Type of paper: Article

Microbial Geochemistry of the Sulfur, Iron, Manganese, and Calcium Cycles in the San Diego River Watershed, Southern California USA

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Received: date; Accepted: date; Published: date

Abstract: Microbial populations involved in forming the distinctive precipitates of the S, Fe, Mn, and Ca cycles in the San Diego River watershed reflect an interplay between mineralogy of the rocks in the watershed, sparse rainfall, ground- and surface-water anoxia, and runoff of high sulfate, treated imported water. In the less developed headwaters, Temescal Creek tributary emerges from pyrite-bearing metamorphic rocks, and thus exhibits both an oxidized Fe and reduced S cycle. In the middle reaches, the river moves through developed land where treated, imported high sulfate Colorado River water enters from urban runoff. Mast Park surrounded by caliche-bearing sedimentary rocks is a site where marl is precipitating. Cobbles in riffles in the river are coated black with Mn oxide. When the river encounters deep-seated volcanic bedrock, it wells up to precipitate both Fe and Mn oxides at Old Mission Dam. Then, directly flowing through caliche-laced sedimentary rocks, Birchcreek tributary precipitates tufa. Further downstream, at a site that periodically receives full sunlight, a sulfuretum sets up during the summer when the river is deoxygenated. Such a rich geochemistry results in activity of iron and manganese oxidizing bacteria, sulfur oxidizers and reducers, and cyanobacteria precipitating calcareous marl and tufa.

Keywords Iron bacteria, sulfate reduction, sulfur oxidizing bacteria, tufa, marl, manganese oxidizing bacteria

1. Introduction

In 2015, amidst the 2012-2017 drought in California, there was a significant increase in the number of complaints from the public about the smell (hydrogen sulfide, H_2S) emanating from the nearby San Diego River (SDR), particularly around the Fashion Valley shopping mall (Fig. 1). Whereas public complaints in the warm-temperature, low-flow months (Aug.-Dec.) were historically common, the number of calls in 2015 was unique. This led public agencies

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Peer-reviewed version available at *Geosciences* **2018**, *8*, 495; doi:10.3390/geosciences8120495

(U.S. Bureau of Reclamation, City of San Diego) and a non-profit organization (San Diego River Park Foundation) to conduct investigations, convene stakeholders, and utilize existing data in an attempt to identify the sources of the H_2S. Biologists from the City of San Diego, Storm Water Division conducted source-tracking investigations to determine if the water quality was being impacted by illicit discharges entering the river via the storm drain system. They concluded that the cause was likely due to natural sources such as sulfate reduction.

Figure 1.pdf

Tracing the sources of sulfur through the watershed monthly as part of San Diego River Park Foundation (SDRPF) protocol resulted in coincidental observations about other microbial geochemical cycles in the SDR. This paper is a qualitative analysis of the S, Fe, Mn, and Ca cycles that were studied through a year and a half of monthly collections. Geology, water chemistry, and water treatment sources for these ions were tabulated to learn which processes dominated or interacted to create ideal conditions for these distinctive natural microbial communities.

Study Area

San Diego River (SDR) (Fig. 1) is centrally located within San Diego County in southwestern California, United States. SDR begins in the Peninsular Range Mountains 2.35 km northeast of Santa Ysabel, California. It extends for 83.68 km and flows west to the Pacific Ocean south of Mission Bay in San Diego. The watershed is 1,124 km^2 and in the near-arid western United States. There are four overlapping seasons: cold (Nov. to Jan.), rainy (Dec. to Feb.), dry (Jun.-Aug.), and hot (Jul. to Oct.). Rainfall during our study interval from 2015-2016 was 61-66 cm in the upper reaches, 20-32 cm in the middle reaches, to 25-26 cm at the river's mouth [2] (Appendix A). Because rainfall is lacking during most months, reaches that are heavily vegetated with aquatic plants slow the flow of water and help drive the water column anoxic [3].

The water in the river is a complex mixture from many sources that include local, treated, and stored imported raw water. The headwater tributaries drain sulfide-bearing metamorphic rocks that weather to supply sulfate and dissolved iron. They drain into the El Capitan Reservoir whose dam is the only impoundment on the main stem of the SDR; the last time the dam overflowed was 1993 [4]. The other major water storage facility, the San Vicente Reservoir, dams a tributary, as do two smaller reservoir lakes (Lakes Murray and Jennings). At the time of our study, water in the El Capitan Reservoir was considered to be an emergency supply; thus, it was only piped to the Alvarado treatment facility from Jan. to April, 2016 in response to drought [5]. At the present time (2018), water in both major reservoirs is being conveyed to the Alvarado treatment plant at Lake Murray. Thus, starting in 2016, river water from the headwaters is being mixed with imported water and reentering the SDR.

The four reservoirs store imported water that is supplemented by sparse local water. The stored water in these reservoirs is treated for municipal use; but the sources vary through the years as San Diego County expands its search for reliable supplies. Treated municipal water within the watershed boundaries is supplied by the San Diego Water Authority, and the Lakeside, Padre Dam, and Ramona Municipal Water Districts [6]. During our study interval, 72% of this municipal water was introduced from the high sulfate Colorado River (100s of mg/L sulfate), 13% from the extremely low sulfate Sacramento Bay Delta water (10s of mg/L sulfate),

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and 15% local supply (100s of mg/L sulfate in Lakeside wells) [7,8]. These water sources are blended primarily to control Colorado River water salinity to levels less than 500 mg/L total dissolved solids [9].

Variable amounts of sulfate are introduced from treated and Colorado River sources. Treated water meets the California Secondary Maximum Contaminant Level for sulfate, which is 500 mg/L [10]. However, analysis of annual water quality reports shows that sulfate values are generally below 250 mg/L, reflecting the fact that Colorado River water is generally below 250 mg/L [11,12]. Sulfate values in the eight analyses from the Colorado River below Hoover Dam for the years 2015-2016 range from 215-243, median 237 [12]. Historically, sulfate in the Lower Colorado River has been as high as 355 mg/L [13].

One additional source of our studied cations and anions are commercial-grade chemicals used by the seven water treatment plants. Depending on the treatment plant and the year, they introduce S (alum, sulfuric acid), Fe (ferric chloride), and Mn (potassium permanganate) [10].

Figure 1 (red arrows) shows where this treated water potentially enters the San Diego River as runoff and discharge. Primarily flowing into storm drains that discharge into the river, the sources of this runoff include residential, commercial, and governmental landscape irrigation and cleaning; leaking pipes and water main breaks; car washing; pool emptying; agricultural runoff; and golf course irrigation.

The watercourse of the SDR also incorporates two shallow alluvial ground-water basins. These are the Santee-El Monte and the Mission Valley basins [14]. Hydraulic head measurements in the USGS SDAQ well (Fig. 2, red dot) were 3-5 m above ground surface (reported from USGS data by [15]) suggesting artesian flow into SDR. Thus, aquifer water may interact with the modern water chemistry, affecting all four cycles. C-14 and Kr isotopic data determined that the water at 12 m depth is 540 ybp, whereas the water at 271 m is 19,100 ybp [16].

2. Materials and Methods

Water quality. Water quality analysis is part of two ongoing programs; data useful for this project were incorporated here from both. The San Diego River Park Foundation (SDRPF) samples 15 sites along the lower SDR monthly. Sampling began in 2004 and follows the SDRPF quality assurance project plan protocol. General water quality measurements include dissolved oxygen (DO), pH, temperature, and conductivity. The measurements are collected using a YSI Professional Plus multiparameter meter. These data and flow which is measured by propeller (ft^3/sec) are published online [17]; additionally, two USGS stream gages provide discharge and peak streamflow data [12].

Storm water biologists from the City of San Diego collected weekly samples from the river between April 2015 and November 2016 to establish baseline water quality measurements. Four sites in the lower watershed were selected based on their proximity to where complaints were reported. These sites overlapped with SDRPF sample locations. Water quality measurements of pH, conductivity, and temperature were taken in the field using portable Hanna and Oakton multiparameter instruments and dissolved oxygen was measured with the YSI ProODO optical DO meter. Additional samples were collected every other week and submitted within six hours of sampling to City laboratories for chemical and bacteriological testing.

Geology and mineralogy. Geology was accessed from published and unpublished maps [18-25], most of which can be accessed online [26]. Mineralogy was accessed from published sources [19, 27-31].

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Water chemistry. Water chemistry for S, Fe, Mn, and Ca is reported in the figures and in Appendix A from published [32-34] and unpublished sources. Unpublished and online sources are [7, 10, 35-41]. Stable isotopes of oxygen and deuterium are reported in [15] for the Mission Valley area (Fig. 1).

Periodically, San Diego State University (SDSU) degree students [42] and class assignments [43,44] have reported on water chemistry. These data are incorporated in the figures and Appendix A.

Monitored site water chemistry is from City of San Diego, Storm Water Division and SDRPF analyses. Chemical analytes tested by City of San Diego, Microbiology and Wastewater laboratory include sulfate and dissolved sulfide, as well as other ions of environmental concern. In general, the analytical techniques used were SO_4 by EPA300.0 or EPA9038, S^{2-} by EPA9034, Fe by SM3111B, and Mn by EPA6010B, Ca by SM3500-D.

Microbiology. For this study, microbial samples were collected systematically during SDRPF sampling days and supplemented with adventitious sampling to assess the entire watershed. Samples were analyzed microscopically. Bacteria in Appendix A were identified using morphological criteria. Most of the bacteria are identified only to genus; species are cited only for monospecific genera or easily recognized ones.

Other microbial analyses are available for the watershed but not reported here. Storm Water biologists collected biweekly bacteria samples to quantify total coliform, *Enterococcus*, and *E. coli*.

3. Results

Figure 1 displays some of the important field sites, the reservoirs, the position where the underground river reemerges, and some of the sources of water. Appendix A reports the details of geology/mineralogy, water chemistry, and microbiology where analyzed for the entire river and its tributaries, beginning near the top of the watershed and ending at the ocean.

The sulfur (S) cycle consists of S-bearing minerals in the watershed, sulfate in the river water, and sulfate-reducing and sulfur oxidizing bacteria (Fig. 2). In the headwaters, sulfate values are in 10s of mg/L, correlating primarily with the presence of pyrite weathering from the surrounding Julian Schist. Further downstream where sulfate values reach into the 100s mg/L, it is hypothesized that the sulfate is being introduced as runoff and drainage from municipal treated water. Figure 3 shows weathering schist along Temescal Creek (Fig. 3a), sulfate reduction (Fig. 3e), bacteria from a sulfuretum (Fig. 3b) that is established in the river under the Friars Road bridge (*Chloroflexus* sp., Figs. 3c and 3l; *Beggiatoa* sp., Fig. 3j; *Chromatium* sp., Fig. 3g, 3h; *Thiospirillum* sp., Fig. 3i), and the colorless sulfur oxidizer *Thiothrix* sp. there and elsewhere (Figs. 3d, 3f, 3k). The colorless sulfur oxidizers require suboxic water and the anoxyphotosynthetic purple and green sulfur bacteria require anoxic water that receives full sunlight. The amount of sunlight required was not analyzed; the sulfuretum is under a double-spanned bridge that blocks sunlight during parts of each day. *Thiospirillum* sp. was first noted in September. Analysis of sulfate values (Appendix A and unpublished data) during the 2015-2016 study interval shows sulfate fell as much as 100 mg/L from the station above the sulfuretum to the station below it from August-October and December in 2015 and June in 2016. Sulfate values decreased most of the other months also, but an order of magnitude less. November 2015 had a significant rainfall event that strongly diluted sulfate.

Figure 2 S cycle watershed .pdf

Figure 3 S bacteria.pdf

The iron (Fe) cycle consists of Fe-bearing minerals in the watershed, iron in the river water, and iron oxidizing bacteria (Fig. 4). Fewer water chemistry analyses are published for Fe, but the values are consistent with the availability of Fe-bearing minerals weathering in the watershed. The seeps at the upper elevations are ascribable to the presence of pyrite in the Julian Schist (Fig. 5m). The presence of iron bacteria (Fig. 5n, 5o) such as *Leptothrix ochracea* (Fig. 5p), *L. cholodnii*, *Siderocapsa* sp., *Siderococcus* sp., *Toxothrix trichogenes*, and *Gallionella ferruginea*, showed where anoxic ground water bearing Fe^{2+} is available in the water, while biofilms formed by *L. discophora* showed where it is discharging along the river banks (Figs. 5o, 5q) [45].

Figure 4 Fe cycle watershed.pdf

Figure 5 Fe bacteria.pdf

The manganese (Mn) cycle consists of Mn-bearing minerals in the watershed, Mn in the river water, and Mn-oxidizing bacteria (Fig. 6). Mn was not studied systematically, and so there are fewer reported sites. Few water chemistry analyses are published for Mn, but the values are consistent with the availability of trace Mn in the watershed rocks. Mn oxide (defined by Tebo et al. [46] as oxides, hydroxides, and oxyhydroxides) is recognized as black coats on rocks in river riffles; Figure 7 displays a cracked open, black-coated rock (Fig. 7r) and the bacteria that precipitate Mn oxide (*Leptothrix discophora*, 7t). Precipitation was tested by submerging microscope slide sets in the river at a riffle at West Hills for a month (Fig. 7s). Mn was also seen at holdfasts of an unidentified diatom that attached to an algal filament (Fig. 7u). Additionally, brown biofilm occurred at two sites; when collected, *L. discophora* holdfasts were present (Fig. 7w), suggesting that these bacteria are precipitating Mn oxide on the biofilm. Furthermore, brown stain is seen sometimes on the foam forming downstream from Old Mission Dam (Fig. 7v); the idea has not been tested with leucoberbelin blue (LBB), but it is hypothesized that the brown may be from colonization by *L. discophora*.

Figure 6 Mn cycle watershed.pdf

Figure 7 Mn bacteria.pdf

The calcium (Ca) cycle consists of minor Ca-bearing minerals in the upper watershed, caliche-rich marine rocks in the lower watershed, Ca in the river water, and hard tufa and

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Peer-reviewed version available at *Geosciences* **2018**, *8*, 495; doi:10.3390/geosciences8120495

soft/gritty marl deposition by cyanobacteria in the lower watershed (Fig. 8). At Birchcreek in Mission Trails Regional Park, the breached cement culvert and the emergent creek bed are lined with a series of small tufa terraces or terracettes (Fig. 9x). The largest terrace is 153 cm wide, 157 cm long, and 18 cm thick. The tufa is coated with embedded *Rivularia* sp. (Figs. 9y, 9z, 9aa). Marl deposition occurs in a backwater at Mast Park (Fig. 9bb) where *Oscillatoria* sp. (Fig. 9cc) dominated the microbial community.

Figure 8 Ca cycle watershed.pdf

Figure 9 Ca cyanos.pdf

4. Discussion

S Cycle (Figures 2 and 3)

In the upper watershed, pyrite is weathering from the Julian schist and percolating into spring pools that display both intense sulfate reduction and iron oxidation. In general, microbial oxidation of pyrite has been found to be a two-step process catalyzed by different bacteria [47,48]. The sulfur moiety of the mineral is attacked first by thiobacilli and oxidized to sulfate,

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ H^+ + 2\ SO_4^{2-}.$$

The iron moiety is released as Fe^{2+} which moves out until it reaches the zone of oxidation where neutrophilic iron bacteria such as *Leptothrix ochracea*, *L. cholodnii*, and *Siderocapsa* sp. form red-orange flocculates and precipitates,

$$2\ Fe^{2+} + ½\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O.$$

In general, the reduction of sulfate to sulfide is catalyzed in anoxic sediment by sulfate-reducing bacteria such as *Desulfovibrio* sp. [47]. This process occurs in one step,

$$SO_4^{2-} + 2\ H^+ + 4\ H_2 \rightarrow H_2S\uparrow + 4\ H_2O.$$

This process is best observed in the soft sediment of the hyporheic zone below the margins of SDR.

Where sulfate-bearing water is suboxic, colorless sulfur oxidizers are typically present when H_2S is available [49]. A distinctive site is in the upper reaches of San Vicente Reservoir where submerged dead tree stumps were covered with colorless sulfur oxidizers that sat directly on black sulfate reducers.

Sulfur oxidizing bacteria are either colorless (white) or are the color of their dominant photosynthetic pigments (bacteriochlorophyll, carotenoids). *Beggiatoa*, *Chromatium*, *Thiothrix*, and *Thiospirillum* store elemental sulfur intracellularly for energy,

$$H_2S + ½\ O_2 \rightarrow S^o + H_2O,$$

and then excrete it as sulfuric acid when H_2S becomes less available [50],

$$S^o + 1.5\ O_2 + H_2O \rightarrow H_2SO_4.$$

In contrast, green sulfur bacteria, including *Chloroflexus*, excrete the sulfide sulfur immediately as sulfuric acid. Thus at the Friars Road sulfuretum (Fig. 1), sulfate and soluble sulfide arrive in the water, get transformed to sulfate, elemental sulfur, sulfuric acid, and H_2S by the sulfur cycle microbial community, and then leave as sulfate, sulfuric acid, dissolved sulfide, and $H_SS\uparrow$ (Appendix A). Lacking sites to accumulate sediment, other than behind upstream dams, the river

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provides no intermediate storage where stable pyrite might form, and thereby might remove naturally some of the excess H_2S.

The major source of sulfate in the SDR below El Capitan dam is hypothesized to be urban runoff from treated, imported high-sulfate Colorado River water. Stable isotopes of oxygen and deuterium are being studied currently by Trent Biggs and Chun-Ta Lai at SDSU to address the question of variable water sources (in preparation [51]). The availability of sulfate feeds sulfate reduction wherever sediment becomes anoxic. Particularly in the hyporheic zone below the river banks, sediment smells of H_2S, and is black from the formation of metastable iron monosulfides [52]. Vibrios which could be *Desulfovibrio* sp. were present in all analyzed black samples. Where the water was suboxic and flowing, long white streamers of the colorless sulfur oxidizer *Thiothrix* sp. were distinctive. Where the SDR itself became fully anoxic, especially in backwaters and in places where the water barely flows in the summer, white biofilms of the sulfur oxidizer *Beggiatoa* sp. spread out over the quiet water. In places where sunlit water is stagnant or flowed slowly over riffle cobbles in full sun, the anoxyphotosynthetic purple sulfur oxidizers *Chromatium* sp. and *Thiospirillum* sp. and green non sulfur *Chloroflexus* sp. were anoxia indicators.

These data allow us to approach the question as to why the smell of H_2S is so intense in the lower reaches in the summer. The river carries a large load of sulfate; hopefully the isotope research will better answer the question of sulfate sources, hypothesized here as being introduced primarily from treated Colorado River water runoff. Colorado River water is the least expensive water available to the County, and so it will continue to be the most attractive resource into the future. In the summer, the river becomes suboxic and anoxic, thereby creating ideal conditions for sulfate reducing bacteria. As seen on Figure 2, most of the sites in the lower reaches had the full range of sulfur bacteria. The sulfur oxidizers use the H_2S provided by the sulfate reducers. Thus, one might expect that the oxidizers should be lowering the sulfide concentration. Instead, analysis of sulfate values during the study interval showed 100 mg/L drop in sulfate values below the sulfuretum during the late summer (August to October in 2015). The sulfate is clearly being reduced to sulfide that is not being lowered even by intense activity of sulfur oxidizers. There are other factors that could accelerate H_2S-production not addressed by our research, such as river velocity being reduced in the lower reaches; or the fact that there is more aquatic vegetation, aiding anoxia; or drought affecting water anoxia. Creative methods for removing or reducing gaseous sulfide, such as being tested by the wastewater community [53,54], await future research.

Fe Cycle (Figures 4 and 5)

In the headwaters, pyrite is weathering from the Julian schist and percolating into spring pools having red flocculates/precipitates formed by iron bacteria. As explained above, microbial oxidation of the pyrite sulfide releases the (reduced) iron during the oxidation of the sulfide. Where the iron feeds into the pools, at the air-water interface the iron oxidizers *Leptothrix cholodnii*, *L. ochracea*, *Siderocapsa* sp. oxidize the reduced iron to red-orange flocculates/ precipitates. Another iron oxidizer, *Toxothrix trichogenes* was rare. The red orange flocculates/ precipitates have been analyzed elsewhere to be the highly hydrated, metastable mineral ferrihydrite [55]. Ferrihydrite cannot dehydrate to stable hematite without application of heat or salinity [56].

The banks of the northern end of the El Capitan Reservoir in particular were lined with iron seeps. Thus, a major source of iron in the reservoir water may be from weathering of iron-

 doi:10.20944/preprints201811.0007.v1

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bearing minerals in the surrounding S-type (sediment derived) granitic rocks [31]. Further downstream, where iron-bearing ground water emerges along the edges of the SDR, the iron bacteria *Leptothrix cholodnii*, *L. ochracea*, *Siderocapsa* sp. oxidized the iron to red-orange flocculates/precipitates. Another iron oxidizer, *Gallionella ferruginea* was rare.

The most distinctive iron cycle was exhibited around the breached, historic Old Mission Dam where ground water emerges from the subsurface aquifer upon encountering the meta-volcanic bedrock massif. The water must be predominantly anoxic, containing sufficient reduced iron to feed a distinctive iron-oxide cycle. When the water table is elevated (February to May, September), the edges of the outcropping rocks have small pools filled with red iron flocculates/precipitates of the iron oxidizers.

Found in all three sections of the river, the red-orange flocculates/precipitates of the iron oxidizers, being exceptionally colorful, are perfect tracers to learn where iron-bearing ground water emerges into the river [45]. Furthermore, where the water is barely moving, the oil-like biofilm of *L. discophora* spreads out onto the water, initiating the precipitation of the hydrated ferric oxide that forms interference colors on the water when the biofilm plates overlap [57]. This iron bacterium also participates in the Mn cycle, where it precipitates Mn oxide on solid surfaces such as rocks, bottles, cans, plastic, etc.

Mn Cycle (Figures 6 and 7)

Mn is typically a trace constituent of river water [58]; it probably only dominates river systems receiving acid mine drainage [59,60]. Chemically, reaction kinetics determines that iron will drop out before Mn [61]. Biologically, many iron bacteria get energy by oxidizing the iron, so Mn stays in solution until the bulk of the iron is removed. Mn typically stays in solution in uncontaminated natural rivers until oxygen levels are raised, which is the process where oxygenated river water flows over cobbles in riffles [62]. The black Mn oxide coatings are predominantly created by mineralization of the holdfasts of *Leptothrix discophora*. The Mn oxidation process occurs on an exopolymer matrix [46] and is considered to be a byproduct reaction, a detoxification mechanism, or a potential protection mechanism (46,63]. In SDR, riffles are coated black from the top of the watershed (Boulder Creek) to the bottom (YMCA). Interestingly, when oxygen in the river water is very low, the coatings dissolve (microbial Mn reduction?).

Mn substitutes in for Fe in many minerals, including pyrite, amphiboles, and pyroxenes [64]. Presumably the Mn measured in the Julian schist by Germinario [28] was present as substitution for Fe in pyrite. Todd et al. [31] analyzed the presence of Mn in most of the Peninsular Range granitic rocks.

Mn concentrations measured in the USGS SDAQ well (Figure 6, red dot) are in the thousands of ug/L (Appendix A). Artesian pressures were measured that would extend 3-5 m above ground surface (reported from USGS data by [15]). Therefore, leakage from the subsurface could supply in-stream Mn.

The mineralogy of biogenic black Mn oxide coatings is complex. The phase precipitated by Mn oxidizing bacteria is a metastable, highly hydrated mineral such as Na-bearing buserite [46]. Unlike the ferrihydrite precipitated by the iron bacteria, buserite dehydrates to stable birnessite [65]. It is suggested that the detoxification or potential protection mechanism used by the Mn oxidizers can co-precipitate other cations in the water; this process explains why the early prospectors would scrape the Mn-oxide rinds for assay of valuable elements such as Ag,

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Ni, and Co (see [61]). Mineralization within the SDR watershed includes Au, Cu, Mo, and U [66]; none of these coprecipitate with Mn.

Other phenomena were noted that might be part of the Mn cycle, but require further testing with LBB for confirmation. Brown biofilm contains *L. discophora* holdfasts; this unusual precipitate was noted at Old Mission Dam, Kumeyaay Lake, West Hills, and Estuary sites. A white foam forms downstream as water falls over Old Mission Dam; where the foam gets caught in a backwater, it turns the brown color of Mn oxide in June, September, and December. If the brown is Mn oxide, two hypotheses are suggested. The foam might store sufficient oxygen to overcome the activation barrier, or the foam might be colonized by an oxidizer such as *L. discophora.*

Ca Cycle (Figures 8 and 9)

The Ca cycle appears where the caliche-bearing Friars Formation is exposed in the watershed. Ca is precipitated in two forms—soft/gritty marl and hard tufa. In both cases, cyanobacteria are implicated in the precipitation of the calcium carbonate. Hard tufa terracettes [67,68] are forming in the Birchcreek tributary where the pH is typically greater than 8. Microscopically, *Rivularia* sp. dominated. The formation of tufa is considered to be enzymatically precipitated using the Rubisco pathway [69], whereas marl precipitation is probably the result of pH increase during photosynthesis. Soft/gritty marl precipitates on cyanobacteria mats in shallow water in a backwater area of the river at Mast Park; *Oscillatoria* sp. was the most abundant cyanobacterium identified in that mat. Marl was observed at other sites in the lower watershed, but not sampled.

5. Conclusions

Sampling the distinctive microbial populations for 18 months has created a deeper understanding of the interplay between abiotic and biotic processes in the San Diego River and its tributaries. Mineralogy of the rocks in the watershed, sparse rainfall, ground- and surface-water anoxia, and runoff of high sulfate treated imported water all appear to create conditions that are favored by S, Fe, Mn, and Ca cycle bacteria.

Furthermore, a surprising amount of geochemical information about the river was provided by the presence of the microbial community that precipitates S, Fe, Mn, or Ca. The presence of the gradient-seeking sulfur oxidizers at the surface of the water showed where the water was suboxic. Black sulfidic sediment produced by the sulfate reducing bacteria highlighted the location of anoxia. Purple and green sulfur oxidizing bacteria also showed the location of anoxia where there is full sun. Iron oxide biofilms at the surface of the water showed where anoxic ground water carrying reduced iron was discharging. Even though Fe and Mn typically travel together, Mn typically moves slightly further downstream. Mn oxide coatings on riffles suggest that iron bacteria upstream have stripped out the Fe, so that Mn was the dominant cation in the water. $CaCO_3$ precipitation showed where the pH was greater than 8 and where leachable Ca was present in the watershed.

Each of these biological cycles is distinct. The S cycle is exhibited by microbial sulfate reduction, sulfur oxidation, and anoxyphotosynthesis. Fe oxidizers create red flocculates/ precipitates and oil-like biofilm. Mn oxidizers create black coatings on rocks in riffles and perhaps on biofilm and foam. The Ca cycle cyanobacteria precipitate $CaCO_3$ in the form of hard tufa and soft/gritty marl.

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These cycles actually rely on many linked and unlinked processes in the watershed. Pyrite in the upper watershed and runoff of high-sulfate treated Colorado River in the middle and lower watersheds drive the S cycle that also relies on low oxygen in the water. The Fe cycle is driven by the availability of iron-bearing minerals such as pyrite, but also requires ground water anoxia. The Mn cycle is similar to that of the Fe cycle, but it additionally requires a source of reduced Mn being carried by oxygenated water over riffles. The Ca cycle is distinct and appears to be exhibited only where watershed sediments contain abundant caliche. Thus, the natural microbial populations of the SDR reflect a complex dynamic system.

Author Contributions: Conceptualization, Eleanora Robbins; Formal analysis, Ming Lai and Janae Fried; Methodology, Ming Lai; Visualization, Shannon Quigley-Raymond; Writing – original draft, Eleanora Robbins and Shannon Quigley-Raymond; Writing – review & editing, Ming Lai and Janae Fried.

Funding: This research was a volunteer activity (ER) done as part of foundation (SQ-R) or City of San Diego (ML) sampling protocol. The Department of Geological Sciences at San Diego State University funded analytical chemicals for JF.

Acknowledgments: Thanks to Vicki Todd for unplublished maps; Lake and Reservoir Keepers (Brian Norris, Budd Murray, Butch Paddock, Gayle Havens, Heidi Couture, Malie Guerrero, Viviana Castellon); San Diego County Parks and Recreation (Patti Hayden); Field partners (Kyle Armendariz, Jon Calderon, Pat Curo, Janis Hernandez, Julie Lubjenkov, Fed Pinongeos, Vicki Todd, Wenje Lee, Kathy Thorbjornarson, Lili Landin); San Diego River Park Foundation volunteers (Chandler Hood, John Kennedy, Duncan Miller, Marty Offenhauer, Gary Strawn); San Diego County Water Authority personnel (Craig Balban, Mark Umphries); U.S. Geological Survey (Wes Danskin, Kelly McPherson, Rob Anders). Appreciation is also given for microbial identification (Margarita Grabovich); for rainfall data (Charles Fisk); and for water chemistry data from City, County, and Federal agencies (Doug Campbell, Doug McPherson, Jeff Pasek, Laralyn Asato, Lori Zajac, Mark Umphries, Mike Clark, Ron Kauble, Tom Burger).

Conflicts of Interest

Storm water biologists from the City of San Diego primarily participated in water sample collection and provided data for this article. Other authors declare no conflict of interest.

Appendix A: Microbiology, water chemistry, and geology/mineralogy of the San Diego River watershed

Explanation of abbreviations and format details in appendix

A) Distances for tributaries are measured where they enter the San Diego River.
B) Geology is reported from each sample locality; the mineralogy reflects the geology of a one-kilometer radius from the upstream side of the sample locality. Mineral and rock abbreviations are as follows: bio, biotite; calc, calcareous; chl, chlorite; cong, conglomerate; epi, epidote; ferrihy, ferrihydrite; hema, hematite; hbe, hornblende; ilm, ilmenite; musco, muscovite; py, pyrite; pyrrho, pyrrhotite; pyrox, pyroxene; volc, volcanic.
C) For water chemistry and microbiology, the numbers from 1-12 in parentheses are months (1=Jan., 2=Feb., etc.).
D) Fe and Mn are in ug/L; other chemical constituents are reported in mg/L.
E) FeOx refers to observations of iron oxide flocculates/precipitates that were not sampled. SOx refers to observations of white filaments and white biofilms that were not sampled.
E) References in [ ]

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F) Minimum-maximum values in samples collected in the reporting interval 2015-2016 are in regular font; values from other years are in italics.

Upper Watershed

Monthly rainfall (in.), Julian CDF Station, [lat. 33.07639, long. -116.5925], 1285 m elev. [2]

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ann
2015	0.49	2.47	2.19	1.61	3.20	0.01	1.94	0.05	1.97	0.52	3.05	6.42	23.92
2016	7.95	0.66	1.98	1.47	0.88	0.00	0.00	0.00	1.20	0.31	3.57	7.88	25.90

SDR at Headwaters (NE of Santa Ysabel), [33.116035,-116.652667], San Diego County unincorporated. The San Diego River (SDR) begins around 1158 m elevation as a seep in the Peninsular Ranges.

Km 83.68		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [24]	gabbro, tonalite		bio, hbe, ilm, mag	bio, hbe, pyrox	pyrox

Coleman Creek (Tributary of SDR), [33.087911,-116.646191], Cleveland National Forest.

Km 79.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [24]	schist, tonalite	py	bio, hbe, ilm, mag, musco, py	bio, hbe, py, pyrox	pyrox
Microbiology		no H_2S↑	FeOx(10)		

Sentenac Creek (Tributary of SDR), [33.073579,-116.651438].

Km 76.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [24]	schist, tonalite	py,pyrrho	bio, hbe, ilm, musco, py, pyrox, pyrrho	bio, hbe, py, pyrox	pyrox
Water Chemistry [36]	*pH 7.3(5)* *DO 5.15 (5)*	SO_4 *50.9(5)*	Fe *101(5)*		

Temescal Creek (Tributary of SDR), [33.055867, -116.662263], Cleveland National Forest. The upper watershed creek flows through a series of spring pools being fed by ground water emerging from fractures in pyrite-bearing, Julian schist bedrock.

Km 74.0		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [24]	schist, tonalite	py,pyrrho	bio, hbe, ilm, musco, py, pyrox, pyrrho	bio, hbe, py, pyrox	pyrox
Water Chemistry	pH 6.91(3)				
Microbiology		H_2S↑ (3,7,8,9,10)	FeOx(3,7,8,9,10) *L.discophora* biofilm(7,10) *L.cholodnii*(11) *L.discophora*(11) *L.ochracea*(11) *Siderocapsa*(11)		

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Ritchie Creek (Tributary of SDR), [33.016086,-116.711658], San Diego County unincorporated. Iron-oxide flocculates were sampled in lined pools dug into the river to provide water for grazing cows.

Km 68.4		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [24]	granodiorite, tonalite	py, pyrrho	bio, hbe, ilm, py, pyrox, pyrrho	bio, pyrox	pyrox
Water Chemistry [36]		SO_4 *51.2(5)*			
Microbiology		no H_2S↑	*L.discophora* biofilm(2) FeOx(2) *L.ochracea*(2)		

Cedar Creek (Tributary of SDR), [33.0022,-116.7089]. 0

Km 66.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [22]	tonalite	py, pyrrho	bio, hbe, ilm, py, pyrox, pyrrho	bio, hbe, py, pyrox	pyrox
Water Chemistry [36-37]	pH 7.66(4)-8.43(4) DO 7.35(4)-8.38(4)	SO_4 *54(3)-83.4(3)*	Fe *26.2(5)*	Mn *5.96(5)*	

Boulder Creek (Tributary of SDR), [32.963674,-116.6639], Cleveland National Forest and San Diego County unincorporated.

Km 65.3		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [22]	granodiorite, quartz diorite, tonalite	py, pyrrho	bio, hbe, ilm, py, pyrox, pyrrho	bio, hbe, py, pyrox	pyrox
Water Chemistry [36]	pH 7.75(4) DO 8.12(4)	SO_4 *12.3(4)-53.8(3)*	Fe *70(5)-181(5)*	Mn *5.14(2)-66/3(4)*	
Microbiology		no H_2S↑	FeOx(7)	*L.discophora* coatings(7)	

Sheep Camp Creek (Tributary of Boulder Creek), [32.982157,-116.673192], Cleveland National Forest. Creek was dry but the soil probe uncovered moist, black, sulfidic sediment.

Km 65.3		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [22]	tonalite, schist	py	bio, hbe, ilm, musco, py, pyrox	bio, hbe, py, pyrox	pyrox
Microbiology		H_2S↑ (10)			

Lake Cuyamaca (Tributary of Boulder Creek), [32.979851,-116.578715], Cleveland National Forest. A tributary entering Lake Cuyamaca was sampled at a seep.

Km 65.3		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [20]	schist, granodiorite, tonalite, quartz monzonite	py, pyrrho	bio, ilm, mag, musco, py, pyrox, pyrrho	bio, hbe, py, pyrox	pyrox
Water	pH *8.3(5)*	SO_4 *7.2(5)*-39(5)			

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Chemistry [33]					
Microbiology		H_2S↑ (2)	*L.cholodnii*(2) *L.ochracea*(2) *cf. Siderocapsa* (2)		

SDR at Eagle Peak Road, [32.962593,-116.749980].

Km 60.7		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [22]	tonalite	py, pyrrho	hbe, ilm, mag, py, pyrox, pyrrho	hbe, py, pyrox	pyrox
Water Chemistry [37]	pH *8.22(5)* DO *7.23(3)*	SO_4 *83.9(4)-105(3)*			

SDR in El Capitan Reservoir, [32.883583,-116.803683], and [32.917314,-116.781290], San Diego County unincorporated. SDR enters the north end of the Reservoir. Iron-oxide seeps are particularly common along the northwestern edge. Seeps were also present along the east side of the dam.

Km 49.1		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [25]	tonalite	py, pyrrho	bio, hbe, ilm, mag, py, pyrox, pyrrho	bio, hbe, py, pyrox	calc-silicate, pyrox
Water Chemistry [40]	pH 7.77(1)-8.45(7)	SO_4 79.8(1)-162(7)	Fe 72.6(4)	Mn 10.4(4)-40.8(4)	Ca 31.1(1)-36(4)
Microbiology		H_2S↑ (3,9) *Beggiatoa*(9) FeS_2 framboids(3)	*L.discophora* biofilm(3,9) FeOx(3,9) *L.discophora*(3) *L.ochracea*(9) *Siderocapsa*(3) *Siderococcus*(3) *Toxothrix trichogenes*(3)		

Conejos Creek and its Tributary King Creek, [32.8903,-116.7631], (Tributary of El Capitan Reservoir).

Km 51.5		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [23]	tonalite, quartz monzonite	py, pyrrho	bio, hbe, ilm, mag, py, pyrox, pyrrho	bio, hbe, py, pyrox	calc-silicate, pyrox
Water Chemistry [36-37]	pH *7.7(11)-8.0(5)* DO *8.0(5)*	SO_4 *18.1(5)*-336(3)	Fe *39.7(5)-640(11)*	Mn *0(11)-6.83(5)*	Ca *11.6(11)*

Chocolate Creek (Tributary of El Capitan Reservoir), [32.8472,-116.8069], City of Alpine. Creek mud was probed where the creek forms a delta into the south end of El Capitan Reservoir. Although iron-oxide-rich rocks crop out along Chocolate Creek, no Fe-oxide flocculates were seen in the delta.

Km 51.0		S cycle	Fe cycle	Mn cycle	Ca cycle

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Geology/ Mineralogy [21]	tonalite, gabbro	py, pyrrho	hbe, ilm, mag, py, pyrox, pyrrho	hbe, py, pyrox	pyrox
Water Chemistry [36]	pH *7.21(5)-8.67(5)* DO *5.72(5)-13.81(5)*	SO_4 *2.16(2)-314(5)*	Fe *500(11)*	Mn *0(11)-64.9(5)*	Ca *11.2(11)*
Microbiology		no $H_2S\uparrow$			

Peutz Creek (Tributary of El Capitan Reservoir), [32.854140,-116.790672].

Km 51.0		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [21]	tonalite	py, pyrrho	hbe, ilm, mag, py, pyrox, pyrrho	hbe, py, pyrox	pyrox
Water Chemistry [37]	pH *7.3(11)*	SO_4 *1(11)-116(3)*	Fe *210(11)*	Mn *0(11)*	Ca *4.8(11)*

Helix Water District Well 101.

Location not published		S cycle	Fe cycle	Mn cycle	Ca cycle
Water Chemistry [41]		SO_4 *178(?)*	Fe *140(?)*	Mn *300(?)*	

SDR below El Capitan Reservoir Dam, [32.883621,-116.814100].

Km 50.5		S cycle	Fe cycle	Mn cycle	Ca cycle
Water Chemistry [32,36]	pH *7.6(?)-8.9(?)*	SO_4 8(11)-*268(?)*	Fe *840(11)*	Mn *0(11)*	Ca *6(11)*

Middle Watershed

Monthly rainfall (in.), El Cajon Station (32.81389, -116.975, 123 m elev.) [2]

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ann
2015	0.62	0.42	1.05	0.15	1.13	0.20	0.57	0.01	0.42	0.75	0.98	1.45	7.75
2016	4.81	0.12	0.96	0.69	0.67	0.00	0.00	0.00	0.49	0.15	1.03	3.76	12.68

Featherstone Creek (Tributary of Padre Barona Creek into San Vicente Reservoir), [32.941147,-116.85681], Barona Indian Reservation. Creek is typically dry, but cobbles in the riffles are coated.

Km 44.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [23]	granite, gabbro, monzogranite		hbe, ilm, mag, pyrox	hbe, pyrox	pyrox
Microbiology		$H_2S\uparrow$ (4)		*L.discophora* coatings(6)	

San Vicente Creek above San Vicente Reservoir (Tributary of SDR), [32.9934,-116.8498], San Diego County unincorporated.

Km 44.9		S cycle	Fe cycle	Mn cycle	Ca cycle

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Geology/ Mineralogy [23]	tonalite, cong	py	bio, hbe, ilm, mag, py	bio, hbe, py	
Water Chemistry [36]	pH *7.92(3)-8.44(5)* DO *2.53(9)-11.19(5)*	SO_4 *128(3)-600(9)*		Mn *6.16(5)-55.6(3)*	
Microbiology		H_2S↑ (9)	*L.discophora* biofilm(9) FeOx(9)		

San Vicente Reservoir (Tributary of San Vicente Creek), [32.937880,-116.90896], San Diego County unincorporated. Four major tributaries enter the San Vicente Reservoir. The S cycle is intense along the drowned tributaries, especially along the east side where a forest was drowned.

Km 44.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [25]	tonalite, granodiorite		hbe, ilm, mag, pyrox	hbe, pyrox	
Water Chemistry [37]	pH *8.3(3,11)*	SO_4 160(3)-211(11)	Fe *10(3)-20(11)*	Mn *0(3,11)*	Ca *9.2(3)-83.2(11)*
Microbiology		H_2S↑ (2) *Beggiatoa*(2)	*L.discophora* biofilm(2) FeOx(2)		

San Vicente Creek below San Vicente Reservoir, [32.910012,-116.924743].

Km 44.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [25]	tonalite, granodiorite		hbe, ilm, mag, pyrox	hbe, pyrox	
Water Chemistry [35,36]	pH *7.1(?)-9.1(?)*	SO_4 *7(?)-390(?)*			Ca *22(?)-112(?)*

Lake Jennings Reservoir (Tributary of unnamed creek), [32.861092,-116.878203], City of Lakeside. This reservoir stores imported raw water. Seeps with Fe-oxide flocculates are prominent along the south and east sides of the lake.

Km 37.5		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [25]	monzogranite, tonalite, meta-andesite	py framboids-2	bio, hbe, ilm, mag, musco, pyrox	bio, hbe, pyrox	
Water Chemistry [36]		SO_4 *167(8)-173(8)*			
Microbiology		H_2S↑ (2)	*L.discophora* biofilm(2) FeOx(2) red rods(2) *L.ochracea*(2)		

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Treated imported water data. Treated imported water from Municipal Water Treatment facilities first enters the watershed as urban runoff here. The sulfate signature is dominated by that of the high-sulfate Colorado River.

Km 37.5		S cycle	Fe cycle	Mn cycle	Ca cycle
Water Chemistry [10]	pH 7.1-8.7	SO_4 154-264	Fe not detected at ppb	Mn not measured	Ca 70-78

Los Coches Creek (Tributary of SDR) (Flinn Springs County Park), [32.8491,-116.8591], City of Lakeside. The park has an extensive iron spring.

Km 37.5		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [21]	tonalite, granite, schist	py	bio, hbe, ilm, mag, musco, py	bio, hbe, py, pyrox	pyrox
Water Chemistry [36]	pH *7.81(5)-8.23(11)* DO *5.4(5)-12.17(4)*	SO_4 *58.1(2)-262(4)*		Mn *5.49(9)-35.9(5)*	
Microbiology		$H_2S\uparrow$ (11)	*L.discophora* biofilm(11) FeOx(11)		

SDR below Riverford Road bridge and Lakeside Park, [32.856443,-116.946952], City of Lakeside. Sampled where the river enters the former gravel pit pond.

Km 33.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [25]	tonalite, granodiorite		bio, hbe, ilm, mag, pyrox	bio, hbe, pyrox	
Microbiology		$H_2S\uparrow$ (8)	*L.discophora* biofilm(3,8) FeOx(3)		

SDR at Chubb Lane "Cottonwood Ave. extension" (RCP gravel stockpile facility), [32.84696,-116.9734], City of Santee. Iron bacteria sampled at seeps along the peripheries of the river and S cycle bacteria in backwater areas.

Km 31.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [25]	Quaternary river sediment				
Water Chemistry	pH 7.14(3)-8.37(2) DO 0.97(6)-5.88(10)	SO_4 224(9)-237(8)			
Microbiology		$H_2S\uparrow$ (2,3,5,9,11) *Thiothrix*(10)	*L.discophora* biofilm(2,10) FeOx(2,3) *L.ochracea*(3,10)	*L.discophora* coatings(5,6)	

SDR below Mast Park pedestrian bridge and backwater sites, [32.844080,-116.989653], City of Santee. SDR at the Mast Park site flows through gravel pit ponds, one of which displays a distinctive Ca cycle in a backwater location that is slightly protected from the mainstream by cattails. The water is around 5 cm deep. The rock source of Ca is not particularly obvious; the river flows in Holocene alluvium, although the caliche-rich Friars Formation crops out both

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north and south of the river there. The cyanobacterial mats in the backwater are coated with soft marl and get exposed by duck activity. Young mat-forming *Oscillatoria* float in the shallow water but are not coated with marl. The larger, presumably older trichomes are coated. Sulfur-cycle bacteria are distinct at a nearby backwater that receives full sun.

Km 29.4		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [25]	sandstone, claystone, Quaternary river sediment		bio, hbe, hema, pyrox	bio, hbe, pyrox	caliche, marl(6,8,9,10)
Water Chemistry	pH 7.03(4)-8.87(11) DO 0.08(11)-4.72(6)	SO_4 100(9)-338(5)			
Microbiology		$H_2S\uparrow$ (1,2,5,6,9,10,11,12) SOx(3,11) *Beggiatoa*(7,8,10,11) *Thiothrix*(11) *Chromatium*(8,9)	*L.discophora* biofilm(9)		*Oscillatoria(7)* cf. *Pseud-anaebaena*(6)

Upper Forester Creek below Prospect Avenue bridge (Tributary of SDR), [32.83179621, -116.986214], City of Santee. The creek changes from an upstream concrete channel to a natural river at the bridge. The creek is particularly polluted, flowing through industrial compounds [34]. Sulfate values are so high that it is suggested that sulfuric acid is periodically being released at a yet undiscovered locality.

Km 28.8		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19,25]	sandstone, cong, tonalite, granodiorite	py framboids(2)	bio, hbe, ilm, mag, pyrox	bio, hbe, pyrox	marl(10), concrete channel
Water Chemistry [33,36]	pH 7.50(8)-8.82(5) DO 5.91(10)-17.4(6)	SO_4 81(3)-643(7)		Mn 0.84*(6)-66.8(12)*	Ca 91(10)
Microbiology		$H_2S\uparrow$ (1,10,12) *Beggiatoa* (10,11,12) *Thiothrix*(12) vibrios(2)	FeOx(10) *L.discophora* biofilm(12) *L.discophora*(11 ,12) red rods(2)	*L.discophora* coatings(6,10)	

Sycamore Creek (Tributary of SDR) (Carleton Oaks, Santee Lakes), [32.84431,-117.0064], City of Santee. Creek receives runoff from Santee Lakes that are discharge ponds created by the Padre Dam Pure Water wastewater treatment facility

Km 28.3		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	monzogranite, granodiorite, Quaternary river sediment		bio, hbe, ilm, mag, pyrox	bio, hbe, pyrox	
Water Chemistry	pH 7.68(6)- 8.54(2) DO 5.16(11)-10.93(5)	SO_4 310(6)-394(7)			

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Microbiology		H_2S↑ (1,2,3,4)	*L.discophora* biofilm(1,3)		

Km 26.2, SDR below West Hills Parkway, [32.839405,-117.024589], City of Santee. USGS stream gage 11022480 (Mast Road).

Km 26.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, claystone, monzogranite, volc cobbles		bio, hbe. hema, pyrox	bio, hbe, pyrox	caliche, feldspar
Water Chemistry	pH 6.97(1)-8.73(12) DO 2.88(8)-11.48(5)	SO_4 235(5)-398(8)			
Microbiology		H_2S↑ (2,3,4,5,6,9,10,11, 12) SOx(10) *Beggiatoa*(9,10) *Chromatium*(5)	*L.discophora* biofilm(2,3,5,6,9,10) FeOx(5,6)	*L.discophora* coatings (3,6,7,8,9,10,11 ,12); gone (12) EPS induced oxide along filaments (6) Brown biofilm(9)	

Wells drilled into alluvial aquifer due east of Mission Gorge.

Km not published		S cycle	Fe cycle	Mn cycle	Ca cycle
Water Chemistry [34]	pH *7.1(5,12)-7.9(12)*	SO_4 *120(6)-200(5,12)*	Fe *20(12)-50(12)*	Mn *8(5)-210(6)*	Ca *42(5)-390(5,12)*

SDR at Kumeyaay Lake (Mission Trails Regional Park), [32.841648,-117.034033]. The lake was a gravel pit in SDR alluvium.

Km 24.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [18,19]	sandstone, claystone, monzogranite, meta-andesite		bio, chl, hbe, hema, pyrox	bio, hbe, pyrox	caliche, feldspar
Water Chemistry	pH *8.5(7)* DO *2(7)*				
Microbiology			*L.discophora* biofilm(9)	*L.discophora* coatings(9) Brown biofilm(9)	

Km 24.8, SDR reemerges upon encountering volcanic bedrock [32.843288,-117.035317]

SDR at Old Mission Dam (Mission Trails Regional Park), [32.83977,-117.0433].
The river flows over the breached Old Mission Dam, often forming extensive white foam directly downstream.

24.1 km		S cycle	Fe cycle	Mn cycle	Ca cycle

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Geology/ Mineralogy [18,19]	sandstone, claystone, monzogranite, meta-andesite		bio, chl, hbe, hema, pyrox	bio, hbe, pyrox	caliche, feldspar
Water Chemistry [33]	pH 7.33(4)-8.56(11) DO 2.29(9)-9.43(11)	SO_4 *36(9)-601(3)*	Fe *20(3,12)-30(6)*	Mn *10(6)-270(12)*	
Microbiology		H_2S↑ (1,2,3,4,5,6,10,11,12)	*L.discophora* biofilm(1,2,3,5,9,10,11) FeOx(1,2,9,10) *L.discophora*(10) *L.ochracea*(10) *Siderocapsa*(2,3,5,6,10)	*L.discophora* coatings(3,9) Brown biofilm (8,9)	

SDR at Jackson Road extension (Mission Trails Regional Park), [32.82124,-117.0621]. The river runs across rock outcrops and the cement barrier of the Second San Diego Aqueduct at Jackson Road extension.

Km 21.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [18,19]	sandstone, claystone, cong, meta-andesite, monzogranite, volc cobbles		bio, chl, hbe, hema, pyrox	bio, hbe, pyrox	caliche
Water Chemistry	pH 7.04(7)-8.31(5) DO 0.36(8)-11.74(5)	SO_4 155(9)-349(4)			
Microbiology		H_2S↑ (2,3,4,5,9,10.12) *Beggiatoa*(3)	*L.discophora* biofilm(2,3,4,11) FeOx(3,4)	*L.discophora* coatings(10,11)	

Birchcreek (Tributary of SDR) along Jackson Road extension (Mission Trails Regional Park), [32.818942,-117.060987]. Emerging from the calcareous Friars Formation, Birchcreek begins as a spring under Mission Gorge Road.

Km 21.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, claystone, cong, meta-andesite, volc cobbles		bio, chl, hbe, hema, pyrox	bio, hbe, pyrox	caliche tufa(1,2,3,6,9,10,12)
Water Chemistry	pH 7.38(8)-8.20(2) DO 7.19(10)-13.55(6)	SO_4 285(5)-355(6)			
Microbiology		H_2S↑ (3,10) Beggiatoa (7) Thiothrix (7)	*L.ochracea*(9)	*L.discophora* coatings(10)	*cf. Gloeocapsa* (1,9,12) *Rivularia*(6,7,9)

Lower Watershed

Monthly rainfall (in.), San Diego WSO (32.73361, -117.18306, 11 m elev.) [2]

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ann
2015	0.42	0.28	0.93	0.02	2.39	0.04	1.71	0.01	1.24	0.43	1.54	0.88	9.89
2016	3.21	0.05	0.76	0.55	0.44	0.00	0.00	0.00	0.32	0.07	0.61	4.22	10.23

 doi:10.20944/preprints201811.0007.v1

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SDR at southern end of Admiral Baker Golf Course, [32.79304,-117.0998].

Km 15.4		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, claystone, cong, volc cobbles		bio, hbe, hema, pyrox	bio, hbe, pyrox	caliche, calc cement
Water Chemistry	pH 7.12(9)-8.43(12) DO 0.99(10)-11.14(5)	SO_4 119(5)-355(7) S^{2-} not detected (1,3,4,6,7,12)-0.97(8)			
Microbiology		H_2S↑ (6,10) *Beggiatoa*(6,10) *Chromatium*(6)	*L.discophora* biofilm(9)	*L.discophora* coatings(6,9,10)	

SDR sulfuretum under Friars Road bridge, [32.790280, -17.102561] No obvious rock source of sulfide or sulfate is present in the surrounding rocks and sediments. The sulfuretum disappears following intense rainfall events.

Km 15.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, claystone, cong, volc cobbles	FeS_x blebs(1,9)	bio, hbe, hema, pyrox	bio, hbe, pyrox	caliche, calc cement
Water Chemistry	pH *7.17(9)*-7.3(7) DO *0.42(9)*				
Microbiology		H_2S↑ (1,2,4,6,7,8,9,10) SOx(5,10) *Beggiatoa*(6,9,10) *Thiothrix*(6,7,9) *Chromatium*(6,7,10) Thiospirillum (9,10) Chloroflexus(6,9,10) vibrios(1,6)	*L.discophora* biofilm(5,6,9,10) FeOx(1,9) Magnetotactics? (10)	*L.discophora* coatings(4,10,12)	

SDR at Kaiser Ponds (San Diego Mission Road), [32.783509,-117.104174]. The ponds are small lakes formed were river alluvium gravel was extracted.

Km 14.7		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, claystone, mudstone, cong, volc cobbles	FeS_x blebs(1)	bio, hbe, hema, pyrox	bio, hbe, pyrox	caliche, mollusk fossils, calc cement
Water Chemistry	pH 7.02(3)-8.12(12) DO 0.08(7)-6.02(1)	SO_4 176(8)-220(7)	Fe *202(1)*	Mn *14.6(1)*	Ca *18.6(1)*
Microbiology		H_2S↑ (1,2,9,10,12) vibrios(1)			

Lake Murray Reservoir (Tributary of Alvarado Creek), [32.787782,-117.035660]. The reservoir was sampled along the Padre Bay embayment at the NE side of the lake.

Km 14.5		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, cong, mudstone, meta-andesite		bio, chl	bio	caliche, calc cement, mollusk fossils

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Water Chemistry [33]		SO_4 *109(12)-290(8)*			
Microbiology		$H_2S\uparrow$ (2)	FeOx(2) *L.discophora* biofilm(2) *Gallionella ferruginea*(2) *L.ochracea*(2) *Siderocapsa*(2)		

Alvarado Creek (Tributary of SDR), [32.779964,-117.071517]. Sampled at the San Diego State University access site along the rocks and upstream where ground water discharged into sandy sediment near the railroad tracks.

Km 14.5		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, cong, mudstone, meta-andesite, volc cobbles		bio, chl, ferrihy, hema	bio	caliche, marl(10), mollusk fossils, calc cement
Water Chemistry [36]	pH 7.84(10)-8.02(10) DO 6.66(10)-9.5(10)	SO_4 257(10)-*377(2)*		Mn *9.25(5)-72.9(2)*	
Microbiology		*Beggiatoa*(10)	FeOx(10) *L.discophora* biofilm(12)	*L.discophora* coatings(10)	

The Mission Valley aquifer underlies all the remaining sites. The aquifer is in a buried channel created during the Last Glacial Maximum of the Pleistocene Epoch [15].

SDR below Ward Road bridge, [32.78024,-117.11003].

Km 13.8		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, cong, mudstone, claystone, marl, Quaternary river sediment, volc cobbles	FeS_x blebs(1)	bio, epi, ferrihy, hbe, hema, ilm, mag, pyrox	bio, hbe, pyrox	caliche, marl, epi, mollusk fossils, calc cement
Water Chemistry	pH 7.04(4)-8.18(11) DO 0.38(10)-7.75(1)	SO_4 178(7)-211(8)		Mn 542(4)	Ca 135(10)
Microbiology		$H_2S\uparrow$ (1,2,4,6,9,12) *Beggiatoa*(9,10) *Thiothrix*(9,10) SOx(9,10) vibrios(1)	*L.discophora* biofilm(1,2) FeOx(2) *L.ochracea*(9)	*L.discophora* coatings(2,10)	

USGS Well SDAQ (Screen elevation 20 ft. a.m.s.l.), [32.778067,-117.120910]. Hydraulic head measurements in the well were 3-5 m above ground surface suggesting the possibility of artesian flow into SDR [16].

Km 12.7		S cycle	Fe cycle	Mn cycle	Ca cycle

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Water Chemistry [15]	pH *7.0(8)-7.1(5)* DO *0.5(5)-2.1(8)*	SO_4 *224(8)-237(5)*	Fe *524(8)-920(5)*	Mn *2790(8)-3050(5)*	Ca *219(5)-221(8)*

City of San Diego DB Monitoring Wells.

Km 12.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Water Chemistry [15]	pH *7.0(6)-7.1(4)*	SO_4 *203(4)-212(6)*	Fe *4.11(4)-7.83(6)*	Mn *1660(4)-2610(6)*	Ca *160(4)-172(6)*

Km ~11.1, Tidal Limit, [32.776899,-117.127259].

SDR at Qualcomm Way (First San Diego River Improvement Project, FSDRIP), [32.76986,-117.1548]. The river was sampled on the upstream side of a pond in a former gravel excavation where the river flows under the road.

Km 9.3		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, mudstone, cong, marl	FeS_x blebs(1)	bio, ferrihy, hbe, hema, ilm, mag	bio, hbe	caliche, marl. mollusk fossils, calc cement
Water Chemistry	pH 7.12(3)-8.23(5) DO 0.57(10)-11.51(4)	SO_4 46(11)-322(9) S^{2-} not detected (1-7,9-12)-1.36(12)			
Microbiology		$H_2S\uparrow$ (1,6,7,9,10) *Beggiatoa*(7,8,9,10) *Thiothrix*(8) *Chromatium*(7) vibrios(1)		*L.discophora* coatings(10,12)	

SDR below California State Route 163 bridge, [32.767190,-117.161806]. Sampling took place in the river under the bridge. The S cycle was intense and *Thiothrix* sp. rosettes covered the underwater parts of invasive *Ludwigia* (Evening Primrose).

Km 8.6		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, claystone, cong, volc cobbles		bio, epi, ferrihy, hema, hbe, ilm, mag	bio, hbe	caliche, calc mollusks, calc cement, epi
Microbiology		$H_2S\uparrow$ (1,8) *Thiothrix*(8)			

SDR under Fashion Valley Mall (Town and Country) bridge, [32.76517,-117.1687]. USGS stream gage 110123000 (Fashion Valley). Sampling took place in the river due south of Fashion Valley Mall under the Town and Country bridge and at the west side of Fashion Valley Road.

Km 7.9		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	sandstone, claystone, cong, volc cobbles	FeS_2 framboids(1) FeS_x blebs(1)	bio, ferrihy, hema	bio	caliche, calc mollusks, calc cement, epi
Water Chemistry	pH 7.12(3)-8.17(11) DO 0.18(9)-7.93(4)	SO_4 69(7)-315(9) S^{2-} not detected (1-7,9-12)-0.88(5)			

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Microbiology		H_2S↑ (1,2,4,6,8,9,10,12) *Beggiatoa*(1-7,8-12) *Chromatium*(8) SOx(4,10) vibrios(1)	FeOx(1)		

SDR at YMCA (River Gardens), [32.76230,-117.1944]. The river flows at the south end of the YMCA complex through an area being developed by SDRPF as River Gardens.

Km 5.4		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	artificial fill, sandstone, siltstone, claystone, cong	FeS_x blebs(1)	bio, ferrihy, hema	bio	mollusk & ostracod fossils, caliche, calc cement
Water Chemistry	pH 7.12(3)-8.54(11) DO 0.62(10)-9.28(4)	SO_4 82(9)-409(9) S^{2-} not detected (1,3,4,6,7,9-12)-1.07(5)			
Microbiology		H_2S↑ (1,2,4,6,7,8,9,10,12) *Beggiatoa*(6,8,9,10) *Thiothrix*(6,7,8,10) *Chromatium*(9) vibrios(1)	*L.discophora* biofilm(6) FeOx(6)	*L.discophora* coatings(6,8)	

SDR at Estuary (east end), [32.76131,-117.2037]. Sampling of the river took place on the west side of Pacific Highway, west of the sewer line crossing the river. Sulfate reduction was common in the muddy sediment around the peripheries of the river. Iron oxidizing biofilms and possible Mn oxide coated biofilms were collected along pools in the floodplain.

Km 4.6		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	artificial fill, sandstone				mollusk & ostracod fossils, marl(12)
Water Chemistry	pH 7.40(4)-8.42(11) DO 1.85(7)-10.57(5)	SO_4 93(9)-503(8)			
Microbiology		H_2S↑ (1,2,9,12) vibrios(1)	*L.discophora* biofilm(10)	Brown biofilm (10)	

Famosa Slough (Tributary of SDR), [32.755377,-117.228585]. Famosa Slough is a protected wetland surrounding a tributary that flows from the south into the river. Brackish water periodically floods the wetland.

Km 2.2		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/ Mineralogy [19]	artificial fill, sandstone				mollusk & ostracod fossils
Microbiology		H_2S↑ (8)			

SDR Mouth (south end of Mission Bay, San Diego), [32.756068,-117.252714].

Km 0.0		S cycle	Fe cycle	Mn cycle	Ca cycle
Geology/	artificial fill				

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Mineralogy [19]					

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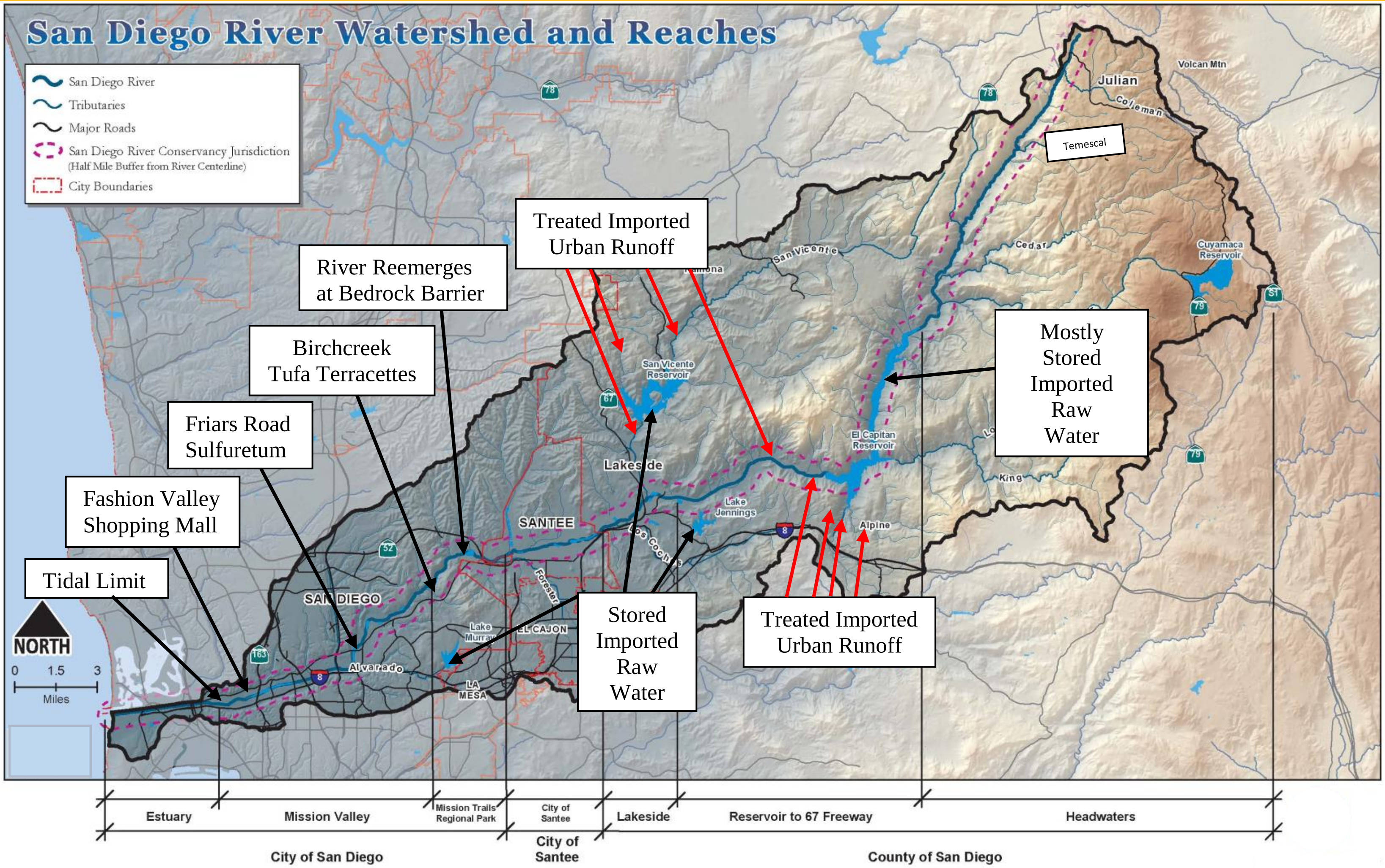

Figure 1. San Diego River watershed and important sites (adapted from San Diego River Conservancy [1])

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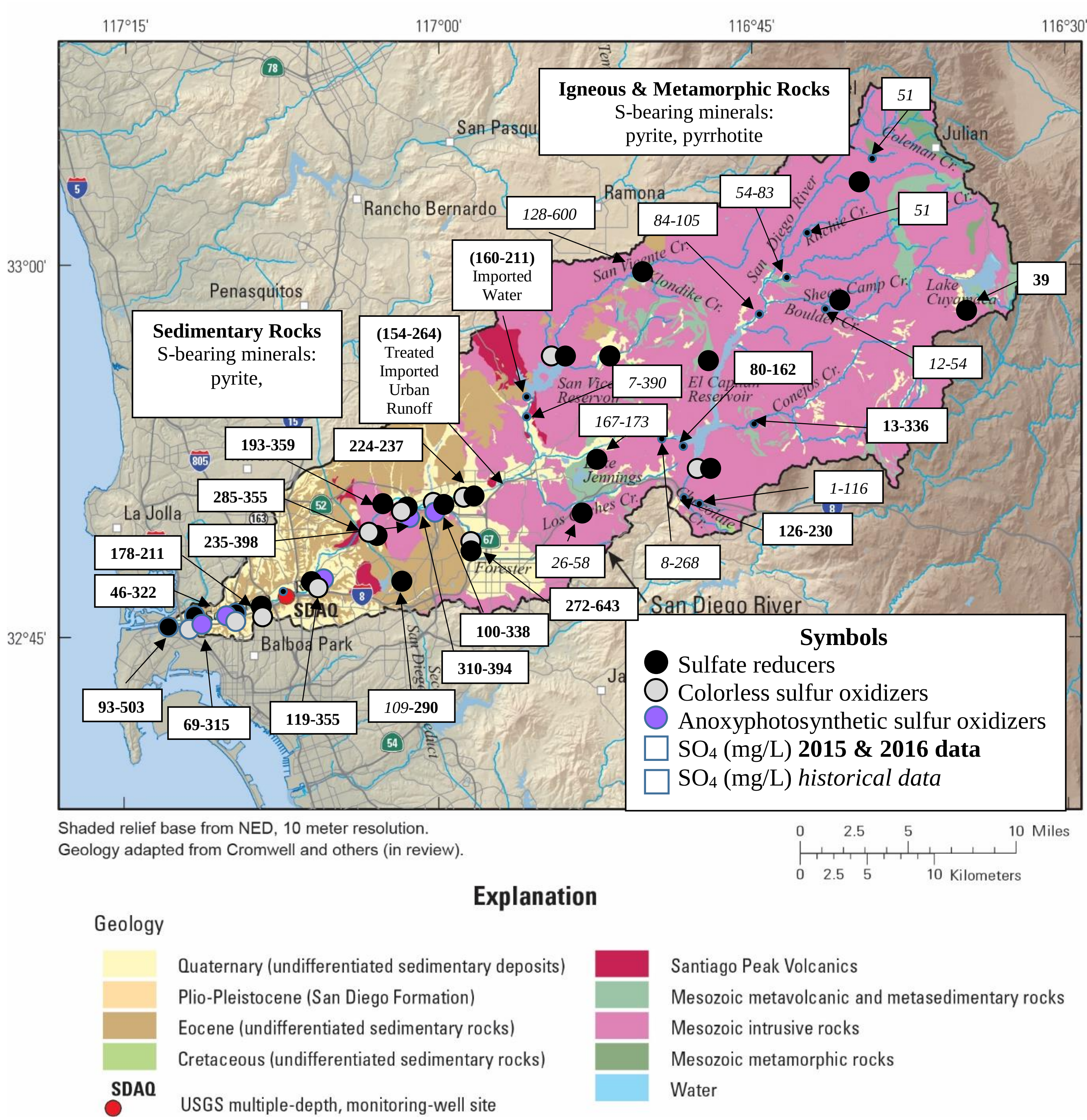

Figure 2. Sulfur cycle of the San Diego River watershed

 doi:10.20944/preprints201811.0007.v1

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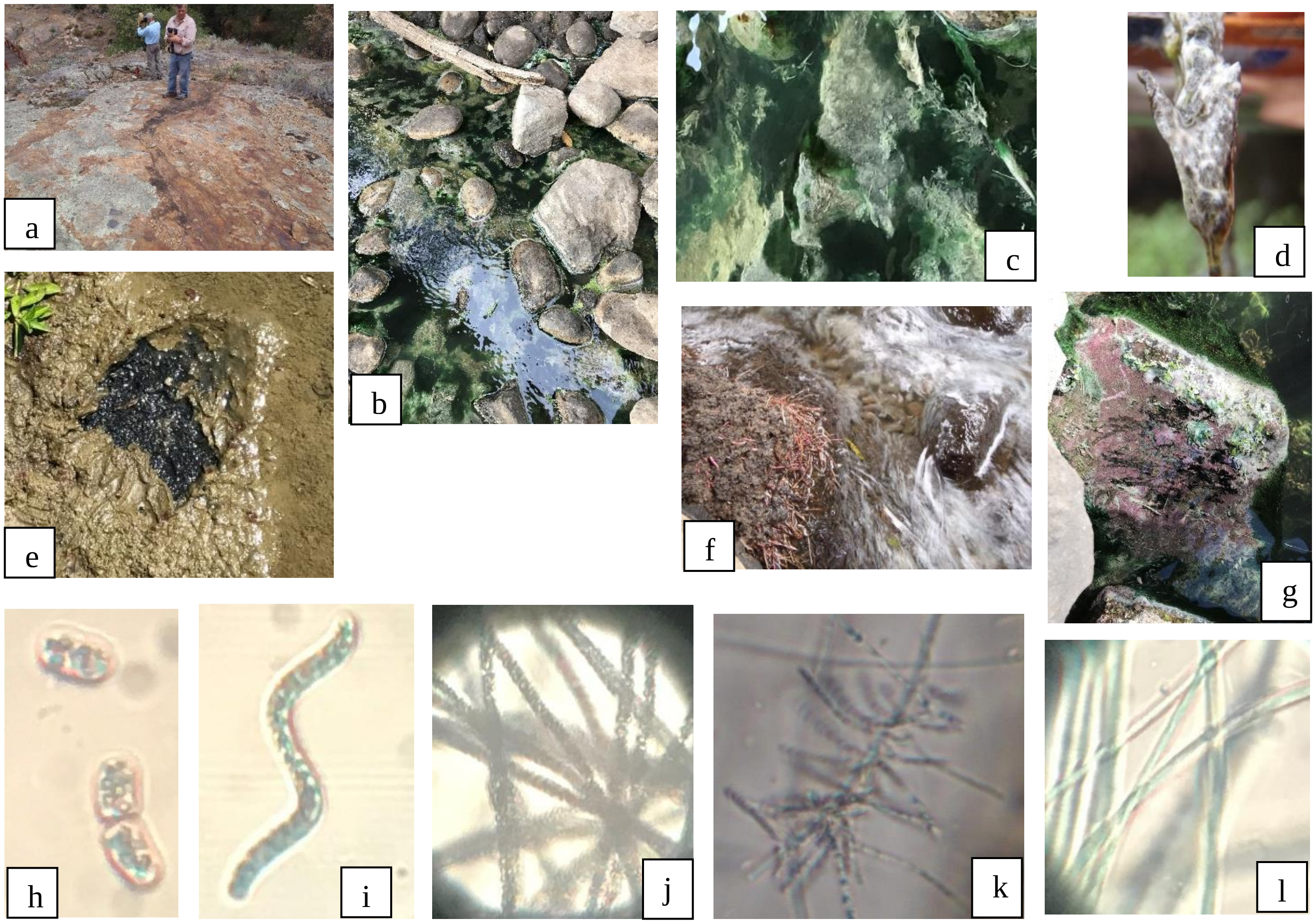

Figure 3. Sulfur cycle images and photomicrographs of the San Diego River watershed
a Rusty red-orange weathering rind from oxidation of pyrite (FeS_2) in Julian Schist (Temescal Ck)
b Sulfuretum in riffle (SDR under Friars Rd bridge)
c *Chloroflexus* sp. (green) coated with *Beggiatoa* sp. (white) (sulfuretum in SDR under Friars Rd bridge)
d *Thiothrix* sp. colonizing *Myriophyllum* (SDR under highway 163 bridge, Fashion Valley)
e Black sulfidic mud under footprint (SDR at backwater at Mast Park)
f *Thiothrix* sp. filaments in flowing river (SDR at Ward Rd)
g *Chromatium* sp. on submerged boulder (sulfuretum in SDR under Friars Rd bridge)
h *Chromatium* sp. sulfuretum in SDR under Friars Rd bridge, 450x)
i *Thiospirillum* sp. (sulfuretum in SDR under Friars Rd bridge, 450x)
j *Beggiatoa* sp. (sulfuretum in SDR under Friars Rd bridge, 450x)
k *Thiothrix* sp. (SDR at Ward Rd., 450x)
l *Chloroflexus* sp. (sulfuretum in SDR under Friars Rd bridge, 450x)

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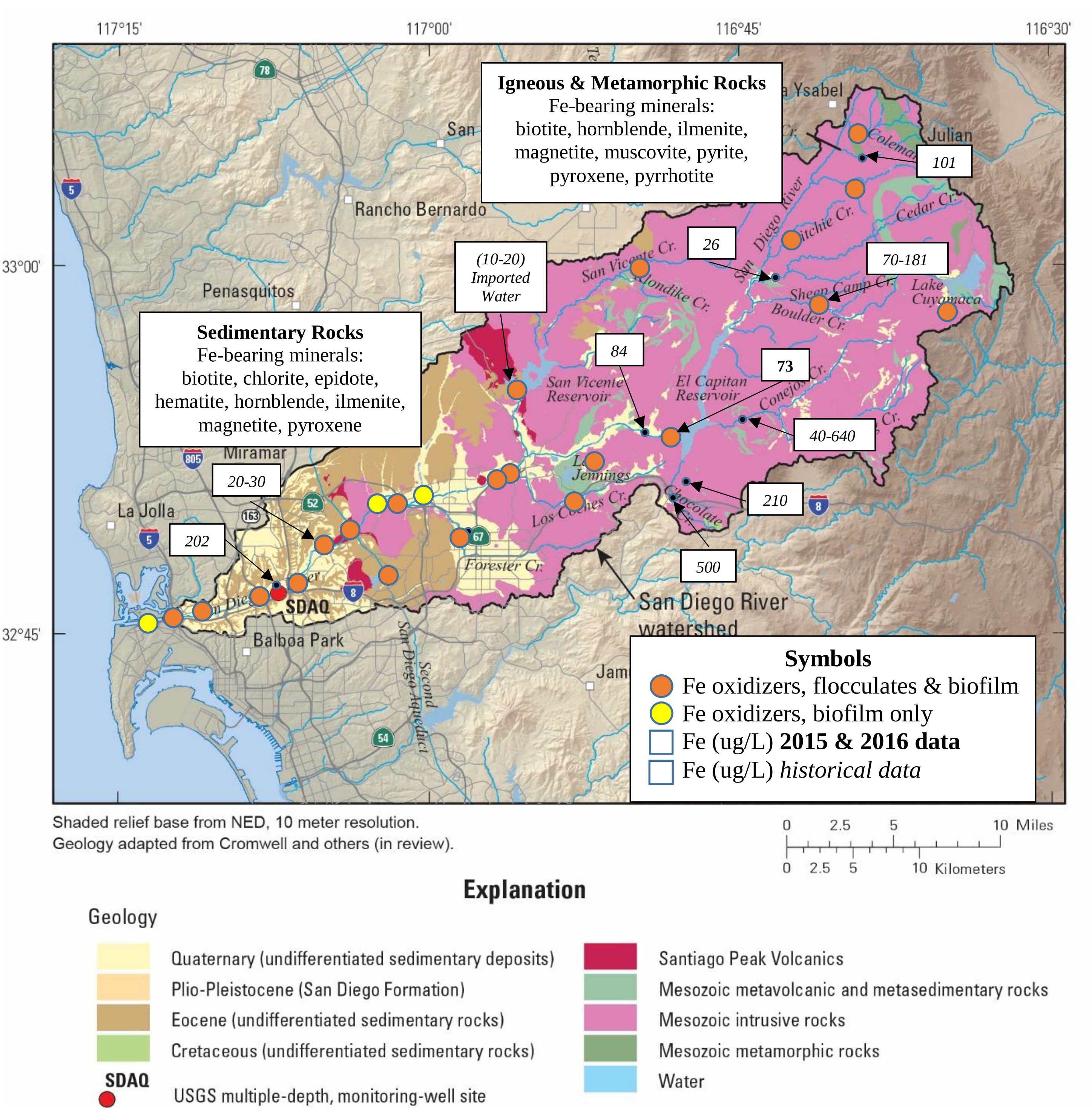

Figure 4. Iron cycle of the San Diego River watershed

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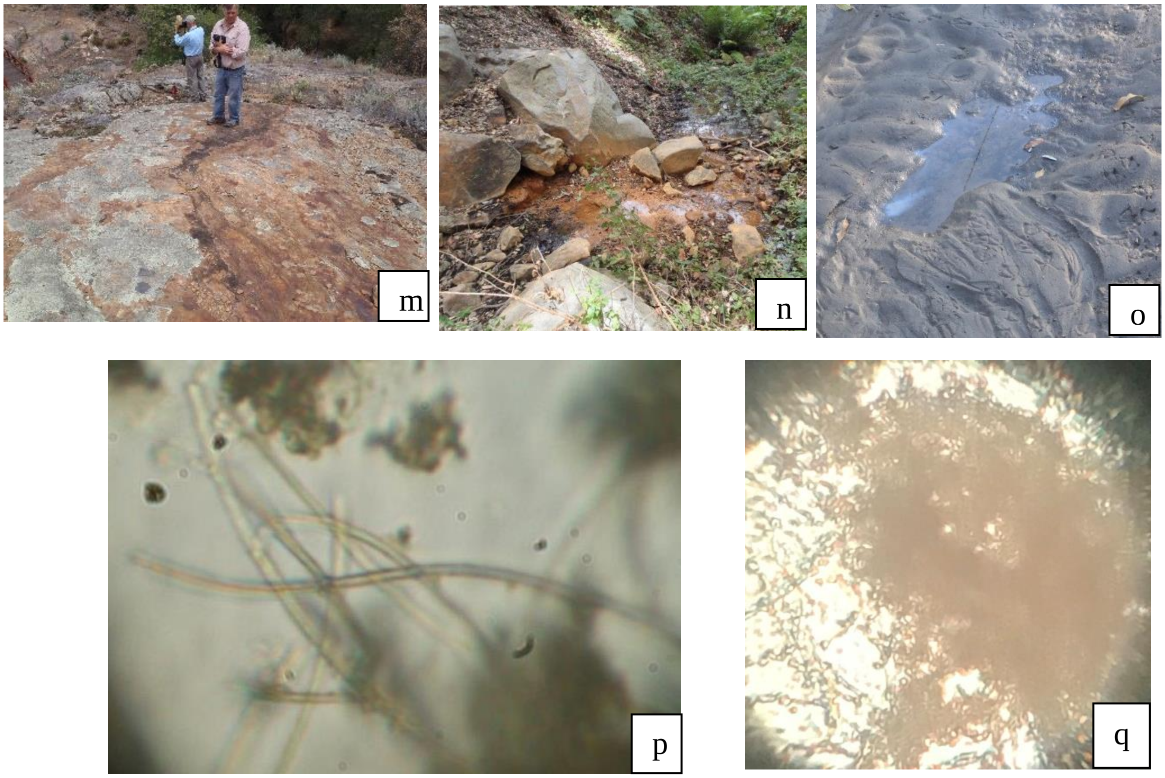

Figure 5. Iron cycle images and photomicrographs of the San Diego River watershed
m Rusty red-orange weathering rind from oxidation of pyrite (FeS_2) in Julian Schist (Temescal Ck)
n Iron spring (Temescal Ck)
o Oil-like *Leptothrix discophora* biofilm floating on water (Alvarado Ck)
p *Leptothrix ochracea* (Lake Murray, 450x)
q *Leptothrix discophora* holdfasts and short rods of oil-like biofilm (SDR at Cottonwood Ave, 450x)

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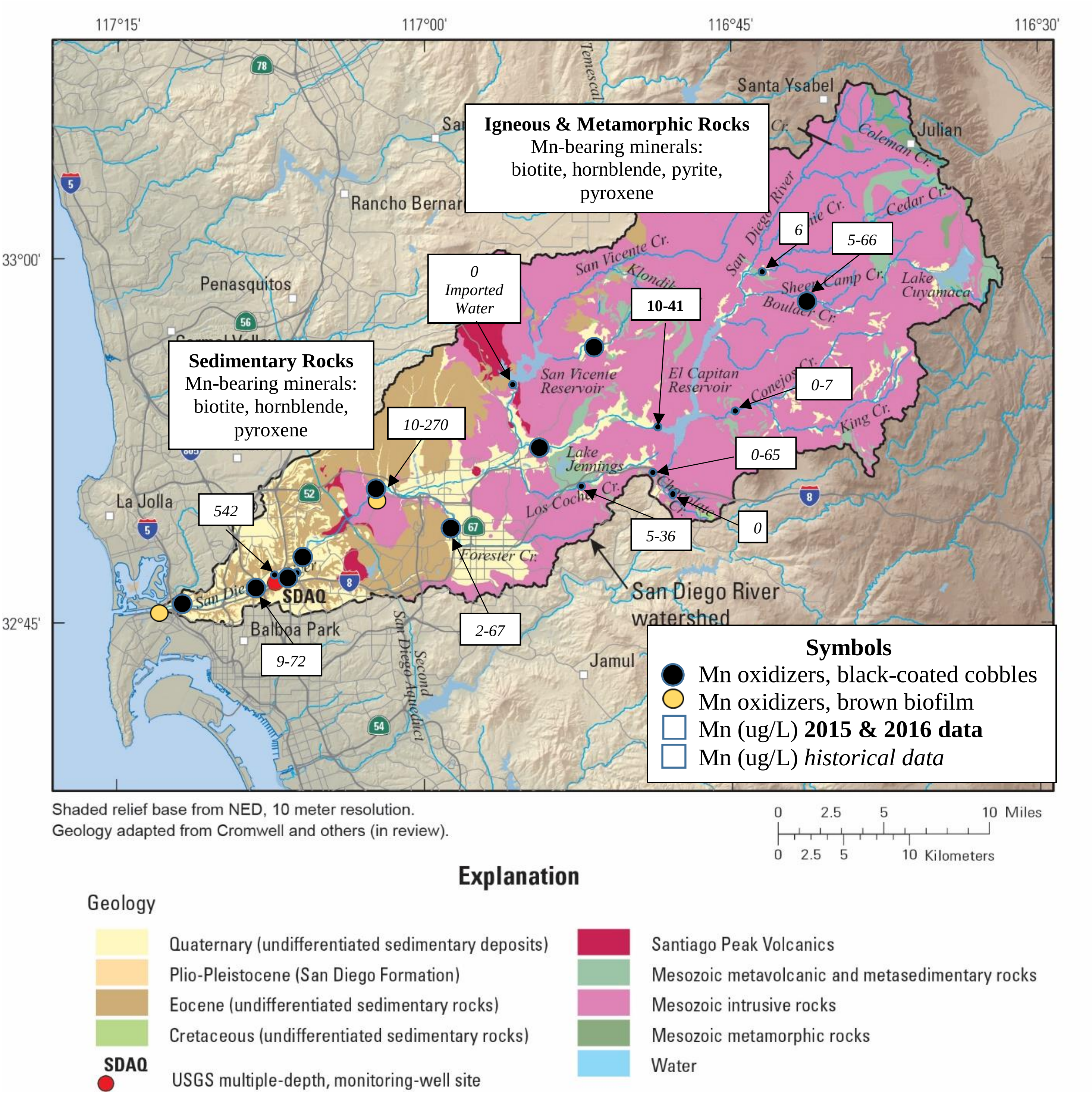

Figure 6. Manganese cycle of the San Diego River watershed

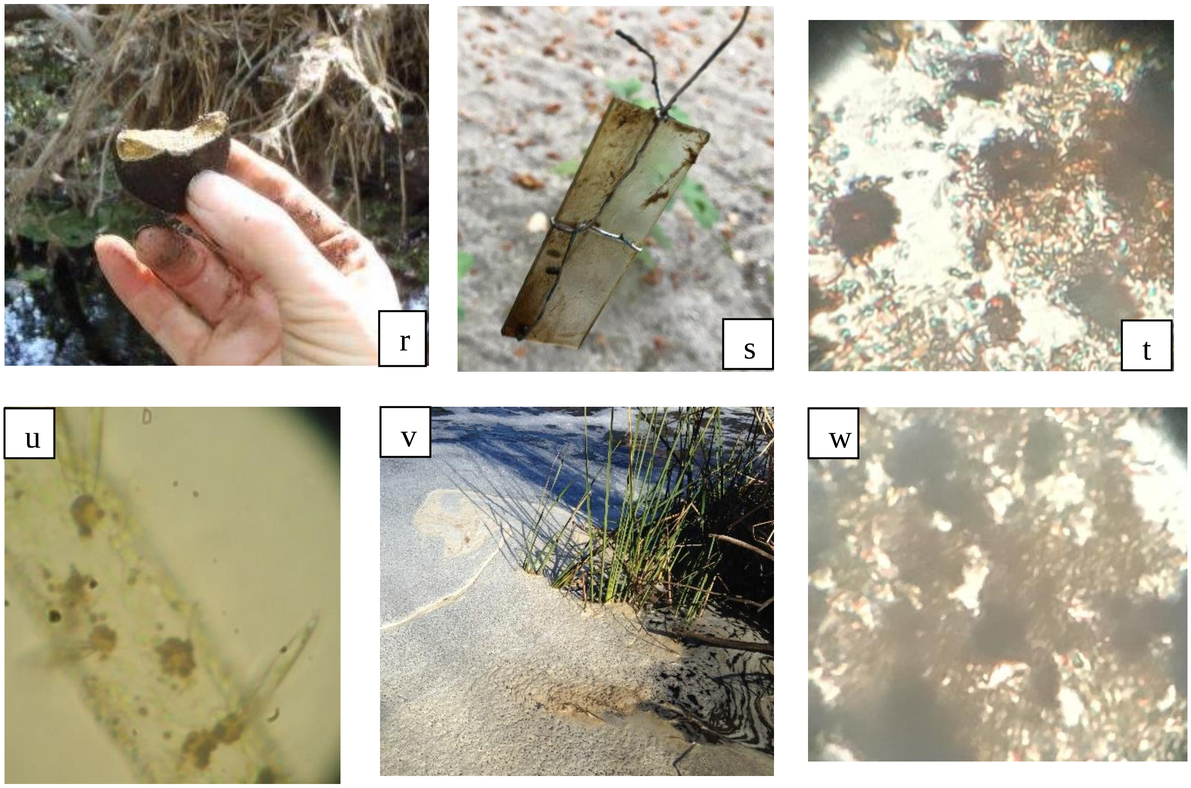

Figure 7. Manganese cycle images and photomicrographs of the San Diego River watershed
r Mn-oxide coated cobble (SDR at Old Mission Dam)
s Mn-oxide coated microscope slide set suspended one month in river (SDR at West Hills)
t *Leptothrix discophora* holdfasts on microscope slide (SDR at West Hills, 450x)
u Unidentified epilithic diatoms precipitating Mn oxide at their holdfasts (SDR at River Gardens, 100x)
v Brown-stained foam (SDR at Old Mission Dam)
w *Leptothrix discophora* holdfasts from brownish biofilm (along Estuary, 450x)

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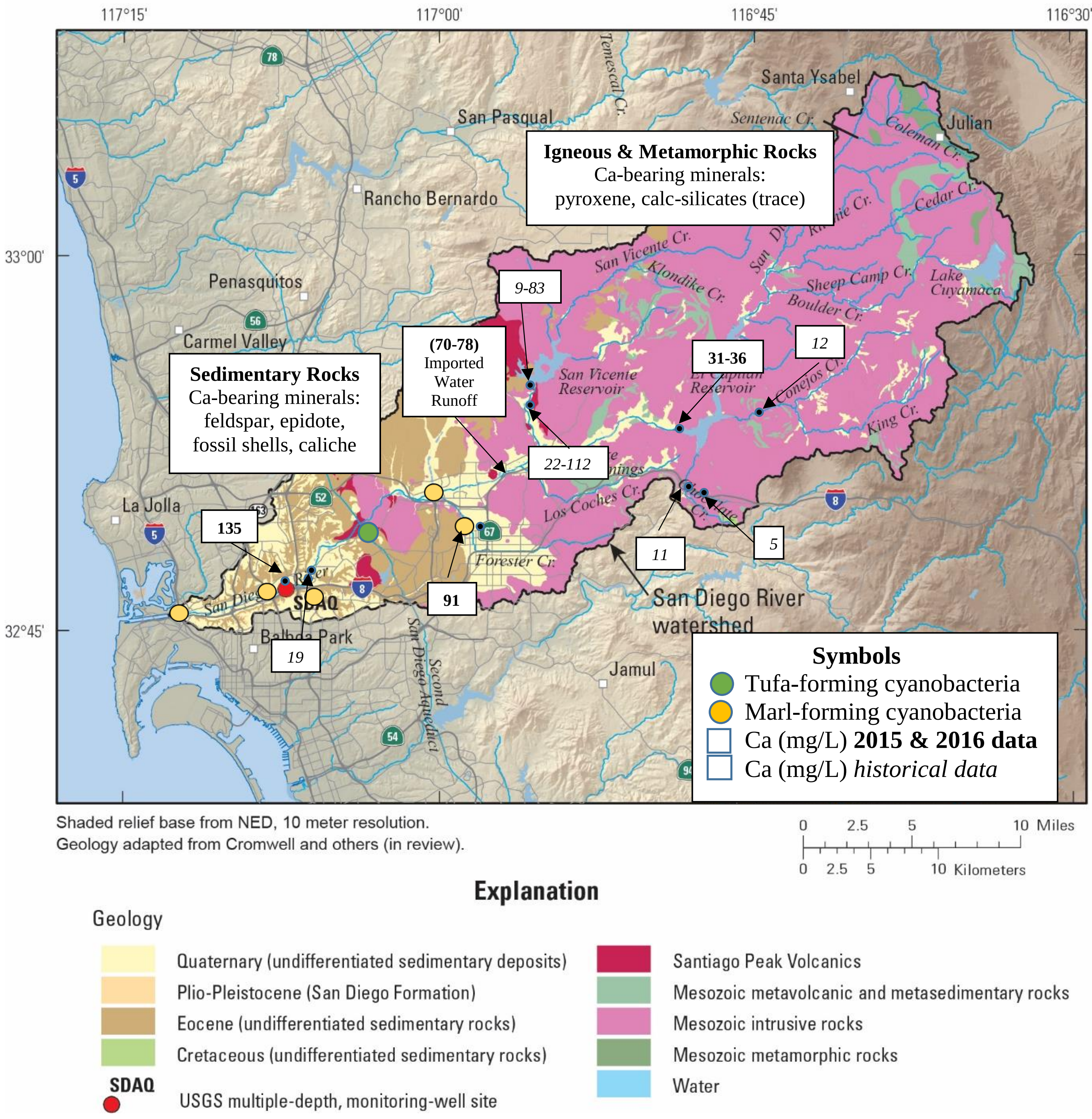

Figure 8. Calcium cycle of the San Diego River watershed

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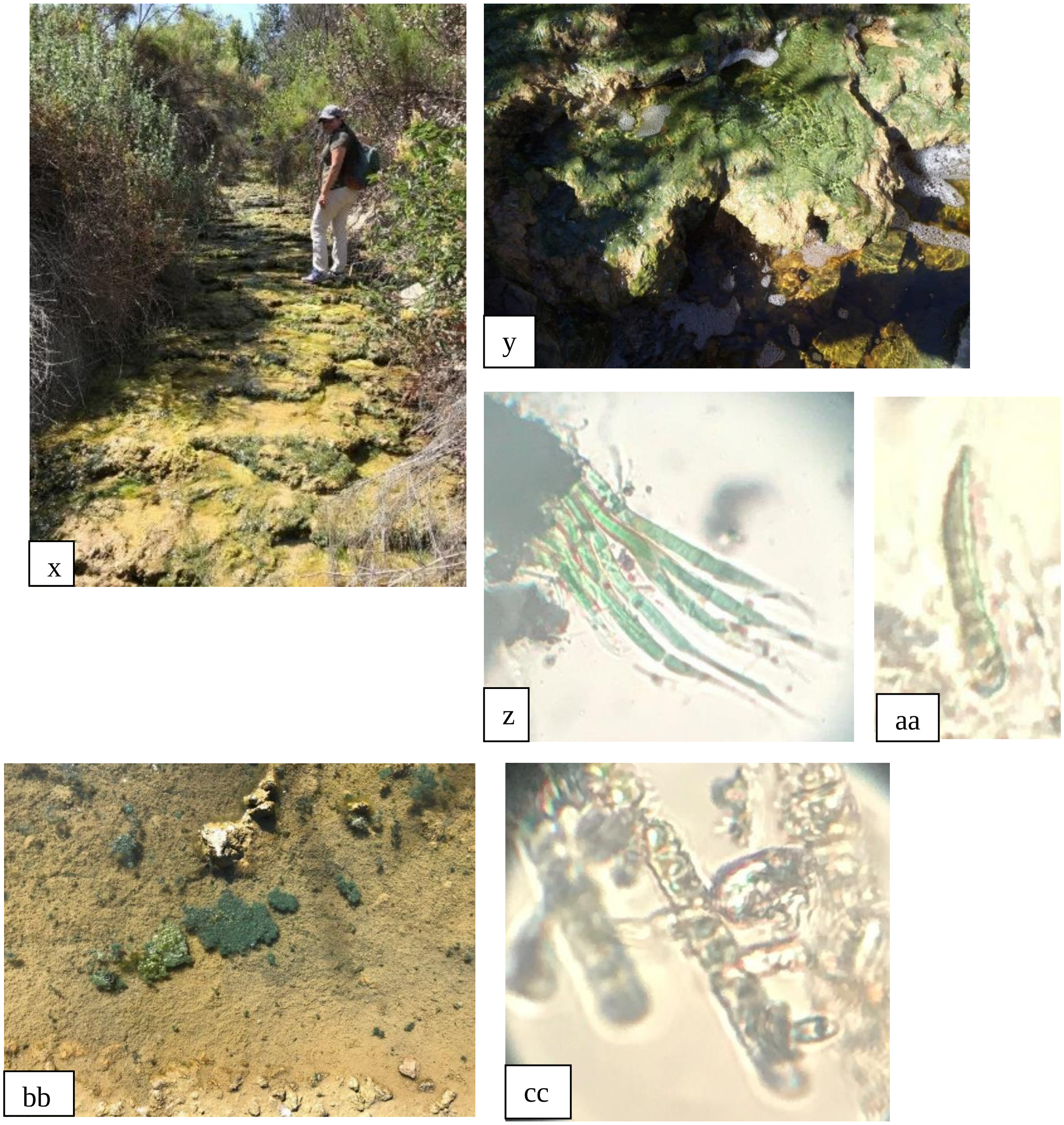

Figure 9. Calcium cycle images and photomicrographs of the San Diego River watershed
x Hard tufa terracettes (Birchcreek)
y Surface of tufa terracette coated by embedded *Rivularia* sp. (Birchcreek)
z *Rivularia* sp. attached to tufa (Birchcreek, 450x)
aa *Rivularia* sp. attached to tufa (Birchcreek, 450x)
bb Cream-colored gritty marl and floating, dislodged *Oscillatoria* sp. (backwater of SDR at Mast Park)
cc Calcite-coated *Oscillatoria* sp. hormogonia from marl (backwater of SDR at Mast Park, 450x)