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Riparian Dendrochemistry: Detecting Anthropogenic Gadolinium in Trees along an Effluent-Dominated Desert River

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Abstract: This research documents spatial and temporal patterns of effluent uptake by riparian trees through development of a new and innovative application for dendrochronology, specifically dendrochemistry. The rare-earth element (REE) gadolinium (Gd) is a known micro-pollutant in its anthropogenic form and enters streams from wastewater treatment plants. Anthropogenic Gd was first used in select medical procedures in 1988 and has since been used as a contrast agent for medical imaging. It is naturally flushed from the body following procedures and is subsequently discharged via treatment plants into waterways. Riparian trees that utilize effluent-dominated surface water take up Gd, which then remains in annual growth rings. The year 1988 serves as presence/absence date stamp for Gd in tree rings, thereby making Gd an ideal marker for this dendrochronological study. Results from this study along the Upper Santa Cruz River in southeastern Arizona show levels of Gd in effluent-dominated surface flows to be elevated above the threshold that distinguishes an anthropogenic anomaly from natural Gd_{SN} abundance in freshwater, thereby confirming that anthropogenic Gd is present. Gd was found in the growth rings of cottonwood trees (*Populus fremontii* var. *arizonica* (Sarg.) Jeps.) that are growing in the floodway adjacent to the effluent-dominated portion of the stream. The presence of Gd in cottonwood annual rings confirms that the trees are utilizing effluent over the course of the growing season. Furthermore, temporal patterns of Gd concentrations in trees directly adjacent to the stream may be reflective of high-frequency changes in surface water quality. Information on the impacts of effluent quality on the chemical composition of tree rings can be a useful monitoring tool to evaluate the spatial and temporal patterns of effluent use in riparian trees and to identify high-frequency changes in surface water quality.

Keywords: dendrochemistry; gadolinium; rare earth elements; riparian; *Populus fremontii*; cottonwood trees; ecological monitoring

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1. Introduction

Functioning riparian ecosystems in the southwestern United States are vital indicators of the health of river basins and play a pivotal role in maintaining streamflow conditions, facilitating groundwater recharge, providing natural water quality enhancement, and supporting biodiversity [1–3]. Despite their importance, these systems are under increasing pressure from human alteration to the quality and quantity of surface and groundwater [4–7]. As one mitigation to these threats, municipal wastewater (effluent) can play an important role in ecosystem restoration by providing in-stream flows for vegetation and recharging local water tables [8–11]. Increasingly, effluent flows may be critical to riparian survival in arid and semi-arid river systems where surface water and groundwater have been de-coupled due to anthropogenic change and drought [10].

While there are many benefits to utilizing effluent for the maintenance of in-stream flows, there are numerous unresolved ecohydrological issues regarding the release of effluent into groundwater dependent riparian systems. Few studies have quantified the full suite of benefits and impacts to ecosystem function in effluent-dominated streams, although this need has been described [12]. There is little knowledge about how native riparian vegetation incorporates and responds to continued inflows of nutrient-rich effluent. The need to address this knowledge gap is particularly compelling within the context of climate variability and the potential for prolonged drought and rising temperatures. This climate variability increases freshwater demands, further degrades riparian systems, and potentially increases the number of streams reliant upon effluent to maintain surface flows and associated riparian habitats. Ultimately, a lack of understanding about the dynamics of effluent-dominated streams has created a void in methods suitable for evaluating the ecological integrity of these systems [9].

To address knowledge gaps in effluent-dominated riparian systems, this research documents spatial and temporal patterns of effluent uptake by riparian trees through development of an innovative application of dendrochronology, specifically dendrochemistry, which is defined as the measurement and interpretation of the concentration of elements in tree rings [13]. Dendrochemical measurements can be utilized to estimate relative temporal changes in the availability of elements in the surrounding air, water, or soil utilized by trees [14].

Dendrochemistry has multiple applications for investigating temporal and spatial variability of elements in the environment. Since trees do interact with their environment both chemically and physically [15], dendrochemistry can be an effective tool for reconstructing environmental change [16]. Numerous studies have focused on heavy metal concentrations in tree rings [17,18] as a method to determine the timing and geographic distribution of metals, including mercury [19], lead [16,20,21], and tungsten [22]. Dendrochemistry has been successfully applied to investigations into groundwater contamination [23,24], and a related branch of dendrochemistry has focused on examining mechanisms of essential plant nutrition, including uptake patterns of nitrogen [25] and forest nutrition [26,27].

Dendrochemistry is an evolving field of research and numerous elements remain unexamined as tracers of environmental contamination. Few if any studies have yet investigated the utility of rare earth element (REE) signatures in tree rings for tracing historic changes in groundwater and surface water quality. The REE gadolinium (Gd) is a known micro-pollutant that enters streams from wastewater treatment plants and has been identified as a tracer for effluent movement in streams and groundwater [28,29]. Gd was first used in select medical procedures in 1988 and subsequently discharged via treatment plants into waterways [30,31]. In effluent-dominated rivers that support functioning riparian forests, trees can display a temporal Gd presence/absence date stamp (before and after 1988) in annual tree rings, thereby making Gd an ideal marker for analyzing effluent-related changes in groundwater and surface water quality in riparian environments.

1.1. Rare Earth Elements

Rare earth elements (REEs) are part of the lanthanide series in the periodic table, and each element shares nearly identical chemical and physical properties. REEs display a systematic decrease in ionic radius as their atomic number increases, a pattern referred to as "lanthanide contraction" [32,33]. This behavior results in coherent behavior in the entire lanthanide series (La-Lu) [34]. Despite this coherence, there is evidence that heavy REEs (Dy-Lu) and light REEs (La-Sm) can behave differently during certain chemical processes such as adsorption and complexation [35].

The most stable oxidation state of REEs in natural waters is trivalent [33]. Because of this, REEs can adsorb strongly on surfaces of rocks or bind to organic substances such as humic acid [36]. As evidence of this condition, suspended material in rivers reflects basin geology [37] and groundwater typically displays an REE signature reflective of the rocks through which the water has flowed or the basin material in which the groundwater resides [38,39]. REE patterns are therefore regionally specific.

Little is known about the relationship between REEs and vegetation. Due to their tendency to adsorb to rock surfaces, REEs are minimally available to plants through soil. However, plants exhibit preferential light REE uptake patterns at the root-water-soil interface along streams and rivers [33]. In addition, some fern species are known REE accumulator plants [36]. Considering that studies have shown REEs to be instructive geochemical tracers of the origins of suspended and dissolved sediments in rivers [37,40], investigating REE uptake patterns in vegetation, and specifically in annual tree rings of riparian plant species, may offer insights into changes in river chemistry.

1.2. Anthropogenic Gadolinium

Notable among the REEs, gadolinium (Gd) can be found in both natural and anthropogenic forms and can serve as an indicator of changing water quality. Anthropogenic Gd (Gd_{ANTHRO}) enrichment results from the use of gadopentetic acid (Gd-DTPA) as a contrasting agent for MRIs [41]. Gd_{ANTHRO} organic compounds were first used in the United States in 1988 as contrasting agents in MRIs. Patients undergoing MRI procedures take Gd-DTPA either orally or intravenously and excrete the substance unaltered. Gd_{ANTHRO} is very stable for over 6 months under natural conditions, is highly water soluble and mobile in surface and groundwater systems, and does not adsorb onto surrounding materials, as do natural REEs [28,42].

Increased concentrations of Gd_{ANTHRO} in river systems that receive treated municipal effluent were reported in 1996 [30]. During the past two decades, elevated levels of Gd_{ANTHRO} in rivers, lakes, and groundwater have been documented in Europe [42–47], Japan [48], and North America [28,41]. Gd_{ANTHRO} has the potential to serve as a tracer for monitoring the pathways and presence of municipal effluent in waterways and drinking water [28,49].

Numerous questions remain about Gd_{ANTHRO} and must be investigated before Gd_{ANTHRO} can be effectively used as a tracer or for monitoring protocols. While research has focused on concentrations of Gd_{ANTHRO} in sources of water, more detailed research is required to understand processes that control the fate and transport of Gd_{ANTHRO} [41]. In particular, Gd_{ANTHRO} uptake patterns in riparian vegetation have not yet been investigated. Relative amounts of Gd_{ANTHRO} within annual growth rings could provide a historical picture of Gd_{ANTHRO} uptake patterns in trees over time. Addressing this knowledge gap surrounding the connection between Gd_{ANTHRO} and riparian vegetation, this study documents spatial patterns of effluent uptake by *Populus fremontii* var. *arizonica* (Sarg.) Jeps along an arid, effluent-dominated river through a new application of dendrochemistry.

1.3. Research Questions

This research investigates the interaction of effluent with riparian vegetation by addressing four key questions:

1. Is gadolinium (Gd) present in effluent-dominated surface and groundwater?
2. Do Fremont cottonwood (*Populus fremontii*) trees along the effluent-dominated stream contain Gd in their growth rings?
3. Do Gd concentrations vary temporally in cottonwood annual rings?
4. Can temporal and spatial variability of Gd concentrations be correlated with ecohydrologic characteristics of the stream, such as clogging layer dynamics?

2. Materials and Methods

2.1. Study Area

The Upper Santa Cruz River (USCR) is a bi-national river that flows through the rapidly growing urban area that encompasses Nogales, Sonora (Mexico) and Nogales, Arizona (United States). The Upper Santa Cruz River relies upon three contributing water sources: surface runoff, effluent from the Nogales International Wastewater Treatment Plant (NIWTP), and groundwater discharge. The Upper Santa Cruz River Basin is located at approximately 1158 m (3800 feet) above sea level and receives approximately 46 cm (18 inches) of precipitation a year. The primary uses of water in the Basin are municipal, industrial, agricultural, and environmental [50].

The river is characterized by a series of shallow and undulating micro-basins that together form the underlying floodplain aquifer. Groundwater can be found in three relatively distinct aquifers. The most accessible aquifer, referred to as the Younger Alluvium, fills a series of seven independent sub-basins immediately bordering and underlying the stream channel (Figure 1). The Younger Alluvium basins are primarily comprised of gravel, sand, and clay of Pliocene and Pleistocene age [50]. Groundwater levels in the USCR basin have varied over time in response to climate conditions and human-use patterns. Due to the shallowness of the aquifer and the permeable nature of the alluvium, the water table is sensitive to climatic changes, rising quickly during heavy precipitation and depleting rapidly during drought. Recharge from the stream into groundwater tables is tightly linked to precipitation patterns. The year 2000 was a flood-dominated year with 61,674,092 cubic meters (50,000 acre-feet (af)) of recharge, while 2002 was the start of a drought and there was less than 24,669,636 cubic meters (20,000 af) of recharge [50]. Surface flow in the river is ephemeral and intermittent from the headwaters, through Sonora, and into Arizona for about 16 km.

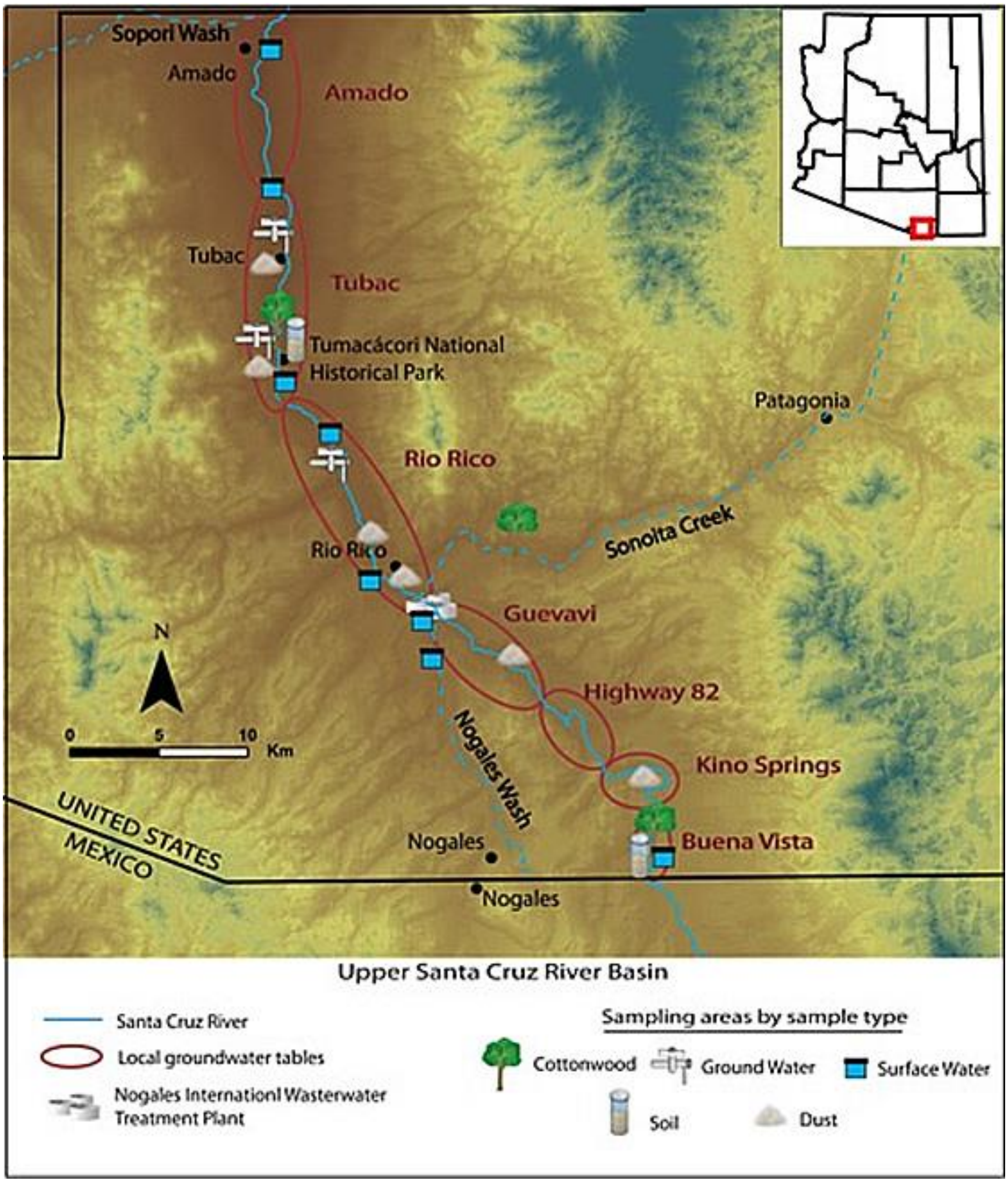

Figure 1. Upper Santa Cruz River Basin sampling locations and types.

At the confluence of Sonoita Creek and the USCR, a perennial reach of the river runs north for about 48 km because of daily effluent discharges from the Nogales International Wastewater Treatment Plant (NIWTP). The NIWTP began operation in the 1950s and reached its current discharge rate after a significant upgrade in 1992. Historic agricultural operations cleared cottonwood and mesquite forests for fields up until the 1930s [51]. However, the daily inflows of effluent from the NIWTP have revived the riparian ecosystem, and almost 600 species of vertebrates and invertebrates now depend upon the river system for either temporary or permanent habitat [52]. The Arizona Department of Water Resources reports that since effluent subsidies began in 1972, the discharge of treated effluent into the channel resulted in an approximately 0.8 m average increase in local groundwater tables [53]. A corresponding analysis of riparian vegetation patterns over time suggests that riparian vegetation has increased in density and extent due to the introduction of effluent into the USCR system. Recent synthesis of historic aerial photographs and current satellite imagery shows that floodplain lands receiving direct effluent subsidies have experienced a rapid increase of mature riparian forests from 1984 to 2004 [54].

Effluent discharged into the Upper Santa Cruz River can potentially enhance or hinder riparian vegetation growth, depending on water quality and hydrologic conditions. Effluent is known to be high in nitrogen, which can benefit riparian vegetation by stimulating growth [10,55]. On the other hand, nitrogen also fosters algae growth that can form thick mats on the bottom of the stream channel and lead to clogging of surface sediments [56,57]. In the absence of seasonal floods, the algal mats, also known as clogging layers, can seal the bottom of the stream channel, decreasing infiltration and recharge and hindering the connection between surface water, subflow, and groundwater [58]. The clogging layer can retain flows in the stream channel while the groundwater tables drop below the root zone of riparian plants. Paradoxically, riparian trees can then suffer from drought conditions even while there is water in the stream.

2.2. Field Sampling

Collections of Fremont cottonwood (*Populus fremontii*) were made from living trees within the 100-year floodplain in the Upper Santa Cruz River (USCR) watershed in 2007–2008 (Figure 1) to utilize for dendrochemical analysis. Increment core samples of radial growth were collected from suitable, mature, and healthy cottonwood trees using a 5.15-mm diameter Haglof borer (Forestry Suppliers, Inc, Jackson, MS). Each sample was taken at a randomized cardinal direction. Increment borers were cleaned with isopropyl alcohol after each sample was taken to minimize contamination between trees. Two samples were taken from each tree, one approximately five inches above the other for replication purposes. Three distinct sites within the USCR watershed were selected for sampling (Figure 1).

1. Effluent Site–Six trees were sampled along the effluent-dominated portion of the USCR through Tumacácori National Historical Park. Three trees were sampled immediately adjacent to the effluent-dominated stream. Three trees were sampled ~200 m from the stream and within a band of mature cottonwoods that most likely germinated shortly after notable flood events in 1977, 1983, and 1993 [51].
2. Control Site (main stem of the river)—Eight trees were sampled at two adjacent ranches immediately north of the U.S.–Mexico border and immediately overlaying the Buena Vista groundwater basin (Figure 1). This site is about 16 km south (upstream) of the NIWTP and therefore does not receive effluent subsidies. Two collections of trees were made at the northern and southern ends of the basin (Figure 1). The southern end of the basin includes a small spring that supports year-round water for about three kilometers in the channel.
3. Control Site (tributary)–Control samples were gathered from trees along Fresno Canyon, a tertiary tributary to the USCR in Sonoita Creek State Natural Area. Fresno Creek is ephemeral and only flows during rainfall events.

Surface water samples were taken to ascertain whether Gd was present in surface flows and/or in the groundwater both upstream and downstream of the effluent discharge point. Samples were collected at publicly accessible points along the river, both north and south of the Nogales International Wastewater Treatment Plant (NIWTP), including the spring located above the Buena Vista groundwater basin at the main stem control site. Two sets of surface water samples were taken before and after the summer monsoon rainy season (July–September) with the aim of keeping the dilution of the Gd_{ANTHRO} signal by precipitation runoff events to a minimum. Groundwater was collected from wells near surface water sampling locations. Soil samples were collected within 30 m of the stream bed at Tumacácori NHP and at the main stem control site. All samples were taken from 0.5 m depth within the floodplain soil. Surface dust samples were taken in three clusters downstream and upstream of the NIWTP to assess airborne transport of anthropogenic Gd [59,60].

2.3. Sample Preparation

Increment core samples were prepared following standard dendrochronological techniques [61]. Each sample was finely sanded to provide clearly polished transverse views of annual growth rings. Cottonwood trees are difficult to precisely crossdate due to variable patterns of complacent and false rings [62]. However, samples were visually inspected under a microscope and confidently assigned approximate dates by counting rings back in time from the bark and matching patterns of narrow and wide rings [63]. Each core includes or pre-dates 1988, the first year that Gd_{ANTHRO} was used in MRI procedures and thus introduced into effluent-dominated streams via water treatment plants. Cores were cut into 2- to 3-year increments for analysis. The wood, soil, and dust samples were chemically digested and analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) at the UA Soil, Water, and Environmental Sciences Arizona Laboratory of Emerging Contaminants (ALEC). Surface and groundwater samples were also measured by ICP-MS at the ALEC and were analyzed for major ions and REE concentrations.

2.4. Data Analysis

To determine the pattern of REE concentrations in all samples (surface water, groundwater, trees, dust, and soil), values of raw concentrations were normalized to the North American Shale Composite [64]. REEs are subject to the Oddo-Harkins effect, which suggests that during the evolution of the solar system, even-atomic-number elements were more stable than neighboring odd-number elements [41]. For example, Gd (atomic number 64) is naturally enriched compared to its nearest neighbor's Eu (atomic number 63) and Tb (atomic number 65). Normalizing to North American Shale Composite removes this effect.

Once normalized, known anomalies may still occur. As a rule, REEs are trivalent; however, cerium (Ce) and europium (Eu) are redox-sensitive and may occur as tetra- and di-valent cations, thus behaving anomalously from other REEs [45]. In addition, vegetation preferentially accumulates Eu [35]. Owing to this documented anomalous behavior, standardized Eu was not included in this analysis.

Elevated levels of Gd in surface water and groundwater are expressed by the geogenic ratio of the standardized measured values of Gd (Gd_{SN}) and the interpolated abundance of Gd ($Gd\,^*_{SN}$) [28,42].

$$Gd_{SN}/Gd\,^*_{SN} = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN}) \quad (1)$$

Equation (1) is derived from the predictable cohesion among REEs by interpolating the expected natural abundances of shale-normalized Gd in water samples from Gd's nearest stable neighbors samarium (Sm) and terbium (Tb).

Gd_{SN} concentrations can vary among sites depending upon complexation patterns across the 15-member series of REEs. Two distinct patterns of complexation behavior exist between the light REEs (La-Eu) and heavy REEs (Tb-Lu), and Gd can alternately behave as a heavy REE for weak complexation or as a light REE for strong complexation [65]. To accommodate this variability, a geogenic ratio of 1.3 is defined as the threshold that distinguishes an anthropogenic anomaly from natural Gd_{SN} abundance in freshwater [42], [66].

The geogenic ratio was calculated for surface water samples pre- and post-monsoon, as well as for groundwater samples. Geogenic ratios were not calculated for tree samples for two primary reasons. First, concentrations of elements found in wood samples are mediated by the exposure of the roots to the elements, selective uptake mechanisms, and the degree of utilization within the tree [67]. Second, absolute concentrations of Gd_{SN} in the trees are extremely small (nanograms/gram). If the input of anthropogenic Gd is small in water samples, the geogenic fraction can be erroneous [42]. Therefore, to avoid erroneous results brought on by using the ratio analysis for the trees, Gd_{SN} trends are compared against standardized trends for all REEs.

3. Results

3.1. Gd_{SN} in Water, Soil, and Dust Samples

Geogenic ratio results from surface water samples show a clear delineation between samples upstream and downstream of the NIWTP. All samples taken from upstream of the NIWTP fall between 0.3 and 1.0, which is below the 1.3 anthropogenic threshold (Figure 2). All the effluent-dominated surface water samples taken from downstream of the NIWTP are between 1.5 and 4.0. These values are well above the 1.3 anthropogenic threshold. All the groundwater samples from both upstream and downstream of the NIWTP fall between 0.5 and 1.0, below the 1.3 anthropogenic threshold.

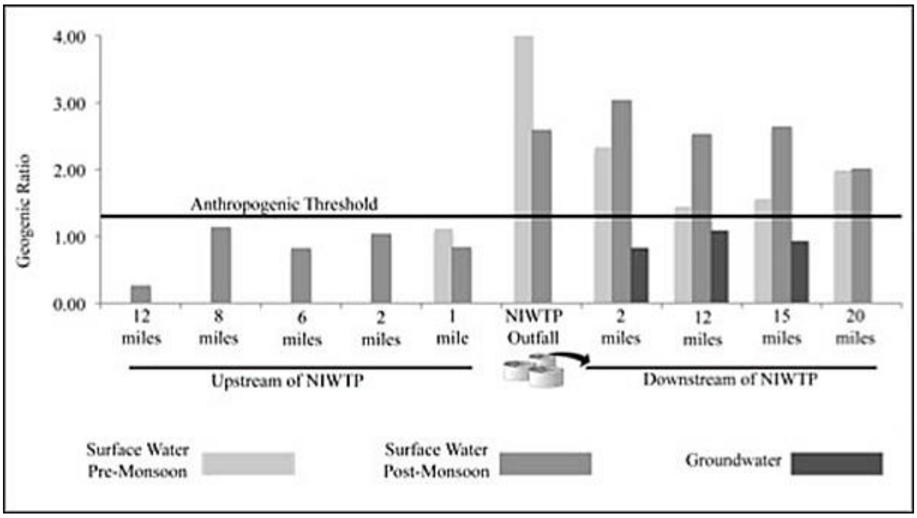

Figure 2. Geogenic Ratio in Upper Santa Cruz River surface and groundwater samples. Values above the anthropogenic threshold of 1.3 indicate the presence of Gd_{ANTHRO}.

For dust and soil samples, standardized values of Gd were analyzed in comparison with other REEs. Values for Gd_{SN} were negligible, just above zero (Figure 3).

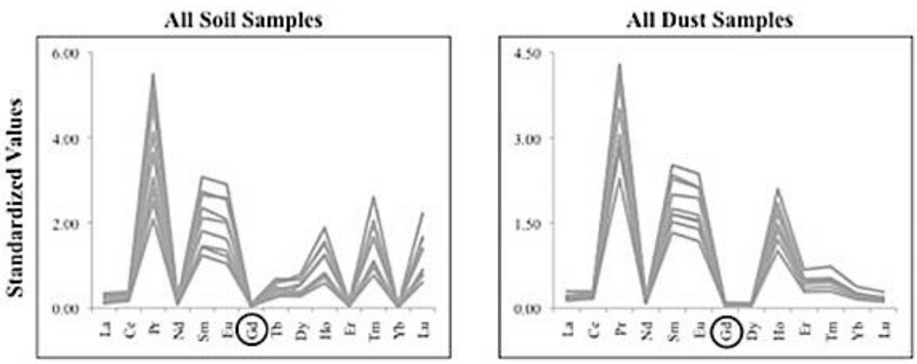

Figure 3. Standardized soil and dust samples from all sampling locations showing negligible amounts of Gd relative to other REEs.

3.2. Gd_{SN} in Populus Fremontii Trees

Under natural conditions, all REE elements (apart from Eu) display coherent behavior, due mainly to their similar physiologic properties [30]. In the cottonwood trees sampled adjacent to the effluent-dominated river, this tight coherence is evident for all the standardized REE values except for Gd_{SN}. Distinct from other standardized REEs, Gd_{SN} is elevated by as much as a factor of two (Figure 4). Furthermore, a common temporal pattern is evident in the three trees sampled directly adjacent to the effluent-dominated stream. Each of the three trees includes a spike in Gd_{SN} concentrations around the year 2005. The temporal pattern is not uniform for the three trees located 200 m from the stream channel. Only one of these trees exhibits a spike in 2005, while the other two trees show a reduction in relative Gd_{SN} concentrations in 2005.

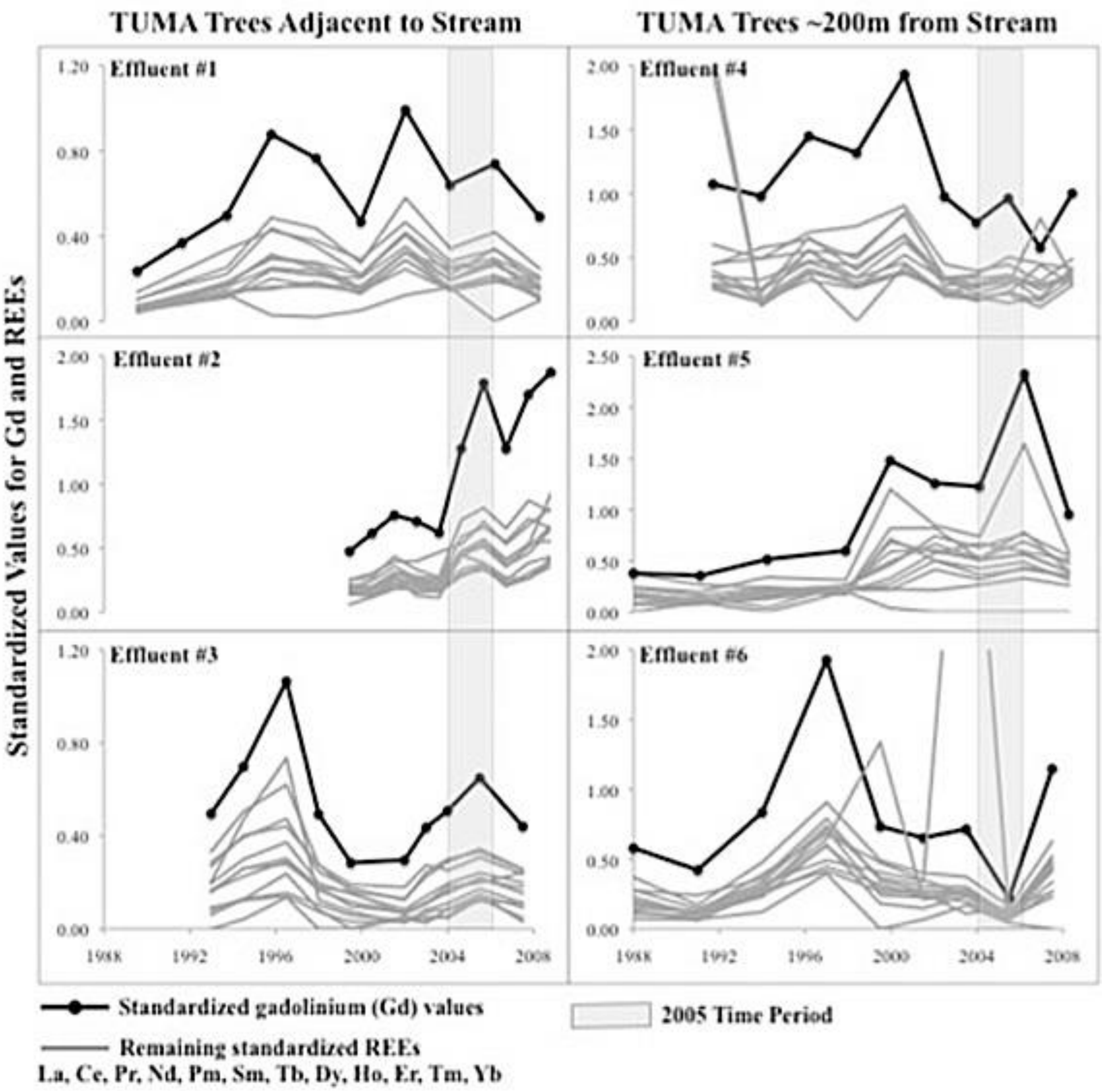

Figure 4. Relative concentrations of REEs in three cottonwood trees adjacent to the effluent-dominated stream (**left column**) and ~200 m west of the effluent-dominated stream (**right column**). The light gray bar highlights the 2005 time-period.

Trees located in the northern portion of the control site also showed elevated levels of Gd_{SN} relative to other REEs. In contrast, trees located in the southern portion of the control site did not demonstrate elevated levels of Gd_{SN}. Trees sampled at the tributary control site did not display elevated levels of Gd_{SN}.

4. Discussion

4.1. Anthropogenic Gd in Surface and Groundwater

Results from surface water samples collected at control sites upstream of the NIWTP indicate that anthropogenic Gd (Gd_{ANTHRO}) is absent in natural stream flows that do not contain treated effluent. However, effluent-dominated surface water flows downstream of the treatment plant do contain elevated levels of Gd_{SN} relative to other REEs and above the anthropogenic threshold. This suggests that Gd_{ANTHRO} is present in effluent-dominated surface water flows and moves downstream through the cottonwood dominated riparian floodplain.

While effluent-dominated surface water samples contain Gd_{ANTHRO}, groundwater tables that underlie the effluent-dominated portion of the stream do not contain detectable amounts of Gd_{ANTHRO}. Considering evidence that effluent is recharging groundwater tables [50,68], this is a surprising result. As one possible explanation for this result, dilution may account for the absence of detectable Gd_{ANTHRO} levels in groundwater. Effluent that does recharge groundwater tables is subsumed by the volume of water already present in the groundwater tables. If Gd_{ANTHRO} is present in groundwater, it may therefore not be present in detectable amounts. More extensive sampling of groundwater at varying depths and distance from the stream would aid in determining the degree of dilution and if Gd_{ANTHRO} values are present at shallower depths or directly underlying the stream.

4.2. Detectable Levels of Gd_{ANTHRO} in Populus Fremontii Trees

Cottonwood trees growing adjacent to the effluent-dominated stream contain elevated levels of Gd_{SN} relative to other standardized REEs in their annual growth rings. These elevated levels of Gd_{SN} in the annual growth rings, paired with detectable levels of Gd_{ANTHRO} in effluent-dominated surface water samples, suggest that excess Gd_{SN} in cottonwood trees is anthropogenic in origin. Furthermore, the presence of Gd_{ANTHRO} in annual growth rings of cottonwood trees serves as an indication that trees are utilizing effluent at some point during their annual growth cycle.

Cottonwood trees along the Upper Santa Cruz River are not long-lived (<40 years), and many of the trees within the riparian area geminated after three major floods in 1977, 1983, and 1993 [51]. As a result, only two of the six trees sampled along the effluent-dominated stretch of the river pre-date 1988, when Gd-DTPA was first used in MRI procedures and discharged into waterways via municipal treatment facilities. Of these two trees, one tree indicates elevated levels of Gd_{ANTHRO} prior to 1988. This result is likely a reflection of the anatomy of cottonwood trees. Populus species have numerous rings in the sapwood, the area of the tree involved in the upward conduction of sap [69,70]. As a result, concentrations of nutrients and elements taken up by a tree over the course of one growth year can be contained within annual rings of previous years. To accommodate this physiological characteristic of the cottonwood in this study, concentrations of Gd_{ANTHRO} were analyzed in 2- to 3-year blocks so that the general trend of uptake patterns would be reflected.

Interestingly, elevated levels of Gd_{ANTHRO} were also found in trees sampled in the northern part of the control site, 10 miles upstream of the NIWTP effluent discharge point (Figure 1). Trees sampled in the southern portion of the control site did not contain elevated Gd levels, nor did the soil, dust, or surface water samples taken from the perennial spring at this location. There is little concrete evidence to suggest why Gd_{SN} would be elevated relative to other standardized REEs in the northern part of the control site while trees in the southern half of the control site show cohesive levels of all standardized REEs, including Gd_{SN}. However, anecdotal evidence may offer a suggestion as to this difference. The northern part of the control site is located approximately two miles north of the U.S.-Mexico border and three miles east of the twin border cities of Nogales, Sonora (population 500,000) and Nogales, Arizona (population 20,000). The northern portion of the control site is also located downstream of a small tributary that originates in Sonora, Mexico and conveys water from Sonora. It is plausible that geologic faults convey groundwater flow away from Nogales, Sonora towards lower-elevation locations such as the northern portion of the control site (K. Nelson, pers. comm.). Many of the washes and much of the surface runoff in Nogales, Sonora contain flows from leaky or broken sewer pipes [71]. While there is little to no data collection on the volume or chemical composition of these flows, it is conceivable that wastewater from broken sewer pipes could contain elevated levels of Gd_{ANTHRO}. These flows could then contribute to the groundwater that is conveyed to the northern portion of the control site for this study. Under this scenario, Gd_{ANTHRO} could be recorded in annual rings of riparian trees.

4.3. Gd_{ANTHRO} Spike in TUMA Trees around the Year 2005

Cottonwood trees from the effluent-dominated portion of the river display temporal differences in relative Gd_{ANTHRO} values. Gd_{ANTHRO} concentrations were measured in 2-year increments at the effluent-dominated site. The temporal pattern and ~2005 spike in Gd_{ANTHRO} in the near-stream trees at Tumacácori complement investigations into clogging layer dynamics along the USCR. A University of Arizona study confirmed the existence of a clogging layer in the stream channel of the USCR north of the NIWTP and concluded that two consecutive floods of 350 cfs or more were needed to scour the riverbed and restore the connection between the stream channel and shallow water tables [72]. In the 1980s and 1990s, above-average precipitation and frequent floods supported gaining stream conditions, which diluted nutrient-rich effluent flows with groundwater to prevent (or at least slow) the formation of the clogging layer. The year 2001 marked the start of a regional drought, and there were few floods in the USCR watershed from 2002 to 2005. Groundwater levels dropped and gaining conditions gave way to losing conditions. Without the mitigating influence of groundwater dilution, the clogging layer grew and ultimately severed the groundwater-surface water connection in the hyporheic zone [72]. In 2005, two consecutive floods above 350 cfs scoured the streambed and removed the clogging layer, thereby restoring the connection between the stream and shallow groundwater tables. A spike in Gd_{ANTHRO} concentrations in the near-stream trees at the effluent-dominated experimental site coincides with the 2005 floods and the break-up of the clogging layer and suggests a general temporal recording of these events in the tree rings.

5. Conclusions

In light of rising demands for freshwater and rapid rates of riparian ecosystem degradation, effluent is becoming an increasingly viable water augmentation option to address escalating competition for water among urban, agricultural, industrial, and environmental demands [73,74]. Effluent can provide consistent flows to rivers and support both restoration and maintenance of riparian vegetation. However, effluent-dominated streams have unique water quality characteristics that distinguish them from natural streams. Numerous questions remain unanswered about the impacts of effluent on riparian function, the degree to which riparian vegetation may be utilizing effluent, and the degree to which effluent may be recharging drinking water tables.

Determining levels of Gd_{ANTHRO} in the annual growth rings of cottonwood trees may offer insights into these questions. For example, measuring the concentrations of Gd_{ANTHRO} in annual growth rings of trees along effluent dominated streams could reveal the degree to which riparian species utilize effluent to meet evapotranspiration requirements. Mapping the spatial distribution of trees with detectable levels of Gd_{ANTHRO} can also provide information on the dispersion patterns of effluent within the riparian ecosystem. Such insights could help inform water management efforts aimed at securing water specifically for environmental needs. Furthermore, if Gd_{ANTHRO} could be developed as a tracer for the presence of effluent in surface water, groundwater, and trees, adaptive policies could be developed to ensure that the quality in effluent is sufficient for both environmental and human uses. Future research on Gd_{ANTHRO} concentrations within other riparian species such as velvet ash (*Fraxinus velutina*) would offer additional insights into the spatial gradient of effluent utilization and temporal differences in Gd_{ANTHRO} concentrations. More information on the impacts of effluent quality on the chemical composition of tree rings can be a useful monitoring tool to evaluate the spatial and temporal patterns of effluent use by riparian trees and to identify changes in surface water quality.

Author Contributions: A.L.M. conducted this research as part of her Ph.D. dissertation research. She led the field visits, sample and data analysis, and was the principal author on this manuscript. P.R.S. served as the Dissertation Advisor to this work, assisting with the collection and analysis of samples and providing key insights to the manuscript. All authors have read and agreed to the published version of the manuscript.

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