UNIVERSIDAD DE CHILE
FACULTAD DE CIENCIAS FÍSICAS Y MATEMÁTICAS
DEPARTAMENTO DE GEOLOGÍA

EL ROL DE LOS BACKGROUNDS GEOQUÍMICOS Y MINERALÓGICOS LOCALES, COMO INFORMACIÓN ESENCIAL PARA CONSTRUIR GUÍAS DE CALIDAD DE SEDIMENTO EFICIENTES, PARA CUENCAS DE ALTA MONTAÑA ALTERADAS HIDROTERMALMENTE (CUENCA RÍO MAPOCHO, CHILE CENTRAL)

TESIS PARA OPTAR AL GRADO DE MAGÍSTER EN CIENCIAS,
MENCIÓN GEOLOGÍA

MEMORIA PARA OPTAR AL TÍTULO DE GEÓLOGO

JOSÉ PABLO CORREA BURROWS

PROFESOR GUÍA:
DR. MANUEL ANTONIO CARABALLO MONGE

MIEMBROS DE LA COMISIÓN:
DR. JAMES MCPHEE TORRES
DR. SANTIAGO MONTSERRAT MICHELINI
DR. BRIAN TOWNLEY CALLEJAS

SANTIAGO DE CHILE
2020

RESUMEN DE TESIS PARA OPTAR AL TÍTULO DE:
Geólogo y grado de Magíster en Ciencias, mención Geología
POR: José Pablo Correa Burrows
FECHA: 31/07/2020
PROFESOR GUÍA: Manuel Antonio Caraballo Monge

EL ROL DE LOS BACKGROUNDS GEOQUÍMICOS Y MINERALÓGICOS LOCALES, COMO INFORMACIÓN ESENCIAL PARA CONSTRUIR GUÍAS DE CALIDAD DE SEDIMENTO EFICIENTES, PARA CUENCAS DE ALTA MONTAÑA ALTERADAS HIDROTERMALMENTE (CUENCA RÍO MAPOCHO, CHILE CENTRAL)

La cuenca alta del río Mapocho (Andes de Chile Central) ha sido estudiada como caso representativo de un sistema hidrológico de alta montaña compuesto por tres subcuencas desarrolladas sobre rocas muy distintas una de otra y, sometidas a diferentes factores antrópicos: 1) un sistema de ARD desarrollado sobre rocas hidrotermalmente alteradas (i.e., Yerba Loca); 2) un río con actividad minera en su cabecera e hidroquímicamente clasificado como no afectado por drenaje minero ácido (i.e., San Francisco); y 3) un río con una baja concentración de metales (i.e., Molina). De este modo, sesenta y tres muestras de sedimentos han sido recolectadas en siete sitios distintos, durante las cuatro estaciones a lo largo de un año hidrológico (2016-2017). En términos generales, la composición geoquímica de los sedimentos clásticos es consistente con la geoquímica inferida a partir del estudio mineralógico. Sin embargo, los sedimentos de menor tamaño de grano (i.e., Arenas y limos) muestran mayores concentraciones que los de mayor tamaño de grano (i.e., Gravas) para elementos tales como Fe, S, Cu y As. Este comportamiento es particularmente evidente en Yerba Loca y ha sido atribuido a la aparición estacional de precipitados ricos en Fe y precipitados ricos en Al como parte de la fracción de sedimentos de menor tamaño de grano. A parir del testeo de distintas metodologías para el cálculo de los *backgrounds* geoquímicos (TIF, MAD y $95\%_{\text{percentil}}$) se han obtenido resultados que sugieren que este último método es el más apropiado para este tipo de sistema montañoso. Así, usando la metodología seleccionada, se han calculado tres *backgrounds* distintos: 1) Cuenca estero Yerba Loca; 2) Cuenca río Molina y; 3) Cuenca alta del río Mapocho. Se observa que el tercer *background* generado (el cual sintetiza la realidad de toda la cuenca alta del río Mapocho, incluyendo a Yerba Loca y Molina) tiende a subestimar o sobrestimar algunos valores comparándolos con los *backgrounds* locales de Yerba Loca y Molina, respectivamente. Además, cuando los *backgrounds* generados son comparados con las guías de calidad de sedimento consensuadas internacionalmente (*Consensus-Based Sediment Quality Guidelines*, en inglés), Fe, Cu, Mn, Zn, Pb, Cu, Cr, Ni y As muestran valores de *background* considerablemente mayores a los valores establecidos como límite para comenzar a considerar efectos adversos probables. El presente estudio establece la importancia primordial de contar con un *background* geoquímico sólido antes de cualquier intento de evaluación de riesgo asociada a calidad de sedimentos en regiones de alta montaña alteradas hidrotermalmente, las cuales cubre una cantidad significativa de los sistemas fluviales de América del Sur y muchas otras áreas del mundo. Además, se expone la necesidad de llevar a cabo estudios ecotoxicológicos específicos del sitio, teniendo en cuenta la flora y fauna locales, a fin de corroborar los posibles efectos tóxicos del *background* geoquímico local.

Muy al Norte, en una tierra llamada Svithjod, se yergue una roca. Tiene cientos de millas de ancho y otro tanto de altura. Una vez cada mil años llega un pajarito hasta ella para afilar su pico.

Cuando a causa de eso la roca llegue a desgastarse enteramente habrá transcurrido nada más que un sólo día de la eternidad.

Hendrik Willem van Loon

Dedicado a Olmo y a América, espero que en algún punto tengan
la posibilidad de encantarse con este maravilloso planeta
tanto como yo… Me esforzaré por ello.

AGRADECIMIENTOS

En primer lugar, quisiera agradecer a Manuel por darme la oportunidad de trabajar con él en este singular trabajo de título, el cual ha significado una serie de aprendizajes, que, en su gran mayoría, van más allá de lo netamente académico. También me gustaría agradecer al Álvaro, al Leo y a Martín, de los cuales sentí un apoyo una guía constante durante gran parte de este tiempo, en especial a Álvaro, que he llegado a considerar un gran amigo y consejero y que, sin él, habría sido mucho más duro abordar y entender esta investigación. A las personas que también formaron parte de mi desarrollo durante mi paso por el AMTC, al grupo de aguas en particular, a Santiago, a Miguel, a Gerardo, al Felo al Salva y a Andreina. A quienes me ayudaron en las distintas labores que este trabajo conllevó, a Roberto Valles por ayudarme y guiarme con la molienda, a Andrés Ibáñez por ayudarme y enseñarme sobre los análisis de difracción de rayos-X y a utilizar los programas de interpretación respectivos. A la Vivi, porque no sólo me ayudo y enseñó durante mis jornadas en el laboratorio de calidad de agua, sino que también porque fue un apoyo y una amiga fundamental en uno de los períodos más duros de mi vida, gracias por presentarme a tu familia e incluirme en tu vida. Y a Maritza y Blanca, quienes, con mucho cariño, siempre estuvieron dispuestas a guiarme y apoyarme en lo que necesitara durante mis pasos por el departamento de geología.

A mi papá y mi mamá, con los cuales no habría podido llegar acá, pues si bien ha costado esfuerzo el caminar por este sendero, son ellos los que me han dado siempre fuerzas para seguir adelante. Son ellos quienes me han enseñado a buscar ser mejor persona, a no rendirme y a intentar generar un mundo mejor. Gracias por siempre darme cariño, por hacerme sentir amado, por apoyarme incondicionalmente, desde siempre, por escucharme, por comprenderme, por aguantarme, por todo. A mis hermanas y a mi hermano, a la Tanza por incluirme en su vida diaria desde que era chico y me llevaba a sus panoramas, gracias hermanita por darme siempre tanto amor, por escucharme, por contarme, por ser mi amiga y por siempre incluirme tanto en tu hogar; al Tavo por enseñarme que lo moralmente correcto no es necesariamente lo correcto, por ser incondicional cuando lo he necesitado y, por día a día enseñarme a ser consecuente y; a la Maripauli por ser siempre tan detallista y preocupada, por enseñarme el peso que conlleva la verdad y, por a pesar de la distancia nunca, dejar de estar presente. Al Marcos y a la Nacha, por hacerse parte de nuestra familia y por hacernos parte de las suyas. Al Olmo y a la América, por haber traído tanta luz a esta familia, por alegrarnos la vida y por darnos un motivo por el cual intentar hacer las cosas siempre lo mejor posible. Les amo. A la Elianita linda, por siempre estar ahí, por regalonearme, por quererme, por confiar en mí, por aconsejarme, por ser prácticamente una abuela más, muy sabia por lo demás. A la Gabi, al Luis y la Gabita por ese amor y cariño gigantes que siempre nos entregan, dentro y fuera de su hogar, gracias por ser parte de mi familia. Y finalmente, al Fritz, por ser el hermano menor que nunca tuve y por tu cariño interminable… No entiendo como un ser puede llegar a entregar tanto amor y cariño, gracias por hacerlo con mi familia, nuestra familia.

También quiero agradecerle a los geoamigues, a la Clau, al Aldo, a la Aileen a la Mila y a la Vale, a todos ustedes que han llegado ser parte fundamental de mi vida. A lo largo de la carrera muchas veces me cuestioné si me gustaba la cosa o no, o si era feliz al respecto o no (como muchos otros quizá), pero, independiente de la respuesta a la que llegaba, el haberlos conocido a ustedes y, el que hoy formen parte de mi vida, hace que deje de cuestionármelo, pues ya no es relevante. Gracias por ser el apoyo que han sido estos últimos años, por esa sinceridad, por ese espacio de honestidad, por las sonrisas, por las risas, por a veces sincronizarnos tanto. Me alegra el alma que sean parte de mi vida, gracias por ser ustedes. Les adoro.

Me gustaría agradecer al Haik, por ser siempre un gran amigo y hermano, sobre todo por el regalo de integrarme en una segunda familia, la suya. A tus padres en particular, Sandra y Kricor, gracias por siempre tratarme como uno más, no saben lo importantes que han llegado a ser para mí. Al Darío, por ser mi gran amigo de la infancia y alguien fundamental en mi desarrollo como persona, no sabes cómo me inspiras muchas veces, sobre todo cuando se trata de conocer, comprender y respetar la naturaleza que nos rodea. Y al Negrito, creo que mi primer mejor amigo de toda vida y el ejemplo claro de que el tiempo y distancia no afectan en nada a una verdadera amistad.

A la Coni, al Pito y la Mariela, con quienes he vivido muchos de los momentos más felices de mi vida y he conocido varios de los lugares más lindos que he visto. Gracias Coni por mostrarme cómo el trabajo duro trae frutos, creo que no he conocido persona más trabajadora y completa que tú, no sabes cuánto te admiro. A ti también Pito, por mostrarme que el cumplir los sueños depende netamente de uno mismo, no sabes lo feliz que me hace saber que eres parte de mi vida hermano, gracias por toda la felicidad que siempre entregas. Y a la Marielita, que me he enseñado que la sinceridad es la base de todo, además de mostrarme cómo el cariño cambia todo al momento de hacer las cosas.

A mi querida hermandad, al Tomate, al Vito, al Coto, a la Fran, la Maca, la Pilvi, la Javi, la Vale, el Benja, el Seba, la Florchi, la Beba y la Isa. Gracias por toda la magia de la que fuimos parte durante tantos años, por todo el cariño y el entendimiento, por el apoyo y la incondicionalidad. Gracias herman@s por formar parte de mi vida y de mi desarrollo. Una parte de lo que soy hoy en día, se los debo a ustedes, de todo lo que me han enseñado y de todo lo que hemos compartido. Sé que, con lo ya construido, el tiempo poco podrá hacer, así, a pesar de la distancia y el tiempo ese lazo de hermandad siempre quedará. Les quiero mucho, gracias por todo.

Al Gaspar a la Ethel y al Pipe. Gracias amig@s por la compañía, por escuchar, por conversar, por cada momento que hemos reído juntos, que hemos disfrutado juntos, que hemos enfrentado juntos. Agradezco el haber podido crecer y aprender junto a ustedes. Son de las personas más importantes que me ha permitido conocer el escultismo, me siento afortunado.

A todos mis amig@s de los *escau*, con quienes he vivido no sólo una serie de momentos, sino que una serie se sentimientos y experiencias que los ha llegado a hacer fundamentales dentro de mi desarrollo como persona y mi ser actual. Al Guajardo y al Claudio, al Pablito, a la Chío, a la Maca Bravo, a la Cota, a la Caro, a la Jose, a la Isi, a la Cata Zamora, a la Nacha Valencia, al Videla, a la Romi, al Cris, a la Javo, a la Paula, al Castro, al Alegría, a la Trini, a la Saide, la Vale Navarro y a tanta gente que formó parte de mi crecimiento. Gracias amig@s por tantas experiencias, por tantos viajes, por tanto aprendizaje, por tanta amistad, cariño y muchas otras cosas que han formado una familia que nunca deja de apoyarse. Creo que al grupo y a cada uno de ustedes le debo tantas cosas, que espero ser capaz de retribuirlas al mundo a lo largo de mi vida. Espero que, junto al fuego, siempre nos volvamos a encontrar.

Y en realidad, a cada persona que ha formado parte de mi desarrollo como persona (valga la redundancia), gracias por todo lo entregado, por todo lo enseñado.

TABLA DE CONTENIDO

ÍNDICE DE TABLAS

ÍNDICE DE FIGURAS

CAPÍTULO 1

1.1. Motivación

Los sedimentos transportados a través de sistemas fluviales tienden a acumular de manera natural una amplia variedad de contaminantes, pudiendo posteriormente servir como fuente de ellos y, más aún, transportarlos y depositarlos en áreas lejos de su origen (Burton Jr., 2013). Esto es perjudicial sobre todo para los organismos bentónicos, los cuales desarrollan gran parte de su vida sobre estos sedimentos, lo cual cobra relevancia si se considera que estos invertebrados son esenciales para el equilibrio de la cadena trófica (Cain et al., 2004). De este modo, adquiere sentido darle importancia a la gestión de la calidad de sedimentos y, el tomar en consideración los posibles factores que pueden influir de un tipo de cuenca a otra.

Este trabajo de tesis consiste en la generación de *backgrounds* locales, geoquímicos y mineralógicos, para los sedimentos transportados a través de la cuenca alta del río Mapocho, la que para estos fines se ha considerado como caso representativo de una cuenca de alta montaña hidrotermalmente alterada. A partir de éstos, se busca levantar la importancia de contar con un *background* local, o al menos uno representativo para cada tipo de cuenca, al momento de llevar a cabo evaluaciones de toxicidad asociada a la carga metálica contenida en los sedimentos.

1.2. Estructura de la tesis

Este escrito se separa en 4 capítulos: en el primero (y presente) se introduce el tema de tesis, dando a conocer su motivación y contexto , además de plantear la hipótesis de trabajo y los objetivos propuestos; el Capítulo 2 corresponde a un manuscrito que actualmente se encuentra en proceso de revisión entre sus coautores, con el fin de enviarlo a la revista *Science of the Total Environment* una vez que esto finalice; el Capítulo 3 es el material suplementario de dicho artículo y; finalmente, en el Capítulo 4 se exponen las principales conclusiones del estudio.

1.3. Relevancia de los sedimentos para su entorno

Los sedimentos transportados a través de sistemas fluviales tienden a comportarse prácticamente como dispensadores de contaminantes, orgánicos e inorgánicos. Esto se debe a que, de manera natural, tienden a acumular una amplia gama de éstos y, a servir como foco de contaminación en los sistemas donde son transportados (Burton Jr., 2002). Más aún, tanto los sedimentos como los compuestos químicos asociados están constantemente sujetos no sólo a procesos de meteorización, sino que además a distintos factores fluviales que dan paso a su deposición en áreas muy lejanas respecto a su origen, pudiendo servir como fuente de contaminación en nuevos sitios (Burton Jr., 2013). Es así como, cada cuenca existente transporta sedimentos con una signatura metálica intrínseca a ella, condiciones a partir de las cuales los ecosistemas locales se han desarrollado, desde los pequeños invertebrados hasta la macrofauna presente en cada localidad (Liu et al., 2017; Khan et al., 2019).

Este *background* regional depende principalmente de las rocas que dan vida a los sedimentos transportados. Sin embargo, es importante considerar la mineralogía que compone esas rocas, debido a que la disponibilidad y movilidad de los metales asociados depende, entre otros factores, de la fase mineral en la cual viajan (Gutiérrez et al., 2015). En ese sentido, un metal que es transportado a través de una fase sulfurada no necesariamente muestra el mismo comportamiento, ni la misma interacción con el medio, que uno que es transportado por una fase mineral más estable, como los silicatos, por ejemplo. De este modo, la interacción agua-roca juega un rol fundamental en cómo los agentes tóxicos potenciales son liberados al medio acuático (Jamieson et al., 2015), lo cual depende de la geología local, el régimen hidrológico y el nivel de intervención antrópica, entre otros factores.

1.4. Guías de calidad de sedimento (*Sediment Quality Guidelines,* SQG).

Para prevenir y controlar los efectos tóxicos asociados a los sedimentos transportados a través de ríos, se han creado una serie de guías que buscan definir los valores de concentración de una serie de compuestos, sobre los cuales, pueden verse afectados los ecosistemas que se desarrollan en torno a los sistemas fluviales asociados; las llamadas Guías de Calidad de Sedimento. Las SQG más recientes se basan en los efectos adversos que, algún compuesto específico en los sedimentos (orgánico o inorgánico), pudiese causar sobre macroinvertebrados bentónicos (Burton Jr., 2018). Si bien se han desarrollado una serie de guías alrededor del mundo (Smith et al., 1996; Chapman et al., 1999a; Simpson et al., 2013) y, a pesar de que estas se han creado en función de la realidad específica de cada sitio, no difieren mucho entre una y otra (Burton Jr., 2002).

Cada SQG suele definir dos valores límite para caracterizar la toxicidad de los sedimentos transportados: un primer nivel bajo el cual es raro que ocurran efectos tóxicos adversos, TEC, por sus siglas en inglés (*Threshold Effect Concentrations*: Concentración umbral de efecto) y; un segundo nivel sobre el cual es esperable que ocurran efectos tóxicos adversos en los organismos asociados, PEC, por sus siglas en inglés (*Probable Effect Concentration*: Concentración de efecto probable). En ese sentido, el trabajo de MacDonald et al. (2000) muestra al menos 6 TECs y 5 PECs distintos aplicados alrededor del mundo, a partir de los cuales homogeniza la información y crea las *Consensus-Based* (CB) TEC y PEC para As, Cd, Cr, Cu, Pb, Hg, Ni y Zn, así como para otros tipos de contaminantes orgánicos e inorgánicos. Estos valores han sido determinados a partir de la media geométrica de los valores de TECs y PECs previamente publicados. Sin embargo, hay que tener en mente que cada SQG ha sido establecida en función de la realidad específica que existe en cada medio, por lo tanto, tanto su aplicabilidad como confiabilidad dependen directamente de las condiciones que gobiernan cuenca a cuenca (Burton Jr., 2002).

Por otro lado, las SQG usualmente se aplican en sitios donde converge más de un potencial agente tóxico, lo que por consiguiente entrega la posibilidad de presentar efectos sinérgicos o antagónicos entre ellos. De este modo, trabajos como el de Michelsen (1999) han propuesto que, en cada sitio específico, debería implementarse una serie de SQGs representativas y biológicamente variadas, para que así estas se apliquen a comunidades, más que sólo a especies específicas. Además, es importante considerar que la biodisponibilidad de los contaminantes es influenciada por una serie de factores que no se han considerado en las SQGs. Por ejemplo: el tamaño de grano y la superficie de contacto de las partículas, la dureza, el tipo de material orgánico, el pH del agua, las dinámicas químicas espaciotemporales, la resuspensión y deposición de material y, la bioturbación, entre muchos otros (Burton Jr., 1991; Burton Jr., 2002).

Un ejemplo donde las guías de calidad se aplican con éxito es el estudio de Liu et al. (2017), en el cual se usan las CB SQG, y otros métodos conocidos, para evaluar la calidad de los sedimentos transportados a través del río *Xiangjiang*. Éste último compone el sistema de ríos más largo de la provincia de Hunan (China) y, su cuenca cubre más del 40% de la superficie de la provincia. Por cientos de años, dentro de esta cuenca se han desarrollado tanto actividad minera como fundiciones de plomo, zinc y cobre. De este modo, producto de la descarga de agua asociada a estos procesos industriales, este curso de agua se ha visto severamente contaminado por metales pesados y metaloides. Así, este sistema se caracteriza no sólo por *clusters* de minas y fundiciones, sino que además por áreas densamente pobladas y, fábricas químicas y metalúrgicas abandonadas, además de suelos destinados a la agricultura. Entonces, a partir de los perfiles de contaminación potenciales, derivados de las distintas actividades que se desarrollan en sitios definidos sobre la cuenca, los autores presentan siete metales pesados y metaloides con serios problemas de toxicidad y, que cubren una gran área de emisión dentro de la cuenca de *Xiangjiang*, acorde a estudios previos (i.e. Cd, Pb, Cu, Zn, Hg, Cr y As).

1.5. Cuencas de alta montaña hidrotermalmente alteradas y la importancia del *bakground* local.

Los sistemas fluviales de alta montaña son completamente distintos a lo expuesto en el caso por Liu et al. (2017). En especial, los desarrollados sobre rocas que han sufrido alteración hidrotermal, tienen ciertas peculiaridades que claramente los diferencia del resto de este tipo de sistema. De este modo, entre algunas de las características que diferencian a este tipo de ríos, las cuales condicionan el tipo de sedimento generado, se tiene:

1. Altas pendientes que dan pie a un intenso transporte de sedimentos.
2. Muy escasa (o completamente nula) presencia de vegetación cubriendo para estabilizar los suelos y disminuir la erosión y generación de sedimentos.
3. Sedimentos clásticos con alta concentración de metales.
4. Número acotado de especies formando parte del ecosistema.
5. Alta variabilidad estacional en los caudales asociados, debido a la nieve y/o a procesos glaciales (Valenzuela-Díaz et al., 2019).

Además, en el caso específico de los ríos afectados por drenaje ácido de rocas (ARD, por sus siglas en inglés), la exposición de minerales sulfurados a procesos de meteorización genera no sólo la acidificación de sus aguas, sino que además la liberación de cationes metálicos al medio (Bingham & Nordstrom, 2000). Así, a medida que el agua se neutraliza aguas abajo (ya se por mezcla con afluentes o por lluvia), los cationes disueltos y los sulfatos adquieren mayor afinidad por fases sólidas, llegando incluso a generarse nuevas fases minerales ricas en metales (Furrer et al., 2002). Esta es una de las vías por la cual, los metales asociados a las fases minerales neoformadas o al material en suspensión, se exponen al medio, siendo capaces de acumularse a altas concentraciones en los sedimentos transportados (Massoudieh et al., 2010). Así, como resultado de la gran variedad de parámetros que controlan la geoquímica y la mineralogía final de los sedimentos de ríos de alta montaña, se hace frecuente la existencia de subcuencas vecinas con signaturas geoquímicas significativamente distintas.

En ese sentido, se recalca la importancia de contar con un *bakground* específico para cada tipo de cuenca estudiada, como base para la evaluación de calidad de suelos y sedimentos. Además, dicho *bakckground* debería considerar la concentración natural de los metales y metaloides asociados, entendiendo que puede haber cuencas cuya concentración natural de metales pueda, teóricamente, dar paso a efectos tóxicos adversos según lo registrado en otro tipo de sistemas. Por otro lado, surge la necesidad de contar con un *background* específico al momento de evaluar cuencas con signaturas contrastantes, como ocurre en el caso de los sistemas de alta montaña hidrotermalmente alterados: cuencas asociadas a hidrotermalismo y subsecuente ARD, versus cuencas equivalentes sin actividad hidrotermal y, cuya variabilidad tanto hidro como geoquímica se ve enmascarada por el sistema adyacente (caracterizado por concentraciones mayores de metales).

1.6. Objetivos

1.6.1. Hipótesis de trabajo

Las Guías de Calidad de Sedimento convencionales no son aplicables en cuencas de alta montaña hidrotermalmente alteradas, se hace necesaria la implementación de *bakckgrounds* locales debido a la gran carga de metales que, de manera natural, lleva asociado el material transportado.

1.6.2. Objetivo general

Descifrar y proponer los criterios geoquímicos y mineralógicos fundamentales que deberían considerarse para la óptima generación de *backgrounds* geoquímicos en cuencas de alta montaña hidrotermalmente alteradas.

1.6.3. Objetivos específicos

- Definir la mineralogía que compone los sedimentos transportados a través de las distintas subcuencas

- Definir la geoquímica de los sedimentos transportados y establecer consistencias con el estudio mineralógico.

- Generar backgrounds geoquímicos y mineralógicos de los sedimentos transportados en las distintas subcuencas bajo estudio y;

- A partir de estos, mostrar su relevancia para los estudios de evaluación de calidad de sedimentos en cuencas de alta montaña hidrotermalmente alteradas.

CAPÍTULO 2

The role of local geochemical and mineralogical backgrounds as essential information to build efficient sediment quality guidelines at high-mountainous hydrothermally-altered basins (Mapocho basin, Chile)

José P. Correa-Burrows[1], Álvaro Navarrete-Calvo[1,2], Santiago Montserrat[2], Leonardo Navarro-Valdivia[1,2], Martín J. Valenzuela-Díaz[4], James McPhee[2,3], Valeria A. Zapata[1], Manuel A. Caraballo[2,4*]

1. Geology Department, University of Chile, Plaza Ercilla 803, Santiago, Chile

2. Advanced Mining Technology Center, University of Chile, Avda. Tupper 2007, Santiago, Chile

3. Civil Engineering Department, University of Chile, Av. Blanco Encalada 2002, Santiago, Chile

4. Mining Engineering Department, University of Chile, Avda. Tupper 2069, Santiago, Chile.

Abstract.

The Mapocho River's upper basin (Chilean Central Andes) was studied as a representative case of a high-mountainous hydrological system comprised by three sub-basins developed over very different rocks and submitted to different anthropic pressure: 1) a natural ARD system developed on hydrothermally-altered rocks (i.e., Yerba Loca), 2) a creek with mining activity in its headwaters and hydrochemically classified as non-affected by acid mine drainage (i.e., San Francisco), and 3) a low metal concentration creek (i.e., Molina). Sixty-three sediments samples were collected at seven different locations, during the four seasons along a hydrological year (2016-2017). In general terms, the geochemical composition of the clastic sediments was consistent with the geochemistry inferred from the mineralogical study. However, sediments with a smaller grain size (i.e., Sands & Silts) showed higher concentrations than the bigger grain size counterparts (i.e., Gravel) for elements such as Fe, S, Cu and As. This behavior was particularly evident in the Yerba Loca basin and it was attributed to the seasonal appearance of Fe-rich and Al-rich precipitates as part of the finer sediments. Different methodologies for the calculation of geochemical backgrounds (TIF, MAD and $95\%_{\text{percentile}}$) were tested. Results suggest that the $95\%_{\text{percentile}}$ method was the most appropriate for this type mountainous systems. Using the selected methodology, three different geochemical backgrounds were calculated: 1) Yerba Loca basin, 2) Molina basin, and 3) Mapocho Upper basin. It was observed that the third geochemical background (synthesizing the reality of the whole Mapocho upper basin, including Yerba Loca and Molina) tends to underestimate or overestimate some values if compared with the local geochemical backgrounds of Yerba Loca and Molina, respectively. In addition, when the generated background levels were compared with the Consensus-Based (CB) Sediment Quality Guidelines, Fe, Mn, Zn, Pb, Cu, Cr, Ni and As showed background values that were consistently higher than the values set by the CB Threshold Effect Concentration and even higher than the CB Probable Effect Concentration (for Fe and Cu). The present study clearly states the paramount importance of having a solid geochemical background before any attempt of a sediment risk assessment is made at hydrothermally-altered high-mountainous regions, which cover a significant amount of the river systems from South America

and many other areas in the world. Also, it exposes the need to carry out site specific ecotoxicological studies considering local flora and fauna, in order to corroborate the possible toxic effects of the natural geochemical background.

Keywords

High-mountainous hydrothermally-altered basins
Sediment Quality Guidelines
Local geochemical background
Water-rock interaction
Environmental sustainability

2.1. INTRODUCTION

Sediments transported through fluvial systems naturally tend to accumulate a wide range of contaminants and, may initially act as pollutants sink. However, with time, they can also be source of both organic and inorganic pollutants (Burton Jr, 2002). They are also constantly subjected to different fluvial transport processes, which lead them to deposit far away from their origin, thus acting as pollution vectors **(**Burton Jr, 2013). Each existing basin transports sediment with an intrinsic geochemical signature, generating local hydrogeochemical conditions influencing the local ecosystems, from the smallest invertebrates to the macro-fauna (Gutiérrez et al., 2015, Liu et al., 2017, Khan et al., 2019). These local geochemical backgrounds are mainly due to the interaction of the weathering processes and the rocks of a specific geological setting. Special attention must be paid to the particular mineralogy comprising these rocks, because of the availability and mobility of the transported metals will strongly depend, among other factors, on the mineral phases hosting them (Gutiérrez et al., 2015). In that sense, a metal transported in sulfide will present a very different interaction with the environment than the same metal transported in a more stable mineral phases, such as silicates for example. Therefore, water-rock interactions play a fundamental role in how the potential toxic agents are released to the aquatic environment (Jamieson et al., 2015), which depends on local geology, hydrology, and the level of anthropological intervention, among other agents.

To address the issue of toxicity effects associated with sediments, a series of Sediment Quality Guidelines (SQGs) have been developed around the world (e.g. Oceania: Simpson et al., 2013; Asia: Chapman et al., 1999a; North America: Smith et al., 1996). The great majority of the most recent and used SQGs seek to define the values at which certain metals, metalloids, and other kind of organic pollutants in the sediments could lead to detrimental effects to riverine ecosystems. Specifically, attention is paid to the study of the toxicological effects on benthic organisms (Burton Jr, 2018), since these invertebrates are essential to food chain’s equilibrium (Cain et al., 2004). On this regard, MacDonald et al. (2000) homogenized the existing information from a series of guidelines developed in different countries around the world, and (based on the geometric mean of the existing values of each parameter), they proposed a Consensus-Based thresholds for As, Cd, Cr, Cu, Pb, Hg, Ni and Zn, among other metals and organic compounds of concern in freshwater sediments. Despite this significant effort to generate general threshold values that could have a broad application to different environmental realities, it's important to keep in mind that every single SQGs was created to be used on the specific reality existing at each environment. Therefore, their applicability and reliability are clearly linked to that specific environment (Burton Jr, 2002).

High-mountainous fluvial systems, and especially those developed over rocks that suffered hydrothermal alteration, have some peculiarities that clearly differentiate them from the rest of riverine systems. Among other, the following characteristics of this type of rivers (conditioning the type of sediments generated) can be highlighted: 1) high slopes and high-velocity creeks transporting high amount of sediments, 2) very limited or complete absence of vegetation cover to stabilize the soils and slow down soil erosion and sediments generation, 3) high metallic concentration of the bedrock generating the river sediments, 4) small number of species comprising the river ecosystems, 5) high seasonal variation on river water flows due to snow and/or glacier melting processes (Valenzuela-Diaz et al., 2019). An even more special, but frequent, case within these types of rivers is the development of acid waters coming from acid rock drainage (ARD). The exposure of sulfide minerals to the weathering processes generates not only acidification of the waters but also the release of metallic cation into the medium (Bingham & Nordstrom, 2000). As the water neutralizes downstream (e.g. by mixing downstream or by raining), the dissolved cations and sulfates get strong affinities with solid phases or even generate new metal-rich mineral phases (Furrer et al., 2002). This is one of the pathways by which metals associated with either neoformed minerals or suspended matter are exposed to the environment, being able to accumulate at high concentrations in the transported sediments (Massoudieh et al., 2010). Another even more direct way is by the transport of metal bearing minerals that were originally part of the surrounding rocks. As a result of the great variety of parameters controlling the final geochemistry and mineralogy of high mountainous river sediments, the existence of neighboring sub-basins (forming a bigger complex basin) having significantly different geochemical signatures is quite frequent.

The current study takes place at the Mapocho River's upper basin (Chilean Central Andes). This basin can be understand as a representative case of a high-mountainous hydrological system, where its three principal sub-basins show three different geological and anthropological contexts: 1) a natural ARD system developed on hydrothermally-altered rocks (i.e., Yerba Loca), 2) a creek with mining activity in its headwaters and hydrochemically classified as non-affected by acid mine drainage (i.e., San Francisco), and 3) a low metal concentration creek (i.e., Molina). Thanks to the diverse realities covered, the main scope of this study is to decipher and propose the fundamental mineralogical and geochemical criteria that should be considered for the optimal generation of geochemical backgrounds in high-mountainous hydrothermally-altered basins. In addition, different methodologies for the calculation of geochemical backgrounds will be tested and the most appropriate for this type mountainous systems will be recommended. Finally, the obtained local geochemical backgrounds will be compared with different toxicity threshold values offered by well-established and worldwide used Sediment Quality Guidelines (SQG). This comparison is intended to show how general SQGs are not directly applicable to high mountainous watersheds and also to highlight the paramount importance of generating local geochemical backgrounds to properly address the complex reality of these systems.

2.2. FIELD BACKGROUND INFORMATION

2.2.1. Geographical and Geological setting

The study area is located at Chilean Central Andes, northwest of Santiago City, and includes the whole Mapocho River's upper basin (). This area ranges between 960 and 5,350 m.a.s.l. and covers a total area around 570 km^2. Three different sub basins were defined: Yerba Loca (YL), Molina (MO) and San Francisco (SF). Yerba Loca's basin is located between 1,350 and 5,350 m.a.s.l. (meters above sea level) covering an area about 108 km^2. Its main stream length is about 20 km, with an average slope of 7%. Although part of its headwaters is located within Los Bronces mining district (Toro et al., 2012), there is no mining activity in this area. Nevertheless, its head waters naturally show low pH values and high sulfate and metals concentrations due to the presence of hydrothermal alterations in the rocks of the region (Gutiérrez et al., 2015). San Francisco's basin is located between 1,150 and 5,350 m.a.s.l. covering an average area about 189 km^2 (Figure 1). Its main stream has an extension of about 34 km and an average slope of 7%. The mining operation of Los Bronces is located in the river's headwaters. As a result, this sub-basin cannot be considered under a natural regime at the time of assessing its sedimentological and hydraulic behavior. Finally, Molina's basin is located between 1,150 and 5,300 m.a.s.l, covering an average area about 300 km^2. Its main stream has a length about 25 km and an average slope of 8%. The rocks of these region do not present any significant hydrothermal alteration and no mining activity is registered.

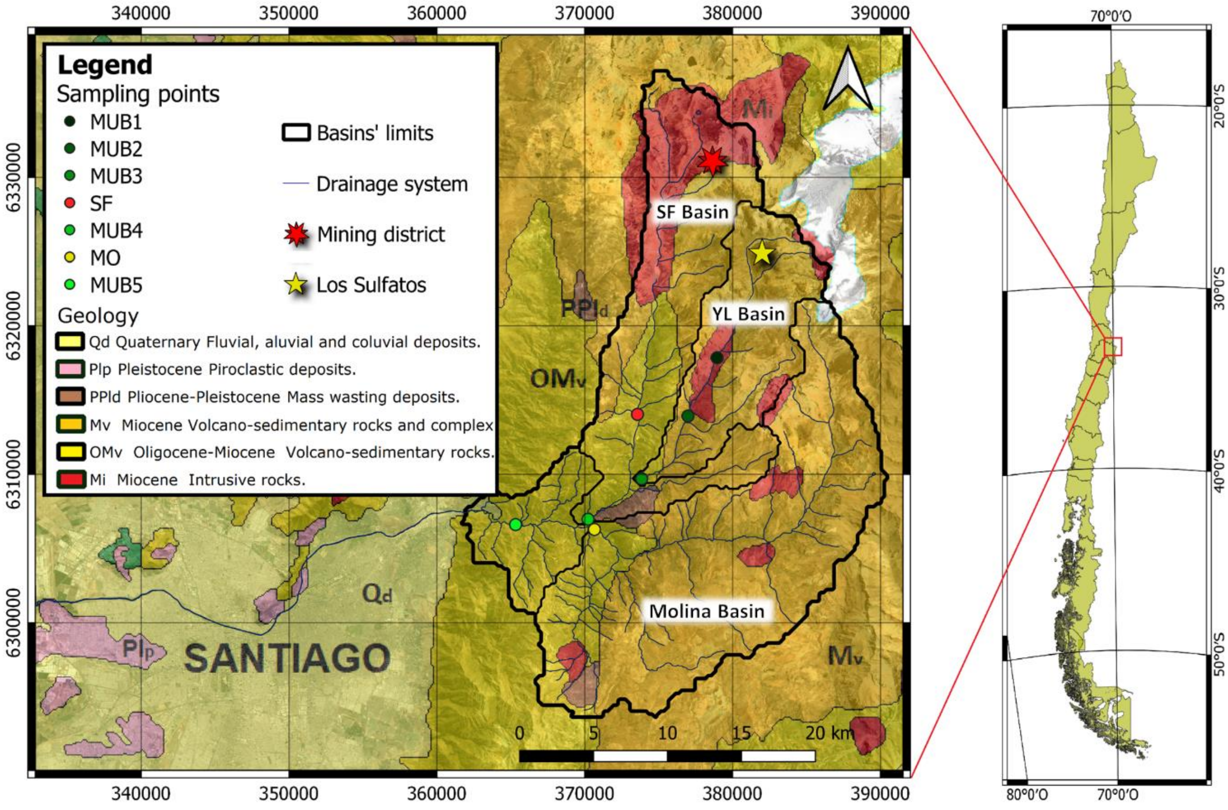


Figure 1. Geological map of the Mapocho's upper basin where the three main sub-basins (black line) and the sampling points (colored circles) have been identified. MUBn= Mapocho Upper

Basin sampling point n (n=5), SF= San Francisco; Mo= Molina. FF= Farellones Formation and; AF= Abanico Fromation. Modified from SERNAGEOMIN, 2003.

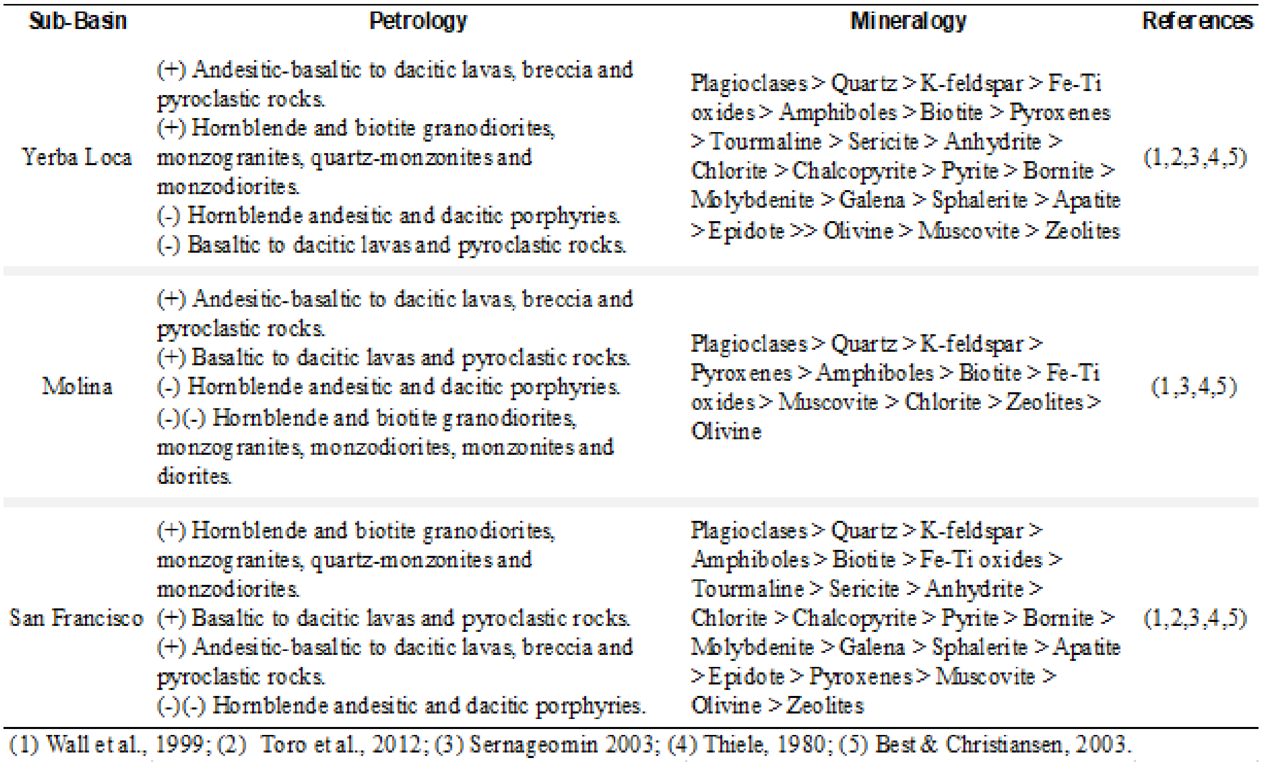
The regional geology (Figure 1) is defined by two principal stratigraphic formations, Abanico Formation (Fm.) (dating from the Upper Eocene?-Early Miocene; Aguirre, 1960; Wyss et al., 1994; Charrier et al., 1996) and Farellones Fm. (Early-Middle Miocene; Klohn, 1960; Nyström et al., 2003). The Abanico Formation is a volcano-sedimentary sequence comprised by andesitic to basaltic lavas sequences intercalated with pyroclastic and continental sedimentary rocks. The pyroclastic deposits within this formation are made by tuffs, breccia and acidic composition ignimbrites, while the sedimentary intercalations correspond to fluvial, alluvial and lacustrine deposits, which can be found in the form of conglomerates, sandstones, breccia, shale and siltstone. Nyström et al., 2003 divided the Abanico Fm. in two predominant members, the inferior one comprised by basic lavas intercalated with acidic composition pyroclastic and lacustrine deposits and, the superior one consisting of basaltic lavas. On the other hand, Farellones Fm. contains two principal members, (Rivano et al., 1990) the inferior one made by tuffs and ignimbrites with dacitic to rhyolitic composition and intercalated by continental sedimentary deposits; and the superior one comprised by lavas with tuffs and breccia intercalations. The composition of the tuff intercalations range between andesitic to basaltic breccia intercalations show rhyolitic to dacitic compositions (Thiele, 1980).

Specifically, San Francisco's and Yerba Loca's sub-basins are characterized by plutons and porphyries mainly comprised by diorites, granodiorites, granites and monzonites, which ages range between Late Cretaceous to Miocene (SERNAGEOMIN, 2003; Deckart et al., 2010; Table 1, Table 6). Los Bronces Breccia Complex (developed adjacent to and within the porphyritic intrusive), is characterized by the presence of Cu sulfide mineralization. The clasts of this Breccia Complex are made by andesite and diorite while the matrix is comprised by different proportions of quartz, tourmaline, specularite, anhydrite, pyrite, chalcopyrite, bornite and molybdenite, among others (Toro et al., 2012). According to Thiele (1980) the intrusive bodies are found only in Farellones Fm.; that is, they don't intrude Abanico Fm. Non-consolidated materials are Pleistocene to Holocene mass movement, colluvial, fluvial and alluvial deposits (Wall et al., 1999; Selles & Gana, 2001). These materials are generally made by poorly sorted sand, gravels and blocks with low consolidation level. Specifically, fluvial deposits are mainly comprised by gravels, sands and, to a lesser extent, silts (Wall et al., 1999). These sediments are typically characterized by clasts with dacitic to andesitic composition and quite common breccia remains, the latter particularly visible along the Yerba Loca stream.

Regarding Molina's sub-basin, it's characterized principally by basaltic to dacitic lavas and pyroclastic rocks mainly comprised by acid tuff and breccia with andesitic, dacitic and obsidian clasts, which ages ranges between Upper Eocene to Middle Miocene (Wall et al., 1999, Nyström et al., 2003; Table 1, Table 6). From the geological map in SERNAGEOMIN (2003), the surface of Molina River's basin is mainly covered by Farellones Fm., followed to a much lesser extent by Abanico Fm. Nevertheless, despite the significant presence of the former geological formation and, unlike the other two sub-basins, Molina's presents a very low quantity of outcrops of plutons and porphyries, with respect to the total area (Figure 1). On the other hand, as well as Yerba Loca's and San Francisco's sub-basins, non-consolidated material are Pleistocene to Holocene mass movement, colluvial, fluvial and alluvial deposits (Wall et al., 1999; Selles & Gana, 2001), which are generally made by poorly sorted silts, sands, gravels and blocks with low consolidation level. According to field observations, fluvial deposits are mainly comprised by silts and sands, reason which would explains the associated turbidity (Figure 7), and in a slightly lesser extent, gravels. As in the other sub-basins, the transported material is typically characterized by clasts with dacitic to andesitic composition.

Table 1 was created to obtain a more synthetic understanding of the main rocks and minerals comprising the different geological formations described in this section. This summarize knowledge of the geological setting will be used to expose the expected connection between the mineralogy at a regional geological scale and the mineralogy from the local sediment sampling campaigns of this study.

Table 1. *Petrological and mineralogical characteristics of the geological units at Mapocho's main Sub-basins.*



Sub-Basin	Petrology	Mineralogy	References
Yerba Loca	(+) Andesitic-basaltic to dacitic lavas, breccia and pyroclastic rocks. (+) Hornblende and biotite granodiorites, monzogranites, quartz-monzonites and monzodiorites. (-) Hornblende andesitic and dacitic porphyries. (-) Basaltic to dacitic lavas and pyroclastic rocks.	Plagioclases > Quartz > K-feldspar > Fe-Ti oxides > Amphiboles > Biotite > Pyroxenes > Tourmaline > Sericite > Anhydrite > Chlorite > Chalcopyrite > Pyrite > Bornite > Molybdenite > Galena > Sphalerite > Apatite > Epidote >> Olivine > Muscovite > Zeolites	(1,2,3,4,5)
Molina	(+) Andesitic-basaltic to dacitic lavas, breccia and pyroclastic rocks. (+) Basaltic to dacitic lavas and pyroclastic rocks. (-) Hornblende andesitic and dacitic porphyries. (-)(-) Hornblende and biotite granodiorites, monzogranites, monzodiorites, monzonites and diorites.	Plagioclases > Quartz > K-feldspar > Pyroxenes > Amphiboles > Biotite > Fe-Ti oxides > Muscovite > Chlorite > Zeolites > Olivine	(1,3,4,5)
San Francisco	(+) Hornblende and biotite granodiorites, monzogranites, quartz-monzonites and monzodiorites. (+) Basaltic to dacitic lavas and pyroclastic rocks. (+) Andesitic-basaltic to dacitic lavas, breccia and pyroclastic rocks. (-)(-) Hornblende andesitic and dacitic porphyries.	Plagioclases > Quartz > K-feldspar > Amphiboles > Biotite > Fe-Ti oxides > Tourmaline > Sericite > Anhydrite > Chlorite > Chalcopyrite > Pyrite > Bornite > Molybdenite > Galena > Sphalerite > Apatite > Epidote > Pyroxenes > Muscovite > Olivine > Zeolites	(1,2,3,4,5)

(1) Wall et al., 1999; (2) Toro et al., 2012; (3) Sernageomin 2003; (4) Thiele, 1980; (5) Best & Christiansen, 2003.

2.2.2. Climate, Hydrology and Hydrogeochemical setting

Central Chile (30–35°S) is characterized by a Mediterranean climate, with wet winters and dry summers (Rütllant & Fuenzalida, 1991), whit maximum and minimum annual temperatures reached during the dry and wet periods, respectively. More specifically, Andean Cordillera at this latitude is characterized by a dry season typically ranging from September to April and a wet season that goes from May to August (Brenning, 2005). Since 2010, Central Chile is suffering one of the worst droughts on record, not only because of its unprecedented duration but also by its severity

(Garreaud et al., 2017). Nevertheless, the so called “Mega Drought” has mainly affected the magnitude of rainfall but not the seasonality of the dry and wet season (Garreaud et al., 2017).

Particularly for the Mapocho’s upper basin, Molina is its main tributary during most of the year due to its bigger catchment area, providing about 70% of the annual discharge (while Yerba Loca provides about the 25%) (Valenzuela-Diaz et al., 2019). However, Valenzuela-Diaz et al., (2019) shown how the maximum discharges of both systems are desynchronized because Molina sub-basin has mainly a nivo-pluvial character whereas Yerba Loca basins has a more snow-glacial character. As a consequence, during summer (December to April) the Mapocho’s discharge is supplied up to about 30-50% by the Yerba Loca stream. This situation leads to Mapocho river showing episodes where it behaves like a natural acid rock drainage (ARD) affected system (such as Yerba Loca does). San Francisco stream usually provides less than 10% of the Mapocho´s annual discharge, situation that remains constant throughout the year (Valenzuela-Diaz et al., 2019).

Valenzuela-Diaz et al. (2019), also studied the water quality of the Mapocho Upper basin. They showed how the Yerba Loca stream is characterized by acidic Ca-SO_4 waters, with relatively high conductivity, high dissolved metals concentrations and low pH values (typical from an ARD). The presence of Fe and Al precipitates on the riverbed in typically concomitant to ARD (Caraballo et al., 2011 and 2019). On the other hand, the Molina stream is characterized by the presence of calcium-carbonated waters with neutral pH, very low electrical conductivity, low concentration of dissolved elements and almost no dissolved metals. As a result, the waters from the upper section of the Mapocho river seasonally varies between Ca-HCO^- to Ca-SO_4^{2-} types, whit pH values ranging from 5.2 to 8.6.

2.3. MATERIAL AND METHODS

2.3.1. Sediment sampling campaigns and sediment treatment

Three groups have been defined for sediment analysis, all of which were used for both, geochemical and mineralogical characterization (Table 2). Seven sampling points have been defined (Figure 1), five of which are located at the Mapocho Upper basin main flow (from MUB1 to MUB5) and, the other two at its main tributaries, MO and SF Rivers (Figure 1). This sampling point arrangement allows not only to study the spatial variations of the main flow from its headwater to its final confluence as Mapocho River, but also to elucidate the geochemical influence of its principal tributaries. Sampling campaigns were carried out almost every month from August 2016 to November 2017, although some months (mainly during winter) theses sampling campaigns had to be discontinued due to bad weather. Additional details about sampling campaign dates, type of samples and chemical analyses are presented in Appendix B. The achieved sampling frequency allowed to generate the needed information to evaluate possible seasonal variations of the sediment’s geochemistry and mineralogy. This seasonal variation of the sediments bulk chemistry could be partially linked to the hydrochemical variations already reported for theses creeks, especially during spring and summer (Valenzuela-Diaz et al., 2019). Sediment samples were always collected at the same sections of the creeks, although the specific sampling point was subjected to the water level during the sampling campaign. Two kilograms of each sample (obtained from the surface layer of the riverbed) were collected using high-density polyethylene shovels, stored in low-density polyethylene bags, in darkness and at room temperature, until they were oven dried at 25-30°C. Subsequently, the samples were sieved with a Sefar-Suiza nylon mesh # 10 (ASTM standard), separating the sand and gravel fractions. Finally, both fractions of each sample were grinded using a RS200 Retsch vibrating disc grinder equipped with an agate mortar, during 9 minutes at 700 rpm. This grinding procedure ensured reducing the grain size of the samples to 0.074 mm (#200 mesh) or lower.

Table 2. *Main characteristics of the three groups differentiated during the Mapocho's solid sampling campaigns.*

Sample Code	**Expected grain size**	**Sampling criteria**	**Sediments type**
Precipitates	$<40\mu m$	Lose precipitates on rocks surface	Chemical
Sands & Silts	$>40\mu m$ and $<2mm$	Went through a 10 ASTM mesh	Detrital
Gravels	$>2mm$ and $> 64mm$	Retained on a 10 ASTM mesh	

Precipitates sampling was conditioned to their seasonal appearance in some very specific and limited sections of the creeks (i.e., the vicinities of sampling point MUB1). As a result, Al-rich precipitates (white ones) were collected only in September 2016, (two samples, at the beginning and at the middle of the month), while Fe-rich precipitates (reddish ones) were collected in November of the same year (one sample). Both Al- and Fe-rich precipitates were developed on the surface of the riverbed as a very thin film that was very difficult to sample on the field. Because of that, it was decided to obtain samples including the gravels with precipitates, to transport them to the laboratory (using low-density polyethylene bags) and to collect there the precipitates by means of brushes with nylon bristles. Once the precipitates were recovered, they were dried at 20-25°C (room temperature), and finally homogenized using a manual agate mortar and pistil.

2.3.2. Chemical and mineralogical analyses

In order to know the geochemical composition of the different sediments sampled, it was decided to submit them to a modified *aqua regia* acid digestion (1:1:1 HNO_3:HCl:H_2O), a well-used extraction procedure (ISO 11466, 1995; Butler, 2020), followed by ICP-MS analyses of the digestion solutions. This type of pseudo total digestion it is not effective at dissolving some silicates (e.g., quartz), but it gives a very good idea about metals which are most likely to be released during the long-term weathering processes into the creek waters. So, this process not only gives detailed information about mobile elements in soils and sediments, but it is also a cost-effective way to extract these elements (Rao et al., 2008; Milicevic et al., 2017). The digestion was developed by mixing 500 mg of sediment with 7.5 ml of aqua regia solution for 30 minutes (stirring occasionally) followed by immediate heating (at approximately 100°C) until complete evaporation of the solution. Once a dry pellet was obtained and cooled, 5 ml of HNO_3 were added and left overnight. The next day, the nitric solution was recovered using 30 ml of Milli-Q water and stored at 4 ºC in 60 mL sterile polypropylene containers until analyzed. The chemical analyses were performed by ICP-MS and ICP-OES at an external analytical company (i.e., Bureau Veritas/Acmelabs) using a commercial analytical package (i.e., ICP-MS AQ250 analysis for soils, sediments and lean rocks). The detection limits for this analytical method are reported in Table 9 (Supplementary material).

The sediments mineralogical semi-quantitative compositions were obtained by powder X-ray diffraction (XRD) of randomly oriented samples on Bruker D5005 X-ray diffractometer with CuKα radiation. Diffractometer settings were: 40 kV, 30 mA, and a scan range of 10–63° 2θ, 0.02° 2θ step size, and 5 s counting time per step. The obtained diffractograms were analyzed using the software XPowderX® and PDF2 database.

2.4. RESULTS AND DISCUSSION

2.4.1. Mineralogical characterization of the Mapocho upper basin's sediments

Table 3 summarize the mineral phases identified in all the Gravels and Sands&Silts samples of the present study, as well as the semiquantitative ranges (in wt%) shown by each identified mineral in each sampling points. These ranges correspond to each sampling points minimum and maximum values calculated for all the individual sampling campaigns during 2016 and 2017. Detailed mineralogical information for each specific sampling campaign is shown in Tables 7 and 8 (Appendix A). The main mineral phases comprising both set of samples (i.e., quartz, plagioclases and phyllosilicates) are in agreement with the mineralogy of the main petrological units discussed in section 2.1. No evidences of metal bearing sulfides or oxides/hydroxides were observed in the X-Ray diffraction study. Also, it is important to notice that the relative abundance of the main detected mineral phases did not show significant monthly variations or discernible tendencies (from September 2016 to July 2017). As a result, sediments main mineralogy is not submitted to significant seasonal variations.

Regarding each individual sub-basin, both Yerba Loca and San Francisco basins show very similar mineralogical signatures including muscovite (phyllosilicate mineral group, $KAl_2(AlSi_3O_{10})(OH)_2$) and albite (plagioclase mineral group, $NaAlSi_3O_8$) or labradorite (plagioclase mineral group, $(Ca,Na)(Si,Al)_4O_8$) as their more characteristic minerals. It can be observed how the relative abundances of the main minerals comprising the gravel size sediments of the Yerba Loca basin (i.e., sampling points MBU1 to MBU3) typically show Pla>>Qtz>Phy (Pla = Plagioclase and Phy = Phyllosilicates), whereas the sand & silt size sediments tend to reduce their relative abundances of plagioclases and increase quartz and phyllosilicates contents (Tables 3, 7 and 8). Since Sand & Silt sediments are the result of Gravel´s physical and chemical weathering, the observed behavior could be explained by the higher hardness and resistance to chemical weathering of quartz. Also, phyllosilicates sheet structure facilitates the generation of small to very small grain sizes (i.e., silts and clay grain sizes). On the other hand, the sampling point at the output of San Francisco´s basin (SF, Figure 1) exhibits a very similar proportion of quartz and plagioclases at the gravel size fraction and also a higher content of quartz and phyllosilicates at the sand & silt fraction; whereas the output of the Molina´s basin is characterized by a very high proportion of plagioclase and quite low quartz and phyllosilicates at both gravel and sand & silt grain sizes. The mineralogical signature of Molina´s sediments is characterized by the presence of andesine (plagioclase mineral group, $(Na,Ca)(Si,Al)_4O_8$) as well as pargasite (amphibole mineral group, $\{Na\}\{Ca_2\}\{Mg_4Al\}(Al_2Si_6O_{22})(OH)_2$) and laumontite (zeolite mineral group, $CaAl_2Si_4O_{12} \cdot 4H_2O$) and the absence of muscovite. The mineralogical signature of MUB4 shows a higher resemblance to the one of the Yerba Loca basin, revealing the higher influence of this basin against San Francisco basin. Finally, the mineralogical signature of MUB5 is clearly a mixture of all the contributing sub-basins (i.e., YL, SF and Molina).

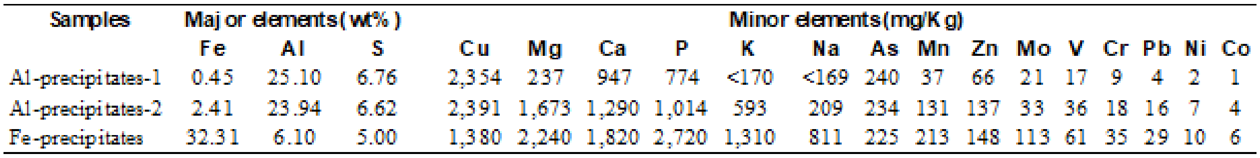
Table 3. *Sediments mineral identification and semiquantification (wt%) by XRD.*

Sample point	Number of samplings		Plagioclases			Phyllosilicates			
		Qz	Alb	Lbr	And	Msc	Ccl	Prg	Lmt
				GRAVELS					
MUB 1	3	25-33	50-63			8-11	3-6		
MUB 2	3	26-39	51-66			4-5	3-4		
MUB 3	3	15-21		65-70		10-11	3-4		
SF	4	36-50		41-57		5-7	1-3		
MUB 4	4	17-27		66-77		2-4	3-5		
MO	4	18-21			68-71		2-3	6-8	1-2
MUB 5	2	17-23			66-73	6		4	
				SANDS & SILTS					
MUB 1	4	39-41	35-44			13-17	4-6		
MUB 2	4	36-54	38-41			13-17	4-6		
MUB 3	6	39-57		28-41		7-17	3-8		
SF	7	38-50		32-47		6-23	1-6		
MUB 4	8	31-41		49-63		4-6	2-5		
MO	5	12-16			72-79		2-3	4-5	1-5
MUB 5	3	25-39			50-66	4-6		5-6	

Numbers correspond to the ranges of the compositions measured in the different sampling campaign
Qz: Quartz, Lbr: Labradorite, And: Andesine, Alb: Albite, Msc: Muscovite, Prg: Pargasite, Ccl: Clinochlore, Lmt: Laumontite

On the other hand, whitish and reddish to brownish precipitates were observed at certain sections of the Mapocho´s upper basin (Figures 5 and 6, Appendix A). Those precipitates appeared in the form of neoformed mineral phases with clay-like texture, as crust-like aggregates on the surface of bed sediments or cementing the riverbed sediments. According to the XRD study performed to three samples obtained from the neoformed mineral with clay-like texture (Figure 9), they are predominantly comprised by amorphous or poorly crystalline mineral phases that may show some occasional peaks corresponding to traces of detrital minerals (like quartz). Based on the comparison of the obtained diffractograms and the geochemical composition shown in Table 4 with previous studies from other similar regions on the world (Furrer et al., 2002; Caraballo et al., 2011 and 2019), schwertmannite ($Fe_8O_8(OH)_{8-2x}(SO4)_x$, with $0.75 > x > 2.58$) and hydrobasaluminite ($Al_4(SO_4)(OH)_{10}\cdot 12\text{-}36H_2O$) are proposed as the most plausible mineral phases forming these precipitates. These precipitate's occurrence is especially predominant along the Yerba Loca stream, (mainly in the vicinities of MUB2 and MUB3), however, there are certain periods of the year in which they've been observed even after San Francisco and Molina confluences with Yerba Loca (MUB4 and after MO, respectively), about 5km before MUB5. It is important to notice that while Yerba Loca basin shows both kind of precipitates (whitish and reddish-brown), those found in MUB4-MO confluence are only white, which in some cases present greenish tones.

Table 4. *Bulk chemistry of the Fe- and Al- rich precipitates obtained at MUB1 sampling point.*



Samples	Major elements (wt%)			Minor elements (mg/Kg)														
	Fe	Al	S	Cu	Mg	Ca	P	K	Na	As	Mn	Zn	Mo	V	Cr	Pb	Ni	Co
Al-precipitates-1	0.45	25.10	6.76	2,354	237	947	774	<170	<169	240	37	66	21	17	9	4	2	1
Al-precipitates-2	2.41	23.94	6.62	2,391	1,673	1,290	1,014	593	209	234	131	137	33	36	18	16	7	4
Fe-precipitates	32.31	6.10	5.00	1,380	2,240	1,820	2,720	1,310	811	225	213	148	113	61	35	29	10	6

Taking into account the previous mineralogical information, a tentative geochemical composition of the sediments could be inferred where Si>Al and Ca>Na>K>Mg>Fe are expected to represent the main major and minor elements, respectively. Also, no evidences of a significant metal pollution could be implied from the mineralogical study alone (apart from the observed Al- and Fe-rich precipitates observed at some limited section of the Mapocho upper basin, mostly at Yerba Loca sub-basin).

2.4.2. Geochemical characterization of the Mapocho upper basin's sediments

It is important to remember that the elemental compositions discussed in this section come from pseudo-total digestions with *aqua regia* that have the ability to completely dissolved most minerals with the exception of certain silicates that are only partially dissolved. As a matter of fact, the summatory of all elements concentrations for each sample typically add up to 10 or 15 wt%, in the best cases. The remaining 85 or 90 wt% corresponds to major elements that were not completely released from the hosting minerals (i.e., Si, Al, Ca, among others) or that could not be analyzed by ICP-MS (i.e., C, O, H, N, among others). Nevertheless, these pseudo-total digestions offer valuable information about the elements availability and can be considered as the maximum concentrations that could potentially be released from the sediments during historic (not geologic) periods of time (Rao et al., 2008; Milicevic et al., 2017; Butler, 2020).

The bulk geochemical composition of the Mapocho´s upper basin is in great consonance with the composition that might be inferred from the mineralogical study. However, some relevant discrepancies on major and minor elements abundances and tendencies, as well as some significant concentrations of various metals and metalloids, are observed in Figure 2.

From a broad perspective, it can be observed that Sand&Silt sediments frequently show higher concentrations than Gravel sediments for elements that should be monitored as potential inorganic pollutants, viz: Fe, S, Cu and As. This behavior is particularly evident in the Yerba Loca Basin (i.e., from MUB1 to MUB3) and could be attributed to the higher amount of Fe- and Al-rich precipitates that commonly appear as part of the fine sediments at the Mapocho upper basin (Figure 5, Appendix A). On the other hand, both sediments fractions show very similar concentrations (slightly higher for Gravel sediments) of the elements typically comprising the main minerals of the detrital clasts, namely: Al, Ca, Mg, K and Na. The relative abundances of these elements are in good agreement with the general mineral proportions observed in the previous section.

Regarding the specific geochemical behavior of the most relevant elements that are typically included (or could/should be included) as potential inorganic contaminants in Sediment Quality Guidelines (SQG), the following 7 elements will be discussed:

Iron concentrations are consistently high in all the sediments at the whole Mapocho Upper basin, roughly ranging from 3 wt% to 6 wt% and from 2 wt% to 4 wt% in the Sand & Silt and Gravel sediments, respectively (Figure 2a). A plausible partial explanation for the general high iron concentrations of both type of sediments and the higher concentration shown by finer sediments (i.e., Sand&Silt) could be the frequent appearance of different proportion of iron precipitates along the whole Mapocho upper basin. As shown in Table 4, these precipitates are made up to a 32 wt% of Fe. However, the formation of these iron precipitates is more predominant in the Yerba Loca sub-basin. Therefore, the high iron concentrations of the samples downstream MUB4 sample point should be attributed to a different reason. On this regard, the existence of Fe mineral phases not detected by XRD or the preferential dissolution of clinochlore (chlorite mineral group, $(Mg,Fe^{2+})_5Al(AlSi_3O_{10})(OH)_8$) during the aqua regia pseudo-total digestion likely contributed to these high Fe concentrations.

Aluminum concentrations are very similar at both sediment fractions (Figure 2a), spanning a short concentration range between 1 wt% and 2.5 wt%. However, some discernible discrepancies can be observed in the extension of the “box plot main bodies” (colored area from 25 to 75 percentiles) if Gravel and Sand&Silt samples are compared. Gravels´ Al concentrations always show a very narrow range close to the median whereas this element concentration in the Sand&Silt samples typically show broader ranges far from the median. This behavior can be explained if the Al in the Gravel samples is mainly attributed to the aluminosilicates comprising the detrital clast whereas the Al in the Sand&Silt samples is assigned to both the aluminosilicates in the detrital fraction of the sediments and to the seasonal presence of the Al-rich precipitates. The seasonal variations for certain elements will be explained later in further detail. This situation is clearly observed in MUB1 sampling point (Figure 2a) where the higher and most frequent formation of Al-rich precipitates was recorded (Figure 5, Appendix).

Sulfur (Figure 2b) and arsenic (Figure 2c) concentrations show very similar trends and distributions in both sediment fractions. It is important to notice both the high sulfur concentrations measured at both sediment fractions (up to 0.3 wt% and 1 wt% in Gravel and Sand&Silt sediments, respectively) and the higher sulfur content in the finer grain sediments. These observations also apply for arsenic. Sulfur (and arsenic) concentrations in Gravel sediments are most probably due to the presence of minor amounts of sulfides that were not detected during the XRD study whereas sulfur concentrations in the Sand&Silt sediments are most likely due to the presence of traces amounts of sulfides (in the detrital fraction) and minor amounts of Fe and sulfate rich minerals in the precipitates (i.e., schwertmannite). Also, the distribution of both elements in the Sand&Silt sediments clearly show a decreasing tendency from the head to the mouth of the Mapocho upper basin that perfectly reproduce the decrease in the influence zone of the ARD generated at the headwaters of the Yerba Loca sub-basin.

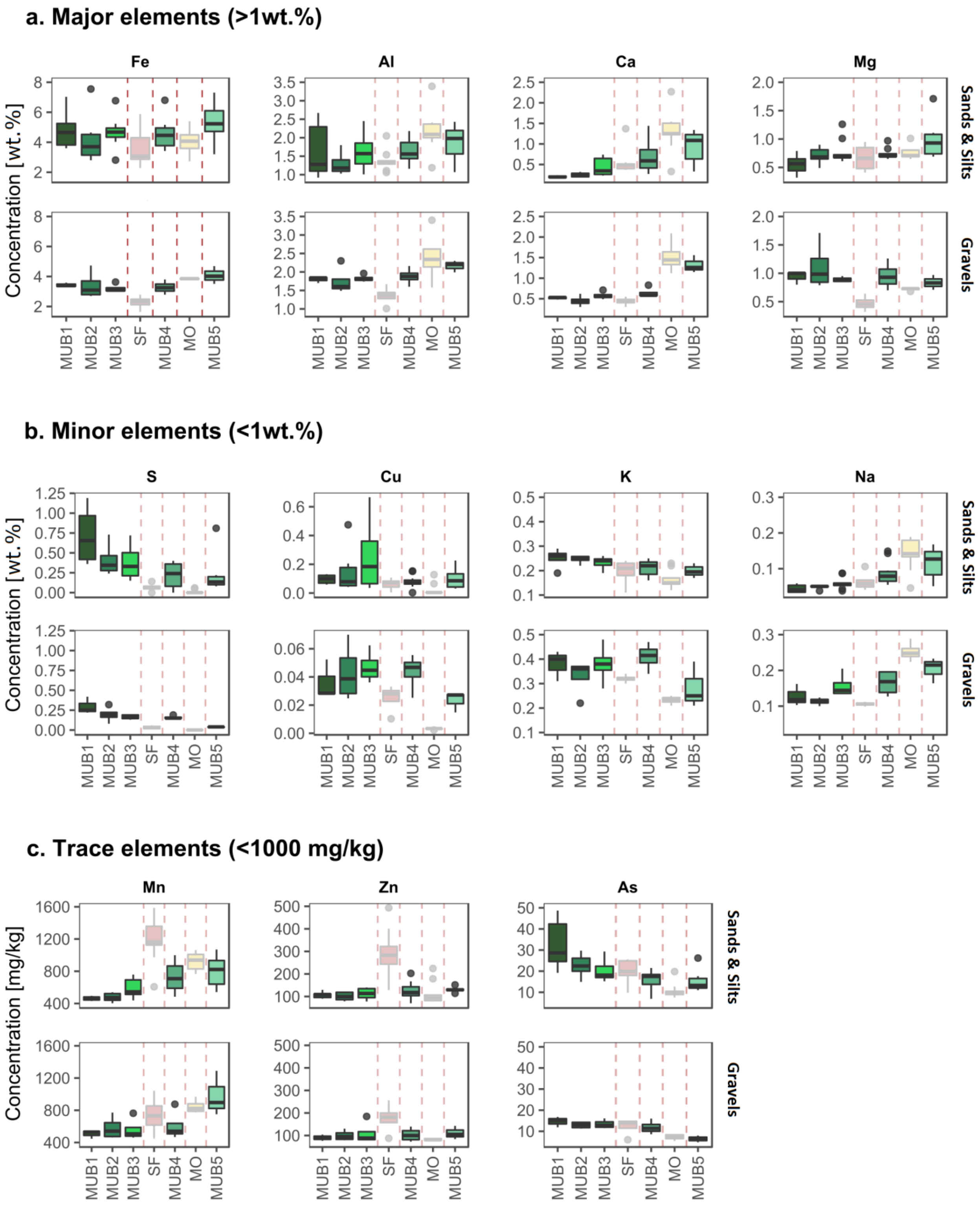


***Figure 2**. Sediments (Gravels and Sands & Silts) bulk geochemical composition. Boxplots central marks indicate median values, bottom and top edges of the boxes represent the 25th and 75th*

percentiles, vertical lines extended to 5th and 95th percentiles and the outliers are marked by a black filled circle. Boxplots from the principal tributaries (San Francisco, SF, and Molina, MO) were faded to clearly differentiate them from the data corresponding to the Mapocho Upper Basin main course (MUB1 to MUB5).

Copper concentrations differ almost one order of magnitude if Gravel and Sand&Silts sediments are compared (Figure 2b). A similar explanation to the one offered for S and As could apply to Cu, where the low concentrations in the Gravel sediments may correspond to very minor concentrations of copper sulfide minerals in the detrital sediments whereas the significant concentrations in the finer sediments could be attributed to the formation of Cu-rich precipitates in the section of the basin more affected by ARD. Several previous studies have reported the adsorption and/or co-precipitation of Cu during the formation of aluminum precipitates (e.g., hydrobasaluminite, $Al_4(SO_4)(OH)_{10}\cdot12\text{-}36H_2O$) in ARD (Caraballo et al., 2011; Sánchez-España et al., 2016; Caraballo et al., 2019). Al-precipitates sampled in MUB1 also show high concentrations of copper, being the fourth most abundant element after Al, S and Fe (Table 4).

Manganese and zinc, in trace concentrations, show very similar distribution in the two studied sediment fractions, with no discernible differences between them (Figure 2c). This is probably because both elements are hosted in some of the minor mineral phases comprising the detrital sediments. Manganese concentrations show an increasing tendency from the head to the mouth of the Mapocho upper basin whereas zinc concentrations remain almost constant along the main course of the Mapocho.

Sand&Silt concentrations for Al and Cu and, Fe and S at MUB3 will be used to exemplify the seasonal variations previously mentioned. As can be observed in Figure 3a, Al and Cu concentrations show very similar trends with higher values during the wet season and lower values during the dry season (inversely related to the hydrochemical seasonality shown for Yerba Loca Stream by Navarrete, 2020). These trends are in agreement with the seasonal observations of whitish to greenish precipitates at MUB3. Fe and S concentrations trends (Figure 3b) show very high resemblance. A clear seasonal pattern (like the one for Al and Cu) cannot be defined with the available data. However, field observations confirmed that the higher Fe and S concentrations of the Sand&Silt samples correspond to the appearance of temporary upstream Fe-rich precipitates.

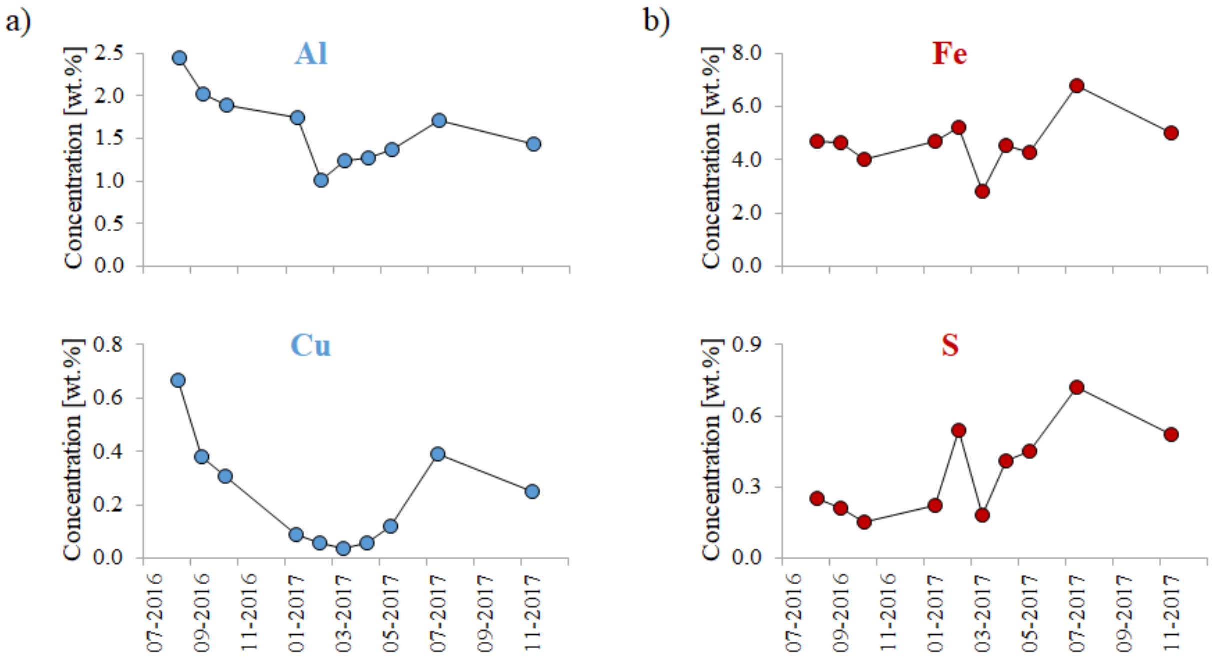


***Figure 3**. Sands & Silts sediments geochemical variations with time at Yerba Loca sub-basin. Samples at a) and b) correspond to MUB3 (lower Yerba Loca).*

2.4.3. Sediments natural geochemical background at the Mapocho upper basin as a proxy of Andean hydrothermally-altered high-mountainous regions

Due to the geochemical and mineralogical complexity shown by the different sub-basins conforming the Mapocho upper basin, it was decided to evaluate the three most frequent and better stablished methods to calculate geochemical backgrounds and threshold limits in soil and sediment metal polluted samples (Reimann and Caritat, 2017; Rothwell and Cooke, 2015; Tume et al., 2019).

The first method is known as "MAD method" and it is proposed as an improvement to the original method of Mean + 2 Standard Deviation (SD) usually used in exploration geochemistry to detect data outliers (Reimann et al., 2005). The MAD method is calculated as Median + 2 Median Absolute Deviation (MAD), which is defined as the median of the absolute deviations from the data's median. This method is quite robust against the effect that data outliers may have on the behavior of the whole population of data, what is very convenient having in mind that outliers are very common in geochemical datasets (Reimann & Caritat, 2017).

The second method is called Tukey Inner Fence (TIF) or upper whisker in a boxplot. It is based on the use of the upper whisker of a Tukey's boxplot (Tukey, 1997) as calculated by Q3 + 1,5 IQR where Q3 corresponds to the value of the third quartile (equivalent to the 75th percentile) and IQR is the inter quartile range (value of Q3 – value of Q1). This method depends only on the data distribution since it is based on the boxplot for its calculation.

The third method is based on the use of percentiles and it propose to use either 90th percentile, 95th percentile or 98th percentile of a given dataset to define the threshold. In this study it is decided to use the 95th percentile (P95) because it is the most frequently used upper percentile for the determination of metals background values in soil (Ander et al., 2013; APAT-ISS, 2006).

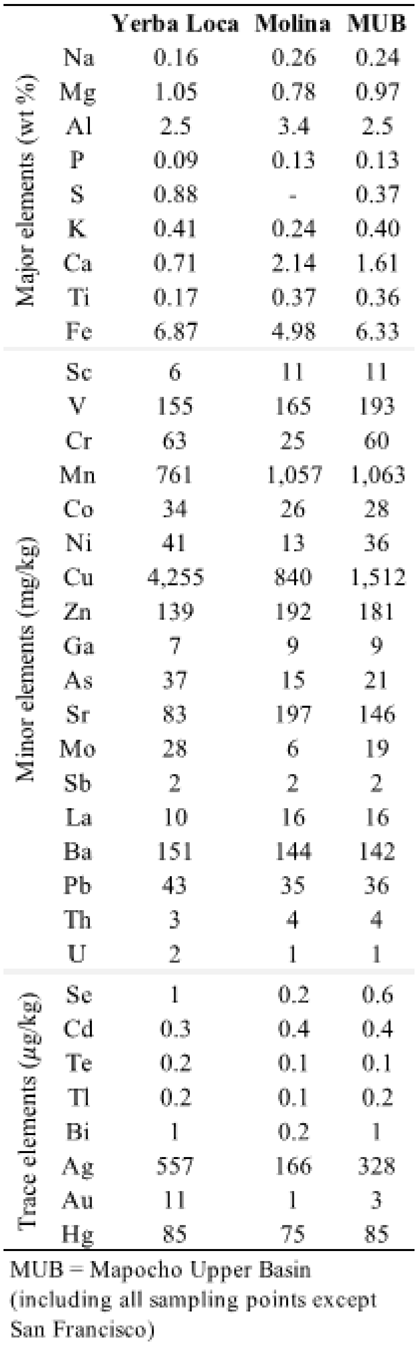
Appendix C (Excel file) offered detailed information of all the concatenated calculations performed until reaching the synthetic information of the geochemical background showed in Table 5. A comparison between the three methods tested (i.e., MAD, TIF and P95) reveals that the TIF method very frequently generate anomalous values that are even higher than the maximum measured value (values in red in the first sheet of Appendix C). This effect is due to both the structure of the equation used in the TIF method and to its application in Non-normal distributed data (Reimann and Caritat, 2017). As a result of these observations, the use of the TIF method to calculate the geochemical background of our samples was ruled out.

Regarding the values obtained with MAD and P95 methods, it was observed that both methods generated very similar values for most elements (MAD/P95 is typically close to 1, first sheet of Appendix C). In the discrepant results, it is always due to a higher value obtained for P95 method. The values obtained for Cu are a good example of an extreme possible discrepancy between MAD and P95. As previously shown, Cu concentrations in Sand&Silt samples is submitted to seasonal variations (Figure 3) that generate Non-normal distributed data with several extreme values with anomalous high concentrations. The equation used in the MAD method has the tendency to prioritize central values vs extreme values in a normal distributed data whereas the P95 method is conceived to prioritize the higher recorded values disregarding the distribution of the data. As a result, it was decided to select P95 as the best approach to generate the background values of our study; because for most elements and sampling points it will show very similar values than the MAD method but it will generated more realistic concentration values for the elements submitted to the appearance of seasonal extreme values (i.e., MAD/P95 values lower than 0.5 marked in red in the first sheet of Appendix C).

Once the P95 method was selected, it was decided to test if there was any significant difference in the results obtained considering just the Sand&Silt samples or combining the data from both Sand&Silt and Gravel samples (named as ALL in the second sheet of Appendix C). A great similarity ($P95_{Sand\&Silt}/P95_{ALL}$ values very close to 1) was observed for the vast majority of the generated data. The few discrepancies where mostly observed for the elements that were previously reported in this study as the main components of the major minerals forming the detrital clast of the Gravel samples (i.e., Ca, Mg, Na and K). For this reason, it was decided to use $P95_{ALL}$ as the most representative values of the heterogenous reality of the main river sediments at the Mapocho upper basin.

Finally, it was decided to generate a proposal with three different geochemical backgrounds to better represent the complex reality of the Mapocho upper basin, namely: Yerba Loca Basin, Molina and Mapocho Upper basin (MUB), using data from sampling points MUB1 to MUB3, just Molina and all the sampling points but San Francisco, respectively. Information from San Francisco River was not considered in the geochemical background of Mapocho Upper basin due to the low sediment transport that this river would have with respect to the other two tributaries. This situation is reflected both, in field observations in sections prior to the confluence with Yerba Loca Stream (Figure 6.a) and, in the very low contribution that this system represents to the annual discharge of Mapocho River, compared to the other studied tributaries (Valenzuela-Díasz et al., 2020). As can be observed on Table 5, the proposed values for most elements at Yerba Loca and Molina sub-basins typically differ from each other. In general, the geochemical background of the Yerba Loca sub-basin is typically enriched in metals. This is especially significant for Cu, but it is also relevant for S, Fe, As and Mo. The third generated geochemical background (MUB data in Table 5) synthesizes the reality of the whole Mapocho upper basin. As a result, it underestimates or overestimates some values if compared with the local geochemical backgrounds of Yerba Loca and Molina, respectively. Again, Cu can be used as a good example, showing concentrations of 1,512 mg/Kg, 4,255 mg/Kg and 840 mg/Kg for MUB, Yerba Loca and Molina, respectively. These differences may have very important implications in the event of the generation of a sediment quality guideline for the Mapocho upper basin and/or its specific sub-basins.

__Table 5.__ Mapocho's upper basin geochemical background.



		Yerba Loca	Molina	MUB
Major elements (wt %)	Na	0.16	0.26	0.24
	Mg	1.05	0.78	0.97
	Al	2.5	3.4	2.5
	P	0.09	0.13	0.13
	S	0.88	-	0.37
	K	0.41	0.24	0.40
	Ca	0.71	2.14	1.61
	Ti	0.17	0.37	0.36
	Fe	6.87	4.98	6.33
Minor elements (mg/kg)	Sc	6	11	11
	V	155	165	193
	Cr	63	25	60
	Mn	761	1,057	1,063
	Co	34	26	28
	Ni	41	13	36
	Cu	4,255	840	1,512
	Zn	139	192	181
	Ga	7	9	9
	As	37	15	21
	Sr	83	197	146
	Mo	28	6	19
	Sb	2	2	2
	La	10	16	16
	Ba	151	144	142
	Pb	43	35	36
	Th	3	4	4
	U	2	1	1
Trace elements (μg/kg)	Se	1	0.2	0.6
	Cd	0.3	0.4	0.4
	Te	0.2	0.1	0.1
	Tl	0.2	0.1	0.2
	Bi	1	0.2	1
	Ag	557	166	328
	Au	11	1	3
	Hg	85	75	85

MUB = Mapocho Upper Basin (including all sampling points except San Francisco)

2.4.4. Sediments geochemical background at the Mapocho upper basin vs Sediment Quality Guidelines (SQG)

Original Sediment Quality Guidelines used to compare bulk chemical concentrations of the sediments with some reference or background values (Burton Jr, 2002) and they were very dependent on local geochemical effects, whereas more recent SQG are based on the adverse effect that a specific compound (organic and inorganic) in the sediments may have on benthic macroinvertebrates (Burton Jr, 2018). Many different SQGs have been developed across the World, like in North America (Smith et al., 1996), Australia and New Zealand (ANZECC, 1997; Simpson et al., 2013), and Hong Kong (Chapman et al., 1999a). Despite being developed for the specific reality of each region of the World, they do not differ too much between them (Burton Jr, 2002). All those approaches typically define two threshold levels to characterize the toxicity of the transported sediments: a first one below which adverse toxic effects rarely occur (threshold effect concentrations, TEC) and a second one above which adverse toxic effects are likely to occur on the associated organisms (probable effect concentration, PEC). On this regard, MacDonald et al. (2000) generated a review paper on this topic and recorded at least 6 different threshold effect concentrations and 5 different probable effect concentrations indexes applied around the World. To homogenize all the existing information, they created the Consensus Based TECs and PECs for As, Cd, Cr, Cu, Pb, Hg, Ni and Zn (as well as for other common organic pollutants) by determining the geometric means of previously published TEC and PEC values. It should also be considered that SQGs are usually applied in places where more than one potential toxic agent converges, with the concomitant possibility of presenting synergistic or antagonistic effects between them. Therefore, some authors like Michelsen (1999) proposed that a set of representative and biologically varied SQG should be implemented for each specific field site, so that they can be applied to communities rather than just specific species. Finally, it’s important to consider that the bioavailability of pollutants is influenced by a series of factors which have not been considered in SQGs, such as the grain size and the surface contact of the particles, the hardness, the kind of organic matter, water pH, space-time chemical dynamics, resuspension and deposition of material and bioturbation, among several other factors (Burton Jr, 1991-2002).

Figure 4 shows a comparison between the concentration ranges of 10 metals and metalloids (typically included in SQG as potential pollutants) in the sediments of the present study and TECs (light blue lines) and PECs (dark blue lines) proposed by the Consensus-Based Sediment Quality Guidelines (MacDonald et al., 2000). Calculated geochemical backgrounds for each specific element and basin is also shown as horizontal red lines. Yerba Loca`s sediment background concentrations for all elements except Cd and Hg are consistently higher than the Consensus-Based TECs and even higher than the Consensus-Based PECs for Fe, Cu and As. Special attention should be placed in Cu, which background concentration is 28 times higher than the Consensus-Based PEC. On the other hand, Molina sub-basin is characterized by fewer elements showing sediment concentrations higher that the Consensus-Bases TECs (i.e., Fe, Mn, Zn, Cu and As) and even fewer slightly higher than the Consensus-Based PECs (i.e., Fe and Cu). Considering the Upper Mapocho Basin as a whole, it can be observed a behavior very similar to the one showed by Yerba Loca but slightly smoothed due to the behavior of the sediments at the Molina Sub-basin. Specifically, all elements except Cd and Hg are consistently higher than the Consensus-Based TECs and just Fe and Cu are higher than the Consensus-Based PECs. According to these results, the Mapocho upper basin as a whole, and specially some natural sub-basins like Yerba Loca, has a natural geochemical background for some elements so high that probable toxic effects on the river ecosystem may be expected. However, it is important to notice that the employed Consensus-Based TEC and PEC values are not specifically obtained using the existing organism in the waters of these particular streams and rivers. In this regard, it’s essential to perform ecotoxicological studies using the local fauna and flora, corroborating these possible toxic effects of the natural geochemical background, to generate a reliable sediment toxicity assessment on any water course at hydrothermally-altered high-mountainous regions.

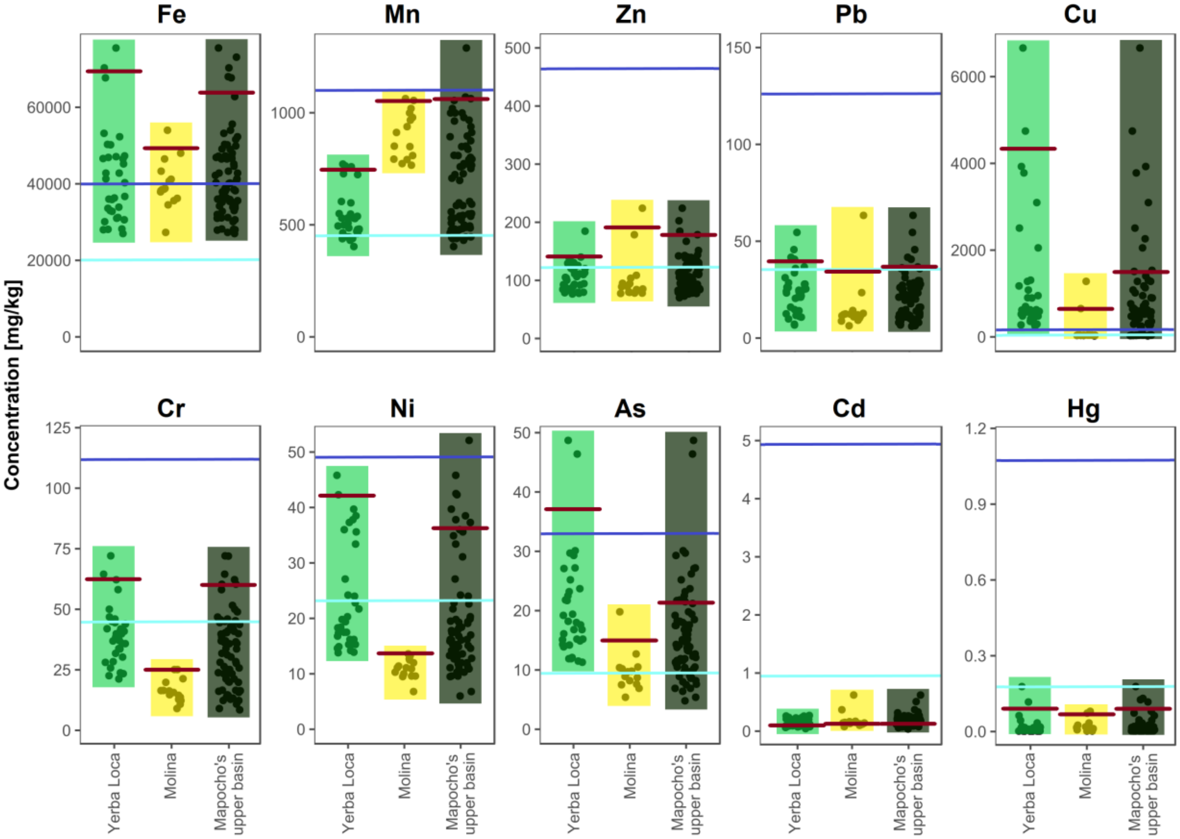


Figure 4. *Comparison between the concentration at Yerba Loca, Molina and Mapocho of some metals and metalloids typically included in Sediment Quality Guidelines (SQG) and some threshold values frequently reported on SQGs. Black dots= individual samples; red lines= background values proposed on Table 5; light blue line= threshold effect concentration (TEC) and; dark blue line= probable effect concentration (PEC) according to the Consensus-Based Sediment Quality Guidelines from MacDonald et al., 2000. Fe and Mn TEC and PEC values are from Bucham et al., 2008.*

2.5. IMPLICATIONS AND CONCLUDING REMARKS

From the study carried out on the behavior of high mountainous basins hydrothermally-altered, focused on the generation and application of a specific background for this kind of hydrological environment; in the next paragraphs are shown the principal implications.

As it may be expected, it was confirmed that the main mineral phases comprising the detrital sediments (i.e. plagioclases, quartz and, phyllosilicates) are consistent with major rock forming minerals of the main petrological units defined in this geological setting. Most importantly, it was observed that the relative abundance of the transported minerals does not present significant monthly variations nor apparent trends during the sampling period (September 2016 to November 2017). On this regard, two of the three sub-basins under study (i.e., Yerba Loca and Molina) showed some differences in the proportion of the main mineral phases comprising their sediments (in accordance with the specific petrology of each sub-basin), resulting the mineralogical signature of the final confluence (Mapocho Upper basin) the sum of the contribution from each of the sub-basins under study.

In general terms, the geochemical composition of the clastic sediments was consistent with the geochemistry inferred from the mineralogical study. This resemblance can be attributed to the fact that the detrital material is basically the same for both sediment fractions (as reported by the XRD study), and as a consequence, they both showed similar concentrations for the elements that typically make up these detrital clasts (Al, Ca, Mg and Na). However, some important discrepancies in the abundance and trends of certain major and minor elements was observed. Specifically, sediments with a smaller grain size (i.e., Sands & Silts) showed higher concentrations than the bigger grain size counterparts for elements such as Fe, S, Cu and As. This behavior was particularly evident in the Yerba Loca sub-basin, because it is developed over the region comprising rocks that suffered hydrothermalism and, as a consequence, the creek suffered a problem of acid rock drainage and the riverbed developed a higher proportion of Al- and Fe-precipitates. Those precipitates are very fine grained and, although may form isolated patches of precipitates, they typically form part of the Sand & Silt fraction of the sediments. Following this reasoning, it was observed that the Sand & Silt fraction showed seasonal trends for the concentrations of Fe-S and Al-Cu that perfectly match the seasonal appearance of reddish-brown and white precipitates at the Yerba Loca.

Regarding the specific sub-basins or the general Mapocho Upper basin backgrounds generated in the present study, it was observed how the geochemical background of the Yerba Loca (where the rocks suffered an important hydrothermal alteration) is typically high for some metals. This situation occurs with the elements that present seasonal variations, which generate a non-normal distribution product of various extreme values with anomalous high concentrations (i.e., especially significant for Cu, but also relevant for S, Fe, As and Mo). On the other hand, the geochemical background proposed for the Molina sub-basin (where the rocks did not suffer almost any hydrothermal alteration) commonly exhibited lower values for most metals. As a result, the third generated geochemical background (synthesizing the reality of the whole Mapocho upper basin) underestimates or overestimates some values if compared with the local geochemical backgrounds of Yerba Loca and Molina, respectively.

When this background levels were compared with the Consensus-Based (CB) Sediment Quality Guidelines, all the elements (except Cd and Hg) showed background values that were consistently higher than the values set by the CB Threshold Effect Concentration (TEC) and even higher than the CB Probable Effect Concentration (PEC) for Fe and Cu. According to these results, the whole basin and, in particular the hydrothermally-altered sub-basin, present a geochemical background so high for some elements that, theoretically, there may cause probable toxic effects on the ecosystem of their watercourses.

The mineralogical similarities between the creek sediments and the bedrocks shown in this study, open the possibility to use the information in geologic maps as a valid first approximation to infer the expected mineralogy and geochemistry of the creek sediments (in the case of non-having a suitable geochemical background). Furthermore, this research has served to lift the geochemical imprint of the sediments transported by this kind of rivers, which may serve as indicators of the presence of hypogenic copper sulfides or, the development of supergene processes, which is relevant to mining exploration. However, our results also clearly state the paramount importance of having a solid geochemical background before any attempt of a sediment risk assessment is made at hydrothermally-altered high-mountainous regions, which cover a significant amount of the river systems from South America and many other areas in the world. Finally, it's essential to carry out site specific ecotoxicological studies considering local flora and fauna, in order to corroborate the possible toxic effects of the natural geochemical background. These studies should lead to the generation of specific TEC and PEC that are more suitable to be used in watercourses draining high-mountainous hydrothermally-altered regions.

2.6. ACKNOWLEDGMENTS

This work was funded under the eaves of the *CONICYT/PIA* Project AFB180004, Advanced Mining Technology Center (AMTC) from the University of Chile, which also provided all the necessary assistance before, during and after the sampling campaigns. We also thank each of the technicians and professionals who in one way or another contributed in this study.

2.7. REFERENCES

Aguirre, L. (1960). Geología de los Andes de Chile Central (provincia de Aconcagua). *Instituto de Investigaciones Geológicas, Boletín, No 9*, 70 p.

Ander, E. L., Johnson, C. C., Cave, M. R., Palumbo-Roe, B., Nathanail, C. P., & Lark, R. M. (2013). Methodology for the determination of normal background concentrations of contaminants in English soil. *Science of the Total Environment*, *454-455*, 604-618. doi:https://doi.org/10.1016/j.scitotenv.2013.03.005

ANZECC. (1997). ANZECC interim sediment quality guidelines. *Report for the Environmental Research Institute of the Supervising Scientist. Sydney, Australia.*

APAT-ISS. (2006). Protocollo Operativo per la determinazione dei valori di fondo de metalli/metalliodi nei suoli dei siti d' interesse nazionale. *Agenzia per la Protezione dell 'Ambiente e per i Servizi Tenici Instituto Superiore di Sanità. 2006 (Revisione 0).*

Best, M. G., & Christiansen, E. C. (2003). *Igneous Petrology. 1st Edition. 729 pp.* Blackwell Science.

Bingham, J., & Nordstrom, D. K. (2000). Iron and aluminum hydroxysulfates from acid sulfate waters. *Reviews in mineralogy and geochemistry*, *40 (1)*, 351-403. doi:http://doi.org/10.2138/rmg.2000.40.7

Brenning, A. (2005). Geomorphological, Hydrological and Climatic Significance of Rock Glaciers in the Andes of Central Chile. *Permafrost and Periglacial Processes*, *16*, 231-240. doi:https://doi.org/10.1002/ppp.528

Buchman, M. F. (2008). NOAA Screening Quick Reference Tables. *NOAA OR&R Report 08-1, Seattle WA, Office or Response and Restoration Division, National Oceanic and Atmospheric Administration*, 34p. Obtenido de repository.library.noaa.gov/view/noaa/9327

Burton Jr., G. A. (1991). Assessing the toxicity of freshwater sediment. *Environmental Toxicology and Chemistry, 10*, 1585-1627. doi: https://doi.org/10.1002/etc.5620101204

Burton Jr., G. A. (2002). Sediment quality criteria in use around the world. *Limnology, 3*, 65-75. doi:https://doi.org/10.1007/s102010200008

Burton Jr., G. A. (2013). Assessing Sediment Toxicity: Past, Present, and Future. *Environmental Toxicology and Chemistry, Vol.32, No. 7:*, 1438-1440. doi:http://doi.org/10.1002/etc.2250

Burton Jr., G. A. (2018). Breaking from tradition: establishing more realistic sediment quality guidelines. *Environmental Science and Pollution Research, 25*, 3047-3052. doi:https://doi.org/10.1007/s11356-016-8338-x

Butler, B. M. (2020). Mineral sources of aqua regia extractable base cations in Scottish soils interpreted from Cubist models trained with quantitative mineralogy data. *Chemical Geology 551*, 119773. doi:https://doi.org/10.1016/jchemgeo.2020.119773

Cain, D. J., Luoma, S. N., & Wallace, W. G. (2004). Linking metal bioaccumulation of aquatic insects to their distribution patterns in a mining-impacted river. *Environmental Toxicology and Chemistry, 23*, 1463-1473. doi: https://doi.org/10.1897/03-291

Caraballo, M. A., Sarmiento, A. M., Sánchez-Rodas, D., Nieto, J. M., & Parviainen, A. (2011). Seasonal variations in the formation of Al and Si rich Fe-stromalites in the highly polluted acid mine drainage of Agua Agria Creek (Tharsis, SW Spain). *Chemical Geology 284,*, 97-104. doi:https://doi.org/10.1016/j.chemgeo.2011.02.012

Caraballo, M. A., Wanty, R. B., Verplanck, P. L., Navarro-Valdivia, L., Ayora, C., & Hochella, Jr., M. F. (2019). Aluminum mobility in mildly acidic minedrainage: interactions between hydrobasaluminite, silica and trace metals from the nano to the meso-scale. *Chemical Geology, 519*, 1-10. doi:https://doi.org/10.1016/j.chemgeo.2019.04.013

Chapman, P. M., Allard, P. J., & Vigers, G. A. (1999a). Development of sediment quality values for Hong Kong special administrative region: a possible model for other jurisdictions. *Marine Pollution Bulletin, 38(3)*, 161-169. doi:https://doi.org/10.1016/S0025-326X(98)00162-3

Charrier, R., Wyss, A. R., Flynn, J. J., Swisher, C. C., Norel, M. A., Zapata, F., . . . Novacek, M. J. (1996). New evidence for Late Mesozoic-Early Cenozoic evolution of the Chilean Andes in the Upper Tinguiririca Valley (35°S). Central Chile. *Journal of South American Earth Sciences, 9*, 393-422. doi:https://doi.org/10.1016/S0895-9811(96)00035-1

Deckart, K., Godoy, E., Bertens, A., Jeréz, D., & Saeed, A. (2010). Barren Miocene Granitoids in the Central Andean Metallogenic Belt, Chile: Geochemistry an Nd-Hf and U-Pb Isotope

Systematics. *Andean Geology, 37*, 1-31. doi:https://doi.org/10.4067/S0718-71062010000100001

Furrer, G., Phillips, B. L., Ulrich, K. U., Pöthig, R., & Casey, W. H. (2002). The origin of aluminum flocs in polluted streams. *Science, 297,* 2245-2247. doi:https://doi.org/10.1126/science.1076505

Garreaud, R. D., Alvarez-Garreton, C., Barichivich, J., Boisier, J. P., Christie, D., Galleguillos, M., . . . Zambrano-Bigiarini, M. (2017). The 2010-2015 megadrought in central Chile: impacts on regional hydroclimate and vegetation. *Hydrology and Earth System Sciences, 21*, 6307-6327. doi:https://doi.org/10.5194/hess-2017-191

Gutiérrez, F., Pincetti, G., Payacán, I., Tristram, E., & Vela, I. (2015). Composición Natural de las Aguas en la Cuenca alta del Santuario de la Naturaleza Yerba Loca, Santiago. *Congreso Geológico Chileno, 14.* La Serena, Chile, 292-295.

International Standard Organization (1995). Soil quality. Extraction of trace elements soluble in Aqua Regia, ISO 11466.

Jamieson, H. E., Walker, S. R., & Parsons, M. B. (2015). Mineralogical characterization of mine waste. *Applied Geochemistry, 57,* 85-105. doi:http://dx.doi.org/10.1016/j.apgeochem.2014.12.014

Khan, R., Parvez, S., Jolly, Y. N., Haydar, A., Alam, F., Khatun, A., . . . Hossain, S. M. (2019). Elemental abundance, natural radioactivity and physicochemical records of a southern part of Bangladesh: Implications for assessing the environmental geochemistry. *Environmental Nanotechnology, Monitoring & Management, 12,* 1-13. doi:https://doi.org/10.1016/j.enmm.2019.100225

Klohn, C. (1960). Geología de la Cordillera de los Andes de Chile Central (provincias de Santiago, O'Higgins, Colchagua y Curicó). *Instituto de Investigaciones Geológicas, Boletín No. 8, 95 p. Santiago*. Obtenido de http://www.sudoc.fr/112356141

Liu, H., Zhang, K., Chai, L., Yang, Z., Yang, W., Liao, Q., . . . Liu, Y. (2017). A Comparative Evaluation of Different Sediment Quality Guidelines for Metal and Metalloid Pollution in the Xiangjiang River, Hunan, China. *Archives of Environmental Contamination and Toxicology, 73:,* 593-606. doi:https://doi.org/10.1007/s00244-017-0436-3

MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystem. *Archives of Environmental Contamination and Toxicology, 39,* 20-31. doi:https://doi.org/10.1007/s002440010075

Massoudieh, A., Bombardelli, F. A., & Ginn, T. R. (2010). A biogeochemical model of contaminant fate and transport in river waters and sediments. *Journal of Contaminant Hydrology, 112*, 103-117. doi:http://doi.org/10.1016/j.jconhyd.2009.11.001

Michelsen, T. C. (1999). Principles for assessing the reliability of sediment quality guidelines (SQGs). *SETAC News 19(4)*, 22-23.

Milićević, T., Relić, D., Škrivanj, S., Tešić, Ž., & Popović, A. (2017). Assessment of major and trace element bioavailability in vineyard soil applying different single extraction procedures and pseudo-total digestion. *Chemosphere, 171,* 284-293. doi:https://doi.org/10.1016/j.chemosphere.2016.12.090

Navarrete-Calvo, A. (2020). Hydrochemical variations of acid rock drainage controlled by hydrological processes and Al-Fe hydroxisulfates pH buffer minerals at high-mountainous basins (Yerba Loca basin, Chile). *Master's thesis. Geology Department, University of Chile.*

Nyström, J. O., Vergara, M., Morata, D., & Levi, B. (2003). Tertiary volcanism during extension in the Andean foothills of Central Chile (33°15'-33°45'S). *Geological Society of America Bulletin, 115,* 1523-1537. doi:https://doi.org/10.1130/B25099.1

Rao, C. R. M., Sahuquillo, A., Lopez Sanchez, J. F. (2008). A Review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. *Water Air Soil Pollution 189*, 291-333. doi:https://doi.org/10.1007/s11270-007-9564-0

Reimann, C., & Caritat, P. (2017). Establishing geochemical background variation and threshold values for 59 elements in Australian surface soil. *Science of the Total Environment, 578,* 633-648. doi:https://doi.org/10.1016/j.scitotenv.2016.11.010

Reimann, C., Filzmoser, P., & Garrett, R. G. (2005). Background and threshold: Critical comparison of methods of determination. *Science of the Total Environment, 346(1-3),* 1-16. doi:https://doi.org/10.1016/j.scitotenv.2004.11.023

Rivano, S., Godoy, E., Vergara, M., & Villarroel, R. (1990). Redefinición de la Formación Farellones en la Cordillera de los Andes de Chile Central (32-34°S). *Revista Geológica de Chile, 17,* 205-214. Obtenido de http://www.researchgate.net/publication/267808429

Rothwell, K. A., & Cooke, M. P. (2015). A comparison of methods used to calculate normal background concentrations of potentially toxic elements for urban soil. *Science of the Total Environment, 532*, 625-634. doi:https://doi.org/10.1016/j.scitotenv.2015.06.083

Rütllant, J., & Fuenzalida, H. (1991). Synoptic aspects of the Central Chile rainfall variability associated with the southern oscillation. *International Journal of Climatology, 11*, 63-76. doi:https://doi.org/10.1002/joc.3370110105

Sánchez-España, J., Yusta, I., & Burgos, W. D. (2016). Geochemistry of dissolved aluminum at low pH: hydrobasaluminite formation and interaction with trace metals, silica and microbial cells under anoxic conditions. *Chemical Geology, 441,* 124-137. doi:https://doi.org/10.1016/j.chemgeo.2016.08.004

Selles, D., & Gana, P. (2001). Geología del área Talagante y San Francisco de Mostazal: regiones Metropolitana de Santiago y del Libertador General Bernardo O'Higgins. Santiago, Chile. *Servicio Nacional de Geología y Minerúa. Mapa a escala 1:100.000*.

SERNAGEOMIN. (2003). *Carta geológica de Chile. Geological Map Scale, 1:1,000,000.* Obtenido de http://bibliotecadigital.ciren.cl/handle/123456789/16327

Simpson, S. L., Batley, G. E., & Chariton, A. A. (2013). *Revision of the ANZECC/ARMCANZ sediment quality guidelines.* CSIRO Land and Water Report 8/07, Lucas Heights, NSW, Australia. doi:https://doi.org/10.4225/08/5894c6184320c

Smith, S. L., MacDonald, D. D., Keenleyside, K. A., Ingersoll, C. G., & Field, J. (1996). A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *Journal of Great Lakes Research, 22*, 624-638. doi:https://doi.org/10.1016/S0380-1330(96)70985-1

Tarbuck, E. J., & Lutgens, F. K. (2005). *Ciencias de la Tierra: Una introducción a la geología física. 8th Edition. 710 pp.* Pearson Prentice Hall.

Thiele, R. (1980). Hoja Santiago. Región Metropolitana. *Instituto de Investigaciones Geológicas de Chile, Carta Geológica de Chile, No.39*, 51p. Obtenido de https://bibliotecadigital.ciren.cl/handle/123456789/20526

Toro, J. C., Ortúzar, J., Zamorano, J., Cuadra, P., Hermosilla, J., & Spröhnle, C. (2012). Protracted Magmatic-Hydrothermal History of the Río Balnco-Los Bronces District, Central Chile: Development of World's Greatest Known Concentration of Copper. *Society of Economic Geologists, Special Publication*, 105-126. doi:https://doi.org/10.5382/SP.16.05

Tukey, J. W. (1977). *Exploratory Data Analysis.* Addison Wesley, Reading.

Tume, P., González, E., Reyes, F., Fuentes, J. P., Roca, N., Bech, J., & Medina, G. (2019). Sources analysis and health risk assessment of trace elements in urban soil of Hualpen, Chile. *Catena, 175*, 304-316. doi:https://doi.org/10.1016/j.catena.2018.12.030

Valenzuela-Diaz, M. J., Navarrete-Calvo, A., Caraballo, M. A., McPhee, J., García, A., Correa-Burrows, J. P., & Navarro-Valdivia, L. (2019). Environmental water quality standards and management in the overlap between natural protected areas and copper mining activities (upper Mapocho River Basin, Santiago, Chile).

Wall, R., Selles, D., & Gana, P. (1999). Área Tiltil y Santiago, Región Metropolitana. Santiago, Chile. *Servicio Nacional de Geología y Minería. Mapa a escala 1:100.000*.

Wyss, A. R., Flynn, J. J., Norell, M. A., Swisher, C. C., Novacek, M. J., McKenna, M. C., & Charrier, R. (1994). Paleogene mammals from the Andes of the central Chile: A preliminary taxonomic, biostratigraphic, and geochronologic assessment. *American Museum Novitates, 3098*, 1-31. Obtenido de https://hdl.handle.net/2246/4994

CAPÍTULO 3

Supplementary material

3.1. Mapocho's upper basin

3.1.1. Yerba Loca Stream

Yerba Loca Stream's is one the three principal sub-basins that make up the upper basin of Mapocho River, which shows great geochemical variability both, spatially and temporarily speaking, evidencing itself as a high mountainous basin affected by ARD. This streams is born from the confluence of two glacial origin watercourses, coming from El Rincón and La Paloma Glaciers, furthermore, this is associated with high turbidity water, which acquires a whitish hue due to the presence of neoformed mineral phases mainly compound by Al. Figure 5.a-b show the turbidity of the stream in its headwaters and, particularly Figure 5.a shows two zooms with a detail of the whitish precipitates: on the left it can be seen how the neoformed phases are stored on the river bed, concentrating among the transported sediments; on the other hand, a 0.5-1.0 cm thickness cobble is shown on the right. Furthermore, these mineral phases, which are presumably resulting from the interaction of both waterways, can either be transported by suspension through the water or decant and store next to the background sediments.

Downstream, and as to the stream converge different watercourses coming mainly from the melting of snow, changes in physicochemical conditions are leading to the precipitation of Fe mineral phases, which are characterized by a shades of orange coloration, for example, in Figure 5.c this coloration can be seen on both edges of the river, while through it it's seen how the water still presents a certain whitish turbidity degree. On the other hand, in Figure 5.d it can be seen how in certain sections of the middle basin it's possible to appreciate old different episodes of amorphous Fe-phases precipitation giving rise to different shades of orange, in addition, in this picture it's also shown a zoom with a detail of the kind of sediments which is transported through Yerba Loca Stream, among which, remains of apparently hydrothermal origin breccias are found. Finally, a few kilometers before the confluence with San Francisco River, it begins to precipitate again whitish neoformed phases, however, they do it in a much smaller amount compared to the headwaters precipitates, in addition, both edges show colorations that account for ancient periods of Fe neoformed phases precipitation (Figure 5.e-g). On the other hand, just before the confluence, there is a period of the year where these precipitates have been seen with greenish hues (Figure 5.f), which has been associated with high Cu concentration (relative to the common whitish neoformed phases).

Figure 5. *Spatial variation in Yerba Loca Stream: a-b. Headwaters; c-d. Middle basin area and; e-g. Lower basin area.*

3.1.2. San Francisco River

Generally, San Francisco River doesn't show so much variation along the basin, which is mainly associated with the ecological regime to which it's subjected as a result of the mining activity in the headwater area, thus, the middle zone of the basin is characterized as a low flow crystalline watercourse surround by vegetation (Figure 6.a). On the other hand, after the confluence with Yerba Loca Stream conditions change markedly, for example, due to the increase in the flow, the system begins to transport a greater amount of suspended material, which is reflected in the turbidity. Furthermore, it also shows an orange coloration in the rocks on both sides of the river (Figure 6.b), which accounts for ancient episodes of Fe mineral phases precipitation. The latter would account for the geochemical influence of Yerba Loca Stream on the upper basin in general, which even becomes reflected in Mapocho River (the final confluence of the studied system), for example, Figure 6.c shows the confluence of San Francisco and Molina Rivers (April 2017) in which it's shown how the former presents a white turbidity with greenish hue, associated with Al-precipitates with high Cu content. This situation has only been seen at the end of summer – beginning of autumn, so the rest of the year San Francisco River (after Yerba Loca Stream) has a medium to high light brown turbidity, which is associated with clastic suspended material transportation.

***Figure 6**. Spatial variation in San Francisco River: a. Middle basin area; b. Lower basin area and; c. San Francisco and Molina River's confluence (April 2017).*

3.1.3. Molina River

The mouth of Molina River is characterized by a large amount of surrounding vegetation, which covers the ground to the watercourse, with the exception of certain beaches which are generated in the internal zones of the associated meanders. Throughout the year its water has high turbidity, presumably given by the large amount of suspended material which carries this system and, whose coloration is earthy hue (Figure 7.a). Valenzuela-Díaz et al. (2019) propose that Molina River represents the largest contribution of water to Mapocho River during the most of the year, which according to this study, is also reflected in a higher amount of transported suspended material, thus, during most of the year (autumn, winter and much of the spring) the influence of Molina River over the turbidity of Mapocho River is seen at the confluence of both rivers, Molina and San Francisco (Figure 7.b).

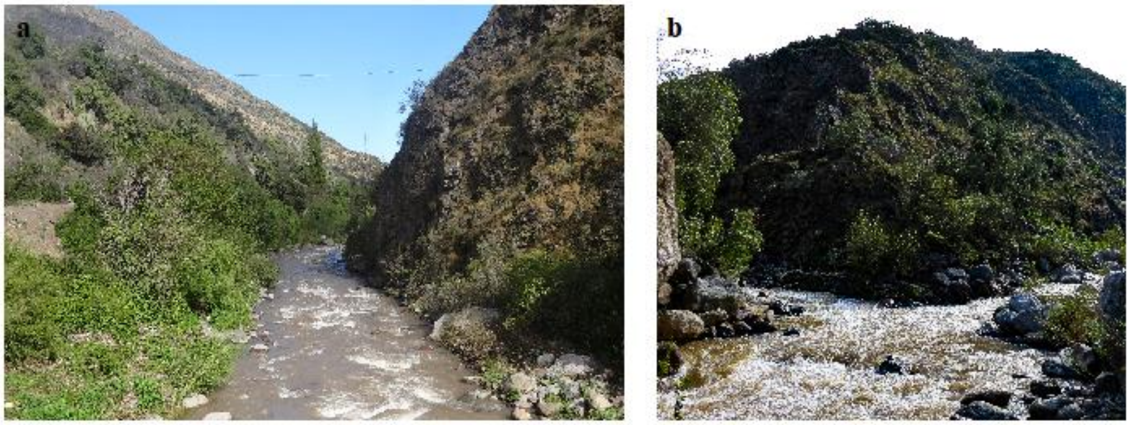


***Figure 7**. Molina River's confluence: a. Nearby vegetation and high turbidity water characterize this area and; b. Molina and San Francisco River's confluence (representative view).*

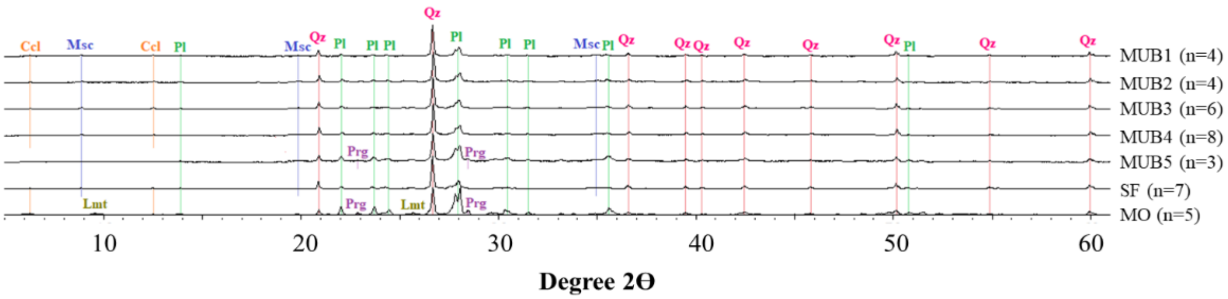
***Table 6.** Petrological and mineralogical characteristics of the geological units at Mapocho's upper basin.*

Geological Units	**Age**	**Petrology**	**Mineralogy**	**References**
Intrusive Units	Eocene-Miocene	Granodiorites to monzogranites and	Hornblende, biotite, quartz, plagioclases	(1, 4, 5)
		Granodiorites to diorites	Plagioclases, amphiboles, pyroxenes, olivines	
Abanico Fm.	Upper Eocene?-Early Miocene	Basaltic to dacitic lavas	Andesine-labradorite, augite, magnetite, hypersthene, olivine, oxihornblende, zeolites, chlorite	(1, 2, 4, 5, 6,7)
		Acid tuff and breccia with andesitic clasts	Quartz, plagioclase, k-feldspar, biotite, Muscovite, orthopyroxene, clinopyroxene, Fe-Ti oxides, glass	
		Fine to medium grain size sedimentary rocks	Quartz, clay minerals, plaglioclase, micas	
Farellones Fm.	Early-Middle Miocene	Andesitic-basaltic to dacitic lavas	Plagioclase, orthopyroxene, clinopyroxene, hornblende, quartz, biotite, k-feldspar, Fe-Ti oxides	(2, 3, 4, 5, 6)
		Acid pyroclastic rocks with andesite, dacite and obsidian clasts	Hematite, quartz, plagioclases	
Rio Blanco-Los Bronces-Los Sulfatos Breccia Facies	Miocene-Pliocene	Granidiorite, quartz-monzonite and diorites clasts	Albite, k-feldspar, chlorite, tremolite, biotite, sericite	(3, 4, 5)
		Matrix (veins)	Quartz, tourmaline, specularite, anhydrite, pyrite, chalcopyrite, bornite, molybdenite, galena and sphalerite, biotite, anhydrite, magnetite, chlorite, k-feldspar, sericite, apatite, epidote	

(1) Wall et al., 1999; (2) Nyström et al., 2003; (3) Toro et al., 2012; (4) Sernageomin, 2003; (5) Thiele, 1980; (6) Best & Christiansen, 2003; (7) Tarbuck & Lutgens, 2005

3.2. Sediments mineralogical analysis

a) Sands & Silts fraction



b) Gravels fraction

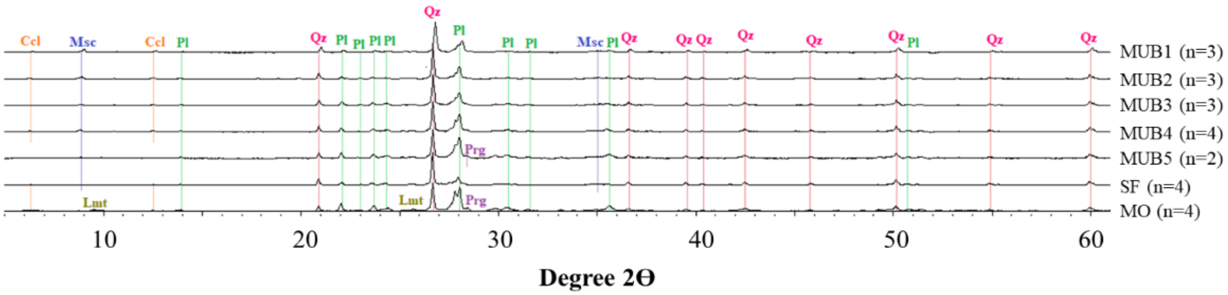


Figure 8. *Diffractograms associated with the representative mineralogy of each sampling point, from the upper Yerba Loca's basin (MUB1) to the final confluence to Mapocho River (MUB5), including San Francisco and Molina Rivers. On the right side of each spectrum, next to the name of the sampling point, the number of analyzed samples by each one es indicated. a. Sands & Silts fraction and; b. Gravels fraction.*

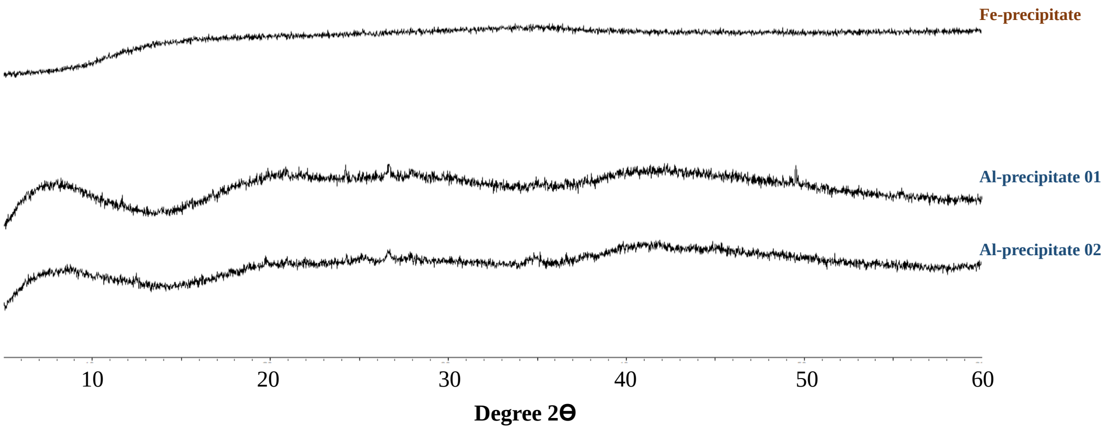
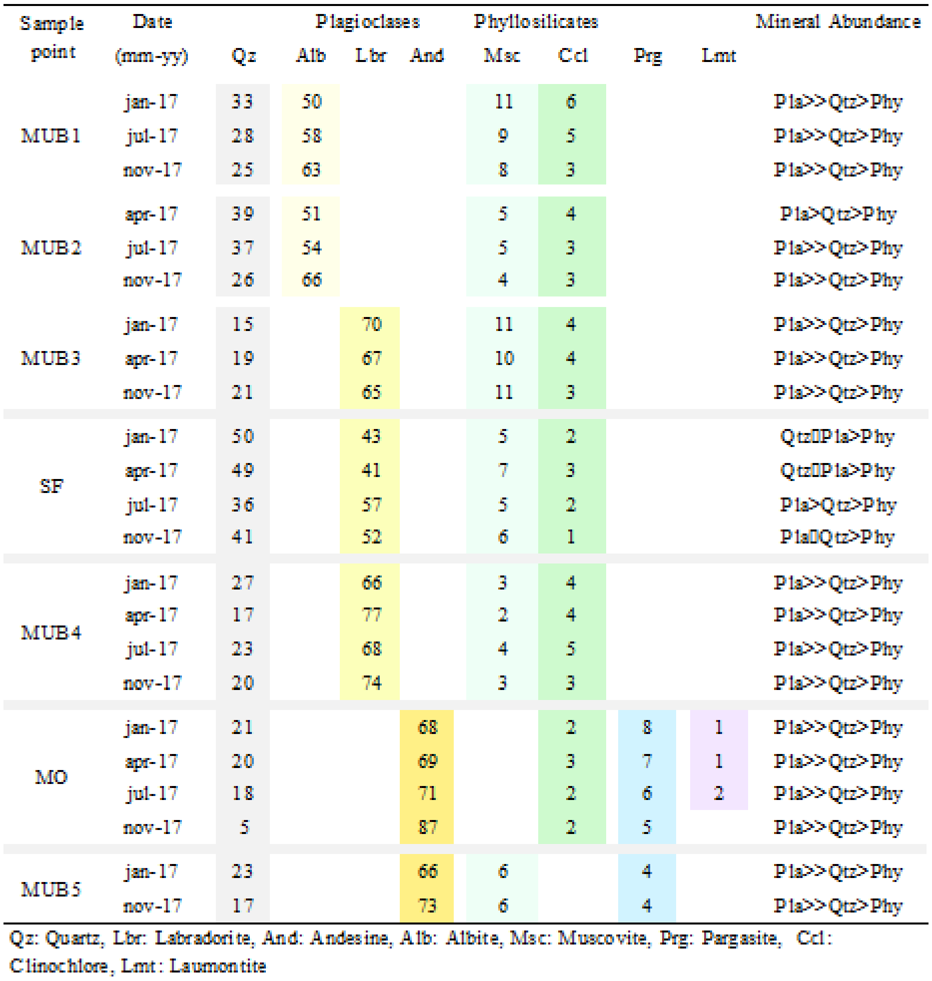


Figure 9. *Diffractograms of the Fe- and Al-rich precipitates at MUB1.*

***Table 7.** Gravels identification and semiquantification (wt%) by XRD.*



Sample point	Date (mm-yy)	Qz	Plagioclases			Phyllosilicates		Prg	Lmt	Mineral Abundance
			Alb	Lbr	And	Msc	Ccl			
MUB1	jan-17	33	50			11	6			Pla>>Qtz>Phy
	jul-17	28	58			9	5			Pla>>Qtz>Phy
	nov-17	25	63			8	3			Pla>>Qtz>Phy
MUB2	apr-17	39	51			5	4			Pla>Qtz>Phy
	jul-17	37	54			5	3			Pla>>Qtz>Phy
	nov-17	26	66			4	3			Pla>>Qtz>Phy
MUB3	jan-17	15		70		11	4			Pla>>Qtz>Phy
	apr-17	19		67		10	4			Pla>>Qtz>Phy
	nov-17	21		65		11	3			Pla>>Qtz>Phy
SF	jan-17	50		43		5	2			Qtz□Pla>Phy
	apr-17	49		41		7	3			Qtz□Pla>Phy
	jul-17	36		57		5	2			Pla>Qtz>Phy
	nov-17	41		52		6	1			Pla□Qtz>Phy
MUB4	jan-17	27		66		3	4			Pla>>Qtz>Phy
	apr-17	17		77		2	4			Pla>>Qtz>Phy
	jul-17	23		68		4	5			Pla>>Qtz>Phy
	nov-17	20		74		3	3			Pla>>Qtz>Phy
MO	jan-17	21			68		2	8	1	Pla>>Qtz>Phy
	apr-17	20			69		3	7	1	Pla>>Qtz>Phy
	jul-17	18			71		2	6	2	Pla>>Qtz>Phy
	nov-17	5			87		2	5		Pla>>Qtz>Phy
MUB5	jan-17	23			66	6		4		Pla>>Qtz>Phy
	nov-17	17			73	6		4		Pla>>Qtz>Phy

Qz: Quartz, Lbr: Labradorite, And: Andesine, Alb: Albite, Msc: Muscovite, Prg: Pargasite, Ccl: Clinochlore, Lmt: Laumontite

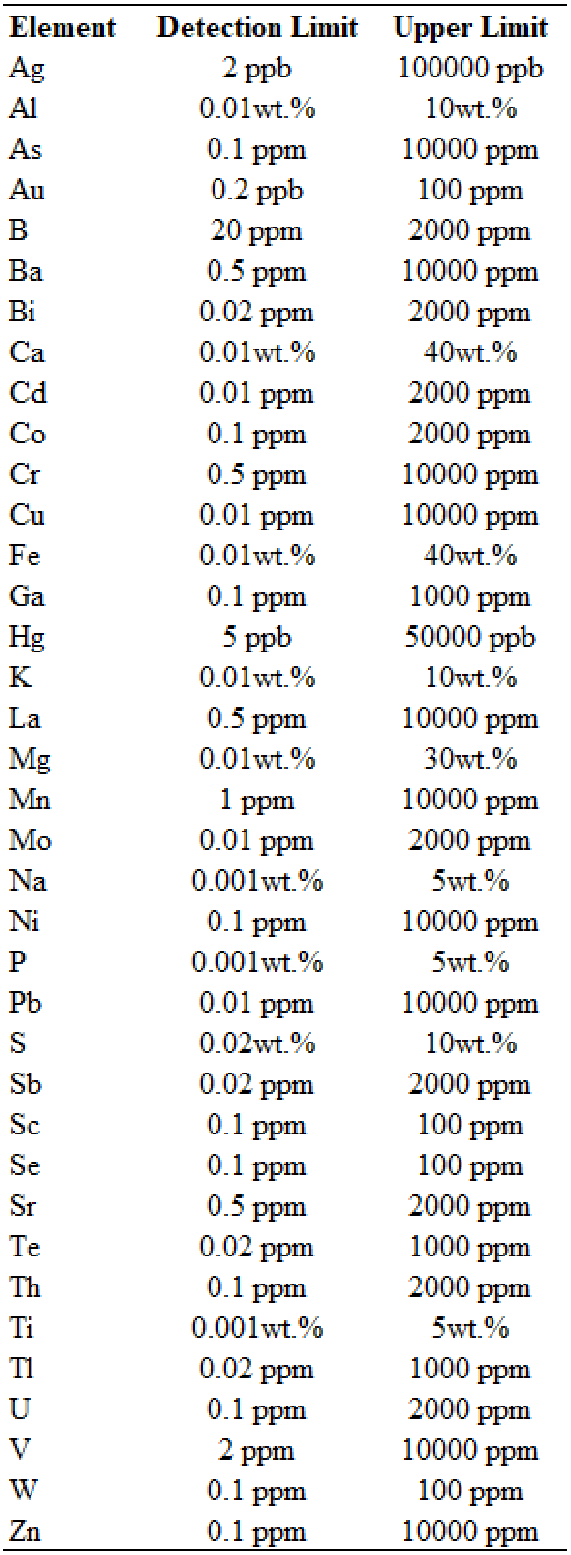
Table 8. *Sands & Silts identification and semiquantification (wt%) by XRD.*

Sample point	Date (mm-yy)	Qz	Plagioclases			Phyllosilicates		Prg	Lmt	Mineral Abundance
			Alb	Lbr	And	Msc	Ccl			
MUB1	sept-16	39	44			13	4			Pla▯Qtz>Phy
	jan-17	39	44			13	4			Pla▯Qtz>Phy
	feb-17	41	38			15	6			Qtz▯Pla>Phy
	mar-17	42	35			17	5			Qtz▯Pla>Phy
MUB2	jan-17	39	41			14	6			Pla▯Qtz>Phy
	feb-17	43	38			13	6			Qtz▯Pla>Phy
	mar-17	43	39			13	5			Qtz▯Pla>Phy
	apr-17	36	43			17	4			Pla▯Qtz>Phy
MUB3	sept-16	54		35		7	4			Qtz>Pla>Phy
	oct-16	46		40		7	7			Qtz▯Pla>Phy
	feb-17	57		28		7	8			Qtz>Pla>Phy
	mar-17	57		30		7	6			Qtz>Pla>Phy
	may-17	49		39		6	6			Qtz>Pla>Phy
	jul-17	39		41		17	3			Pla▯Qtz>Phy
SF	oct-16	43		38		17	1			Qtz▯Pla>Phy
	jan-17	50		32		16	2			Qtz>Pla>Phy
	feb-17	41		38		18	3			Qtz▯Pla>Phy
	mar-17	38		32		23	6			Qtz▯Pla>Phy
	apr-17	45		42		8	4			Qtz▯Pla>Phy
	may-17	41		47		8	4			Qtz▯Pla>Phy
	jul-17	45		46		6	2			Qtz▯Pla>Phy
MUB4	oct-16	31		63		4	2			Pla>>Qtz>Phy
	nov-16	33		58		5	3			Pla>>Qtz>Phy
	jan-17	39		53		4	3			Pla>Qtz>Phy
	feb-17	35		56		5	4			Pla>>Qtz>Phy
	mar-17	40		50		5	5			Pla>Qtz>Phy
	apr-17	40		50		5	5			Pla>Qtz>Phy
	may-17	41		49		5	5			Pla>Qtz>Phy
	jul-17	41		49		6	4			Pla>Qtz>Phy
MO	sept-16	12			79		3	4	2	Pla>>Qtz>Phy
	oct-16	12			78		3	5	2	Pla>>Qtz>Phy
	jan-17	16			75		2	5	1	Pla>>Qtz>Phy
	feb-17	15			75		3	5	2	Pla>>Qtz>Phy
	jul-17	16			72		2	5	5	Pla>>Qtz>Phy
MUB5	jan-17	26			61	6		6		Pla>>Qtz>Phy
	feb-17	39			50	6		5		Pla>>Qtz>Phy
	may-17	25			66	4		5		Pla>>Qtz>Phy

Qz: Quartz, Lbr: Labradorite, And: Andesine, Alb: Albite, Msc: Muscovite, Prg: Pargasite, Ccl: Clinochlore, Lmt: Laumontite

3.3. Sediments geochemical analysis

Table 9. *Detection and upper limits reported by ACME Labs for their analytical package ICP-MS AQ250 for soils, sediments and lean rocks.*



Element	Detection Limit	Upper Limit
Ag	2 ppb	100000 ppb
Al	0.01wt.%	10wt.%
As	0.1 ppm	10000 ppm
Au	0.2 ppb	100 ppm
B	20 ppm	2000 ppm
Ba	0.5 ppm	10000 ppm
Bi	0.02 ppm	2000 ppm
Ca	0.01wt.%	40wt.%
Cd	0.01 ppm	2000 ppm
Co	0.1 ppm	2000 ppm
Cr	0.5 ppm	10000 ppm
Cu	0.01 ppm	10000 ppm
Fe	0.01wt.%	40wt.%
Ga	0.1 ppm	1000 ppm
Hg	5 ppb	50000 ppb
K	0.01wt.%	10wt.%
La	0.5 ppm	10000 ppm
Mg	0.01wt.%	30wt.%
Mn	1 ppm	10000 ppm
Mo	0.01 ppm	2000 ppm
Na	0.001wt.%	5wt.%
Ni	0.1 ppm	10000 ppm
P	0.001wt.%	5wt.%
Pb	0.01 ppm	10000 ppm
S	0.02wt.%	10wt.%
Sb	0.02 ppm	2000 ppm
Sc	0.1 ppm	100 ppm
Se	0.1 ppm	100 ppm
Sr	0.5 ppm	2000 ppm
Te	0.02 ppm	1000 ppm
Th	0.1 ppm	2000 ppm
Ti	0.001wt.%	5wt.%
Tl	0.02 ppm	1000 ppm
U	0.1 ppm	2000 ppm
V	2 ppm	10000 ppm
W	0.1 ppm	100 ppm
Zn	0.1 ppm	10000 ppm

CAPÍTULO 4

4.1. Conclusiones

A partir del estudio llevado a cabo sobre el comportamiento de las cuencas de alta montaña hidrotermalmente alteradas, enfocado en la generación y aplicación de un *background* específico para este tipo de ambiente hidrológico, se desprende lo siguiente:

Las principales fases minerales que componen los sedimentos detríticos (i.e., plagioclasas, cuarzo y filosilicatos) son consistentes con la mineralogía de las principales unidades petrológicas previamente definidas. Además, la abundancia relativa de la mineralogía definida no presenta variaciones mensuales significativas, ni tendencias aparentes durante el período que ha durado el muestreo (septiembre de 2016 a noviembre de 2017), por lo tanto, se desprende que los minerales que componen los sedimentos transportados no presentan variaciones estacionales significativas. Por otro lado, dos de las tres subcuencas bajo estudio muestran diferencias en las proporciones de las principales fases minerales que componen las distintas fracciones granulométricas definidas, sin embargo, este comportamiento no se repite en el material transportado en la tercera subcuenca. De cualquier forma, se observa que la signatura mineralógica de la confluencia final al río Mapocho, es la suma de la contribución de cada una de las subcuencas estudiadas, cada una en diferente proporción.

Respecto a los precitados observados en algunas secciones de la cuenca, acorde a los estudios de difracción de rayos-X, se trata de fases minerales amorfas o pobremente cristalinas, las cuales muestran *peaks* ocasionales asociados a minerales detríticos (cuarzo, por ejemplo). Por otro lado, basado en la geoquímica obtenida, los precipitados blanquecinos y rojizos, denominados precipitados de Al y Fe, respectivamente, han sido definidos como fases minerales ricas en Al, S, Cu y As, agregando Fe y Mo en el caso de los precipitados de Fe. Además, basado en la comparación de los difractogramas y la geoquímica obtenidos, con estudios previos en otros sitios similares del mundo, se proponen hidrobasaluminita y schwertmannita como las fases minerales más plausibles para los precipitados de Al y Fe, respectivamente.

La composición geoquímica de los sedimentos clásticos es altamente consistente con la geoquímica inferida a partir del estudio mineralógico, excepto por ciertas discrepancias importantes en la abundancia relativa y las tendencias de ciertos elementos mayoritarios y minoritarios. En esa línea, la fracción de menor tamaño muestra concentraciones más altas que la fracción de mayor tamaño para elementos tales como Fe, S, Cu y As, comportamiento que es particularmente evidente en la subcuenca asociada a hidrotermalismo. Éste es atribuido a la alta proporción de precipitados de Al y de Fe que comúnmente forman parte de la fracción de sedimentos de menor tamaño en dicho sistema. En la misma subcuenca, se observa que la fracción más fina muestra tendencias muy similares en las concentraciones de Fe-S y Al-Cu, comportamiento que es consistente con las observaciones estacionales de los precipitados rojizos y blanquecinos, respectivamente. Por otro lado, ambas fracciones de sedimentos muestran concentraciones similares en elementos que típicamente forman parte de las fases minerales principales que componen los sedimentos detríticos (Al, Ca, Mg y Na), donde la abundancia relativa de estos elementos es consistente con la mineralogía definida a partir del estudio de DRX.

Respecto a los *backgrounds* generados para las dos subcuencas no intervenidas y, el generado para estas dos como un todo (MUB), se aprecia que para muchos elementos difieren los valores entre una y otra, donde la asociada a hidrotermalismo muestra un claro enriquecimiento en metales. Esta situación es significativa no sólo para Cu, sino que además para S, Fe, As y Mo. Es así como, el *background* generado para toda la cuenca, generalmente sobrestima y subestima algunos valores cuando se les compara con los de la subcuenca hidrotermalmente alterada y la que no lo está, respectivamente. Particularmente en la primera subcuenca, esta situación ocurre con elementos que presentan variaciones estacionales, lo cual genera una distribución no gaussiana producto de la presencia marcada de valores extremos con concentraciones anómalamente altas. De este modo, comparado con las CB, las concentraciones de los *backgrounds* generados para todos los elementos (excepto Cd y Hg), son consistentemente más altas que los valores planteados por la CB TEC e, incluso mayores que los propuestos en la CB PEC, en el caso de Fe y Cu. Acorde a los resultados obtenidos, la cuenca entera y, en particular la subcuenca con hidrotermalismo, presentan un *background* geoquímico tan alto para algunos elementos que, teóricamente, se tienen efectos tóxicos probables sobre el ecosistema desarrollado entorno a su curso de agua. Así, se hace esencial desarrollar estudios ecotoxicológicos considerando la flora y fauna locales, en principio, para corroborar los posibles efectos tóxicos del *background* geoquímico natural y, así, generar evaluaciones de toxicidad confiables para cualquier curso de agua en regiones de alta montaña afectadas por hidrotermalismo.

Finalmente, estos resultados establecen la importancia de contar con un *background* (tanto geoquímico como mineralógico) sólido antes de cualquier intento de desarrollar evaluaciones de toxicidad en los sedimentos transportados en este tipo de cuencas. Especialmente, considerando los distintos niveles de complejidad presentados por las regiones de alta montaña hidrotermalmente alteradas, las cuales cubren una cantidad significativa del total de sistemas fluviales de Sudamérica y muchas otras áreas en el mundo.

4.2. Bibliografía

Bingham, J., & Nordstrom, D. K. (2000). Iron and aluminum hydroxysulfates from acid sulfate waters. *Reviews in mineralogy and geochemistry, 40 (1)*, 351-403. doi:http://doi.org/10.2138/rmg.2000.40.7

Burton Jr., G. A. (1991). Assessing the toxicity of freshwater sediment. *Environmental Toxicology and Chemistry, 10*, 1585-1627. doi: https://doi.org/10.1002/etc.5620101204

Burton Jr., G. A. (2002). Sediment quality criteria in use around the world. *Limnology, 3*, 65-75. doi:https://doi.org/10.1007/s102010200008

Burton Jr., G. A. (2013). Assessing Sediment Toxicity: Past, Present, and Future. *Environmental Toxicology and Chemistry, Vol.32, No. 7:*, 1438-1440. doi:http://doi.org/10.1002/etc.2250

Burton Jr., G. A. (2018). Breaking from tradition: establishing more realistic sediment quality guidelines. *Environmental Science and Pollution Research, 25*, 3047-3052. doi:https://doi.org/10.1007/s11356-016-8338-x

Cain, D. J., Luoma, S. N., & Wallace, W. G. (2004). Linking metal bioaccumulation of aquatic insects to their distribution patterns in a mining-impacted river. *Environmental Toxicology and Chemistry, 23:, 23*, 1463-1473. doi: https://doi.org/10.1897/03-291

Chapman, P. M., Allard, P. J., & Vigers, G. A. (1999a). Development of sediment quality values for Hong Kong special administrative region: a possible model for other jurisdictions. *Marine Pollution Bulletin, 38(3)*, 161-169. doi:https://doi.org/10.1016/S0025-326X(98)00162-3

Furrer, G., Phillips, B. L., Ulrich, K. U., Pöthig, R., & Casey, W. H. (2002). The origin of aluminum flocs in polluted streams. *Science, 297*, 2245-2247. doi:https://doi.org/10.1126/science.1076505

Gutiérrez, F., Pincetti, G., Payacán, I., Tristram, E., & Vela, I. (2015). Composición Natural de las Aguas en la Cuenca alta del Santuario de la Naturaleza Yerba Loca, Santiago. *Congreso Geológico Chileno, 14*. La Serena, Chile, 292-295.

Jamieson, H. E., Walker, S. R., & Parsons, M. B. (2015). Mineralogical characterization of mine waste. *Applied Geochemistry, 57*, 85-105. doi:http://dx.doi.org/10.1016/j.apgeochem.2014.12.014

Khan, R., Parvez, S., Jolly, Y. N., Haydar, A., Alam, F., Khatun, A., . . . Hossain, S. M. (2019). Elemental abundance, natural radioactivity and physicochemical records of a southern part of Bangladesh: Implications for assessing the environmental geochemistry. *Environmental Nanotechnology, Monitoring & Management, 12*, 1-13. doi:https://doi.org/10.1016/j.enmm.2019.100225

Liu, H., Zhang, K., Chai, L., Yang, Z., Yang, W., Liao, Q., . . . Liu, Y. (2017). A Comparative Evaluation of Different Sediment Quality Guidelines for Metal and Metalloid Pollution in the Xiangjiang River, Hunan, China. *Archives of Environmental Contamination and Toxicology, 73:*, 593-606. doi:https://doi.org/10.1007/s00244-017-0436-3

MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystem. *Archives of Environmental Contamination and Toxicology, 39*, 20-31. doi:https://doi.org/10.1007/s002440010075

Massoudieh, A., Bombardelli, F. A., & Ginn, T. R. (2010). A biogeochemical model of contaminant fate and transport in river waters and sediments. *Journal of Contaminant Hydrology, 112*, 103-117. doi:http://doi.org/10.1016/j.jconhyd.2009.11.001

Michelsen, T. C. (1999). Principles for assessing the reliability of sediment quality guidelines (SQGs). *SETAC News 19(4)*, 22-23.

Simpson, S. L., Batley, G. E., & Chariton, A. A. (2013). *Revision of the ANZECC/ARMCANZ sediment quality guidelines.* CSIRO Land and Water Report 8/07, Lucas Heights, NSW, Australia. doi:https://doi.org/10.4225/08/5894c6184320c

Smith, S. L., MacDonald, D. D., Keenleyside, K. A., Ingersoll, C. G., & Field, J. (1996). A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *Journal of Great Lakes Research, 22*, 624-638. doi:https://doi.org/10.1016/S0380-1330(96)70985-1

Valenzuela-Diaz, M. J., Navarrete-Calvo, A., Caraballo, M. A., McPhee, J., García, A., Correa-Burrows, J. P., & Navarro-Valdivia, L. (2019). Environmental water quality standards and management in the overlap between natural protected areas and copper mining activities (upper Mapocho River Basin, Santiago, Chile).