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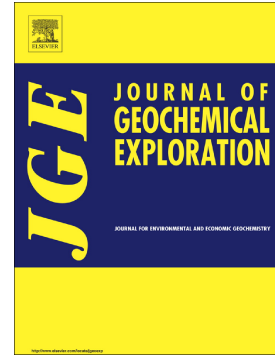
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Potential contamination of stream waters by ultramafic mining sediments: identification of geochemical makers (New Caledonia)

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Abstract:

The ultramafic massifs of New Caledonia are mainly composed of regolites with lateritic soils rich in metals such as Co, Fe, Mg and Ni. The nickeliferous ore is exploited by opencast mines. After rainfalls, erosion and particle runoff cause the mobilization of metals and metalloids in surface waters. The objective of this study is (i) to determine the geochemical background of metals and metalloids in surface waters draining a mining ultramafic massif, (ii) to identify the geochemical markers influenced by the mining of nickeliferous ore (iii) and to define discriminant values of the mining impact. Hydrochemical monitoring was carried out on five streams draining the Koniambo massif over a 15-years period. Twenty-four elements were analyzed for their total concentration and 18 for their dissolved concentration (<0.45µm). The descriptive analysis shows that one river has higher total concentrations of As, Co, Cr, Ni, Mn, Al, Fe, Si and Mg and higher dissolved concentrations of Al, Cr, Ni than the other 4 rivers. This difference results from an old mine whose erosion exacerbates sediment transport. These 5 rivers drain the same ultramafic massif of small surface area (21 km²). The description by the boxplot method of the 4 non-impacted rivers allowed us to define a geochemical background. The graphical comparison between the geochemical background with the median values of the river impacted, validated by the ANOVA one way, allowed us to identify markers of the mining anthropization. The use of a supervised classification as a decision tree ranks the markers according to their discriminating power. In addition, this method determines the range of threshold values that separate impacted from non-impacted rivers. The elements Cr, As, Si, Mg and Al are identified as discriminating markers for total concentrations. Only Cr has been identified as a discriminating metal for the dissolved fraction with an interval around 58 µg/l. This concentration is close to the limit defined by the WHO for drinking water which is 50 µg/l.

Keywords: hydrogeochemical background, ultramafic complexes, surface waters, total metal concentration, dissolved metal concentration, machine learning

1 Introduction

Over the last decades, global awareness has led to a consensus on the need to reconcile economic expansion and ecosystem protection/preservation. Accordingly, an environmental impact assessment predates any mining project to highlight environmental impact and risk. The regulations require an environmental inventory (zero state) before any exploitation (Glasson and Therivel, 2013; Nikièma et al., 2019) as mining affects the natural environment (huge waste production, stripping of fertile soils, transport and storage of mines tailings, release of metallic elements through aerosols or suspended particles, etc.). Hydrosystems, because they are a vital resource at the interface of all ecosystems, require rigorous quality monitoring. As part of environmental monitoring in mining areas, the freshwater geochemical background compiles the concentration values characteristic of the environment prior to mining activity (Nordstrom, 2015). Water quality monitoring consists of comparing the new concentrations to those of the geochemical background, so chemical elements whose concentrations differ significantly are impacted by mining activity. These elements become tracers, or indicators, of the impact or worse, pollution and guide environmental monitoring protocols (Matschulatt et al., 2000; Salminen et al., 2000; Reimann et al., 2005; Guillén et al., 2011; Hao et al., 2014; Levitan et al., Li et al., 2014; 2014; Nordstrom, 2015; Rezza et al., 2018; Zuluaga et al., 2017; Sahoo et al., 2020).

The main task is to define a robust statistical approach to assess the threshold values of the geochemical background. This method must be able to distinguish between "normal" variations of concentrations, representative of water not impacted by mining activity from "abnormal" variations. The distinction in surface waters between the concentrations resulting from naturally occurring mineralization (geogenic) and those resulting exclusively from mining (anthropogenic) turn out to be very complex. This is particularly true when mining reshapes the land constituting by homogeneous geological units. In this case, no imported chemical elements contaminate the environment. If so, to discriminate impacted and non-impacted waters a very dense ante-exploitation database is needed. Data collected must cover a sufficiently long period to define the natural chemical variability within the required precision (Biddau and Cidu, 2005; Plumlee et al., 1999). However, there are no strict regulations defining a "universal" protocol for determining pre-mining water quality databases. Very often, the location of sampling sites, sampling methods, monitoring schedules and parameters compiled in the database are the result of choices made by mining companies or, at best, of case-by-case negotiations with public authorities. So, the methodology used to define a geochemical background must overcome all of these recurrent difficulties (Nordstrom, 2015; Zuluaga et al., 2017; Sahoo et al. 2020).

The classic approach is to use descriptive statistics. The BoxPlot method, according to Turkey, 1977, represent the variability of the concentrations, around the median value. The BoxPlot also singularizes the extreme values, considered to be outside the representative range of variability. Reimann et al, 2005, refines the method and specifies that beyond 15% of extreme values, it is necessary to take into account the median $\pm 2\text{MAD}$. For each chemical element, it is thus possible to visualize the representative variation of an initial state of a river. This variability in a non-impacted context is very dependent on the set of environmental parameters (precipitation rate, climate, substrate geology, proportion of rocks and minerals for the same geology...) that influence the geochemical signature (Reimann et al., 2005; Cohen et al., 2013; Sahoo et al., 2020). It is therefore necessary to take into account this spatial variability in the definition of a geochemical background for large drainage catchments or catchments located in different regions, even if the substrate is of the same geological nature. Despite this better consideration of concentration variability in defining the geochemical background, the approach remains comparative between new analyses and background values. Most often, representative contamination remains subject to the expert's appreciation during graphical comparisons. If the geochemistry of the impacted environment is strongly contrasted or very distinct in terms of elements detected, compared to the initial signature, this interpretation bias can weaken but not call into question the scientific conclusions. On the other hand, for a less contrasting difference, as in the case of mining by only mobilization of natural outcrops, it is absolutely necessary to free oneself from all subjectivity. It is therefore imperative to explore new, more discriminating and robust approaches to test the existence of an anthropogenic impact on an initial environment under any circumstances.

Data mining methods allow global comparisons of a set of values and provide parameters that evaluate whether differences between two domains are statistically significant (Quinlan, 1986). Data mining methods thus seem to offer the possibility of improving the classification between waters impacted and non-impacted by mining activity, even in contexts where there are great similarities.

The environmental monitoring of the catchment areas of the ophiolitic complexes of New-Caledonia (southwest pacific), is part of these complex contexts.

New-Caledonia is the third producer of nickel in the world exploiting nickeliferous mineral deposit with open-pit mines. Extraction consists of stripping the sterile soil (on average 50 m deep) to reach the lateritic and saprolitic nickel ore (Latham 1986; Trescases 1969b, Dublet et al., 2015). Mining, by stripping and storing un-cohesive laterites, can strongly mobilize

sediments with high concentrations of potentially toxic metallic and metalloid elements during heavy tropical rains. Sediments dispersion into adjacent watersheds, and mineral leaching influence the chemical composition of fresh water (Gunkel-Grillon et al. 2014; Pasquet et al., 2018; Merrot et al., 2019).

The Koniambo Massif Pre-Mining Environmental Study (North-West New Caledonia) collected on hydrochemical and hydrological data over a 15-year period (1994-2010, data provided by Koniambo Nickel SAS) from one to twenty-four sampling per year. The database contains over 27700 values including dissolved and total (dissolved + particulate) stream concentrations. This database, is exceptional by the duration of the pré-mining monitoring. The latter is a perfect illustration of the difficulties in establishing a geochemical background to monitor river water quality after the start of a mining operation. This example is one of the complex cases of identifying a potential anthropogenic contribution even though this activity simply remobilizes naturally eroded land.

The main objective of this study is to establish a geochemical background from the environmental database acquired before exploitation by KNS of streams from catchments on ultramafic substrate considered as non-impacted.

In this article, we propose to extract knowledge from these environmental data using data mining and machine learning methods rounds off conventional statistical methods. This approach will allow:

1. to identify, in fresh water, chemical elements highly disturbed by open-mine activities
2. to statistically validate the significant differences per chemical element
3. to build a predictive model to discriminate between impacted and non-impacted surface water.

2 Site description

New-Caledonia is an archipelago located in the South Pacific Ocean and the main island is called “Grande Terre” (Figure 1). Its climate is tropical with a wet season (December to March) and a dry season (June to September). The wet season is characterized by heavy rains with intensities often exceeding 500 mm in 24 hours (Bonvallot et al., 2012). For the streams and rivers, it involves flash flooding with high concentrations of suspended matter and significant flows of sediments. The surface area of the catchments accentuates this effect: the smaller the catchment, the faster the flood. In New-Caledonia, streams are supplies for drinking water, crop watering and fishing. Thus, quantify mining geochemical influence on stream compositions, and identify impact indicators, is of major interest for environment and health population preservation.

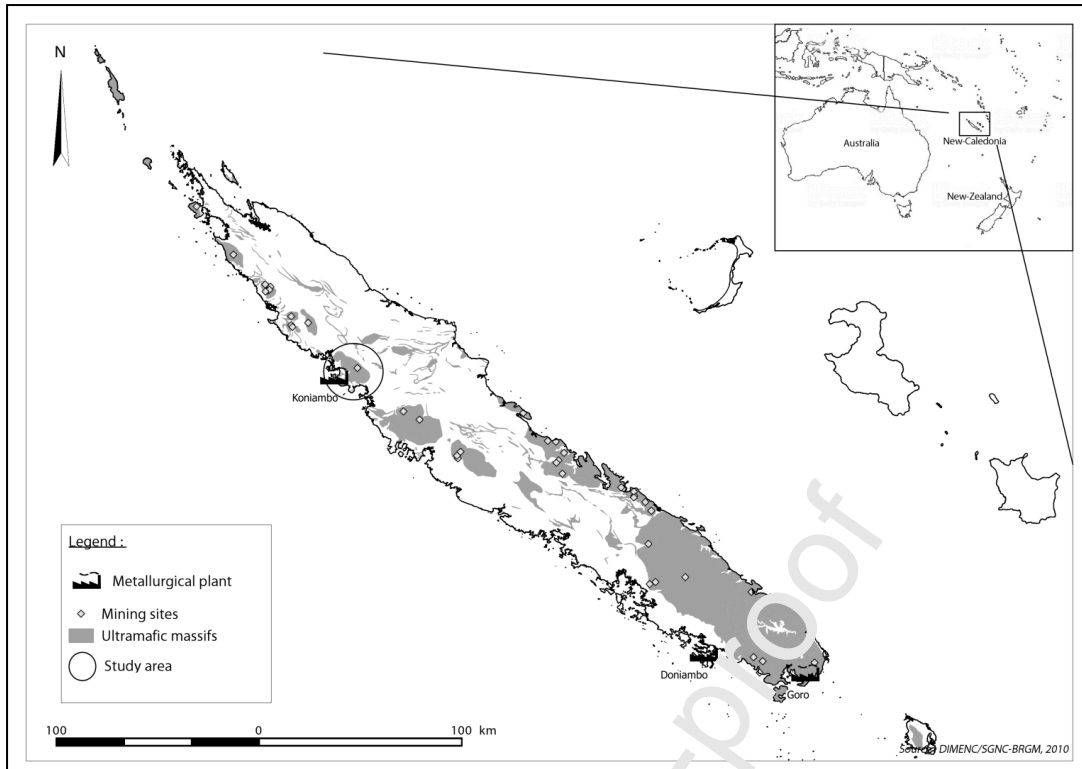


Figure 1 : Repartition of ultramafic massifs (in grey) in the main island “Grande Terre” of New-Caledonia with the localisation of the study area and the mining sites (source : DIMENC/SGNC-BRGM, 2010 – modified).

Some ultramafic klippes cover a third of the New-Caledonia surface and forms the highest mountains (≈ 1500 m). The steep slope, the dominance of un-cohesive rocks, and heavy tropical rainfall are among the natural factors that contribute to the significant erosion of these massifs and mineralized sediment dispersion in stream (Flouvat et al. 2020). The extraction of nickel ores affects the same regoliths.

On the west coast of the "Grande Terre" Koniambo's massif is a klippe of peridotites (Figure 1). It is a mountainous massif over 100 km^2 with a maximum altitude gradient over 850 m. In accordance with the ultramafic nature of the Caledonian ophiolitic massifs, alteration resulting of 11 million years of humid tropical climate replace the peridotites of Koniambo.

The alteration profile reaches a depth of about 50 m (Figure 2). From the depth to the surface, via an increasing alteration, the peridotites (rocks composed essentially of ferro-magnesium silicate minerals) changed into saprolite (formation of nickel phyllosilicates such as willemseite, nepouite, garnierite) then laterites main minerals are goethite - $\alpha\text{FeO}(\text{OH})$, with subordinate hematite, and a basal level of manganese and cobalt oxides (asbolane), as well as serpentines veins, until the final alteration represented by an iron crust (“cuirasse de fer”),

mostly hematite with few goethite (Audet, 2008; Fandeur et al., 2009; Teitler et al., 2019). These mineralogical transformations necessarily impact the distribution of chemical elements within the alteration profile. More soluble elements, such as Si and Mg, have concentrations that decrease towards the surface. On the contrary, elements that are poorly soluble or form alteration-resistant mineral phases such as Fe, Al, and Cr have concentrations that grow towards the surface. This accumulation is promoted by the presence of manganese and mainly iron oxides and hydroxides which can represent "traps" for these elements (Figure 2) (Audet, 2008; Dublet et al., 2015, 2012; Myagkiy et al., 2017; Teitler et al., 2019).

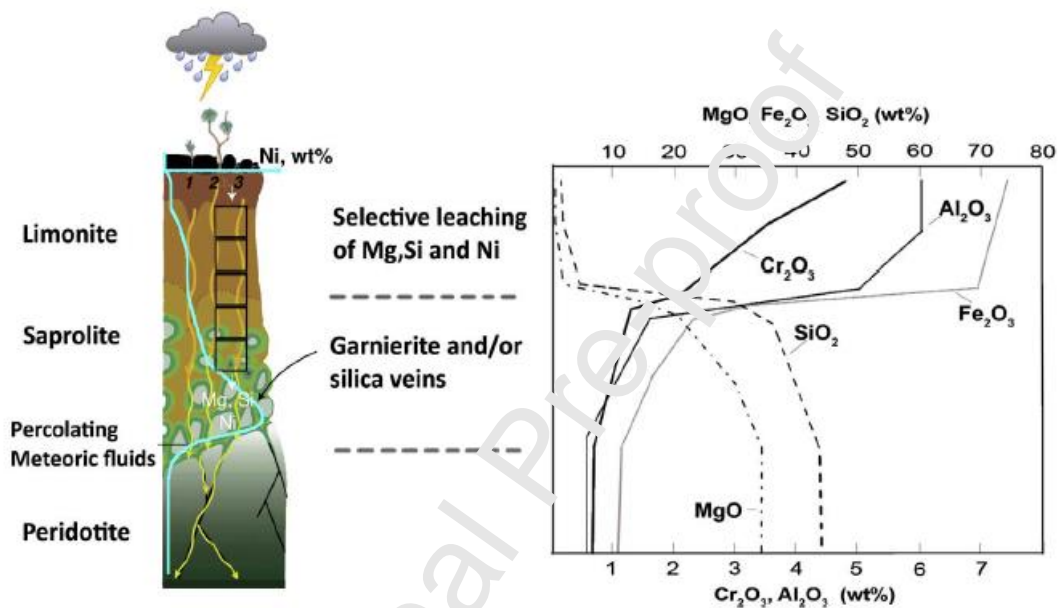


Figure 2 : A schematic log (50 m depth) of the New Caledonian Peridotite Nappe correlated with approximate elemental composition of different zones. (Myagkiy et al., 2017)

The weathered rocks in the alteration profile form the main sediment supply source for the watersheds of the Koniambo massif. Solid transport and hydrochemistry of the surface waters are strongly impacted by lateritic soils which are very sensitive to erosion due to tropical precipitations and important altitudinal gradient. These sediments, besides to nickel, have high concentrations of Fe, Mn, Co and Cr (Ambatsian et al., 1997; Fernandez et al., 2006; Migon et al., 2007). The Koniambo massif is drained by seven main streams, five of which are on an entirely ultramafic substrate: Coco, Confiance, Népia, Pandanus, and Foachiamboué (Figure 3 and Table 1).

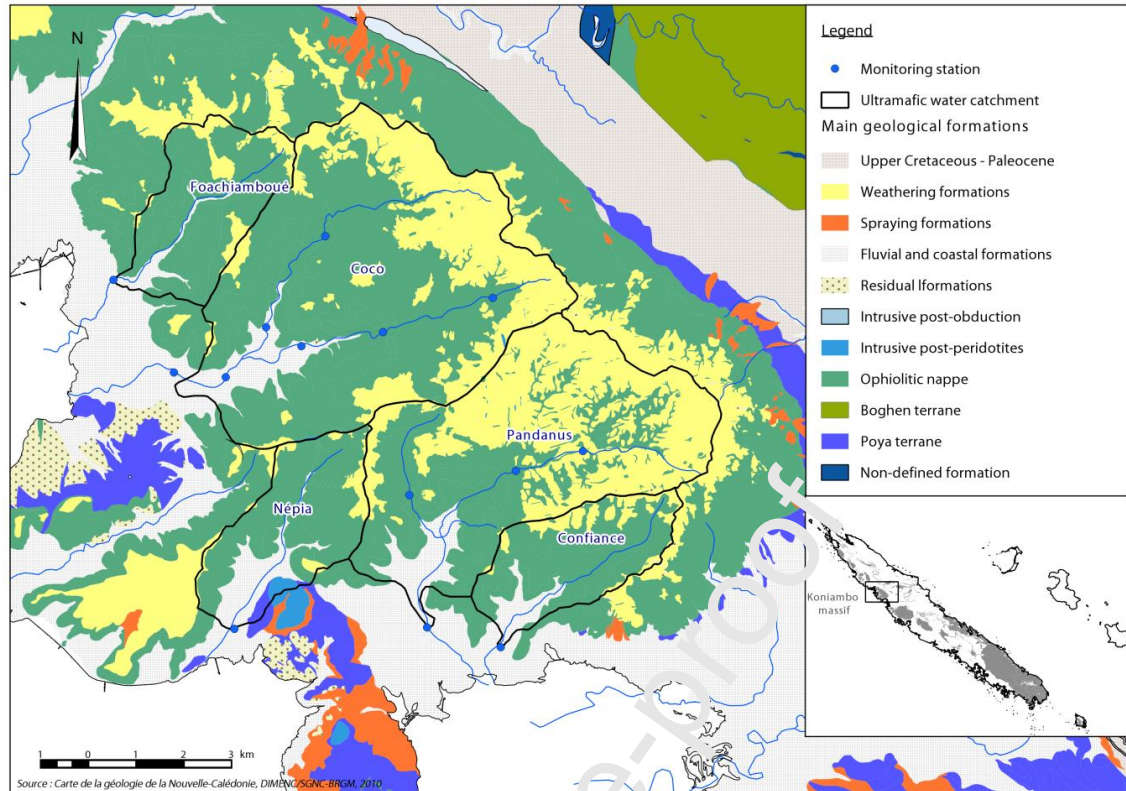


Figure 3: Ophiolitic nappe of Koniambo massif drained by five streams and monitored with 14 hydrological stations (source: Geological map of New-Caledonia. DIMENC/SGNC-BRGM, 2010 - simplified)

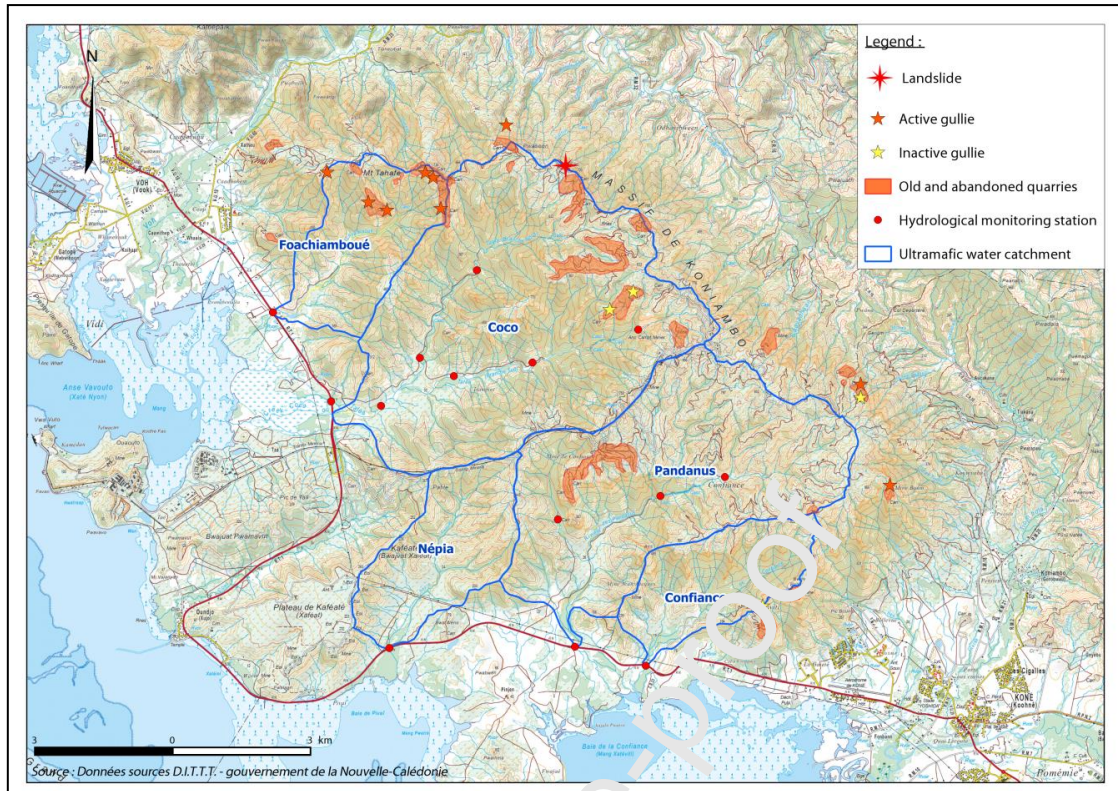
Table 1: Main characteristics of Koniambo's catchments and physicochemical parameters of streams. EC: electrical conductivity; TOC: total organic carbon

Catchments and their area	Main rocks (%)	Land cover and characteristic flow	EC ($\mu\text{S}/\text{cm}$)	pH	TOC (mg/l)
Coco 35.1 km ²	Peridotites (54%) Laterites (28%) Serpentinities (8%)	Few exploration roads and few old quarries Perennial and turbulent streamflow	Min :95.5 Mean:231 Max :416 <i>n</i> =37	Min : 7.22 Mean:8.3 Max : 12.8 <i>n</i> =31	Min :0.1 Mean:4.7 Max :7 <i>n</i> =6
Confiance 7.6 km ²	Peridotites (62%) Laterites (13%) Serpentinities (12%) Silts (5%)	Few exploration roads Non-perennial stream with a turbulent flow	Min :95.5 Mean:221 Max :354 <i>n</i> =18	Min :6.7 Mean:8.7 Max :12 <i>n</i> =16	Min :0.1 Max :3 <i>n</i> =2
Foachiamboué 8.1 km ²	Peridotites (63%) Laterites (10%)	Few exploration roads and many old open-cast mines	Min :87.6 Mean:206 Max :862 <i>n</i> =37	Min :6.8 Mean:8.2 Max :12.6 <i>n</i> =33	Min :0.1 Max :0.1 <i>n</i> =1

	Serpentinities (18%)	Non-perennial and turbulent streamflow			
Népie 8.9 km ²	Peridotites (57%), Serpentinities (10%) Laterites (7%) Silts (14 %)	Thick vegetative cover with rare erosion gullies Non-perennial and turbulent streamflow	Min :102 Mean:519 Max :864 <i>n=11</i>	Min :6.8 Mean:8.8 Max :12.7 <i>n=8</i>	Min :0.1 Max :20 <i>n=2</i>
Pandanus 25.8 km ²	Peridotites (31%) Laterites (50%) Serpentinities (7%) Silts (6%)	A large exploration roads network and a vegetative cover of maquis Perennial and turbulent streamflow	Min :90.2 Mean:147 Max :285 <i>n=57</i>	Min :6.6 Mean:7.9 Max :12.6 <i>n=47</i>	Min :0.1 Mean:4.0 Max :8 <i>n=3</i>

The geological substrate of each watershed consists of the same main rocks: peridotites (mostly serpentinitized harzburgites, and dunités), laterites, serpentinites with mixed fine particles of the previous rocks. Only the respective proportions of these rocks vary from one basin to another. Catchment areas vary from small (8 km²) to medium (more than 35 km²). In the 19th century, the Koniambo massif has been exploited with opencast quarries for manganese and chromium ores located on Foachiamboué's catchment (Figure 4). This previous mining activity left scars at the top of the Foachiamboué watershed, in the form of active ravines. They result from stripping during mining of the upper parts of the soil (humus, iron crust, laterites). Revegetation has been made impossible by the absence of humus horizons, and erosion is still active. The Foachiamboué watershed is the only one of the five draining the Koniambo massif that was subject to significant mining pressure before the environmental monitoring period (Maurizot et al., 2007).

Figure 4: Koniambo's catchments with former mines and quarries before 2010 with localisation of monitoring stations represented by the red points (Source: DITTT – Government of New-Caledonia - modified)



3 Materials & Methods

3.1 Data description and preparation

A pre-mining survey has been conducted by Koniambo Nickel SAS and hydrochemical data were collected from 1995 to 2009 (in 2010, the mining society have begun the earthworks to prepare the exploitation of the nickeliferous ore). There is an exceptional hydrogeochemical database covering a period of 15 years. This database capitalizes 5474 values for the five ultramafic catchments, including 991 measurements of physico-chemical parameters (pH, total organic carbon, suspended matter, electrical conductivity), and 4483 concentrations of chemical elements. Several monitoring stations from upstream to downstream have been deployed for Coco (7), and for Pandanus (4) and for Confiance, Népia and Foachiamboué only 1 at the outlet. The number of geochemical data per catchment area is also variable: 1489 for Pandanus, 1140 for Coco, 1074 for Foachiamboué, 446 for Confiance and 334 for Népia, making a total of 4483 measures for the ultramafic catchments. Sampling was performed manually with a portable automatic water sample (Teledyne Isco model) when the water level was low, because during rainfall access to stations is prohibit, for safety reasons. Analyses were performed by certificate private laboratories by ICP-MS and ICP-AES according to normalized procedures (Table 2). The mining company has, of course, called in several analytical laboratories over the 15 years of environmental monitoring. However, the accreditation of all these laboratories and the standardized analytical procedures guarantee

the accuracy, reproducibility of the results, and the compliance with the values of the standards. Thus, the rigorous protocol for determining analytical blanks followed the NFX06-021 standard or equivalent. The analytical blanks conformed the recommended limit: blank concentration + $\sigma < (u / 3)$, with σ is the standard deviation and u the analytical uncertainty.

Concentrations of twenty-four elements (Al, Fe, Ca, Na, K, Si, Mg, B, Mn, Ni, Zn, Ag, As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Pb, Sb, Sn and V) were analyzed on the raw water samples, identified as "total" (suspended matter + dissolved fraction). The concentrations of eighteen elements (Al, Fe, Mg, B, Mn, Ni, Zn, As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Pb, Sb, and Sn) were analyzed in the filtrates, obtained after a 0.45 μm filtration of the total water samples, and represent the concentrations of dissolved elements. So, two databases were obtained: element concentrations of total and dissolved fractions, which concern 200 samples for dissolved elements and 225 samples for total elements, with, sometimes, missing values.

Table 2: List of normalized analytical procedures used for total and dissolved elements concentration in stream waters

Normalized analytical procedure	Analyzed elements
FD T90-112	Zn*
FD T90-119	Al, Cd, Cr, Cu, Fe, Pb, Mn, Mo, Ni, Ag, V
NF ISO 15 586	Ca, Co*, Cu, Pb, Ni, Mn*, Ba*, Sb*, Al*, Cr, Fe*, Mo*, As, Sn
NF EN 1483 ; NF T90 131	Hg
NF T90 020	K*, Na*
NF T90 005	Ca*
NF ISO 7980	Mg*, Ca*
VARIAN SI	Si*
US EPA 6020	Al, Sb, As, Ba, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Ag*, V, Zn
US EPA 6010	Na*, K*, Ca*, Mg*, Fe* and B*
US EPA 6011	Fe** and B*
* :dissolved element	

In order to identify geochemical indicators and thresholds marking the influence of mining activity, we use the machine learning methods (supervised classification), which require samples of the same dimensions without missing values. Thus, in this case, all samples with missing values and elements with less than 25% of concentration occurrences have been removed from each database (8 elements and 81 samples for dissolved concentrations; 11 elements and 124 samples for total concentrations).

3.2 Data analysis

The variability of each element concentration was analyzed with the Tukey boxplot (Tukey, 1977). This method graphically depicts numerical data and it has been recommended by Reimann et al. (2005) as a first step to define the geochemical background (Fok et al., 2013; Hao et al., 2014; Levitan et al., 2014; Reimann and Garrett, 2005). In the first instance, the ultramafic watersheds of the Koniombo massif cover a reduced surface area and have sufficient geological homogeneity for analysis by BoxPlot alone to describe their geochemical variability. This method does not require removing samples with missing concentrations from the database. The interpretation is made for each chemical element. The median value defines the central value of each element concentrations.

The difference between Q1 and Q3 (called also InterQuartile= $Q3 - Q1$) provides concentration variability of each element. Boxplots have been also used to identify extreme values, which are above P_s ($P_s = \text{quartile}_3 + 1.5 \times \text{InterQuartile}$) or below P_i ($P_i = \text{quartile}_1 - 1.5 \times \text{InterQuartile}$).

In addition, the graphical comparison of median values for the non-impacted and the impacted basins allows us to identify as geochemical indicators, elements whose concentrations are significantly different between the two groups of samples (positive and negative examples). This method was applied on total and dissolved concentrations datasets. To statistically validate these indicators, we used ANOVA tests (Hogg and Ledolter, 1987) to compare impacted and non-impacted groups of samples. P-Values calculated for each indicator identified in the case of dissolved elements and the case of total elements will confirm this difference significantly on identified indicators.

Moreover, we performed a supervised classification method on labeled datasets on two classes (positive examples from impacted basins, negative examples from non-impacted). We used a well-known supervised classification method, decision tree (Quinlan, 1986) implemented in Weka software (Frank et al., 2016). The decision tree, which is easy to interpret (a simple way to visualize a decision of classification), is used to build a hierarchical model on element concentrations to differentiate (possibly predict) samples of impacted and non-impacted basins. The higher the discrimination, the more the measurement of the classification rate called accuracy rate (global percentage of well classified samples) is near 100%. The classification tool provides statistical Kappa coefficient which quantifies the quality of the classification. Furthermore, this method allows us to obtain a ranking of elements from strongest to weakest with respect to discrimination accuracy, by using information gain measure. In addition to the accuracy rate, the decision tree method provides the concentration values of each element that contributes to the discrimination of samples.

4 Results and Discussion

4.1 Data cleaning

The data analysis by the BoxPlot method identifies extreme values. It is among these extreme values that outliers have been extracted. These extreme data accumulate maxima or minima either really representative of the measured values or erroneous, resulting from various errors (input error, analytical error...). Data cleaning must remove these latter from the database.

The selection is based on three criteria:

- *Consistency of values with a homogenous geogenic contribution.* All watersheds lie on ultramafic substrates, with a similar mineralogy. The surficial horizons make up the alteration profile of the New Caledonian ultramafic massifs. These degraded rocks feed the watercourses with sediments (suspended matter, SM). It is therefore logical to expect consistency between the chemical element composition of ultramafic and weathered rocks, and the dissolved concentrations of chemical elements in surface waters. In addition, aquifers of mining massifs display geology dominated by ultramafic rocks (Genthon et al., 2017; Jaupart, 2017). The water supplied to streams by aquifers should therefore not have a radically different geochemical composition from surface water.
- *Repetition over the 15-year period of the highest concentration values.* Cyclones encountered in tropical climates are extreme events of heterogeneous rainfall. They impact suspended matter, chemical element concentrations of water. They are erratic events, several decades apart. A geochemical background can only be established from data with the same variability over a long period. This criterion is necessary for the geochemical background to be a perennial reference when monitoring freshwater quality. Cyclone temporality is thus incompatible with the definition of a geochemical background (Reimann et al., 2005; Nordstrom, 2015). The extreme values corresponding to this type of events have therefore been removed from the processed database. Only the recurring extreme concentrations over the 15-year period are considered representative of the geochemical background.
- *The correlation between increasing concentrations of suspended matter and concentrations of chemical elements concentrated in the laterites:* The watersheds studied are not subject to chemical inputs except geogenic origin. The weathered ultramafic substrates and eroded sedimentary particles provide the geochemical composition of surface waters. Lateritic minerals are characterized by high concentrations of Mg, Fe, Ni, Co, Mn and Cr (Perrier et al., 2006; Fandeur et al.,

2009; Dublet et al., 2012, 2015). Suspended matter thus enriches the alkaline waters of the Koniambo Massif with these same chemical elements. In this context, high concentrations of lateritic derived chemical elements not correlated with high concentrations of suspended matter appear aberrant and be removed from the treated base.

These criteria guided the testing of each extreme value. A total of 82 outlier values have been excluded from the two datasets.

4.2 *Physicochemical parameters of streams*

The main characteristics and physicochemical parameters of the 5 studied catchments are summarized in Table 1. The water pH values range from 6.6 to 12.8, which is consistent with known alkaline values for freshwater on ultramafic substrates (Bolaños-Benítez et al., 2018; Cipolli et al., 2004; Neal and Shand, 2002; Nikić et al., 2013). Sediments resulting from the erosion of Koniambo laterites include essentially iron oxides and hydroxides (goethite, hematite), (Perrier et al., 2006; Fandeur et al., 2009; Dublet et al., 2012, 2015). The alkalinity of surface water favors the release of the most mobile fraction of the metallic and metalloid elements adsorbed on these minerals surface (maximum effect for $\text{pH} \approx 12$). Leaching experiments for pH values varying from 6 to 10, carried out on sediments from the Caledonian ultrabasic mining massif, confirmed these results, particularly for the elements Al, Co, Cr, Fe, Mn and Ni (Gunkel-Gallon et al., 2014, Myagkiy et al., 2017; Pasquet et al., 2018; and personnel experiments). Surface waters therefore have pH values that facilitate the release of metallic and metalloid elements. Unfortunately the KNS database does not have enough relevant data to testify the impact on variability of the geochemical background.

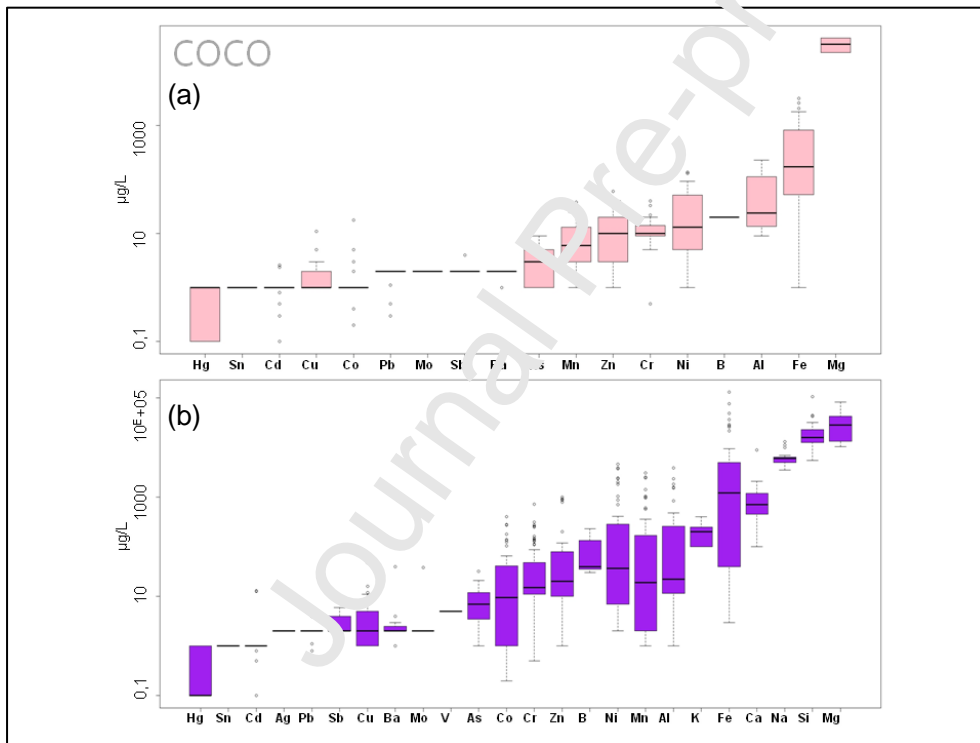
Conductivity values range from 87.6 $\mu\text{S}/\text{cm}$ to 864 $\mu\text{S}/\text{cm}$. Nepia's water has the highest mean (519 $\mu\text{S}/\text{cm}$) and the maximum (864 $\mu\text{S}/\text{cm}$) conductivity (median = 628 $\mu\text{S}/\text{cm}$). This stream also has the most extensive vegetation cover (table 1), and the few data on TOC attribute the maximum value to this river (TOC = 20 mg/l). The mineralogy of the ultramafic watersheds of Koniambo excludes a mineral origin of carbon and favors the organic origin. The organic matter promotes the release of Ni, Co, Cr, adsorbed on the surface of goethite and hematite particles, under the pH conditions of Nepia (Quantin et al., 2020; Pasquet et al., 2018). The higher conductivity values in Nepia are probably the result of increased solubilization of metallic and metalloid elements due to the presence of higher concentrations of organic matter. TOC values measured in the rivers studied range from 0.1 to 20 mg/l. However, the base has few TOC values. The highest and lowest TOC are measured in the Confidence (3 mg/l) and the Foachiamboué (0.1 mg/l), which are almost not vegetated. As

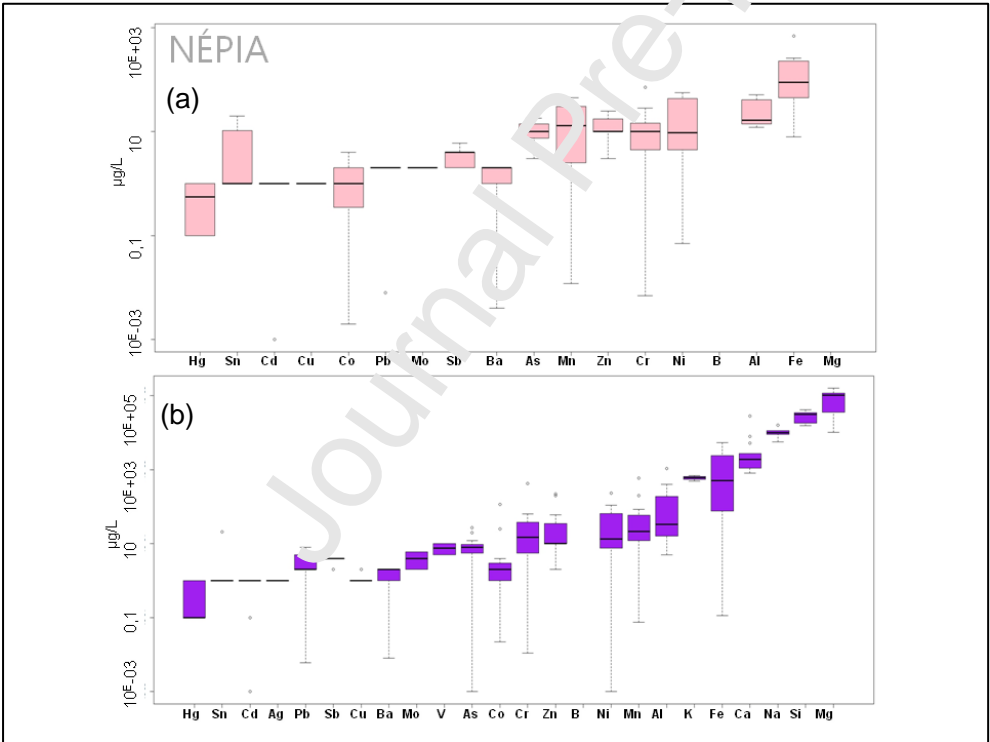
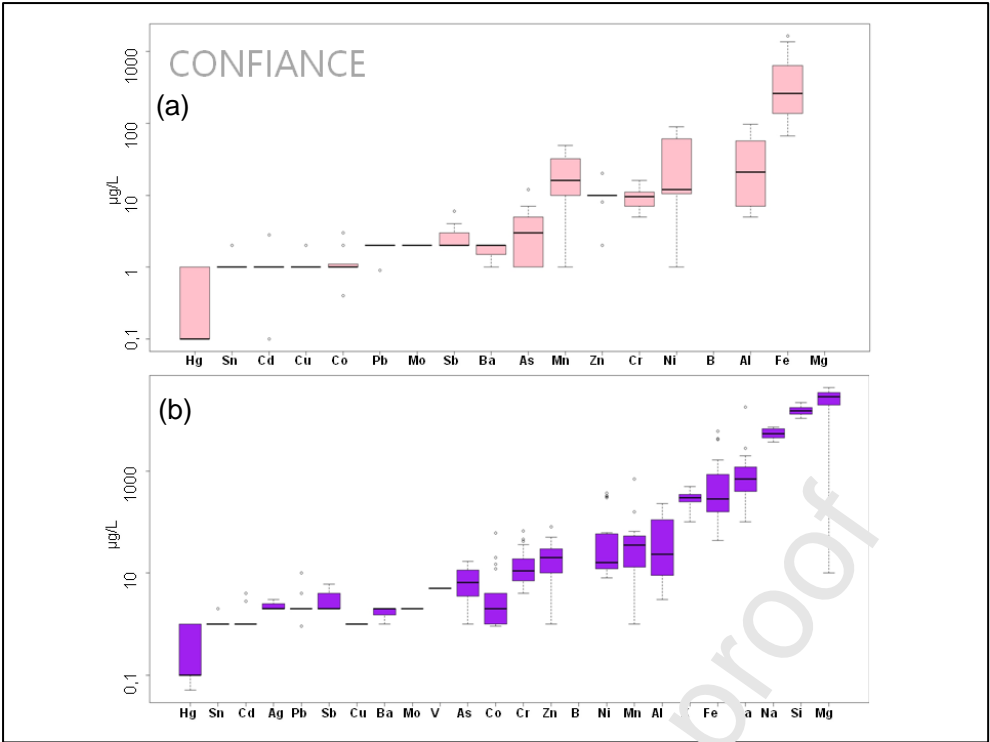
mentioned above, the highest TOC value (20mg/l) belongs to Nepia, the most vegetated river. The limited data available would therefore seem to correlate the TOC value with the proportion of vegetation cover. This is consistent in an environment almost devoid of mineral carbon.

4.3 Geochemistry of streams on ultramafic substrates

Results of descriptive statistic for total concentrations and for dissolved concentrations, of all Koniambo watersheds are listed respectively in Table 3 and 4. Figure 5 cumulates all BoxPlot graphics (Coco, Confiance, Népia Pandanus and Foachiamboue). For each stream, the BoxPlots show lower variabilities for dissolved concentrations than total ones.

Figure 5: Concentrations of (a) dissolved elements in pink, (b) total elements in purple in $\mu\text{g/L}$ for all Koniambo's catchments.





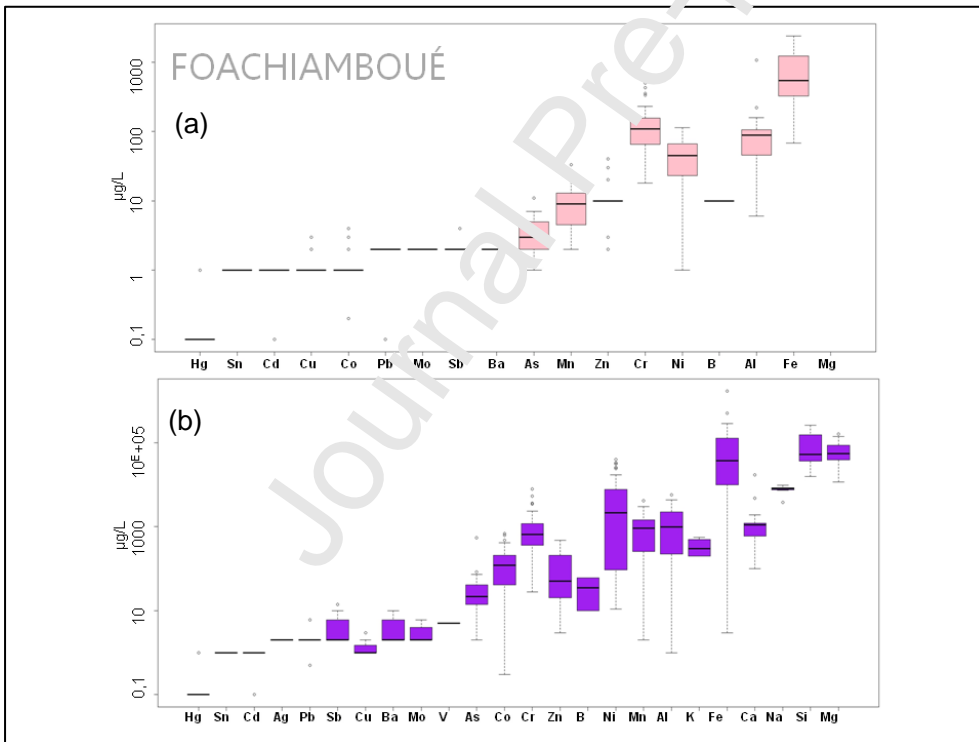
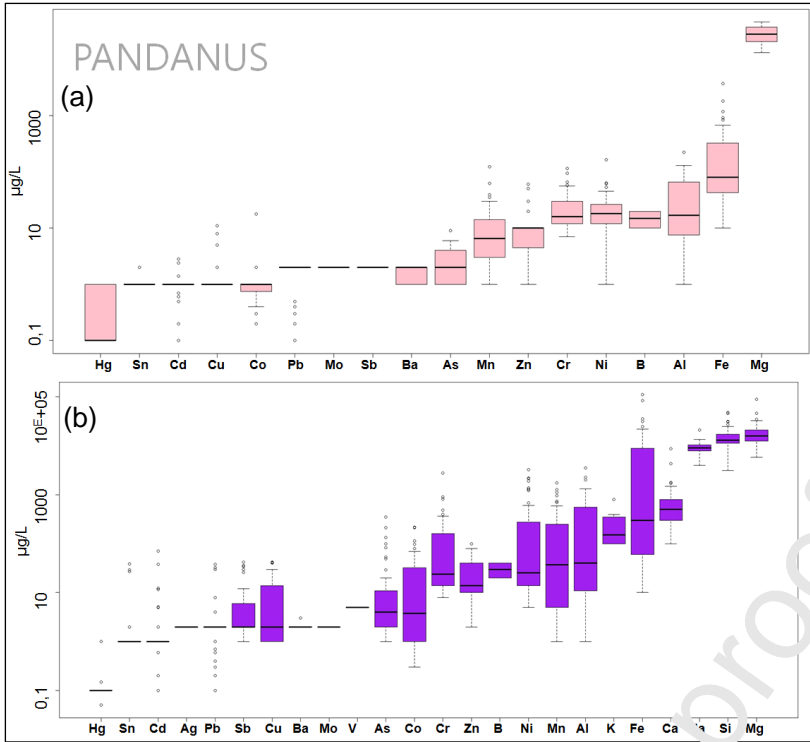


Table 3: Statistical summary for total concentrations of studied catchments: Coco, Confiance, Népia, Pandanus, and Foachiamboué – first quartile (Q1), median (Med), third quartile (Q3), interquartile (IQ), number of values (n), number of value <LDL excluded (n_i), units : µg/L

	Coco						Confiance						Népia						Pandanus						Foachiamboué					
	Q1	Med	Q3	IQ	n	n _i	Q1	Med	Q3	IQ	n	n _i	Q1	Med	Q3	IQ	n	n _i	Q1	Med	Q3	IQ	n	n _i	Q1	Med	Q3	IQ	n	n _i
Hg	0,1	0,1	1	0,9	34	6	0,1	0,1	1	0,9	11	4	0,1	0,1	1	0,9	13	3	0,1	0,1	0,1	0	48	8	0,1	0,1	0,1	0	34	3
Sn	1	1	1	0	15	0	1	1	1	0	7	0	1	1	1	0	5	0	1	1	1	0	30	0	1	1	1	0	29	0
Cd	1	1	1	0	40	10	1	1	1	0	14	4	1	1	1	0	12	4	1	1	1	0	55	13	1	1	1	0	35	5
Ag	2	2	2	0	31	2	2	2	2,5	0,5	3	1	1	1	1	0	2	2	2	2	2	0	21	8	2	2	2	0	23	3
Pb	2	2	2	0	38	12	2	2	2	0	14	4	2	2	4,5	2,5	1	4	2	2	2	0	55	13	2	2	2	0	34	5
Sb	2	2	4	2	23	15	2	2	4	2	9	4	4	4	4	0	5	4	2	2	6	4	35	18	2	2	6	4	32	5
Cu	1	2	4,7	3,7	26	15	1	1	1	0	9	5	1	1	1	0	7	5	1	2	14	13	41	14	1	1	1,5	0,5	31	6
Ba	2	2	2,2	0,2	12	13	1,5	2	2	0,5	3	3	1,1	2	2	1	3	4	2	2	2	0	61	7	2	2	6	4	35	5
Mo	2	2	2	0	10	16	2	2	2	0	2	2	3	4	5	2	2	0	2	2	2	0	41	8	2	2	4	2	30	0
V	5	5	5	0	23	13	5	5	5	0	2	2	6,2	7,5	8,7	2,5	2	2	5	5	5	0	21	8	5	5	5	0	23	3
As	3,7	7	12	8,2	40	10	3,7	6,5	9,7	6	16	2	5,5	8	9,5	4	15	1	2	4	10,5	8,5	54	13	14	21	39	25	37	3
Co	1,2	9,5	40	38,7	42	7	1	2	4	3	17	0	1	2	3	2	15	0	1	3,8	32	31	61	66	41,7	12,5	22,6,5	18,4,7	38	1
Cr	11	15	48	37	61	0	7	11	19	12	21	0	5,5	15	38	32,5	15	0	14	24	16	14	73	37	36,4	66,0	11,99	83,4,5	39	0

																							5							
Zn	10	20	80	70	43	7	10	20	30	20	15	3	10	10	22,5	12,5	1	4	10	14	40	30	60	8	20	50	20	180	37	3
B	35	40	135	100	3	12	-	-	-	-	-	4	-	-	-	-	-	4	25	30	35	10	27	17	22,5	35	47,5	25	2	3
Ni	7	37	285	278	49	1	12	16	58	46	21	0	8,2	13,5	64	55,5	16	0	14	25,5	27,2	25,2	70	0	96	2189	7479	7383	40	0
Mn	2	19	168,5	166,5	47	3	13	35	53,5	40,5	19	0	12,5	21,5	57	44,5	16	0	5	37,5	24,2	24,2	68	2	29,8	94,5	1433,2	1135,4	40	0
Al	11,5	22	260,5	249	47	3	11,2	23,5	97,5	86,2	18	0	17	33,5	180	163	0	11	40	559	548	65	3	24,8	1000	2695	2446,2	40	0	
K	100	200	250	150	1	2	275	300	325	50	8	0	550	900	650	100	3	1	100	150	325	225	12	5	200	300	500	300	5	0
Fe	42,5	1213,5	4495,2	4452,7	4	4	170,2	280,5	826	655,8	2	0	904	504	2336	2256	16	0	60	300	8941	8881	67	3	1010	3742,5	1332,73	1231,73	39	1
Ca	450	700	1200	750	43	0	400	700	1150	750	2	0	1100	1900	2700	1600	13	0	300	500	800	500	59	1	625	1100	1200	575	38	0
Na	5000	6000	6275	1275	26	0	4475	5350	5650	2175	8	0	9100	10100	11325	2225	6	0	4100	9000	5350	1250	35	0	7550	8000	8325	775	8	0
Si	12650	15800	23050	10400	31	0	13100	15100	17600	4500	17	0	20525	31100	34500	13975	1	0	11200	12900	17100	5900	45	0	35900	50750	15100	115100	34	0
Mg	13350	28500	42700	29350	39	0	19600	28700	34500	14900	1	0	35500	102000	118000	82500	1	0	12500	15950	20875	8375	56	0	38325	53300	84800	46475	38	0

4.3.1 Total concentration of chemical elements

For the total element concentrations, prevailing major elements are Mg and Si, followed by Fe, Na, Ca, K and Al with high concentrations of heavy metals Mn, Ni, Cr and Co (Table 3). Among these leading elements, Fe, Al, Mn, Ni and Co present the greatest variability in concentrations, as shown by the calculation of the quotient $(Q3-Q1)/Q3$. The closer the ratio $(Q3-Q1)/Q3$ is to 0, the smaller the gap is between the two quartiles, and the closer this ratio is to 1, the larger the gap is between Q3 and Q1. The value of $(Q3-Q1)/Q3$ of the total concentrations of Fe, Al, Mn, Ni and Co are between 0.8 and 1.0 for all Coko, Nepia, Pandanus and Confiance streams. Logically the Q3/Q1 ratios are also high with maximum values of 32 for Co, 40.7 for Ni, 50.8 for Al, 84.2 for Mn and 149 for Fe. Note that Zn has median and Q3 values that may be higher than those of Co, while Zn concentrations are about 5 times lower than Co concentrations, in laterites of the Koniambo massif (Audet, 2008; Ulrich, 2010). High concentrations of Zn are therefore not expected in these non-impacted influenced streams on ultramafic substrates (absence of non-geogenic inputs). It should also not be forgotten that the sustainability of river flows in the Koniambo massif is ensured by groundwater supplies during low-rain periods (Dewandel et al., 2017; Jeanpert et al., 2019). The water qualitative monitoring of the peridotite aquifers of the Koniambo massif, from 2009 to 2011, indicates a Q3 value of 93.3 $\mu\text{g/L}$ (maximum: 830 $\mu\text{g/L}$) for Zn against 1 $\mu\text{g/L}$ (maximum: 69.1 $\mu\text{g/L}$) for Co (data provided from groundwater monitoring of KNS). The higher concentrations of dissolved Zn in surface water might therefore highlight a contribution from peridotite aquifer water.

Finally, boron has high median and Q3 values in total samples (respectively, 30 to 40 $\mu\text{g/L}$, and 35 to 135 $\mu\text{g/L}$) close to those of Ni. B is relatively concentrated in asbolane minerals (manganese oxide-hydroxide) of New Caledonia lateritic units (Trescases, 1973). So weathering of the asbolane particles, could explain the high concentrations of Boron in natural waters of ultramafic catchments.

4.3.2 Dissolved concentrations of chemical elements:

The dissolved element concentrations of ultramafic watersheds display a less variability (Table 4). Indeed, the highest values of Q3/Q1 do not exceed a factor of 12, compared to a factor > 100 for total concentrations. The ratios $(Q3-Q1)/Q3$ closest to 1 are again obtained for Fe, Al, Mn and Ni, in the same way as total concentrations. These elements are still the most fluctuating. It should be noted that during KNS pre-mining monitoring, concentrations of Si, Ca, Na, K (as well as Ag and V) were not measured on the dissolved fractions. Comparison of the median values per element and per watershed of the total sample and its

dissolved fraction shows that only Mg has higher concentrations in the dissolved fraction: Coco $Mg_{median-total} = 28\ 500\ \mu\text{g/L}$; Coco $Mg_{median-dissolved\ fraction} = 32\ 050\ \mu\text{g/L}$; Pandanus $Mg_{median-total} = 15\ 950\ \mu\text{g/L}$; Pandanus $Mg_{median-dissolved\ fraction} = 28\ 200\ \mu\text{g/L}$. These results are explained by the high solubility of magnesium in alkaline and hyper alkaline surface waters as on ultramafic watersheds (McClain and Maher, 2016; Neal and Shand, 2002; Nikić et al., 2013). As a reminder, the surface waters of the 5 catchments of the Koniambo massif have average pH values between 6.6 and 12.8. All other major elements have similar or lower concentrations in the dissolved fraction compared to the total sample. Among the trace elements, boron remains highly concentrated in the dissolved fraction. In particular, it is the most concentrated trace element in the filtered water of the Coco. These results confirm the presence of Boron in soluble form in ultramafic rocks and particularly in serpentinites (Boschetti and Toscani, 2008; Neal and Shand, 2002; Stefánsson et al., 2015). Comparison of dissolved median values with guidelines for drinking water quality (WHO, 2008) reveals that dissolved As concentrations can be upper the recommended value of $10\ \mu\text{g/L}$. Népia median value is $10\ \mu\text{g/L}$ with a Q_3 value of $14\ \mu\text{g/L}$ (Table 4). Dissolved Ar concentrations can “naturally” occurs at levels harmful to human health. The health impact of this result is important since this river supply fresh water and drinking water to the New Caledonian populations.

Table 4: Statistical summary for dissolved concentrations of studied catchments: Coco, Confiance, Népia, Pandanus, and Foachiamboué – first quartile (Q1), median (Med), third quartile (Q3), interquartile (IQ) number of values (n), number of value <LDL excluded (n₁), units : µg/L. NA = No Acquisition

	Coco						Confiance						Népia						Pandanus						Foachiamboué							
	Q1	Med	Q3	IQ	n	n ₁	Q1	Med	Q3	IQ	n	n ₁	Q1	Med	Q3	IQ	n	n ₁	Q1	Med	Q3	IQ	n	n ₁	Q1	Med	Q3	IQ	n	n ₁		
Hg	0,1	1	1	0,93	23	3	0,11	0,11	1	0,9	10	1	0,11	0,15	1	0,9	60	0	0,1	0,1	1	0,9	25	5	0,11	0,11	0,1	0	32	0		
Sn	1	1	1	0	13	1	1	1	1	0	81	1	1	1	5,77	4,7	40	0	1	1	1	0	21	1	1	1	1	1	1	0	29	0
Cd	1	1	1	0	29	7	1	1	1	0	12	0	1	1	1	0	72	2	1	1	1	0	34	9	1	1	1	0	33	2		
Cu	1	1	1,7	0,7	22	2	1	1	1	0	82	2	1	1	1	0	62	2	1	1	1	0	27	3	1	1	1	0	30	3		
Co	1	1	1	0	25	9	1	1	1,1	0,1	10	0	0,14	1,15	1,1	1,1	80	0	0,7	1	1	0,25	31	9	1	1	1	0	31	2		
Pb	2	2	2	0	26	10	2	2	2	0	11	1	2	2	2	0	72	2	2	2	2	0	33	10	2	2	2	0	32	2		
Mo	2	2	2	0	10	2	2	2	2	0	20	0	2	2	2	0	20	0	2	2	2	0	44	4	2	2	2	0	30	0		
Sb	2	2	2	0	21	13	2	2	2	0	35	2	2	4	4	2	52	2	2	2	2	0	22	17	2	2	2	0	29	3		
Ba	2	2	2	0	11	12	1,5	2	2	0,5	31	1	1	2	2	1	32	2	1	2	2	1	83	1	2	2	2	0	33	3		
As	1	3	5	4	24	14	1	3	4,7	3,75	10	2	7,5	10	14	6,5	72	2	1	2	4	3	25	2	2	3	5	3	3	3		
Mn	3	6	13	10	28	6	10,5	16	29,2	19,5	10	0	2,7	13	27,8	25	80	0	3,2	6,5	13,75	10,5	38,0	2	4,75	9	12,5	7,75	32	1		
Zn	3,2	10	20	16,7	30	4	10	10	10	0	100	0	10	10	17,5	7,5	71	1	4,5	10	10	5,5	35	5	10	10	10	0	33	0		

The most concentrated trace elements in laterites resulting from the alteration of New Caledonian ultramafic massifs are Ni, Cr, Co and Mn, (Audet, 2008; Dublet et al., 2015, 2012; Myagkiy et al., 2017; Teitler et al., 2019). The ranking of the median values in total concentration in water samples mainly gives $Co_{median-total} < Cr_{median-total} < Ni_{median-total} < Mn_{median-total}$, with a median for Mn that reaches a value 18 times higher than that of Co (Confidence samples). However, this classification becomes for the median values of the dissolved fraction $Co_{median-dissolved\ fraction} \ll Mn_{median-dissolved\ fraction} < Cr_{median-dissolved\ fraction} \leq Ni_{median-dissolved\ fraction}$. Among these elements, cobalt always displays the lowest concentrations ($Co_{median-dissolved\ fraction} = 1\ \mu\text{g/L}$) as for total concentrations. Mn has the highest median values of trace element concentrations in total samples but lower dissolved concentration (6 to $16\ \mu\text{g/L}$) than Cr and Ni (respectively 9.5 to $16\ \mu\text{g/L}$ and 9.5 to $18\ \mu\text{g/L}$). These two elements therefore have the ability to concentrate in the surface water of these ultramafic watersheds. Cr seems to be the element most likely to solubilize since the median values, and Q3 values of chromium are lower than those of Ni and Mn in the total samples but higher in the dissolved fractions. Cr occurs naturally as Cr (III), an immobile micronutrient poorly toxic, and as Cr (VI), a strong oxidizing agent, soluble and carcinogen (Fendorf, 1995). The most soluble fraction of Cr is the exchangeable Cr (VI) which is reduced by iron-oxides and oxidized by manganese-oxides (Beccmer et al., 2003; Dublet et al., 2015; Gunkel-Grillon et al., 2014).

The highest chemical concentrations of samples are linked in the database with a period of large increase in suspended matter (SM) concentrations. These values can be high as indicated by the maximum concentrations of suspended matter: 2867 mg/L for Pandanus, 1700 mg/L for Coco, 374 mg/L and 332 mg/L respectively for Confiance and Nepia. During intense rain events, these streams become highly turbid, with a red/orange color specific of iron oxide/hydroxide clasts. The violence of rainfall in tropical climates and the steep slopes of the Caledonian ultramafic massifs cause natural strong erosion of the altered soils (Figure 6).

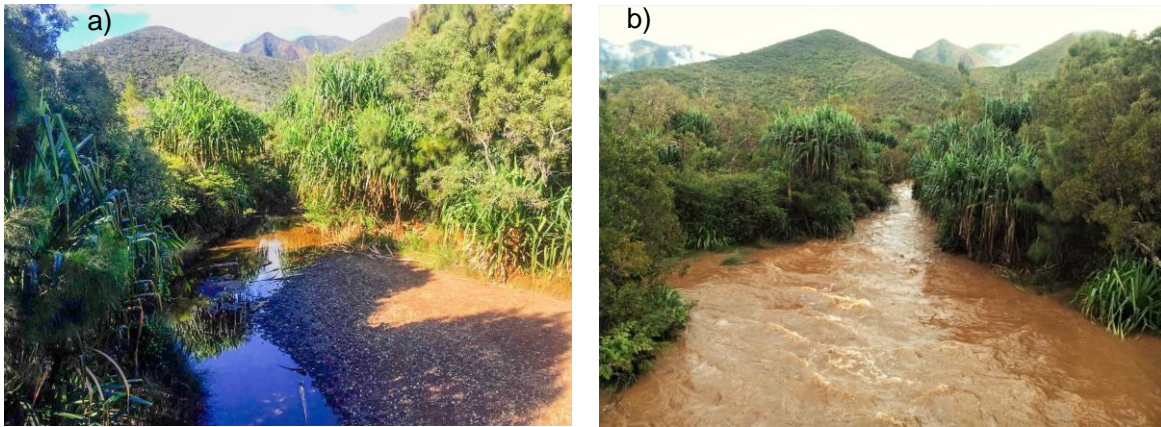


Figure 6: Pandanus stream during low waters (a) and floods (b)

Considering the low concentrations of total organic carbon in water catchments (Table 1), the water geochemistry is related to geogenic fractions with an almost null organic fraction. The database did not include information on the mineralogy of suspended matter in the streams of the Koniambo massif watersheds over the period 1954-2009. However, the geology of their substrates and the alteration profile of the Koniambo massif are similar to the other watersheds on New Caledonia's ultra-basic substrate. X-ray diffraction analyses of suspended matter present in the streams of New Caledonia's ultramafic catchments almost systematically identify serpentine minerals (ferro-magnesium silicate, lizardite, chrysotile and antigorite), willemseite (nickel silicate), goethite, hematite (iron oxides-hydroxides), quartz (silicate) and occasional asbolane (manganese oxide-hydroxide) (Audet, 2008; Gunkel-Grillon et al., 2014; Pasquet et al., 2016; Teitler et al., 2019). The water compositions of the ultramafic non-anthropized watersheds result from chemical interaction with both lateritic suspended particles and substrate.

The geochemistry of New Caledonian surface waters on ultramafic substrate obtained by descriptive statistics is close to the data in the literature (Binda et al., 2018; McClain and Maher, 2016; Neal and Shand, 2002; Tashakor et al., 2018). However, mineralogical transformations resulting from the alteration of ultramafic rocks in warm tropical climates impact the geochemical signatures of surface waters. Our results confirm that concentrations of Fe, Ni, Cr, Mn and Co increase in tropical waters compared to unaltered ultramafic watersheds (Echevarria, 2018; Tashakor et al., 2018). The rivers of the Koniambo massif contain significantly higher geogenic Fe, Ni and Cr concentrations than those analyzed on water collected on weathered peridotites in other parts of the world (*e.g.* $Fe_{median-total} = 862 \mu\text{g/L}$, $Ni_{median-total} = 33 \mu\text{g/L}$, $Cr_{median-total} = 8 \mu\text{g/L}$ in Tashakor et al., (2018), up to respectively $1213 \mu\text{g/L}$, $37 \mu\text{g/L}$ and $24 \mu\text{g/L}$ in Caledonian surface waters). These naturally

high concentrations result from ultramafic alterations leaving residual nickel ores (Massoura et al., 2006).

4.4 Markers of mining activities

The graphical representation of the descriptive statistic values of the Koniambo surface waters show that (Figure 7a, 7b):

- The Coco, Confidence, Nepia, Pandanus rivers have median values of similar variation. This result concerns both dissolved and total element concentrations. The similarity of the environmental parameters (surface area, substrate geology, relationship between peridotite aquifers and surface water, climate...) of these four ultramafic watersheds explains this result. It should be remembered that these four watersheds have not retained any active erosion patterns related to previous anthropogenic activities.
- The median values of Foachiamboué data are partly distinct from those of other Koniambo catchments. For total concentrations As, Co, Cr, Ni, Mn, Zn, Al, Fe, Si and Mg display median values above the interval median of all the others ultrabasic watersheds (Figure 7-a). Ratios, $\text{median}_{\text{total Foachiamboué}} / \text{Maximum median}_{\text{total other koniambo watersheds}}$ are for Ni (59.2), for Fe (30.8), for Cr (27.5) for Mn (25) and for Al (25), (Table 5). This ratio decreases for Co (13.5), As (2.6), Zn (2.5), Si (1.6) and Mg (0.5). In the dissolved fraction, median values above the maximum median value defined by the 4 other rivers of Koniambo are Cr, Al, Ni and Fe ones. The enrichment coefficient is lower than that for the total fraction. The ratios $\text{median}_{\text{dissolved Foachiamboué}} / \text{Maximum median}_{\text{dissolved other koniambo watersheds}}$ are respectively Cr (6.8), Al (3.7), Ni (2.5) and Fe (2.1), (Table 5).

The Foachiamboué watershed is the only one of the 5 watersheds that has preserved active gullies as relics of previous mining activity. The similarities in descriptive statistics parameters of the 4 watersheds Coco, Confidence, Nepia and Pandanus, calculated from a 15 years monitoring, could allow to associate the interval between the maximum values of Q3 and the minimum values of Q1 as representative of the geochemical background of the watersheds on ultrabasic substratum of the Koniambo massif. The waters of the Foachiamboué River characterize the impact of a mining activity on the geochemical composition of surface water.

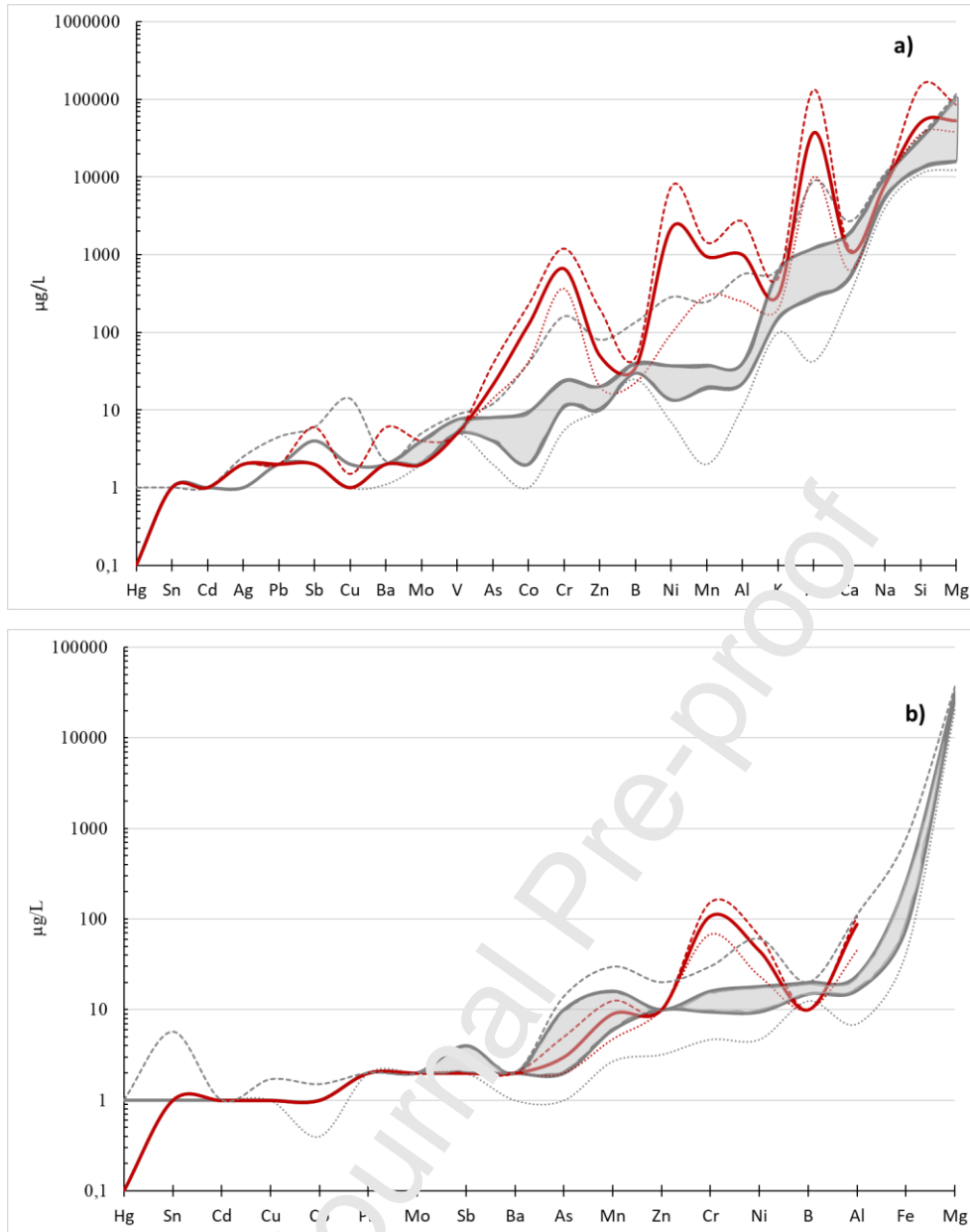


Figure 7: Graphic of the BoxPlot parameters values. Foachiamboué data in red: dashed line = Q3 values; solid line = median values, point line = Q1 values. Geochemical Interval of the Coco, Confiance, Nepia and Pandanus ultramafic catchments in gray: dashed line = maximum value of Q3; gray area = median interval (minimum and maximum) and point line = minimum value of Q1. a) Total concentrations and b) dissolved fractions.

Interpretation of higher enrichment of Foachiamboué total and dissolved concentrations as a relic of previous mining activity is consistent.

Table 5: Geochemical background of surface waters in ultramafic catchments for the metallic and metalloid elements (total and dissolved concentrations) - units in $\mu\text{g/L}$

Total concentration			Dissolved concentration		
	Med _{min}	Med _{max}		Med _{min}	Med _{max}
Hg	0,1	0,1	Hg	0,1	1
Sn	1	1	Sn	1	1
Cd	1	1	Cd	1	1
Ag	1	2	Cu	1	1
Pb	2	2	Co	1	1
Sb	2	4	Pb	2	2
Cu	1	2	Mo	2	2
Ba	2	2	Sb	2	4
Mo	2	4	Ba	2	2
V	5	7,5	As	2	10
As	4	8	Mn	5	16
Co	2	9,5	Zn	10	10
Cr	11	24	Cr	9,5	16
Zn	10	20	Ni	9,5	18
B	30	40	B	15	20
Ni	13,5	37	Al	16,5	24
Mn	19	37,5	Fe	80	260
Al	22	40	Mg	28200	32050
K	150	600			
Fe	280,5	1213,5			
Ca	500	1900			
Na	5350	10100			
Si	12900	31100			
Mg	15950	192000			

Mining operations amplify the erosion and the mobilization of suspended particles. Due to their high concentrations and via runoff, mining sediments are the major conveyors of metal elements to surface waters. The highest concentration of suspended particules (SP) measured in Foachiamboué is 5740 mg/L, which is twice the maximum concentration of SP measured in the streams not influenced by mining (2867 mg/L). In the same way, the median values achieve 364 mg/L for Foachiamboué compared to 88 mg/L for the maximum median of the other ultramafic catchments. Thus, the chemical elements with increasing concentrations in streams under mining influence are mainly those already identified as highly concentrated in alteration residues of peridotite. In addition to the quantitative aspect, mining also modifies the mineralogy of sediments. Open-cast mines erode deeper rocks in the alteration profile of ultramafic massifs to reach the ores (Dublet et al., 2015; Sellier et al., 2021). While "natural" erosion mainly mobilizes superficial laterites, mining reaches the more weakly altered deep horizons in which relics of the initial peridotites persist and include the most nickel-rich

horizons. This explains the strong increase in Ni concentrations in the Foachiamboué's stream, and the significant presence of Al (the silicates indicators, Si and Mg, are not discussed since they were not analyzed in the dissolved fraction of the Foachiamboué). The lack of enrichment of the Co median in the dissolved fraction of the Foachiamboué in relation to the geochemical background is explained by the low solubility of this element under the physico-chemical conditions encountered. The highest $Q3_{total}$ values for Co, 40 $\mu\text{g/L}$ and 32 $\mu\text{g/L}$ originate from the two non-impacted Coco and Pandanus streams respectively. The dissolved Co concentrations of the same samples do not exceed 1 $\mu\text{g/L}$. The absence of Mn enrichment in the dissolved fraction also seems to be explained by its relatively low solubility, as suggest the low $Q3_{dissolved}$ of 12.5 $\mu\text{g/L}$ compared to the high $Q3_{total}$ of 1433.2 $\mu\text{g/L}$ obtained for the Foachiamboué stream.

The identification of an enrichment in As and Zn in impacted waters does not seem to be immediately linked to mining sediment inputs due to the absence of carrier mineral and to their relatively low concentrations in the lateritic profile (Pasquet et al., 2018). However, these elements are also concentrated in the silicates that make up the Koniambo serpentinites and peridotites with concentrations from 14 to 219 $\mu\text{g/g}$ and 0.08 to 24 $\mu\text{g/g}$ for Zn and As respectively (Deschamps et al., 2013, 2010, Petriglieri et al., 2020; Secchiari et al., 2016). These peridotites and serpentine rocks also form the geology of aquifers connected with surface waters of the Koniambo Massif (Dewandel et al., 2017; Genthon et al., 2017; Jeanpert et al., 2019). These two elements have a higher solubility under alkaline pH and reducing conditions prevailing in underground reservoirs (Peters, 2008; Ryan, Peter et al., 2011; Smedley and Kinniburgh, 2002, 2001; Verma et al., 2019). The lack of median values higher than the geochemical background of the dissolved values probably indicates a more significant contribution of groundwater in dissolved As and Zn than sedimentary leaching. This hypothesis is supported by the concentrations of As higher than the WHO recommendations (10 $\mu\text{g/L}$) obtained for Nepia, which is not impacted by the excess sediment supply resulting from mining activity.

Although the presence of chromite (Cr oxide, FeCr_2O_4) in peridotites and altered soils can result in high concentrations of Cr in watershed under mining, the enrichment is especially high. The Cr median $_{total\ Foachiamboué}$ is 27.5 times higher than the maximum median $_{geochemical\ background}$. The high adsorption of Cr, especially the CrVI, by iron oxides and hydroxides, such goethite, is well known (Boschetti and Toscani, 2008; Fandeur et al. 2009; Dublet et al., 2015; Gunkel-Grillon et al., 2014; Kierczak et al., 2016). Gunkel-Grillon et al. (2014) demonstrated that the dominance of iron oxides and hydroxides plus immersion/dehydration

cycles in settling tanks significantly increase Cr concentrations in captured mining sediments. The overflow of the settling tanks during major rain events releases these chromium-enriched sediments. These processes can account for the higher chromium concentrations in streams impacted of mining.

The identification of chemical elements indicative of mining anthropization must be supported by robust statistical validation. While the method using the enrichment of statistical parameters values relative to geochemical background to identify geochemical indicators of anthropization is simple to implement, it requires consolidation. Table 6 shows the P-Value estimated by ANOVA method to differentiate the two groups of samples from non-impacted and impacted watersheds (Foachiamboué). The p-values obtained from the total concentrations confirm that Al, Si, Mg, Cr, Co, Ni, Mn, Fe, As are significantly different between the two groups. In contrast to the result obtained by comparing the median values, and with a p-value of 0.479, Zn concentrations are likely to be similar between the impacted and non-impacted catchments.

Table 6: One-way ANOVA results for the total concentration and the dissolved fraction

Chemical element	P_Value	
	Dissolved fraction	Total concentration
Al	0,0263	1,1915E-08
As	0,5220	0,0023
Ca _t	-	0,6428
Cd	1	0,3553
Co	-	6,8068E-07
Cr	6,6333E-12	2,0405E-07
Cu	0,3818	0,2141
Fe	0,2156	0,0011
Hg	0,0468	0,0483
Mg	-	7,6563E-08
Mn	0,1990	1,7145E-06
Ni	0,0326	1,1306E-06
Pb	1	0,2999
Sb	0,1991	0,5902
Si	-	1,8338E-10
Zn	0,2982	0,4789

The p-values calculated from the concentrations of dissolved elements show that only the Cr concentrations are significantly different between the two groups of impacted and non-impacted watersheds (p-value $6.63 \cdot 10^{-12}$). Al and Ni with p-value 0.026 and 0.032 respectively are the only two other elements that also have p-value below 5%, but which

remain very close to this accepted limit. Finally, Fe concentrations, with a p-value of 0.21, cannot be considered statistically different between the two groups of catchment areas. Thus, the total concentrations of Zn and dissolved Fe can no longer be considered as undeniably influenced by mining. By this way, the elements As, Co, Cr, Ni, Mn, Al, Fe, Si and Mg for the total samples and Cr, Al, Ni for the dissolved fraction are identified as geochemical indicators of the impact of mining activity on surface waters on ultramafic substrate by the two statistical methods used. Of all elements studied, Cr measured in the dissolved fraction has the lowest p-value (6,63.10⁻¹²), which attests that Cr is a good indicator of mining activities.

The application of the BoxPlot descriptive statistics method remains essential to describe the variability of the data defining the geochemical background. However, the approach comparing the values of Q3 and Q1 of potentially impacted surface water to those of the geochemical background is not sufficiently robust statistically. This approach may lead to misinterpretation, especially when the mining impact consists almost exclusively in exacerbating the sedimentary inputs of otherwise naturally eroded massifs. The identification of geochemical impact indicators requires complementing the BoxPlot with an additional statistical method such as ANOVA.

As part of surface water quality monitoring, the identification of geochemical indicators is essential but not sufficient. It is also necessary to access the discriminative values for the concentration of these elements to differentiate impacted from non-impacted streams.

4.5 Determination of indicators discriminating values

Tree decision method provides a tree (see figure 8) with Cr, As, Si, Mg and Al (ranked in discriminating power order) as good geochemical indicator for the total concentration. Accuracy rate of this classification is 91.12 % with Kappa statistic near 0.76. The discriminative concentration for Cr is around 367 µg/L, for As around 10 µg/L, for Si around 15.1 µg/L and for Mg around 46.3 µg/L.

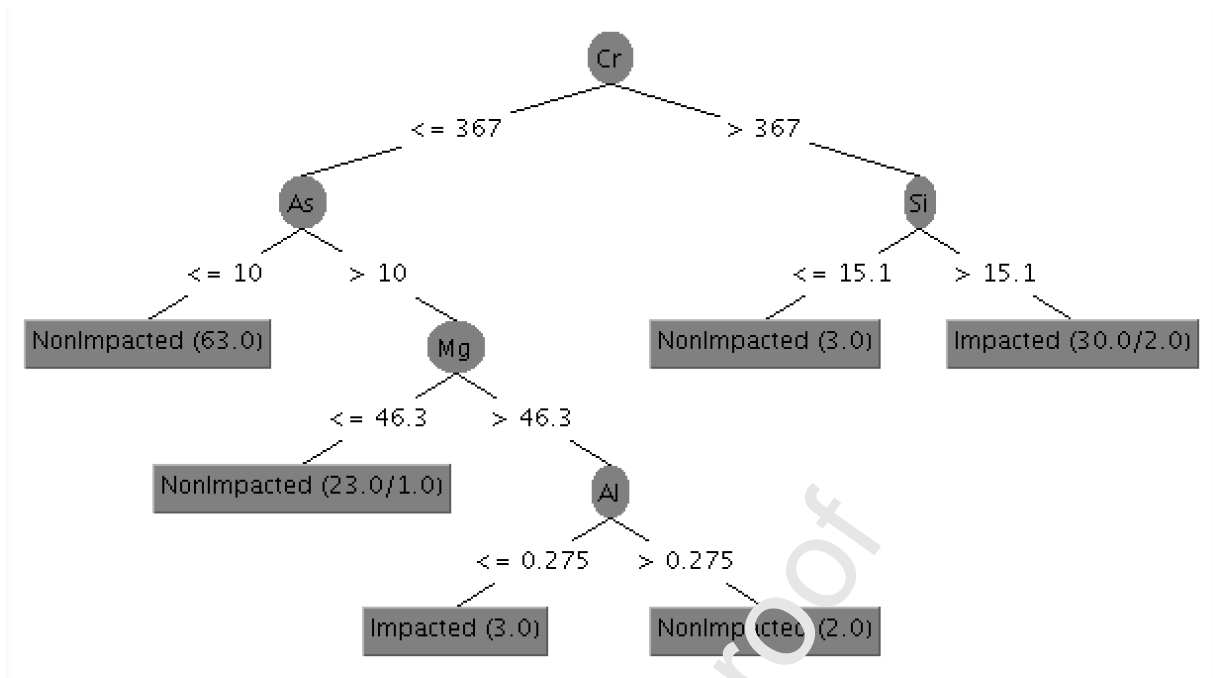


Figure 8: Decision tree based on total concentration of marker elements (units: $\mu\text{g/L}$)

As shown in figure 9, the tree decision, with an accuracy rate of 92.94% and Kappa statistic around 0.84, shows only that Cr appears as a good indicator to discriminate efficiently between non-impacted and impacted basins in data. In addition, that confirms the threshold value for this indicator Cr around $58\mu\text{g/L}$.

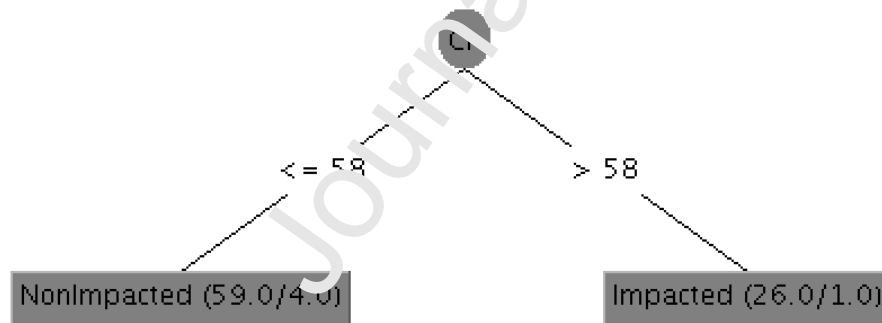


Figure 9: Decision tree based on dissolved concentration on markers elements (units: $\mu\text{g/L}$)

It should be noted here that the decision tree method does not highlight the other geochemical elements despite the fact that their P-Value is very significant. This comes from the decision tree method, which is asked to prune the tree when the accuracy rate is sufficient.

The comparison of dissolved median values measured in this impacted catchment with guidelines for drinking water quality (WHO, 2008) reveals that Cr concentration is upper than $50\mu\text{g/L}$ which is the recommended value. Cr median value is $108\mu\text{g/L}$ with a Q_3 value

of 152.5 $\mu\text{g/L}$ (Table 4). This high chromium value could also lead to sanitary problems like As mentioned in section 4.3, but in the case of Cr, its concentration is enhanced by mining activity when surface waters have not been managed.

5 Conclusion and perspectives

Our approach is original and offers the possibility, even in a context of anthropization very close to the natural geogenic evolution, not only to identify the geochemical impact of mining activity but also to obtain discriminating values that can be used for the environmental monitoring.

This study provides for the first-time values for naturally occurring inorganic chemicals in surface waters draining ultramafic catchments. With the significant dataset provided for this study for non-impacted catchments, the geochemical background of 24 elements in the total fraction and of 18 elements in the dissolved fraction has been established. Results underline that in ultramafic catchments As can naturally occur at levels harmful to human health. The comparison between the geochemical background and the median concentrations measured in a draining stream of former open-pit mines, determined that As, Co, Cr, Ni, Mn, Al, Fe and Si are markers of mining anthropization for total concentrations and that Cr, Ni and Al are markers for dissolved concentrations. Results also underline that in ultramafic catchments Cr can occur at levels of health significance as a consequence of mining operations.

The geochemical background obtained from data of the Koniambo massif must be reinforced and consolidated by other hydrogeochemical monitoring of watersheds on ultramafic substrates. But in any case, our study shows the usefulness of long-term water quality monitoring to assess the impact of human activities on river quality and ecosystem sustainability.

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Declaration of competing interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Author statement

Aurélie Boula: Conceptualization, Methodology, Data Curation, Writing-Original draft preparation, Formal analysis

Christine Laporte-Magoni.: Conceptualization, Methodology, Writing-Original draft, Supervision, Validation, Funding acquisition

Peggy Gunkel-Grillon: Conceptualization, Writing- Reviewing and Editing, Funding acquisition

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Highlights:

- First geochemical background of rivers in ultramafic context in New Caledonia.
- Work based on a database on more than 15 years of hydrochemical monitoring.
- The developed method combines classical statistic analysis and machine learning
- Identification of chemical markers and threshold values of mining anthropisation.

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