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Hydrologic tracers and thresholds: A comparison of geochemical techniques for event-based stream hydrograph separation and flowpath interpretation across multiple land covers in the Panama Canal Watershed

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ABSTRACT

Stream hydrograph separation using naturally occurring geochemical tracers holds great potential for elucidating mineral weathering and solute transport. This study addresses a critical need to characterize catchment runoff generation in the humid tropics using multiple natural tracers for hydrograph separation and concentration/discharge (*C*/*Q*) hysteresis analysis. We use hydrometric and geochemical data collected at the start of the wet season from three small, steep catchments located in the humid seasonal tropics of central Panama that differ primarily in land cover. We apply a dual source hydrograph separation model between two end-members: new event water precipitation and pre-event water stored in the catchment. We compare the effectiveness of electrical conductivity (EC) and stable water isotopes (δD and $\delta^{18}O$) tracers for identifying precipitation event water in stream runoff using across forested (1.43 km^2), mixed land use 'mosaic' (1.82 km^2) and pasture (0.42 km^2) catchments. Hysteretic *C*/*Q* loops are analyzed for flowpath interpretation using δD, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-}. During a medium-large magnitude event on May 23, 2013, forest and mosaic stream δD, Ca^{2+}, Mg^{2+}, and Na^+ exhibited clockwise hysteresis, SO_4^{2-} exhibited anticlockwise hysteresis, and K^+ and Cl^- each showed no hysteresis. EC as a surrogate for total dissolved solids agrees acceptably with stable water isotope hydrograph separations during small peak runoff events (<3 mm/h). However, isotope and conductivity tracers strongly disagree during a large runoff event (>10 mm/h) in the mosaic catchment. Early wet-season events indicate lower event water fractions than events farther into the wet season. Despite previous work showing land cover strongly controls storm runoff efficiencies, hydrograph separation and hysteresis analyses only indicate weak event water delivery differences between the paired forest and mosaic catchments.

1. Introduction

Many flowpath and runoff studies have been conducted in temperate regions, but the understanding of hydrologic processes in tropical catchments pales in comparison (Wohl et al., 2012). Further study in the humid tropics, which covers about 25% of the earth's land surface, becomes more urgent as the tropics face rising land cover disturbance pressures owing to population growth (Foley et al., 2005). Anthropogenic landscape disturbances to soil morphologies in the humid tropics further alter the flow regime, creating challenges in understanding hydrologic system behavior as land covers undergo change. Hydrograph separation studies using stable water isotopes and naturally occurring ion tracers present an opportunity to elucidate runoff process thresholds and infer flowpaths across a spectrum of anthropogenically altered tropical land covers (Buttle et al., 2004). Improved hydrological mechanistic understanding using natural tracers may advance hydrologic model development for predicting the impacts of change, with potential benefits for society (e.g. flood forecasting and hydropower) and interdisciplinary research (e.g. climate change,

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chemical weathering zones, plant water use and availability). Yet, only a few investigations have recently described event-based tracer studies in the tropics (e.g. Kurtz et al., 2011; Schellekens et al., 2004; Goller et al., 2005; Muñoz-Villers and McDonnell, 2012 and Bonell et al., 1998).

This study aimed to identify event-based runoff characteristics and evaluate electrical conductivity (EC) effectiveness as a hydrograph separation tracer relative to the stable water isotopes deuterium (δD) and oxygen-18 ($\delta^{18}O$) in three humid tropical catchments. These experimental catchments each span a spectrum of recovery from anthropogenic activity as part of the Agua Salud Project in the Panama Canal Watershed. The same study catchments are described in detail in Ogden et al. (2013). We also utilized major ion hysteresis analysis (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, and Cl^{-}) in conjunction with the hydrograph separation results to interpret storm runoff water sources. Event scale runoff behavior in the Panama Canal Watershed is characterized by highly responsive streams that rapidly deliver water as interflow (Niedzialek and Ogden, 2012). Variations in the effectiveness of EC and stable isotopes for hydrograph separation are analyzed based upon antecedent catchment conditions and event-based runoff behavior. This research presents potential applications for identifying storm runoff flowpaths and discriminating runoff fluxes from different sources in hydrologically responsive humid tropical catchments. Study results serve as a critical physical process characterization for later evaluating biogeochemical transport and cycling in the Panama Canal Watershed.

Naturally occurring geochemical constituents resulting from mineral weathering and biogeochemical processes can serve as flowpath tracers to help identify runoff generation processes. Hydrograph separation quantifies the relative contributing source water fractions (event water vs. pre-event water) to stream runoff during precipitation events. Decades of research on hydrograph separations using geochemical tracers have shown that in most alpine and temperate upland forested basins, the pre-event fraction is 50% or more of streamflow at peak discharge (Buttle, 1994). Past studies have compared different naturally occurring tracers on their effectiveness for hydrograph separation in temperate climates (e.g. LaDouche et al., 2001; Wels et al., 1991) and tropical montane Puerto Rico (Schellekens et al., 2004), yet there is a paucity of hydrograph separation studies comparing major ion tracers with stable water isotopes across small, steep, humid tropical catchments.

The ideal event-based tracers for humid settings are stable water isotopes δD and $\delta^{18}O$, as they are generally considered to behave conservatively when evaporative fractionation processes are negligible. Major ions and EC have also been successfully applied as tracers (e.g. Rice and Hornberger, 1998; Muñoz-Villers and McDonnell, 2012), but this can be problematic due to their non-conservative behavior. Regardless of conservative behavior, *C/Q* hysteresis analysis can help determine solute flowpaths. Cl^{-} and Br^{-} are often assumed to act relatively conservatively in terrestrial ecosystems, though there is some variation as to how different naturally-occurring geochemical tracers behave in different settings. In a meta-analysis of Cl^{-} conservative behavior in forest ecosystems, Svensson et al. (2010) found that Cl^{-} is more likely to be conservative in regions with high Cl^{-} deposition than in areas with low (<6 kg ha^{-1} yr^{-1}) Cl^{-} deposition. Given the proximity to both the Atlantic and Pacific Oceans, the Cl^{-} deposition rate in the Agua Salud catchments is expected to be high. Sklash et al. (1986) also report that Cl^{-} and EC both exhibit non-conservative behavior relative to the stable water isotopes in the Mai Mai catchment in New Zealand. EC can also exhibit non-conservative behavior (Pilgrim et al., 1979). Prior to this study, it was unknown how EC and Cl^{-} behave during runoff events in the Agua Salud catchments.

1.1. Runoff production in the Panama Canal Watershed

Hydrograph separation studies across varying land uses in the humid the tropics are lacking (Buttle et al., 2004). The initiation of the wet season is of particular interest for conducting a runoff tracer study, as anomalously high runoff ratios have been observed during this period in the Panama Canal Watershed (Calvo et al., 2005). Coupling hydrometric monitoring with event water and pre-event water fraction estimations using natural geochemical tracers could elucidate flowpath and runoff mechanisms as the Agua Salud Project catchments undergo a transition in moisture states. A dual component, rather than three component hydrograph separation influenced our approach per the Q-mode factor analysis by Kinner and Stallard (2004) of chemical constituents in the Lutz Creek catchment located 11 km from the Agua Salud sites. They found that 95% percent of variance in Ca^{2+}, Cl^{-}, K^{+}, Mg^{2+}, Na^{+}, NO_3^{2-}, PO_4^{2-}, $Si(OH)_4$, and SO_4^{2-} can be explained by surface and subsurface runoff-contributing end members.

The objectives of this study are two-fold (i) to identify effective geochemical tracers for hydrograph separation purposes, and (ii) compare and contrast geochemically-derived hydrograph components and hydrometric runoff behavior among catchments of different land uses during the dry- to wet-season transition in moisture states.

1.2. Study location

In 2008, the Smithsonian Tropical Research Institute (STRI) began a landscape-scale study called the Agua Salud Project in the Panama Canal Watershed to investigate land use impacts on ecosystem services. The Agua Salud Project addresses tropical studies in biodiversity, forestry, and ecosystem services including hydrology across a spectrum of common tropical land uses (Stallard et al., 2010). Our study investigates early wet season precipitation runoff events using naturally occurring geochemical tracers across three catchments in Agua Salud Project.

We studied three catchments draining into the Agua Salud River in the Panama Canal Watershed (Fig. 1). The 1.43 km^2 forest catchment is contained entirely within Soberanía National Park. Roughly 80% of the forest catchment is a mature forest (>80 years old) while secondary succession forest (<35 years old) makes up the remaining 20%. The second catchment is a mixed land-use mosaic watershed draining 1.82 km^2 adjacent to the forest catchment. It is characterized by a mix of young secondary forest (<15 years in age), older secondary forest (>15 years in age), actively grazed cattle pasture, and patches of subsistence agriculture. The third study sub-catchment is a 0.423 km^2 actively grazed cattle pasture embedded within the mosaic catchment. All three study catchments share similar morphology, soils, underlying geology and rainfall.

1.3. Climate

Panama is located between 7° and 10° north of the equator with distinct wet and dry seasons governed by Inter-Tropical Convergence Zone movement. On average, the wet season begins on May 4 with a standard deviation of 11 days and ends end on December 20 with a 15 day standard deviation (Smithsonian Tropical Research Institute (STRI), 2013). We monitored the geochemistry of the three streams during rainfall events during a six week hydrologic transitional period at the start of the wet season beginning in May, 2013 and ending in mid-June, 2013. Average annual rainfall between 1960 and 2010 at Barro Colorado Island located about 11 km