

DEPTO. CONSERVACIÓN Y PROTECCIÓN DE RECURSOS HÍDRICOS PROCESO N° 18732729

MINUTA:	DCPRH № 33/					
MAT.:	Recomendaciones para el plan de descontaminación de la cuenca del río Maipo derivadas de la Tesis de Magister "Water Quality Evolution of The Maipo Basin in Central Chile" (Evolución de la calidad del agua de la cuenca del río Maipo en Chile Central) donde se analizan 8 años de datos de calidad de agua (2014-2022)"					
SANTIAGO,	24 de diciembre del 2024					

#### 1. Introducción

La presente minuta tiene por objetivo extraer los principales hallazgos de la tesis "Water Quality Evolution of The Maipo Basin in Central Chile" (Evolución de la calidad del agua de la cuenca del río Maipo en Chile Central) donde se analizan 8 años de datos de calidad de agua (2014-2022) (Fredes 2024), en función de los parámetros conductividad eléctrica, oxígeno disuelto, nitrato, ortofosfato y DBO<sub>5</sub>, levantados bajo la NSCA de la cuenca del río Maipo. En análisis temporal identificó lo siguiente:

1. Se identifica un aumento en el tiempo de los parámetros Conductividad específica, nitrato y ortofosfato en la mayoría de las áreas de vigilancia.

Los resultados que muestra esta tesis indican que desde el año 2018 aproximadamente se percibe un aumento de los valores de conductividad, nitrato y ortofosfato en las distintas áreas de vigilancia. Este aumento al ser ubicuo no tendría una fuente puntual, pudiendo ser reflejo de la sequía vigente en el país hace 14 años.

Respecto a los datos de DBO<sub>5</sub>, se detectó un aumento entre 2018 y 2022 en diferentes áreas de vigilancia con el más alto valor el año 2021 (Figura 2 y Figura 3). En la estación MA3 (Figura 2) este aumento se dio en los 3 años citados, al revisar las precipitaciones ocurridas en las estaciones meteorológicas San José, Colorado, Lo Prado y el Paico (Figura 1) para el año 2018 el día que se registra el valor (51 mg\*L-1) 08/10/2018 y el día anterior, se ve que solo ocurrieron precipitaciones en la estación Colorado con 0.5 mm el 08/10/2018, esta cantidad de agua es menor respecto a otros eventos de lluvia donde no se alcanzaron similares concentraciones de DBO<sub>5</sub>, no pudiendo entonces atribuirse a la lluvia de forma exclusiva, sumado a eso debe considerarse la distancia que tiene la estación meteorológica Colorado respecto a la estación MA3 donde difícilmente se puede pesquisar los efectos de esta lluvia.

En el año 2021 se produjeron aumentos de DBO<sub>5</sub> en julio, agosto, septiembre y noviembre. El aumento en julio se produjo el día 22/07/21 en las estaciones MA5 y PU2, identificándose lluvia sólo en la estación meteorológica el Paico con 0.2 mm, esta estación no recoge la influencia de los puntos antes mencionados, pudiendo descartarse la influencia de la lluvia en el valor de DBO<sub>5</sub> encontrado. El aumento de agosto se produjo en la estación LA1 el día 18/08/2021 con 20,8 mg\*L-1, produciéndose precipitaciones en dicha oportunidad y el día anterior (26.6 mm registrados en Lo Prado Cerro San Francisco 33111 el 18/08/2021 y 3.1 mm el 17/08/2021), por tanto, podría ser un factor influyente en la concentración de DBO5 encontrada. Los aumentos en septiembre se produjeron en las estaciones MP2 y MA3 con 24,4 mg\*L-1 el 15/09/21 y 20,9 mg\*L-1 el 14/09/21,

respectivamente, sin registrarse lluvia en las estaciones meteorológicas más cercanas, a mencionar San José Guayacán 330112 ni en Lo Prado Cerro San Francisco 33111 el día 14 y 15. En noviembre se repite el aumento en LA1 el 24/11/2021 con 21.5 mg\*L-1 registrándose 0.2 mm en la estación Lo Prado Cerro San Francisco 33111 el día anterior, no obstante, y en comparación con lo descrito en agosto para LA1, se considera improbable que esta cantidad de precipitación contribuyese a la DBO<sub>5</sub> registrada.

En el año 2022 durante febrero, en el tramo del río Maipo que comprende las estaciones MA1 a MA3, se identificaron valores de DBO<sub>5</sub> altos respecto a lo histórico (20,6 y 21.0 mg\*L-1 el 22/02/22), sin la ocurrencia de precipitación el mismo día ni el anterior en las estaciones atmosféricas más cercanas, San José Guayacán 330112 y Eulogio Sánchez Tobalaba 330019, descartándose entonces una influencia de este factor, aumentando entonces el peso de otras variables ya descritas en el documento de tesis, como el aumento de los asentamientos informales.

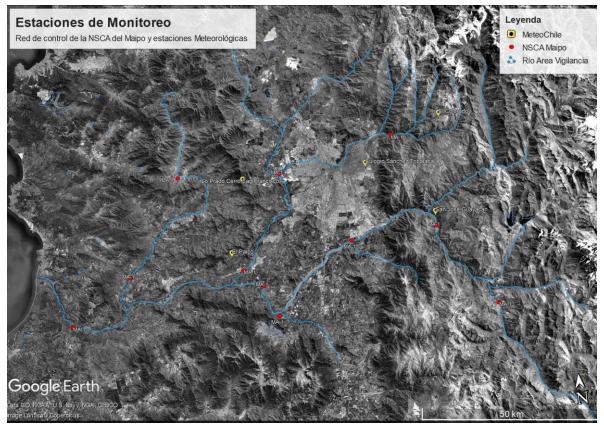


Figura 1. Mapa con la ubicación de las estaciones meteorológicas del catastro de estaciones SACLIM en MeteoChile cercanas a las estaciones de la NSCA del Maipo (red de control).

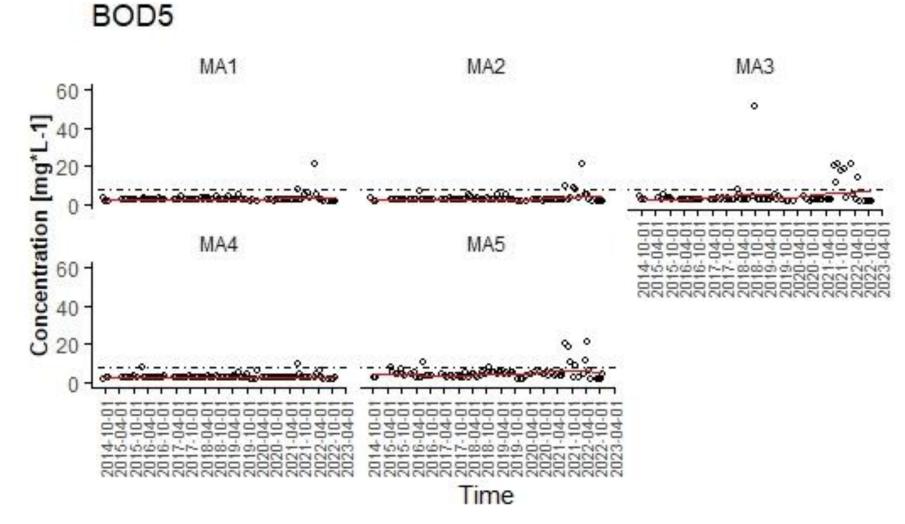


Figura 2. Gráficos de series de tiempo de las campañas de monitoreo del río Maipo para DBO5. La línea punteada muestra los valores objetivo asociados con la NSCA, la cual es específica para cada área de vigilancia y la línea roja es una curva de regresión polinómica local. Los nombres de los sitios son los siguientes MA1 = Río Maipo en las Melosas, MA2 = Río Maipo en San José de Maipo, MA3 = Río Maipo antes de río Clarillo, MA4 = Río Maipo en Puente Naltahua y MA5 = Río Maipo en Cabimbao.

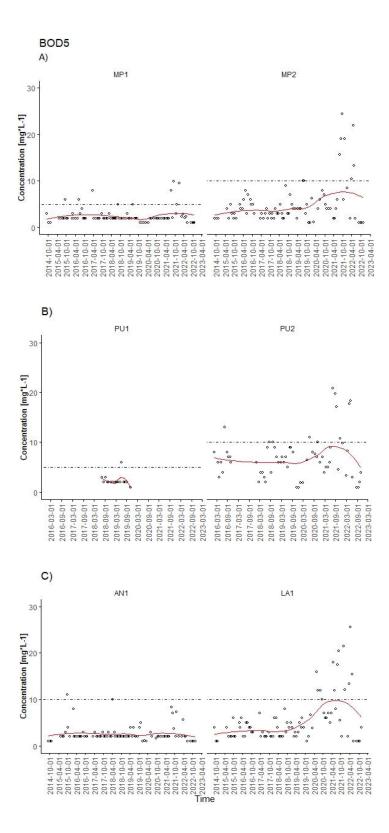


Figura 3. T Gráficos de series de tiempo de las campañas de monitoreo del río Maipo para DBO5 de A) río Mapocho, B) estero Puangue and C) río Angostura and estero Lampa para Demanda Bioquímica de Oxígeno (BOD5La línea punteada muestra los valores objetivo asociados con la NSCA, la cual es específica para cada área de vigilancia y la línea roja es una curva de regresión polinómica local. Los nombres son MP1 = río Mapocho en los Almendros, MP2 = río Mapocho en el Monte, PU1 = Estero Puangue antes de Puente Curacaví, PU2 = Estero Puangue en Ruta 78, AN1 = río Angostura en Valdivia de Paine, y LA1 = Estero Lampa antes del río Mapocho.

2. Aguas abajo de la cuenca del río Maipo y Puangue se identifica un empeoramiento de la calidad del agua.

Considerando los datos analizados se identifica que los parámetros que han empeorado su calidad son la conductividad, nitrato y ortofosfato y su detrimento no responde a eventos puntuales, sino a una tendencia. Estos parámetros se asocian a contaminación difusa, el nitrato estaría asociado a la aplicación de fertilizantes y su rápida movilización a través del agua por ser un compuesto muy soluble. En el caso del ortofosfato, el mecanismo es diferente pues se asocia al material particulado, este material se desplaza por acción del agua pero no disuelto. Tanto para el nitrato como el ortofosfato la sobre concentración de estos tiene un origen multivariado (gestión territorial, uso ineficiente de fertilizantes, entre otros), sin embargo, la prolongada sequía podría ser un factor importante en su aumento detectado en el tiempo.

- 3. Las recomendaciones para atender los hallazgos mencionados son los siguientes.
- Aumentar el número de estaciones de monitoreo continuo de la calidad del agua en la cuenca, particularmente en la salida de la subcuenca del estero Puangue (PU2) y en la salida de la cuenca del río Maipo (MA5), donde la infraestructura para medir caudales existe y se encuentra en uso.
- En el mismo esquema anterior, es necesario medir parámetros básicos de calidad de agua en MA5 y PU2, como pH, Conductividad Eléctrica, Oxígeno Disuelto y temperatura, y se recomienda incorporar la medición de turbidez en todas las estaciones de monitoreo de forma sistemática para mejorar el conocimiento de los impactos que aporta el cambio estacional y separarlos de las alteraciones antrópicas, como la extracción de áridos y descargas de aguas residuales. La turbidez puede ser incluida en las estaciones de monitoreo continuo o ser medidas de forma puntual en cada campaña dependiendo de los recursos disponibles.
- Según los resultados de DBO5, hay una brecha de información en datos de contaminantes orgánicos que debe ser abordada en el programa de monitoreo del río Maipo. La recomendación es monitorear indicadores microbiológicos (Ej.: coliformes totales, fecales, E.Coli), y completar el esquema de los parámetros nitrogenados, incluyendo el nitrógeno Kjeldahl y nitrito para estimar el valor total de nitrógeno, los cuales tienen estrecha relación con la contaminación orgánica. Esta información se relaciona con las inquietudes levantadas en los análisis desarrollados por la DGA para los PERHC y se considera idónea esta última herramienta para abordarlos.
- Se debe incluir los datos hidrológicos en el programa de monitoreo del río Maipo, estos datos son fundamentales para comprender mejor las cargas de los compuestos y sustancias normados y para evaluar la efectividad de cualquier medida futura tendiente a controlar esta contaminación.
- Considerar recurrir a técnicas complementarias que permitan mejorar el modelo conceptual de las emisiones en la cuenca, como por ejemplo la hidrología isotópica. Esta técnica podría ser abordada desde los PERHC.

Estas recomendaciones no poseen una jerarquización, son básicas considerando las presiones presentes en la cuenca del río Maipo y están pensadas como un insumo relevante para el diseño del programa de descontaminación a desarrollar.

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## 2. Referencias

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## Water quality evolution of The Maipo Basin in Central Chile

Thesis presented by

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## **MSc Freshwater Quality Monitoring and Assessment**

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# MSc in Freshwater Quality Monitoring and Assessment

## **Research Dissertation Cover Sheet**

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Assignment details: .....Research Dissertation......

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#### Abstract

The Maipo basin is a basin shared by 3 regions, the largest being the Metropolitan region (Chile's capital), which overlaps with 90.7% of the total area of the basin. This basin has an intensive use satisfying diametrically different needs through water such as energy, industry, mining, agriculture, urban and rural settlements, and ecosystemic services. It also represents the most studied basin in Chile, with a monitoring network that begins in 1966 and developed until 2014 when an environmental management tool named Secondary Normative of Environmental Quality implemented by the Supreme Decree 53/2014 (S.D. 53/2014) enforced its surveillance, turning its previous monitoring objective from the characterization for irrigation purposes towards the protection of ecosystems health, a task that is developed until this day by the General Water Directive (Direccion General de Aguas in Spanish, DGA). With an imminent decree of 'Saturation' and a consequent definition of a decontamination plan from the Ministry of the Environment triggered by the S.D 53/2014, it's an urgent matter to perform a temporal analysis of the data gathered in these 8 years of monitoring, focusing on the parameters that reflect anthropic activities developed in the basin.

This data comes from the control surveillance areas of the Maipo river (MA1, MA2, MA3, MA4 and MA5), the Mapocho river (MP1 and MP2), the Puangue creek (PU1 and PU2), the Angostura river (AN1) and the Lampa creek (LA1), and the parameters Dissolved Oxygen (DO), Specific Conductivity (SC), Nitrate-Nitrogen (N-NO3), Phosphorus Phosphate (P-PO4) and BOD5. The results show that SC, N-NO3 and P-PO4 are affecting water quality in surveillance areas downstream of the urban centres (MA5, PU2 and LA1) by increasing their values over time. SC have changed from infrequent overcoming of the target values in the first years towards often overcomes from mid-2018 on in MA2 (7 vs 24), MA3 (3 vs 17), MA5 (13 vs 45), MP2 (8 vs 15), PU2 (1 vs 45) and LA1 (2 vs 25). Regarding N-NO3, PU2 and LA1 show an important increase in values from a steady base of 9.000 mg·L<sup>-1</sup> in July 2014 to 50.120 mg·L<sup>-1</sup> in June 2020 in PU2, and in LA1 from October 2016 with 0.200 mg·L<sup>-1</sup> to February 2022 with 1.249 mg·L<sup>-1</sup>. There's a marked peak in BOD5 values between 2019 and 2022 in MA3 (51.0 mg·L<sup>-1</sup> in October 2018), MA5 (28.0 mg·L<sup>-1</sup> in April 2022), MP2 (24.4 mg·L<sup>-1</sup> in September 2021), PU2 (20.8 mg·L<sup>-1</sup> in July 2021), and LA1 (25.6 mg·L<sup>-1</sup> in April 2022).

The increase in salinity and nutrients could be associated with the historic drought (since 2010 on) that concentrates substances when flow is reduced, regarding BOD5 the explanation might be a multifactor phenomenon, yet the higher values found between 2019 and 2022 might be an increase

in non-treated domestic wastewater discharge along with several years of drought. Several measures are to be taken to have a better understanding of the increase in nutrients and organic matter input, being the most important to increase the continuous monitoring network by including MA5 and PU2 surveillance areas, gather and collate flow measurements with physicochemical analysis to calculate loading and to broaden the range of parameters related to organic pollution, namely total and faecal coliforms, E.coli, Kjeldahl Nitrogen, Nitrite and Chemical Oxygen Demand.

#### 1. Introduction

#### 1.1. The Maipo basin: the dichotomy of development and preservation

The Maipo river Basin (at latitude 33.5°S, and an area of 15,274 km<sup>2</sup>) covers three administrative regions of Central Chile: the Metropolitan, Valparaiso and the Libertador General Bernardo O'Higgins. The Metropolitan region covers 90.7% of the surface of the basin (Borgias and Bauer, 2018, Peña-Guerrero et al., 2020). This basin has a predominantly mediterranean climate, with a long dry season and a winter period that concentrates over 75% of the annual rainfall. This means that there are two periods of permanent runoff, with floods due to rainfall in the winter months and melting in the spring-summer months (DGA, 2016a).

This basin has intense human activity, being one of the most developed in the country and the most degraded in environmental and ecological terms (Pasten et al., 2019). It's home to 40% of the national population, which means a great pressure on water resources, the demand for water is sorted by superficial water (70%) and groundwater (30%) (BCN, 2024a), water use permits data shows that more than 262 m<sup>3</sup>/s are for consumption and more than 1042 m<sup>3</sup>/s for non-consumptive use (DGA, 2016b). This basin has around twenty sewage treatment plants, with an agricultural activity identified as the fourth-most important at national level (Pasten et al., 2019); electric generation has an installed capacity of 871 MW (SEC, 2019). The main legal instrument that rules how water is managed within the country is called the Water Code of Chile (Codigo de Aguas in Spanish and CDA from now on); it defines water permits as a right on water and consists of its temporal use aligned with current regulation, requisites and limitations that the Water Code describes (Article 6 of the Water Code). This permit is not linked to the terrain where it flows so it can be treated separately (Bjornlund and McKay, 2002); water usage also has an organizational component where water users can gather in committees to distribute water. There should be an organization per basin, yet the Water Code allows the coexistence of several, dividing one river in several sections which can be managed 'independently' for legal and administrative purposes. Even with the benefits that this regime could imply for water distribution there're several other material and discursive implications (Borgias and Bauer, 2018).

The landscape of the basin presents high degradation, representing 5% of its formations of sclerophyllous and thorny forests. Its drainage basin presents a mosaic of land uses with scrub (43%), agricultural (17%) and urban (5%) coverage (Cheval et al., 2020). In addition to the latter, channel degradation due to gravel mining extraction has caused important changes such as reduced braiding pattern and channel-narrowing, endangering of river infrastructure (Arrospide et

al., 2018). These changes in the river also impact ecosystems through habitat disturbance, riparian zone alteration and sediment transport imbalance (Koehnken et al., 2020).

Besides the condition summarized above, there's also the effect caused by the mega drought in Chile (CR2, 2019). Since 2010 there's evidence of a permanent drought condition within the country showing its consequences at a national level (Peña-Guerrero et al., 2020, Xu, 2023). This drought has caused a lack of precipitation, change of its usual regime and location and increase in extreme climate events (e.g. landslides, out of season rain events, heat waves, fires, among others) (CR2, 2023). In 2022 there was a 22% deficit in precipitation being the 13th driest year with 567 mm national average (MMA, 2022) and from the Copiapo to Aysen river (26° and 49°, Nort to Austral region) there's a 5 - 15% decrease forecast in precipitation by the year 2030 (MMA, 2023). This condition accompanying the Chileans translates in a readily exhaustion of aquifers and river courses deriving from the activation of administrative mechanisms within the CDA to prevent deeper damage and facilitate access for the population, these are: Exhaustion declarations (for superficial waters), Reserve decree, Restriction areas (for groundwaters), Prohibition zones (for groundwaters) and Protected Aquifers (DGA, 2024b). There's also the Scarcity decree, a temporal tool mend to ensure potable water supply and support for agriculture; from 2018 until 2021 this tool was invoked exponentially according to Figure 19 (Appendix) going from 12 to 38 decrees (DGA, 2023). Since the 13<sup>th</sup> of June 2022 Chile has the Law 21455 from the MMA named Climate Change Framework Law<sup>1</sup> which provides the legal environment to implement measures that tackle climate change challenges, particularly to reduce greenhouse effect emissions by 2050, adapt to climate change, and meet international commitments in the matter. As a consequence of drought, Chile has an evident stress in its Northern and Central regions with a water average availability of less than 1000 m<sup>3</sup> hab<sup>-1</sup> yr<sup>-1</sup> (WB, 2011), which is accompanied by negative impacts in agriculture and cattle activities deriving in socioeconomic instability (Vüllrath Ramirez et al., 2022) among other factors. Nevertheless, the stress condition of these macroregions is overlooked by the national water average availability of 54000 m<sup>3</sup> hab<sup>-1</sup> yr<sup>-1</sup>; along with this, according to SDG indicator 6.4.2, Chile gualifies as not stressed with a stress level of 8% in 2021 (UN-Water, 2024). These values drive us to highlight that each region or groups of regions have their own behaviour and impacts regarding climate change, thus measurements to tackle this must be, when possible, site specific.

<sup>&</sup>lt;sup>1</sup> Ley Marco de Cambio Climatico in Spanish. Source:

https://www.bcn.cl/leychile/navegar?idNorma=1177286&idParte=10341110&idVersion=2022-06-13

#### 1.2. The study of the Maipo basin: DGA and its role on water quality knowledge of the basin

The General Water Directive of Chile (Direccion General de Aguas in Spanish, and DGA from now on) is a public organization within the Ministry of Public Works in charge of the management of natural waters, specifically continental, promoting governance, protecting its guality and guantity for a sustainable, resilient and inclusive development and strengthening its governance (DGA, 2024a). The DGA's main obligation is linked to water research is to establish and maintain a monitoring network of quantity, level and quality of glacial, superficial and groundwaters, being the data gathered of public access and up to date (CDA, Art. 129 bis 3.). This obligation allows it to fulfill several other attributions related to water protection and knowledge: to plan and provide recommendation on water uses, to act as the police of water (prevent or sanction acts against water quality and quantity), and to research water resources towards its preservation and conservation. The latter is achieved through the National Hydrometric Service, which measures water guality and quantity, providing knowledge to the public. This Service maintains several monitoring networks; groundwater level, lake level, glacial, fluviometric, sediment and water quality. Water quality has been monitored since 1959, gathering over 1.4 million data<sup>2</sup>; monitoring occurs under an annual programme that dictates a seasonal monitoring on rivers, semestral in groundwater and differentiated in lagoons and lakes reaching a minimum of once every 4 years (DGA, 2019). River monitoring is performed by each regional DGA office in Chile, whereas most water quality analysis is done by the Environmental DGA laboratory located within the Metropolitan region. The Metropolitan office, in charge of monitoring the Maipo basin, has gathered over 131,150 data between 16-05-1966 and 22-12-2022, covering an inorganic span of parameters mostly<sup>3</sup>.

The DGA is the only organisation that monitors water historically and systematically at a national level, co-existing with other organizations that perform monitoring at a small, and sometimes more specific level (e.g.: MMA, Agricultural and Cattle Service, Directive of Hydraulic Works, NGOs, academia, private sector, etc.) (Donoso, 2018).

#### 1.3. Protecting the Maipo basin: control, review and take action

It's clear that the Maipo basin is one of the most important basins in the country, mainly from an economic angle but also from ecosystemic and social angles. The latter two aspects are a concern that has grown through the years where several environmental and social NGOs that advocate for

<sup>&</sup>lt;sup>2</sup> Until 2018

<sup>&</sup>lt;sup>3</sup> Field parameters, trace metals, metalloids, phosphorus and nitrogen compounds, organic matter indicators, among others.

the right to live in an environment free of pollution<sup>4</sup>, and for the passivity of the State in its regulatory role (Borgias, 2018). The main social activities concentrate within the Metropolitan region (economy, politics, culture, technology, among others), a centralized point of view from which Chile constantly tries to change, yet this factor has an important weight when studying the basin because more resources are available<sup>5</sup>, and logistics allows to narrow the data gaps quickly (i.e. high connectivity, more laboratories and consultant agencies available, established capacities, etc.). These characteristics, among others, settles this basin as an object of protection through regulation.

There is an environmental management instrument at place to protect this basin (Supreme Decree 53/2014, S.D 53/14 from now on) (Cheval et al., 2020), born from the Law of General Environmental Basis of the Environment N°19300/2000 (LGBM 19300 in Spanish). It was a response to international scrutiny of Chile as a country moving from a dictatorship regime to a democracy, with an increasing pressure to tackle environmental and social problems withing the country. The LBGM was born in 1994; it settles the basis for environmental institutions to work supervised by the CONAMA, an organism in charge of the coordination of the different public institutions for the creation and implementation of legislation, institution and policy that integrates society, economy and the environmental aspects under a sustainable management of our natural resources (Garcia-Carmona, 2023). Among the several environmental instruments created by the LGBM (e.g.: environmental impact assessment, strategic environmental evaluation, regulation for emission to the environment, etc.) are the secondary normative for the protection of ecosystems, being one of them for the Maipo river basin. This instrument regulates the presence of pollutants in the environment to prevent their levels, concentrations and periods from representing a risk to the protection or conservation of the river ecosystems and of nature. To date, seven of these instruments are in place, one for each different water body along the country (Cheval et al., 2020) (from a total of 101).

<sup>&</sup>lt;sup>4</sup> Chilean Constitution, article 8.

<sup>&</sup>lt;sup>5</sup> The resources that a region has depend on its expenses, investments, activities developed and inputs from the Regional Development Subsecretary. These amounts depend also on poverty indicators and territorial characteristics DIPRES. 2017. *Financiamiento de los Gobiernos Regionales en Chile [Financing of the Regional Governments of Chile]* [Online]. Available: https://www.dipres.gob.cl/598/articles-160346\_doc\_pdf.pdf [Accessed 20-06-2024].

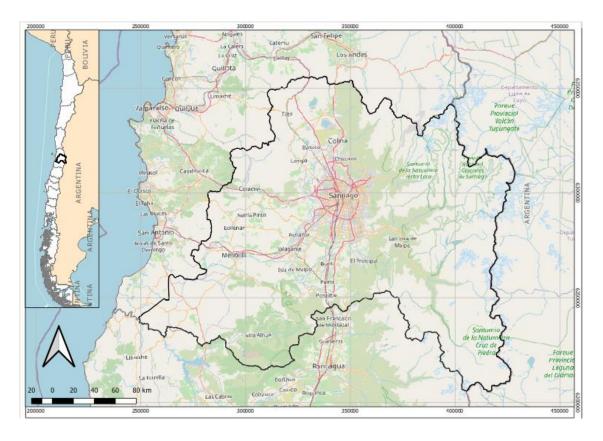


Figure 1. The Metropolitan region of Chile and its location within the country.

The S.D 53/2014 states in its Title IV, Article 6, that "Compliance with the secondary environmental quality standards<sup>6</sup> (Table 1) contained in this decree must be verified annually according to the Environmental Quality Monitoring and Control Programme (PMCCA in Spanish), based on monitoring for each control parameter and at the final section of each of the indicated surveillance areas". A surveillance area is one or multiple sections of a river and are the study units of the Monitoring Programme. According to Title VI Article 12, "The PMCCA must include, at least, a monthly monitoring for each control parameter and must include the use of ecotoxicological tests or trials and the sampling of bioindicators in the defined surveillance sections, as complementary tools to determine the effects of water quality on aquatic communities. Additionally, the S.D 53/2014 considers the intensification of monitoring in case of observing a trend towards exceeding the levels of environmental quality established in these regulations. Monitoring under the S.D 53/2014 started in July 2014 when the decree was published in the Official Newspaper<sup>7</sup>.

<sup>&</sup>lt;sup>6</sup> This environmental protection tool is named secondary to all standards not meant to protect human health (primary standards) but the environment.

<sup>&</sup>lt;sup>7</sup> It publishes documents regarding public and private acts that hold relevance to law, economy, commercial, financial, and social living of the country.

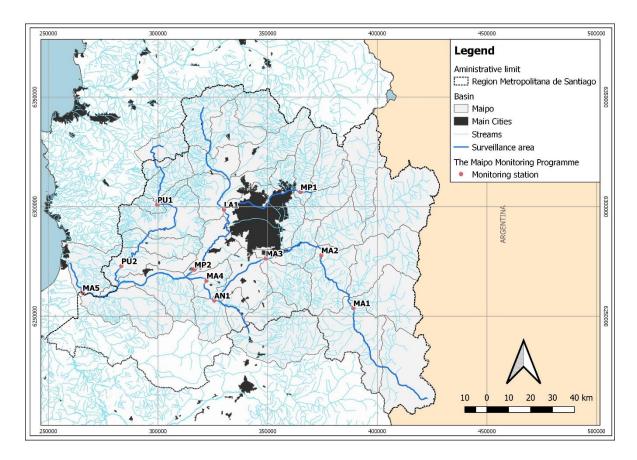


Figure 2. The Maipo basin in central Chile (inset) as the focus of this study. The major cities, stream network, surveillance areas and monitoring stations used in the monitoring programme are outlined.

PARAMETER	Unit	MA1	MA2	MA3	MA4	MA5	MP1	MP2	PU1	PU2	AN1	LA1
Dissolved												
Oxygen	mg/L	8	8	8	8	6	8	6	8	5	6	5
Specific												
Conductance	Us/cm	1900	1900	1900	1600	1600	400	1600	400	1750	1600	1900
pН	pH Units	6,5-8,7	6,5-8,7	6,5-8,7	6,5-8,7	6,5-8,7	6,5-8,5	6,5-8,5	6,5-8,5	6,5-8,5	6,5-8,5	6,5-8,5
Chloride	mg/L	300	240	240	180	180	30	240	30	240	180	240
Sulphate	mg/L	430	380	380	380	380	150	380	150	380	380	480
BOD5	mg/L	8	8	8	8	8	5	10	5	10	10	10
N-NO3	mg/L	0.5	0.5	0.5	4	8	1.5	10	1.5	10	4	4
P-PO4	mg/L	0.08	0.08	0.08	0.15	1	0.08	2.5	0.6	2.5	0.15	0.6
Dissolved												
Lead	mg/L	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007
Dissolved												
Nickel	mg/L	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Dissolved Zinc	mg/L	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Total												
Chromium	mg/L	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Table 1. Target concentrations of each parameter in each surveillance area (S.D 53/2014)

The PMCCA, which is a complementary tool named Resolution N° 1799/2020 (BCN, 2024b) was elaborated by the DGA, MMA and Superintendency of Environment (SMA). It works as a monitoring programme and considers the following topics: Objective and scope of application; Definitions; Surveillance area and monitoring; Station location; Environmental quality levels by surveillance area; Compliance criteria and exceedances; Sampling and analysis methodologies; and the water quality report. Regarding surveillance areas and monitoring stations the most important information

is that the S.D 53/2014 defines two types of monitoring; control and observation. Control monitoring is used to evaluate compliance of water quality standards; it involves a monthly monitoring of parameters shown in Table 1 whereas observation monitoring is used as a complement to understand the changes of the basin, it is monitored by semester, it considers of a broad set of parameters (Figure 14, Appendix), and its execution depends on budget availability (i.e.: it is not compulsory).

The monitoring mandated by S.D 53/2014 is carried out by the regional DGA together with the Environmental Laboratory of the DGA and the MMA. The DGA sends the SMA and MMA an annual report of the monitoring data gathered in each period; the SMA must review each year that the data meets all the standards required (e.g.: sampling methodology, analysis methods, holding time of analysis, frequency of sampling, among others), whereas the MMA concludes after 5 years of monitoring if the water quality targets of the basin were met. After this period of monitoring and evaluation of the information the MMA must inform the Presidency if the basin is in a latency or saturated (polluted) state. A latency state derives in changes in the monitoring programme to narrow and identify the source(s) of pollution (e.g.: higher monitoring frequency, more chemical parameters, other bioindicators, modelling, among others). A saturated state instead derives in a decontamination plan that should tackle the main pollution sources; in this case discharging industries could be obliged to incorporate new technologies to pollute less.

To date there are 8 years of monitoring effort within the S.D 53/2014 scheme and a saturation declaration<sup>8</sup> of the state of the basin and its surveillance areas is in process, which indicates that the basin is below the desired quality in chloride, sulphate, nitrate and dissolved oxygen; the detail reveals that chloride and dissolved oxygen are constantly over and below, respectively, the target values whereas pH, electric conductivity, BOD5, nitrate, and sulphate are moving away from the desired levels gradually (MMA, 2019). According to the most recent review of S.D. 53/2014 data, the areas where water quality is more affected are MA3, MA5, MP1 and PU2 whereas less-affected areas are AN1, MA4 and MP2. Areas MA1 and MP1 have water quality problems regarding field parameters and chloride, however area MP1 seems to have a constant problem with dissolved zinc, and until this later analysis (covering data until 2021), with nitrate. MA1 and MP1 areas seem to show effects of human intervention, but they're monitored as reference condition sites to compare with areas located in the middle and lower part of the basin.

<sup>&</sup>lt;sup>8</sup> Recognition of the basin's status is made through a supreme decree from the Minister of Environment. To date this document hasn't been released mainly because the actions derived from this will impact the industry sector becoming also a political issue.

Regarding the total universe of data gathered under the S.D. 53/2014, the parameters with less representation are those of the Observation monitoring with less than 300 data (Figure 14, Appendix), whereas the Control parameters are over 900. BOD5 is the only Control parameter with the lowest amount; this is because the parameter cannot be analysed in the DGA laboratory and had to be externalized to the private sector. The logistic of sending the sample (within the region and even to another region) and to follow up its timely reception in the external laboratory causes discoordination with the consequent loss of analysis. This has been improved in time by using services only within the region to develop this analysis.

Biomonitoring within the basin was performed for benthic macroinvertebrate, chronic and acute biotoxicity and ichthyofauna by the MMA in 2015, 2016 and 20179 (MMA, 2019), and in another study covering the period 2020 and 2021 (MMA, 2021). Benthic macroinvertebrate showed higher abundances in the lowest reaches of the Maipo river (MA4 and MA5) as well as the lower reach of the Mapocho river (MP2) during 2016 and 2020, in 2021 AN1 and LA1 showed higher average abundances, PU2 and MA1 showed the lowest values in 2020 and 2021. Richness on the other hand pointed at AN1 and MA4 as the sites with the greatest diversity of taxa during 2016 and 2020, and MP1 in 2016. In both studies LA1 showed the poorest quality compared to the other rivers which is related to anthropic disturbances along the river. The chronic and acute biotoxicity test concluded that MP1 was the only site that resulted in a statistically significative inhibitory effect on the growth of Raphidocelis subcapitata<sup>10</sup> 100% of its concentration in 2016, in 2017 the results showed that in most of the monitoring stations was identified a mild growth inhibition (but statistically significant) except for MA4, PU2, AN1, MA1, and MA4 showed an inhibitory effect during 2021, PU2 also shown this effect in 2020. Ichthyofauna was studied in 2016 and 2017 in three sections of Maipo river: MA1, MA4 and MA5, the findings showed presence of *Trichomycterus areolatus* (Vulnerable) and Percichthys trucha (Almost threatened) in MA4 and Percichthys trucha and Basilichthys sp (Vulnerable) in MA5, but no presence of fish in MA1. In the following study the Ichthyofauna was monitored in the middle of the Maipo basin showing a hotspot location represented by Trichomycterus areolatus in MP2, MA4, AN1, and MA5, Basilichthys australis nativa in AN1, MA4 and MA5, all classified as Vulnerable. Additionally, Percichthys trucha nativa (Almost threatened) was found in AN1, MA4 and MA5, and Percilia gillissi ('coloradita') (In danger) was also

<sup>&</sup>lt;sup>9</sup> The first year of monitoring the indicators used were ChSIGNAL and ChBMWP, but since ChNMWP index results better represent the ecologic state and physicochemical water quality it was decided to use it for future campaigns. <sup>10</sup> A microalgae used for bioassays according to the Chilean Normative 2706. Of 2002.

found in AN1. Higher surveillance areas do not show presence of Ichthyofauna because they're very steep and highly turbid.

As seen, this basin has a protection scheme that goes many years back and covers several aspects of water quality, yet this protection scheme is oriented to understand if the basin has overcome its target values, without considering a vision of what has been occurring during the 8 years of monitoring, or in general, where is water quality going, if there're more measures that should be taken to improve monitoring outcomes. As seen, water quality is evaluated in the Maipo basin through field parameters, organic pollution, macroelements, nutrients and microelements (heavy metals). The parameters that summarise the main anthropogenic activities of the basin (urban centres, agriculture and industry) are specific conductivity (SC), dissolved oxygen (DO), nitrate (N-NO3), phosphate (P-PO4) and BOD5 (Biochemical Oxygen Demand), this subgroup and its implication to understand how the basin works will be described next.

SC is a measurement of the ability of a solution to conduct an electric current, it's unit of measurement is uS/cm. Most substances in the environment have an electric charge (organic and inorganic substances), thus they might contribute to the variations found in SC, yet these variations are small compared to the contribution of mineral salts<sup>11</sup> (Jeffery et al., 2009), making them the most important focus when analysis SC results (Wetzel, 2001a). SC in natural waters ranges from 10 to 1000 uS/cm, in Chile some water bodies reach 56550 uS/cm, the latter value reflects the far north salty lagoons that have high salinity (DGA, 2020). Besides these water bodies a value above 1000 uS/cm might represent a pollution condition or situation (Maybeck et al., 1996). SC data might not be as precise as using concentrations of each mineral present in the water, however, it's a powerful tool because it's highly correlated with total dissolved solids (in mg·L<sup>-1</sup>)<sup>12</sup> which is a measure of water mineralization, it speaks clearly through its magnitudes, and it's easy and cost-effective to measure (Maybeck et al., 1996).

Dissolved oxygen (DO) is an essential gas for aquatic life and it governs most of the chemical and biological reactions (Wetzel, 2001b). This parameter indicates the amount of oxygen a water body has; it can be expressed in concentration (mg·L<sup>-1</sup>) or percentage of saturation (%) and its fluctuation depends on several factors: temperature, atmospheric pressure (and thus altitude), turbulence, salinity and presence of algae and plants. The measurement of DO allows us to know and estimate general characteristics of a water body, such as: biologic activity, presence of anthropic and

<sup>&</sup>lt;sup>11</sup> Mineral salts are inorganic compounds, the mineral part divide into macroelements (calcium, sodium, magnesium, potassium), microelements (heavy metals like copper, iron, zinc) and trace metals (cadmium, bromine, nickel, chrome), whereas the salts group considers chloride, sulphate, carbonate, among others.

<sup>&</sup>lt;sup>12</sup> Total dissolved solids = SC · factor. This factor is between 0.55 and 0.75 depending on the nature of each water body.

industrial activities, seasonal changes, mixing, among others, as well as more specific aspects such as daily fluctuation, which is a manifestation of temperature and biologic activity. DO is constantly monitored in water because of its importance; its field measurement is not as highly-accurate as that of a chemical analysis (Winckler Method) but accurate enough to implement it compared to the efforts that a chemical analysis represents. Where no information on organic pollution is available the changes in this parameter might serve as an indicator of its occurrence, even as an input to other specific parameters related with organic pollution (BOD) (DGA, 2020).

Nitrate is an inorganic nitrogen compound with negative charge, very reactive and soluble in water when it's part of a salt (i.e. it dissociates readily in water); its importance in the environment lies in its role as one of the two basic nutrients required by algae metabolism (phosphorus is the other nutrient) and thus primary productivity in water bodies. Nitrate occurs naturally through bacterial activity that uses nitrogen from the atmosphere (e.g. Clostridium, Bacillus, Azotobacter, among others) but its main source is considered anthropic, particularly from land runoff in agricultural areas (non-point source pollution) where fertilizers are applied<sup>13</sup> (Apello and Postma, 2005); this, added to the fact that nitrate is highly soluble, makes nitrate a threat not just to surface water but also groundwater for different reasons. In surface waters a nitrogen imbalance (surplus specifically) can alter the trophic state of a water body towards a nutrient-enriched ecosystem, which can derive in an eutrophication condition, with the consequent loss of biodiversity and ecosystemic services (e.g.: drinking water sources, loss of amenities, etc.) (Wetzel, 2001c). In groundwater the effect of nitrogen through nitrate is well known to affect human health, not just by the 'blue baby syndrome', which has an acute effect on babies, but it is also responsible for stagnant growth in children who drink water with high concentrations of nitrate (Damania et al., 2019). In addition to the latter, groundwater connections to superficial water bodies also represents a pathway of pollution to groundwater compromising its sustainability. These, among other reasons, is why nitrate is monitored systematically in several water bodies and why it's important to control its sources.

Orthophosphate, or phosphate, is a compound of phosphorus; as with nitrate, it is also inorganic with negative charge yet its cycle is not as dynamic as nitrogen's because it is associated mostly with particulate matter from organic sources (> 95% as biological matter decay) (Wetzel, 2001d). Phosphate is the most reactive (and soluble) form of phosphorus in nature and as such it is used as a nutrient source; phosphorus is usually less abundant than nitrogen in aquatic ecosystems,

 <sup>&</sup>lt;sup>13</sup> The common composition of fertilizers is 12% nitrogen (N), 32% phosphorous (P2O5) and 16 % potash (K2O) FAO. 2024. NSP
 *Fertilizer Specifications* [Online]. Available: https://www.fao.org/agriculture/crops/thematic-sitemap/theme/spi/plantnutrition/fertspecs/en/ [Accessed 07-06-2024].

which means that it's considered a limiting nutrient of primary productivity (der Grift et al., 2014). The reactivity of phosphate also has important effects on chemical equilibria because it readily forms insoluble compounds with many cations (e.g.: calcium, magnesium and iron, among others), changing their concentration, and it also adsorbs easily into mineral particles (e.g.: clays, hydroxides and carbonates) and colloids, reducing its own concentration in solution (Wassen et al., 2013, Wang et al., 2024). This last characteristic is important when considering sediment as a source of phosphorus and metals, and the risk it poses to become a pollution source when reductive conditions are in place (Wassen et al., 2013, Wang et al., 2024). Phosphorus sources can be natural or anthropic, the latter being the most significant input to aquatic ecosystems through point and diffuse sources (Leone et al., 2008) where the main activities that contribute phosphates are: agriculture, industrial waste and urban sewage (Wei et al., 2021). The reactive nature of phosphate are in the box of phosphate and urban sewage (Wei et al., 2021).

Biological Oxygen Demand (BOD) is an indirect indicator of organic matter content; this parameter accounts for the mg·L-1 of dissolved oxygen consumed in 5 days (BOD5) at 20°C by aerobic microorganisms when they metabolize organic matter to an inorganic stable form (i.e. it relates with the amount of biodegradable organic matter) (Chapman and Kimstach, 1996). This parameter is a useful tool to estimate the organic matter charge in a water body, which depending on its magnitude might imply it's a pristine water body ( $\leq 2 \text{ mg} \cdot L - 1$ ), it has an anthropogenic source of organic matter (≥10 mg·L-1) or it's an industrial discharge (up to 25000 mg·L-1) (Chapman and Kimstach, 1996). BOD5 measurement should be interpreted with care because, as it depends on microorganisms, these might be affected by toxic substances present in the water that alter its metabolisms, underestimating the ultimate oxygen consumption; thus its interpretation requires more information. BOD5 is usually measured with Chemical Oxygen Demand (COD), a parameter with the same principle (i.e. indirect measurement of organic matter content) but that estimates the amount of oxygen needed for degradation of biodegradable and non-biodegradable organic matter (Lee et al., 2016); BOD5 is usually less than COD. BOD5 analysis has a limited holding time (24 hrs) because of its dependence of microorganisms (SMWW, 2017), which constrains it to be measured systematically if there're no laboratories within a certain distance (Muller et al., 2014), yet in the case of the Maipo river the offer of laboratories is enough to implement its monitoring.

#### 1.4. Aim and objectives of this study

The aim is to study the evolution over time of water quality in the Maipo basin and its sub-basins (Mapocho river, Puangue creek, Angostura river and Lampa creek) from the beginning of the Maipo

Monitoring Programme in 2014 to the end of 2022 (when last measurements were available). To achieve this the following objectives will be pursued:

- Analyse time series of the key parameters related to anthropogenic stress, namely: DO, CE, N-NO3, P-PO4 and BOD5.
- Compare each parameter against the target values designed by the S.D. 53/2014 to protect each surveillance area to understand the evolution of water quality.
- Interpret these findings against the Maipo basin development (i.e. river basin administration) and stressors (e.g.: historic drought, urban and industrial development, gravel mining).

#### 2. Materials and Methods.

#### 2.1. Study area

As described in the introduction, the study area covers the Maipo basin with its surveillance areas monitored by a law enforcement instrument (S.D. 53/2014). The surveillance areas under analysis are shown in Figure 3, and its main characteristics regarding anthropic influence are summarized in Table 2. The criterion to assign a degree of anthropic influence is self-made, inferred based on proximity of the city and land uses. A 'null' influence indicates minimum to no proximity to rural or urban areas, a 'mild' influence means location within a rural area and/or proximity to an urban centre and 'important' influence represents a location within an urban area or an intensive land use area, or an area highly influenced by these stressors.

The two main anthropic activities affecting water resources (agriculture and industry) are also depicted in Figure 3, the first as the canal irrigation network provided by the Center of Information of Natural Resources of Chile (ID\_Minagri, 2019) and the second as the data base of regulated discharges located within the Maipo basin until 2022 provided by RETC from the Ministry of Environment (SMA-SISS, 2022). This information will be used to interpret water quality results.

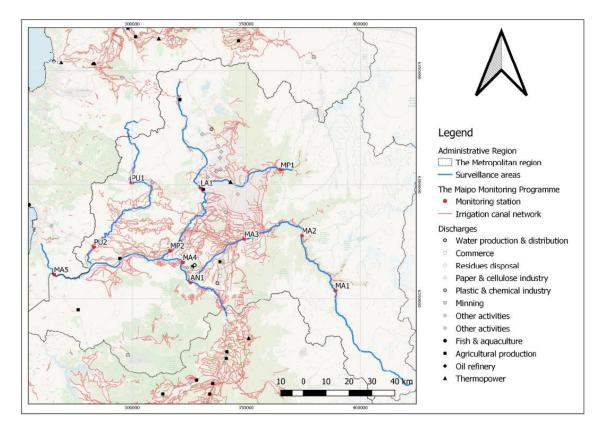


Figure 3. Map of the irrigation canal network and industrial discharges in the Maipo basin along with the surveillance areas and control monitoring stations of the monitoring programme.

The Maipo river has mixed sources; one pluvial and the other from snow melting (Meza et al., 2014); another important feature to be considered is that most of the flow from the upper part is diverted by an important canal called San Carlos, which feeds the agricultural and urban demand of the lower part of the Mapocho river (Genova and Wei, 2023); this alters water balance of the basin noticeably. The Maipo has different intervention levels depending on the surveillance area; MA1 has null intervention because there's little to no anthropic activities in its vicinity; there is also a scarce presence of rural settlements narrowing it to a small group of houses. The following section is MA2, which is subjected to a higher intervention compared to MA1 yet still considered not important. In MA3 surveillance area the impact becomes evident from the increase in activities close to the river surroundings, one example is the number of discharges located shown in Figure 3. From MA4 on the intervention degree becomes evident; this surveillance area collects the impact of the main urban centres until MA5 surveillance area starts, where the last input of agricultural land is collected. The Mapocho river also has a nivo-pluvial regime as the Maipo, yet its main water source comes from ice melting during spring, from its interaction with the urban areas this river is considered highly polluted and physically stressed (Segura et al., 2006). The Lampa creek receives recharges from groundwater and pluvial regime also (DGA, 2004), yet these sources have decreased considerably with the drought and other stressors which means that it carries water intermittently. The Puangue creek is fed by groundwater in its origin (DGA, 2004); it receives water from the Mapocho river through a canal named Las Mercedes (DGA, 2006). The Angostura river has a pluvial regime most of the time (UTEM, 2019); its intervention level is low compared to the other rivers, yet it's immersed in a strongly-agricultural area, thus there are evident alterations related to this activity (e.g.: animal presence within and in the proximity of the river, crops close to the riverbank, among others.).

River	Name	BNA Code	Monitoring	Surveillance	Location	Degree of
			frequency	area	within the	intervention
					Maipo basin	
Maipo (main	The Maipo river in Las Melosas	5701002		MA1	Upstream	Null
basin)	The Maipo river in San Jose de			MA2	Upstream	Mild
	Maipo	5704008				
	The Maipo river before Clarillo river	5710009		MA3	Central	Important
	The Maipo river before Naltahua			MA4	Central	Important
	bridge	5717005				
	The Maipo river in Cabimbao	5748001		MA5	Downstream	Important
Mapocho	The Mapocho river in Los		Monthly	MP1	Upstream	Null
	Almendros	5722002				
	The Mapocho river in El Monte	5737005	1	MP2	Central	Important

Table 2. Main division areas of the Maipo basin and its surveillance areas. The degree of intervention has as a reference the proximity to the main city (Santiago).

River	Name	BNA Code	Monitoring frequency	Surveillance area	Location within the Maipo basin	Degree of intervention
Puangue	The Puangue creek before the Curacavi bridge	5742002		PU1	Upstream	Null
	The Puangue creek in route 68	5746001	-	PU2	Central	Important
Lampa	The Lampa creek before El Maipo	5716001		LA1	Central	Important
Angostura	The Angostura river in Valdivia de		-	AN1	Upstream	Null
	Paine	5736001				

#### 2.2. Software

The software used to process the data were Microsoft Excel (Version 2405), R (Version 4.3.1) (R, 2023), and R Studio (2023.09.1-494) (PositTeam, 2023). Basic packages of R were used for formatting data and producing graphs. Detail the main packages used will be provided when considered necessary.

#### 2.3. Database selection

The raw data base consists of the historical water quality data of the Maipo basin under the monitoring plan implemented by the S.D. 53/2014 established in the Introduction, the data is collected through monthly monitoring campaigns performed by the DGA technical team, standardized protocols<sup>14</sup> are followed to ensure robustness of sampling. Physicochemical analysis performed by the DGA Environmental laboratory are also performed under a strict quality assurance programme (ISO 17025).

A subset of this data base was created selecting only relevant parameters for the purpose of this research which are DO, SC, N-NO3, P-PO4 and BOD5 (Table 3). The parameters selected respond to what other sources have recommended considering anthropic effects in water quality relatable to urban and agricultural activities (Chapman and Kimstach, 1996).

The surveillance areas selected comprehend those with official control, leaving aside those considered as ancillary support (observation monitoring stations) because the latter are monitored in a less frequent manner (twice a year). PU1, a surveillance area of the Puangue creek has less measurements compared to the rest of the surveillance areas because there's an intermittent flow caused from the mega drought and water abstraction (Consult column N in Table 4, Appendix), thus the data from this surveillance area will be used as a reference when comparing with PU2 and other surveillance areas outside the Puangue creek.

<sup>&</sup>lt;sup>14</sup> APHA, AWWA, WPCF, Standard Methods for Water and Wastewater Examination (2005), 21st Edition.

The period selected under study is from 01/07/2014 until 31/12/2022, which is the latest update of available data in the DGA repository (Table 3).

Basin	Parameters	Unit	Studied Period
The	Dissolved Oxygen (DO)	mg∙L-1	
Maipo	Specific Conductivity (SC)	uS·cm⁻¹	
	Nitrate nitrogen (N-NO3)	mg∙L-1	01/07/2014 to 31/12/2022
	Phosphate (P-PO4)	mg∙L-1	
	Biological Oxygen Demand (BOD₅)	mg·L <sup>-1</sup>	

Table 3. Parameters and time to be analysed in each surveillance area of the Maipo basin.

A summary statistic of each surveillance area and parameter was created to understand the main characteristics of data distribution and improve ulterior discussion (Table 4, Appendix).

#### 2.4. Data processing

#### 2.1. Time series

Time series plots of each surveillance area within the Maipo were elaborated to understand the evolution of values and concentrations of DO, SC, N-NO3, P-PO4 and BOD5. Target values of each surveillance area and parameter were added to the corresponding graphs for comparison<sup>15</sup>, a smoothing curve was also used along the plotted data with the LOESS tool in R (Local Polynomial Regression Fitting)<sup>16</sup> (Cleveland et al., 2017). This tool fits a polynomial curve using observation within the dataset and a weighted local regression; it is used to identify a possible trend in data, remove background noise, unveil characteristics, trends and cycles to facilitate discussion. The window of observations used for calculation can be adjusted, in this case 75% of observations was found to be visually effective (i.e. a span of 0.75).

The data from the monitoring campaigns were graphed without further treatment (besides the one described in Database Selection, whereas data from continuous monitoring (Figure 16, Appendix) were averaged by day to improve resolution of the graphs.

<sup>&</sup>lt;sup>15</sup> For DO two target values were used, a lower cut provided by the normative and an upper cut to emphasize optimal conditions.

<sup>&</sup>lt;sup>16</sup> LOES source: https://www.rdocumentation.org/packages/stats/versions/3.6.2/topics/loess

## 3. Results and Discussion

#### 3.1. Time series

The following figures show the time series of DO, SC, N-NO3, P-PO4 and BOD5 in each surveillance area (the Maipo river, the Mapocho river, the Puangue creek, the Angostura river and the Lampa creek) within the Maipo basin.

#### Dissolved Oxygen

The Maipo shows for DO that concentrations decrease downstream of the surveillance areas, with the lowest average values in monitoring station MA4 and MA5 ( $8.53 \pm 1.58$  and  $7.66 \pm 1.70$  mg·L<sup>-1</sup>, respectively) (Table 4, Appendix). DO concentrations maintain above the minimum target value in most surveillance areas of these rivers, yet MA4 shows values below its target more frequently (Figure 4). The latter could be associated with the location of MA4, which not only receives the influence of Pirque (agricultural commune of 445.3 km<sup>2</sup> 26521 habitants) upstream of MA3, but also of Isla de Maipo, another agricultural commune with a similar population to Pirque (189 km<sup>2</sup> and 36219 habitants) (INE, 2024), along with several discharges of agricultural and miscellaneous activities. This might increase the input of organic matter impacting DO concentration in MA4.

In the Mapocho river, concentrations seem more disperse compared to the Maipo (upstream and downstream); MP1 shows a clear distance in quality from MP2, having the first close to pristine conditions (9.44  $\pm$  1.40 mg·L<sup>-1</sup> over 8.25  $\pm$  2.00 mg·L<sup>-1</sup>, respectively) (Table 4, Appendix). MP1 surveillance area shows a higher frequency of values below its target (8 mg L<sup>-1</sup>) compared to MP2 (6 mg·L<sup>-1</sup>) (Figure 5 A). The latter becomes evident when considering that MP1 is in an area with minimal intervention and in a guarded location. MP2 on the other hand is located almost 30 km southwest of the city, receiving discharges from two WWTPs (La Farfana and El Trebal), from irrigation canals, and also from the rural communes located outside (southwest) of the urban centre (Peñaflor, Talagante and Calera de Tango communes) (Figure 1). The Puangue creek also shows a marked difference between PU1 and PU2, having higher concentrations upstream compared to downstream (9.48  $\pm$  1.80 mg·L<sup>-1</sup> and 6.32  $\pm$  1.30 mg·L<sup>-1</sup> respectively), which is an effect of the location of PU2 within an intensive agricultural area. PU2 surveillance area shows a group of values below its target (5 mg·L<sup>-1</sup>) with an almost consecutive frequency between April 2018 and June 2019 (Figure 5 B). PU2 receives the impacts of its entire subbasin (heavily agricultural area), which has one of eldest irrigation canals of the Metropolitan region starting in 1854 (ACCLM, 2021). This canal not only receives irrigation water but also multiple minor domestic and industrial discharges (food industry and reuse of water for irrigation) (DGA, 2004). Surveillance area in the Angostura river (AN1) has a good quality compared to its own target value (8.02  $\pm$  1.41 mg L<sup>-1</sup> against 6 mg L<sup>-1</sup>),

with just one value below its target (Figure 5 C). As mentioned in the Introduction, this river is the shortest of the ones considered in this study, being the monitoring station not far from the rivers origin (Figure 1). This certainly allows an observation of good water quality in its area. Lampa creek, LA1, which is located downstream of the city (but before MP2), shows an impaired quality with an average of  $6.41 \pm 1.56 \text{ mg} \cdot \text{L}^{-1}$  (Table 4, Appendix) and with values below its target (5 mg  $\cdot \text{L}^{-1}$ ) across the studied period (Figure 5 C). LA1 receives discharges from one WWTP<sup>17</sup>, in addition with industrial and agricultural activities (SMA-SISS, 2022), domestic and industrial discharges are regulated by law yet not agriculture, which ultimately might be responsible for the lower average of DO.

Considering time evolution, most rivers under study show a similar fluctuation between years. In the Maipo river the fluctuation in MA1, MA2 and MA3 seem less pronounced and more frequent than in MA4 and MA5 where there's a delay (Figure 4). A similar pattern is observed in the Mapocho river, i.e. The upstream surveillance area (MP1) has a more frequent fluctuation than MP2 (Figure 5 A) which instead seems to increase from 2020 on. Puangue creek shows the similar pattern as the Maipo and Mapocho river in PU2 monitoring station (PU1 doesn't have enough data to discuss) (Figure 5 B). Angostura river shows the same fluctuation as the latter river yet with an increase in concentrations on the last period of the curve compared to the first period. Lampa creek shows a mild pattern (almost stable) compared to the other rivers (Figure 5 C). There're two evident outcomes from the data; first, that monitoring stations close and at the outlet of the basin, MA4 and MA5, have lower DO levels because they group most of the discharges from the city and surrounding areas, and second, that in most monitoring stations DO seems to increase over time, which is good considering the natural intensification of activities within the Maipo basin. LA1 monitoring station is the only one whose condition regarding DO remains stable and closer to the minimum required values, i.e. no increase observed. This might occur because of the extensive canal network that exists that overflow during floods (Mellado-Tigre, 2008), which changes the natural response of the river to rain and recharge events and thus makes difficult identify water quality responses in DO. The latter should be taken into consideration when monitoring control and improvements measures in this creek.

As described in the Introduction, biomonitoring data greatly complements physicochemical results, matching some of the findings, such as the lower water quality found in LA1. Considering the imminent saturation condition of part of the Maipo basin, biomonitoring frequency and coverage

<sup>&</sup>lt;sup>17</sup> This WWTP treat the domestic discharge of most part of Lampa commune SACYR-AGUA. 2024. *Concessiones [Concessions]* [Online]. Available: https://www.sacyragua.cl/sacyragua\_areas\_concesion [Accessed 15/03/2024].

efforts should be reconsidered specially to evaluate pollution control measurements for a decontamination plan.

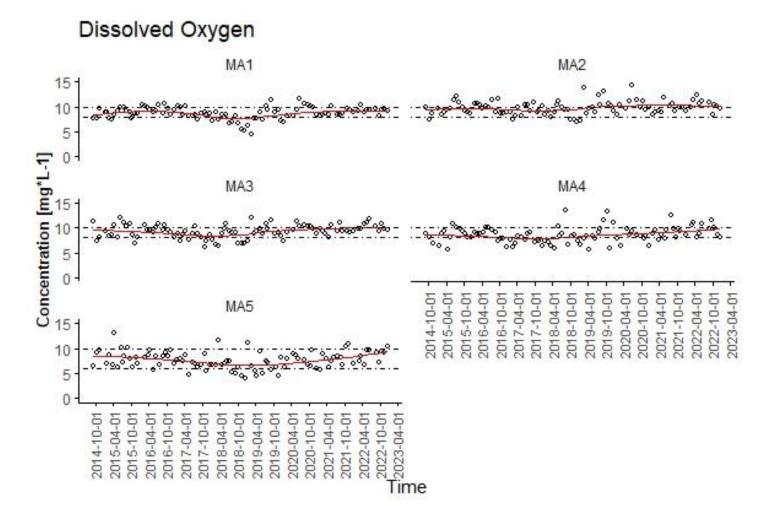


Figure 4. Time series plots of the monitoring campaign data from The Maipo river for Dissolved oxygen (DO) in mg·L-1. The dashed lines show the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MA1 = Maipo river in the Melosas, MA2 = Maipo river in San Jose de Maipo, MA3 = Maipo river Clarillo river, MA4 = Maipo river in Naltahua bridge and MA5 = Maipo river in Cabimbao.

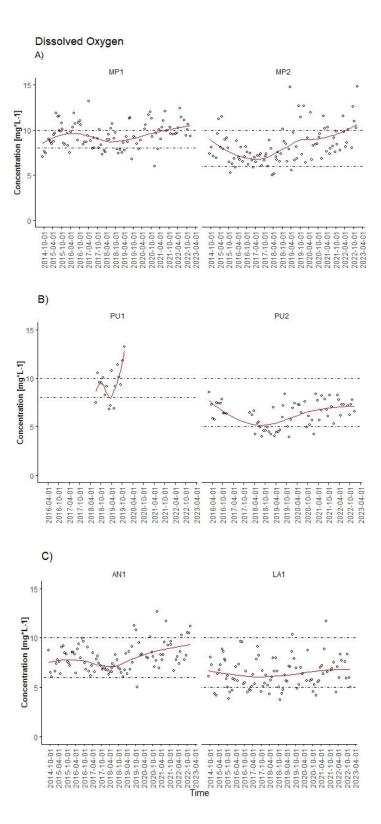


Figure 5. Time series of monitoring campaign data from A) Mapocho, B) Puangue and C) Angostura and Lampa creeks for dissolved oxygen and the red line is a local polynomial regression curve. The dashed line shows the target values associated with local normative which is specific for each surveillance area. Site codes MP1 = Mapocho river in los Almendros, MP2 = Mapocho river in El Monte, PU1 = Puangue creek before Curacavi bridge, PU2 = Puangue in route 78, AN1 = Angostura river in Valdivia de Paine and LA1 = Lampa creek before Mapocho river

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#### Specific Conductivity (SC)

As described in the Introduction, SC is one of the most important water quality parameters to measure, firstly because it reveals pressures on water quality beyond natural sources; it might lack specificity yet it's how the question 'is there something going on with water quality?' is answered (Kney and Brandes, 2007), secondly it is cost-effective to measure, which is essential to build long-term history of water quality and to compare between water bodies (Thorslund and van Vliet Michelle, 2020) and thirdly, SC is directly related to drought conditions in water quality becoming a critical parameter when taking decisions (Peña-Guerrero et al., 2020). SC shows a similar fluctuation in all rivers with evident spatial and time trends; this parameter explains greatly the variation within the Maipo basin along with TDS, turbidity and ORP (according to (MMA, 2021). In the Maipo, surveillance areas upstream of the city, MA1, MA2 and MA3, show a more disperse distribution of SC (1548 ± 431 uS cm<sup>-1</sup>, 1691 ± 468 uS cm<sup>-1</sup> <sup>1</sup> and 1531  $\pm$  395 uS·cm<sup>-1</sup>) compared to downstream MA4 and MA5 (1347  $\pm$  167 uS·cm<sup>-1</sup> and 1581 $\pm$ 219 uS cm<sup>-1</sup>), yet with similar averages and percentiles (25 and 75) and with slighter lower values in MA4 (Table 4, Appendix) (Figure 6), a situation that can be attributed to a higher number of effluents this surveillance area receives (Figure 3), which causes a dilution effect. The target value of SC shows that most surveillance areas, except MA4, have measurements overcoming the respective target, yet this occurs more frequently from October 2018 on in MA2 (target value 1900 uS cm<sup>-1</sup>, overcoming before October 2018 = 7, after October 2018 = 24), MA3 (target value 1900 uS cm<sup>-1</sup>, overcoming before October 2018 = 3, after October 2018 = 17) and MA5 (target value 1600 uS cm<sup>-1</sup>, overcoming before October 2018 = 13, after October 2018 = 45) (Figure 6).

The Mapocho river shows an important difference between monitoring stations reflecting their current location and stressors, i.e. MP1 is in a reference site with lower SC ( $308 \pm 93 \text{ uS} \cdot \text{cm}^{-1}$ , N = 99), whereas MP2 receives the discharges from two WWTPs (La Farfana and El Trebal) and also from the rural communes located outside (Southwest) of the urban centre (Peñaflor, Talagante and Calera de Tango communes) ( $1547 \pm 164 \text{ uS} \cdot \text{cm}^{-1}$ , N = 95) (Table 4, Appendix). Most of the measurements in MP1 are located below the target value until April 2019 where overcoming measurements became more frequent (target value 400 uS \cdot \text{cm}^{-1}, overcoming before April 2019 = 2, after April 2019 = 9); in MP2 this occurs from October 2018 on (target value 1600 uS \cdot \text{cm}^{-1}, overcoming before October 2018 = 8, after October 2018 = 15) (Figure 7 A). The Puangue creek also shows an important difference between upstream and downstream surveillance areas; PU1 shows an average almost two times lower than PU2 ( $194 \pm 23 \text{ uS} \cdot \text{cm}^{-1}$  and  $314 \pm 31 \text{ uS} \cdot \text{cm}^{-1}$ ) (Table 4, Appendix); PU1 monitoring station

characterizes by having small flow and abundant riverine vegetation compared to PU2, which is within a highly intervened area. PU2 shows that across the studied period there are measurements higher than the designated target value (Figure 7 B), yet this is almost constant from March 2018 (target value 1750 uS·cm<sup>-1</sup>, overcoming before March 2018 = 1, after March 2018 = 45). The Angostura river (AN1) is also considered a high-quality water body with an average SC of 1305 ± 177 uS·cm<sup>-1</sup> (Table 4, Appendix), in the beginning of the monitoring study it showed a higher variation that has decreased from 2019 on. AN1 surveillance area also shows a high stability when comparing with target values because no measurements have overcome it within the entire studied period (Figure 7 C). The Lampa creek (LA1) has a high dispersion on its measurements (1633 ± 448 uS·cm<sup>-1</sup>), similar to MA1, MA2 and MP1 (Table 4, Appendix), yet it also shows similar magnitudes compared to the rest of the rivers within the Maipo basin. Regarding its target value, LA1 shows that from April 2018 on the measurements overcome the target often (target value 1900 uS·cm<sup>-1</sup>, overcoming before April 2018 = 2, after April 2018 = 25) (Figure 7 C). 104

The study of temporal trends for SC shows that in every river and creek there is a similar fluctuation with higher values in upstream surveillance areas than downstream showing a possible delay and higher values in late 2014 and again from 2018 until late 2021. There seem to be an increase in SC from 2018 in most monitoring stations, this could also be associated with an important decrease in flow from 2016 to 2019 (Figure 15, Appendix) (DGA, 2024c). The data is telling that water quality according to SC might be influenced greatly by drought conditions. When a decrease in rainfall occurs during an extended period substances concentrate on the soil, then rain occurs, and the substances dissolved and along with particulate matter then change water quality and thus its possibilities of use (Liu et al., 2022). The latter aligns with the data gathered from continuous monitoring in MP1 (Figure 16, Appendix) where higher values are observed from the end of 2018, yet this data has several time gaps that doesn't allow solid statements. Nevertheless, this information, along with DO, Turbidity and Total Suspended Solids (TSS), could greatly improve interpretation of punctual monitoring data; in the same way, to gather this data in the outlet of the basin will help robust any analysis on loading made from this basin.

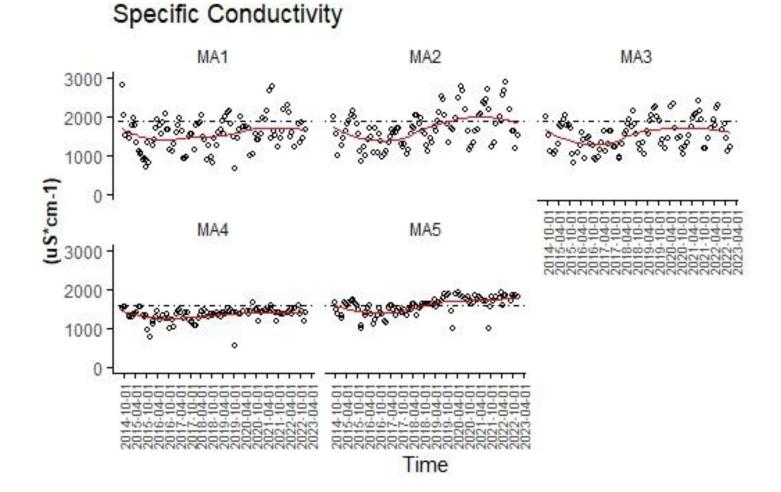


Figure 6. Time series plots of the monitoring campaign data from The Maipo river for Specific Conductivity (SC). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MA1 = Maipo river in the Melosas, MA2 = Maipo river in San Jose de Maipo, MA3 = Maipo river before Clarillo river, MA4 = Maipo river in Naltahua bridge and MA5 = Maipo river in Cabimbao.

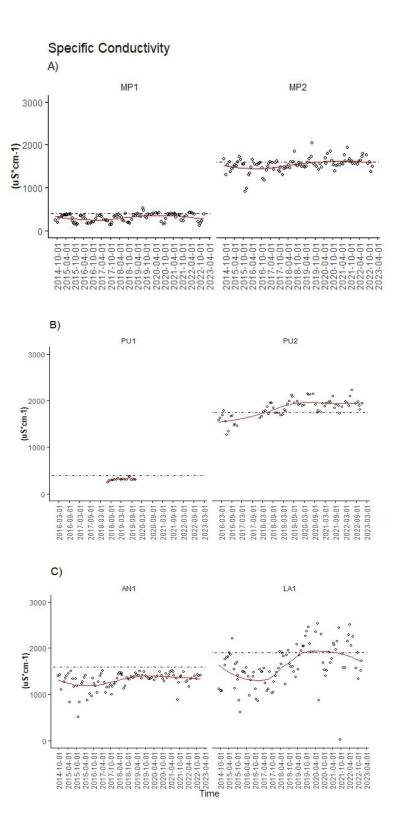


Figure 7. Time series of monitoring campaign data from A) Mapocho, B) Puangue and C) Angostura and Lampa creeks for Specific Conductivity (SC). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MP1 = Mapocho river in los Almendros, MP2 = Mapocho river in El Monte, PU1 = Puangue creek before Curacavi bridge, PU2 = Puangue in route 78, AN1 = Angostura river in Valdivia de Paine and LA1 = Lampa creek before Mapocho river.

#### Nitrate Nitrogen (N-NO3)

N-NO3 shows increasing concentrations downstream of the Maipo (MA4 and MA5), with values in MA5 higher than MA4 (7.565  $\pm$  4.721 mg·L<sup>-1</sup> over 2.591  $\pm$  1.821 mg·L<sup>-1</sup>) (Table 4, , Appendix). The latter becomes evident, considering the location of MA4 and MA5 monitoring stations, especially MA5 which gathers the discharges of the entire basin through its tributaries (Figure 3). Regarding target values comparison, monitoring stations overcome their assigned target values, yet MA4 and MA5 are the ones where this occurs more frequently (Figure 8).

The Mapocho river shows a marked differentiation between MP1 (upstream) and MP2 (downstream) surveillance areas; MP1 concentrations are lower and less disperse than MP2, indicating that MP2 gathers more sources of this nutrient (0.604  $\pm$  0.416 mg·L<sup>-1</sup> against 7.000  $\pm$  3.964 mg·L<sup>-1</sup>); as detailed in the analysis of DO and SC, MP2 receives discharges from point (e.g.: WWTPs and irrigation canals) and diffuse sources (runoff). Both surveillance areas maintain most of their measurements below the respective target values (1.5 and 10.0 mg·L<sup>-1</sup> respectively) (Figure 9 A). The Puangue creek also shows evident differences between upstream (PU1) and downstream monitoring stations (PU2). Even the few measurements available in PU1 shows 29 times smaller average concentrations of N-NO3 than PU2  $(0.393 \pm 0.486 \text{ mg} \cdot \text{L}^{-1} \text{ against } 11.503 \pm 7.127 \text{ mg} \cdot \text{L}^{-1} \text{ respectively})$  (Table 4, , Appendix). The latter is explained by the high intervention that this river has in some stretches upstream, and the intermittent water flow regime due to complete abstraction for small dams which after using the water returned it to the river via canals. PU2 also shows 2 outlier values in June and November 2020 (with 50.120 and 49.460 mg L<sup>-1</sup>, respectively), the value of June is similar to the one obtained in MA5 and MP2 in the same month (32.830 and 36.610 mg·L<sup>-1</sup>, respectively), whereas the value of November relates to a similar value in MA5 the same month (35.500 mg·L<sup>-1</sup>). In June 2020 it rained 110 mm, almost 5 times more than 2021 (22.2 mm) and 4 times more than 2022 (27.5 mm) (DMC, 2024), the runoff of this rain could explain the peak in the monitoring stations already mentioned, which by being located downstream of the main city centre (MP2) and agricultural areas (MA5 and PU2) gather most discharges showing their effects in water quality. The values of N-NO3 from November 2020, where no rain occurred, could be related to overconcentration from lower flows during the year 2020 compared to the other years monitored (Figure 15, Appendix). As expected, meeting the target values of each surveillance area also shows differences, where PU2 has frequently overcome its target (10 mg·L<sup>-1</sup>) across the studied period as to PU1 that has only one measurement above it (1/17 measurements over a 1.5 mg·L<sup>-1</sup> target) (Figure 9 B). The Angostura river (AN1) shows in general values below 4 mg·L<sup>-1</sup> (its target value), with a moderate dispersion toward lower values  $(3.552 \pm 2.108 \text{ mg}\cdot\text{L}^{-1})$  (Table 4, Appendix) (Figure 9 C). These values reflect a low intervention within the surveillance area (MMA, 2021), which it's possible to observe by AN1 location where no discharge points are identified (Figure 3). As already mentioned, there are few values over the target limit (12/91 measurements). The Lampa creek (LA1) shows fluctuating concentrations of N-NO3 (2.377 ± 2.036 mg·L<sup>-1</sup>) (Table 4, Appendix) with less dispersion the first years (from 2014 to late 2017) to higher dispersion the last years of monitoring (from early 2018 to the end of 2022). There's an impaired water quality in the present years with higher values than the assigned target value (4 mg·L<sup>-1</sup>) (Figure 9 C), particularly from early 2018 on. The latter could be attributed to an expansion of the city limits towards Lampa commune, along with an increase in population from 40,228 in 2002 to 102,034 in 2017 (INE, 2018, INE, 2024) and an overall change in lifestyle, in which agricultural settlements are changing towards semi-luxurious households. This change in land use has an intensive use of water, where its consequent disposal doesn't match the growth speed of population (Lukas and Fragkou, 2014).

The time series of N-NO3 indicates that in the Maipo river there's an increase in MA5 starting in October 2017 approximately (Figure 8). In the Mapocho river, MP1 doesn't show a particular time trend, yet MP2 shows a fluctuation of N-NO3 from the beginning of the monitoring programme (July 2014) to October 2018 approximately, then most measurements (75%) seem to stabilize until late 2022 (Figure 9 A). The Puangue creek, PU2 particularly, shows an opposite trend to MP2 where similar values persist within 9.000 mg·L<sup>-1</sup> in the first years (July 2014 to September 2019) to increase noticeably from early 2020 on reaching a maximum of 50.120 mg·L<sup>-1</sup> in June 2020 (Figure 9 B). In the Angostura river values fluctuate, yet most of them do it between a narrow range (4 to 3 mg·L<sup>-1</sup>) with a stable shape (Figure 9 C). The Lampa creek shows that its fluctuation in time seem to increase according to the smoothing curve from 2.000 mg·L<sup>-1</sup> in August 2015 until 9.711 mg·L<sup>-1</sup> in October 2021 (Figure 9 C). Even though this increase seems mild, there should be at least 3 years of additional monitoring to assure that statement as in other cases here analysed (Downes et al., 2002).

The increase in concentration of N-NO3 through the monitoring campaigns might be based on several factors detailed as follows. The growth of agriculture as the main economic activity of the basin, the discharge points identified within the basin (except for electric power generation) and also those non-identified (without a permit) and thus absent in Figure 3; most discharge points shown in Figure 3 count within its emission nitrogen compounds (Table 5, Appendix). There's also the mixed regime of the basin and the mega drought settled in Chile since 2010 (Xu, 2023). Peña-Guerrero *et al.* (2020) indicate in

its study of the Maipo basin that higher concentrations of nitrate could be associated to a lower dilution capacity of the water bodies and the constant discharge and input from diffuse sources, which aligns with the findings from this data. Taking action to control nutrients, particularity nitrate, is complex due to its strong mobility; this means an effective way to control its input might be through water use, particularly water efficiency. From the last SDG 6 report performed in 2021 Chile declared a low efficiency use of water (0.21 USD/m<sup>3</sup>) (UN, 2024), which is attributed to its main user, agriculture, using around 70% of it. This means that any measure to control this nutrient should address water practices that ensure more water efficiency; it's important to understand that it might not be possible to reduce the percentage of water used by agriculture, considering its huge role in food production for Chile and other countries, yet it could be a goal to produce more using the same amount of water. Additionally, if measures are taken to reduce nitrate emissions to water bodies, it is necessary to improve monitoring extending the analysis performed so far (general water quality) to calculate nutrient loading. This implies that fluviometric data should be gathered along with chemical analysis. This is a basic requisite to strengthen the study of water quality (Maybeck et al., 1996).

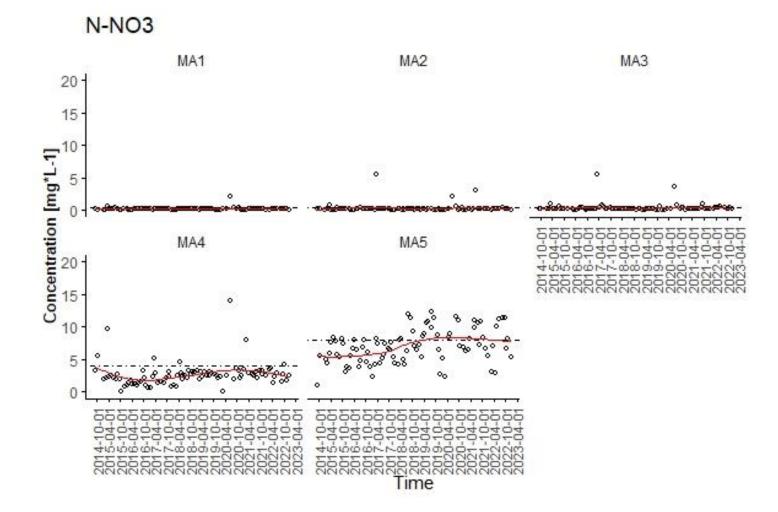


Figure 8. Time series plots of the monitoring campaign data from The Maipo river for Nitrate Nitrogen (N-NO3). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MA1 = Maipo river in the Melosas, MA2 = Maipo river in San Jose de Maipo, MA3 = Maipo river before Clarillo river, MA4 = Maipo river in Naltahua bridge and MA5 = Maipo river in Cabimbao.

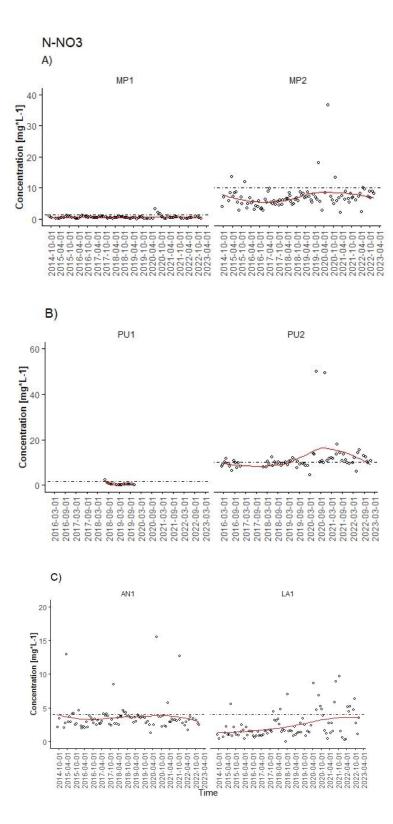


Figure 9. Time series of monitoring campaign data from A) Mapocho, B) Puangue and C) Angostura and Lampa creeks for Nitrate Nitrogen (N-NO3). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MP1 = Mapocho river in los Almendros, MP2 = Mapocho river in El Monte, PU1 = Puangue creek before Curacavi bridge, PU2 = Puangue in route 78, AN1 = Angostura river in Valdivia de Paine and LA1 = Lampa creek before Mapocho river.

# Phosphorus Phosphate (P-PO4)

In the Maipo river P-PO4 shows smaller concentrations (below the detection limit) in upstream surveillance areas, they become detectable in MA4 to increase in MA5 where the higher average concentration of this compound was found ( $0.386 \pm 0.417 \text{ mg} \cdot \text{L}^{-1}$ ) (Table 4, Appendix). Regarding target values, from MA3 to MA5 measurements overcome each target ( $0.08 \text{ mg} \cdot \text{L}^{-1}$  in each surveillance area), yet this occurs rarely (Figure 10).

In Mapocho river, MP1 (upstream) differentiates from MP2 (downstream) evidently, the latter with an average concentration 94 times greater than MP1 and a higher dispersion also (0.753 ± 0.903 mg L<sup>-1</sup> over  $0.008 \pm 0.015$  mg·L<sup>-1</sup>) (Table 4, Appendix). The target values of each surveillance area (MP1 0.08 mg·L<sup>-1</sup> and MP2 2.5 mg·L<sup>-1</sup>) are met with 2 values overcoming it in MP1 and none in MP2 across the studied period (Figure 11 A). The Puangue creek, as in the Mapocho and Maipo rivers, shows an evident difference between upstream (PU1) and downstream surveillance areas (PU2) (0.008 ± 0.005 mg·L<sup>-1</sup> and 0.979  $\pm$  0.489 mg·L<sup>-1</sup>, respectively), even considering the few values gathered from PU1. Most measurements in each surveillance area met their respective target value, except for one value in PU2 (1/68 measurements) (Table 4, Appendix), and Figure 11 B). The Angostura river (AN1) shows a higher dispersion in its measurements  $(0.182 \pm 0.364 \text{ mg} \text{ L}^{-1})$  compared to upstream surveillance areas in the Maipo river, Mapocho river and Puangue creek (Table 4, Appendix). From Figure 11 C it's possible to observe frequent overcoming of measurements from the target value (0.15 mg L<sup>-1</sup>) across the studied period. Lampa creek (LA1) evidences a strong presence of pressures that cause higher concentrations of P-PO4, as to in other downstream monitoring stations (MA5, MP2 and PU2) reaching an average of 0.604  $\pm$  0.526 mg L<sup>-1</sup> (Table 4, Appendix). The target value for P-PO4 in this surveillance area (0.6 mg·L<sup>-1</sup>) is overcome frequently since March 2018 (Figure 11 C).

The time series of P-PO4 in the Maipo river shows a mild increase in time in MA5 which started in late 2017 and that stabilizes around 0.5 mg·L<sup>-1</sup> until October 2021 when it decreases again (Figure 10). The Mapocho river, particularly MP2, shows a soft increase which occurs from July 2018 until December 2022 (Figure 11 A). The Puangue creek shows an increase of concentrations from March 2017 until March 2021 in PU2, then decreasing until the last measurement (Figure 11 B). The Angostura (AN1) river shows a steady trend across the monitoring period (Figure 11 C) and Lampa creek (LA1) shows an evident increase of concentrations from October 2016 with 0.200 mg·L<sup>-1</sup> until February 2022 with 1.249 mg·L<sup>-1</sup> when a decrease starts (Figure 11 C). This means that there's evident

disturbance on water quality in the Lampa creek regarding phosphorus, with an evolution that separates greatly from what it's desirable.

Phosphorus is not a parameter that rises many alarms so far because the focus of it impact is mainly on the outlet of the Maipo basin (beyond MA5) where there's a wetland, but now it's important to maintain its control also upstream considering a recent environmental management tool named 'Declaration of Urban Wetlands' from the MMA. This is a process born from the Law 21.202<sup>18</sup> of 2020 that allows the declaration of an urban wetland with consequent development of protection actions towards them, an urban wetland is defined as "surfaces covered with water, whether natural or artificial, permanent or temporary, stagnant or flowing, fresh, brackish or salty, including areas of marine water, whose depth at low tide does not exceed six meters and that are totally or partially within the urban *limit"* (Article 1<sup>st</sup>, Law 21.202/2020). There're no urban wetlands declared in the Lampa surveillance area, yet the possibility exists because there's a water course representing a habitat for several ecosystems. The latter also raises the need to change the location of PU1 monitoring station to a place with constant water flow that allows to gather more data, because there's a declaration in place of an urban wetland over the surveillance area of PU1<sup>19</sup> (MMA, 2024), and the need to overview the P-PO4 data of MA4 and MA5 where another urban wetland was declared<sup>18</sup>. The impact that wetlands have as nutrient sink is an interesting angle to explore in the Maipo basin because even though their function has been overlooked from the point of view of this monitoring programme, there's a chance to do so through decontamination actions that should develop when the saturation declaration of this basin finally becomes public.

In a similar manner how nitrate removal must be managed, phosphate transportation to water courses must be prevented with measures oriented to diminish soil erosion where most of the phosphate concentrates, and to control stormwater flow, which transports particulate phosphorus (River and Richardson, 2018).

<sup>&</sup>lt;sup>18</sup> Law 21.202 Modifies several legal bodies with the purpose of protecting urban wetlands. Source: https://www.bcn.cl/leychile/navegar?idNorma=1141461

<sup>&</sup>lt;sup>19</sup> Code of declaration: HU-0082 for the wetland in the Puangue river, and Code of declaration: HU-0095 and HU-0055 for the wetland in the Maipo river.

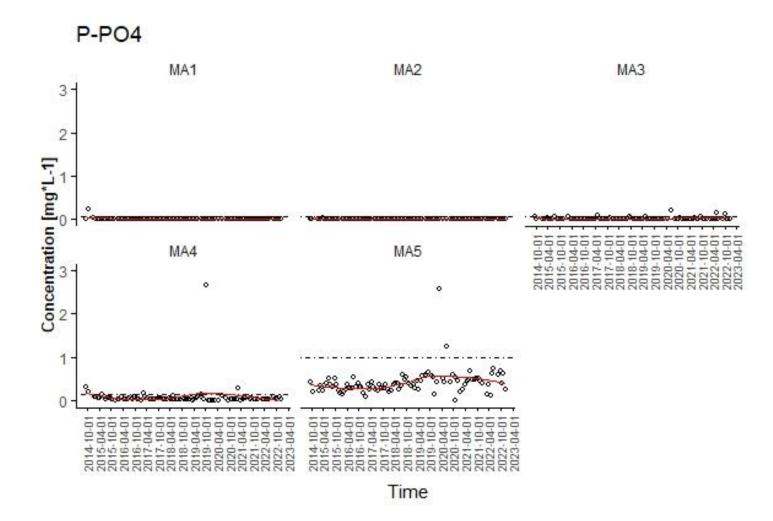


Figure 10. Time series plots of the monitoring campaign data from The Maipo river for Phosphorus Phosphate (P-PO4). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MA1 = Maipo river in the Melosas, MA2 = Maipo river in San Jose de Maipo, MA3 = Maipo river before Clarillo river, MA4 = Maipo river in Naltahua bridge and MA5 = Maipo river in Cabimbao.

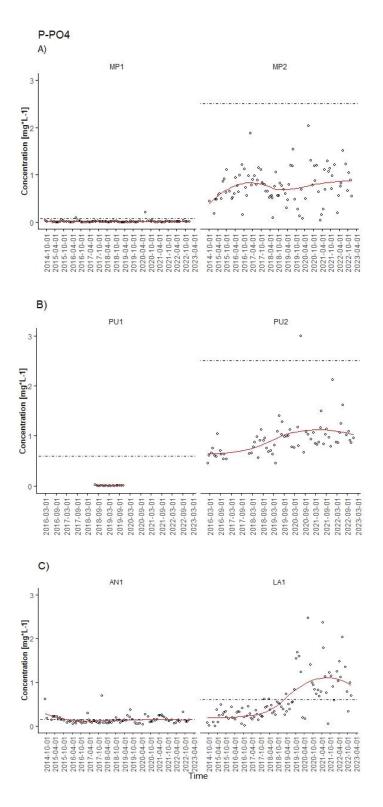


Figure 11. Time series of monitoring campaign data from A) Mapocho, B) Puangue and C) Angostura and Lampa creeks for Phosphorus Phosphate (P-PO4). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MP1 = Mapocho river in los Almendros, MP2 = Mapocho river in El Monte, PU1 = Puangue creek before Curacavi bridge, PU2 = Puangue in route 78, AN1 = Angostura river in Valdivia de Paine and LA1 = Lampa creek before Mapocho river.

#### Biochemical Oxygen Demand (BOD5)

A general view of BOD5 in the Maipo river shows that the measurements locate below the detection limit of the analytical technique (>50%) in most surveillance areas except for MA5 (only 11%) (Table 4, Appendix). It's also possible to observe more dispersion of the data from the surveillance areas located downstream, such as MA3 and MA5 ( $4.3 \pm 6.9 \text{ mg} \cdot \text{L}^{-1}$  and  $4.4 \pm 3.6 \text{ mg} \cdot \text{L}^{-1}$ , respectively) (Table 4) and the highest values of the river (51.0 mg $\cdot \text{L}^{-1}$  in October 2018 and 20.8 mg $\cdot \text{L}^{-1}$  in April 2022, respectively). Target values assigned for each surveillance area are met most part of the studied period, yet there're frequently overcome from July 2021 on in most of the surveillance areas (Figure 12).

The Mapocho river shows more dispersion (MP1 2.6  $\pm$  1.9 mg·L<sup>-1</sup> and MP2 5.0  $\pm$  4.6 mg·L<sup>-1</sup>) (Table 4, Appendix) compared to the Maipo in the entire studied period. As mentioned in previous parameters, MP1 has lower values compared to MP2 corroborating that MP1 has a better water guality than MP2. MP1 shows an overcome of its target value (5 mg·L-1) across the studied period, MP2 group its overcome from September 2021 on (MP2 target value 10 mg  $L^{-1}$ , overcome before September 2021 = 0, after September 2021 = 9) reaching a maximum of 24.4 mg  $L^{-1}$  in September 2021 (Figure 13 A). Puangue creek has few values in PU1 that cannot allow to make further interpretations, PU2 on the other hand show several measurements trough the studied period (Figure 13 B). These measurements distribute along a range of 1.0 to 20.8 mg·L<sup>-1</sup> with a P<sub>25</sub> of 4.0 mg·L<sup>-1</sup> and P<sub>75</sub> of 9.0 mg·L<sup>-1</sup> showing that its values are below the value of a non-treated domestic sewage (100-400 mg L<sup>-1</sup>) (Sancha (nd)) yet comparable to a very polluted water body (EuroStat, 2024). The values of BOD5 in PU2 are located mostly under the target value (10 mg L<sup>-1</sup>), yet concentrations that overcome the target mostly occurred between July 2021 and June 2022, reaching a maximum of 20.8 mg·L<sup>-1</sup> in July (Figure 13 B). The Angostura river (AN1) show less fluctuation of its measurements across the studied period compared to the rest of the monitoring stations located upstream  $(2.6 \pm 1.9 \text{ mg} \cdot \text{L}^{-1})$  (Table 4, Appendix), identifying 2 set of peaks in its data set, one between October 2014 and march 2015, and another between June 2021 and April 2022 (Figure 13 C). The target value of this surveillance area is 10 mg·L<sup>-1</sup>, which is 5 times higher than its median (2.0 mg·L<sup>-1</sup>) (Table 4, Appendix), registering only one measurement above it (1/85 with a concentration of 11.0 mg·L<sup>-1</sup>). The Lampa creek (LA1) has a noticeable dispersion (5.6  $\pm$  5.1 mg·L<sup>-1</sup>) as also shown in MA3 and MP2 surveillance areas (Table 4, Appendix). The target value (10 mg·L<sup>-1</sup>) was not overcome until May 2020, a situation that extended until July 2022 reaching a maximum of 25.6 mg L<sup>-1</sup> in April 2022 (Figure 13 C).

The time series of BOD5 shows in the Maipo river that a soft increase occurred in all surveillance areas, yet more pronounced in MA3 and MA5, this increase became evident around 2019 and 2022 depending on the monitoring station, MA4 on the contrary shows a steadier trend (Figure 12). The Mapocho river shows a similar increase as the one described for the Maipo river but occurs only in MP2 (downstream), the increase starts smoothly from the beginning of the monitoring program (2 mg·Lmg·L<sup>-1</sup> approximately) reaching a stabilization between march 2016 and April 2018, and then it increases again to reach a maximum in October 2021 (Figure 13 A). The Puangue creek, particularly PU2, shows a smooth decreasing trend from the beginning of the monitoring programme until December 2021 where it increases until September 2021 and then decreases again to the last measurement in 2022 (Figure 13 B). The Angostura river shows a steady pattern of concentrations in general whereas the Lampa creek increases its BOD5 concentrations abruptly from August 2018 until May 2021

The last results show a peak in concentrations in all rivers, particularly noticeable in the monitoring stations located downstream of the urban centres, these peaks overlap with the pandemic period in Chile (03/03/2020 – 31/10/2021) (MINSAL, 2022), but also with the consequent increase in poverty and the immigration wave (Veliz et al., 2023). When discussing the pandemic effect, this might become a reasonable explanation for the results considering the fact that the population was compelled to spend more time in their homes, which could increase the production of domestic wastewater between that period yet this doesn't align with the results gathered by the SISS (SISS, 2024) where the highest production of wastewater in the region from the period covering 2012 to 2021 occurred between 2017 and 2019, i.e. previous to the pandemic. A complementary explanation could also be that WWTPs might have relaxed their operations considering the restrictions (i.e.: people circulation, supplies chain disruption, etc.), which ultimately impacts wastewater treatment and disposal, but the data again shows that the highest sanction numbers in the region occurred between 2015 and 2019, decreasing in number until the last report in 2021 (Figure 17, Appendix). Another view of this could be that the control of the WWTPs was not performed as usual or their processes also were underdeveloped considering the circumstances, unfortunately this analysis cannot be addressed in this research.

approximately where it starts to decrease (Figure 13 C), in a similar manner as found in P-PO4.

When considering lack of access and immigration, it's important to note the important factor is the increase of informal settlements around the Metropolitan region (Figure 18, Appendix) that do not have sanitary access and disposal of wastewater (Lopez-Morales et al., 2018), discharging it directly to watercourses. Since the Metropolitan region concentrates most of the immigrant population (SNM,

2024) and it's the most expensive region to live within Chile (INE, 2022), the increase in informal settlements and their consequences (irregular wastewater discharge) could have an important weight to what's observed in BOD5, particularly when its peaks coincides (SNM, 2024) with the ones observed in the data (between 2020 and 2022). Finding an explanation to the increase of BOD5 between 2020 and 2022 is not a straightforward process because there are other factors not considered here, yet there're several measures to take that could improve interpretation of this data in the future, for example, to monitor other parameters that better reflect these stressors (e.g.: faecal coliforms, E. coli, pharmaceutical products, TSS, NTK, COD, among others.), to collate this data with flow to calculate loading and estimate a balance of organic input, and also to set new monitoring stations that capture the impact of informal settlements.

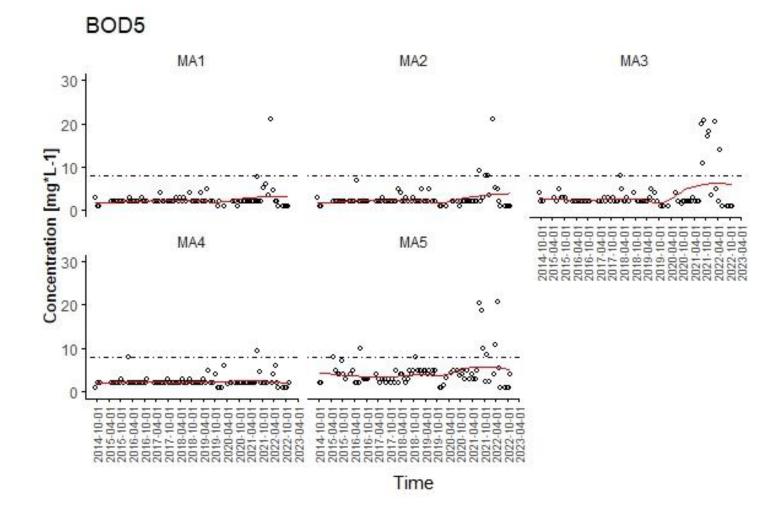


Figure 12. Time series plots of the monitoring campaign data from The Maipo river for Biochemical Oxygen Demand (BOD5). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MA1 = Maipo river in the Melosas, MA2 = Maipo river in San Jose de Maipo, MA3 = Maipo river before Clarillo river, MA4 = Maipo river in Naltahua bridge and MA5 = Maipo river in Cabimbao.

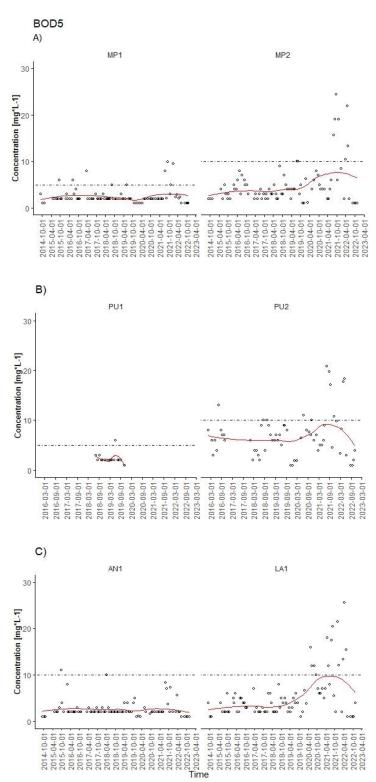


Figure 13. Time series of monitoring campaign data from A) Mapocho, B) Puangue and C) Angostura and Lampa creeks for Biochemical Oxygen Demand (BOD5). The dashed line shows the target values associated with local normative which is specific for each surveillance area and the red line is a local polynomial regression curve. Site codes MP1 = Mapocho river in los Almendros, MP2 = Mapocho river in El Monte, PU1 = Puangue creek before Curacavi bridge, PU2 = Puangue in route 78, AN1 = Angostura river in Valdivia de Paine and LA1 = Lampa creek before Mapocho river.

# 4. Conclusions and recommendations

The 8 years of data (2014 to 2022) from the Monitoring Programme of The Maipo river basin have derived the following findings:

- Dissolved Oxygen shows fluctuation in each surveillance area (the Maipo, Mapocho, Angostura and Puangue) within historic values, except for the Lampa creek surveillance area where a mild decrease was found over time.
- Specific conductivity in most surveillance areas, except for the Mapocho and Angostura river, showed an increase in values over time, relating this pattern to a decrease in flow and precipitation caused by the historic drought.
- Nitrogen Nitrate and Phosphorus Phosphate are causing a decrease in water quality in the Maipo river (in MA5 monitoring station, located close to the outlet of the basin), in the Puague creek (in PU2 monitoring station) and the Lampa creek (LA1) over time. The effect caused by Nitrate Nitrogen is higher and at a higher rate compared to phosphorus. In both cases the decrease in flow from rivers might be the main reason for the increase in concentrations found.
- BOD5 revealed a mild fluctuation and change through time in each surveillance area until 2020 where it increases noticeably. This increase coincides with an appearance of informal settlements located close to the rivers, yet further investigation must be done to ensure a correlation.

From the latter, the recommendation is to intensify monitoring and include parameters that narrow the knowledge gap for future actions as detailed next:

- To increase the number of continuous monitoring stations within the basin, particularly in MA5 (outlet of the Maipo basin) and in PU2 (outlet of the Puangue creek subbasin), which is where fluviometric infrastructure from the DGA already exists.
- Within a continuous monitoring scheme, it's necessary to measure basic field parameters in MA5 and PU2, such as pH, specific conductivity, dissolved oxygen and temperature, and it is recommended to include turbidity measurements in all monitoring stations systematically to understand better the impact of seasonality changes and separate them from anthropic alterations, such as gravel mining and wastewater discharges. Turbidity can be included in the continuous monitoring scheme within the Maipo basin or be measured in each monitoring campaign depending on the resources available.

- Based on BOD5 results, there's a gap in information regarding organic pollutants that need to be filled within the Maipo Monitoring Programme. The recommendation is to monitor microbiological indicators (e.g.: total, faecal and/or E. coli) and complete the nitrogen scheme parameters including Kjeldahl nitrogen and nitrite to estimate total nitrogen values, which are closely related to organic input.
- Include hydrology data within the Maipo Monitoring Programme which will help to better understand loading changes for any future measurement implemented to control pollution.

These recommendations are basic considering the stressors present in the Maipo basin and are thought to work as input for any measure taken once the decontamination programme on this basin is in place.

#### 5. Disclaimer

This analysis does not represent a formal evaluation of the target values settled for each surveillance area established by the S.D.53/2014 in the Maipo basin, there are designed mechanisms and organisms responsible within this normative to execute such validation. Comparison with target values made by the author is just an exercise to enrich interpretation of the results.

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"Science is not just to make discoveries: it is also important to value the knowledge, clean the straw, organize it in an accessible way, socialize it and found its utility".

Jose Manuel Mechado

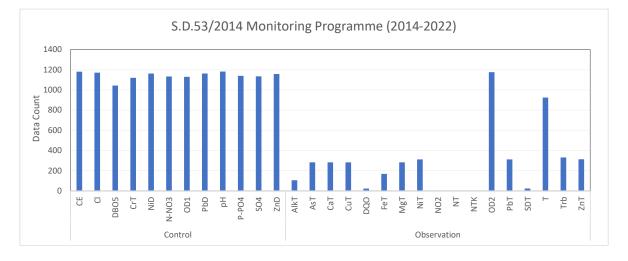
# 8. Appendix

			Surveillance										
Parameter	River System		Area	Ν	N <dl< th=""><th>min</th><th>max</th><th>median</th><th>mean</th><th>sd</th><th>se</th><th>P25</th><th>P75</th></dl<>	min	max	median	mean	sd	se	P25	P75
DO [mg*L-1]	Maipo	Upstream	MA1	96	-	4.41	11.61	8.78	8.72	1.22	1.25	8.07	9.47
		Upstream	MA2	94	-	6.88	14.32	9.77	9.80	1.36	0.14	8.88	10.50
		Upstream	MA3	93	-	6.22	12.04	9.27	9.24	1.31	0.14	8.48	10.19
		Downstream	MA4	95	-	5.50	13.50	8.43	8.53	1.58	0.16	7.64	9.42
		Downstream	MA5	95	-	4.08	12.98	7.48	7.66	1.70	0.17	6.56	8.72
	Mapocho	Upstream	MP1	97	-	6.00	13.16	9.39	9.44	1.40	0.14	8.47	10.31
		Downstream	MP2	95	-	5.00	14.80	7.89	8.25	2.00	0.20	6.86	9.14
		Upstream	PU1	17	-	6.80	13.25	9.51	9.48	1.80	0.44	8.28	10.53
	Puangue	Downstream	PU2	67	-	3.97	8.55	6.42	6.32	1.30	0.16	5.27	7.32
	Angostura	Upstream	AN1	94	-	5.02	12.68	7.80	8.02	1.41	0.15	6.93	8.62
	Lampa	Downstream	LA1	95	-	3.75	11.69	6.24	6.41	1.56	0.16	5.28	7.30
		Upstream	MA1	98	-	676	2802	1549	1548	431	44	1276	1818
SC (uS*cm-1)	Maipo	Upstream	MA2	95	-	841	2869	1637	1691	468	48	1327	2008
		Upstream	MA3	94	-	801	2400	1487	1531	395	41	1223	1803
		Downstream		95	-	564	1667	1378	1347	167	17	1288	1431
		Downstream		97	-	985	1913	1622	1547	219	22	1471	1749
		Upstream	MP1	99	-	124	532	342	308	93	9	223	384
	Mapocho	Downstream		95	-	909	2047	1547	1542	164	17	1480	1610
		Upstream	PU1	17	-	253	386	309	314	31	8	302	316
	Puangue	Downstream		68	-	1272	2233	1885	1840	194	23	1731	1954
				95	-	509	1522		1305		18	1731	1954
	Angostura	Upstream	AN1					1355		177			
	Lampa	Downstream		98	-	18	2530	1590	1633	448	45	1392	1918
N-NO3 [mg*L-1]	Maipo	Upstream	MA1	92	0	0.010	2.200	0.232	0.259	0.225	0.023	0.185	0.290
		Upstream	MA2	92	0	0.010	5.585	0.226	0.354	0.668	0.070	0.180	0.281
		Upstream	MA3	91	0	0.010	5.561	0.282	0.417	0.673	0.071	0.219	0.364
		Downstream		92	0	0.010	14.040	2.424	2.591	1.821	0.190	1.777	3.021
		Downstream		93	0	0.919	35.500	6.924	7.565	4.721	0.490	5.272	8.564
	Mapocho	Upstream	MP1	90	0	0.050	3.270	0.529	0.604	0.416	0.044	0.376	0.700
		Downstream	MP2	92	0	2.117	36.610	6.521	7.000	3.964	0.413	5.325	8.013
		Upstream	PU1	17	0	0.025	2.099	0.306	0.393	0.486	0.118	0.128	0.393
	Puangue	Downstream	PU2	67	0	4.447	50.120	10.000	11.503	7.127	0.871	9.066	11.75
	Angostura	Upstream	AN1	91	0	1.295	15.480	3.177	3.552	2.108	0.221	2.641	3.714
	Lampa	Downstream	LA1	91	0	0.027	9.711	1.560	2.377	2.036	0.213	1.031	2.913
P-PO4 [mg*L-1]		Upstream	MA1	92	14	0.003	0.251	0.008	0.012	0.026	0.003	0.006	0.010
		Upstream	MA2	92	12	0.003	0.039	0.008	0.009	0.006	0.001	0.006	0.011
		Upstream	MA3	91	2	0.004	0.217	0.013	0.024	0.033	0.003	0.009	0.021
		Downstream	MA4	93	1	0.003	2.660	0.044	0.087	0.274	0.028	0.029	0.072
	Maipo	Downstream	MA5	94	0	0.016	2.572	0.386	0.417	0.284	0.029	0.265	0.507
		Upstream	MP1	91	20	0.003	0.203	0.008	0.015	0.024	0.003	0.004	0.017
	Mapocho	Downstream		93	0	0.035	7.101	0.753	0.903	0.987	0.102	0.546	1.048
		Upstream	PU1	17	4	0.003	0.019	0.007	0.008	0.005	0.001	0.004	0.010
	Puangue	Downstream		68	0	0.457	3.520	0.892	0.979	0.489	0.059	0.709	1.063
	Angostura	Upstream	AN1	92	0	0.042	3.500	0.121	0.182	0.364	0.038	0.090	0.158
	Lampa	Downstream		92	0	0.0042	2.469	0.429	0.604	0.526	0.055	0.236	0.822
BOD5 [mg*L-1]		Upstream	MA1	82	57	1.0	21.0	2.0	2.5	2.4	0.3	2.0	2.0
		Upstream	MA1 MA2	83	55	1.0	21.0	2.0	2.3	2.4	0.3	2.0	2.0
		•	MA3	83	42	1.0	51.0	2.0	4.3	6.9	0.3	2.0	3.0
		Upstream											
		Downstream		87	52	1.0	9.4	2.0	2.3	1.3	0.1	2.0	2.0
	Maipo Mapocho	Downstream		83	9	1.0	20.8	4.0	4.4	3.6	0.4	2.7	5.0
		Upstream	MP1	86	58	1.0	9.9	2.0	2.6	1.9	0.2	2.0	2.1
		Downstream		84	14	1.0	24.4	4.0	5.0	4.6	0.5	2.0	6.0
B		Upstream	PU1	16	11	1.0	6.0	2.0	2.3	1.1	0.3	2.0	2.0
	Puangue	Downstream		64	4	1.0	20.8	6.3	7.0	4.4	0.6	4.0	9.0
	Angostura	Upstream	AN1	85	29	1.0	11.0	2.0	2.6	1.9	0.2	2.0	2.0
	Lampa	Downstream	LA1	85	19	1.0	25.6	4.0	5.6	5.1	0.6	2.0	6.0

Table 4. Summary of statistics performed for El Maipo river basin using monitoring campaign data for DO, SC, (N-NO3, P-<br/>P-PO4, and BOD5. N<DL: Measurements below DL, "-": Not applicable.</th>

	Discharge sources characterization											
Parameter	Water production & Distribution	Comerce	Residues disposal	Paper & cellulose industry	Plastic & chemical industry	Minning	Other	Fish and aquaculture	Agricultural production	Oil	Thermopower	
Oil & grease	1	9	2	7	5	3	54	4	16	2	10	
Aluminium	1	5	1	6	4	3	35	5	9	2	8	
Arsenic	1	5	2	6	1	3	32	4	8	1	8	
Bencene	-	1	-		-		3		2			
Boron	1	2	2	6	2	2	32	2	9		9	
Cadmium	1	5	2	7	1	3	34	3	8	1	8	
Cyanide	1	5	1	7	1	3	32	3	8	1	7	
Chloride	1	3	2	6	3	2	33	2	11	-	9	
Copper	1	5	2	6	1	3	33	4	9	2	10	
Hexavalent Chromium	1	5	1	7	1	2	33	3	8	1	7	
Total Chromium	_	3	_		_	1	2	2		1	4	
Tin		3	1			1	2	2		1	2	
Fluoride	1	5	2	6	2	3	32	5	8	2	9	
Total phosphorus	1	4	1	7	2	2	52	5	13		8	
Fixed Hidrocarbons	1	3	2	6	2	2	32	1	6		7	
Total Hidrocarbons		3	1	2		1	2	2		2	2	
Volatiles Hidrocarbons		3	1	1			2	2		2	2	
Iron/dissolved iron	1	3	1	6	4	3	31	4	10		9	
Phenol index	1	4	1	6	2	3	31	3	6	2	7	
Manganese	1	5	2	6	1	3	37	3	8	2	8	
Mercury	1	5	1	7	1	3	31	4	9	2	8	
Molibdene	1	5	2	6	1	3	32	5	8	2	8	
Nickel	1	5	1	7	1	3	34	3	8	1	9	
Nitrite + Nitrate		2			3		5		2			
Ammonia Nitrogen (N-NH3)							1					
Total Kjendahl Nitrogen	1	6	1	7	5	3	57	5	16		8	
PCP	1	2	1	6	1	2	30	1	8		5	
Lead	1	5	1	7	1	3	35	3	8	1	9	
Selenum	1	5	1	6	1	3	32	5	8	2	8	
TSS	1	7	2	7	2	3	61	5	14	2	11	
Sulphate	1	3	2	7	5	2	43	2	8		8	
Sulphur	1	6	1	6	2	2	33	3	8	2	8	
Methylene Blue Active		3				1	2	3		1	3	
Tetrachloroethene	1	2	1	6	2	2	30	1	8		5	
Toluene / methylbenzene /												
Toluene / Diphenylmethane	1	2	1	6	1	2	29	1	8		5	
Triclorometano	1	2	1	6	2	2	33	1	9		7	
Xilene	1	2	1	6	1	2	29	1	8		5	
Zinc	1	6	1	7	1	3	36	3	8	2	10	

# Table 5. Characterization of the contaminants (parameters) of the point source discharges identified in El Maipo Basin (SMA-SISS, 2022).





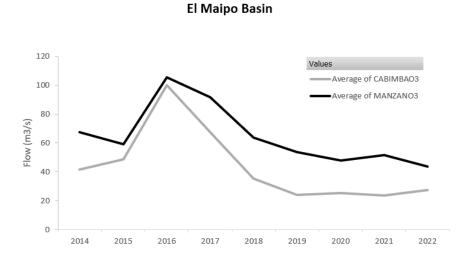


Figure 15. Annual average flow between 2014 and 2022 from Maipo en el Manzano (upstream) and Maipo en Cabimbao (downstream) continuous monitoring stations. Source: self made

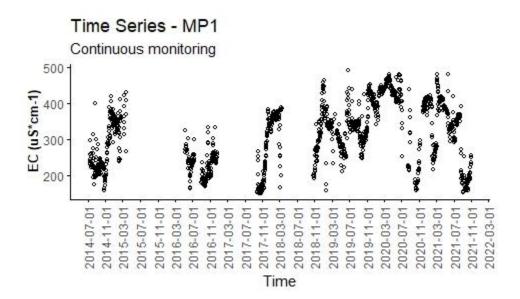


Figure 16. Daily average SC between 2014 and 2022 from the Mapocho in Los Almendros (upstream) continuous monitoring station. Source: self made

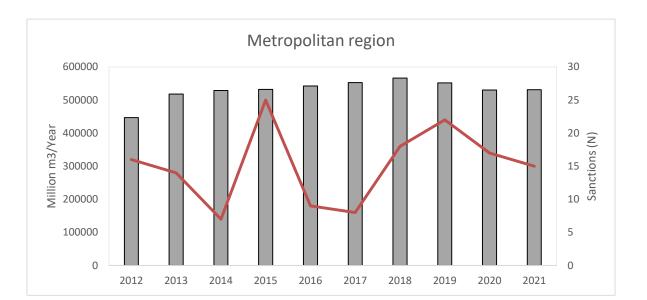


Figure 17. Volume of wastewater treated in the Metropolitan region under the sanitary concession scheme between 2012-2021 and the number of sanctions registered for the same period. Source: (SISS, 2024)

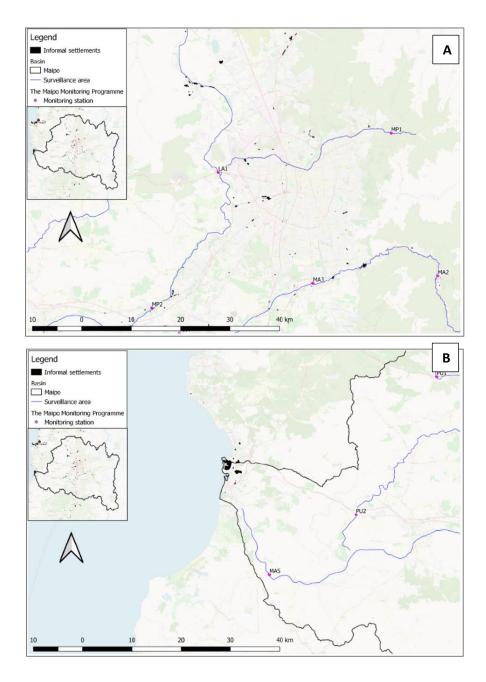


Figure 18. Cadastre of informal Settlements within the Metropolitan Region. A) Zoom to the settlements located in the and around the city centre and B) Zoom to the settlements located in the outlet of the Maipo basin. Source: (MINVU, 2022)

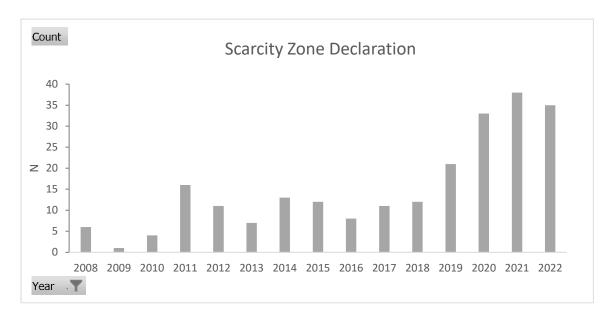


Figure 19. Scarcity declaration zone in Chile between 2018 and 2022. Source: (DGA, 2023)

