# INFLUENCE OF VEGETATION ON ORGANIC PHOSPHORUS AND CARBON FORMS IN WETLAND SOILS

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## INTRODUCTION

Treatment wetlands sequester inorganic and organic forms of phosphorus (P), the bioavailability of which regulates the potential P flux from soil to the overlying water column. Stormwater treatment areas (STAs) in the Everglades, Florida were designed to remove P from agricultural runoff prior to discharging them into the Everglades Protection Area. The quality of organic P accreted in these wetlands is influenced by the type of vegetation and nutrient status. At the same time carbon (C) source in wetlands could be sustained through C fixation by vegetation and its subsequent decomposition. Therefore, understanding the chemical nature of the forms of inorganic and organic P (OP) and organic C (OC) is critical in developing management strategies to maintain desired effluent P concentrations and for the long-term sustainability of these systems. This study was performed to address the question on how and to what extent the type of vegetation and nutrient loading alter the storage and reactivity of P and C and their forms in wetland soils.

**Objective:** To determine the forms and distribution of P and C in floc (surface layer), recently accreted soil (RAS), and pre-STA native peat soils along the flow path of STAs with emergent aquatic vegetation (EAV) and submerged aquatic vegetation (SAV). We hypothesized that EAV dominated flow-ways (FWs) produce more stable organic P and C than SAV dominated FWs.

## MATERIALS AND METHODS

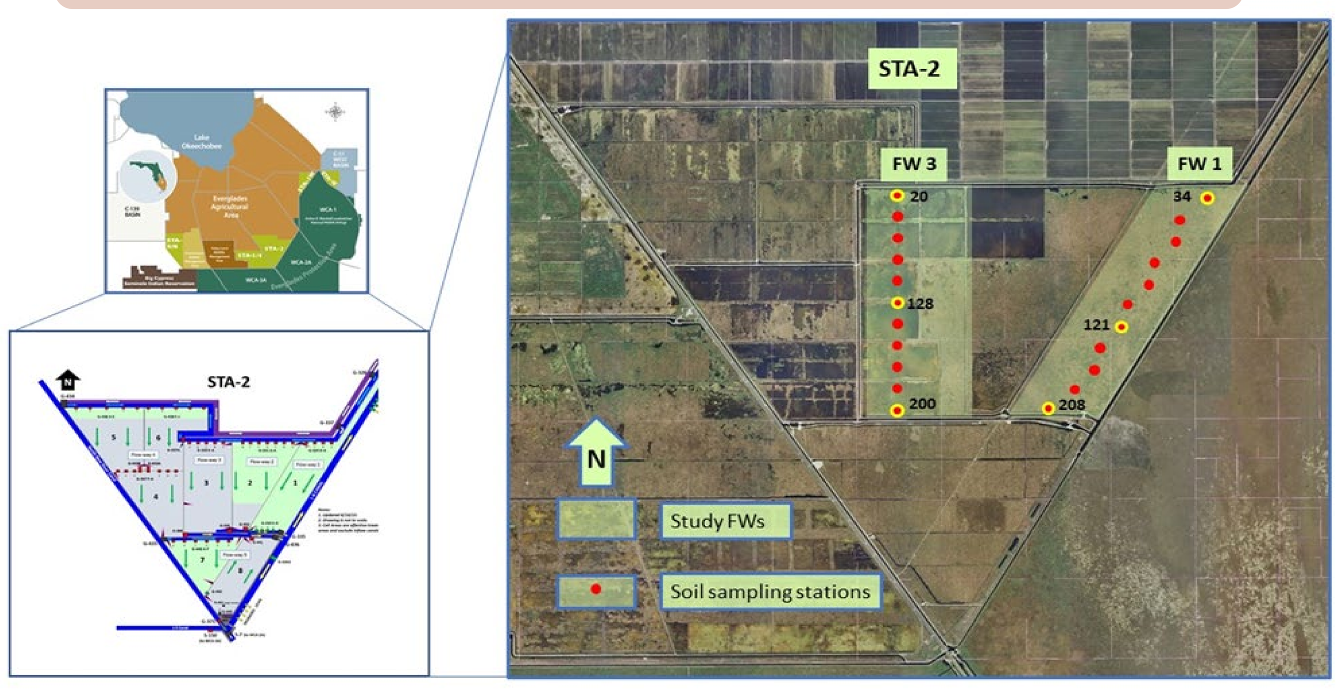

Figure 1. Study sites

### Study sites:

- **STA-2 FW-1** is a 743 ha constructed wetland (also called Emerged Aquatic Vegetation - EAV FW), consists primarily of cattail (*Typha domingensis*).
- **STA-2 FW-3** is a 928 ha constructed wetland (also called Submerged Aquatic Vegetation - SAV FW).

Both flow-ways in STA-2 operate as parallel treatment flow-ways and receive inflows originating from the same source/watershed.

### Soil Samples:

Intact soil cores from 9 transect stations in STA-2 FWs 1 and 3 were obtained (Figure 1). The inflow, midflow, and outflow locations along each transect were designated as benchmark sites where triplicate soil cores were collected. Soil cores were sectioned into floc (detrital floc material), RAS, and pre-STA soil (Figure 2). All samples were stored at 4°C until used for chemical analysis.

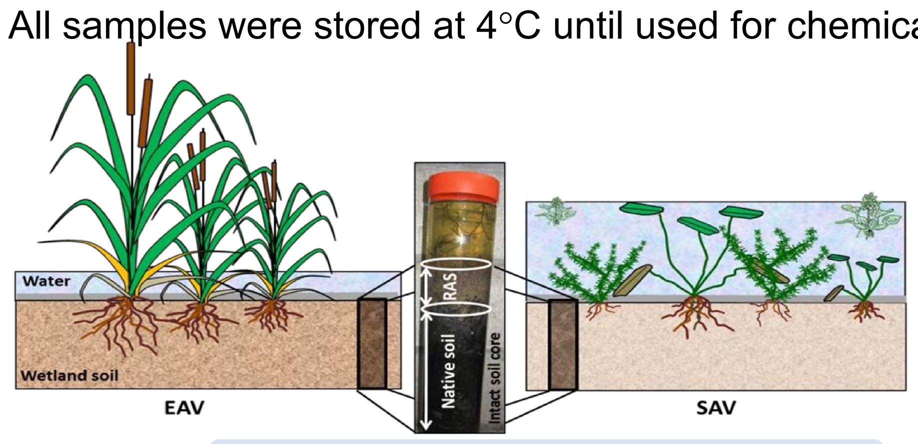

Figure 2. Soil core sampling

### Methods used:

- Solution state $^{31}P$ Nuclear Magnetic Resonance Spectroscopy (NMR). NMR spectra were acquired using an Avance III spectrometer manufactured by Bruker Bio-Spin operating at a field strength of 14 tesla (600 MHz) with an 51mm bore. Spectroscopy data were collected using TopSpin software (Version 3.2 pl5) while imaging data was collected using ParaVision 6.
- Solid state cross polarization magic angle spinning $^{13}C$ NMR, using 3.2mm Low-E® CP-MAS.
- Conventional operationally defined P fractionation of soils.

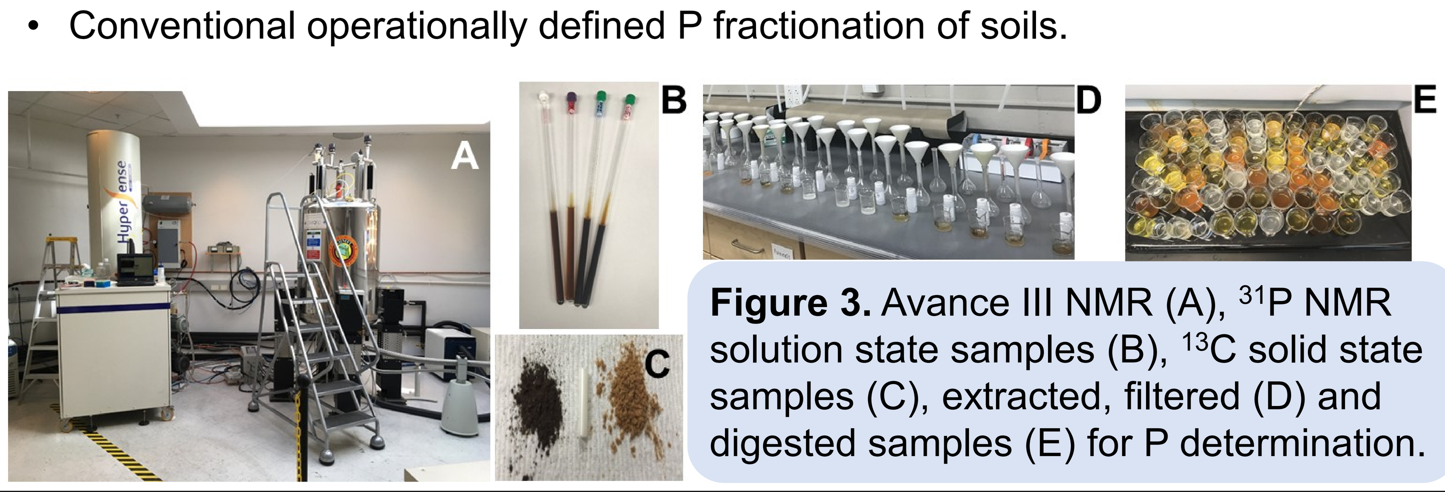

**Figure 3.** Avance III NMR (A), $^{31}P$ NMR solution state samples (B), $^{13}C$ solid state samples (C), extracted, filtered (D) and digested samples (E) for P determination.

## Acknowledgements

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## RESULTS

**FW-1 EAV**

| | Diester | Pyro-P | Alkyl-C | O-alkyl | Aryl-C | Carboxyl | MBP | Labile Po | HCl-Po | NaOH FA- P | NaOH HA- P | Residual P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Monoester | 0.94 | 0.52 | -0.69 | -0.14 | -0.78 | -0.74 | 0.68 | 0.86 | 0.70 | 0.88 | 0.77 | 0.74 |
| Diester | | 0.60 | -0.71 | 0.07 | -0.84 | -0.87 | 0.72 | 0.91 | 0.76 | 0.89 | 0.80 | 0.79 |
| Pyro-P | | | -0.18 | 0.69 | -0.48 | -0.56 | 0.73 | 0.47 | -0.02 | 0.29 | 0.53 | 0.01 |
| Alkyl-C | | | | 0.25 | 0.68 | 0.78 | -0.32 | -0.52 | -0.67 | -0.59 | -0.57 | -0.67 |
| O-alkyl-C | | | | | -0.07 | -0.17 | 0.45 | 0.07 | -0.36 | -0.13 | 0.21 | -0.31 |
| Aryl-C | | | | | | 0.90 | -0.66 | -0.72 | -0.58 | -0.73 | -0.69 | -0.64 |
| Carboxyl-C | | | | | | | -0.51 | -0.66 | -0.65 | -0.62 | -0.70 | -0.63 |
| MBP | | | | | | | | 0.79 | 0.24 | 0.71 | 0.73 | 0.40 |
| Labile Po | | | | | | | | | 0.76 | 0.95 | 0.85 | 0.84 |
| HCl-Po | | | | | | | | | | 0.82 | 0.61 | 0.97 |
| NaOH FA- P | | | | | | | | | | | 0.77 | 0.90 |
| NaOH HA- P | | | | | | | | | | | | 0.69 |

**FW-3 SAV**

| | Diesters | Pyro-P | Alkyl-C | O-alkyl-C | Aryl-C | Carboxyl | MBP | Labile Po | HCl-Po | NaOH FA- P | NaOH HA- P | Residual P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Monoester | 0.17 | -0.05 | 0.25 | 0.19 | 0.32 | 0.27 | -0.01 | 0.24 | 0.46 | 0.19 | 0.23 | 0.28 |
| Diester | | 0.44 | -0.58 | -0.55 | -0.58 | -0.53 | 0.84 | 0.31 | -0.35 | -0.13 | -0.26 | 0.49 |
| Pyro-P | | | -0.51 | -0.53 | -0.59 | -0.52 | 0.55 | 0.59 | 0.22 | -0.25 | -0.25 | 0.41 |
| Alkyl-C | | | | 1.00 | 0.99 | 0.97 | -0.82 | -0.57 | 0.29 | 0.51 | 0.82 | -0.73 |
| O-alkyl-C | | | | | 0.98 | 0.97 | -0.80 | -0.60 | 0.24 | 0.53 | 0.84 | -0.75 |
| Aryl-C | | | | | | 0.98 | -0.83 | -0.54 | 0.32 | 0.55 | 0.78 | -0.66 |
| Carboxyl-C | | | | | | | -0.79 | -0.56 | 0.35 | 0.69 | 0.87 | -0.70 |
| MBP | | | | | | | | 0.62 | -0.24 | -0.35 | -0.45 | 0.73 |
| Labile Po | | | | | | | | | 0.50 | -0.25 | -0.38 | 0.90 |
| HCl-Po | | | | | | | | | | 0.45 | 0.33 | 0.26 |
| NaOH FA- P | | | | | | | | | | | 0.70 | -0.28 |
| NaOH HA- P | | | | | | | | | | | | -0.60 |

**Table 1. Correlations of Organic P forms, Organic C forms and P fractions in EAV and SAV flow-ways of STA-2**

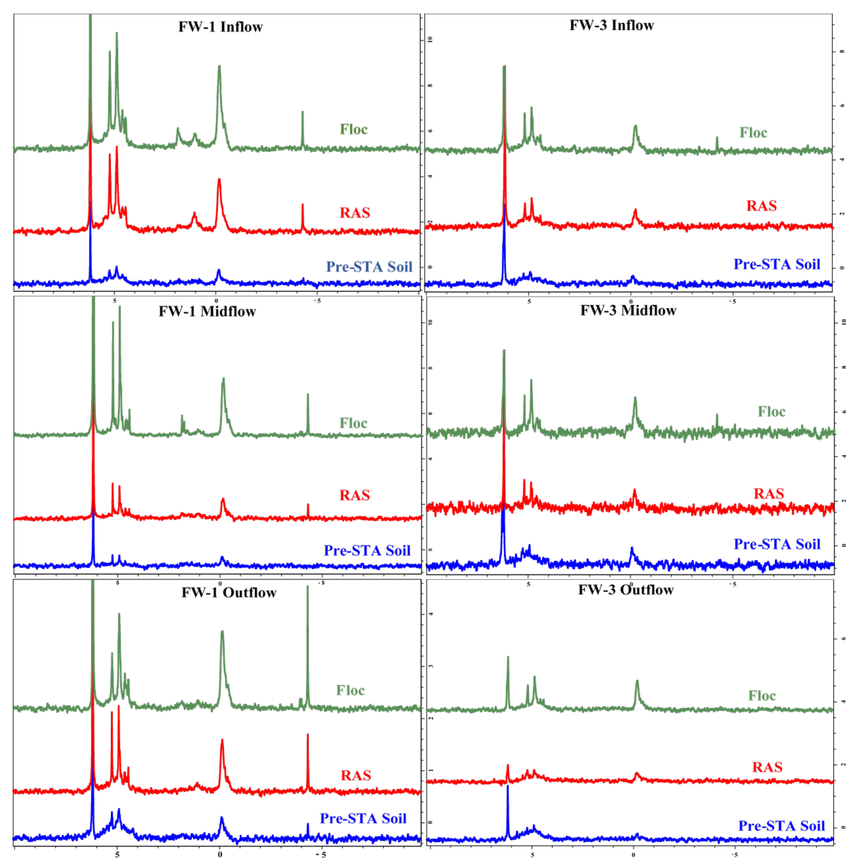

**Figure 4. $^{31}P$ NMR spectra for the Floc Ras and Pre-STA Soil samples from inflow, midflow, and outflow of FW-1 and FW-3.**

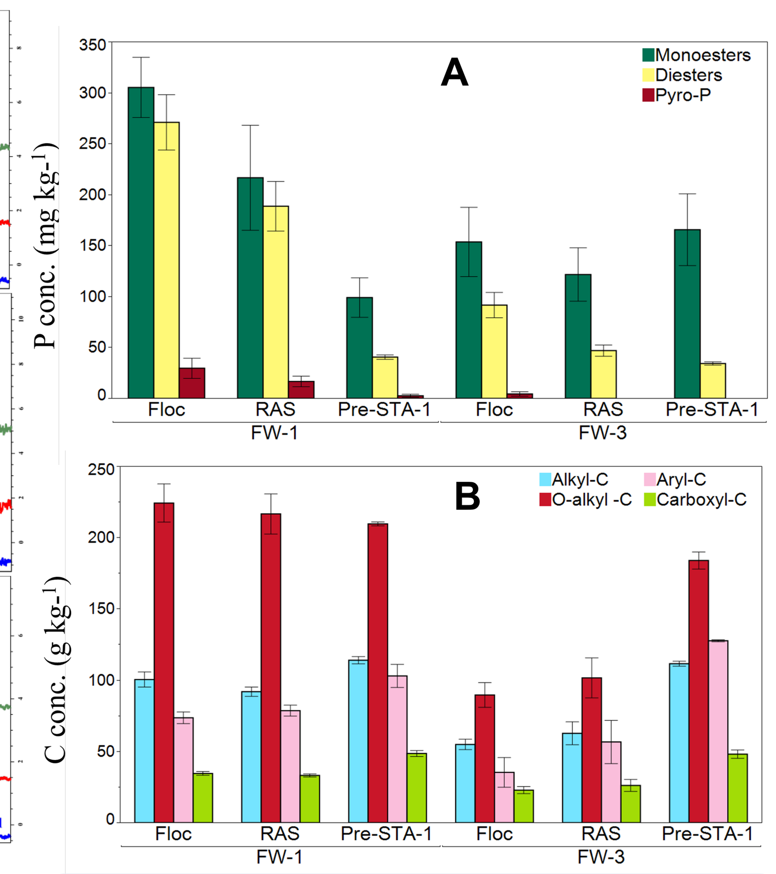

**Figure 5. Organic P (A) and C (B) forms of the Floc Ras and Pre-STA Soil samples of FW-1 and FW-3 of STA-2.**

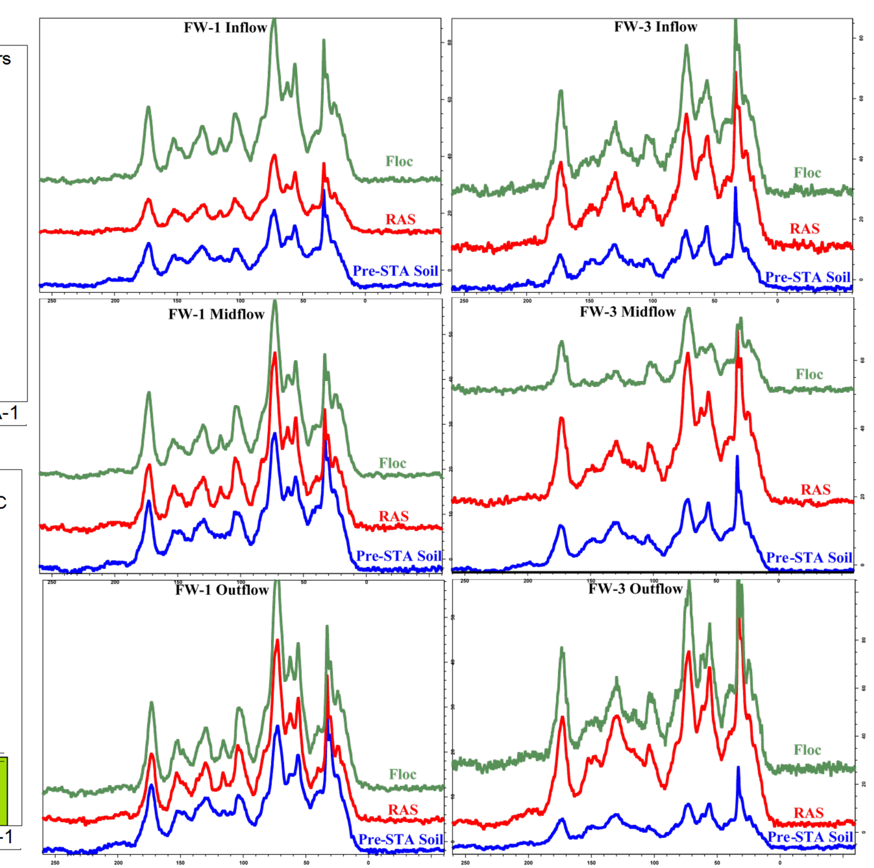

**Figure 6. $^{13}C$ NMR spectra for the Floc Ras and Pre-STA Soil samples from inflow, midflow, and outflow of FW-1 and FW-3.**

| FW | Sample Location | Sample Depth | Phosphorus (mg kg$^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|
| | | | NaOH-TP | Ortho phosphate | Phospho monoester | Phospho diester | Pyro phosphate |
| FW-1 | Inflow | Floc | 855 | 165 | 351 | 325 | 14 |
| | | RAS | 702 | 141 | 312 | 237 | 12 |
| | | Pre-STA | 191 | 41 | 102 | 45 | 3 |
| | Midflow | Floc | 1091 | 500 | 315 | 249 | 27 |
| | | RAS | 481 | 176 | 135 | 159 | 11 |
| | | Pre-STA | 194 | 91 | 64 | 39 | ND |
| | Outflow | Floc | 761 | 225 | 250 | 239 | 48 |
| | | RAS | 566 | 165 | 203 | 170 | 27 |
| | | Pre-STA | 255 | 82 | 131 | 38 | 5 |
| FW-3 | Inflow | Floc | 508 | 224 | 193 | 84 | 7 |
| | | RAS | 347 | 146 | 155 | 46 | ND |
| | | Pre-STA | 302 | 116 | 150 | 36 | ND |
| | Midflow | Floc | 259 | 92 | 86 | 75 | 6 |
| | | RAS | 189 | 80 | 70 | 38 | ND |
| | | Pre-STA | 237 | 88 | 114 | 36 | ND |
| | Outflow | Floc | 362 | 64 | 182 | 116 | ND |
| | | RAS | 215 | 18 | 140 | 57 | ND |
| | | Pre-STA | 330 | 66 | 233 | 31 | ND |

**Table 2. Organic P forms (mg kg$^{-1}$) of floc, RAS and Pre-STA soil samples identified by $^{31}P$ NMR.**

| FW | Sample Location | Sample Depth | Carbon (g kg$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | Alkyl-C | O-Alkyl-C | Aryl-C | Carboxyl-C |
| FW-1 | Inflow | Floc | 94 | 203 | 73 | 32 |
| | | RAS | 86 | 189 | 71 | 31 |
| | | Pre-STA 1 | 109 | 207 | 117 | 52 |
| | Midflow | Floc | 97 | 221 | 67 | 37 |
| | | RAS | 97 | 235 | 83 | 35 |
| | | Pre-STA 1 | 115 | 211 | 89 | 45 |
| | Outflow | Floc | 111 | 249 | 81 | 34 |
| | | RAS | 93 | 226 | 82 | 34 |
| | | Pre-STA 1 | 118 | 211 | 103 | 49 |
| FW-3 | Inflow | Floc | 52 | 80 | 34 | 21 |
| | | RAS | 53 | 80 | 42 | 21 |
| | | Pre-STA 1 | 114 | 190 | 127 | 43 |
| | Midflow | Floc | 51 | 82 | 18 | 20 |
| | | RAS | 57 | 97 | 41 | 23 |
| | | Pre-STA 1 | 112 | 190 | 129 | 53 |
| | Outflow | Floc | 62 | 107 | 54 | 28 |
| | | RAS | 79 | 128 | 87 | 35 |
| | | Pre-STA 1 | 108 | 172 | 127 | 48 |

**Table 3. Organic C forms (g kg$^{-1}$) of floc, RAS and Pre-STA soil samples identified by $^{13}C$ NMR.**

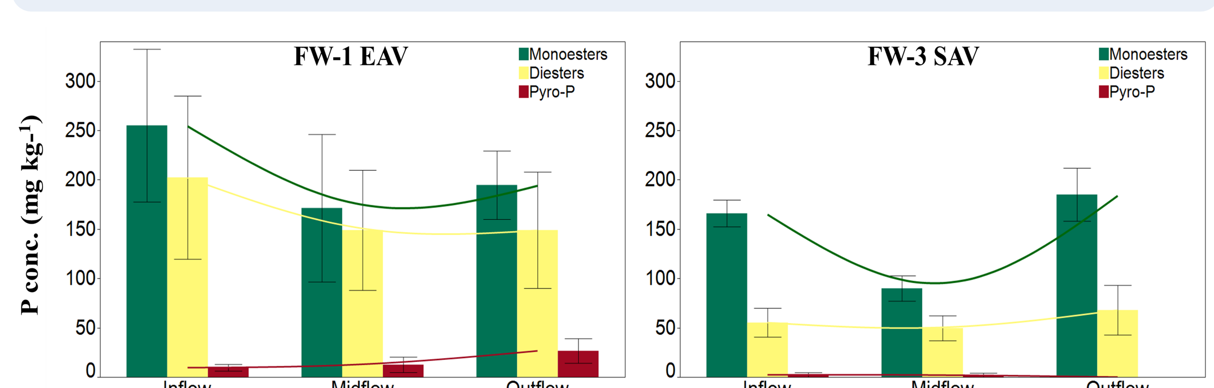

**Figure 7. The concentration of the organic P forms along the flow path (from inflow to outflow).**

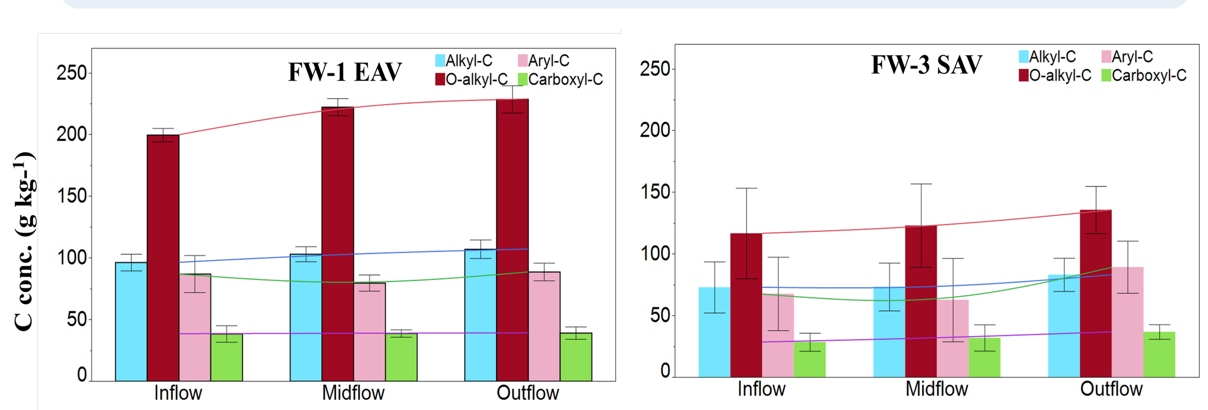

**Figure 8. The concentration of the organic C forms along the flow path (from inflow to outflow).**

## DISCUSSION AND CONCLUSIONS

- As the Everglades restoration efforts progress and water quality continues to improve, P and C cycle and associated pools will also respond in accordingly.
- Total P extracted by NaOH-EDTA and total organic P determined by solution $^{31}P$ NMR were positively correlated with the microbial biomass P (MBP) in EAV FW ($P$<0.005). Similarly, orthophosphate monoesters and diesters were positively strongly correlated with the acid and alkali extractable P in the EAV FW (P<0.005). Organic P forms showed negative correlation with all organic C forms except with O-alkyls.
- By contrast, apart from a correlation between diesters and MBP ($P$<0.005), there were no other correlations between OP forms with the P pools in the SAV FW. No correlation of monoesters with OC forms was recorded, while diesters had strong negative correlations with all OC forms.
- Significant gradients of P concentrations were observed both as a function of distance from inflow and with soil depth (floc, RAS, and pre-STA soils).
- Phosphorus loading increased the proportion of P stored as inorganic P in SAV systems and as organic P in EAV systems. The ratio of TPi/TPo in floc and RAS of EAV system was 0.5 and decreased with distance from inflow, suggesting accumulation of OP, while high ratios of up to 2.5 in SAV system indicated towards inorganic P accumulation in the floc and RAS.
- Although most soil P was stored as orthophosphate monoesters, soil organic P inputs were dominated by diesters, implying that plants and microorganisms highly controlled the composition of P forms.

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