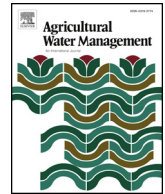




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## Assessment of water sources and their contributions to streamflow by end-member mixing analysis in a subtropical mixed agricultural catchment

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## ABSTRACT

Knowledge of the dominant water sources and their relative contributions to streams in time is important for understanding the underlying hydrological processes as well as managing the quantity and quality of water resources. In many subtropical regions, the complexity of mixed agricultural land and water use in combination with lack of data further inhibits such understanding of the dominant catchment scale runoff generation processes. This study provides new insights into the time-variable interactions of natural and anthropogenic influences on the catchment response through integrated hydrometric and multi-tracer (stable water isotopes,  $Mg^{2+}$ ,  $Na^+$ ,  $Si^{4+}$ ,  $Cl^-$ , and Electricity Conductivity) analyses. The combined diagnostic tools of mixing models (DTMM) and end-member mixing analysis (EMMA) were successfully used to evaluate the spatiotemporal variability in key water sources of a subtropical catchment in China. This study site is characterized by rain-fed uplands and irrigated water paddy fields. The EMMA results for one year of data showed that irrigation water, rainwater and ground water were the three main sources, which contributed to 64%, 19% and 17% of the streamflow on average, respectively. However, temporal patterns in rainfall and irrigation practices did cause significant variability in these relative contributions. Overall, we found that routine agricultural practices to optimize crop growth (especially during paddy growth periods) was a more important factor than hydro-meteorological conditions in controlling the regime and properties of water sources. The relatively simple but successful application of EMMA and DTMM in a complex environment demonstrates that it is a valuable approach for understanding water sources and hydrologic processes concerning agricultural or mixed-land use catchments.

### 1. Introduction

Information about the sources and flow pathways that generate streamflow is essential for understanding hydrologic and biogeochemical processes. Especially in cultivated catchments, this further relates to characterizing contaminant transport of non-point source agricultural pollution (Jin et al., 1999; Birkel et al., 2010; Zhao et al., 2013). Mixing models using isotopic and chemical tracers as a hydrograph separation technique have been widely and successfully used to trace streamflow sources and flow paths at the catchment scale. They have provided new insights into hydrological processes with respect to (time-variable) water sources and dominant flow pathways in catchment hydrology (e.g. Liu et al., 2008, 2013; Munyanza et al., 2012). These hydrograph separation techniques assume conservative mixing and require specific definitions of the endmembers. However, considerable uncertainties remain due to the spatial and temporal

variability in end member chemistry composition (Soulsby et al., 2003; Schmieder et al., 2016). In agricultural catchments, this is further complicated by human activities (Durand and Torres, 1996; Soulsby et al., 2003). For example, soil tillage and the application of fertilizers and pesticides can remove the chemical gradients in catchment soils, which in turn affect the original chemical properties of different hydrological sources. As such, most of the chemical or isotopic hydrograph separation studies have been carried out in semi-natural ecosystems. These include forested catchments (Scholl et al., 2015; Klaus et al., 2015), mountain regions (Hugenschmidt et al., 2014; Rahman et al., 2015), and other (semi-) natural ecosystems such as in Arctic river basins (Blaen et al., 2014) and glaciated regions (Wu et al., 2016; Wilson et al., 2016). Relatively few of these studies concern agricultural or mixed-land use catchments (Exner-Kittridge et al., 2016; Tweed et al., 2016). Yet, in order to minimize agricultural pollution and manage water resources efficiently, knowledge on the sources and pathways of

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water that contributes to the stream is of crucial importance.

In non-irrigated agricultural catchments, precipitation, ground water and riparian zone water are generally assumed to be the major contributors to stream flow generation (Hyer et al., 2001). However, where rain-fed and irrigated fields co-exist, understanding the relative contribution of irrigation water with respect to the other potential sources in agricultural catchments is required (Unal et al., 2004). In particular, for subtropical rural irrigated environments, a lack of data has contributed to a limited understanding of the (time-variable) contributions of rainwater and irrigation water to streamflow generation. For example, in subtropical China, paddy field irrigation is common, yet the influence of different irrigation phases to streamflow generation is poorly understood. Previous studies focused only on specific storm events when the migration of substances is most active (Hugenschmidt et al., 2014; Farrick and Branfireun, 2015). However, such specific focus studies are known to bias the physical interpretation of contributing end-members (James and Roulet, 2006). A study on streamflow generation in a 19.8 ha agricultural catchment previously showed significant differences in hydrologic flow paths and sources between non-stormflow periods and stormflow periods (Pionke and DeWalle, 1994 I; DeWalle and Pionke, 1994 II). At the seasonal to annual time-scale, the geochemical character of particular water sources can vary significantly due to different pathways providing distinct opportunities for interaction of the water with soil and bedrock (Yang et al., 2009). In addition, fractal behavior may occur across time scales and affect long-term observations of streamflow chemistry (Kirchner et al., 2000). Hence, it is essential to understand the validity and applicability mixing models in different environments.

Here, we aimed to gain new insights into the spatiotemporal variability of streamflow generation in a mixed subtropical agricultural catchment. We focused on a region within the Poyang Lake drainage area in subtropical China, where common agricultural areas typically consist of small patches of uplands mixed with paddy fields. Streamflow is composed of overland flow, irrigation water and soil water (Zhang et al., 2011) but the temporal variability in the relative contributions is largely unknown. The specific objectives of this study were a) to explore the chemical characteristics of the key potential water sources of streamflow, including rainfall, irrigation water and ground water; and b) to quantify their relative contribution to streamflow under different hydrological conditions throughout the year.

## 2. Materials and methods

### 2.1. Study area

This work was carried out in the Sunjia experimental research catchment (50.5 ha), located in the headwater region of Poyang Lake, near Yingtan, Jiangxi Province, in South Eastern China (Fig. 1). The humid subtropical climate is characterized by hot summers (up to 40 °C) and mild winters (5.1 °C). The mean annual temperature is 17.8 °C. Mean annual potential evapotranspiration is ~1200 mm, while mean annual precipitation totals ~1800 mm, of which half occurs between March and June. The catchment elevation ranges from 34 to 55 m and slopes are around 5% to 8%.

The geology in the study region consists of Cretaceous sandstone and deeply weathered Quaternary red clay. Clay mineralogy is dominated by kaolinite with some hydro-mica and vermiculite, as a result of the weathering of feldspar and other silicate minerals. This weathering may cause higher cationic concentrations (e.g. Ca<sup>2+</sup>, Mg<sup>2+</sup>) in ground water than in rainwater and irrigation water. Desilicating and ferrallitic weathering in this subtropical environment is liable to remove Si<sup>4+</sup>, resulting in Si-depleted minerals. Soils in this region are red soils, which are derived from the Cretaceous sandstone and Quaternary red clay and are classified as Ultisols based on the USDA Soil Taxonomy (Soil Survey Staff, 2010). These soils are strongly acidic with pH (H<sub>2</sub>O) varying from 4.5 to 6.0. They are also rich in sesquioxides with an iron-oxides

content of about 20–60 g kg<sup>-1</sup> in the soils.

The dominant agricultural land uses during the observation period were rain-fed upland peanut (*Arachis hypogaea*) (39%) and double rice (*Oryza sativa*) in the terraced irrigated paddy fields (25%). Other land uses in the upland areas included mandarin orange (*Citrus reticulata*) tree (6%), an agroforestry system consisting of peanut intercropped with mandarin orange (*Citrus reticulata*) tree (8%), grape (*Vitis vinifera*) orchard (10%) and other forested land (6%). The remaining land (6%) was occupied by ponds and residential use. Irrigation water to supply the paddy fields originates from the Luxi River. It enters the catchment through two inlet weirs channels (Fig. 1). Stream flow exhibits strong seasonality, reflecting patterns in both precipitation and irrigation practices. High flow coincide with the irrigation period and the rainy season, while ephemeral drying-up occurs after irrigation stopped in October during the dry season (Tang et al., 2007, 2008).

### 2.2. Field monitoring and sample collection

We collected hydrometric data and water samples for chemical analyses between January and December 2015. Rainfall was recorded by an automatic tipping bucket (Resolution: 0.5 mm) connected to an event data logger (Onset Computer Corporation, USA) installed near the foot of the peanut hillslope (Fig. 1). Rainfall samples were collected 24 times during the study year, just before times which coincided with stream water sampling. All water samples were stored in the refrigerator prior to analysis. Four weirs were installed to measure irrigation inflows (No.1 and No.2) and stream outflows (No.3 and No.4) within the Sunjia catchment (Fig. 1). Two different types of weirs, a rectangular and sharp-crested weirs, were installed at the inlet (No.1) and at the other stream flow stations (No.2, No.3 and No.4), respectively. The No.3 weir was installed at the outlet of the irrigation channel to another catchment. Water level was measured with a HOBO data logger (Onset Computer Corporation, USA) and recorded at 30-min intervals. The recorded water levels were then converted to flow by adopting theoretical rating equations for the specific weirs. For the sharp-crested weirs at No.2, No.3 and No.4, this also involved additional gauging data. The total irrigation flow into the catchment was calculated as the sum of inflow at No.1 and No.2 weirs minus the irrigation outflow at No.3 weir. There was no additional water source for the irrigation channel between the weirs at sites No.1 and No.3. The weir at No.4 was located at the primary outflow channel of the catchment.

Shallow ground water samples were collected monthly from three wells across the catchment (see Fig. 1). Wells 1 and 2 were used by local farmers for drinking water and used for water sampling only. At observation Well 3 ground water table was also monitored by a HOBO water level data logger at 30-min intervals (Onset Computer Corporation, USA). Irrigation water at the inlet, stream water at the outlet and spring water that seeps from the soil at the foot of the hillslope (Fig. 1) were collected every fortnight.

### 2.3. Laboratory sample analysis

The rainfall, irrigation, spring, well, and stream water samples were analyzed for major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Si<sup>4+</sup>) and anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) using a Dionex ICS1100 Ion Chromatograph (IC). Analytical precision (1σ standard deviation) for all ions was less than 1% and the detection limit was less than 0.1 mg L<sup>-1</sup>. Electricity conductivity (EC) and the pH of water samples were also measured. δD and δ<sup>18</sup>O analyses were conducted by a Liquid-Water Isotope Analyzer (Model 908-0008, Los Gatos Research, Inc.) and results were expressed relative to VSMOW in ‰(permil) following Eq. (1):

$$\delta(\text{‰}) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

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