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Geologically-derived nitrogen and phosphorus as a source of riverine nutrients

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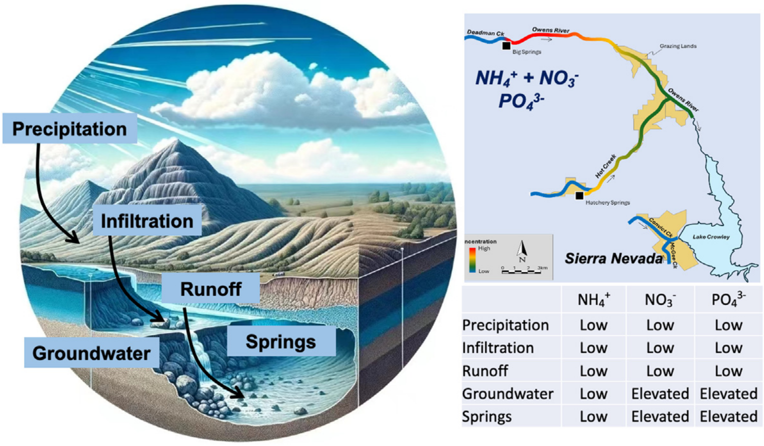
HIGHLIGHTS

- Water samples were collected from snow-melt runoff and volcanic spring-fed rivers.
- Spring waters contained elevated nitrate and phosphate concentrations.
- Nitrogen originated from lacustrine deposits in the shallow aquifer of the caldera.
- Phosphate derived from weathering of apatite and volcanic glass in volcanic deposits.
- Geologically-derived nutrients are often overlooked as a source of riverine nutrients.

GRAPHICAL ABSTRACT



	NH_4^+	NO_3^-	PO_4^{3-}
Precipitation	Low	Low	Low
Infiltration	Low	Low	Low
Runoff	Low	Low	Low
Groundwater	Low	Elevated	Elevated
Springs	Low	Elevated	Elevated

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ABSTRACT

The role of geological-derived nitrogen (N) and phosphorus (P) as sources of riverine nutrients was investigated in the Long Valley caldera of eastern California. Stream and spring waters were collected during the biologically-critical summer dry season when spring water/ground water inputs comprised >90% of streamflow. Samples were collected above and below major spring water inputs and irrigated pastures grazed by beef cattle to isolate the effects of spring waters versus cattle grazing as potential sources of riverine N and P. Inputs of N and P from geologic materials were identified as the primary source of elevated nutrient concentrations throughout the study area. Nitrogen, in the form of NO_3–N (0.11–0.33 mg/L), originated from the slightly-thermal, shallow aquifer subsystem that intersected lacustrine/fluvial materials incorporating nitrogen-bearing geologic materials. Phosphorus, as PO_4–P (0.132–0.255 mg/L), originated from both the shallow and deeper (thermal) groundwater systems and was attributed to its rapid release from weathering of the volcanic deposits. Grazing activities generated no discernible increases in mineral N or TP loads when comparing streamflow above and below grazed locations. There was a substantial loss of NO_3–N during flood irrigation of pastures that was attributed to denitrification and/or vegetation uptake, with a corresponding increase of dissolved organic nitrogen ascribed to leaching of plant and/or fecal materials. This study demonstrates that geologically-derived nutrients (N and P)

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from volcanic terrains can be an important source of stream water nutrients. Results of this study are consistent with our previous results in volcanic areas of northern California and highlight that geologically-derived nutrients are often overlooked as a source of riverine nutrients and can have a profound effect on aquatic ecosystems.

1. Introduction

Eutrophication due to anthropogenic nutrient inputs is one of the greatest threats to freshwater and coastal marine ecosystems throughout the world. While anthropogenically-derived point and non-point source inputs of N and P to aquatic systems are undoubtedly the dominant source of these nutrients, the release of N and P from weathering of geologic materials can be an important nutrient source for some aquatic ecosystems (Lusardi et al., 2016, 2021). Phosphorus is released from the mineral apatite in geologic materials, and from the glass fraction of volcanic deposits, providing a long-term source of P to ecosystems (Nanzyo et al., 2003). Similarly, nitrogen release from geologic materials, especially bedrock of sedimentary origin (e.g., carbonaceous shale, mudstone, mica schist), has been implicated as an ecologically important source of nitrogen (Holloway et al., 1998; Morford et al., 2011, 2016b). These natural (background) nutrient sources can contribute to elevated levels of N and P in soils (Strathouse et al., 1980; Dahlgren, 1994), rivers (Lusardi et al., 2016, 2021), lakes/reservoirs (Holloway et al., 1998; ODEQ, 2002; Klamath Tribal Water Quality Consortium, 2018) and groundwater (Roberson and Whitehead, 1961; Evans et al., 2002; Lusardi et al., 2021), thereby affecting the trophic status of aquatic ecosystems. Notably, these geologically-derived nutrients are largely overlooked as a potential nutrient source for aquatic ecosystems, and as a contributing source to nutrient impairment of natural waters. This is especially the case in semi-arid rangelands where elevated streamwater nutrient levels are often erroneously attributed to livestock grazing, leading to confusion and conflict in resolution of water quality remediation efforts (Kattelmann, 1997).

Nitrogen inputs from weathering of geologic materials are often overlooked in the overall nitrogen cycle, yet rocks contain >99% of Earth's reactive nitrogen reservoir (Houlton et al., 2018). Nitrogen release by bedrock weathering can lead to soil N-saturation and acidification in northern California owing to NH_4^+ release from mica minerals in bedrock and subsequent nitrification of NH_4^+ generating both NO_3 and H^+ (Dahlgren, 1994). Nitrogen availability in excess of biological demands leads to leaching of the NO_3 to the aquatic system. For instance, the leaching of NO_3^- from N-bearing bedrock was identified as an appreciable source of NO_3^- to a downstream reservoir in the Mokelumne River watershed (California) where it contributed to periodic algal blooms (Holloway et al., 1998). In this case, the elevated NO_3 concentrations were erroneously attributed to forest harvest activities. Phosphorus enrichment in surface and ground waters is especially prevalent in volcanic terrains where rapid weathering of volcanic glass along with the fine particle size and high porosity/permeability leads to the rapid release of P (Dahlgren et al., 2004; Lusardi et al., 2021).

Under the arid to semi-arid conditions of eastern California and Oregon, groundwater/spring water contributions to streamflow can comprise the majority of the annual stream discharge, except for the snowmelt runoff period (Reimers et al., 1955; Lopes and Allander, 2009; Sterle et al., 2019). Several of these spring-fed streams are among the most productive cold-water fish habitats in the western USA (Lusardi et al., 2016, 2021). The consistent discharge and temperature of spring waters are an important aspect of these excellent fisheries, but natural inputs of N and P also enhance the food resources and growth rates of these cold-water fishes (Lusardi et al., 2021, 2023). As such, these spring-fed aquatic systems have been termed “keystone habitats” owing to their resilience and importance for conservation (Lusardi et al., 2023). In the lotic environment, the low stream water residence time prevents the elevated background nutrient levels from inducing eutrophication, although aquatic macrophytes are often found in the streambed immediately downstream of the spring water inputs (Supplemental Fig. 1a). Conversely, the geologically-sourced nutrients can contribute to serious eutrophication in downstream lentic environments where impoundment leads to high water residence times allowing for the proliferation of algal blooms, as well as notable deviations in saturated dissolved oxygen and pH. The elevated PO_4^{3-} levels are especially notable as they promote the growth of N-fixing algal species, as well as harmful algal blooms (e.g., *Aphanizomenon flos aquae*, *Microcystis* sp.) (Jellison et al., 2003; Eldridge et al., 2012).

The primary purpose of this paper is to bring greater awareness to the role of natural (geologic) N and P sources in aquatic ecosystems. These results are especially relevant to the ~70% of the global land area having bedrock of sedimentary origin (often N-enriched), and areas with recent volcanic/hydrothermal activity (often P-enriched). Background nutrient inputs can enhance (lotic) or degrade (lentic) aquatic ecosystems and therefore should be recognized as a potentially important source of nutrients in waterbodies being classified as impaired by excess nutrients. This study integrates our research results from eastern California's Upper Owens River watershed (Long Valley caldera) with our previous studies examining natural N/P sources in the Cascade Volcanic Range of northern California and Oregon (Oliver et al., 2014; Lusardi et al., 2016, 2020, 2021, 2023). The Upper Owens River provided an excellent opportunity to assess nutrient inputs (N/P) from adjacent snowmelt systems originating in the Sierra Nevada (granitic bedrock) and volcanic spring-fed systems associated with the Long Valley caldera. By sampling various stream segments above/below livestock grazing and above/below spring water inputs, we were able to clearly distinguish nutrient inputs from natural versus livestock sources. Stream runoff from this watershed area is impounded in Lake Crowley, which experiences persistent summer eutrophication (Mackie and Zhang, 2005; Jellison et al., 2003; Jellison and Dawson, 2003; Regional Water Quality Control Board Lahontan Region, 2005). Results of this study provide critical information for watershed managers and remediation activities to alleviate eutrophication in regions with natural nutrient inputs (e.g., Upper Klamath Lake, Iron Gate Reservoir, Eagle Lake and Lake Crowley in Oregon and California).

1.1. Study area

The Upper Owens River watershed (~984 km^2 above Lake Crowley) is located at the boundary between the Sierra Nevada (granitic bedrock) and the Basin and Range Province in eastern California (Fig. 1). The watershed extends from the Sierra Nevada (peak elevations >3660 m) in the west and flows through the Long Valley Caldera to Lake Crowley (surface elevation = 2067 m). The Long Valley caldera (32 km E-W x 18 km N–S) formed from a massive eruption (600 km^3) about 760,000 years ago creating the extensively-distributed Bishop tuff (rhyolite). Subsequent deposits above the Bishop tuff consist of intercalated volcanic flows/tuffs and fluvial/lacustrine materials that form aquifers capable of storing and transmitting large amounts of groundwater (Sorey et al., 1978). The Long Valley Caldera hosts an active hydrothermal system that includes hot springs and fumaroles (Sorey et al., 1978; Sorey, 1985).

Climate is characterized as hot-summer Mediterranean (Koppen-Geiger Climate Zone - Csa) with the majority (70–80%) of precipitation falling as winter snow. The watershed lies in the rain shadow of the Sierra Nevada with mean annual precipitation ranging from more than 2500 mm along the Sierra Nevada crest to less than 300 mm at Lake Crowley (Sorey et al., 1978). Dominant vegetation communities grade from barren granite bedrock at higher elevations, to montane coniferous forests (e.g., *Pinus jeffreyi, Pinus contorta, Abies magnifica, Abies concolor*),

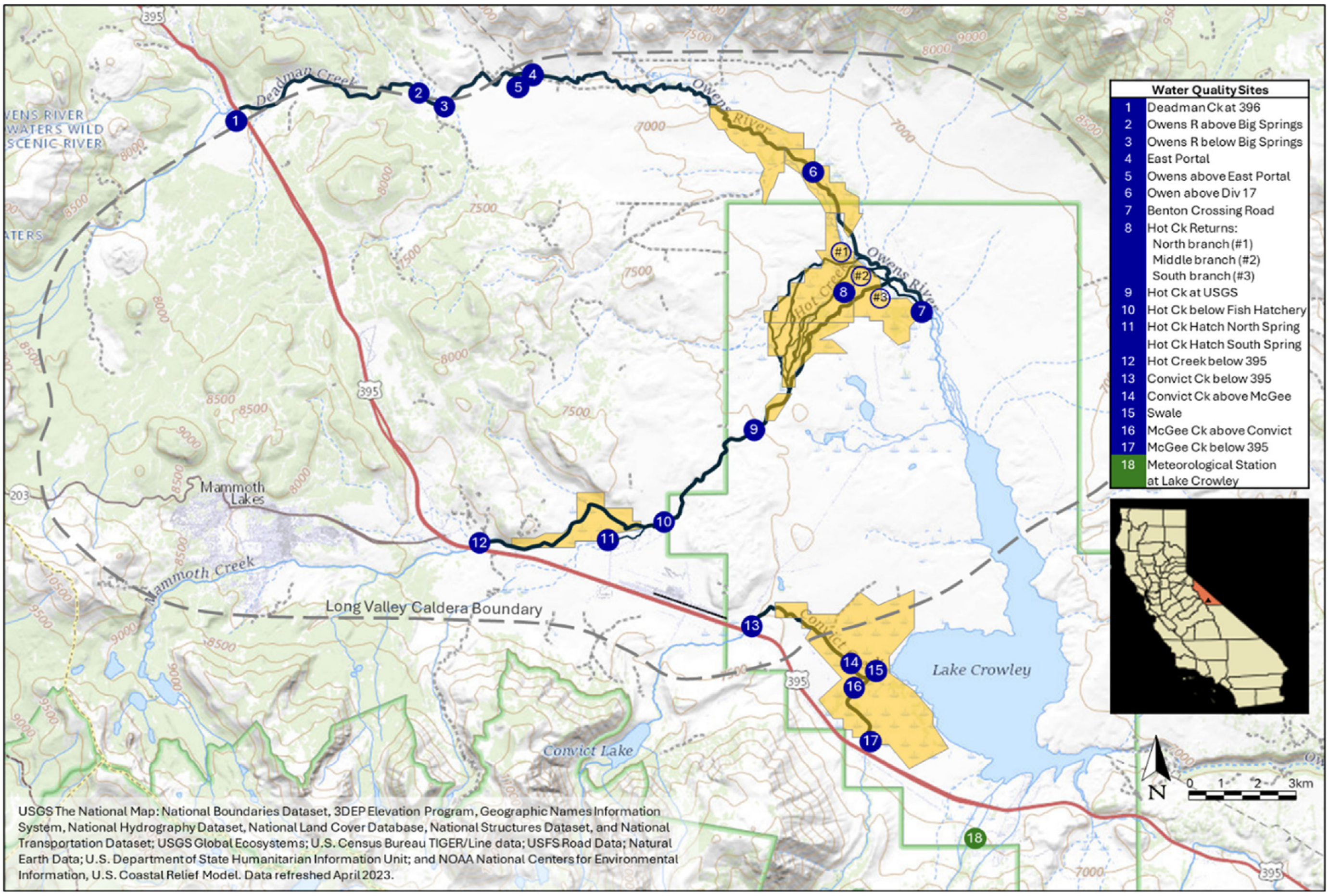

Fig. 1. Study area and locations of water sampling sites and meteorological station in the Long Valley caldera of eastern California. Water quality was assessed in the stream segments highlighted in black.

and semi-desert shrublands (e.g., *Artemisia tridentate, Purshia tridentate, Sarcobatus vermiculatus*) with riparian/wetland species along waterways on the valley floor. Land ownership in the watershed is dominantly public (~90%) with approximately 2750 ha (2430 ha City of Los Angeles lands, 320 ha private lands) of Long Valley utilized for flood-irrigated pasture for grazing by beef cattle, estimated to be ~2600 head, (Inyo and Report, 2019; UC Extension, 2018) during the late-spring through fall period.

We examined water quality along the three major stream segments within the Upper Owens River watershed above Lake Crowley: Deadman Creek-Glass Creek-Owens River, Mammoth Creek-Hot Creek, and Convict-McGee Creeks. Deadman and Glass Creeks form the headwaters of the Owens River, which provide a pulse of snowmelt runoff, but little water input (<0.1 m^3/s) during the summer/fall dry season. A complex of high volume springs, hereafter termed Big Springs, discharge a relatively consistent 1.4 m^3/s into the river over several hundred meters of the Owens River at approximately river km (RK) 45.6 (RK 0 at the high water mark at Lake Crowley for this stream segment). Sulfur hexafluoride (SF6) dating provides a minimum age of 12 years for Big Springs discharge waters (Evans et al., 2002). These findings established the presence of a slow groundwater flowpath in the permeable, thick sequences of fractured and layered volcanic rocks from Mammoth Mountain to Big Springs (Evans et al., 2001). Additional inputs to the Upper Owens River include interbasin flows from the East Portal (RK 36.8) and three distributaries of Hot Creek (RK 10 to RK 13.5). East Portal is the discharge point for the Mono Craters Tunnel (MCT) that includes water diverted from Grant Lake Reservoir in the Mono Basin via the MCT, as well as groundwater contributions that infiltrate into the tunnel from the surrounding volcanic deposits (average groundwater contribution ~0.34 m^3/s). The Upper Owens River has a continuous gaging station located within the Big Springs input segment at RK 45.6 (Fig. 1- site 3). Beef cattle grazing was present below RK 24 to Lake Crowley during the June–October portion of the study period.

The headwaters of Mammoth Creek that becomes Hot Creek where the Hot Creek Fish Hatchery springs enter the creek at RK 15.6 (RK 0 at confluence with Owens River for this stream segment) consists primarily of intrusive and extrusive igneous rocks at higher elevations, areas of glacial till and alluvial deposits at the transition to the valley floor, and volcanic and lacustrine deposits within the caldera. A series of slightly-thermal springs and geothermal fumaroles/springs discharge to Hot Creek at approximately RK 11.5 and provides the majority of Hot Creek flow outside of the snowmelt period. The groundwater originates as snowmelt from the Sierra Nevada that emerges along a fault zone from a fractured basalt unit. The hot springs/fumaroles below the Hot Creek Fish Hatchery are heated to temperatures as high as 220 °C by interaction with a resurgent magma dome underlying the central portion of Long Valley (Sorey, 1985) (Supplemental Fig. S1b). Continuous gaging stations along the Mammoth/Hot Creek segment are located at RK 9.8 (USGS) and RK 23.1 (City of Los Angeles). Beef cattle grazing was present below the Hot Creek USGS gaging station (RK 9.8/site 9) and confluence with the Upper Owens River during the June–October portion of the study period (Fig. 1).

Convict and McGee Creeks originate as snowmelt and groundwater inputs from granitic bedrock in the Sierra Nevada and associated glacial till and alluvium in the valley and discharge directly into Lake Crowley. There are no identified spring inputs to the segments of Convict and McGee Creeks examined in this study. Continuous gaging stations for Convict (site 13) and McGee (site 17) Creeks are located at RK 4.8 and RK

4.1, respectively (RK 0 at Lake Crowley), and water discharge for each creek was measured at the time of sampling just above the McGee/Convict confluence. Beef cattle grazing was present between Highway 395 and the downstream water sampling locations during the June to October portion of the study period.

1.2. *Field and laboratory methods*

A total of 10 streamwater collections occurred on an approximately monthly basis for the summer-fall grazing period (the biologically critical period for the local aquatic ecosystems) from July 2018 to October 2019 (two grazing seasons). Samples were obtained from a well-mixed, center/mid-depth of the stream channel, placed on ice and transported to the laboratory for chemical analyses. A YSI 6600 (Xylem, Yellow Springs, OH, US) was used to collect field measurements of temperature, specific conductance (SC), pH, turbidity, and dissolved oxygen (DO) at the time of sample collection. For all three stream systems, water collection sites were located above/below grazing, and above/below spring water inputs when present (Fig. 1). The Convict-McGee segment represented only snowmelt runoff with no known spring water inputs within the studied portion of the watershed. The Deadman-Glass-Owens and Mammoth-Hot Creek segments contained snowmelt runoff at their headwaters and spring water inputs in their lower reaches within Long Valley. Daily flow data were acquired from existing gauging stations, direct flow measurements, and estimates based on a water balance. A Marsh McBirney Flo-Mate 2000 (Marsh-McBirney Inc., Frederick, MD, US) or SonTek Flowtracker (SonTek, San Diego, CA, US) were used for all field flow measurements. Additionally, we obtained historical water quality data for three major springs at the Hot Creek Fish Hatchery that contribute inputs to Mammoth-Hot Creek and seven groundwater wells from the US Geological Survey NWIS database that covered various time periods between 1986 and 2022 (see Supplemental Information Fig. 2; https://nwis.waterdata.usgs.gov).

A subsample of stream water was filtered through a pre-rinsed 0.2 μm polycarbonate membrane (Millipore) for quantification of soluble reactive phosphorus (SR-PO_4), nitrate-N (NO_3–N) + nitrite-N (NO_2–N), ammonium (NH_4–N), and dissolved organic carbon (DOC). SR-PO_4 was determined using the ammonium molybdate spectrophotometric method (LOD ~0.005 mg LP^{-1}) (Clesceri et al., 1998). The vanadium chloride method was used to spectroscopically determine NO_3+NO_2–N (LOD = 0.01 mg/L). As NO_3–N constituted >95% of the combined NO_3+NO_2–N concentration, we report the NO_3+NO_2–N concentration as NO_3–N in this study. NH_4–N was determined spectroscopically with the Berthelot reaction, using a salicylate analog of indophenol blue (LOD ~ 0.010 mg/L; Forster, 1995). Analyses for SR-PO_4, NO_3–N + NO_2–N, and NH_4–N were completed within 72 h of sample collection. TN and TP (unfiltered sample) were determined following oxidization with 1% persulfate and subsequent quantification of nitrate and phosphate, respectively, using the methods described above (Yu et al., 1994; SM 45000-N C; Clesceri et al., 1998). DOC was measured using a Dohrmann UV enhanced-persulfate TOC analyzer (EPA Standard Method 5310C; Phoenix 8000; LOD ~0.1 mg/L).

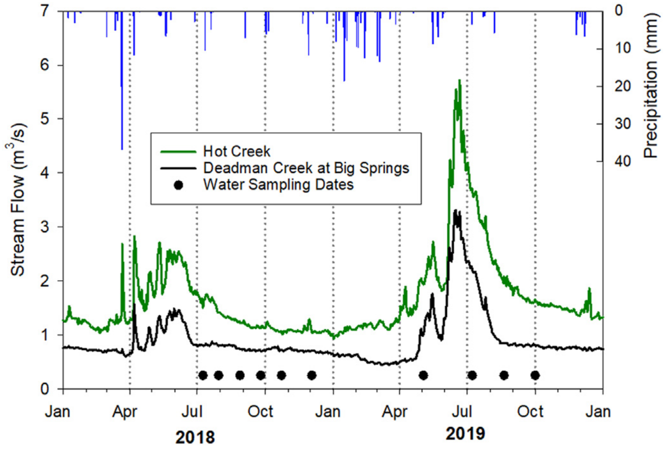

Fig. 2. Stream hydrographs for Deadman Creek (USGS 10265100; Site 3 in Fig. 1) and Hot Creek (USGS 10265150; site 9 in Fig. 1) gauging stations along with the daily precipitation record (blue bars) from the Lake Crowley meteorological station (see Fig. 1 for station location). Total calendar year precipitation was 179 and 190 mm in 2018 and 2019, respectively. Water chemistry sampling dates are indicated by solid dots below the hydrographs. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

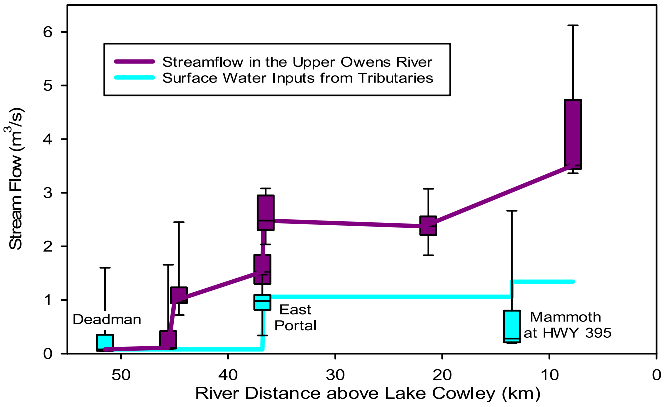

Fig. 3. Median surface water inputs to Lake Crowley from the Owens River (Purple line) during the June–October period, 2018–2019. Median surface water tributary inputs are indicated with blue line with box plots showing overall data distribution among sampling dates. The difference between streamflow and tributary inputs is attributed to spring/groundwater accretions. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Laboratory quality assurance/quality control included implementation of Surface Water Ambient Monitoring Program (SWAMP) compatible standard laboratory procedures including replicates, spikes, reference materials, setting of control limits, criteria for rejection, and data validation methods (Puckett, 2002). For each sample collection date, 10–20% of the analyses were replicated and analyzed with a laboratory blank, two matrix spikes, as well as a certified control standard. Relative percent difference of laboratory replicates for all analyses were <5%, and the mean value of replicates was used for data analysis of replicated samples.

2. Results

2.1. *Spring/groundwater contributions to Owens River stream flow*

The Owens River and Mammoth/Hot Creek systems exhibited a combined snowmelt-springs hydrograph (Fig. 2). During the study period, the hydrograph displayed a snowmelt runoff period (late-April to mid-August) followed by relatively stable baseflow conditions during the late-summer through winter. Median surface water inputs to Lake Crowley from the Owens River was 3.51 m^3/s across our sampling dates (Fig. 3). Of this flow, Big Spring contributed ~1.34 m^3/s (1.44 m^3/s above East Portal and <0.10 m^3/s from Deadman Creek above Big Springs) and Hot Creek Spring contributions were ~1.20 m^3/s (1.48 m^3/s Hot Creek USGS gauge minus 0.28 m^3/s Hot Creek at Hwy 395). Accordingly, 72.4% (2.54 m^3/s Spring inputs/3.51 m^3/s Owens River at Benton Crossing) of the median water inputs to the Owens River above Lake Crowley originated from spring/groundwater inputs across our sampling dates. A small portion of the Hot Creek water was lost to evapotranspiration (June–September ET = 6.23 mm/d; CIMIS, 2012) from the flood irrigation of ~750 ha of rangeland within the distributary portion of the stream prior to entering the Owens River.

Table 1
Median values for flow and field measurements of selected water quality parameters during the study period. Site ID numbers refer to sites located on Fig. 1.

Sample ID	Flow (m^3/s)	Temp (°C)	DO% Saturation	DO (mg/L)	pH	Specific Conductivity (μS)	Turbidity (ntu)
#13 Convict Creek below 395	2.1	14.3	77.8	7.9	7.9	132	1.0
#14 Convict Creek above confluence	0.4	13.1	76.1	7.6	7.8	148	0.9
#17 McGee Creek below 395	0.7	7.9	77.5	8.8	7.8	115	1.0
#16 McGee Creek above confluence	0.6	9.4	77.5	8.7	7.8	132	1.6
#1 Deadman Creek above 395	0.1	7.4	71.9	8.7	7.8	52	1.2
#2 Deadman Creek above Big Springs	0.1	9.3	73.5	8.3	7.9	127	1.3
#3 Owens River below Big Springs	1.0	10.4	71.5	7.9	7.6	229	0.4
#5 Owens River above East Portal	1.4	11.5	89.8	9.3	8.2	232	1.2
#6 Owens River at Diversion 17	2.4	12.8	90.1	9.5	8.0	206	1.5
#7 Owens River at Benton Crossing	3.5	16.8	89.0	9.0	8.4	309	2.2
#4 East Portal	1.0	13.7	71.7	6.9	7.5	172	1.2
#12 Hot Creek below 395	0.3	12.1	73.2	8.0	7.9	100	2.0
#10 Hot Creek below Hatchery	1.0	15.4	99.7	10.0	7.8	198	1.2
#9 Hot Creek at USGS Gauge	1.5	30.8	103.0	7.7	7.9	484	1.8
#8 Hot Creek Confluence - North	0.7	17.9	92.8	8.8	8.6	515	2.5
#8 Hot Creek Confluence - Middle	0.7	22.2	93.4	7.9	8.8	380	3.0
#8 Hot Creek Confluence - South	0.4	21.0	78.5	7.6	8.6	423	3.2
#11 Hatchery Spring S1 - south	0.2	15.0	62.6	6.2	7.4	224	0.5
#11 Hatchery Spring S2 - north	0.2	14.7	62.5	6.3	7.4	221	0.6

Travel times for the median flow regime were estimated from flow velocity measurements. Travel time of the Owens River from Big Springs to Benton Crossing was 10.7 h, whereas travel times for Mammoth/Hot Creek from Highway 395 to Benton Crossing via the North, Middle and South distributaries were approximately 22, 14.9 and 14.5 h, respectively (D. Vance pers. comm.; Geosyntec October 11, 2020). Flows within the three Hot Creek distributary channels were deemed approximately 40:40:20% (North, Middle, South confluences) during the summer irrigation season.

The Convict-McGee system has median upstream flows of 2.84 m^3/s (2.12 m^3/s Convict Creek at Hwy 395 plus 0.73 m^3/s McGee Creek at Hwy 395) compared to 1.03 m^3/s (0.42 m^3/s Convict Creek above McGee Creek plus 0.61 m^3/s McGee Creek above Convict Creek) below the downstream confluence of the two streams (Table 1). The loss of water resulted from diversion of water, primarily from Convict Creek, for upland pasture irrigation on the alluvial fans above Lake Crowley. Average travel times during the study period for Convict Creek from Hwy 395 to Lake Crowley was estimated as ~8 h and McGee Creek from Hwy 395 to the confluence with Convict Creek was estimated as ~4 h.

2.2. Nutrient dynamics

2.2.1. General water quality characteristics

Median seasonal water temperatures showed an upstream-to-downstream increase within the Upper Owens (7.4–16.8 °C) and Mammoth/Hot Creek (12.1–30.8 °C) river segments across our sampling events (Table 1). Water temperature within the Big Spring's discharge zone was 10.4 °C and showed a narrow range (10.1–11.9 °C) reflecting the dominance of groundwater inputs. Median spring water temperature at the fish hatchery springs were ~15 °C and increased rapidly to 30.8 °C due to thermal spring water inputs below the fish hatchery. Notably, the water temperature decreased from 30.8 °C to 17.9–22.2 °C in the lower Hot Creek between the USGS Gauge and the confluence with the Owens River, as these waters cooled during transport in response to meteorological conditions. After mixing of the Upper Owens and Hot Creek water sources, the median temperature was 16.8 °C (maximum 20.8 °C on July 28, 2018) at Benton Crossing, thereby providing appropriate thermal conditions for the cold-water fishery, despite the appreciable influence from the thermal springs. For the snow-melt streams entering the valley, Convict Creek had a considerable higher median temperature (14.3 °C) than McGee Creek (7.9 °C) owing to regulation at Convict Lake at RK 15.4 (69 ha and 1233 m^3 water storage; Reimers et al., 1955).

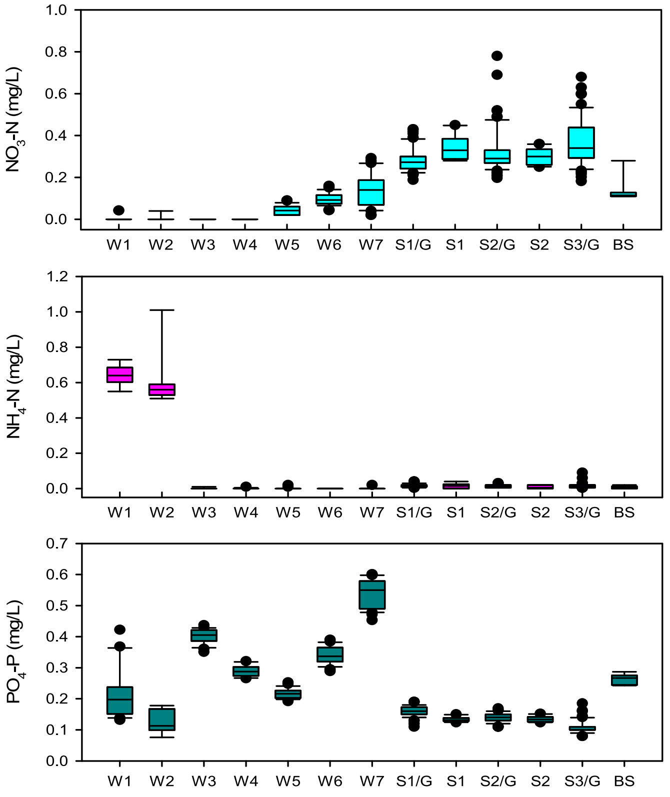

Fig. 4. Nitrate (NO_3–N), ammonium (NH_4–N) and phosphate (PO_4–P) concentrations at seven groundwater wells (W1–W7) monitored by the US Geologic Survey (see Supplemental Information Fig. S2 for well characteristics), three slightly thermal springs monitored by the US Geological Survey (S1/G, S2/G, S3/G) over the period 1986–2021, two springs monitored during our study (S1, S2; same springs as S1/G and S2/G) and the Big Springs (BS) river site during the non-snowmelt period of our study.

Specific conductance (SC) clearly distinguished snow-melt runoff from spring/groundwater inputs (Table 1). Snow-melt river segments had a lower SC (100–150 μS) compared to 200–250 μS for the slightly-thermal groundwater inputs below Big Springs and >500 μS for the thermal spring segment of Hot Creek. The spring outlets at the fish hatchery had SC values of ~220 μS, similar to that of Big Springs.

Dissolved oxygen saturation percentages were 76–78% in McGee/Convict, 72–90% in Upper Owens and 73–103% in Mammoth/Hot Creek (Table 1). The slightly-thermal springs at the fish hatchery had a 63% DO saturation, whereas the river segment receiving Big Springs water had a 72% DO saturation. DO saturation decreased from 103% to 79–93% across the irrigated pasture reach in the Hot Creek distributaries. This decrease may result from both oxygen consumption by organic matter decomposition in the saturated, irrigated pasture soils/stream sediments, as well as the decrease in water temperature (30.8–18–22 °C) that increases oxygen solubility (DO solubility 5.8 mg/L at 30 °C vs. 7.0 mg/L at 20 °C at 2100 m). Similarly, the higher DO saturation percentage at the Hot Creek USGS gauge than below the fish hatchery was likely a function of increasing water temperature rather than any primary production (photosynthesis) over the short river reach (5.6 km; ~5.6 h travel time).

The pH of non-grazed river segments were generally in the range of 7.6–8.4 and spring/groundwater inputs were ~7.6 for Big Springs and 7.4 for the fish hatchery springs (Table 1). The pH values tended to increase during downstream transport in the Owens and Mammoth/Hot Creek systems, which we attributed to CO_2 degassing from the CO_2-supersatured groundwaters; the lower DO saturation of spring waters further implied CO_2 supersaturation. Turbidity levels were low (<2 ntu) in all non-grazed river segments and increased only slightly (2.5–3.2 ntu) across the irrigated pasture zone due to grazing activities, indicating little particulate transport.

2.2.2. Ground and surface water nitrogen dynamics

Among the seven groundwater wells (depths 116–491 m; Supplemental Fig. S2), the two hydrothermal wells (W1, W2) had remarkably high median NH_4–N concentrations (median values W1 = 0.64 and W2 = 0.56 mg/L) indicative of NH_4 release from geologic materials under anoxic conditions (Fig. 4). Four wells had non-detectable (<0.04 mg/L) NO_3–N concentrations (W1–W4), whereas three wells (W5–W7) had median NO_3–N concentrations in the range of 0.04–0.14 mg/L. The variable nature of the NO_3–N concentrations likely reflected the groundwater flowpath relative to the N-bearing geologic materials, namely the lacustrine deposits within the caldera. Spring water sources had median NH_4–N concentrations <0.01 mg/L, whereas NO_3–N concentrations ranged from 0.11 mg/L for the Big Springs input reach along the Owens River to 0.30–0.33 mg/L for the spring inputs at the fish hatchery. Notably, the USGS median NO_3–N values (S1/G = 0.27 and S2/G = 0.29 mg/L) over the period 1986–2021 were similar to our median values (S1 = 0.33 and S2 = 0.30 mg/L) for these same springs during our study period. Hence, we posit that our short-term results (2 years) were representative of the spring water NO_3–N concentrations over the past three decades.

Mineral N concentrations (NH_4+NO_3) were generally low (<0.10 mg/L) across most river sampling sites (Table 2). The two notably exceptions were Hot Creek below the fish hatchery with elevated NH_4–N (0.04 mg/L) and NO_3–N (0.23 mg/L) and the Owens River below Big Springs with slightly elevated NO_3–N (0.11 mg/L). At both locations, the elevated mineral N values were distinctly higher than their respective upstream sampling sites. Organic nitrogen (total N minus mineral N) was the dominant form of N is all three stream systems (Owens 0.05–0.25; Mammoth/Hot Creek 0.15–0.23; McGee/Convict 0.08–0.12 mg N/L).

The distinct increase in NO_3–N (0.03–0.11 mg/L) in the Big Springs discharge reach was attributed to groundwater inputs as ~90% of the streamflow across the sampling events consisted of spring water inputs. Similarly, the large increase in NO_3–N (0.01–0.23 mg/L) below the fish hatchery was ascribed to spring water inputs, with some inputs from fish wastes from the hatchery. For example, two springs used as source waters for the fish husbandry contained median NO_3–N concentrations of 0.30 and 0.33 -mg/L during the study period and each spring contributed ~0.23 m^3/s of flow during the sampling events. In contrast, the McGee/Convict system representing snowmelt runoff had consistently low mineral N concentrations throughout the study period, both above and below the grazed areas.

To assess the role of pasture flood irrigation/grazing on nutrient dynamics, we compared N concentrations at the confluence of the three Hot Creek distributaries with the Owens River to the irrigation input waters from the Hot Creek at USGS gauge immediately above the irrigated pasture. Median NO_3–N concentrations decreased across the irrigated pasture (0.10 to <0.02 mg/L), NH_4–N concentrations showed no change, and organic N increased (0.18 to 0.29–0.58 mg/L). The larger increase in organic N concentrations in the North Confluence was likely associated with its longer travel time (22 h versus 14–15 h) allowing more time for water interactions with the vegetation/grazing (cattle excrement) on the landscape. Similarly, DOC concentrations were considerably higher in the North Confluence (7.9 vs 2.6–3.7 mg/L), further supporting the role of travel time in controlling organic carbon and nutrient transformations across the irrigated landscape.

Median TN, NH_4–N and NO_3–N loads remained similar or decreased within the grazed reaches of both Convict and McGee Creeks, with the decreased TN load in Convict Creek being associated primarily with a

Table 2
Median values for nutrient (N and P) and dissolved organic carbon concentrations during the study period. Site ID numbers refer to sites located on Fig. 1.

Site ID	TN (mg/L)	NH_4–N (mg/L)	NO_3–N (mg/L)	Organic N (mg/L)	TP (mg/L)	PO_4–P (mg/L)	DOC (mg/L)
#13 Convict Creek below 395	0.12	0.02	0.00	0.10	0.010	0.000	0.9
#14 Convict Creek above confluence	0.12	0.02	0.03	0.08	0.012	0.000	0.9
#17 McGee Creek below 395	0.15	0.01	0.05	0.09	0.013	0.000	0.7
#16 McGee Creek above confluence	0.18	0.01	0.04	0.12	0.012	0.000	1.2
#1 Deadman Creek above 395	0.17	0.01	0.00	0.16	0.054	0.031	1.0
#2 Deadman Creek above Big Springs	0.20	0.01	0.03	0.16	0.131	0.116	1.0
#3 Owens River below Big Springs	0.17	0.01	0.11	0.05	0.271	0.255	0.4
#5 Owens River above East Portal	0.13	0.01	0.03	0.08	0.273	0.261	0.7
#6 Owens River at Diversion 17	0.15	0.02	0.00	0.13	0.168	0.148	1.1
#7 Owens River at Benton Crossing	0.27	0.02	0.00	0.25	0.161	0.125	1.5
#4 East Portal	0.19	0.01	0.08	0.09	0.016	0.000	1.1
#12 Hot Creek below 395	0.17	0.02	0.01	0.15	0.041	0.022	1.4
#10 Hot Creek below Hatchery	0.50	0.04	0.23	0.23	0.172	0.134	0.8
#9 Hot Creek at USGS Gauge	0.31	0.02	0.10	0.18	0.180	0.142	1.2
#8 Hot Creek Confluence - North	0.60	0.02	0.00	0.58	0.149	0.102	7.9
#8 Hot Creek Confluence - Middle	0.38	0.02	0.01	0.35	0.172	0.127	2.6
#8 Hot Creek Confluence - South	0.33	0.02	0.02	0.29	0.183	0.127	3.7
#11 Hatchery Spring S1 - south	0.42	0.01	0.33	0.07	0.143	0.132	0.4
#11 Hatchery Spring S2 - north	0.36	0.01	0.30	0.05	0.143	0.134	0.5

Table 3
Median values for nutrient (N and P) and dissolved organic carbon loads (kg/d) during the study period. Site ID numbers refer to sites located on Fig. 1.

Site ID	TN (kg/d)	NH_4–N (kg/d)	NO_3–N (kg/d)	Organic N (kg/d)	TP (kg/d)	PO_4–P (kg/d)	DOC (kg/d)
#13 Convict Creek below 395	14.6	1.1	<0.1	13.6	1.8	<0.1	154.6
#14 Convict Creek above confluence	5.2	0.7	1.2	3.3	0.4	<0.1	44.9
#17 McGee Creek below 395	9.3	0.9	3.1	5.3	0.9	<0.1	37.5
#16 McGee Creek above confluence	8.2	0.6	2.4	5.2	0.5	<0.1	65.3
#1 Deadman Creek above 395	1.3	0.1	<0.1	1.2	0.4	0.2	5.4
#2 Deadman Creek above Big Springs	2.0	0.2	0.4	1.4	1.2	1.1	8.2
#3 Owens River below Big Springs	16.0	0.5	10.2	5.4	24.0	22.3	36.3
#5 Owens River above East Portal	17.1	1.7	6.3	9.1	36.8	35.3	92.3
#6 Owens River at Diversion 17	33.1	3.6	<0.1	29.6	34.2	31.6	226.5
#7 Owens River at Benton Crossing	82.4	6.8	<0.1	75.6	56.8	47.9	495.7
#4 East Portal	14.0	0.7	7.3	5.9	1.1	<0.1	96.8
#12 Hot Creek below 395	4.6	0.3	0.5	3.9	1.1	0.6	32.3
#10 Hot Creek below Hatchery	37.0	3.0	21.4	12.6	12.6	11.2	78.9
#9 Hot Creek at USGS Gauge	37.4	3.2	17.7	16.5	23.9	18.6	138.4
#11 Hatchery Spring S1 - south	9.6	0.3	6.0	3.3	2.9	2.6	8.6
#11 Hatchery Spring S2 - north	8.4	0.1	6.1	2.2	3.1	2.8	8.6

large decrease in discharge due to irrigation diversions (Table 3). In the Upper Owens River, TN, NH_4–N and NO_3–N loads were very low (<2 kg/d) above Big Springs. Below Big Springs, the median NO_3–N load displayed a longitudinal decrease to non-detectable levels at Benton Crossing, despite a 7.3 kg N/d input from the East Portal inter-basin transfer and possible inputs from Hot Creek. Conversely, both median TN and NH_4–N loads showed a progressive increase during downstream transport below Big Springs. In Hot Creek, median TN, NH_4–N and NO_3–N loads showed increases below the slightly-thermal springs at the fish hatchery and remained similar across the thermal spring input zone between the hatchery and USGS gauge, a distance of 5.6 km. This pattern indicates that the slightly-thermal springs in both the Upper Owens and Hot Creek were an appreciable source of NO_3–N, whereas the thermal springs in Hot Creek contributed little additional nitrogen to streamwaters.

2.2.3. Ground and surface water phosphorus dynamics

All the groundwater wells had notable median PO_4–P concentrations that ranged from 0.113 to 0.550 mg/L (Fig. 4). The lower PO_4–P concentrations were associated with higher water temperatures (Supplemental Fig. S2). Spring water sources had PO_4–P concentrations ranging from 0.100 to 0.160 mg/L for the spring waters at the fish hatchery to 0.255 mg/L for the Big Springs input reach along the Owens River. As found for NO_3–N concentrations, the USGS median PO_4–P values (S1/G = 0.160 and S2/G = 0.140 mg/L) over the period 1986–2021 were similar to our median values (S1 = 0.132 and S2 = 0.134 mg/L) for these same springs.

Concentrations of TP (0.010–0.013 mg/L) and PO_4–P (<0.005 mg/L) were very low in the snow-melt creeks (Convict/McGee) (Table 2). Low TP/PO_4 concentrations were also found in the Owens and Hot Creek systems above the spring water inputs. Below the springs, PO_4–P was the dominant form of TP, as opposed to organic and sediment bound forms (TP minus PO_4). Similar to NO_3 concentrations, median PO_4–P concentrations showed an increase from spring water inputs at Big Springs (~0.260 mg/L), the fish hatchery springs (~0.133 mg/L) and the Hot Creek slightly-thermal (0.134 mg/L) and thermal (0.142 mg/L) spring segments. In contrast to NO_3 concentrations that substantially decreased with downstream transport and during pasture irrigation, there were only small reductions in PO_4–P concentrations along these transport pathways.

TP (<2 kg/d) and PO_4–P (<1 kg/d) loads were very low in the snowmelt segments of Convict, McGee, Mammoth/Hot Creek and the Owens River above Big Springs (Table 3). Phosphorus loads increased downstream of spring water inputs on the Owens River and Hot Creek, with TP/PO_4–P loads for Owens at Benton Crossing (56.8/47.9 kg/d) being approximately equal to the combined load of Hot Creek at USGS gauge (23.9/18.6 kg/d) plus Owens at Diversion-17 (34.2/31.6 kg/d).

3. Discussion

The groundwater system in the Long Valley caldera is comprised of two major components: (1) a shallow subsystem in which temperatures are slightly higher than ambient land-surface temperatures, and the concentrations of dissolved solids are relatively low; and (2) a deeper subsystem in which temperatures are much higher than ambient surface temperatures, and concentrations of dissolved solids are relatively high (Sorey et al., 1978). These two groundwater sources are clearly distinguished in the spring water chemistry with the slightly-thermal springs having temperatures of 10–15 °C and SC values of 200–250 µS, compared to boiling water inputs and SC > 500 µS for the thermal spring segment of Hot Creek. The shallow subsystem is contained within deposits above the densely welded Bishop Tuff, which various boreholes identify as ranging from 865 to 1280 m (Fournier, 1989). The fill above the densely welded Bishop Tuff consists chiefly of lava flows and tuffs intercalated with lacustrine and fluvial sediments (Murphy et al., 2016). Long Valley Lake formed in the caldera shortly after the eruption (760 ka) and surface waters were subsequently drained by about 150 ka (Hildreth and Fierstein, 2016). Fine-grained pelagic sediments, representing the lacustrine deposits, were prevalent in the upper 300 m of one borehole (Abers, 1985), and a second borehole indicated that ~15% of a 700 m core consisted dominantly of lacustrine deposits (Fournier, 1989). The disappearance of ostracods (carbonates) and the appearance of diatoms within the lacustrine sediment record indicate a transition from saline to relatively freshwater conditions sometime after 550 ka (Fournier, 1989).

The low NO_3–N concentrations (<0.10 mg/L) in the snow-melt dominated streams indicate that atmospheric N deposition provides a low background signal to streamwaters. Total annual N deposition in the study area based on the Community Multiscale Air Quality model (CMAQ) is < 3 kg/ha/yr (Fenn et al., 2010). Relative to snow-melt runoff dominated stream segments, streamwaters originating from spring inputs on the Owens and Hot Creek systems displayed appreciably higher NO_3^- and PO_4^{3-} concentrations. The elevated nutrient concentrations in spring water dominated stream segments are consistent with previous reports for spring water nutrient concentrations in the Long Valley Caldera (Evans et al., 2002; Jellison and Dawson, 2003; Jellison et al., 2003). This infers that the groundwater/spring hydrologic system is delivering geologically-derived nutrients to streamwaters. This inference is strongly corroborated by our direct nutrient measurements from spring outlets at the fish hatchery (Table 2), as well as USGS historical measurements (1986–2021) of three slightly-thermal springs (Fig. 4) used as input waters for the hatchery operations. While direct sampling of spring waters was not possible from Big Springs on the Owens River due to its diffuse inputs, there was a distinct increase in both NO_3^- and PO_4^{3-} concentrations in the river reach with spring water accretions (RK 46 to ~RK 40); these median nutrient values were comprised of 90% spring water inputs at this site. The TN load slightly decreased in the thermal spring input segment of Hot Creek (below hatchery to USGS gauge = 5.7 km) inferring that the thermal water inputs had a lower N concentrations as the TN load did not increase across this stream reach. In contrast, the TP and PO_4–P loads increased in this thermal water input zone indicating that the thermal water inputs had appreciable TP/PO_4–P concentrations.

The mineral N and PO_4–P concentrations are consistent with several spring waters that we have previously investigated in groundwater and spring waters from volcanic terrains in the Cascade Range of northeastern California (Lusardi et al., 2016, 2021). We attribute the high PO_4 concentrations to chemical weathering of apatite minerals $[Ca_{10}(PO_4)_6(OH,F,Cl)_2]$ and glassy volcanic materials (incorporating P), similar to that reported in the Klamath River basin, Oregon/California (ODEQ, 2002; Klamath Tribal Water Quality Consortium, 2018). The large surface area and porosity/permeability of volcanic ejecta coupled with the rapid weathering of volcanic glass contribute to the rapid release of P from the volcanic materials (Dahlgren et al., 1999, 2004). While P release from geologic materials is generally assumed to be associated with the mineral apatite, volcanic glass can contain a considerable amount of P as well (Derkachev et al., 2023; Kuznetsova and Motenko, 2014). The globally-compiled phosphorus content of rhyolite bedrock, the composition of the Bishop Tuff that dominates the volcanic ejecta comprising the Long Valley caldera, is 305/493 mg P/kg (median/mean, n = 14194; Porder and Ramachandran, 2013). An extensive analysis (n = 219) of the glass fraction from several Bishop Tuff units found phosphorus median/mean contents of 70/158 mg P/kg (range = 28–2104 mg /kg; PGualda et al., 2022). In addition to the rapid dissolution kinetics of volcanic glass (Wolff-Boenisch et al., 2004), the Long Valley groundwater flow pathway provides a favorable weathering environment in terms of water availability and the elevated temperatures resulting from the hydrothermal system.

Using detailed water chemistry data from Evans et al. (2002) for the Big Springs water source, we calculated that spring waters are near equilibrium with hydroxyapatite (saturation index = +0.246 as determined by MINEQ ver 3.1; Gustafsson, 2015) (See Supplemental Table S1). These results are consistent with results from several volcanic springs in the Mt. Shasta region of northern California (Lusardi et al., 2021). Attainment of equilibrium conditions is made possible by the appreciable groundwater transport times, such as the estimated minimum age of 12 years for Big Springs discharge waters (Evans et al., 2002). Differences in PO_4^{3-} concentrations among different volcanic spring water sources is attributed primarily to differences in water pH, Ca^{2+} activity and temperature. Notably, there was a trend of decreasing P concentrations in the seven groundwater wells as the water temperature increased. This is consistent with the solubility of hydroxyapatite decreasing at higher temperatures (McDowell et al., 1977; Gustafsson, 2015).

We ascribe the primary source of nitrogen in the spring water to organic matter and/or NH_4^+ incorporated into silicate minerals (e.g., mica) comprising the shallow aquifer materials formed from fluvial/lacustrine deposits. Once released from the rock/organic matter as NH_4^+, nitrification transforms the NH_4^+ to NO_3^- in oxygenated groundwater systems. While streamwater nitrogen is often attributed to atmospheric deposition, instream N fixation or anthropogenic activities, bedrocks of sedimentary origins often contain appreciably concentrations of nitrogen (Holloway and Dahlgren, 2002; Morford et al., 2016a). A survey of bedrock in California found coarse and fine-grained siliciclastic rocks and their low-grade metamorphic counterparts to have median nitrogen contents of 271 and 698 mg N kg^{-1}, respectively (Morford et al., 2016a). The source of nitrogen in these sedimentary deposits is biological materials (e.g., algae, fecal materials) incorporated into the sediments. As such, pelagic sediments have appreciable nitrogen contents (600–1000 mg N kg^{-1}) that become incorporated into the rock during diagenesis. Nitrogen exists in sedimentary rocks either as organic N forms, or as NH_4^+ substituting for K^+ in mica and feldspar minerals. The NH_4^+ can be formed by microbial or thermal mineralization of organic nitrogen in anoxic environments (Boudou et al., 2008). This NH_4^+ accumulates in the sediment porewaters and may become incorporated into silicate minerals during diagenesis or transported in hydrothermal fluid flows (Bebout and Fogel, 1992). The fluvial/lacustrine sediments that are intercalated with the volcanic flows/tuffs were previously recognized as an important component of the shallow groundwater subsystem supporting the slightly-thermal springs in the Long Valley caldera (Sorey et al., 1978). The prevalence of ostracods and diatoms identified in the lacustrine deposits are the likely biological source of nitrogen in these sedimentary deposits.

In contrast to the shallow groundwater system in Long Valley, the thermal water inputs originating from the deeper groundwater system to Hot Creek showed no apparent nitrogen inputs, consistent with their origin from deeper volcanic deposits largely devoid of nitrogen. However, two groundwater wells (W1 and W2), located near the northwestern edge of the caldera demonstrated daily fluctuations in water temperature alternating between 55/105 °C (W1) and 50/180 °C (W2) (Fig. 4). Interestingly, these two wells contained elevated median NH_4–N concentrations of 0.64 (W1) and 0.56 (W2) mg N/L. These findings provide compelling evidence for thermal mineralization of organic N to NH_4^+ [Boudou et al., 2008] and/or hydrothermal release of NH_4^+ from silicate minerals. Previous studies have documented the direct release of NH_4^+ from sedimentary rocks by thermal waters in volcanic regions of New Zealand (Ellis and Mahon, 1964, 1967). These NH_4^+-rich groundwater conditions appear to occur at locations where the deeper hydrothermal waters interact with the shallower fluvial/lacustrine sediments that have incorporated N. The NH_4^+ released by these hydrothermal interactions may become nitrified to NO_3^- should it encounter oxygen due to mixing with oxygenated waters along the groundwater flowpath. As such, NH_4^+ inputs from the major springs in the Long Valley caldera were at or below the analytical detection limit (<0.01 mg N/L).

3.1. *Effects on aquatic ecosystems*

Nutrient inputs associated with volcanic spring water inputs can have profound effects on aquatic ecosystems leading to their designation as 'keystone habitats' (Lusardi et al., 2016, 2021, 2023). Under the arid to semi-arid conditions of eastern California, groundwater/spring water contributions to streamflow in the project area comprise the majority of the annual stream discharge, except for the snowmelt runoff period. The spring water inputs play a disproportionate role in aquatic ecosystem productivity during the summer/fall period. Similar to other spring-fed rivers investigated in northern California (Lusardi et al., 2016, 2021), aquatic macrophytes and a prominent benthic community of primary producers and associated biofilm communities prosper in the nutrient-rich waters below spring inputs in the Owens and Hot Creek systems (Supplemental Figs. S1a and c). These instream primary producers prominently remove NO_3^- from the water column during downstream transport resulting in no-detectable NO_3 (<0.01 mg NO_3–N L^{-1}) in waters entering the downstream Lake Crowley (as measured at Benton Crossing). Denitrification may also contribute to nitrate removal from the water column, but was deemed negligible relative to that of aquatic plant retention due to the short water travel times in the Upper Owens River (e.g., 10.7 h from Big Springs to Benton Crossing). In contrast, PO_4–P loads/concentrations were not appreciably attenuated during downstream transport owing to a much lower P requirement relative to N; aquatic plants have a N:P atomic ratio of ~26 (Duarte, 1992). Thus, PO_4–P rich waters (median = 0.125 mg/L) enter Lake Crowley wherein they can stimulate algal blooms of N-fixing cyanobacteria (dominant N-fixing species were *Lyngbya*, *Gloeotrichia,* and *Aphanizomenon*; Jellison et al., 2003). The high instream primary productivity in turn contributes

Table 4
Mass balance for median nutrient (N and P) and dissolved organic carbon loads (kg/d) above and below the lower Hot Creek grazing area during the study period.

Site ID	TN (kg/d)	NH_4–N (kg/d)	NO_3–N (kg/d)	Organic N (kg/d)	TP (kg/d)	PO_4–P (kg/d)	DOC (kg/d)
Above Irrigation/Grazing	70.5	6.8	17.7	46.0	58.0	50.3	364.9
Below Irrigation/Grazing	82.4	6.8	0.0	75.6	56.8	47.9	495.7
Change due to Irrigation/Grazing	11.9	0.0	−17.7	29.6	−1.2	−2.4	130.8

to high secondary productivity of macroinvertebrates that provides ample food to support the trophy trout fishery (Lusardi et al., 2016, 2020). Thus, nutrient-rich volcanic spring inputs support highly productive/high trophic level lotic ecosystems, whereas impoundment in lentic ecosystems can be detrimental to water quality/aquatic ecosystems as the high P inputs leads to nuisance algal blooms as water residence time allows for biological conversion of nutrients to aquatic biomass.

3.2. *Impact of grazing on streamwater nutrient dynamics*

Grazing activities during the summer/fall period showed no distinct increases in N and P loads as the streams pass through the upland grazed areas of the irrigated Convict/McGee pastures (Table 3). TN/TP loads in Convict Creek decreased owing primarily to irrigation water diversion (i.e., decreased water flux), whereas TN/TP loads in McGee Creek remained relatively unaffected.

Irrigated pastures in the lower Hot Creek catchment consisted of flood-irrigated riparian areas located between three primary distributary channels before the irrigation tailwaters ultimately enter the Owens River downstream of Division-17 (Fig. 1). Hence, to evaluate grazing impacts on water quality in the lower Hot Creek catchment, we compared the non-grazed input waters (Hot Creek at USGS gauge plus Owens River at Divsion-17) to the combined water sources below the grazed lands for Owens at Benton Crossing. There was no appreciably change in median TP/PO_4–P loads associated with irrigation/grazing activities (Table 4). In contrast, the NO_3–N load was effectively reduced to zero across these same reaches. We attribute the loss of NO_3^- to a combination of vegetation uptake and denitrification in the often saturated pasture soils (due to flood irrigation). While NH_4–N loads were not appreciably affected, the TN load increased by 11.9 kg/d. Based on the difference between TN and mineral N loads, the organic nitrogen component increased by 29.6 kg/d across the irrigated/grazed landscape. This suggests that a portion of the NO_3–N load input to the irrigated pasture in lower Hot Creek was taken up by the vegetation and subsequently released as organic nitrogen, from leaching of living/dead vegetation and/or fecal material from the grazing cattle. As particulate matter was low below the grazed area, we posit that much of the organic N load occurs as dissolved organic N (DON). This is supported by an increase in the DOC load (130.8 kg/d), which equates to a C:N atomic ratio of 11.8 for the dissolved organic matter (DOM), assuming that the entire TN load is contained within the DOM fraction. This C:N ratio is similar to the range of 11.0–14.6 for DOM found in streams draining improved grasslands in the United Kingdom (Yates et al., 2019).

Overall, the impacts of irrigation/grazing on P dynamics were negligible, whereas the NO_3–N was deemed largely converted to DON. The resulting increase of DOM to Lake Crowley will contribute to increased biological oxygen demand (both C-BOD and N-BOD) and to mineral N ($NH_4^+ + NO_3^-$) concentrations upon microbial mineralization, thereby potentially contributing to increased primary productivity in Lake Crowley. However, the 11.9 kg/d increase in TN associated with irrigation/grazing activities in the lower Hot Creek catchment was considerably lower than the 49.9 kg/d TN inputs from spring water inputs (Hot Creek = 32.8 kg/d and Big Springs = 17.1 kg/d). Hence, the spring water input of nutrients plays a substantially more important role than irrigation/grazing on N/P inputs to the Owens River and downstream Lake Crowley. Notably, flood irrigation may play a valuable role in cooling the Hot Creek waters prior to joining the trophy Owens River trout fishery (30.8 °C to 17.9–22.2 °C).

4. Conclusions

Large volume spring water inputs play a disproportionate role in the hydrology, streamwater chemistry and aquatic ecosystems of the Upper Owens River watershed during the critical biological period of summer-to-fall. Consistent discharge from springs provides a stable, reliable water source throughout the summer-fall dry period. Most notably, inputs of nitrogen and phosphorus from geologic materials were identified as the source of elevated nutrient concentrations below spring water inputs. Nitrogen, in the form of NO_3^-, originated from the slightly-thermal, shallow aquifer subsystem that intersected lacustrine/fluvial materials that incorporated nitrogen-bearing biological materials (e.g., ostracods and diatoms). Phosphorus, as PO_4^{3-}, originated from both the shallow and deeper (thermal) groundwater systems and was attributed to rapid release from the volcanic deposits (e.g., apatite and volcanic glass). In the lotic environment, the elevated N and P levels generated prolific instream primary and secondary productivity that supports a trophy trout fishery. However, when impounded in the downstream reservoir, the increased nutrient loads along with longer residence time and lack of transport generates summer algal blooms and subsequent reservoir hypoxia. Grazing activities generated no discernible increases in mineral N, TP or PO_4–P loads when comparing above-versus below-grazing river locations. When Hot Creek spring water inputs were used for downstream flood-irrigation of pastures, there was a substantial loss of NO_3–N, attributed to denitrification and/or vegetation uptake, with an increase of organic nitrogen, ascribed to leaching of plant and/or fecal materials. Overall, this study demonstrates the role of geologic nutrients (N and P) originating from large volume springs in volcanic terrains as an important source of stream water nutrients. Inputs of geologically-derived nutrients are often overlooked, and in semi-arid rangeland systems are often erroneously attributed to livestock grazing activities.

CRediT authorship contribution statement

Mike Deas: Writing – review & editing, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jeff Laird:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Stacy Tanaka:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Randy A. Dahlgren:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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