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## CHARACTERIZATION OF GROUNDWATER AND SURFACE WATER GEOCHEMISTRY IN AN AGRICULTURAL SETTING AT EKU MEADOWBROOK FARM, MADISON COUNTY, KENTUCKY

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Agricultural activities often contaminate watersheds with excess nutrients leading to poor water quality and eutrophication. Eastern Kentucky University (EKU) Meadowbrook Farm raises crops and livestock, which contribute dissolved nutrients to the neighboring Muddy Creek watershed. Consequently, the Farm is developing methods to sequester phosphorous and limit nutrient contamination.

Before phosphorous sequestration methods can be tested, Farm surface water and groundwater geochemistry must be better understood to determine hydrological pathways for nutrients. We use naturally-occurring dissolved cations, pH, oxidation-reduction potential (ORP), specific conductivity (SC), dissolved oxygen (DO%), total hardness, and alkalinity as chemical tracers to parse the contribution of dissolved ions from different water sources, to recognize different water source chemistries, and to interpret storm events. To measure discharge from a proximal, intermittent stream that drains a representative and critical portion of the Farm, we used an instrumented, V-notch weir to examine storm-water flow during Tropical Storm Cindy (June 22-25, 2017).

Water samples taken from springs (groundwater), surface water, and storm water on the Farm were analyzed for various dissolved constituents. Dissolved cations were measured via ICP-OES (ACT Labs) for sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>), and magnesium (Mg<sup>2+</sup>). pH, ORP, SC, and DO% were determined with YSI and Vernier probes. Alkalinity and total hardness were measured via the bromocresol green - methyl red and the EDTA digital titration methods, respectively. Dissolved ammonium (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and phosphate (PO<sub>4</sub><sup>3-</sup>) concentrations were determined by colorimetry with a UV-VIS spectrophotometer via the sodium hypochlorite, cadmium reduction, and ascorbic acid methods, respectively.

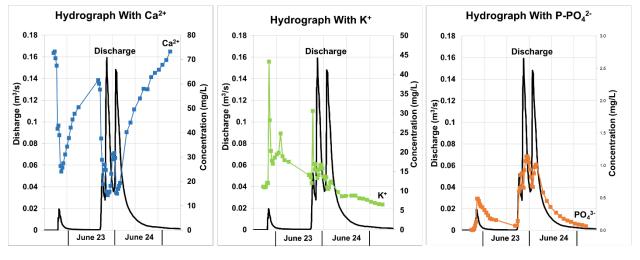
Both groundwater and surface water sources exhibit similar ranges of pH (neutral to basic), ORP (oxidizing), alkalinity, total hardness, DO%, and SC. Source waters generally have high  $Ca^{2+}$  and  $Mg^{2+}$ , and low K<sup>+</sup>, Na<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, and NH<sub>4</sub><sup>+</sup> concentrations. This strongly suggests that background chemistries of source groundwater and surface water are controlled by local limestone bedrock dissolution. Groundwater is further characterized by relatively high NO<sub>3</sub><sup>-</sup> concentrations and low temperatures; in contrast, surface waters exhibit higher temperatures and lower NO<sub>3</sub><sup>-</sup> concentrations.

During the Cindy event, concentration of  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  within baseline source waters decreased with increasing discharge through the weir (Fig. 1), along with SPC, pH, and alkalinity. This behavior represents dilution of Farm groundwater by storm precipitation and subsequent overland flow. However, K<sup>+</sup> increased from baseline concentrations, spiking

concurrently with increased discharge through the weir, and then progressively decreased in magnitude over the duration of the storm (Fig. 2). These data suggest that  $K^+$  was flushed from soil by rain waters.

Nutrient concentrations increase with increased discharge indicating transport by surface runoff. For example,  $PO_4^{3-}$  concentrations closely track and are proportional to discharge, which suggests  $PO_4^{3-}$  transport from the surficial soil substrate via flushing by precipitation (Fig. 3).  $NO_3^{-}$  exhibited nearly identical transport behavior as K<sup>+</sup>; concentration spikes occur simultaneously with K<sup>+</sup> and discharge. However,  $NO_3^{-}$  levels reached a higher baseline concentration than pre-storm levels. The Cindy event suggests infiltration and retention of  $NO_3^{-}$  within soil and groundwater during fair weather, initial flushing during the rain event, and then prolonged  $NO_3^{-}$  release from Farm soil and groundwater.

Background concentration of  $NH_4^+$  is generally 0.0 to 0.2 mg/L. Immediately prior to water flow over the weir during the Cindy event, concentrations were unusually high (~1.7 mg/L). During the first storm pulse, these high concentrations decreased significantly to <0.4 mg/L. Later in the main storm event,  $NH_4^+$  tracked discharge from the weir and afterward returned to typical background concentrations. This behavior suggests rapid release of  $NH_4^+$  from soil followed by accumulation within the weir pool and then subsequent flushing during the precipitation event.



*Fig. 1.* Discharge hydrograph and Ca<sup>2+</sup> concentration during Tropical Storm Cindy.

Fig. 2. Discharge hydrogrpah and K+ concentration during Tropical Storm Cindy.

*Fig 3.* Discharge hydrograph and PO<sub>4</sub><sup>3-</sup> concentration during Tropical Storm Cindy.