Scientific Research

Domestic Water Supply Dynamics Using Stable Isotopes δ^{18}O, δD, and d-Excess

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Abstract

Surface water is the greatest contributor to many water supplies in urbanized areas. Understanding local water sources and seasonality is important in evaluating water resource management, which is essential to ensure the sustainability of water supplies to provide potable water. Here we describe the municipal water cycle of Columbus, Ohio, USA, using δ^{18}O, δD, and d-excess, and follow water from precipitation through surface reservoirs to a residential tap between May 2010 and November 2011. We show that trends in water isotopic composition of Ohio precipitation have a seasonal character with more negative values during the winter months and more positive values during the summer months. The year of 2011 was the wettest year on record in Central Ohio, with many months having high d-excess values (>+15‰), suggestive of increased moisture recycling, and possibly moisture introduced from more local sources. Tap waters experienced little lag time in the managed system, having a residence time of ~2 months in the reservoirs. Tap waters and reservoir waters preserved the isotopic signal of the precipitation, but the reservoir morphology also influenced the water residence time, and hence, the isotopic relationship to the precipitation. The reservoirs supplied by the Scioto River function like a river system with a fast throughput of water. The other reservoirs display more constant solute concentrations, longer flow-through times, and more lacustrine qualities. This work provides a basic understanding of a regional water supply system in Central Ohio and helps characterize the water flow in the system. These data will provide useful baseline information for the future as urban populations grow and the climate and hydrologic cycle changes.

Keywords

Ohio Precipitation, Municipal Water Supply, Moisture Recycling, Reservoir Residence Time

1. Introduction

Anticipation of the future relationship between water resources and climatological conditions and population growth is essential for developing strategies to ensure the long-term sustainability of water supplies [1]. Surface reservoirs provide approximately 63% of all public water supplies in the USA [2]. The stability of water resources in regards to monitoring and planning represents a major challenge for water managers. The timing of precipitation and evaporative water loss from reservoirs can significantly affect water storage, proving difficulty in developing reservoir-planning models [3] [4]. In addition, changes in precipitation amounts, recharge rates, and land use can affect the residence time of water through watersheds altering reservoir storage capacity. In Ohio, the total water withdrawals in 2000 were 42.0 Mm^3/d, with 39.0 Mm^3/d from surface water and only 3.0 Mm^3/d from groundwater [2]. The primary uses of this water are domestic supply, irrigation for agriculture, livestock usage, and aquaculture. For Ohio in 2000, the public water supply usage, water withdrawn by public and private water suppliers, was 5.6 Mm^3/d [2].

The public water supply of Columbus, Ohio, utilizes surface water from Griggs and O'Shaughnessy Reservoirs on the Scioto River, Hoover Reservoir on Big Walnut Creek, supplemental water from Alum Creek Reservoir on a tributary of Big Walnut Creek, and groundwater. This mix of water is distributed to residents via three water plants, Dublin Road Water Plant (DRWP), Hap Cremean Water Plant (HCWP), and Parsons Avenue Water Plant (PAWP) (**Figure 1**). With increasing suburbanization in nearby Franklin and Delaware counties and population growth in the city of Columbus, the need to understand current water resource dynamics is extremely important. Our goal in this paper is to provide data that documents the current status and stability of regional water supply so this information can serve as a baseline in the future.

Stable isotope analyses can provide an important method in determining the sources and residence times of water, monitoring the rates of water loss, and regional water resource sensitivity to evaporation. Although, the
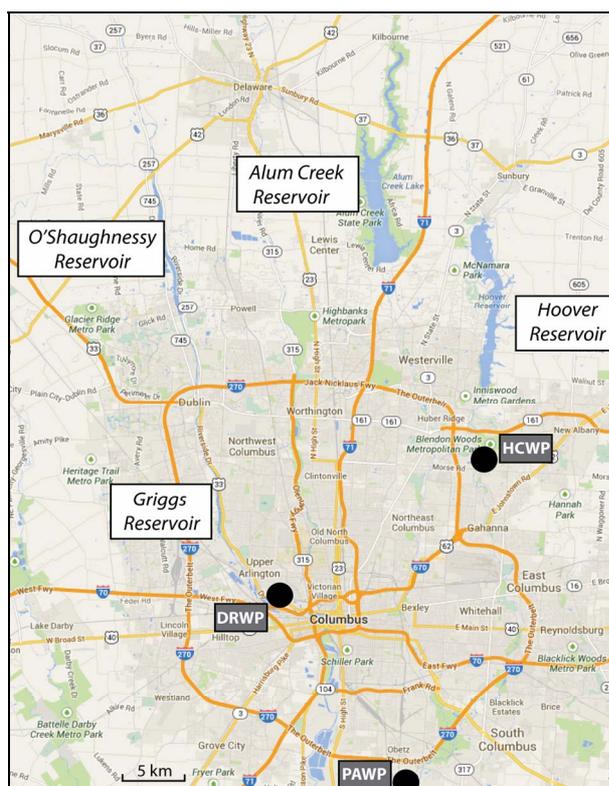

Figure 1. Reservoirs that contribute to the Columbus, Ohio water supply are Griggs, O'Shaughnessy, Alum Creek, and Hoover. The Dublin Road Water Plant (DRWP) extracts water from Griggs and O'Shaughnessy for water supply usage, while the Hap Cremean Water Plant (HCWP) utilizes water from Hoover Reservoir. Alum Creek Reservoir provides supplemental water to Hap Cremean Water Plant (adapted from Google maps). Parsons Avenue Water Plant (PAWP) distributes groundwater from wells.

isotopic evidence for evaporation does not in itself provide a warning signal of water resource sensitivity, data collected over time and analyzed in combination with information on regional climate and hydrology could be used to characterize and monitor surface water resource susceptibility to climate change [1]. The comparison of the isotopic signature of precipitation to potable water can also provide important information regarding the residence time of water in human-dominated hydrologic systems. At a regional level, the difference in isotopic ratios between precipitation and tap water can be attributed to hydrological factors such as water transit times from the source to the consumer. Management of water resources requires that the human interactions, known perturbations, and natural processes in the hydrologic cycle be fully understood. This information will enhance knowledge about site-specific hydrology, water management, water supply infrastructures, and regional hydroclimatological impacts [1]. This work utilizes stable isotopes $\delta^{18}O$ and δD to delineate the residence time of water in a human-controlled watershed-reservoir system, based on the lag between precipitation and residential tap water over time. Our observations will contribute an important dataset for interpreting regional water sources and supplies in order to evaluate water management. A major justification for this study is to provide the initial database for future comparisons of the water distribution system in Columbus, Ohio.

2. Methods

2.1. History of Columbus, Ohio, Water Supply

In 2010, Columbus, Ohio, was the 15th largest city in the United States with a population of 787,033 [5]. Water availability played a crucial role in population growth of Columbus over the past 100 years. In 1904, the city constructed Griggs Dam on the Scioto River to provide an adequate water supply. For 20 years, Griggs Reservoir served as the only reservoir providing water to Columbus. With the completion of the O'Shaughnessy Dam, an additional storage dam further upstream on the Scioto River from Griggs Reservoir, in 1925, Columbus had a water supply to serve a population of 0.5 million—twice the city's size. By 1945, population growth increased the demand for water. In 1955, Hoover Dam was completed on Big Walnut Creek. By the late 1960s, additional water supply was needed, and Alum Creek Reservoir was built in 1978, as a supplement to Hoover Reservoir. In 1983, wells in Southern Franklin County Ohio were constructed in an aquifer between the Scioto River and Big Walnut Creek. Currently three reservoirs, Griggs, O'Shaughnessy, and Hoover, provide 85% of the more than 4.9×10^5 m^3 of daily water supplied to the metropolitan area, while the remaining 15% is drawn from wells in southern Franklin County, Ohio (**Table 1**) [6].

2.2. Site Description-Reservoirs and Water Plants

Griggs Reservoir (**Figure 1**) is associated with the Scioto River (which remains the main water source for Columbus) (**Table 1**). It is ~9.7 km long, and located on the NW side of Columbus, Ohio. Approximately 16 km upstream of Griggs Dam on the Scioto River is the O'Shaughnessy Dam separating the slightly larger O'Shaughnessy Reservoir (**Figure 1**) from Griggs Reservoir near Dublin, Ohio. Together, these two reservoirs have a capacity of 2.3×10^7 m^3 [6]. Approximately 30% of drinking water for the city of Columbus comes from the Griggs and O'Shaughnessy Reservoirs. The Griggs and O'Shaughnessy Reservoirs retain only a small percentage of the Scioto River water that flows through Columbus. Griggs and O'Shaughnessy reservoirs are more of a riverine system connected to the Scioto River, and this creates a very weather- and flow-dependent system [8].

Table 1. Columbus, Ohio, water supply information.

Reservoirs/Wells	Water Source	Surface Area (km^2)	Capacity (m^3)	Average Raw Water Demand[*]
Griggs	Scioto River	1.5	5.3×10^6	6.4×10^4
O'Shaughnessy	Scioto River	3.4	1.8×10^7	1.1×10^5
Hoover	Big Walnut Creek	13.2	7.9×10^8	3.8×10^5
Alum Creek Lake	Alum/Big Walnut Creek	13.7	8.9×10^8	5.0×10^5
South Well-Field	Groundwater	na	na	5.7×10^5

[*]Average raw water demands assume 6% loss through treatment plant [7].

Hoover Dam (**Figure 1**) forms the Hoover Memorial Reservoir, which supplies water for the entire northeast portion of Franklin County (**Table 1**). Alum Creek Dam is located on Alum Creek, a tributary of Big Walnut Creek that drains into the Scioto River south of Columbus (**Table 1**). Hoover Reservoir can be supplemented with Alum Creek Reservoir water. The maximum amount allowed to be transferred from the Alum Creek Reservoir to Hoover is an average of 1.2×10^6 m³/d per calendar year [7]. Hoover and Alum Creek reservoirs are more characteristic of a lacustrine environment, resulting in a more classic reservoir system [8].

Columbus Division of Water manages water delivered to residents of the Greater Columbus Area. Three water plants, Dublin Road Water Plant, Hap Cremean Water Plant, and Parsons Avenue Water Plant (**Figure 1**), distribute water. The Dublin Road Water Plant utilizes surface water from the Griggs and O'Shaughnessy Reservoirs on the Scioto River, and provides water to downtown Columbus, western, and southwestern Franklin County. The Dublin Road Water Plant is designed to treat up to 2.5×10^5 m³/d. The Hap Cremean Water Plantutilizes surface water from the Hoover Reservoir on Big Walnut Creek and serves water to The Ohio State University and the northern half of Franklin County. The Hap Cremean Water Plant is designed to treat up to 4.7×10^5 m³/d of surface water. Alum Creek Reservoir also provides supplemental water to the Hap Cremean Water Plant. The Parsons Avenue Water Plantutilizes groundwater from wells and provides water to southeastern Franklin County, Ohio. The PAWP is designed to treat up to 1.9×10^5 m³/d of groundwater.

2.3. Sample Collection and Storage

Precipitation was collected from rain events using a precipitation collector located on the Ohio State University campus (latitude: 40.0025; longitude: −83.0390). This collector consisted of a plastic funnel (top diameter = 248 mm; height = 319 mm), silicone tubing, and a 1000 mL Nalgene® high-density polyethylene (HDPE) bottle with two fittings in the cap to allow the displaced air out as the bottle is filled with precipitation. The sample collection tubing line was contorted with a loop near the funnel to help minimize evaporation between the funnel and sample bottle. Each precipitation sample was collected once daily during events and as soon as possible after each event. Precipitation aliquots were collected for stable isotope and anion analysis, and samples were not filtered. Samples for isotopic analysis were collected in 20 mL glass scintillation vials with polyethylene cone shaped liners in the caps to help eliminate any headspace. Stable isotopic water samples were filled to the top to prevent evaporation, and lids were wrapped in parafilm to prevent any leakage or evaporative loss. All samples were then stored dark and chilled until time for analysis, usually within 2 - 3 months of collection.

Reservoir water collection was done weekly at Griggs Reservoir, and all other reservoirs were sampled on a monthly basis (May 2010-November 2011) by an individual wearing vinyl gloves. Water was collected from the reservoir pier. Reservoir samples were syringe filtered in the field using 0.4 µM Whatman™ Nucleopore syringe filters into a 60 mL pre-cleaned Nalgene® low density polyethylene (LDPE) bottle into glass 20 mL scintillation vials for stable isotopic analysis. For the isotopic samples, scintillation vial caps were wrapped in parafilm. Samples were refrigerated and stored dark until analysis.

Tap waters were collected from a residential tap in downtown Columbus supplied by the Dublin Road Water Plant weekly over the study from May 2010 to November 2011. Hence, the water collected originated from the Griggs/O'Shaughnessy reservoir system. Water from the tap was allowed to flow for ~5 seconds, and then aliquots for stable isotopes and anion analyses were collected and stored in the same way as precipitation samples.

2.4. δ^{18}O and δD Analysis

Stable isotopic samples were analyzed for δ^{18}O and δD using a Picarro Wavelength Scanned-Cavity Ring Down Spectroscopy Analyzer for Isotopic Water-Model L1102-*i* within 2 - 3 months of collection [9]. The stable isotopic analysis includes a calibration using internal laboratory standards of waters spanning the isotopic range of the samples. Our internal laboratory standards were deionized water aliquots from Florida (δ^{18}O = −2.3‰; δD = −12.3‰), Ohio (δ^{18}O = −9.3‰; δD = −64.6‰), Nevada (δ^{18}O = −14.2‰; δD = −106.0‰) and Colorado (δ^{18}O = −17.0‰; δD = −129.0‰). Our internal laboratory standards were standardized relative to Standard Light Antarctic Precipitation (SLAP) and Vienna Standard Mean Ocean Water (VSMOW), at the Ice Core Paleoclimatology Laboratory at The Ohio State University using standard gas-source mass spectrometry techniques [10]. Isotopic values are presented as per mil (‰) values. The accuracy was ≤4.2% for δD and ≤3.4% for δ^{18}O, calculated by relative standard error comparing the Picarro isotopic measurement for an internal laboratory standard and the Ice Core Paleoclimatology Laboratory isotopic measurement for an internal laboratory standard. Preci-

sion was calculated as ≤1.0% for δD and ≤0.5% for δ^{18}O, for 100 measurements using relative standard deviation.

Deuterium excess (d-excess) values were calculated as d-excess = δD − 8*δ^{18}O, using the Global Meteoric Water Line [11]. Deuterium excess reflects non-equilibrium fractionation characterized by temperature and relative humidity in the precipitation source region [12] [13].

2.5. Weather Station Data Collection

Temperature and precipitation amount data were gathered at the Waterman Farm of Ohio State campus weather station within the network of Ohio Agricultural Research and Development Center (OARDC) of the Ohio State University [14]. This station is ~1.4 km from the precipitation collector, and it has been collecting data since January 1986. This long-term record was used to calculate the average 25-yr monthly temperatures and precipitation amounts. Data from this study were also compared to the long-term climate records maintained by the National Weather Service.

3. Results

3.1. Meteorology

The precipitation totals for this study were above the 25-yr average monthly precipitation totals for Central Ohio for more than half of the months in this study (May 2010 to November 2011, **Figure 2**). Monthly mean temperatures were slightly above normal compared to the 25-yr monthly average temperature (**Figure 2**). Spring 2011 (February, March, April, and May) had precipitation totals much greater (as much as 2× the 25-yr average). Fall 2011 (September, October, and November) also had greater amounts of precipitation than the 25-yr monthly average. April 2011 was the wettest April on record, with total precipitation of 18.1 cm, breaking the record of 18.0 cm set in 1893. The wettest year on record in Columbus was 2011 (139.6 cm). The previous record was 135.0 cm in 1990. Columbus also experienced the third wettest spring (44.8 cm, with previous record of 48.8 cm in 1882), and the second wettest fall on record (38.1 cm, with the previous record of 39.4 cm in 1881) [15].

3.2. Isotopic Composition of Precipitation

Values of δ^{18}O and δD for precipitation ranged from −19.5‰ to −0.23‰ and from −148‰ to +4.5‰, respectively (n = 119; [16]). These ranges are typical of mid-continental stations globally [17]. The δ^{18}O volume-weighted precipitation values followed a similar trend to the precipitation δ^{18}O monthly average, with a more
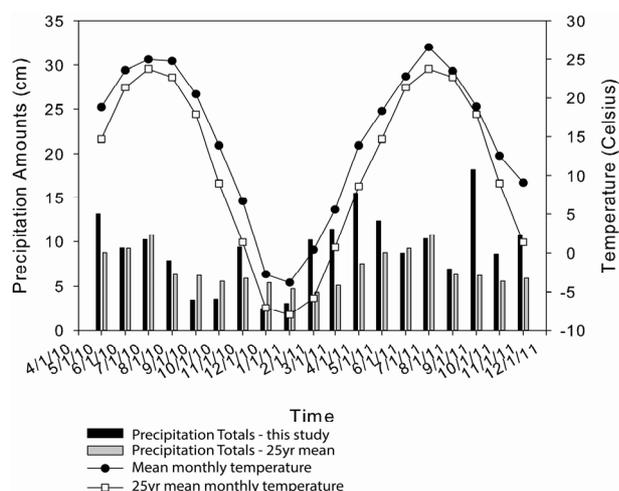

Figure 2. Monthly precipitation totals and average monthly air temperatures across the study during May 2010 to November 2011 in comparison to the 25-yr monthly precipitation totals and mean monthly air temperatures. Data gathered from a weather station within the network of OARDC.

positive signature in the spring and summer seasons and more negative signature in the fall and winter seasons (**Figure 3**). The $\delta^{18}O$ of precipitation displayed a significant relationship with the $\delta^{18}O$ monthly volume-weighted and 25-yr monthly mean temperature ($r^2 = 0.66$; $p < 0.05$). However, no statistically significant relationship existed between the stable isotopic value and the amount of precipitation per event throughout the entire data series (**Figure 3**). Although in the fall of 2011 (e.g. the 2nd wettest fall on record), precipitation values display an "amount effect" with more negative values with larger events (**Figure 3**). Individual precipitation samples span ~20‰ range for $\delta^{18}O$ and ~150‰ range for δD, with as expected more negative values from winter precipitation and more positive values from summer precipitation. The air temperature and $\delta^{18}O$ relationship form a linear regression of $\delta^{18}O = 0.27*T - 11.3$ with $r^2 = 0.44$. Precipitation d-excess values spanned +0.1‰ to +29‰, and had a positive significant relationship with δD ($r^2 = 0.23$). The majority of data fall along or above the Global Meteoric Water Line (GMWL) ($\delta D = 8.0*\delta^{18}O + 10$; [11]) (**Figure 4**). These data have a linear regression of $\delta D = 8.04*\delta^{18}O + 15.64$ ($r^2 = 0.96$; $p < 0.001$) (**Figure 4**), suggesting minimal evaporation has occurred.

3.3. Reservoir Waters

The reservoir data also display a seasonal pattern, with an isotopic transition from more positive waters during
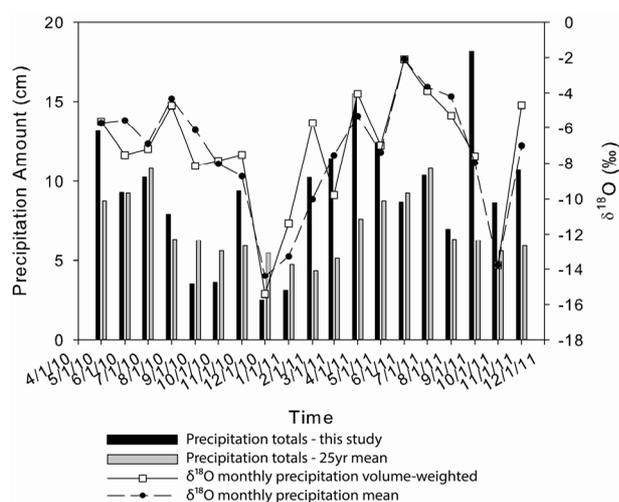

Figure 3. Precipitation $\delta^{18}O$ monthly mean and volume-weighted value from May 2010 to November 2011, in relation to the monthly precipitation amount totals compared to 25-yr monthly precipitation amount mean.
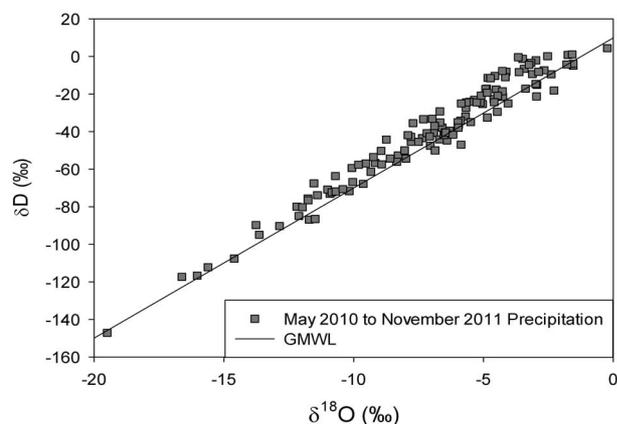

Figure 4. Precipitation isotopic values of May 2010 to November 2011 plotted in relation to the GMWL.

the warmer periods to more negative values during cooler periods (**Figure 5**). Reservoir isotopic values ranged from $\delta^{18}O$ of −8.9‰ to −4.7‰ and δD of −62‰ to −18‰, with d-excess values from +1.4‰ to +23‰ [16]. The most isotopically positive reservoir waters in 2010 occurred ~September 2010, while the 2011 seasonal enrichment occurred earlier, during August. The most negative signatures in the reservoirs were a $\delta^{18}O$ of −8.9‰ in March 2011, and in May 2010 in Hoover Reservoir. Reservoir waters follow along the GMWL, within the same range of the precipitation samples. The majority of these data fall above the line but some fall below ($\delta D = 6.0 * \delta^{18}O − 1.9$; $r^2 = 0.64$; **Figure 6**). In all reservoirs, the $\delta^{18}O$-δD values displayed a positive significant correlation.

3.4. Residential Tap Waters

Residential tap water distributed via the Dublin Road water plant ranged from $\delta^{18}O$ of −9.0‰ to −4.3‰ and δD
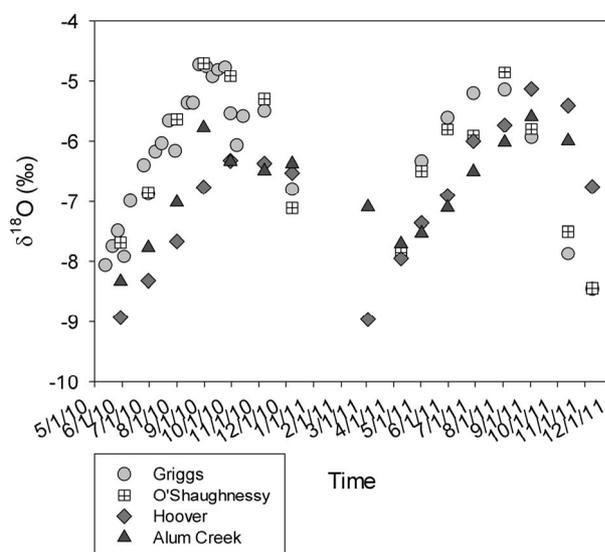

Figure 5. Reservoir $\delta^{18}O$ values from Griggs, O'Shaughnessy, Hoover, and Alum Creek from May 2010 to November 2011.
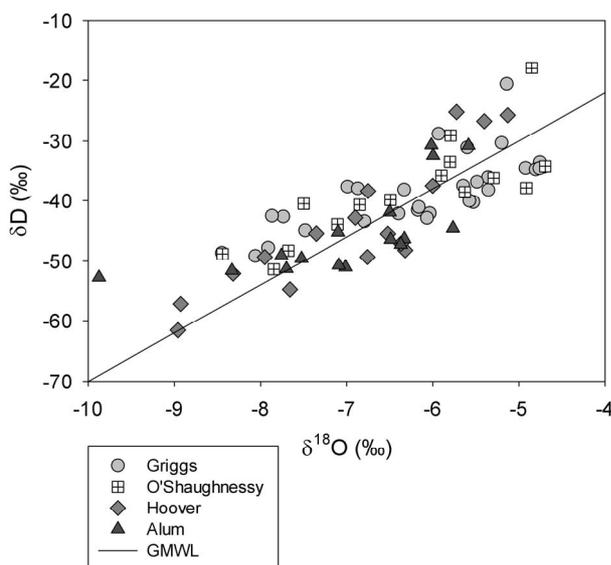

Figure 6. Reservoirs isotopic values over May 2010 to November 2011 plotted in relation to the GMWL.

of −59‰ to −19‰, respectively (n = 53; **Figure 7**; [16]). D-excess values range from +1.2‰ to +23‰, with lower d-excess occurring during July-October 2010, and the most positive d-excess occurring October 2011. The tap water (**Figure 7**) displays a seasonal pattern similar to the reservoirs (**Figure 5**). Tap water was isotopically the most positive in September 2010 and August 2011, and the most negative from January 2011 to mid-March 2011. Pearson positive correlations of significance (p < 0.05) of the tap water variables existed between temperature-δ^{18}O, temperature-δD, δ^{18}O-δD, and δD-d-excess. A significantly negative relationship occurred between δ^{18}O-d-excess. Tap waters data fall both above and below the GMWL (δD = 6.6*δ^{18}O + 4.1; r² = 0.69; **Figure 8**), plotting in a similar manner as the reservoir and precipitation data.

4. Discussion

4.1. Isotopic Records of Central Ohio Precipitation

Records of the isotopic composition of Central Ohio precipitation exist for two previous time intervals: January 1966 to December 1971, which are monthly samples from Coshocton, Ohio [18] and October 1992 to mid-December 1994 for all precipitation events from Oxford, Ohio [19]. These Ohio precipitation data collected in 1966-1971 have a range of δ^{18}O from −17.7‰ to −1.2‰, δD ranges from −126‰ to +3.6‰, and d-excess ranges from +0.64‰ to +24.6‰ and the precipitation data collected from 1992-1994 has a range of δ^{18}O = −20.1‰ to
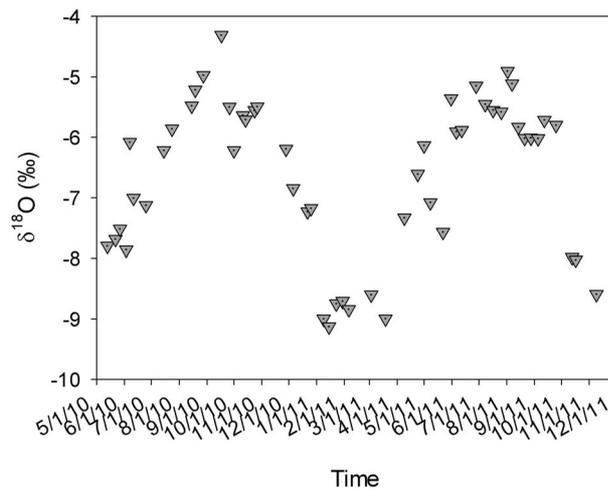

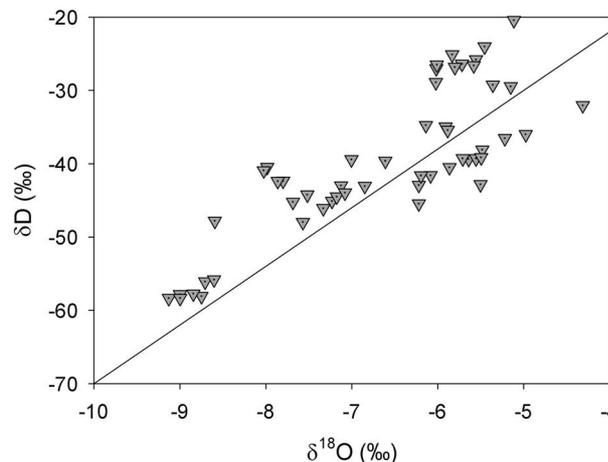**Figure 7.** Residential tap waters δ^{18}O signatures distributed from DRWP over May 2010 to November 2011.

Figure 8. Residential tap water isotopic values from May 2010 to November 2011 plotted in relation to the GMWL.

−0.47‰; δD = −147‰ to −3.2‰; d-excess = −8.6‰ to +25.7‰. These previous Ohio precipitation data collected in 1966-1971 and 1992-1994 also have similar local meteoric water line (LMWL) equations − δD = 7.5*δ^{18}O − 8.8 (r^2 = 0.97; [18]) and δD = 7.8*δ^{18}O − 11.2 (r^2 = 0.97; [19]). Compared to our 2010-2011 precipitation equation of δD = 8.0*δ^{18}O + 15.6 (r^2 = 0.96), our data have a similar slope but a positive intercept. This positive intercept signifies enhanced moisture cycling as the precipitation data plot mostly above the GMWL, while a negative intercept would imply greater evaporation loss, plotting below the GMWL [20] (**Figure 8**).

The monthly δ^{18}O and δD values of IAEA [18] and Coplen and Huang [19] are similar to ours as well. All data sets follow a similar trend of more negative isotopic values from January to March, increasingly more positive values until June, and then declining to more negative values until December (**Figure 9(a)**). Overall, the monthly mean δ^{18}O signatures range over ~15‰, the δD over ~120‰, and there is a smaller variation from the mean in the summer precipitation (April-September) than in the winter precipitation (October to March) (**Figure 9(b)**). Colder temperatures in the winter months produce greater amounts of snow with more negative isotopic values, compared to warmer and isotopically heavier rain (Columbus 2010-2011 snow δ^{18}O = −24.2‰ to −9.4‰ and δD = −185‰ to −58‰), and this could contribute to the greater isotopic variation across the seasons (**Figure 9**).

These similar trends suggest that the sources of moisture to Central Ohio and the processes affecting isotopic variation in Ohio precipitation have not changed dramatically over the last 45 years. However, the data on an event, and even seasonal basis, can be used, in part, to detect differences in moisture sources throughout the calendar year. The d-excess data from 2010-2011 provide the best information of changes in moisture sources, as these data have a deviation from the expected modern worldwide sample value of +10‰ (**Figure 9(c)**). The mean d-excess of precipitation varies globally with the majority falling in the +10‰ to +15‰ range, signifying meteoric origin (+10‰). In the United States, d-excess cannot be explained by a single parameter, but varies strongly with geographic location. It is very much related to different source air masses, differences in temperature, aridity, and the contribution from evapoconcentration and other moisture sources [21]. Higher d-excess can be caused by evaporation that leaves the remaining water vapor more positive in δD and δ^{18}O values, with a GMWL slope less than 8 [21]. Precipitation with a large d-excess value may result from the downwind admixture of the evaporated moisture [22]. Therefore, an increased d-excess in precipitation (>+15‰) could be linked to the significant addition of re-evaporated moisture within continental locations. If moisture from precipitation with an average d-excess of 10‰ is re-evaporated, the lighter $^2H^1H^{16}O$ molecule may contribute preferentially to the isotopic composition of the water vapor and this, in turn, leads to a more positive d-excess in precipitation.

The monthly d-excess values in the Northern Hemisphere follow a U-shaped trend with January d-excess of ~+12‰, steadily dropping to ~+6.5‰ in June, and rising back to ~+12‰ in November [20]. Hence, the d-excess values of >+15‰ during January-April and September-December could signify that the resultant precipitation is from increased moisture cycling from a more inland location, while in May-August d-excess of >+10‰ could indicate that this recycled moisture component is less. If re-evaporation and moisture cycling are the controls of these d-excess values, the possible moisture source could be from the Great Lakes Region, rather than from Ohio's primary precipitation source, the Gulf of Mexico. D-excess in May-June 2010 (+17.7‰ and +19.4‰) and August-November 2011 (+20.7‰, +22.4‰, +20.4‰, +22‰) display consistently higher than +10‰ d-excess values (**Figure 9(c)**). In 2010, the d-excess values represent averages from 11 and 10 sampling events in May and June respectively, due to the high number of precipitation events that occurred in this interval. Water recycling might have played a more important role that resulted in higher d-excess values during this time. In 2011, the higher d-excess values occurred during the wettest fall on record for Columbus with 26 rain events sampled between August to November. This interpretation supports the dependence of the isotopic signatures on the amount effect with the moisture source influenced by more continental sources, as signified by the higher d-excess values measured.

4.2. Comparison to Previous Riverine and Tap Water Studies in Central Ohio

Kendall and Coplen [23] conducted an isotopic study to describe the δ^{18}O and δD in river waters across the United States, and reported the Ohio LMWL derived from river water to be δD = 5.2*δ^{18}O − 8.2 (r^2 = 0.73; n = 82). Their river sampling locations within Ohio were located along the state borders, and precipitation was collected in a central northeast section of Ohio. The goal of their work and their river isotopic dataset was to serve as a proxy for the isotopic composition of modern precipitation in the USA. The slope of the LMWL for their
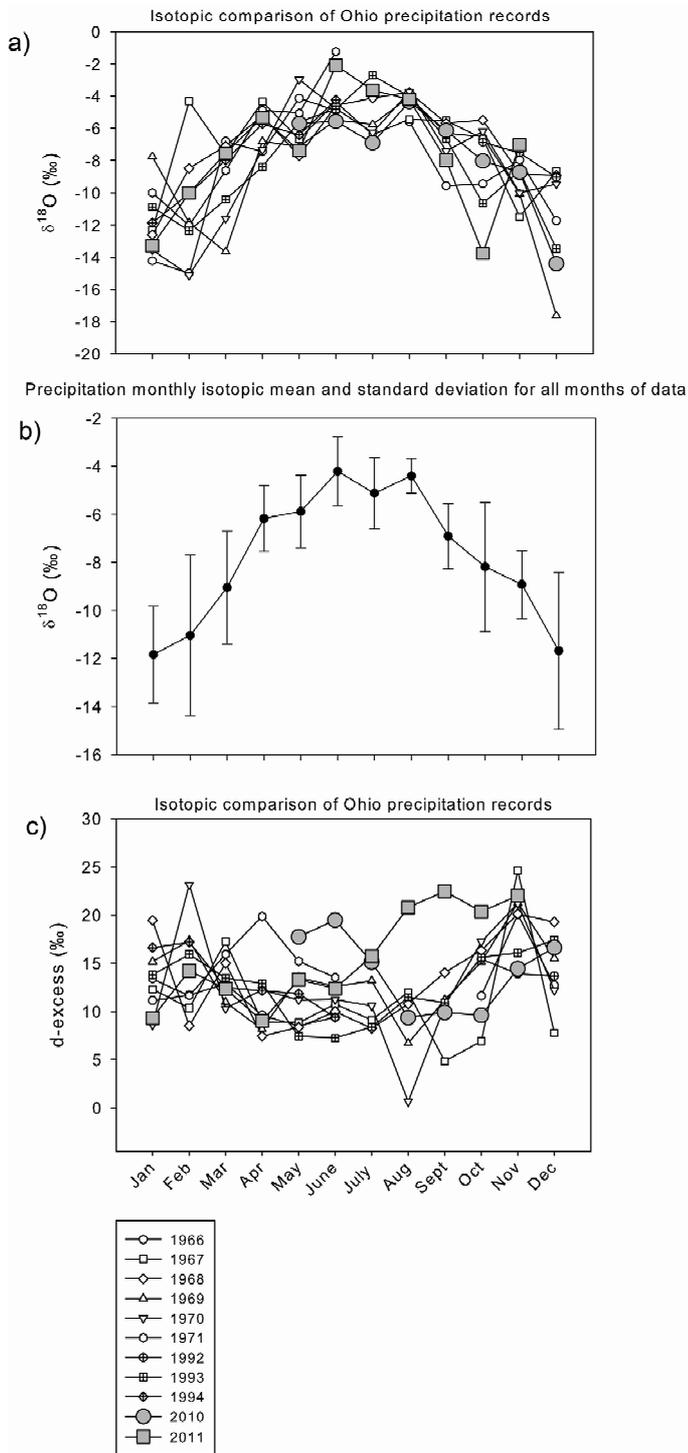
Figure 9. a) Average of monthly δ^{18}O precipitation signature comparison within Ohio from January 1966 to December 1971 [18], October 1992 to mid-December 1994 [19], and May 2010 to November 2011; b) The Ohio monthly δ^{18}O precipitation mean with error bars of 1 standard deviation of the mean, using all Ohio data [18] [19]; c) comparison of average monthly d-excess in precipitation within Ohio from January 1966 to December 1971 [18], October 1992 to mid-December 1994 [19], and May 2010 to November 2011.

dataset is lower than our 2010-2011 data (precipitation = 8.0; reservoir = 6.0; tap water = 6.6), reflecting the influence of other processes such as evaporation on the river waters, as well as potentially geographical variations [23]. Our reservoir waters of 2010-2011 have the most similar LMWL slope to their river water. The lower slopes of the LMWLs might imply significant post-rain evaporation of river samples prior to collection; if so, the data would not be representative of local rainfall. A slope lower than 6 in the LMWL for river water is indicative of evaporation, but it is unclear if this occurs during rainfall, within the soil zone as the water moves through the watershed, or in the streams themselves. Kendall and Coplen [23] predict, d-excess values in precipitation of >10‰, whereas the d-excess values of our study range from +1.4‰ to +23‰. The 2010-2011 d-excess has a wide range of values, and the range represents seasonal influences, water vapor sources, and moisture cycling creating higher d-excess. The Kendall and Coplen [23] prediction does overlap with the d-excess range observed in our study, as might be expected for river systems draining larger watersheds. Based on the discharge-weighted means of the spatial isotopic distribution in rivers, Kendall and Coplen [23] predicted precipitation values of $\delta^{18}O$ of −8‰ to −6‰ and δD of −60‰ to −40‰ for Ohio. These compare, but are more negative than our precipitation averages $\delta^{18}O$ of −6.9‰ and δD of −40.2‰. This supports the general contention that large-scale isotopic signatures of precipitation are preserved in the river isotopic compositions in Central Ohio [23].

Bowen *et al.* [1] described the distribution of $\delta^{18}O$ and δD in tap water across the United States as "dominated by spatially patterned variability." Bowen *et al.* [1] demonstrated that spatially coherent patterns in tap water reflect pervasive regionally features of water supply hydrology, and described the tap water isoscape of the United States through isotopic mapping of measured tap waters from across the country. Tap water patterns of $\delta^{18}O$ and δD were explained in terms of water sources and post-precipitation processes (*i.e.* seasonality, recharge, evaporation) affecting surface and groundwater resources.

The predicted isotope composition of Ohio tap water from interpolated precipitation data was $\delta^{18}O$ of −10‰ to −6.1‰ and δD of −59‰ to −49‰ [1]. Tap water samples were collected monthly in Columbus, Ohio, from January 2005 to June 2006 [1] [16]. These data henceforth will be referred to as the 2005-2006 tap waters. These 2005-2006 tap waters ranged between $\delta^{18}O$ of −9.4‰ to −6.1‰, δD of −63.4‰ to −42.6‰, and with a d-excess of +3‰ to +15‰. While the May 2010 to November 2011 tap waters ranged between $\delta^{18}O$ of −8.9‰ to −4.9‰, δD of −57.8‰ to −23.5‰, and d-excess of +1.8‰ to +23‰ for the monthly isotopic mean. Overall, the 2010-2011 tap waters were at times isotopically more positive and spanned a larger range of values than the 2005-2006 tap waters. All monthly average temperatures in both 2005-2006 and 2010-2011 were higher than the 25-yr average monthly temperatures except for January 2006. The monthly precipitation amounts were higher than the 25-yr average precipitation amount only 7 out of 17 months during 2005-2006 compared to 11 out of 19 months in 2010-2011, with 2011 being the wettest year on record. The total precipitation amount over the 17 months during 2005-2006 was 138 cm with no data available for June 2006, and the 19 months over 2010-2011 had a total precipitation amount of 175 cm. It should be noted that 2005-2006 tap waters were distributed from the HCWP using water from Hoover Reservoir, while the 2010-2011 tap waters were distributed from the DRWP with water from Griggs/O'Shaughnessy Reservoir.

In a comparison of 2010-2011 and 2005-2006 tap water data, the waters demonstrated different isotopic trends (**Figure 10(a)**). Seasonal transitions were seen in both tap water studies, but they occurred at different times of the year. The 2005-2006 data demonstrate a seasonal "lag" time in the precipitation-reservoir-tap system, as more negative isotopic winter waters were associated with the summer tap waters and more positive summer waters with the winter. The 2010-2011 tap waters match much better with seasonal isotopic precipitation patterns, with a faster, steeper gradient during the seasonal transition compared to the 2005-2006 tap waters. There appears to be a lag time of ~2 - 4 months when comparing the $\delta^{18}O$ of the 2005-2006 tap waters to the 2010-2011 data, depending on the time of year. This difference in lag time between precipitation and tap could be explained by the difference in reservoir type, innate differences in water flow paths in the different watersheds, or longer residence times of water due to the differences in precipitation amounts, temperatures, and vegetative growth between the years.

All else being equal, the lacustrine type flow system of Hoover Reservoir should have a longer water residence time resulting in a greater seasonal lag and a lower slope of the seasonal isotopic transition. This supports the work of Allen [8] who calculated an average residence time of 152 days in the Hoover Reservoir; in comparison to the calculated O'Shaughnessy Reservoir residence time as an average of 26 days. Hoover Reservoir's capacity is an order of magnitude greater than O'Shaughnessy's, and Hoover's water plant provides a larger
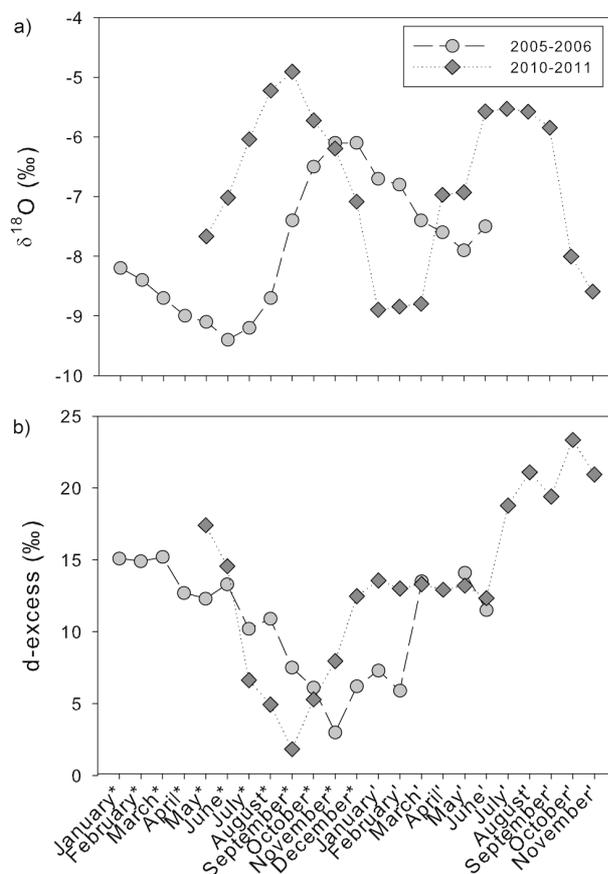
Figure 10. a) DRWP tap water δ^{18}O signature from May 2010 to November 2011 compared with the January 2005 to June 2006 tap waters distributed from the HCWP [1]; b) DRWP tap water d-excess from May 2010 to November 2011 compared with the January 2005 to June 2006 tap waters distributed from the HCWP [1].

amount of water daily. When comparing each reservoir's capacity to their daily volume of treated water, Hoover's ratio (7.9×10^8 m³: 4.7×10^5 m³/d = 16,808 days) is 2 orders of magnitude larger than O'Shaughnessy's (1.8×10^7 m³: 2.5×10^5 m³/d = 720 days). These differences support the concept that the O'Shaughnessy/Griggs reservoir system acts more like a riverine system with a smaller capacity but of faster flow-through than the Hoover reservoir system.

In a comparison of the 2005-2006 and 2010-2011 tap waters d-excess values, both waters each follow a V-shaped trend (**Figure 10(b)**). The 2005-2006 tap waters decreased from +15‰ in March 2005 to +2‰ in November 2005, and then increased to ~+13‰ in March 2006 until June 2006. The 2010-2011 tap waters d-excess values decreased from +17‰ in June 2010 to +2‰ in September 2010, and then increased to +14‰ in December 2010 until June 2011. D-excess of tap waters from July 2011 to November 2011 varied over +20‰ to +23‰. The 2010-2011 tap waters have their lowest d-excess in September 2010, while the 2005-2006 lowest d-excess occurs in November 2005. These data suggest a lag time of ~2 months, a shorter lag time than the δ^{18}O comparison, but both retained the primary precipitation signal. This difference in lag time may be explained by the idea that the d-excess responds more sensitively to seasonal changes in water source, as its main controlling factors are humidity, wind speed, and moisture availability. Also the d-excess seasonal slope transitions were steeper in the 2010-2011 tap waters compared to the 2005-2006 tap waters. This could be a function of each reservoir/water plant system, as the 2005-2006 tap waters came from the lacustrine system (Hoover) with a greater holding capacity and the 2010-2011 waters of the smaller riverine system (Griggs/O'Shaughnessy). The 2010-2011 d-excess tap water values followed closely with the d-excess values of precipitation during May 2011 to

November 2011, with d-excess values >+20‰. This period also coincides with the wettest fall on record, and supports the idea that the Griggs/O'Shaughnessy system retains the precipitation signature even with its "fast" flow-through characteristics, especially during periods of higher precipitation. This isotopic tap water comparison helps describe how differing reservoir types, lacustrine versus riverine, can potentially influence a municipal water cycle.

4.3. Water Cycle of Precipitation to Tap

The precipitation, Griggs reservoir waters, and the tap water are compared in **Figure 11**. The tap water values are similar to the reservoir (**Figure 11**). Even with the large amounts of precipitation during the study period, the reservoir and tap water signatures are similar, with the reservoir level kept at its normal pool level of 258.6 masl. Columbus tap waters have the most negative signature during January 2011 to March 2011, but winter reservoir data were unavailable because of the inability to sample during those times because of an ice cover. However, this lag suggests that the precipitation residence time from reservoir to tap is about two months.

If precipitation is rapidly utilized in the domestic supply and has a short residence time in the reservoir, the $\delta^{18}O$ values should have a similar time series trend. In the comparison of monthly 2010-2011 $\delta^{18}O$ averages of tap waters and volume-weighted precipitation, there are many months (December 2010, February 2011, April 2011, June 2011, and October 2011) during the study period that the tap water $\delta^{18}O$ does not relate well to the precipitation (**Figure 12**). Months that fall on the left side of the tap water: precipitation line have tap waters that
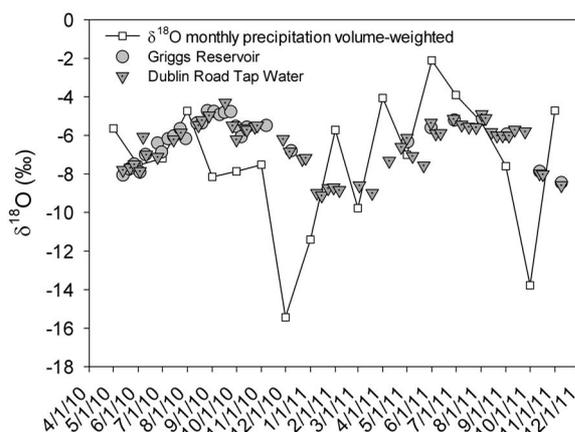

Figure 11. A comparison of Griggs reservoir, tap waters, and precipitation $\delta^{18}O$ volume-weighted signature over May 2010 to November 2011.
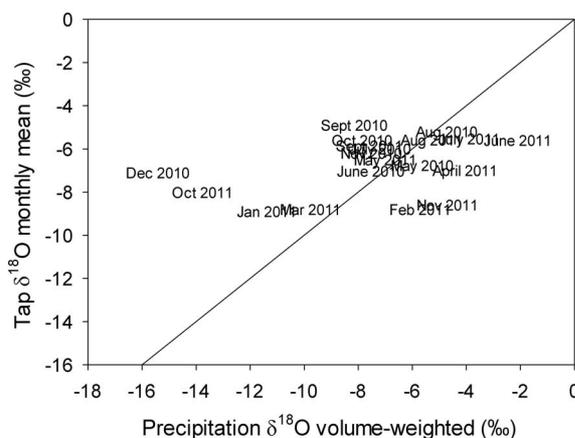

Figure 12. A comparison of tap water $\delta^{18}O$ monthly averages and precipitation $\delta^{18}O$ monthly averages over May 2010 to November 2011.

isotopically resemble summer to fall signatures, while the precipitation was of a more negative isotopic signature, suggestive of winter precipitation. Griggs/O'Shaughnessy Reservoir levels were close to the normal pool levels during both December 2010 and January 2011, while slightly higher in October 2011 at 258.8 masl. This discrepancy suggests some lag from the precipitation falling on the watershed to the tap, possibly due to longer residence times of water in the watershed, reservoir management, or water being drawn from deeper depths, as reservoir had ice covers during December 2010 and January 2011. The more negative values in October 2011 during the wettest fall on record can be explained by the isotopic amount effect, where a greater amount of rainfall produces lower isotopic values with water quickly exiting the reservoir without being captured. The February 2011, April 2011, June 2011, and November 2011 values fall to the right of the 1:1 tap water: precipitation line, with both tap and precipitation reflecting more positive summer isotopic values. These values had precipitation slightly more positive than the tap water, and this suggests mixing with slightly more negative reservoir waters to achieve the tap water signature, as reservoir pool levels were normal. In general however, the 2010-2011 tap waters retain the primary isotopic signal of the precipitation within the riverine system of Griggs/O'Shaughnessy over very short (*i.e.* weekly) time intervals.

4.4. Reservoir Susceptibility to Evaporation

Adeloye *et al.* [3] performed reservoir storage-yield-reliability planning analyses on two multiple reservoir systems, one in England and other in Iran, to investigate the possible effects of reservoir surface net flux from both baseline and climate-change conditions. The behavior of the two systems was different because of the great differences in climate (humid versus semi-arid). Implications for reservoir management and water supply, especially under future climate change scenarios, are important in order to anticipate water resources availability. Through applying different scenarios and using general circulation climate models, it was discerned that reservoirs with lower water yields, designed to meet the seasonal discrepancy between runoff and demand, will be the most prone to climate-change impacts [3].

The very high d-excess in precipitation during 2010-2011, as previously noted, may suggest re-evaporation of the precipitation moisture source to Central Ohio or upwind of Central Ohio during times of higher than average rainfall or at times of higher rates of precipitation. D-excess measurement could potentially be used to describe evaporation effects within reservoirs [24]. In this study, the d-excess values in the reservoirs displayed lower values (<+10‰) in August to December 2010, and the months of April 2011 to November 2011 all had values >+10‰. The summer lowering of the reservoir d-excess did not occur to the same extent in 2010 as in 2011, likely the result of higher than average precipitation amounts. The 2010 reservoir d-excess was the lowest (+2‰) in October 2010, with other times only decreasing to ~+10‰. Also the Griggs/O'Shaughnessy experienced greater d-excess changes than Alum/Hoover, again supporting the idea that hydrologic dynamics of riverine-type compared to lacustrine-type reservoirs can be different and can be seen using isotopic measurement. This suggests that on-going measurements of d-excess in the reservoir could provide information pertaining to both water source and/or reservoir evaporation. Clearly, a better understanding of the impact of precipitation sources on this value is needed before it can be used as a diagnostic tool.

5. Conclusion

This work establishes an isotopic characterization of precipitation, surface waters, and residential tap waters to describe the flow of water in the human-hydrological system of Columbus, Ohio. Signatures of δ^{18}O and δD in precipitation follow similar trends of previous data from 1970s and 1990s with seasonal characteristics of more negative values during winter months and more positive values during summer months. It was evident that tap waters were not experiencing as large of a seasonal lag as previously observed in tap waters from 2005-2006. The 2010-2011 residence time of precipitation to tap was about two months compared to four months in 2005-2006. While 2011 proved to be the wettest year on record for Columbus, Ohio, one implication of this was increased moisture source cycling resulting in higher d-excess (>+15‰) during April 2011 to November 2011. The higher precipitation rates during 2011 contributed to a shorter residence time of reservoir water to the residential tap, with reservoir morphology also playing a significant role concerning water cycling. Each reservoir system dynamic was important in its water and solute cycling as Griggs and O'Shaughnessy reservoirs act as a riverine system with a faster flow-through while Alum and Hoover reservoirs are more of a lacustrine environment of more constant concentrations and greater mixing. Even though much of this study was conducted during

a time with above average precipitation amounts, the basis of understanding about the municipal system of Columbus, Ohio, concerning the travel of precipitation to the reservoir and distribution to a residence has grown. This work provides local water resource managers with information about Ohio precipitation sourcing and a basis of isotopic reservoir dynamics that could aid in the protection of future water resources.

Acknowledgements

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