Scientific Research Publishing

Estimating Evapotranspiration Using Chloride Mass Balance in a New Mexico Paired Basin Study 2009-2019

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Abstract

A paired basin study in the upper Santa Fe River watershed following forest thinning and prescribed burns successfully measured water budget components in a treated and an untreated (control) basin. The paired basin study was established to investigate questions that have arisen regarding changes in water yield from forest treatments. Precipitation, stream flow, soil moisture, and chloride concentrations in precipitation and stream flow were measured to quantify the water budget components. The results from eleven years of data collection and analysis have a high degree of confidence with respect to measuring the water budget components based on the mass balance of water and chloride. The differences in the geologic structure and topography between the two paired basins appeared to impact the water budgets more than the forest treatments, except during periods when winter precipitation and snowmelt represented a significant component of inflow. Although this paired basin study was not able to portray a simple relationship between forest thinning and water yield, the chloride concentration methodology used to estimate evapotranspiration (*ET*) was successful. These detailed observations of chloride deposition and transport characteristics may be relevant for other researchers working in forested basins with substantial *ET*. *ET* rates were estimated by examining the cycle of chloride entering and exiting each basin over six integration periods. *ET* was estimated to be about 90% to 94% of precipitation in the treated basin and 77% to 86% in the control basin. The higher *ET* in the treated basin both before and after forest treatments may be due to the much greater area of west-facing hillslopes in the treated basin, which receive warm afternoon sun, and the greater area of rock cover in the control basin. Variation in the chloride concentration of collected precipitation samples from different sites indicates that horizontal precipitation of

chloride in the tree canopy is an important consideration when using the chloride mass balance approach to calculate water budget components.

Keywords

1. Introduction

In 2001, the City of Santa Fe, New Mexico and the Santa Fe National Forest began thinning and using prescribed fire on dense ponderosa pine forest surrounding two municipal water supply reservoirs in the Santa Fe River watershed to reduce the risk of a catastrophic wildfire. The dense condition of the forest developed after heavy livestock grazing and logging in the 1800s followed by closure of the forest and wildfire suppression. Similar forest restoration activities, aimed at reducing the fuel load and the potential for catastrophic fire, have been widely implemented in the Western United States. Yet questions persist about the response of the water budget to changes in vegetation.

To investigate the impact of forest treatments on evapotranspiration (ET), runoff and recharge, a paired watershed study was implemented in 2008 under a Joint Powers Agreement between the New Mexico Interstate Stream Commission, the City of Santa Fe, and the Santa Fe National Forest to evaluate differences between the treated and untreated basins. The paired basins (**Figure 1**) were initially established in 2001 as part of the NEPA process to understand impacts on turbidity in stream flow. The first phase of mechanical thinning and prescribed burns occurred in 2004, followed by prescribed burns in 2010 and 2011. The areas of the treated basin and control basins are 1.8 km² (443 acres) and 1.5 km² (377 acres), respectively.

Details of the study are available in Lewis (2018) [1] and additional information including the data can be found online [2]. A clear correlation between forest treatments and increased stream flow was not identified from this study. However, the study successfully estimated evapotranspiration rates using chloride mass balance in the two mountain watersheds. This paper summarizes the approach to calculating evapotranspiration and does not emphasize the response of water budgets to forest treatments.

2. Methods

Quantification of evapotranspiration (ET) was based on the mass-balance of chloride in each watershed [3] which assumes that the only source of chloride is derived from precipitation and that all chloride is discharged from the watershed after some period of time. Chloride is present in the atmosphere in suspended liquid droplets or as solid particulates, which are then delivered to the land surface by gravity through wet precipitation or dry deposition.
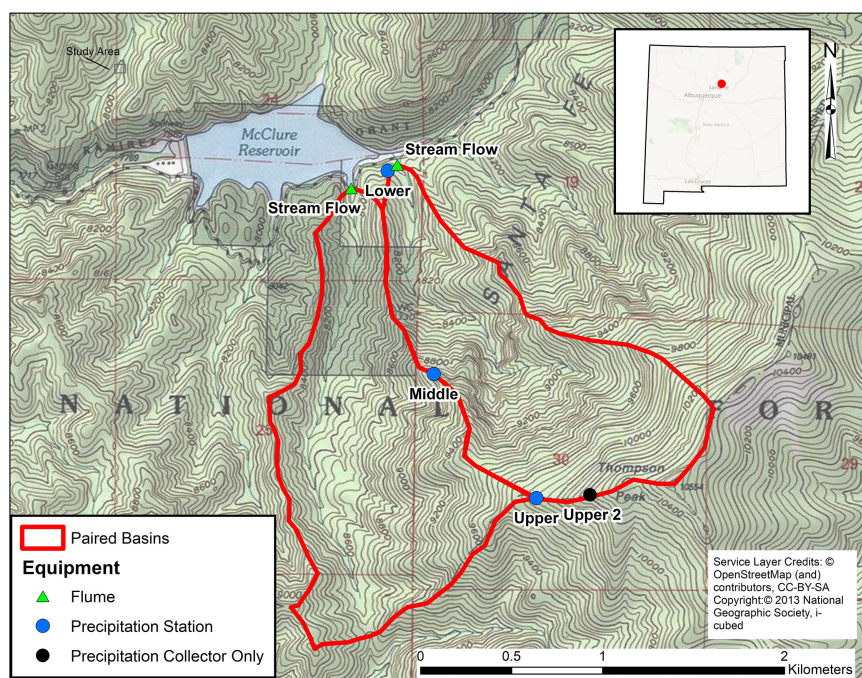
Figure 1. Location of monitoring stations in the paired watersheds.

As described in more detail in Lewis (2018) [1], the mass of chloride entering each basin was estimated by measuring the depth of rain and snow (liquid water equivalent) at three precipitation stations located between the paired basins (Table 1). Data collection began in January 2009. Precipitation samples were retrieved monthly (where possible) from passive composite precipitation collectors, and the chloride concentration of the water was analyzed. An additional precipitation collector was added in 2018 to investigate the impact of chloride deposition by occult precipitation in the form of cloud condensation onto vegetation. To estimate the mass of chloride leaving each basin, the volumetric flow of water was continuously monitored at each outlet stream using a flume and logging pressure transducer. Stream water samples were collected twice a month as grab samples, and these were also analyzed for chloride concentration.

Accuracy of the chloride mass balance method depends on the assumption that there are no other sources of chloride entering the watersheds or dissolving into the flow, and that subsurface inter-basin flow and recharge are a small fraction of *ET*. The watersheds are in a high elevation (2400 m to 3200 m amsl) area of the Santa Fe National Forest that was closed to the public by the US Secretary of Agriculture in 1932. Thus grazing, logging, and recreational activities that might have delivered chloride anthropogenically have been prohibited for nearly a century. The Proterozoic plutonic and supracrustal rocks, called the Thompson Peak metamorphic suite [4], that crop out in the basin are composed of quartzites and schists that are not a source of chloride. Furthermore, bromide, an indicator of anthropogenic sources [5], was below the detection limit in all stream and precipitation samples. Thus, the assumption that there are no other chloride sources appears reasonable.

Table 1. Descriptions of monitoring stations.

Station Name	Coordinates		Elevation (meters)	Drainage Area (km²)	Equipment	Measurement interval
	Latitude	Longitude				
Stream flow & stream temperature & chloride concentration						
Control basin stream	35.68806	−105.82352	2418	1.53	9-inch and 30-inch Parshall flumes, INW AquiStar PT2X transducer	Instantaneous stream flow: 15 minutes Chloride concentration: stream samples collected twice monthly
Treated basin stream	35.68688	−105.82631	2415	1.79		
Precipitation volume and chloride concentration						
Lower	35.6878	−105.8241	2458	NA	Campbell Scientific TE-525 tipping bucket rain gage with snowfall adapter, 5-foot-tall precipitation collector, 12-inch diameter	Precipitation rate: hourly Chloride concentration: composite sample submitted for laboratory analysis monthly
Middle	35.6777	−105.8212	2767	NA		
Upper	35.6716	−105.8149	3021	NA		
Precipitation chloride concentration only						
Upper 2	35.6718	−105.8117	3112	NA	5-foot precipitation collector, 12-inch diameter	Chloride concentration: composite sample submitted for laboratory analysis (two samples)
Soil moisture content (change in storage)						
Lower	35.6878	−105.8241	2458	NA	12 cm Water Content Reflectometer (CS655-L50DS)	hourly

A water level map would help reveal the potential for inter-basin flow; however, no wells are installed in the steep rugged basins, thus the groundwater level gradients are not known. The flow direction in the regional aquifer is from east to west, which is perpendicular to the slope of each stream. If infiltrated water did not reemerge into the stream as baseflow, but flowed towards the west with the regional gradient, then the assumption regarding no inter-basin flow would not be valid. To determine if a significant volume of inter-basin flow (or recharge) was occurring, the mass of chloride entering through precipitation was compared to the mass exiting through stream flow. An imbalance would suggest that chloride was leaving the basins through recharge to the underlying aquifer. The cumulative mass imbalance of chloride was quantified to assess the amount of chloride that may be exiting the watersheds in the subsurface, and concentrations were used to estimate the volume of water that was flowing to the regional groundwater as mountain block recharge.

To estimate evapotranspiration in each basin, the water budgets for each of the basins were calculated assuming [3]:

$$P = RO + E + T + R + \Delta S \tag{1}$$

where P is precipitation, RO is runoff, E is evaporation, T is transpiration, R is recharge, and ΔS is a change in storage, all in units of volume per time (e.g., m³/yr).

The relation between the mass of chloride entering the basin and the mass ex-

iting the basin [3] is:

$$\sum_{n=0}^{n=N} P_n * \left[Cl_p \right]_n = \int_0^{\tau} \left(RO * Cl_s \right) dt \tag{2}$$

where, P_n is the volume of the nth precipitation event, Cl_p is the concentration (mass per volume) of chloride for the associated precipitation event, N is the number of precipitation events, RO is the volumetric discharge of runoff, Cl_s is the concentration (mass per volume) of chloride in the associated streamflow, t is time, and τ is the total time over which chloride flux was integrated.

If recharge to the regional aquifer is a sink for chloride (and if we assume that the chloride concentration of recharge water is equivalent to the chloride concentration in stream flow) then the water budget equation for each time period [3] is:

$$Cl_p * P = Cl_s * RO + Cl_r * R \tag{3}$$

Here, Cl_p and Cl_s are the equivalent volume-weighted chloride concentrations over the full time period from Equation (2), and Cl_r is the chloride concentration in recharge (mass per volume) and assumed to be equal to Cl_s.

Substituting Cl_s for Cl_r and rearranging Equation (3) yields:

$$R = \frac{Cl_p * P - Cl_s * RO}{Cl_s} \tag{4}$$

Assuming that the change in storage is negligible compared to the other terms, and combining E and T into evapotranspiration (ET), Equation (4) can be substituted into Equation (1) and rearranged to give:

$$ET = P - RO - \frac{Cl_p * P - Cl_s * RO}{Cl_s} \tag{5}$$

$$ET = P - RO - \frac{Cl_p * P}{Cl_s} + \frac{Cl_s * RO}{Cl_s} = P \left(1 - \frac{Cl_p}{Cl_s} \right) \tag{6}$$

The volume of recharged water drops out of Equation (5); therefore, we can use the chloride mass balance approach to estimate ET without knowing the volume of regional groundwater recharge. Although the volume of runoff is not explicit in Equation (6), the amount of runoff is used to calculate the volume-weighted chloride concentration in stream flow.

The assumption that $Cl_r = Cl_s$ is based on the idea that once water seeps below the rooting zone, most ET losses will cease and the chloride concentration will stabilize. To the extent that streamflow is derived from the subsurface as base flow, it should be chemically similar to the water that continues deeper into the aquifer. Analysis of samples collected at various times and locations upstream of the flume supported this assumption [1]. Most of the flow at the flumes was derived from groundwater discharging from shallow soil drainage (completed in a few days or weeks after a storm event) and deep groundwater drainage. During dry periods, when no flow reached the flumes, a small spring could usually be found about 45 meters upstream of the flume in the treated basin [1]. The con-

centration in the spring water (representing the deeper groundwater component) was nearly the same as the concentration in stream water sampled at the flume before and after dry periods. Therefore, the concentration of chloride in recharged water was very likely to have been the same as the concentration in the stream.

ET as a percent of precipitation was estimated using Equation (6) based on the volume-weighted concentration of chloride entering and exiting the basins in each stream over a specific time period. Six time periods, or integration periods, were selected to reflect the cycle of chloride entering and exiting the basins. The integration periods coincided with the water years, starting on October 1 and ending on September 30, and ranged from one water year to four water years in length of time. In general, the stream flow subsides at the end of September after the monsoon season has ended, defining the end and beginning of each integration period. The integration periods that are longer than one water year include dry periods or periods when significant rainfall occurred in September and the stream flow had not subsided.

To obtain the total mass of chloride, the average chloride concentration in precipitation was multiplied by the average volume of precipitation per day from the three stations. The total mass of chloride deposited through precipitation as well as dry deposition, which was also captured by the collectors, onto the 1.5 km^2 control basin and the 1.8 km^2 treated basin was calculated for each integration period.

The mass of chloride exiting in stream flow was calculated by multiplying the mean daily stream flow by the mean daily chloride concentration. The volume-weighted concentration in precipitation for each integration period was calculated by dividing the total mass of chloride by the total volume of precipitation and the volume-weighted concentration in stream flow was calculated similarly.

3. Results

ET was estimated to be as much as 94% and 86% of the total precipitation in the treated and control basins, respectively (Table 2). *ET* was consistently higher in the treated basin (90% - 94% of precipitation in the various integration periods) than the control basin (77% - 86% of precipitation). The volume-weighted chloride concentration in precipitation ranged from 0.18 to 0.24 mg/L (Table 2). The flow-weighted mean concentration in the treated basin stream ranged from 2.2 - 3.2 mg/L as compared to 0.9 - 1.4 mg/L in the control basin stream.

Using Equation (6) and the volume-weighted chloride concentrations in precipitation and stream flow, *ET* is overwhelmingly the largest component of outflow. The cumulative water budgets are illustrated in Figure 2 (treated basin) and Figure 3 (control basin) for the six integration periods. Recharge is estimated to be 1.7% - 7.2% of precipitation in the treated basin and 1.1% - 13.1% in the control basin using Equation (4). Changes in soil moisture storage were not significant between the basins or at the start or ending of the six integration periods. The amount of error in the water budgets is equivalent to the estimated

inflow or outflow into in soil moisture storage because the calculations assumed that the change is soil moisture was zero.

Because the chloride mass-balance technique for estimating *ET* assumes that all chloride entering the basins will exit the basin over some integration period, the total mass of chloride input in precipitation and outflow through stream flow is examined. **Figure 4** and **Figure 5** show the cumulative mass of chloride deposited through precipitation and exiting through stream flow in the treated and control basins respectively. Chloride continues to be deposited through precipitation and dry deposition even in dry years, but clearly none exits the stream
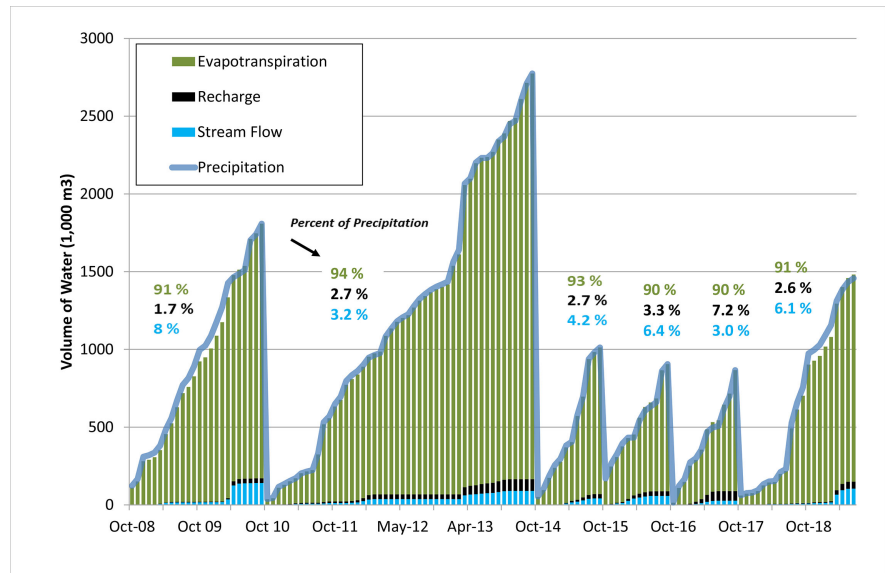

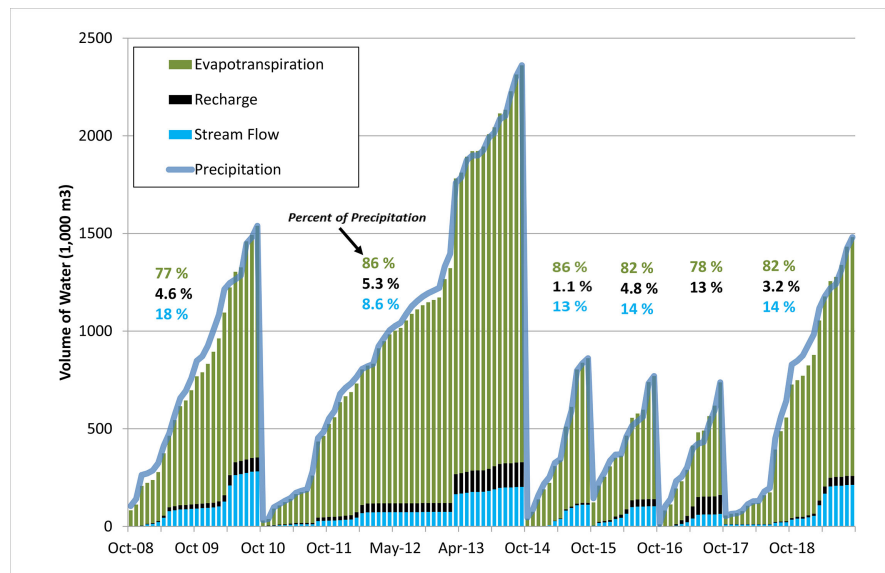**Figure 2.** Cumulative water volume entering and existing the Treated Basin for six integration periods.

Figure 3. Cumulative water volume entering and exiting the control Basin for six integration periods.

Table 2. Evapotranspiration (*ET*) estimates for six integration periods.

| Parameter	Integration Period											
	1		2		3		4		5		6	
	10/2008 thru 9/2010 (2 years)		10/2010 thru 9/2014 (4 years)		10/2014 thru 9/2015 (1 year)		10/2015 thru 9/2016 (1 year)		10/2016 thru 9/2017 (1 year)		10/2017 thru 9/2019 (2 years)	
	Treated	Control	Treated	Control	Treated	Control	Treated	Control	Treated	Control	Treated	Control
Area (km²)	1.79	1.53	1.79	1.53	1.79	1.53	1.79	1.53	1.79	1.53	1.79	1.53
Precipitation (cm)	101		155		56		50		48		97	
Precipitation (cm/year)	*50*		*39*		*56*		*50*		*48*		*49*	
Volume of Precipitation (1000 m³)	1809	1539	2775	2362	1012	861	910	775	867	738	1740	1481
Mass of chloride deposited through precipitation (1000 grams)	381	324	537	457	178	152	204	174	211	180	424	361
Volume-weighted chloride in precipitation (Cl_p) (mg/L)	0.21		0.19		0.18		0.23		0.24		0.24	
Volume of stream flow (1000 m³)	141	282	90	203	42	111	58	103	27	64	105	212
Mass of chloride discharged through stream flow (1000 grams)	314	259	291	282	108	140	135	128	63	72	297	296
Weighted chloride in stream flow (Cl_s) (mg/L)	2.2	0.9	3.2	1.4	2.6	1.3	2.3	1.2	2.4	1.1	2.8	1.4
$ET = (Cl_s - Cl_p)/Cl_s$	91%	77%	94%	86%	93%	86%	90%	82%	90%	78%	91%	82%
ET (1000 m³)	1638	1186	2609	2032	943	741	817	630	778	577	1591	1222
ET (cm per year)	46	*39*	36	*33*	53	*49*	45	41	*43*	38	*44*	*40*
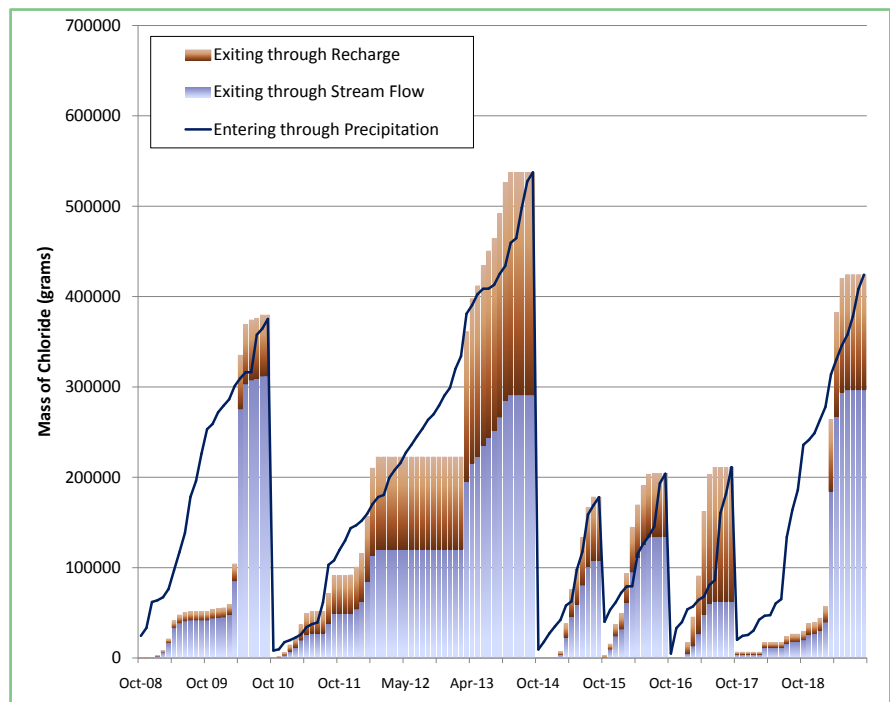
Figure 4. Cumulative mass of chloride deposited through precipitation in the treated basin and existing through stream flow and recharge.
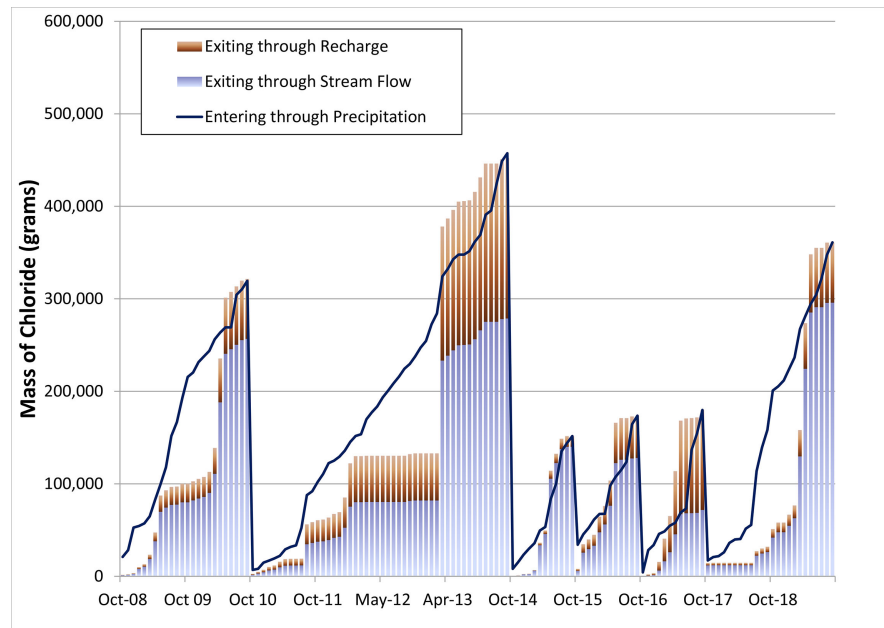
Figure 5. Cumulative mass of chloride deposited through precipitation in the control basin and exiting through stream flow and recharge.

when it is dry. Thus, the chloride builds up in the soil profile during dry periods. For instance, from June 2012 through August 2013 very little chloride exited the basins because both streams had minimal or no flow. Then, in September 2013, twenty centimeters of rain fell resulting in the highest measured flows and relatively high chloride concentrations [1].

Both estimates of recharge and evapotranspiration are sensitive to the chloride concentration in precipitation. The chloride deposition rates vary from 0.8 to 1.2 and are within the national observed values [6]. However, uncertainty in the chloride concentrations in precipitation samples is introduced by the variability in concentrations between the upper station and the other two stations. The chloride concentrations from the lower and middle precipitation stations track relatively closely compared to the concentrations from the upper precipitation station (Figure 6). The upper site generally collected much higher chloride concentrations than the other two stations.

Precipitation samples collected at the upper station usually contained more debris and tannins as compared to the other two stations as well. While the overstory coverage at the upper station is greater than ideal, it is not much greater than the overstory coverage at the lower station. To examine the potential impact of the overstory on the chloride concentrations, a site was installed in an open clearing about 91 meters (300 ft) higher in elevation than the upper station. Results of two samples collected at the new site (upper 2) showed much lower chloride concentrations than samples collected from the upper site. The high chloride concentration in samples from the upper site had a notable influence on the calculated average chloride concentration in precipitation (Cl_p) used in Equation (5).
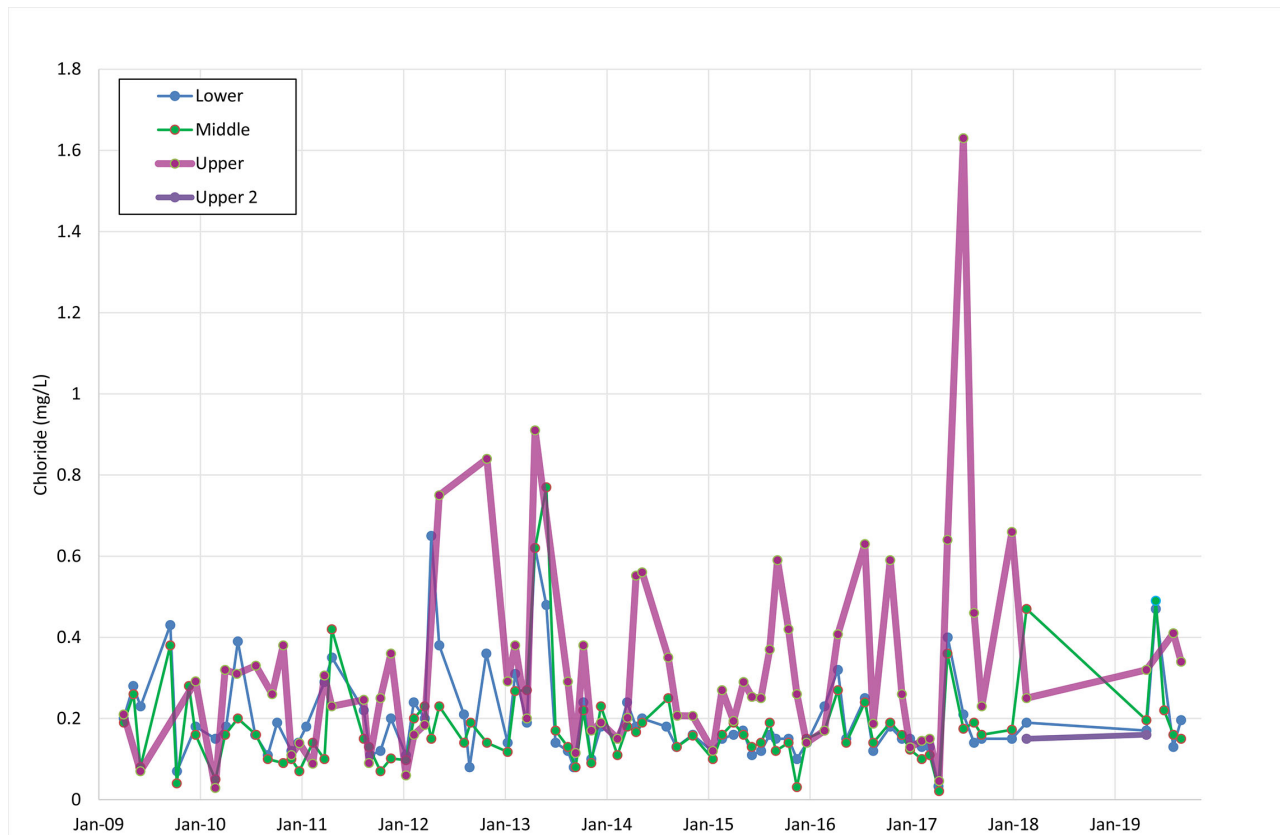
Figure 6. Time series of chloride concentrations from precipitation station samples.

4. Discussion

Calculation of water budgets for six integration periods reflect periods for the cycling of chloride through the watersheds. The difference between the measured amount of water and chloride entering and exiting each basin shows that some chloride and water is not exiting through stream flow but leaving each basin to recharge the regional aquifer. Another possible explanation for a gap in chloride mass exiting through stream flow could be chloride accumulation in the soil as found by Chen *et al.* (2002) [7] and Kauffman *et al.* (2003) [8]. However, given the shallow regolith (<0.5 m) and colluvium with 60% rock fragments [1], frequent flushing of the soil by infiltration, steep terrain (40% - 70%), and low porosity of the bedrock in each of the watersheds, the potential for significant storage of chloride is low in the Santa Fe watershed.

ET as a percent of precipitation is relatively consistent in the treated basin, ranging from 90% - 94% of precipitation over the six integration periods. The control basin on the other hand, is more variable, ranging from 77% - 86%. The error in the water budgets is ~0.02% - 1.5%, which is equivalent to the estimated change in soil moisture.

The chloride concentrations may be impacted by horizontal precipitation from clouds (also known as occult precipitation) occurring more frequently at higher elevations. Similar to this work, previous researchers have found that

samples collected from throughfall in an old spruce stand had chloride concentrations more than twice the concentration from samples collected in an open field [9]. Likewise, Kirchner *et al.* (2010) [10] and Page *et al.* (2010) [11] found significant occult precipitation of chloride. Even when cloud-water deposition does not contribute significantly to the hydrologic input, cloud deposition of major ions (e.g., chloride) can be 10% to 28% of the total wet deposition [12]. And elevation has been observed to influence cloud-water and atmospheric compositions [13], which may contribute to the elevational differences in chloride concentration in the Santa Fe watershed.

The vegetation at higher elevations in the paired basins is predominantly spruce and fir with abundant lichens (Figure 7). These contribute more surface area to collect horizontal precipitation than the ponderosa pines with fewer lichens present at lower elevations. While the recommended location for installing precipitation stations is in an area with no tree canopy, such locations may miss the deposition of chloride through horizontal precipitation on vegetation.

The results of sampling precipitation at the two upper (upper and upper 2) sites point directly to the overstory and debris as the cause of the higher chloride, but it does not explain why samples collected from the lower site are not equally impacted by the overstory. The type of overstory and the elevation could both impact the potential for horizontal precipitation to occur. As suggested above, lichens likely collect moisture from clouds and, where present, will enhance horizontal precipitation and associated chloride deposition onto vegetation surfaces, which may then be flushed off by subsequent rainfall events. The presence of clouds at the land surface is also necessary for this process, and the frequency of their presence is a function of elevation. Examination of cloud ceiling height at the Santa Fe Airport reveals that the cloud cover at 2438 m (8000 ft) occurs less than half as often as it occurs at 3048 m (10,000 ft). Thus, the horizontal precipitation from cloud cover is likely greater at 3048 m than at 2438 m, and this would contribute to increased deposition of chloride onto the tree canopy and eventually onto the ground.

Figure 7. Upper precipitation station showing lichens on surrounding trees.

If indeed chloride is deposited from water droplets in clouds, it is important to measure because it is a source of chloride in the mass balance. This horizontal, or occult, precipitation of water is not recorded by the tipping bucket and likely evaporates without providing a measurable water supply. Horizontal precipitation is also unlikely to be captured directly by collectors, unless they are under a tree that drips. Thus, while the recommended location of precipitation stations is in an open area without any obstructions (within a 45-degree angle of line of sight), such locations may underestimate chloride deposition.

The sensitivity analysis of chloride concentrations in precipitation on the calculated evapotranspiration rates shows the impact of the estimated chloride concentrations in precipitation (**Figure 8** & **Figure 9**). If we eliminate the chloride data from the upper precipitation station, *ET* estimates are greater by 0.5% - 9% compared to using the concentrations from all three stations.

While the chloride mass balance and water budget equations force agreement in the water budget components, the choice of integration periods impacts the estimated *ET* and recharge rates. Integration periods that do not consider the cycling of chloride through each basin can result in apparent negative recharge rates (or inter-basin flow). The cumulative mass of chloride entering the basin through precipitation in the selected integration periods is always more than the amount exiting through stream flow, thus some chloride must exit through recharge and no inter-basin flow is occurring.

The variation in *ET* in each basin appears to be impacted by the seasonality of precipitation (**Figure 10**). Because each of the basins are facing north, in the winter, less sunlight reaches the snow in the canopy and the forest ground as compared to the summer months. *ET* is likely higher in the treated basin than
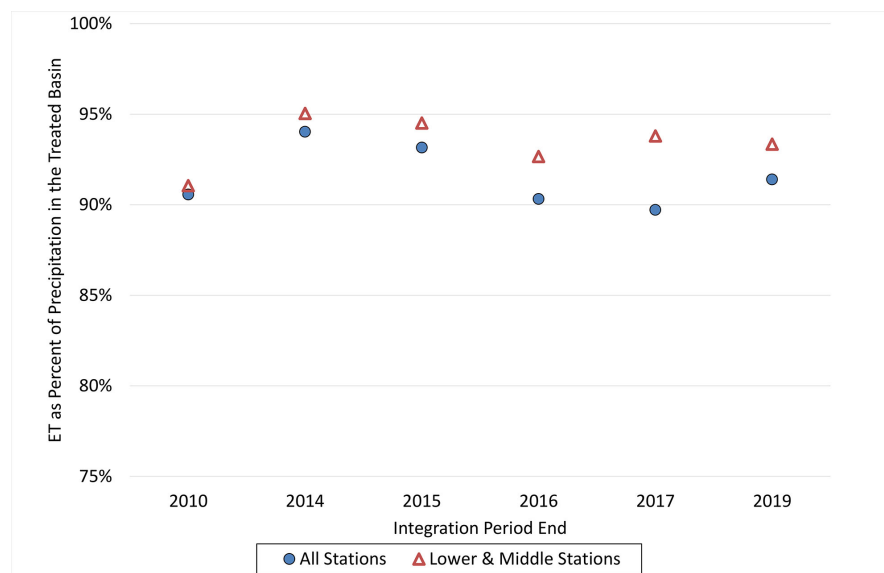

Figure 8. Sensitivity analysis of chloride concentrations in precipitation on calculated *ET* in the treated basin. Triangles only use precipitation collected from the lower and middle stations to determine the chloride concentration of precipitation. Circles include all three stations.
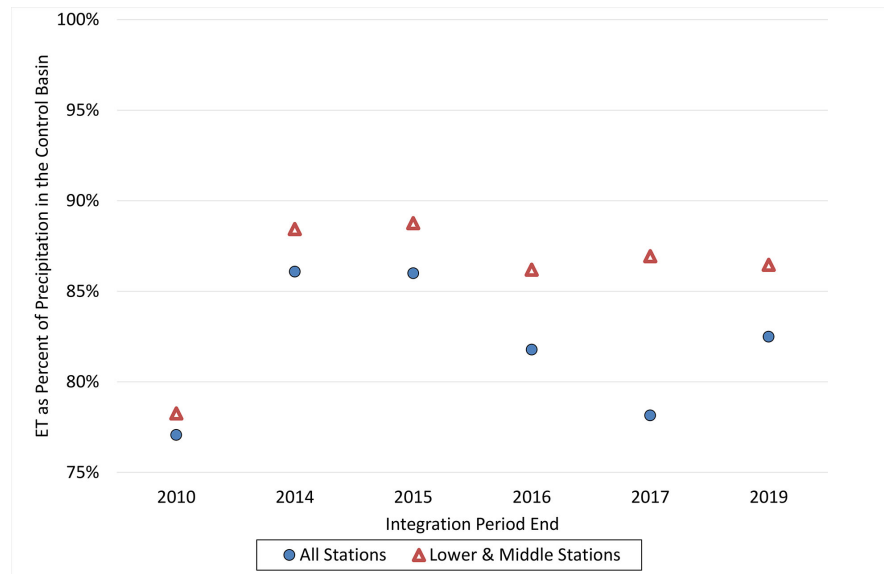
Figure 9. Sensitivity analysis of chloride concentration in precipitation on calculated *ET* in the control basin. Triangles only use precipitation collected from the lower and middle stations to determine the chloride concentration of precipitation. Circles include all three stations.
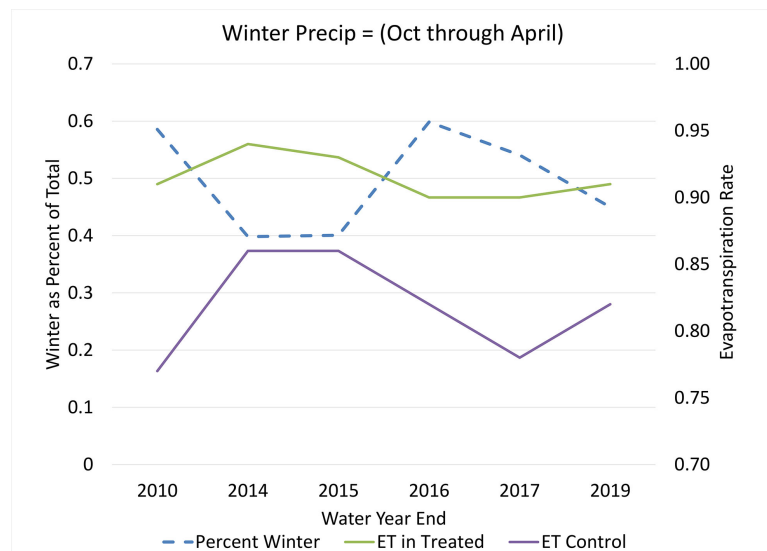

Figure 10. Comparison of percent of winter precipitation to *ET* in the treated and control Basins.

the control basin because the large west-facing slope in the treated basin receives more afternoon sun than the control basin during summer months when the sun is at a higher angle. The greater area of talus in the control basin likely enhances the recharge rate and reduces the rate of *ET* compared to the treated basin.

5. Conclusions

The results of this paired basin investigation have shown that *ET* can be estimated using a chloride mass-balance approach if the following considerations

are met:

1) The chloride concentration in the stream flow is equal to chloride concentration in water that recharges the regional aquifer.

2) The chloride in precipitation is the only source of chloride.

3) An appropriate integration period is selected. This is required because the cycling of chloride through each watershed varies from year to year. Chloride continues to be deposited during dry periods, thus sufficient precipitation is needed to flush the chloride after an extended dry period. The integration periods selected for this study range from one water year to four water years.

4) Chloride from horizontal or occult precipitation is appropriately sampled. In the Santa Fe watershed, this issue appears to be most significant at higher elevations due to the presence of lichens and greater cloud cover. Any application of the chloride mass-balance approach should consider the placement of precipitation collectors and weather stations in relation to tree canopy. A weather station located beneath a covered forest will underestimate the precipitation rate, as compared to a station located in an open clearing. However, the chloride precipitation rate may be underestimated in an open area.

Based on the mass balance of chloride entering and exiting the paired basins in this study, *ET* was calculated to range from 90% - 94% of precipitation in the treated basin, which receives more sunlight, and from 77% - 86% of precipitation in the control basin, which has a greater area of rock cover. In other words, although *ET* was greater in the treated basin compared to the control basin, this was also true prior to treatments due to the geography of the landscape. During the study period, *ET* varied from year to year based on the amount of precipitation that occurred in the winter versus summer. When a greater percentage of the precipitation occurred in the winter, the *ET* rate was lower than in those years when more precipitation occurred in the summer. These practical observations regarding *ET* in the study watersheds were only made possible by careful and appropriate use of the chloride mass balance method.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Lewis, A.C. (2018) Monitoring Effects of Wildfire Mitigation Treatments on Water Budget Components: A Paired Basin Study in the Santa Fe Watershed, New Mexico. *New Mexico Bureau of Geology and Mineral Resources Bulletin*, **163**, 52 p. https://doi.org/10.58799/B-163.

[2] Lewis, A. (2023) Santa Fe Watershed Paired Basin Data, HydroShare. http://www.hydroshare.org/resource/7a29154c0c724c6d91add3b24a127a09

[3] Claassen, H.C. and Halm, D.R. (1996) Estimates of Evapotranspiration or Effective Moisture in Rocky Mountain Watersheds from Chloride Ion Concentrations in Stream Baseflow. *Water Resources Research*, **32**, 363-372.

https://doi.org/10.1029/95WR03111

[4] Bauer, P.W., Ralser, S., Daniel, C. and Ilg, B. (1996) Preliminary Geologic Map of the McClure Reservoir Quadrangle, Santa Fe County, New Mexico. New Mexico Bureau of Geology and Mineral Resources Open-file Digital Geologic Map OF-GM 7.

[5] Mullaney, J.R., Lorenz, D.L. and Arntson, A.D. (2009) Chloride in Groundwater and Surface Water in Areas Underlain by the Glacial Aquifer System, Northern United States: U.S. Geological Survey Scientific Investigations Report 2009-5086, 41 p. https://doi.org/10.3133/sir20095086

[6] NADP (2015) National Atmospheric Deposition Program. http://nadp.sws.uiuc.edu/maplib/pdf/2013/Cl_conc_2013.pdf

[7] Chen, J., Wheater, H.S. and Lees, M.J. (2002) Identification of Processes Affecting Stream Chloride Response in the Hafren Catchment, Mid-Wales. *Journal of Hydrology*, **264**, 12-33. https://doi.org/10.1016/S0022-1694(02)00049-5

[8] Kauffman, S.J., Royer, D.L., Chang, S. and Berner, R.A. (2003) Export of Chloride after Clear-Cutting in the Hubbard Brook Sandbox Experiment. *Biogeochemistry*, **63**, 23-33. https://doi.org/10.1023/A:1023335002926

[9] Probst, A., Viville, D., Fritz, B., Ambroise, B. and Dambrine, E. (1992) Hydrochemical Budgets of a Small Forested Granitic Catchment Exposed to Acid Deposition: The Strengbach Catchment Case Study (*Vosges massif*, France). *Water, Air, & Soil Pollution*, **62**, 337-347. https://doi.org/10.1007/BF00480265

[10] Kirchner, J.E., Tetzlaff, D. and Soulsby, C. (2010) Comparing Chloride and Water Isotopes as Hydrological Tracers in Two Scottish Catchments. *Hydrological Processes*, **24**, 1631-1645. https://doi.org/10.1002/hyp.7676

[11] Page, T., Beven, K.J., Freer, J. and Neal, C. (2006) Modelling the Chloride Signal at Plynlimon, Wales, Using a Modified Dynamic TOPMODEL Incorporating Conservative Chemical Mixing (with Uncertainty). *Hydrological Processes*, **21**, 292-307. https://doi.org/10.1002/hyp.6186

[12] Herckes, P., Mirabel, P. and Wortham, H. (2002) Cloud Water Deposition at High-Elevation Sites in the Vosges Mountains (France). *The Science of the Total Environment*, **296**, 59-75. https://doi.org/10.1016/S0048-9697(02)00037-2

[13] Kalina, M.F., Stopper, S., Zambo, E., *et al.* (2002) Altitude-Dependent Wet, Dry and Occult Nitrogen Deposition in an Alpine Region. *Environmental Science and Pollution Research*, **9**, 16-22. https://doi.org/10.1007/BF02987473