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# A Preliminary Study on Metal and Nutrient Concentrations in Running Water Systems in Southern New Caledonia

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**Abstract** Metal and nutrient concentrations were measured in five running water sampling sites of New Caledonia. Metal concentrations were homogeneous (Ni; 22.7–50.6 µg $L^{-1}$) or not (Fe; 37–749 µg $L^{-1}$). Concentrations of Ni, Cr, Fe were high, including high dissolved fractions (up to 47.8, 70.8 and 417 µg $L^{-1}$, respectively). Concentrations of anthropogenic metals (Ag, As, Cd, Cu, Pb, Sb, V, Zn) were low (maximum: total Cu, 0.6 µg $L^{-1}$). The contamination of waters is presumably due to soil weathering and mining activities. Metal concentrations and phosphate depletion (<0.04 µmol $L^{-1}$) suggest constrained conditions for the development of aquatic life.

**Keywords** Running waters · Metals · Nutrients · New Caledonia

Soils on ultramafic rocks (peridotites) exhibit very high concentrations of iron (Fe) and magnesium (Mg), and transition metals such as cobalt (Co), chromium (Cr), manganese (Mn) and nickel (Ni) (Becquer et al. 2001). Soils in Southern New Caledonia (SNC) are developed on peridotites that degrade into residues (laterite and saprolite layers) highly enriched by weathering in Ni and Cr, either adsorbed onto Fe or Mg oxides or incorporated into mineral lattice (Quantin et al. 2002). These layers are subject to intense mining extraction and strong soil erosion due to tropical rainfall. The combination of these processes results in the potential mobilisation of high amounts of metal-enriched terrigenous dissolved and particulate material likely to affect the quality of rivers and surface grounds. New Caledonia is one of the "hot spots" of biodiversity described by Myers et al. (2000). Indeed, specific metal concentrations that occur on soils of SNC yield specific conditions for the development of organisms. For example, certain plant species hyperaccumulate certain metals, notably Ni, i.e. accumulate up to more than 0.1% Ni in their leaves (Proctor 2003). However, less is known about metal concentrations in running waters in such environments.

We present here an investigation on the dissolved and particulate concentrations of fourteen metals at five freshwater sites in SNC, together with the concentrations of macronutrients (phosphate and nitrogen). Relatively abundant literature on New Caledonia geology (e.g., Becquer et al. 2001; Perrier et al. 2006), suggests specific chemical and biogeochemical conditions for the development of life, but studies dealing with inorganic chemistry of freshwaters in SNC are still scarce. The purpose of this work was to present a preliminary outline of this peculiar geochemical system.

## Materials and Method

Five sampling sites were selected in SNC (Fig. 1). Stations 1, 2 and 4 (Creek Pernod, Madeleine Falls and Trou Bleu River, respectively) are characterised by permanent, moderate water flow. Stations 3 and 5 (former Cr–Co mine and

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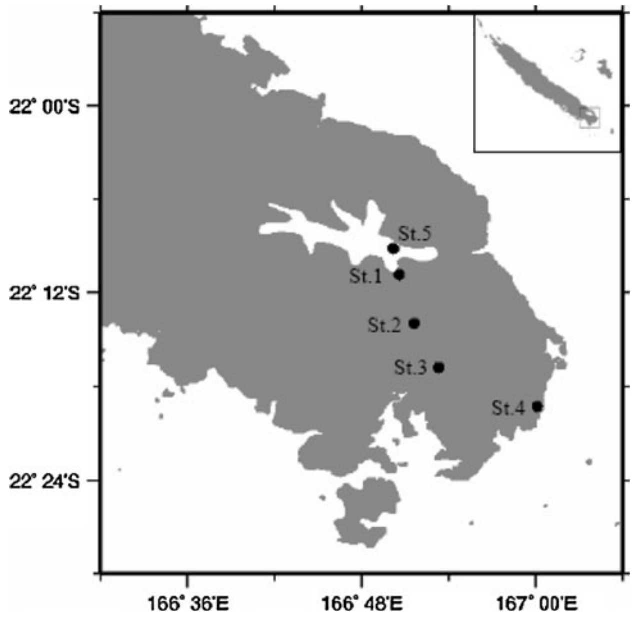

**Fig. 1** Location of the five sampling sites: Creek Pernod (St1 on the map), Madeleine Falls (St2), Cr–Co former mine (St3), Trou Bleu River (St4), and Lake Yaté (St5)

Lake Yaté, respectively) are characterised by very low water flow. Waters are almost totally still at st. 3, an abandoned Cr and Co mine where samples were collected close to a well from which water springs. Station 5 (Lake Yaté) is located close to the inflow area of two non-named streams that feed the lake. It is expected that water flow mobilises particulate material in st. 1, 2 and 4, while water flows at site 3 and 5 yield negligible particle mobilisation. Samples were collected on 7 and 16 November 2008. Meteorological conditions were similar (~a week after a rain event), in order to study standard situations, i.e., not significantly affected by changes in freshwater dynamics, nor resulting from drought. Metal and nutrient samples were separately collected, each in triplicates. Sample collection was performed by hand 10–20 cm below surface with polyethylene bottles (500 and 60 mL for metals and nutrients, respectively). Water samples were filtered in situ on cellulose acetate membranes (porosity 0.2 µm) and stored in the dark at 5°C. Nutrient samples were poisoned immediately after filtration to limit the bacterial consumption of nutrients: 1 mg $HgCl_2$ (Suprapur quality) was added to the sample (60 mL), i.e. 20 µg $mL^{-1}$.

Analyses were carried out under laminar airflow benches in a class 100 clean room. Concentrations of Fe, Mn, Co, Cr, Ni, aluminium (Al), copper (Cu), silver (Ag), cadmium (Cd), lead (Pb), zinc (Zn), vanadium (V), arsenic (As) and antimony (Sb) were analysed. Particulate samples were dissolved by acid treatment including blank filters and two certified reference materials (CRMs). The mineralisation protocol can be found in Heimbürger et al. (2010). Digested and dissolved metals were analysed by ICP-OES, using a Perkin-Elmer Optima 3000, axial torch instrument. An ultrasonic nebuliser (CETAC) was used as sample introduction to improve the sensitivity. Quality of measurements was controlled by analysis of CRMs (SRM 1643e, standard reference freshwater from National Institute of Standards & Technology, USA). Detection limits (d.l.) and CRM recovery are given in Table 1. Phosphate ($PO_4^{3-}$), nitrite ($NO_2^-$) and nitrate ($NO_3^-$) dissolved concentrations were analysed by colourimetry (Technicon autoanalyser). Detection limits (using a light path of 10 cm) are given in Table 1.

## Results and Discussion

Metal and nutrient concentrations measured at the five sites are recorded at Table 2.

Some metals (Ni, Cr, Fe) exhibited high total (dissolved + particulate) concentrations (up to 50.1, 71.6, and 749 µg $L^{-1}$ for Ni, Cr, and Fe, respectively). This is consistent with the chemical nature of ultramafic (i.e., ultrabasic) soils, where high concentrations of Fe, Cr, Ni and Co

**Table 1** Detection limits (d.l.) and CRM recovery (%) for each metal

| Metal | Ag | Al | As | Bi | Cd | Co | Cr | Cu |
|---|---|---|---|---|---|---|---|---|
| d.l. (µg $L^{-1}$) | 0.03 | 1.5 | 3.2 | 0.95 | 0.03 | 0.06 | 0.03 | 0.09 |
| CRM recovery | 68 | 98 | 115 | 99 | 99 | 92 | 90 | 86 |

| Metal | Fe | Mn | Ni | Pb | Sb | V | Zn |
|---|---|---|---|---|---|---|---|
| d.l. (µg $L^{-1}$) | 0.297 | 0.01 | 0.07 | 0.52 | 0.8 | 0.04 | 8.3 |
| CRM recovery | 96 | 104 | 95 | 99 | 110 | 90 | 90 |

| Nutrient | $NO_3^-$ | $NO_2^-$ | $PO_4^{3-}$ |
|---|---|---|---|
| d.l. (µmol $L^{-1}$) | 0.05 | 0.02 | 0.02 |

Nitrogen (N) concentrations are the sum of nitrate and nitrite concentrations

**Table 2** Dissolved and particulate metal concentrations ($\mu$g L$^{-1}$) and dissolved inorganic nutrient concentrations ($\mu$mol L$^{-1}$)

| | Station 1 | Station 2 | Station 3 | Station 4 | Station 5 |
|---|---|---|---|---|---|
| $[Al]_{diss}$ | 3–6 | 5.5–7.5 | <d.l.–3 | <d.l.–2 | 4.5–3 |
| $[Cd]_{diss}$ | <d.l.* | <d.l. | <d.l. | <d.l. | <d.l. |
| $[Co]_{diss}$ | 0.7–1.0 | 0.5–0.8 | 1.1–1.15 | 0.3–0.3 | 0.7–1.1 |
| $[Cr]_{diss}$ | 5.0–6.2 | 3.7–4.6 | 58.8–70.8 | 13.8–14.9 | 16.2–16.8 |
| $[Cu]_{diss}$ | <d.l. | 0.3–0.3 | <d.l.–0.2 | 0.2–0.3 | 0.3–0.4 |
| $[Fe]_{diss}$ | 406–417 | 126–143 | 1.5–6 | 28–36 | 74–79 |
| $[Mn]_{diss}$ | 37.28–39.46 | 14.89–18.88 | 0.25–1.05 | 5.40–6.66 | 15.42–11.20 |
| $[Ni]_{diss}$ | 29.3–35.3 | 37.7–40.5 | 38.9–38.4 | 21.9–28.0 | 38.9–47.8 |
| $[V]_{diss}$ | <d.l. | <d.l.–0.1 | <d.l. | <d.l. | <d.l. |
| $[Al]_{part}$ | 2.5–3.5 | 10.0–11.5 | 2.0–2.0 | 5.0–5.5 | 10.5–11.0 |
| $[Cd]_{part}$ | 0.20–0.25 | 0.05–0.15 | <d.l. | 0.05–0.20 | 0.05–0.05 |
| $[Co]_{part}$ | 0.20–0.20 | 0.55–0.50 | <d.l.–0.05 | 0.10–0.15 | 0.25–0.35 |
| $[Cr]_{part}$ | 1.10–1.20 | 2.60–2.90 | 0.75–0.80 | 1.95–2.45 | 3.50–3.90 |
| $[Cu]_{part}$ | <d.l.–0.1 | <d.l.–0.3 | <d.l. | <d.l. | 0.2–0.1 |
| $[Fe]_{part}$ | 302–332 | 128–145 | 37–31 | 77–80 | 154–161 |
| $[Mn]_{part}$ | 3.89–5.04 | 6.25–7.57 | 0.36–0.40 | 0.80–1.02 | 3.00–2.95 |
| $[Ni]_{part}$ | 1.2–2.3 | 1.5–1.8 | 1.3–1.1 | 1.1–1.3 | 2.4–2.8 |
| $[V]_{part}$ | <d.l. | 0.05– <d.l. | <d.l. | <d.l. | 0.05–0.05 |
| $PO_4^{3-}$ | <d.l. | <d.l.–0.03 | <d.l. | <d.l. | <d.l.–0.04 |
| Total N[†] | 0.955–1.652 | 3.640–8.197 | 1.678–4.930 | 9.430–14.382 | 0.886–2.330 |

* (See Table 1 for d.l. values). Silver, As, Bi, Pb, Sb and Zn concentrations (dissolved and particulate) were always <d.l

[†] The sum $NO_3^- + NO_2^-$ is taken as an approximation of total N

are generally found. Concentrations of total Mn were moderately high (0.61–44.5 $\mu$g L$^{-1}$). Total Ni concentrations were remarkably similar in the various sites, with variability less than a factor of two. On the contrary, concentrations of total Fe varied by more than an order of magnitude (from ~38 $\mu$g L$^{-1}$ at st. 3 up to ~728 $\mu$g L$^{-1}$ at Creek Pernod). Chromium and Co concentrations were also relatively constant, with the exception of dissolved Cr concentrations at st. 3, higher by a factor of ~6 than concentrations elsewhere. Conversely, particulate Cr occurred at lower concentrations at st. 3 than at other sites (e.g., 0.75–0.8 $\mu$g L$^{-1}$ at this station vs. 1.1–3.9 $\mu$g L$^{-1}$ at the other ones). The percolation of water through the naturally Cr-enriched soils of st. 3 likely yields high dissolved Cr concentrations, while it is believed that the very low (close to zero) water flow leads to low weathering of soil, and, therefore, to low particle mobilisation. To a lesser extent, this behaviour is observed for Co at this site, but also for Mn. The highest concentrations of dissolved Fe (417 $\mu$g L$^{-1}$) and Mn (39.5 $\mu$g L$^{-1}$) were found at Creek Pernod. Dissolved Cd was always <d.l., and Cu and V were detectable only at some sites. Concentrations of Ag, As, Bi, Pb, Sb and Zn were <d.l. whatever the station.

The solubility of metals varied from a site to another as follows: the dissolved fraction represented 22 (st. 5) to 63% (st. 1) of total Al, 27 (st. 3) to 56% (st. 1) of total Fe, 41 (st. 3) to 90% (st. 1) of total Mn, 52 (st. 2) to 96% (st. 3) of total Co, 59 (st. 2) to 99% (st. 3) of total Cr, and 94 (st. 5) to 97% (st. 3) of total Ni. In general, metals exhibited relatively low solubility (e.g., the dissolved fraction was 27% of total Fe, and 41% of total Mn at st. 3, where the dissolved contribution is expected the lowest). This is probably due to the mineral character of metals in this environment. Basically, metals associated with mineral material occur within three-dimensional crystalline networks in which dissolution is low. On the contrary, metals associated with anthropogenic material occur within amorphous and soluble structures (Chuang et al. 2005). However, this was not always observed. For example, the soluble fraction of Ni was always high. In surface horizons, the weathering of ultramafic rocks leads to the formation of laterite, which contains large amounts of Fe and Mn oxides, with which the Ni mobilised during the weathering process may co-precipitate. However, Quantin et al. (2002) have shown that metals such as Co and Ni, once they have co-precipitated with ferric hydroxide $\alpha$–Fe(OOH).$H_2O$ (goethite) and with Mn oxides, can be released by anaerobic reducing bacterial activity, which leads to the solubilisation of Fe oxides and, to a lesser extent, that of Mn oxides. This is consistent with observations at st. 3, where the absence of water flow may favour reducing conditions. Concentrations of dissolved Co, and, to a lesser extent, Ni steeply increased at st. 3, compared with other stations. This process might be responsible for the release of significant amounts of Ni in SNC topsoils. This is important because solubility of metals can be viewed as a proxy of their bioavailability. Another example is Cr, which occurred mainly in dissolved form (up to 99% at st. 3), presumably due to the presence of Mn oxides that oxidise Cr(III) into exchangeable, and highly toxic, Cr(VI) (Becquer et al. 2003). Dissolved concentrations of Fe and Cr were sometimes higher than the maximum permissible levels of the World Health Organization drinking water standards. Dissolved Ni was close to this limit, and episodic concentrations beyond the permissible level may be expected.

Table 3 compares some dissolved metal concentrations measured in the present work with concentrations found in variously polluted freshwaters, and concentrations averaged from pristine sites. Apart from Ni, Cr and Fe, and, to a lesser extent, Mn and Co, other metals comparatively occurred at low or very low concentrations at every sampling station. In particular, several metals of which emissions are strongly related to human activities (Ag, As, Cd, Cu, Pb, Sb, V, Zn) were found at very low concentrations, sometimes <d.l. (e.g., dissolved Cd and V at any station, dissolved Cu episodically, and particulate Cd, Co, Cu and V at some stations; see Table 2). Together with the relatively poor solubility of crustal metals such as Fe or Mn, this suggests that the contamination of waters in this region is almost totally due to the weathering of soils, this process being strongly enhanced by former or current mining activities. For example, all sites exhibited very low (<d.l.) concentrations of Zn, which is known as an ubiquitous urban tracer. One can infer that anthropogenic influences from Nouméa, the main city in New Caledonia, do not significantly affect the studied area. Taking into account that the main transport route for urban pollutants is the atmospheric pathway, this is consistent with the direction of prevailing winds in this region (Migon et al. 2007). This assumption may be strengthened by the relatively low Mn and Co concentrations found in this study, compared with concentrations found elsewhere. While high concentrations were reported in wastewater and freshwaters affected by sewage effluents (Buzier et al. 2006), and despite the scarcity of Co literature data, Mn and Co concentrations in the poorly inhabited SNC, were lower by up to several orders of magnitude than in variously contaminated rivers.

Anthropogenic contaminations generally yield relatively high nutrient concentrations (Cheung et al. 2003). However, the metal contamination observed in the present work is presumably due to the natural, lithogenic emission source, although mining activities may be viewed as an anthropogenic contribution. In such a specific environment,

**Table 3** Range of dissolved and total metal concentrations (Metal$_{diss}$ and Metal$_{tot}$, respectively) measured in SNC running waters, compared with values from unpolluted and polluted freshwaters. Concentrations are expressed in µg L$^{-1}$

| | This study | Pristine river water[a] | Seine river France[b] | Vistula river Poland[c] | Lake Kanyaboli Kenya[d] | Yangtze river China[e] |
|---|---|---|---|---|---|---|
| Fe$_{diss}$ | 1.5–417 | 0.56–47.47 | | | | |
| Fe$_{tot}$ | 37–749 | | | | | 174.5–350.5 |
| Mn$_{diss}$ | 0.25–39.5 | | 6.26 | 5.3–583.8 | 284.27 | |
| Mn$_{tot}$ | 0.6–44.5 | | | | | 4.3–8.8 |
| Co$_{diss}$ | 0.3–1.15 | | | 250–3030 | 16.38 | |
| Co$_{tot}$ | 0.4–1.45 | | | | | |
| Ni$_{diss}$ | 21.9–47.8 | 0.29 | | | | |
| Ni$_{tot}$ | 23–50.6 | | | | | 5.6–24.3 |
| Cr$_{diss}$ | 3.7–70.8 | | | | | |
| Cr$_{tot}$ | 6.1–71.6 | | | | | 17.2–24.3 |
| Cu$_{diss}$ | <d.l.–0.4 | 0.13–2.22 | 2.23 | 0.9–90.0 | | |
| Cu$_{tot}$ | <d.l.–0.5 | | | | | 8.6–12.3 |
| Cd$_{diss}$ | <d.l. | $3 \times 10^{-4}$–0.09 | 31 | 510–730 | | |
| Cd$_{tot}$ | <d.l.–0.25 | | | | | 3.2–6.4 |
| Zn$_{diss}$ | <d.l. | 0.02–1.83 | | 16.2–168.7 | 32.79 | |
| Zn$_{tot}$ | <d.l. | | | | | 7.6–11.6 |
| Pb$_{diss}$ | <d.l. | 0.001–0.5 | 353.6 | 240–390 | 20.65 | |
| Pb$_{tot}$ | <d.l. | | | | | 44–734 |

[a] Summary from Prego and Cobelo-Garcia (2003)

[b] Elbaz-Poulichet et al. (2006)

[c] Guéguen and Dominik (2003)

[d] Ochieng et al. (2008)

[e] Wu et al. (2009)

very low phosphate concentrations were found in running waters (<d.l. to 0.04 µmol $L^{-1}$; Table 2), whatever the sampled site. Ultramafic soils have generally low concentrations of P (Proctor 2003). However, such low phosphate concentrations may be partly due to the occurrence of particulate oxides/oxyhydroxides. Indeed, orthophosphate is strongly adsorbed onto oxides and oxyhydroxides, mainly goethite, and also Cr oxides/oxyhydroxides, and organic matter (Golterman 1998). To a lesser extent, nitrate can be adsorbed onto the same surfaces (Duwig et al. 1999), although the concentrations of nitrate and nitrite ranged between 0.9 (st. 5) and 14.2 µmol $L^{-1}$ (st. 4). The weathering of ultramafic rocks under the SNC tropical climate has led to the accumulation of trace elements in lateritic soils widely dominated by Fe-oxyhydroxides (Quantin et al. 2002). The chemical nature of soils for all sampling sites provides good conditions for significant sorption processes. It is hypothesized that rain events and subsequent water flows may not release significant amounts of P by weathering, but, on the contrary, scavenge phosphates from water by re-mobilisation of particles and subsequent sorption processes. The combination of high concentrations of potentially toxic metals and shortage of nutrients in SNC running waters results in a specific, extreme freshwater environment. While the strategies by which certain endemic plants are capable of partitioning and hyperaccumulating metals, and adapting to ultramafic soils, has been documented (e.g., Proctor 2003; Perrier et al. 2004), much less has been done on freshwater systems in such environments. Together with a broader understanding of geochemical parameters that rule the mobility of metals in the topsoils of SNC, and their bioavailability in running waters, future studies should focus on the biological response to this environmental stress, e.g., bacterial dynamics.

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