º46'39.58"W
6	Paxton Ave North	40º56'19.20"N	73º50'15.11"W
7	Paxton Ave South	40º56'19.20"N	73º50'15.11"W
7B	Paxton Ave Southwest	40º56'19.20"N	73º50'15.11"W
8	Sprain Brook	40º56'19.20"N	73º50'15.11"W
9	233rd St City Line (between Westchester and Bronx)	40º53'42.74"N	73º51'43.77"W
10	New York Botanical Garden (old snuff mill)	40º51'34.42"N	73º52'33.70"W
11	Bronx Zoo (south of Mitsubishi waterfall, north of Gate B, Bronxdale Parking lot)	40º51'10.20"N	73º52'27.45"W
12	East Tremont Ave Bridge (East Tremont Ave& Boston Rd)	40º50'26.47"N	73º52'40.95"W
13	Bronx River Estuary (old Sound View Park water testing station, facing meat and fish wholesale markets)	40º48'42.89"N	73º52'07.30"W
14	Sound View Park Station	40º48'28.89"N	73º51'33.67"W

saved in waterproof double-track zipper bags (10.2 × 15.2 cm; made by Fisher Scientific Co., USA), and stored at 4˚C until they were used for further analysis. A portion of each homogenized sediment sample was dried at 70˚C for 72 h, thereafter, finely ground and used for selected physico-chemical analysis (17, 22). The fresh water samples were analyzed of EC, pH, SRP, OP and TP in 28 days after sampling. The water samples were also put in 25 ml vials and frozen for future analysis.

2.3. Assessment of Potential BAP

Sediment samples were analyzed for EC, pH, total organic matter (OM), TP, SRP or (total IP = Pi) and OP. Sediments were sequential extracted by $NaHCO_3$, NaOH, and HCl, and TP was sum of $NaHCO_3$-P, NaOH-P, HCl-P and residue-P. The sum of $NaHCO_3$-P and NaOH-P was considered as BAP here [6,23-25]. Sediments were hydrolyzed by commercial PDEase and NPase at 37˚C [12]. Phosphorus sorption characteristics were determined from batch incubation experiments under aerobic conditions [26-27]. Water samples were analyzed for EC, pH, for SRP using ascorbic color metric method [28]; ash TP was determined by persulfate digestion block method [29] for comparison with sum TP, and OP was calculated from the difference between sum TP and SRP [25]. P compounds in sediments were identified by ^{31}P-NMR. NPase hydrolyzed water sample at 37˚C (modified methods from [11,15,30]). Enzymatic method together with sequential extraction provides a tool to understand sediment P and water P [7].

3. Results and Discussion

3.1. Headwater

Site 1, headwater of the Bronx River is located at Davis Brook, Valhalla, beside the railway station. Sediments collected in this site during summer 2006 were sandy texture. The only major P compound in sediments is GlyP [17]. Bioavailable P (sum of $NaHCO_3$-P and NaOH-P, 146 $mg\cdot kg^{-1}$), sediment total IP (Pi) (393 $mg\cdot kg^{-1}$), sediment total organic P (Po) (99 $mg\cdot kg^{-1}$) and sediment TP (sum of P fractionation of $NaHCO_3$-P, NaOH-P, HCl-P and residue-P, 492 $mg\cdot kg^{-1}$), plus PDEase-P (42 $mg\cdot kg^{-1}$) and NPase-P (41 $mg\cdot kg^{-1}$) [12] were blow average (BAP-246 $mg\cdot kg^{-1}$, TP-580 $mg\cdot kg^{-1}$, PDEase-P-80 $mg\cdot kg^{-1}$, and NPase-P-59 $mg\cdot kg^{-1}$) but around median level concentrations (BAP-185 $mg\cdot kg^{-1}$, TP-479 $mg\cdot kg^{-1}$, PDEase-P-54 $mg\cdot kg^{-1}$, and NPase-P-44 $mg\cdot kg^{-1}$) among the 15 sample sites (**Table 2** and **3**, **Figure 3**)). Total Pi was 80%, and Po was 20% of TP, which were around average percentages. River water is quite clear in this site; SRP in water (SRP_{water}), OP in water (OP_{water}) and TP in water (TP_{water}) (**Table 5**, **Figure 4**) in were the lowest at headwater [43]. $NPase_{water}$ concentration was the second lowest.

Table 2. Selected physico-chemical characteristics of sediments collected in 2006 and 2007.

#	BAP		Pi		Po		TP		Pi%		Po%	
	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007
	mg·kg^{-1}								%			
1	146 cde	45 f	393 cdef	300 b	99 cd	7 a	492 cdef	306 b	80 abc	98 a	20 abc	2 a
2	315 bc	39 f	538 c	209 b	165 bc	15 a	703 c	219 b	77 abc	95 a	24 abc	6 a
3	145 cde	77 ef	445 cde	381 b	61 d	15 a	506 cde	396 b	88 ab	97 a	12 bc	3 a
4	919 a	66 ef	1205 a	296 b	358 a	22 a	1563 a	311 b	77 abc	96 a	23 abc	6 a
5	95 e	41 f	353 cdef	313 b	46 d	6 a	398 ef	318 b	88 ab	98 a	12 bc	2 a
6	122 de	76 ef	231 f	387 b	58 d	8 a	288 f	393 b	80 abc	98 a	20 abc	2 a
7	86 e	317 c	251 ef	732 b	61 d	4 a	312 ef	735 b	81 abc	99 a	19 abc	1 a
7b	245 cde	69 ef	379 cdef	332 b	145 bc	2 a	523 cde	335 b	72 bc	99 a	28 ab	1 a
8	246 cde	62 ef	324 def	237 b	154 bc	2 a	479 def	239 b	68 c	99 a	32 a	1 a
9	186 cde	44 f	363 cdef	254 b	114 cd	4 a	477 def	257 b	76 abc	98 a	24 abc	2 a
10	185 cde	41 f	373 cdef	252 b	97 cd	4 a	470 def	255 b	80 abc	98 a	20 abc	2 a
11	109 e	601 a	314 ef	1049 b	63 d	3 a	376 ef	1051 b	83 abc	99.7 a	17 abc	0.3 a
12	160 cde	137 de	423 cdef	5360 a	50 d	0 a	473 def	5360 a	89 a	100 a	11 c	0 a
13	289 bcd	171 d	522 cd	604 b	142 bc	17 a	663 cd	621 b	79 abc	97 a	21 abc	3 a
14	435 b	491 b	774 b	1092 b	200 b	21 a	974 b	1106 b	79 abc	98 a	21 abc	2 a
Ave	246	152	459	787	121	9	580	793	80	98	20	2
median	185	69	379	332	99	6	479	335	79	99	21	2

Table 3. Enzymatic hydrolysis and microbial activity of sediments collected in 2006 and 2007 (Wang and Pant, 2010b and 2011a).

#	PDEase-P		NPase-P		Microbial P		OM		pH		EC	
	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007
	mg·kg^{-1}						%				μs·cm^{-1}	
1	42 cde	14 d	41 bc	83 b	–72 ab	1 d	0.7	1	7.1	7.2	66	17
2	68 bcde	73 abcd	0 c	21 b	–56 ab	3 d	3.3	0.5	6.8	7.5	298	9
3	13 e	33 cd	0 c	39 b	–27 ab	8 d	1.9	1.2	6.7	7.4	133	12
4	352 a	76 abcd	170 a	67 b	–154 c	13 d	10.7	1.1	6.5	7.3	342	14
5	25 de	13 d	21 bc	24 b	–15 a	–3 d	0.1	0.3	7.4	7.9	220	34
6	54 cde	26 d	44 abc	41 b	–32 ab	14 cd	0.1	0.8	7.5	7.7	158	60
7	70 bcde	237 a	56 abc	95 b	–13 a	34 bcd	0.3	3.5	7.0	7.1	167	62
7b	137 b	53 bcd	84 abc	37 b	–81 b	7 d	1.7	1	6.7	7.4	160	14
8	101 bcd	45 bcd	49 bc	34 b	–78 b	4 d	1	1.1	7.0	7.8	103	10
9	40 cde	83 abcd	34 bc	30 b	–56 ab	5 d	1.7	0.6	6.8	7.7	209	10
10	118 bc	89 abcd	91 abc	32 b	–84 b	5 d	3.7	0.3	7.0	8.2	108	12
11	33 de	216 abc	44 bc	495 a	–39 ab	82 a	3.2	6.7	6.8	7.1	133	23
12	26 de	15 d	13 bc	13 b	–33 ab	51 abc	3.8	1.1	7.8	7.1	254	13
13	35 de	226 ab	110 abc	46 b	–79 b	6 d	4.9	16.7	7.8	8.2	1917	277
14	91 bcde	63 abcd	122 ab	32 b	–162 c	63 ab	3.6	3.4	7.8	8.3	4290	363
Ave	80	84	59	73	–67	18	2.7	3				
median	54	63	44	37	–56	7.4	1.9	1.1				

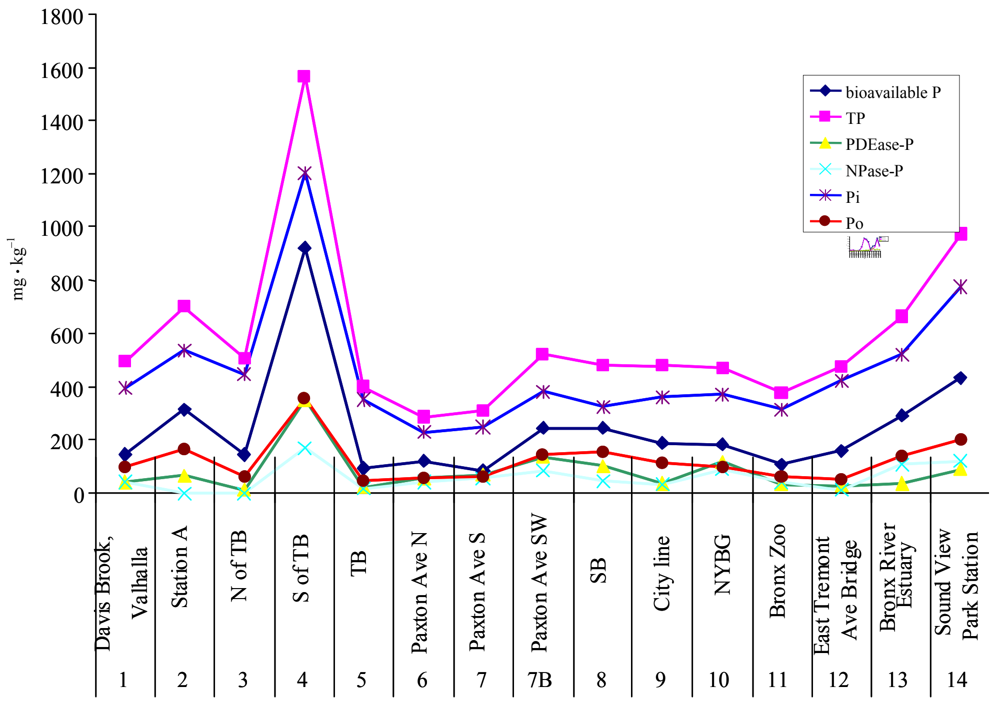

Figure 3. BAP and EHP analysis of sediments collected in 2006.

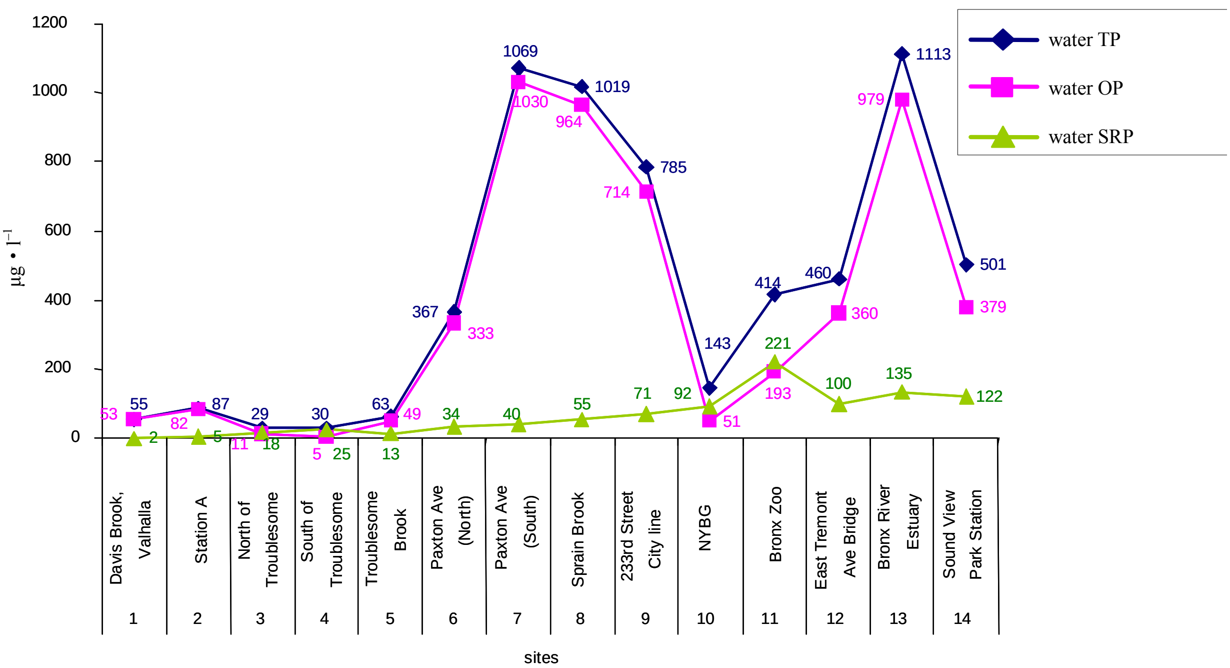

Figure 4. 2006 Water SRP, OP and TP.

Sediments collected in 2007 were also sandy sediments. P compound is GlyP remained the same as 2006 sample [17]. Total P, BAP, and Pi were all lower than median and average concentrations; Po was slightly higher than median and lower than average; and all of these concentrations were decreased from 2006 significantly. Microbial P was lowest (other than site 5) in positive concentrations. PDEase-P in 2007 was less than median and average, and also lower than 2006; NPase-P in 2007 was the third highest (**Table 3**), which was higher than average and median and around twice as in 2006. SRP_{water} increased from 2 in 2006 to 28 $\mu g \cdot l^{-1}$ (lower than median and average) in 2007; OP_{water} (much higher than median and average, third highest) in 2007 was similar as in 2006; TP_{water} increased 1.5 times from 55 to 83 μg·l^{-1} (lower than median and average) (**Table 5**, **Figure 5**). $NPase_{water}$ was the fourth lowest (below average and median), and also decreased from 2006. There is not significant difference between 2006 and 2007 in sediment and water samples at Headwater-Davis Brook, Valhalla.

3.2. Bronx River Valley

Site 2, Station A located at Virginia Road in Bronx River Valley, East of Bronx River Parkway (Pkwy) North (N), beside a bike path in Town of Mt Pleasant. There is a gas station on west of Virginia road. Bronx River Valley has been the major transportation corridor of the region, and people commute with cars, bicycles, and trains [20]. Sediment collected in 2006 was mostly fine sand (33%), silt (19%) and clay (19%) and total fine sediments were up to 71% from granulometric fraction analysis. Bioavailable P (315 mg·kg^{-1}), Pi (538 mg·kg^{-1}, 76% of TP), Po (165 mg·kg^{-1}, 24% of TP), and TP (703 mg·kg^{-1}) (**Table 2**, **Figure 3**) were the third highest concentrations among the 15 sites. NPase-P was nearly zero in concentration, and PDEase-P (68 mg·kg^{-1}) was higher than median (54 mg·kg^{-1}) and lower than average (80 mg·kg^{-1}) (**Table 3**) values of the 15 sites [12]. Major P compound was GlyP, minor P compounds are NMP, PolyN, and IMP [17]. S_{max} was the third highest and Ox-Al was the second highest, Ox-Al associated with OM affected P sorption process [27]. Clay-sized particles and sediments usually have higher sorption of nutrients and pollutants [31]. Both PDEase and NPase-P were strongly correlated with OM with correlation coefficients of 0.745 and 0.683 respectively), correlated TP (r = 0.814, 0.719; p < 0.01), Po (r = 0.872, 0.755; p < 0.01) and BAP (r = 0.887, 0.751; p < 0.01) (**Table 6**), indicating enzyme hydrolysis was related with OM associated BAP [12]. Water samples collected in 2006 showed that SRP_{water} was higher than site 1 but lower than most other sites; TP_{water} and OP_{water} were the highest in the first five sites. SRP_{water} OP_{water} and TP_{water} were higher than in headwater (**Table 5, Figure 4**), while much lower than average and median [14]. $NPase_{water}$ concentration was the highest, indicating potential threat on river water quality when temperature increases [8,9,11,12]. This site is around 1 mi from headwater, however the P characteristics were much different from site 1. Residential in Town of Pleasant commute to the city by automobiles and the gas station activity could affect on P transport and deposit here [1].

Sediment collected in 2007 was sandy sediment, and

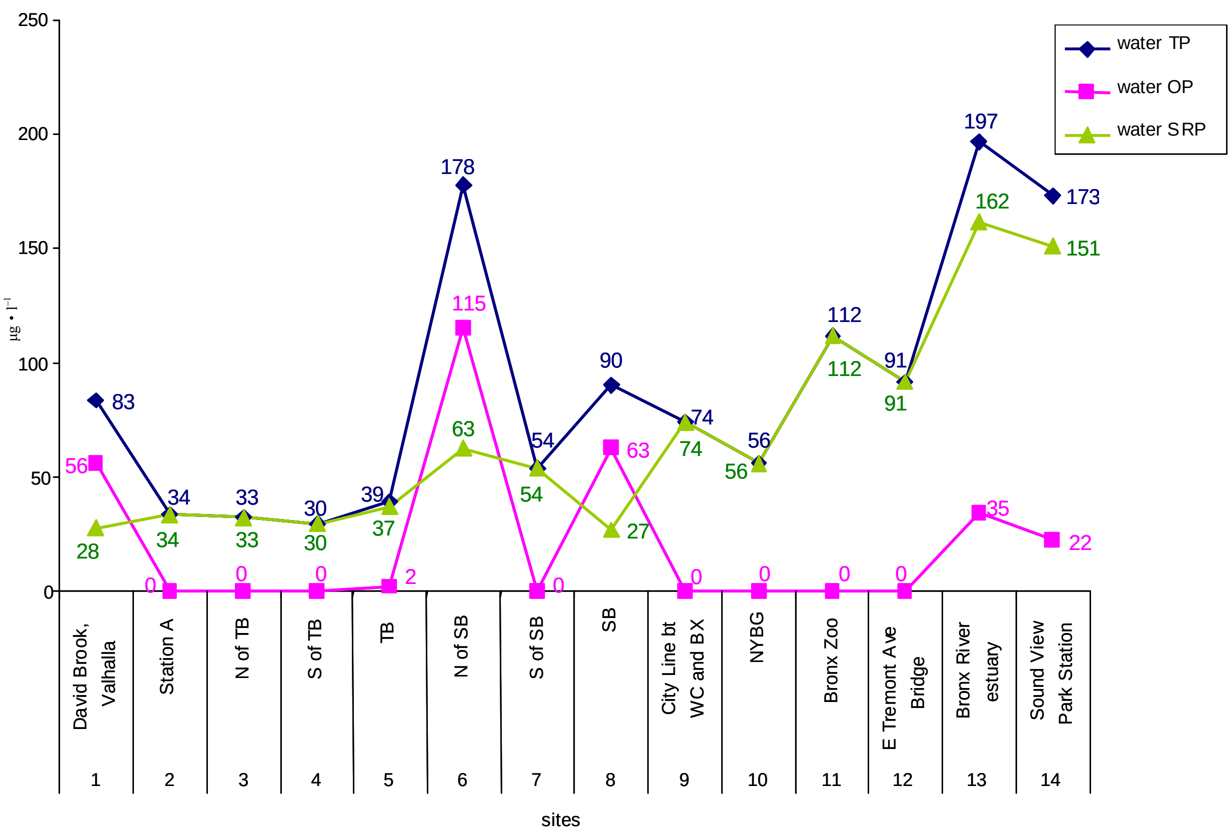

Figure 5. 2007 Water SRP, OP and TP.

its texture was different from that of 2006. GlyP is the only P compound in 2007, and trace amounts of NMP, PolyN, IMP in 2006 not showing up here [17]. Bioavailable P, Pi, and TP concentrations were the lowest among the 15 sites; TP, BAP, OM, Pi and Po were all decreased significantly from 2006 (**Table 2**), and other than Po were all lower than median and average concentrations. PDEase-P and NPase-P were increased from 2006 and both lower than median and average. TP_{water} in 2007 was the third lowest (lower than median and average concentrations), lower than background concentration in natural waters, also lower than water samples collected in 2006. SRP_{water} increased from 2006, which was still lower than median and average; OP_{water} in 2007 is 0, and only SRP_{water} in this site. $NPase_{water}$ (Table 5, Fig.5) was higher than median but lower than average, and much lower than that of in 2006. Perhaps the decreased OP_{water} was the reason of decreased EHP and consequently decreased NPase hydrolysis activity in water column [7, 15,16].

3.3. Troublesome Brook Tributary

Site 3, 4, and 5 were located at Troublesome Brook tributary (TB), east of Westchester County Center and Bronx River Parkway (Pkwy) North (N). Westchester County Center was built in 1930, adjacent to the Pkwy [20]. Sediment textures were different among these three sites. Fine sandy sediments (coarse dand 19%, medium sand 26%, and fine sand 41%) collected in 2006 at site 3 N of TB, silty clay (fine sand 38%, silt 30%, and clay 17% from Granulometric fraction analysis) in site 4, S of TB, and sandy sediments in site 5 (coarse sand 42% and medium sand 16%), TB. Site 4 is a very representative tributary site, and it had highest TP, Pi (1205 $mg{\cdot}kg^{-1}$, 77%), Po (358 $mg{\cdot}kg^{-1}$, 23%), BAP (919 $mg{\cdot}kg^{-1}$) (Table 2), PDEase-P, NPase-P, OM, Ox-Al, S_0; the third highest Ox-Fe, HCl-Ca and HCl-Mg, and the lowest S_{max}. Major P compound was DHAP, and GlyP, NMP, and IMP were in trace amounts [17]. BAP% was also the highest of 59%, which was higher than BAP% in Great Lake tributaries (25% - 50%) [31]. Al, Fe, Mg, Ca associated with OM affected P sorption. Original sorbed P-S_0, P absorption energy K_f and bonding strength (k) were highest among 15 sites [27]; S_{max} was the lowest among the 15 sites, relative high EPC_0 values (more than average 0.36 $mg{\cdot}l^{-1}$), indicating there was high original sorbed P-S_0 in sediments that was correlated with P absorption energy-K_f (0.883), constant relates to bonding strength-k (0.569), and sorption coefficient K_d (0.796) meanwhile there was low sorption capacity in sediments [27]. Site 4 had the second most negative value of microbial P. Wang and Pant [25] mentioned that the negative values of microbial P were possibly caused by different microorganisms or bacteria which were resistant to cell lysis/inhibition, and they could not be paralyzed by chloroform. Those resistant microorganisms and bacteria continue to proliferate and uptake the SRP/BAP resulting in negative values. The more negative the value, the more resistant microorganism/bacteria biological activities occurred and uptake more P [4,25]. The high negative microbial P at site 4 indicated there were more P microbial available, and enzyme could hydrolyzed those microbial P to SRP for plants use. PDEase-P was strongly correlated with BAP, TP, Pi, Po, k, K_f , and OM at $p < 0.01$, S_0 and Ox-Al at $p < 0.05$. NPase-P was correlated with BAP, TP, Pi, Po, OM at $p < 0.01$, with EPC_0, S_0, k, and K_f at $p < 0.05$ (**Table 6**), indicating enzyme hydrolysis, microbial activity, BAP, potential BAP, and P sorption processes were correlated and impacted each other. PDEase-P and NPase-P were strongly correlated with S_0 (r = 0.589, 0.556; $p < 0.05$), NPase-P was negatively correlated with microbial P (r = –0.677; $p < 0.01$) (because microbial-P concentrations were in negative values), and indicating P sorption is connected with microbial activity and enzyme hydrolysis process [4]. Microbial P was negatively correlated (because microbial P were in negative values) with BAP, TP, Po, Pi and NP, indicating that the highest TP, Po, Pi values could probably resulting in a second most negative microbial P, and the more negative value, the more microbial activity could have occurred that might have provided more inherent EHP resulting in highest NPase-P. However, the negative values of microbial P were still need further exploration in the future. It is known that physico- chemical activity such as sorption/desorption and biological activity such as microbial activity/enzyme hydrolysis were interaction each other and controlled P cycling and transport in rivers [4]. Site 4 TB was a narrow small low flow rate tributary that could result in OM and other metal associated P deposition [17]. Clay-sized particles and sediments usually have higher sorption of nutrients and pollutants [31]. Clay-sized sediments are easily suspended and settle slowly, and usually have high sorption rates of OM and cation (Al, Fe, Ca, Mg) associated P [33,39]; and P content increased as sediment size decreased [25, 32]. SRP_{water} was 25 $\mu g{\cdot}l^{-1}$, TP_{water} was 30 $\mu g{\cdot}l^{-1}$, OP_{water} was 5 $\mu g{\cdot}l^{-1}$ (**Table 5**), and all of them were lower than average and median concentrations. Algal growth is linear correlated with P concentration ranged from 10 to 200 $\mu g{\cdot}l^{-1}$ [5], indicating that there was potential possibility of algal growth at this site.

Bioavailable P and TP in sites 3 and 5 were much lower, and significantly lower PDEase-P and NPase-P concentrations than most of other sites (lower than median and average concentrations). Microbial P was in lower negative concentrations, much less negative than concentration in site 4. Phosphorus compounds in sites 3 and 5 were controlled by GlyP, and minor P compounds in site 3 is Poly-N and Pyro-P; and the Pyro-P was possibly related with P fertilizer application from lawn and golf course along Bronx River Pkwy near city of White Plains [5,17]. SRP_{water}, OP_{water}, and TP_{water} were quite low in TB estuary sites [43], and TP_{water} was higher in site 5 than sites 3 and 4 that might be caused by the down stream P accumulation in the water column. $NPase_{water}$ concentrations in these three TB sites were distinguished higher than other freshwater sites, indicating that OP could become bioavailable during increased temperature and changed hydro-climatic conditions [8-12].

In 2007, sandy sediments were collected in sites 3, 4 and 5; texture in site 4 showed different pattern. Total P, BAP and Pi were higher at site 3 (slightly higher than median concentration and lower than average) than sites 4 and 5 (both lower than median and average). Overall, Pi, Po, TP, and BAP of these three TB sites were much lower than values in 2006 (**Table 2**). P compounds in site 4 showed difference that main compound was GlyP in 2007 instead of DHAP in 2006 [17]. PDEase-P, NPase-P, and microbial P all had higher concentration at site 4 than sites 3 and 5 in 2007 (**Table 3**). NPase-P was significantly correlated with microbial P (r = 0.718, p < 0.01), meaning that microbial activity was associated with enzyme hydrolysis [12]. Compared with PDEase-P and NPase-P in 2006 at site 4, both values decreased in 2007; sediment texture changed from silty clay dominated to sandy sediments. It was known that small-grained sediments adsorb more OM and OP; therefore increase phosphatase activity in sediments [33]. $NPase_{water}$ concentrations of these three TB sites in 2007 were much lower than in 2006 (Table 5), $NPase_{water}$ at site 3 in 2007 was higher than median lower than average, $NPase_{water}$ of site 4 and 5 in 2007 were all much lower both median and average; SRP_{water} increased slightly in 2007, OP_{water} decreased significantly in 2007 and so did TP_{water}, other than OP_{water} at site 5 (slightly higher than median but much lower than average), all other concentrations in 2007 were much lower than median and average.

3.4. Sprain Brook Tributary

Sites 6, 7, 7b, and 8 were represented Sprain Brook tributary (SB) sites, located beside Sprain Brook Pkwy East of Bronx River Pkwy in Village of Bronxville, south to City of Yonkers. Sandy sediments were found in SB estuary (site 7b: coarse sand 42%, medium sand 34%, total around 76%). Other than site 7B, GlyP was the major compounds at sites 6 (PolyN and IMP were in trace amounts other than GlyP), 7 and 8. NMP was the major P compound at site 7b, PolyN, NMP, and Pyro-P were minor P compounds in trace amounts. The raw sewer discharge from city of Yonkers since 2002 could possibly result in the various OP and IP compounds in SB sediments [17,34]. Site 7b had the highest TP, Pi, PDEase-P, NPase-P, Ox-Al, Ox-Fe, OM, EPC_0 and the most negative microbial P values among these four SB sites. Site 8 had the highest Po and BAP among SB sites. Strong correlations between PDEase and BAP, TP, Pi and Po, between NPase-P and BAP, TP, Pi and Po mean that if more P bioavailable, predicted there was more enzymatically hydrolysable OP [7,13]. Sites 6, 7 and 8 had comparatively higher NPase-P and PDEase-P (**Table 3**) than most of other sites (PDEase: Site 6-close to median value, site 7, between median and average, site 8-higher than average; NPase-site 6, 7, and 8 all close to median value); and sites 6 and 7 had comparatively lower values of BAP and TP (all lower than median, and Site 7 had the lowest BAP and site 6 had the lowest TP). Site 7b is located at SW of SB; a sandy bar formed here and water flowed very slowly, therefore P accumulation in site 7b could be the reason of more intense enzymatic hydrolysis and microbial activity [12,17,25,27]. TP_{water} of sites 7 and 8 were much higher than other freshwater sites: TP_{water} in site 7 was the second highest and site 8 was the third highest, OP_{water} of site 7 was the highest in and site 8 was the second highest [14]. SRP_{water} at site 7 was 40 $\mu g \cdot l^{-1}$, and it was close to background concentration in natural water (42 $\mu g \cdot l^{-1}$) (**Table 5**); SRP_{water} at site 8 was 55 $\mu g \cdot l^{-1}$ that was higher than background concentration and still lower than national median concentration (250 $\mu g \cdot l^{-1}$) [1]; however the TP_{water} at SB tributary sites 6, 7 and 8 were way higher than national median concentration (site 6 - 1.5 times, site 7 and 8 both around 4 times) and background concentration in natural water (site 6 - 9 times, site 7 - 26 times, site 8 - 24 times). Both TP_{water} and OP_{water} in sites 7 and 8 were first and second highest among fresh water sites; water P levels could possibly associated with the raw sewer spill from City of Yonkers since 2002, possibly the raw sewer accelerating nutrient accumulation [7]; and it could also associated with runoff from golf course and residential activity along the river [1].

In 2007, SB tributary sites showed some different characteristics especially at site 7 compared with 2006 data. Sediments were silty clay sticky type of finer sediments at site 7 in 2007. Site 7 had significantly higher TP, Pi, BAP, PDEase-P, NPase-P, OM and microbial P in 2007 among the 15 sites; other than TP and Pi (around 2.2 times of median but slightly lower than average) all these parameters were much higher than average and medians, higher than all other SB sites 6, 7b and 8. Meanwhile, these concentrations were higher in 2007 than those in 2006. SB sites other than site 7 have lower BAP, TP concentrations in 2007 than in 2006. Po concentrations were much lower in 2007 than 2006 on four SB sites (sites 7, 7b and 8 were lower than median and average; site 6 between median and average). P compounds showed difference, that PolyN, NMP showed up trace amounts in 2007 at site 7, main P compound in 2007 was GlyP instead of DHAP [17]. SRP_{water} (other than site 11) and TP_{water} were highest at site 6 among the first 12 fresh water sites; OP_{water} and $NPase_{water}$ were highest among all sites. OP_{water} and SRP_{water} were lower than concentrations in 2006; however $NPase_{water}$ was much higher than that of 2006 (nearly 22 times) (Table 5); indicating that the high P content and NPase hydrolysis activity in the water column at SB tributary [14]. Water P levels and $NPase_{water}$ in site 7 were decreased from 2006.

3.5. City Line-Boundary between Westchester and the Bronx

Site 9, City Line at 233rd St and Nereid Ave, boundary between WC and the Bronx, east of Woodlawn cemetery, close to Metro-North Woodlawn station. River had been straightened to accommodate the parkway in the border of Bronx/WC [20]. There was sandy sediment (coarse sand 32%, medium sand 22%, fine sand 21%) in this site. BAP and TP were quite close to median, but lower than average (**Table 2**). PDEase and NPase-P were lower than median and average (**Table 3**). Po is 114 $mg \cdot kg^{-1}$, between median and average; Pi is 363 $mg \cdot kg^{-1}$, lower than average and median concentrations. Microbial P was close to median negative concentration, but less negative than average negative concentration. Microbial P was negatively correlated with NPase-P, BAP, TP, Po and Pi, indicating that less bioavailable P and less EHP could possibly explain the less negative value of microbial P. Gly P is the only P compound in sediment at site 9 [17]. All SRP_{water}, OP_{water} and TP_{water} were higher than average and median concentrations (Table 5). TP_{water} was the fourth highest among 14 water sampling sites, and is the third highest among fresh water sites (sites 1-11); SRP_{water} is the highest in the first nine sampling sites around 1.7 times of background concentration, and still much lower than lower river fresh and saline water sites, OP_{water} is the fourth highest among total sites and the third highest among fresh water sites [14]. $NPase_{water}$ is 5 $\mu g \cdot l^{-1}$, the lowest among 14 sites, showing that limited amount EHP and fair amount of non-hydrolyzable OP in river at this location [7].

In 2007, sediment collected in the City Line had decreased BAP, TP, Pi, Po, OM, and NPase compared with sediment collected in 2006; and all these parameters were also lower than median and average concentrations of 2007 data. Only PDEase-P in 2007 was greater and around twice of 2006 concentration, which was higher than median and close to average. P compounds showed up pyro-P in trace amounts other than major compound in GlyP [17]. TP_{water}, OP_{water}, $NPase_{water}$ (**Table 5**) were also lower in 2007 than in 2006. There was construction near Woodlawn Metro-North train station near the city line during sample collection in July 2007, which was one of the P source in urban area and could possibly explain the temporal variations [1].

3.6. Bronx Park-New York Botanical Garden and the Bronx Zoo

Bronx Park includes New York Botanical Garden (NYBG) and the Bronx Zoo, which was covered by dense trees and vegetation. Bronx River runs through a 50-acre native forest in NYBG, which was home to trees nearing 300 years old [35]. Site 10, NYBG, at Old Snuff Mill; Site 11, Bronx Zoo, south of Mitstubish waterfall, entered from Gate B, Bronxdale Parking lot. Both sites had fine sandy sediments (Site 10: coarse sand 31%, medium sand 41%, fine sand 18%; site 11: coarse sand 14%, medium sand 45%, fine sand 34%). Both sites TP, Pi, Po and BAP were lower than median and average. Site 10 had the third highest PDEase-P concentration, fourth highest NPase-P, and third most negative microbial P; it had higher BAP, TP, Po, Pi, OM, Ox-Fe, HCl-Mg, Kd, S_{max}, and K_f than site 11. The larger BAP, Po values and more negative microbial P could possibly explain the higher values of EHP in site 10 than site 11[7], and it might be associated with the fertilizer management in NYBG and animal manure management and runoff from the Wildlife Conservation Society's (WCS) Bronx Zoo [5,17,19]. GlyP was the major P compound for both sites, but site 10 also had PolyN, IMP and Pyro-P in trace amounts [17]. P levels in water samples were higher in site 11 than 10. P levels increased from upper river down stream to lower river, sites 10 and 11 had higher SRP_{water} values than upstream sites, and site 11 had highest SRP_{water} among 14 sampling sites, and its TP_{water}, SRP_{water}, and OP_{water} were higher than site 10. EPC_0 was significantly correlated with SRP_{water} ($r = 0.749$, $p < 0.01$), which could possibly explain the higher water P levels in site 11 and site 10. $NPase_{water}$ concentration is the second highest in Bronx Zoo, that again indicates a potential threat to water quality in an increased temperature [12,14].

In 2007, Site 10 had decreased BAP, TP, Po, Pi, PDEase-P, NPase-P and OM compared with sediments in 2006. Other than PDEase-P, all these concentrations were lower than median and average. P compound is GlyP only; other trace amounts compounds not show up in 2007. It could relate with P fertilizer management in NYBG [17]. In contrast, it had much lower P content than that of Bronx Zoo. Site 11 had the highest BAP, microbial P, and NPase-P; third highest TP, Pi, and

PDEase-P, second highest OM. Other than Po, all these parameters were increased from 2006 to 2007. Sediment texture in 2007 at site 11 was silty clay fine sediments, and OM associated P, microbial and enzymatic activities, EHP, BAP and overall P content increased as sediment size decreased [25,32,33]; which might be also related to animal manure management from Wildlife Conservation Society (WCS) in the Bronx Zoo [17]. In 2007, P compounds were DHAP 10% and GlyP 90% instead of 100% GlyP in 2006 [17]. In 2007, $NPase_{water}$ is higher in site 10 (higher than median and average) than site 11(lower than median and average), however, SRP_{water} and TP_{water} were higher in site 11 (higher than median and average concentrations). Compared with 2006, SRP_{water}, OP_{water} and TP_{water} concentrations all decreased for both sties, $NPase_{water}$ increased at site 10 and decreased at site 11.

3.7. East Tremont Avenue Bridge-Boundary between Fresh and Saline Water

Site 12, East Tremont Avenue (Ave) Bridge is the boundary of fresh and saline water in the Bronx River. Sediment and water samples were collected at the East Tremont Bridge between East Tremont Ave and Boston Road, east of West Farm, and west of Bronx Art Center. There were many abandoned tires on east bank of the river, and there was busy traffic on East Tremont Ave. Bridge with buses, automobiles. Sediments were mixed with shell and pebbles collected at this site, below E Tremont Bridge. Bioavailable P, Po, TP were lower than median and average, Pi was in between median and average; and microbial P was in lower negative value less negative than median and average. PDEase-P and NPase-P were in third lowest values compared with other sites, below median and average. Ox-Fe, HCl-Ca, HCl-Mg and S_{max} were highest here, and Ox-Al is the third highest; indicating large sorption capacity [17,25,27]. P compounds were GlyP (major), PolyN and IMP (trace amounts). During sample collection, there was oil spill found on the river (might either from CSOs or runoff from the bridge), and it might have inhibited microbial activity and enzymatic hydrolysis, resulting comparatively lower EHP (PDEase and NPase-P) and less negative microbial P values [25]. SRP_{water}, OP_{water} and TP_{water} in this fresh and saline water mixed site were higher than most of the freshwater sites, much higher than average and median (other than OP_{water} is higher than median but slightly lower than average concentrations). Sediment EPC_0 was less than TP_{water}, and sediment could adsorb P from water column whenever P is available, plus it had the highest Ox-Fe, HCl-Ca, HCl-Mg, and third highest Ox-Al and those cations binds P in a stable form (under aerobic conditions) [27]; resulting in the highest P sorption capacity-S_{max} [17,25,27,36]. $NPase_{water}$ was the fourth highest, indicating potential threat on water quality in this fresh and saline water boundary site [12,14].

Sediments collect in 2007 at East Tremont Ave Bridge was sandy sediments. It had distinguished highest TP, third highest microbial P, highest Pi but lowest Po, OM was the same as median but lower than average; showing that IP composed of the largest amount of TP due to highest HCl-P [25]. Oil spill was not found during sampling in 2007, this could enhance microbial activity. Sediments in 2006 had largest S_{max}, and they could adsorb P whenever it was available; those P was HCl extractable, and which was why highest HCl-P, Pi, and TP [25-27]. Phosphorus compound is GlyP only; trace amounts of PolyN and IMP in 2006 were not showing in 2007. In 2007, PDEase-P and NPase-P were both lower than median and average; PDEase-P decreased from 2006, NPase-P was similar as 2006, and OM was also decreased from 2006. In 2007, $NPase_{water}$ was slightly lower than median but only 27% of average concentration; SRP_{water} was higher than average and median (Table 5); OP_{water} was 0; TP_{water} was higher than median and slightly higher than average, which was composed of SRP_{water} only and it was 2.2 times of background concentration 42 $\mu g \cdot l^{-1}$ but only 37% of median concentration 250 $\mu g \cdot l^{-1}$ of national streams. Overall, SRP_{water}, OP_{water}, TP_{water} and $NPase_{water}$ were much lower in 2007 than 2006.

3.8. Bronx River Estuary

Bronx River estuary, along Sound View Park, connected to the East River. Site 13, located at old Sound View Park water testing station, facing meat market, close to river channel marker 7 and 8. Currently local businesses are working with the city to create new parks, walking trails and boating launching sites on Hunts Point and between the Cross Bronx and Bruckner Expressways [20]. Sediments were fine sandy (coarse sand-27%, medium sand-21%, and fine sand-15%,) at Site 13. Sediments were fine sandy but a little sticky at site 14 (coarse sand 0.5 - 1 mm: 28%, medium sand 0.25 - 0.5 mm: 17%, and fine sand 0.125 - 0.25 mm: 12%), sediment depth was very shallow at mouth of the river and stream bed was rocky [4,41]. Wholesale fish market moved to Hunts Point from Fulton Street in lower Manhattan in 2005; wholesale meat market is also close by, besides HP WWTP. Sound View Park is along the east of river estuary, rounding off the southern end of the Bronx River, was built on a former landfill, 158-acre, becoming sport fields, fishing spots with beautiful views across Hunts Point to Manhattan [20]. Mixture of fresh and saline waters in the river provides diverse plants, fisheries, benthic mcaroinvertebrates and migratory birds such as herons and egrets [19]. Many people were fishing in summer during sample collection time. Fishes in Bronx Estuary includes striped bass, American eel, blue fish, summer flounder etc.

Electrical Conductivity (EC) in water and sediments were much higher than fresh water sites. Site 14 sediments had second highest BAP, TP, Po, Pi and NPase-P, the most negative microbial P, the fifth highest PDEase-P (all of these values were above average and median concentrations), indicating intense microbial activity provided more available P for enzyme hydrolysis activities [26]. The most negative microbial P could represent a significant amount of TP [25,26,37]. Site 13 had the fourth highest TP, BAP, and Pi, sixth highest Po. Site 14 had higher S_{max} than site 13, even though Ox-Al, Ox-Fe, HCl-Ca, and HCl-Mg were not as high as site 13, because there were higher P levels (BAP, Pi, Po and TP in sediments) and higher P retained (92% in site 14 vs. 88% in site 13) [25,27]. Bioavailable P was the second highest (435 μg^{-1}) (**Table 1**), and BAP% (BAP/TP%) was the fifth highest (45%) in site 14; BAP was the fourth highest (289 μg^{-1}) (**Table 1**) and BAP% (44%) was sixth highest in site 13; both BAP and BAP% were higher than average and median levels in both sites; showing the larger amount BAP in estuary because discharges from HP WWTP sewer overflow during summer storms [12,17,27]. Similarly, other studies found that BAP% was higher in effluents from WWTP (average 72%) than other urban drainage discharges with BAP of 53% [5]. Furthermore, S_{max} was correlated with BAP ($r = 0.641$, $p < 0.05$), TP ($r = 0.613$, $p < 0.05$) and Pi ($r = 0.623$, $p < 0.05$), site 14 had significant higher BAP, TP and Pi than site 13 and other 12 sites, therefore, it had second highest S_{max}. Major P compound in estuary was GlyP; trace amounts of polyN in site 13 and NMP in site 14 [17]. Sewer overflow from HP WWTP during summer storm, CSOs from fish and meat wholesale markets, potential pollutants from East River could result in higher P in river water [38] and substantial microbial activity and enzyme hydrolysis process in estuary [1,12]. In site 13, TP_{water} (1113 $\mu g \cdot l^{-1}$) was the highest and OP_{water} (979 $\mu g \cdot l^{-1}$) was the second highest among the 14 water sampling sites (**Table 4**), showing a second peak of P concentrations in estuary other than the first peak at SB (sites 7 and 8). In the water column, SRP_{water}, OP_{water} and TP_{water} in site 13 were all higher than those of site 14; TP_{water} and OP_{water} concentrations in both estuary sites were above median and average values and greater than national median P concentration (250 $\mu g \cdot l^{-1}$) in waters, showing the highest nutrient concentrations in urban rivers were downstream of WWTP facilities [1]. $NPase_{water}$ of these two estuary sties were lower than median and average, meanwhile, $NPase_{water}$ in site 14 was slightly higher than that of site 13 (**Table 4**). Fishing is popular in summer at Bronx River estuary. P levels in water and sediments could be a potential threat to water quality and fish consumption safety in estuary area.

Table 4. Sorption characteristics of sediments collected in 2006 (Wang and Pant, 2010c).

#	EPC_0	S_0	S_{max}
	mg·kg^{-1}		
1	0.15	9	120
2	0.04	4	333
3	0.28	20	244
4	0.45	66	81
5	0.15	2	167
6	0.15	3	175
7	0.02	0	192
7b	0.73	29	179
8	0.44	53	370
9	0.42	24	169
10	0.41	13	208
11	0.58	13	120
12	0.33	46	476
13	0.54	31	333
14	0.67	42	435
Ave	0.36	24	240
median	0.41	24	192

In 2007, sediments collected at site 13 were silty clay sticky sediments, and at site 14 were mixed sandy and silty sediments. Total P, Pi, Po, BAP and microbial P were second highest in site 14 (**Table 2**); Site 13 had the fifth highest TP and Pi, third highest Po, fourth highest BAP, and highest OM (16.7%, around 6 times of average). Similar as data showed in 2006, it was indicating higher P levels in estuary sediments. PDEase-P was second highest in site 13, which was higher than site 14 (**Table 3**); NPase was also higher in site 13 than 14. As had mentioned earlier, it was showing that fine-grained silty clay type of sediments tends to adsorb more OM consequently increased enzymatic hydrolysis activities [33]. Microbial P was significantly correlated with BAP ($r = 0.879$, $p < 0.01$), Pi ($r = 0.547$, $p < 0.05$), and TP ($r = 0.547$, $p < 0.05$); therefore similar as 2006, site 14 had both second highest microbial P and P concentrations, further proved higher P levels and intense microbial activity in estuary [1,12]. Compared with data in 2006, BAP, TP, Po, NPase-P decreased, PDEase-P and OM

Table 5. physico-chemical characteristics and native enzyme hydrolysis of OP of water samples collected in 2006 and 2007 (Wang and Pant, 2011b).

#	NPase-Pwater		SRPwater		TPwater		OPwater		pH		EC	
	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007
	$\mu g \cdot l^{-1}$										$\mu s \cdot cm^{-1}$	
1	28	10	2	28	55	83	53	56	7.9	7.9	530	540
2	1818	79	5	34	87	34	82	0	7.8	7.8	396	621
3	154	135	18	33	29	33	11	0	7.9	7.9	651	739
4	286	17	25	30	30	30	5	0	8.0	7.9	674	786
5	428	22	13	37	63	39	49	2	7.9	7.7	1257	1415
6	80	1731	34	63	367	178	333	115	7.9	7.9	853	770
7	208	60	40	54	1069	54	1030	0	7.9	7.9	846	777
8	55	61	55	27	1019	90	964	63	7.9	8.0	806	701
9	5	0	71	74	785	74	714	0	8.0	7.9	766	678
10	42	507	92	56	143	56	51	0	8.0	7.9	820	727
11	1165	40	221	112	414	112	193	0	8.0	7.9	685	569
12	404	47	100	91	460	91	360	0	7.9	7.9	786	569
13	88	145	135	162	1113	197	979	35	7.4	7.5	34500	25400
14	109	0	122	151	501	173	379	22	7.3	7.5	35300	37800
ave	348	204	67	68	438	89	372	21	7.9	7.8		
median	132	54	47	55	391	79	263	0				

Table 6. Pearson correlation coefficient and significance of sediment and water data in 2006.

Variables	PDEase-P	Npease-P	S0	SRPwater	TPwater
BAP	0.887**	0.751**	0.705**		
TP	0.814**	0.719**	0.677**		
Po	0.872**	0.755**	0.683**		
Pi	0.773**	0.690**	0.658**		
OM	0.745**	0.683**	0.660**		
Kf	0.785**	0.588**	0.883**		
k	0.895**	0.630**	0.569*		
Kd			0.796**		
EPC0	-	0.565*	0.602*	0.749**	
Ox-Al	0.608*	-	0.534*		
S0	0.589*	0.556*			
Smax			0.720**		
Microbial P	-	–0.677**			
OPwater					0.989**

**correlation is significant at the 0.01 level (2-tailed). *correlation is significant at the 0.05 level (2-tailed).

Table 7. Pearson correlation coefficient and significance of sediment and water data in 2007.

	PDEase-P	NPase-P	TP_{water}
BAP	0.582*	0.717**	
Microbial P	-	0.718*	
OM	0.724*	-	
$NPase_{water}$	0.563*		
SRP_{water}			0.789**

**correlation is significant at the 0.01 level (2-tailed). *correlation is significant at the 0.05 level (2-tailed).

significantly increased and Pi slightly increased in site 13 (**Table 2**); in site 14 Pi, TP, and BAP increased (**Table 1**); and Po, PDEase and NPase-P decreased (**Table 1** & **2**). SRP_{water}, OP_{water} and TP_{water} in both estuary sites were higher than median and average concentrations (**Table 5**). TP_{water} of estuary sites was higher than national background concentration (5 times in site 13 and 4 times in site 14); but lower than national median concentration. TP_{water} and SRP_{water} were highest in site 13, TP_{water} was third highest and SRP_{water} was second highest in site 14 (Table 4), indicating increased P concentrations in waters downstream [1]. However, TP_{water} and OP_{water} were much lower than concentrations in 2006. In 2007, $NPase_{water}$ in site 13 was the third highest (higher than in 2006), indicating P levels and enzymatic hydrolysis increased in estuary site downstream where close to HP WWTP [1, 14]. But there was no native enzyme activity showed at site 14 (lower than in 2006) indicating that substantial portion of the P pool was inaccessible to phosphatases/enzymes to be hydrolyzed at this site [12].

Overall, in 2006 sites 2, 4, 7b and 14 had finer sediments, and highest BAP, Pi, Po and TP. Sites 4 and 14 had most negative microbial P. Sites 4, 14, 7b and 10 had higher NPase and PDEase-P. Estuary and TB had higher TP in water samples. Station A at Bronx River Valley upstream in Westchester, S of TB, SW of SB, NYBG, and the mouth of the river in estuary showed more intense microbial activity and more EHP, BAP and potential BAP. The TP, BAP, Pi, and Po content variations are related to land use and other characteristics of the Bronx River [12,39]. TP_{water} showed peaks at sites 7, 8 and 13, $NPase_{water}$ showed peaks at sites 2 and 11.

In 2007, sediments collected in sites 7, 11, 13 and 14 had finer texture, silty/clay type of sediments, and these sites had high TP, BAP, Pi and Po (other than site 7). Site 12 had the distinguished highest TP and Pi. Sites 7, 11, 12, and 14 also had higher microbial P values. Sites 7, 11 and 13 had significantly higher PDEase-P, and site 11 had highest NPease-P, followed by site 7. TP_{water} showed peaks at site 6, 11 and 13. $NPase_{water}$ showed peaks at sites 3, 7, 10 and 13. Overall, SB, Bronx Zoo, fresh and saline water boundary and estuary showed distinguished P characteristics in 2007. TP_{water} peaks showed in SB and estuary for both years, indicating the raw sewer discharge in Yonkers since was affected P levels and microorganism and enzyme hydrolysis at SB, and downstream HP WWTP facility probably affect Bronx River estuary water P and enzymatic activity as well.

4. Bronx River Ecosystems Improvement and Future Research Perspective

It would be very interesting to continuously survey on P levels in water and sediments under changing hydro-climatic conditions in near future. For instance, this summer is the hottest summer in NYC history; the inherent EHP could increase under increased temperature, threatening freshwater quality. Bronx EcoAdventure organized canoe trip along the Bronx River through NYBG and the Bronx Zoo currently, and canoes were launched at the Concrete Plant Park between Westchester Avenue and Bruckner Boulevard, near the nexus of the Sheridan and Bruckner Expressways (Expy) [40,41]. With effort from Bronx River Alliance, Concrete Park, a waterfront park along the Bronx River, was built up from abandoned site used to contain trash and tries through re-establishing salt marshes on riverbank, completed in Sep 2009, and currently open to public for canoe/kayak trips [40]. It was showing the ecosystem improvement with effort from Bronx River Alliance (migratory birds, shoots along the banks and shell of a small crab discovered). [41].

New York City Parks Department, the Hudson River Foundation, and the Bronx River Alliance are working together on an oyster project that laid about 50,000 oysters into Bronx River on Thursday (10/28/10) morning [42]. High school students placed live oysters onto an experimental oyster reef in the shallow waters off of Sound View Park near the mouth of Bronx River on Oct 28, 2010 [43]. Students from Harbor School, a public school on Governors Island raised the oysters. The reefs located in the Bronx River, Jamaica Bay, off the shores of Governors Island, Staten Island, Bay Ridge, and Hasting in Westchester will be monitored for the next two years [24]. NYC harbor were once flourished oysters in mid-19th century before over-harvesting and pollution nearly wiped out entire population. If oysters are able to survive, the reef will provide shelter for fish and crabs and improve the biodiversity of New York harbor. Water quality could be improved as a result of the oyster's ability to filter contaminants out of the water and improve water clarity [42]. Those oysters are not safe to eat because they grow in water that is contaminated when raw sewage discharges into the river estuary during heavy rain [43]. Ecologists hope to restore New York harbor's oysters, plan 500 acres of oyster beds by 2015, and 5000 acres of oyster beds by 2050 [43].

5. Conclusions

Phosphorus transport varied spatially along the Bronx River. Distinguished characteristics appeared at Bronx River Valley upstream in Westchester, TB, SB, NYBG and estuary in 2006; in SB, Bronx Zoo, fresh and saline water boundary at East Tremont Ave Bridge, and estuary in water and sediments samples collected in 2007. Two years data showed temporal variations as well. Sediment texture, transport, deposition, assimilation, P adsorption and desorption, land use and anthropogenic activities including raw sewer discharge, oil spill, urban construction, fertilizer application and manure management along the Bronx River as well as local hydro-climate changes (such as temperature and precipitations) affected BAP, potential BAP, potential EHP, microbial activity and enzyme hydrolysis; resulting in spatial and temporal variations. Analyses of land use impacts on P transport in the Bronx River, help regulate P in river's watershed and restore river ecosystems. Efforts to restore Bronx River ecosystems and wildlife habitat have been made by community, NY Dept of Park and Recreations, showing improvement and future research perspective. How to coordinate P application, land use and recreation is a key to improve water quality of the Bronx River.

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