

Development of a Field Preconcentration/Elution Unit for Routine Determination of Dissolved Metal Concentrations by ICP-OES in Marine Waters: Application for Monitoring of the New Caledonia Lagoon

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An iminodiacetate chelating resin was optimised for the rapid determination of Co, Cu, Fe, Mn and Ni in seawater. Using inexpensive, high-capacity, reusable cartridges allowed high flow rates of up to 25 ml min⁻¹. High preconcentration factors, of up to 500, were obtained in order to analyse samples using an ICP-OES. The requirement for a buffer was eliminated due to the high tolerance of the ICP-OES to interfering matrix elements, thereby further reducing the potential for contamination. Quantification limits in seawater were: Co = 6 ng l⁻¹, Cu = 8 ng l⁻¹, Fe = 6 ng l⁻¹, Mn = 5 ng l⁻¹ and Ni = 6 ng l⁻¹. The method was verified by the analysis of near shore seawater (CASS-4) and open ocean seawater (NASS-5) reference materials. In order to satisfy the high sampling demands using the iminodiacetate cartridges, a portable off-line preconcentration unit was developed for routine analysis. The multi-channel preconcentration unit, was capable of treating up to eight samples simultaneously with concentrating times as little as 30 minutes. The technique was also used to determine dissolved metals in fresh and interstitial waters. The technique has been successfully used in a number of environmental studies and impact assessments to evaluate the effects of mining on the New Caledonian lagoon.

Keywords: preconcentration, seawater, ICP-OES, dissolved metals.

Pour l'analyse de Co, Cu, Fe, Mn et Ni dans l'eau de mer, la technique de préconcentration des métaux sur lit de résines chélatantes (Iminodiacetate) a été retenue pour les capacités de rétention que ces dernières offrent. Conditionnées dans des colonnes réutilisables à faible coût, ces résines permettent des débits rapides de percolation jusqu'à 25 ml min⁻¹. Les facteurs de préconcentration élevés qui ont été obtenus (500) permettent d'analyser aisément les solutions d'éluion par ICP-OES. Cette technique étant relativement peu sensible aux effets de matrice de l'analyte, l'emploi d'un tampon pH pour la percolation a été écarté, réduisant ainsi les risques potentiels de contamination de l'échantillon. La méthode a été vérifiée avec des échantillons standard d'eau de mer côtière et hauturière de références CASS-4 et NASS-5. Les limites de quantification en eau de mer sont les suivantes : Co = 6 ng l⁻¹, Cu = 8 ng l⁻¹, Fe = 6 ng l⁻¹, Mn = 5 ng l⁻¹ et Ni = 6 ng l⁻¹. Pour répondre à une demande analytique importante avec cette méthodologie, un banc de préconcentration off-line portable a été conçu pour le dosage en routine. Le banc se compose de 8 lignes de préconcentration des métaux pouvant traiter les échantillons simultanément en un peu plus de 30 minutes. La méthodologie développée peut être indifféremment mise en œuvre pour les eaux douces comme pour les interstitielles des sédiments. La technique a été employée avec succès dans plusieurs programmes d'études environnementales et d'évaluations des impacts miniers dans le lagon de Nouvelle Calédonie.

Mots-clés : préconcentration, eau de mer, ICP-OES, métaux dissous.

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In the field of environmental monitoring, accurate determinations of dissolved metal concentrations in seawater are being increasingly requested by regulatory authorities. However, the analysis of this geochemical fraction is a challenging task, particularly in highly dynamic environments where large sample series are required. The difficulties of accurately assessing dissolved metal concentrations are widely documented and principally relate to the low concentrations of dissolved metals, often below the limit of detection for most analytical instruments, and the presence of a highly saline matrix which generates significant analytical interferences (Ferrarello *et al.* 2001) and/or physical effects (e.g., clogging of the nebuliser and injector).

Historically, a number of direct and indirect techniques have been employed to determine dissolved metal concentrations in seawater. To directly determine trace metals, electrothermal atomisation (GF-AAS) has been successfully used (e.g., Cabon and Le Bihan 1994, Chan and Huang 2000, Cabon 2002). However, the mono-element capabilities, combined with the relatively long temperature programmes used, greatly restrict the quantity of samples analysed. Another family of techniques developed for the direct analysis of metals relates to electro-chemical stripping (e.g., Van den Berg and Khan 1990) and, in particular, to potentiometric stripping (Riso *et al.* 1997). These techniques are particularly useful because of their capabilities in determining metal speciation, but are also limited in terms of sample throughput and simultaneous metal determinations.

While these techniques have their merits they are progressively being replaced by multi-elemental methods, principally based on plasma mass spectrometry. Field *et al.* (1999) is one of the few published studies whereby direct dissolved metal analysis was successfully performed on natural seawater samples using high resolution (HR) ICP-MS. The lack of references is an indication of the difficulty encountered when attempting direct seawater analysis.

In addition to the limitations imposed by the specific instrumentation, all these direct analytical techniques present another disadvantage related to their application after the collection of natural samples. Either the samples have to be stabilised (often by acidification) before their analysis, to preserve sample integrity during transportation to the laboratory, or they have to be analysed immediately (e.g., van den Berg and Achterberg 1994, Achterberg *et al.* 1999).

To overcome these problems the quantitative determination of dissolved trace metals is being carried out more and more frequently following separation of the metals onto an ion exchange resin (e.g., Cuculic *et al.* 1997, Willie *et al.* 1998, Pesavento *et al.* 2001, Beck *et al.* 2002, Hirata *et al.* 2003, Matsumiya *et al.* 2004, Biesuz *et al.* 2006). Resins are used to simultaneously concentrate the metals of interest and eliminate from the eluate a high proportion of the matrix components, such as Na from seawaters. This methodology eliminates part of the problem of maintaining sample integrity by immobilising the dissolved metals.

Numerous ion exchange resins have been used for the separation of trace metals from seawater and some of the more popular resins include immobilised 8-hydroxyquinoline (8-HQ) and iminodiacetate resins (IDA):

- The large operating pH range is one of the reasons 8-hydroxyquinoline resins have been popular. However, 8-HQ resins have several drawbacks. Firstly, the absence of any commercial source, makes synthesis necessary (e.g., Willie *et al.* 1998, Hirata *et al.*, 2003 and Matsumiya *et al.* 2004), this being a time consuming step and a potentially contaminating process. Secondly, the release of trace impurities has been reported due to the partial dissolution of the silica gel to which the 8-HQ is typically immobilised (Seubeut *et al.* 1995).

- IDA resins possess a high selectivity for transition metals by virtue of two carboxylic acid functional groups. This capability has led to their widespread use, initially for metal preconcentration in natural waters. In addition, the resin's low affinity for the alkaline earth metals at lower pH has led, more specifically, to their use in the determination of trace metals in seawater (e.g., Bloxham *et al.* 1994, Willie *et al.* 1998, 2001). High cross-linkage IDA resins have been popular for determining dissolved metal concentrations in seawater (e.g., MetPac CC1, Dionex), however, these columns are extremely expensive and the high cross-linkage limits the use of high flow rates. Within the last few years, several manufacturers have developed cheap disposable IDA resin cartridges (OnGuard II M, Dionex and IC-Chelate, Alltech) that are more suitable for high volume, high flow purposes.

On-line or flow injection trace metal preconcentration and elution procedures using ion exchange resins coupled with ICP-MS have been used frequently (e.g., Nicolai *et al.* 1999, Beck *et al.* 2002, Ndung'u *et al.* 2003, Hirata *et al.* 2003). The low detection limits of

ICP-MS instruments reduce the requirement for high sample enrichment (preconcentration) factors. Unfortunately ICP-MS is equally sensitive to matrix interferences and, in particular, the formation of polyatomic species resulting from the strong saline matrix in seawater. High resolution (HR)-ICP-MS has sufficient resolving power to eliminate these polyatomic effects. However, both these instruments are still uncommon around the tropical belt of the South Pacific.

ICP-OES is increasingly commonplace in analytical laboratories due to the lower initial purchase cost and simultaneous multi-elemental analytical capability, and therefore developing techniques that employ the use of readily available instruments is important for their wide application. Vassileva and Furuta (2003) describe an alternative on-line system incorporating an ion exchange column using ICP-OES. However, sample throughput times were between 25 and 40 minutes, due to the higher concentration factors required for the analysis with ICP-OES. Consequently, the resulting high running costs, due particularly to the use of bottled argon, prohibited the analysis of large numbers of samples. Short analytical run times are a requirement in many developing countries.

Reducing the analytical costs was partly solved by Nickson *et al.* (1999) when they developed an off-line preconcentration seawater sample unit. However, the extremely expensive cartridges used (MetPac CC-1, Dionex) meant that only two samples could be preconcentrated simultaneously; additional samples could only be pre-concentrated after elution and reconditioning of the cartridges. Furthermore, flow rates were extremely low (0.5 ml min^{-1}), necessitating a long preconcentration time (> 2 hours), due to the high cross-linkage IDA resin used.

This paper presents the development of a preconcentration/elution method, including the design of a portable preconcentration unit, for the determination of dissolved metals in a range of natural waters. The development of the method was born from the necessity to provide regulatory authorities and organisations charged with surveillance with a simple solution to meet all the requirements of present and future environmental demands in New Caledonia, the world's third largest nickel producer. This growing concern for the environment has recently been accentuated by the construction of a new opencast mining development in the southern part of New Caledonia and the prospect of a similar sized mining development in the north of

the country. In a wider context, national and international governmental and public concerns for the marine environment are being increasingly expressed through a multitude of policies and scientific programmes. The study of the transfer of terrigenous, natural and anthropogenic inputs into coastal environments forms part of the French National Coastal Environmental Programme (PNEC) in which the method presented here has played a vital role in assessing the terrestrial to coastal dissolved metal exchanges.

The paper describes the use of readily available high flow OnGuard II M (Dionex) reconditionable cartridges as a cost effective alternative to the MetPac CC-1 columns and uses an off-line preconcentration procedure allowing up to fourteen samples (two parallel units) to be treated simultaneously in less than 1 hour. The elution was performed in the laboratory and the analysis of the eluates was carried out using ICP-OES in just a few minutes.

Experimental

Reagent and artificial seawater sample preparation

All apparatus were soaked in 10% nitric acid for a minimum of five days and rinsed with ultra pure water (Milli-Q), and then stored in acid-cleaned plastic bags until needed. While analytical acid grades were used for all cleaning steps, high purity reagents were used for all parts of the following procedure.

A stock 5 mol l^{-1} ammonium acetate buffer ($\text{pH} = 5.3$) was prepared by weighing 193 g of ammonium acetate and 25.15 ml of glacial acetic acid (Suprapur, Merck) and completing to 500 ml. Conditioned Chelex 100 (Bio-rad) iminodiacetate resin was then added to the solution, to remove any metal contamination. Prior to use, the ammonium acetate stock solution was then diluted to 0.5 mol l^{-1} and, again, Chelex 100 added.

For the purposes of resin efficiency (recovery) measurements, an artificial seawater solution was made up by mixing ultra pure Milli-Q water ($\text{pH} = 6-6.5$) with Na, Mg, Ca and K at respectively 26.96, 3.17, 0.78 and 0.76 g l^{-1} . A small quantity of iminodiacetate resin (Chelex 100) was added to the artificial solution and mixed, in order to remove any metal contaminants present. The artificial seawater was then spiked with Co, Cu, Fe, Mn and Ni to produce a final concentration of $50 \mu\text{g l}^{-1}$, after removal of the Chelex.

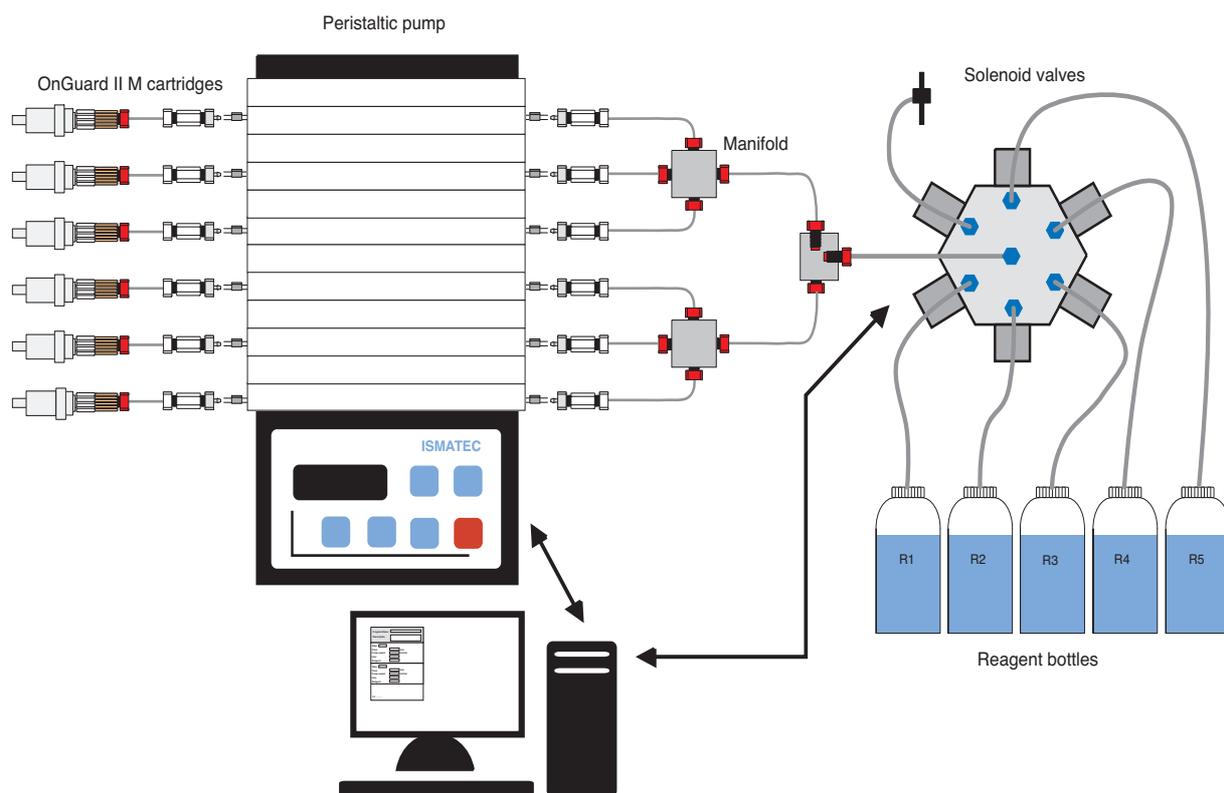


Figure 1. Schematic diagram of the fully automated resin conditioning unit for the simultaneous treatment of six preconcentration/elution cartridges.

Cartridge conditioning

Before any sample pre-concentrations were carried out the OnGuard II M iminodiacetate chelating resin, cartridges were conditioned in a laminar flow hood using the following procedure: (a) Treatment with successive reagents passed through each cartridge (variable flow rate), 10 ml of 1 mol l⁻¹ hydrochloric acid (Suprapur, Merck), 20 ml of ultra pure water (Barnstead), 0.8 ml of 1 mol l⁻¹ ammonia solution (Ultrapur, Prolabo) and 20 ml of ultra pure water and a final rinse with 5 ml of 0.05 mol l⁻¹ ammonium acetate buffer; (b) Cartridges were plugged with a plastic stopper at each end and sealed in an acid-cleaned airtight plastic container for storage prior to their use.

For this critical step a fully automated resin conditioning unit was designed to reduce potential contamination during manipulation and, in particular, to standardise and facilitate pre-treatment of the resin cartridges (e.g., eliminate operator bias). The unit comprised a six port solenoid valve (NRResearch, USA) coupled with a controllable peristaltic pump (Ismatec, IPC, Switzerland) (Figure 1). Six cartridges were conditioned

simultaneously with a conditioning time of approximately six minutes.

Seawater collection

Seawater samples were collected from various locations within the New Caledonian lagoon using 5 litre Teflon-lined Go-flo water samplers (General Oceanics Inc, USA). The Go-Flo water samplers were primed to be open at the site and lowered into the water, rinsed thoroughly and closed using a Teflon-coated messenger. Once at the surface samples were transferred *in situ* into acid-cleaned HDPE bottles and sealed in clean plastic bags. The seawater samples were filtered on-line at 0.45 µm (Millipore acetate filters) during the preconcentration step. In addition, for method optimisation seawater samples were collected from Aquarium des Lagons (Noumea, New Caledonia), via an outlet, into 50 litre acid-cleaned HDPE Nalgene carboys. All the acetate filters were previously acid-cleaned and rinsed with ultra pure water.

Sediment samples were collected by means of a Van Veen grab to extract interstitial seawater. Wet

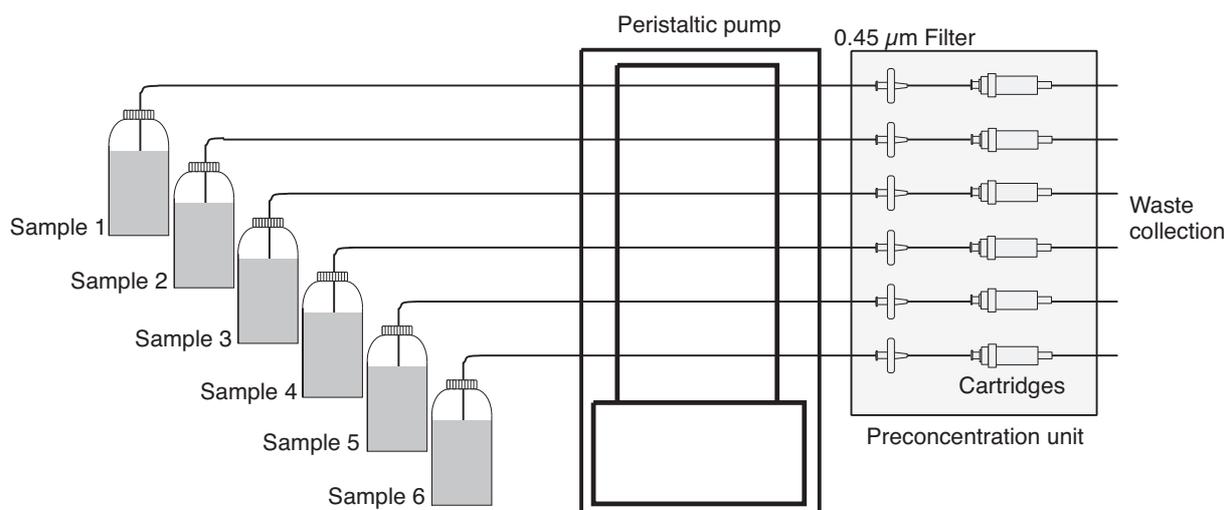


Figure 2. Schematic diagram showing six sample preconcentration units.

sediments were then transferred into cleaned 250 ml centrifuge tubes and spun at 3000 rpm for 20 minutes. The supernatant liquid fraction was then carefully transferred after being filtered at 0.45 µm (Millipore acetate filters) into acid-cleaned bottles.

Portable preconcentration unit

A portable preconcentration/elution unit was used for all experiments and routine determinations (Figure 2). The unit consisted of a clear Perspex support to which the filter holders and resin cartridges were attached. A sixteen channel peristaltic pump (Ismatec, IPC) was operated using either battery or mains power. Two preconcentration units were constructed, one with six sample lines and the other with eight sample lines, that were run in parallel. PTFE Teflon tubing (0.8 mm i.d.) was used for all sample transfer lines. Connections were made using 1/4-28 fittings and Luer lock fittings for resin cartridges and filter holder connections. When *in situ* operations were carried out (e.g., monitoring) the unit was housed in a simple lightweight foldable plastic tent to minimise atmospheric contamination by air-borne dust.

For the preconcentration step, collected sample bottles were removed from the plastic bags and a rigid PEEK plastic sampling probe introduced into the bored cap of each bottle. The samples were subsequently filtered on-line using acid cleaned 0.45 µm porosity filters. The seawater samples were then passed through the resin cartridges or, if pH alteration was required, mixed via an on-line manifold and a 1.5 m

Table 1. ICP-OES operating conditions

Spray chamber	Cyclonic
Nebuliser	Low-flow Gem-cone nebuliser
RF power	1300 W
Plasma gas flow	15 l min ⁻¹
Auxiliary gas	0.5 l min ⁻¹
Nebuliser gas	0.8 l min ⁻¹
Sample flow rate	1 ml min ⁻¹
Plasma view	Axial
Read time	5 s
Replicate readings	3

Teflon mixing coil. The sample effluent was recovered in one litre sampling bottles for volume measurement necessary to determine the preconcentration factor.

Instrumentation

Analysis was performed using an inductively coupled plasma-optical emission spectrometer (Optima 3200DV, Perkin-Elmer). Instrument conditions are detailed in Table 1. Two CRMs (TM-26.3 and TMDA-61, Environment Canada) were used to verify calibration accuracy during each analytical run.

Elution procedure and analysis

The elution of the metals from the resin was performed using a 2 mol l⁻¹ HNO₃ solution following the work of Nickson *et al.* (1999); concentrations above 2 mol l⁻¹ would rapidly degrade the column (Bloxham *et al.* 1994). Both on-line and off-line elution procedures

were evaluated. On-line elution was performed using a simple manifold, whereby the eluent could be alternated to pass directly into the ICP-OES sample introduction system or first through the resin. The on-line system was calibrated by injecting a known mass of each analyte and calculating the sum of the total intensities determined from 100 replicates using a 5 s read time sequence. Sample flow rate was set at 1 ml min⁻¹.

Off-line elution was performed using the same automated conditioning unit (described above) with a specific elution programme. Cartridges were eluted (2.5 ml min⁻¹) after a water rinse and drying step. Samples were eluted directly into clean pre-weighed test tubes. Due to minor differences in the pump tubing length, sample tubes were pre-weighed and after elution weighed again to calculate preconcentration factors accurately.

Although both methods produced satisfactory results, the on-line procedure was more time consuming due to the manual operation of the manifold. In addition, more data treatment was required than the off-line procedure. The off-line procedure was adopted for all subsequent tests.

Standard preconcentration conditions for optimisation experiments

Optimisation experiments using artificial seawater were conducted using a standard 100 ml preconcentration volume with the addition of metallic elements (Co, Cu, Fe, Mn, Ni) to obtain a final concentration of 50 µg l⁻¹. Experimental results conducted on natural seawater, unless otherwise stated, were determined after preconcentration of 900 ml of sample and the final concentrations determined after correction of the resin retention efficiency determined during the pH optimisation tests. Unless otherwise stated, triplicate samples were performed for each experimental point. Preconcentration flow rates were initially set at 5 ml min⁻¹.

Results and discussion

pH optimisation

Preconcentration pH is one of the most decisive factors affecting accurate determination of dissolved metals at trace levels, as it determines both the quantity of both those elements of interest and matrix elements retained on the resin. The effect of pH retention

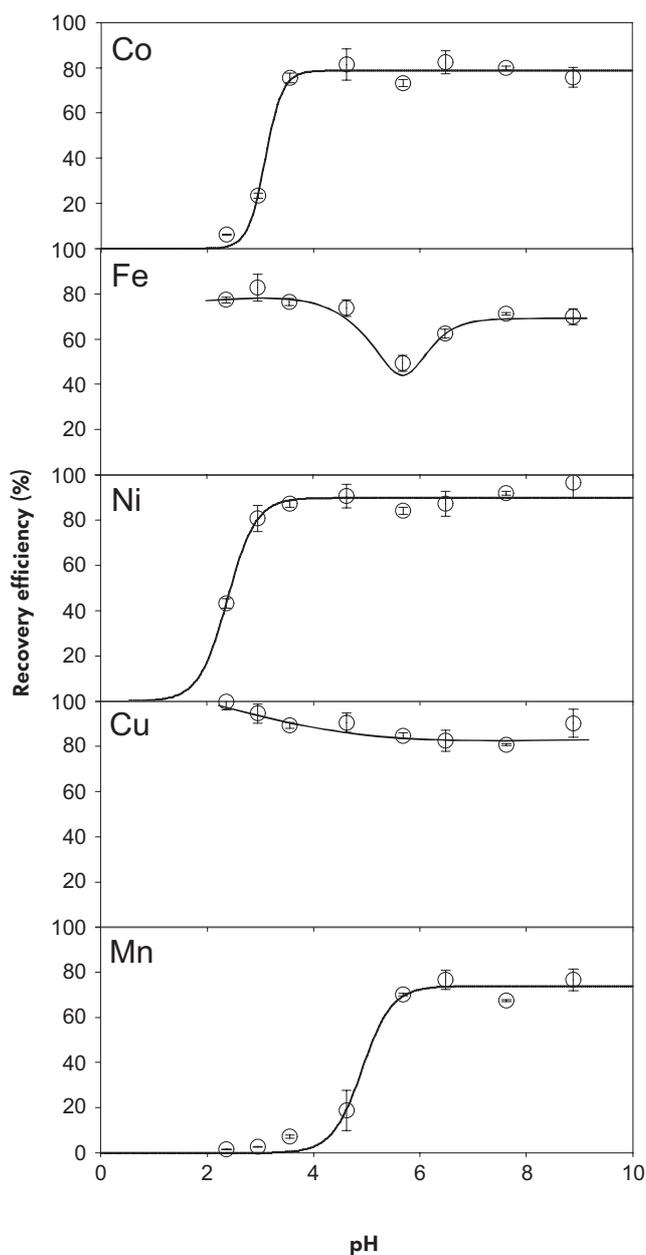


Figure 3. Plots showing the effect of pH on Co, Cu, Fe, Mn and Ni recovery.

efficiencies of the OnGuard II M resin was tested using a pH range from 2 to 9 (Figure 3) on spiked artificial and natural seawater samples.

Copper showed high recoveries (> 80%) over the entire pH range tested, whereas Co and Ni showed satisfactory recoveries (> 80%), but from pH 3 up until pH 9. In the case of Mn, the recovery dropped sharply below pH 6, which agrees with work by Beck *et al.* (2002), Willie *et al.* (2002) and Warnken *et al.* (2000) who found Mn recoveries were best observed at pH 9.

The majority of studies determining dissolved metal in seawater use quadrupole ICP-MS as the instrument of detection. For this reason, the dissolved metals are typically concentrated onto iminodiacetate resins at pH 5-5.5 (Bloxham *et al.* 1994, Nickson *et al.* 1999, Willie *et al.* 2001) to avoid excessive retention of alkaline earth metals present in the seawater matrix, given that the resolving power of quadrupole ICP-MS is often not sufficient to separate molecular or isobaric interferences (principally from Ca, Mg, K, Na) from the isotope of interest. However, pH adjustments below 6 eliminate the possibility of accurate quantification of Mn. Alteration of the preconcentration pH is not absolutely necessary if ICP-OES is used as the instrument of detection. In addition, in order to recover Mn simultaneously with the other trace metals (Co, Cu, Fe and Ni), the preconcentration has to be carried out between pH 6 and 9 (Figure 3); this range of pH corresponds to natural values measured in the environment (around pH 8.2 for seawater and typically between 5 and 8 for most rivers; Chester 1993). In New Caledonian rivers, pH values of around 8 are often observed due to the weathering of ultramafic rocks such as peridotites (Trescases 1973). Moreover, the elimination of a chemical reactant (buffer) reduces significantly the possibility of contaminating the sample with impurities.

Effect of column size/matrix reduction

While ICP-OES is not affected in the same ways as ICP-MS (polyatomic interferences), the presence of the matrix may still cause some undesirable effects, including ionisation suppression and physical deposition on torch ware, affecting both the stability and sensitivity

Table 2.
Comparison of metal concentrations ($\mu\text{g l}^{-1}$) determined using 1 cm^3 and 2.5 cm^3 OnGuard II M cartridges

Element	1 cm^3 (n = 6)	2.5 cm^3 (n = 6)
Co	0.032 \pm 0.002	0.038 \pm 0.003
Cu	0.84 \pm 0.05	0.96 \pm 0.03
Fe	0.43 \pm 0.01	0.43 \pm 0.01
Mn	0.67 \pm 0.03	0.66 \pm 0.02
Ni	1.00 \pm 0.03	0.98 \pm 0.04

of the instrument (Bloxham *et al.* 1994, Wen *et al.* 1999). Ensuring the plasma is robust will help to reduce some physical effects; however it is always preferable to remove the maximum amount of alkaline earth metals from the eluate to maintain instrument stability.

Reducing the amount of matrix elements present in the eluate could be achieved by selecting an appropriate volume of resin, given that the exchange capacity is inherently linked to the amount of active sites capable of retaining matrix elements. However, the reduction in active sites to avoid excess matrix retention should not negatively affect the resin's principal function of retaining the element of interest. OnGuard II M chelating resins are available in two column sizes (1 cm^3 and 2.5 cm^3), therefore, a test was carried out to determine whether any difference in the efficiency could be observed.

An identical seawater sample was passed through each size of resin column. The results showed that determined concentrations for the five listed metals were no different for both column sizes, particularly for Fe, Mn and Ni (Table 2). For Co and Cu, their concen-

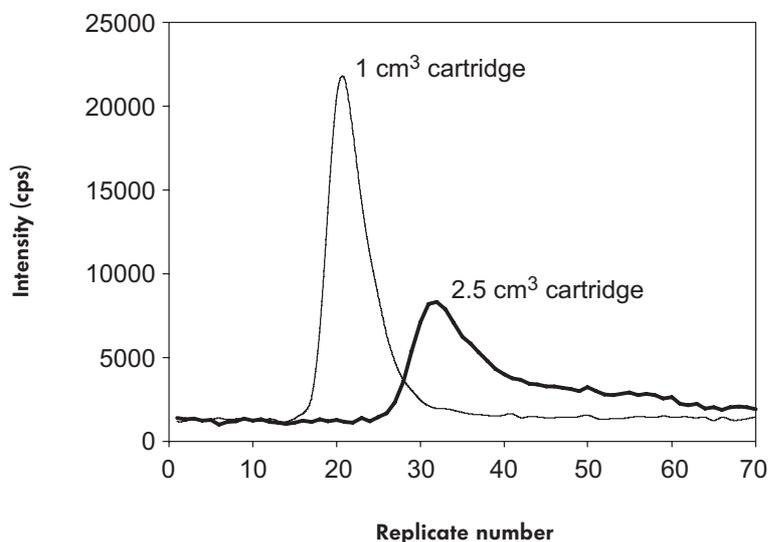


Figure 4. Example of on-line elution plots of Ni determined from 1 cm^3 and 2.5 cm^3 cartridges.

trations were slightly reduced (respectively 15% and 12%) using the smaller 1 cm³ column. However, the concentration of alkali earth metals, in particular Ca, K and Na, was approximately 2.5 times lower in the smaller column. Therefore any EIE (easily ionisable elements) effects during analysis were likely to be significantly reduced.

Another aspect of the effect of the resin column size was demonstrated by performing on-line elutions of the two column sizes. The generated times series elution peaks showed that wash out of the metals was considerably longer using the larger resin column (2.5 cm³). The Ni elution peak generated using different cartridge sizes is presented in Figure 4. Indeed, the use of larger columns for off-line preconcentration would also require greater volumes of elutant and therefore reduce preconcentration factors.

Elution volume

Lowering the volume of elutant increases the overall preconcentration factor, which is particularly important when analysing samples with less sensitive instruments (ICP-OES) than mass spectrometry. For this reason the volume of elutant required for the most complete recovery as possible of the retained elements was tested using between 1 and 5 ml of 2 mol l⁻¹ nitric acid solution (Bloxham *et al.* 1994, Nickson *et al.* 1999).

The results of the tests performed on filtered natural seawater showed stable recoveries were obtained for all of the five metals using an elution volume of 3 ml and above (Figure 5). However, the elution volume was set at 3.5 ml to allow sufficient volume for analysis with ICP-OES.

Preconcentration speed (flow rate)

One of the objectives of this study was to develop a method capable of treating a large number of samples necessary for an adequate monitoring system of the New Caledonian lagoon. Therefore, flow rate constitutes an important parameter in determining sample throughput.

In order to assess the effect of the flow rate on the recovery of metals from the resin, five tests were carried out using filtered natural seawater. Five flow rates of 5, 10, 15, 20 and 25 ml min⁻¹ were studied (Figure 6).

The tests demonstrated that Fe, Mn and Ni were quantitatively absorbed onto the resin over the range

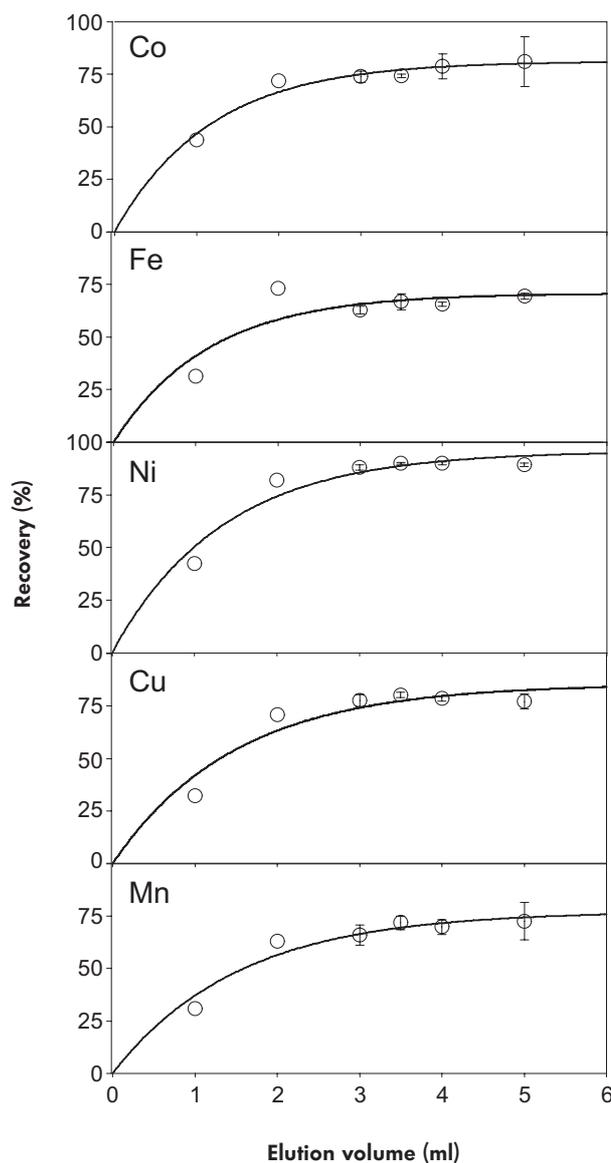


Figure 5. Plots showing the effect of elution volume on Co, Cu, Fe, Mn and Ni recovery.

studied. On the other hand, slight reductions of about 10% and 15%, respectively, in the recovery of Co and Cu were observed above a flow rate of 10 ml min⁻¹.

Where possible, a flow rate of 5 ml min⁻¹ should be used. However, a flow rate of 15 ml min⁻¹ was selected as the best compromise between a long preconcentration time and potential cavitation effects observed at higher flow rates. Due to the small bore size of the tubing, cavitations caused some bubbles to partially block the filter. Although no detrimental effect was observed, this may have an impact on preconcentration volumes for samples particularly rich in particulate material, because clogging of the filter would be accelerated.

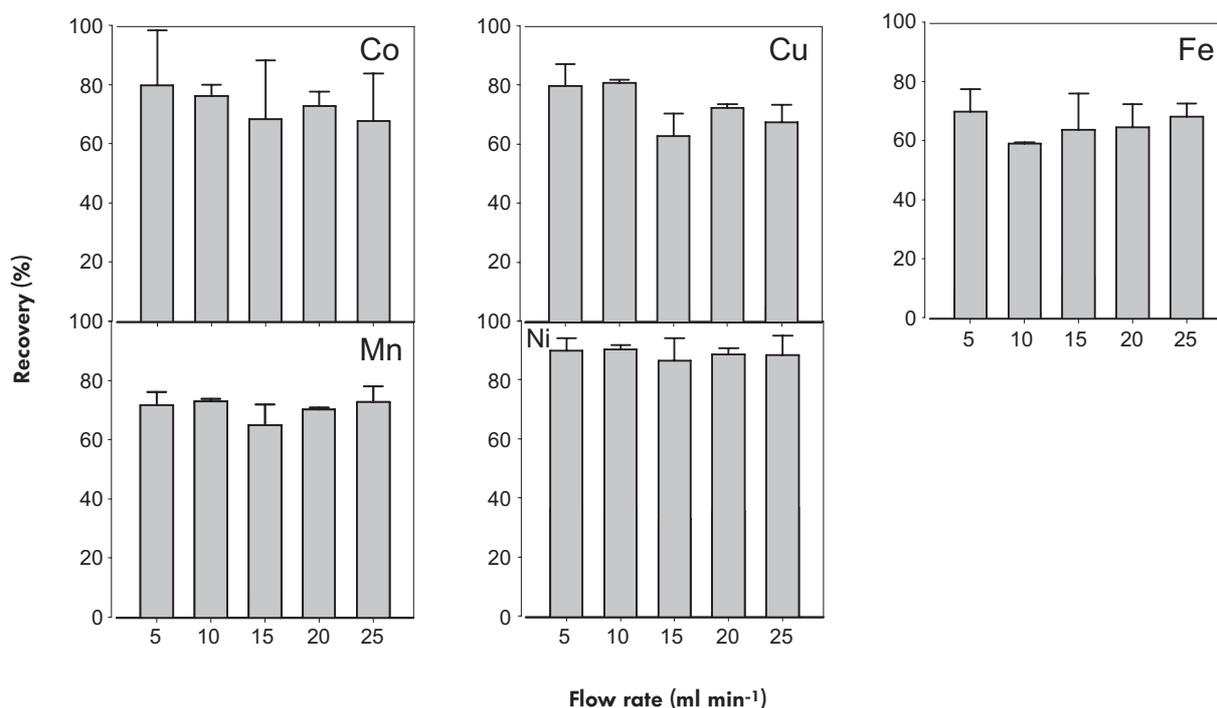


Figure 6. Recovery of dissolved metals as a function of preconcentration flow rate (ml min⁻¹) for Co, Cu, Fe Mn and Ni.

Sample volume versus recovery

The influence of sample volume on the recovery was studied by passing seven different volumes (between 250 and 1800 ml) of filtered natural seawater through the cartridges. Due to the lower sensitivity of ICP-OES compared to mass spectrometers, the ability of the resins to quantitatively recover dissolved metals using large volumes of seawater is crucial to obtain sufficiently high preconcentration factors without exceeding the capacity of the resin.

The metallic elements studied showed a linear response up 1800 ml (Figure 7). The linear response is likely, however, to extend beyond this value; this would incur preconcentration times of over two hours. Cobalt, due to lower concentrations observed in the sample, was not quantifiable below 700 ml and Fe not detected below 120 ml. Although tests demonstrated that it is possible to pre-concentrate up to 1800 ml, in reality the volume will depend on the expected concentration, as smaller preconcentration volumes allow increased sample throughput. Using an elution volume of 3.5 ml, concentration factors ranged between 70 and 500 times for pre-concentrated volumes of 250 to 1800 ml, respectively.

Detection limits and blank values

The quantification limits for this technique varied as a function of preconcentration volume and elution volume and are therefore based primarily on the instrument's detection limits. Quantification limits were determined after adjustment of the retention efficiency and divided by the preconcentration factor (Table 3). The blank values observed during the procedure were in all cases below the detection limits of the instrument. The preconcentration technique presented here would allow determination of dissolved metals in coastal regions and in the majority of cases in the open ocean, providing high preconcentration factors are applied. Only in areas where very low concentrations of dissolved metals are found would the concentrations be below the limit of detection. The concentrations of Fe and Co, in particular, in the Pacific Ocean have been reported as low as 1 ng l⁻¹ and 0.2 ng l⁻¹, respectively (Stumm and Morgan 1996).

Certified reference materials

Accuracy and validation of the proposed method were examined and carried out by determining trace metals in two certified reference materials, CASS-4 a near shore seawater sample and NASS-5 an open

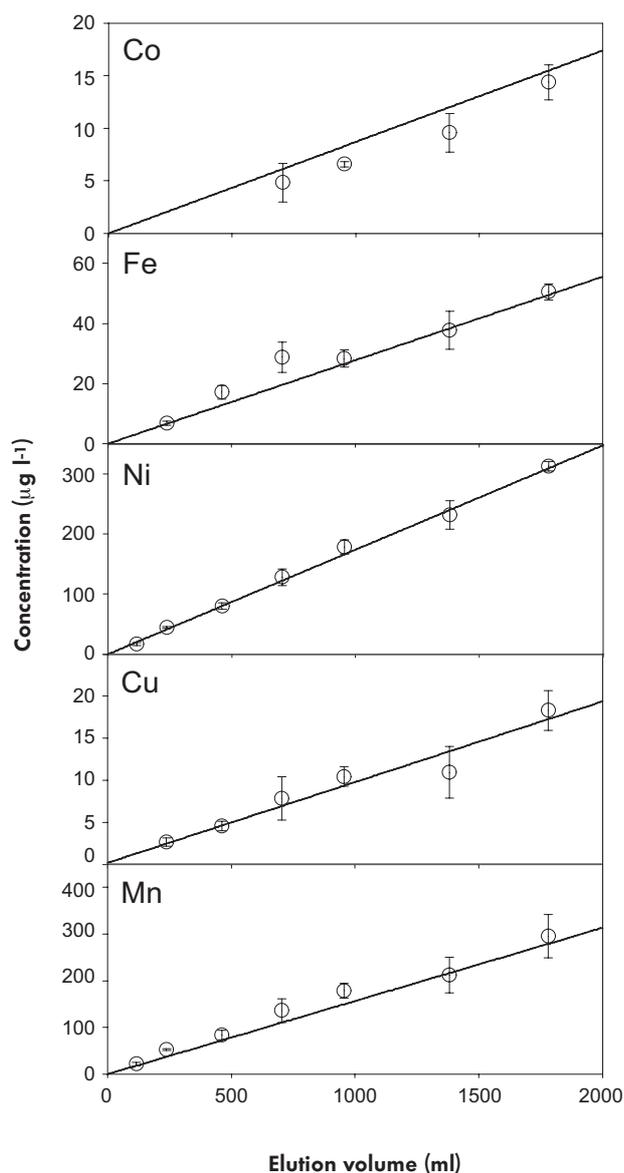


Figure 7. Concentration versus volume pre-concentrated plots for Co, Cu, Fe, Mn and Ni (n = 3). Concentration was determined before the application of pre-concentration factors.

Table 3. Quantification limits (LOQ) determined for a 900 ml and 1800 ml seawater sample after pre-concentration and analysis using axial viewing

Element	QL 900 ml sample (µg l ⁻¹)	QL 1800 ml sample (µg l ⁻¹)
Co	0.012	0.006
Cu	0.015	0.008
Fe	0.011	0.006
Mn	0.011	0.005
Ni	0.012	0.006

ocean seawater sample (National Research Council, Canada). The pre-concentration of the certified samples on the IDA resin cartridges required the adjustment of pH to 8 using aqueous ammonia. Pre-concentration flow rate was 5 ml min⁻¹. In general the results (Table 4) were in good agreement with certified values except for Fe determined in the CASS-4 samples. Iron concentrations were systematically slightly lower than the certified values (approximately 0.02 µg l⁻¹). The deficit in Fe was probably due to a change in speciation of the Fe(II) as a result of the increase in pH to 8.

Application area: New Caledonia

New Caledonia's rich metallic ore body has meant that since the 1870s the exploitation of saprolitic layers has been extensive. Initially small operations, exploitation expanded to industrial levels from the 1950s (Bird *et al.* 1984).

This growing industrialisation by opencast mining techniques has led to the widespread release of contaminants into the surrounding marine environment. Metal enrichment of the coastal sediments of the

Table 4. Analysis of CASS-4 and NASS-5 certified reference seawater

Element	CASS-4 (µg l ⁻¹) n = 5		NASS-4 (µg l ⁻¹) n = 3	
	Determined	Certified	Determined	Certified
Co	0.023 ± 0.007	0.026 ± 0.003	< QL	0.023 ± 0.003
Cu	0.558 ± 0.034	0.592 ± 0.055	0.272 ± 0.019	0.297 ± 0.046
Fe	0.635 ± 0.05	0.713 ± 0.058	0.188 ± 0.010	0.207 ± 0.035
Mn	2.790 ± 0.06	2.78 ± 0.19	0.873 ± 0.062	0.919 ± 0.057
Ni	0.295 ± 0.025	0.314 ± 0.030	0.229 ± 0.012	0.253 ± 0.028

< QL Less than quantification limit.

Table 5.
Dissolved metal concentrations (Co, Cu, Fe, Mn and Ni) in $\mu\text{g l}^{-1}$ for the different selected sites in the SW and S lagoons of New Caledonia

Sampling location	Co	Cu	Fe	Mn	Ni
1 Grande Rade (end of bay) ($n = 7$)	0.09–0.13	0.08–0.17	0.12–0.20	1.44–2.01	3.29–4.35
2 Grand rade transect ($n = 4$)	0.028–0.109	0.02–0.13	0.13–0.16	0.38–1.74	0.57–3.98
3 Anse Vata ($r = 21$)	0.035 ± 0.007	0.06 ± 0.01	0.22 ± 0.06	1.32 ± 0.12	1.00 ± 0.04
4 Port Moselle ($r = 9$)	0.20 ± 0.02	1.63 ± 0.04	0.57 ± 0.05	2.53 ± 0.03	2.08 ± 0.01
5 Baie de St Vincent ($n = 10$)	0.04–0.09	0.02–0.25	0.71–2.65	0.94–2.48	1.95–7.10
6 Dumbea Bay ($n = 10$)	0.01–0.04	0.03–0.19	0.23–1.41	0.32–2.32	0.13–4.52
7 Boulari Bay ($n = 10$)	0.03–0.07	0.03–0.30	0.24–1.38	0.29–0.83	0.95–3.92
8 Canal de la Havannah ($n = 6$)	0.025–0.033	0.05–0.15	0.08–0.18	0.13–0.24	0.18–0.26
9 Reserve Merlet ($n = 2$)	< QL–0.009	0.07–0.07	0.09–0.10	0.09–0.11	0.09–0.10
10 Bay de Prony ($n = 4$)	0.058–0.082	0.08–0.09	0.05–0.10	0.25–0.43	0.44–0.54
11 Baie de Prony interstitial water ($n = 10$)	5.64–59.28	0.25–1.24	5.2–25.4	443–1964	6.6–37.4
12 La Coulée River ($n = 3$)	0.069–0.072	< QL	0.07–0.15	2.10–2.50	8.93–10.65
13 Dumbea River ($n = 3$)	0.011–0.018	< QL	0.14–0.17	0.66–0.86	5.63–7.05
14 La Tontouta River ($n = 3$)	0.012–0.023	< QL	0.05–0.06	1.17–1.68	1.92–2.12
15 Middle lagoon ($n = 3$)	< QL	< QL	0.17 ± 0.04	0.13 ± 0.02	0.15 ± 0.02
16 Outside Barrier reef ($n = 3$)	< QL	< QL	0.03 ± 0.02	0.05 ± 0.02	0.09 ± 0.02

n = number of sampling stations, n = number of replicate samples collected from the same location on different days and r = number of replicates, < QL = less than quantification limit.

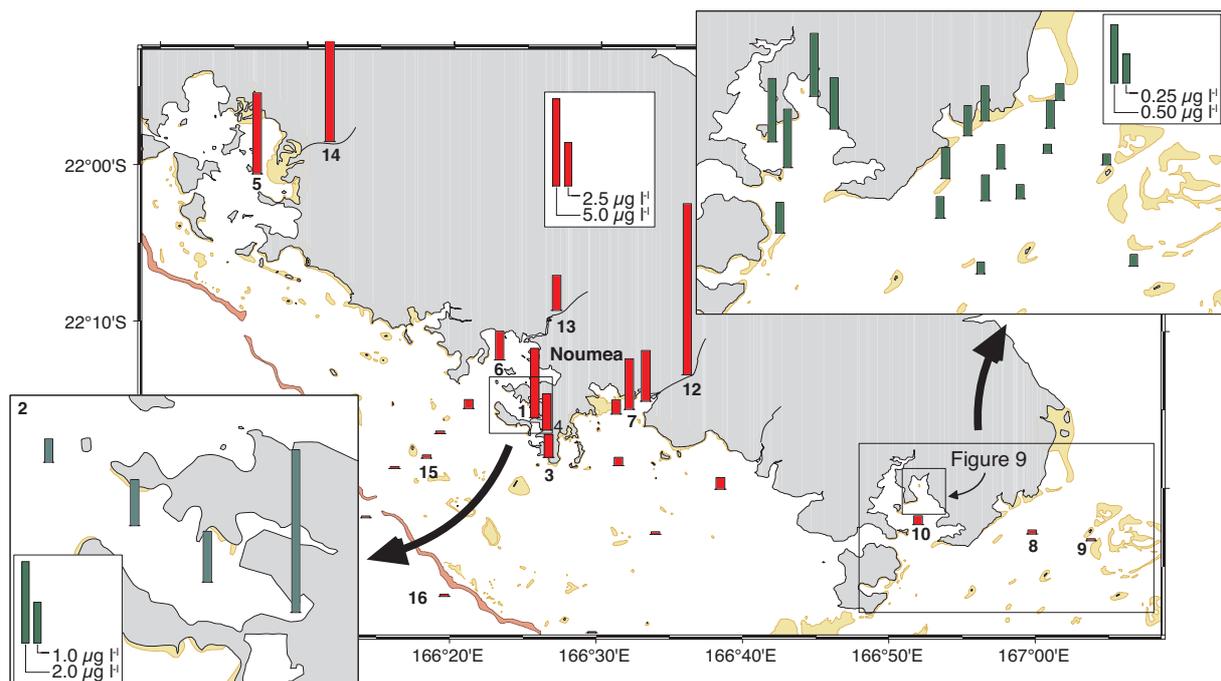


Figure 8. Dissolved Ni concentrations determined in the south-west lagoon of New Caledonia. Numbers correspond to sampling locations listed in Table 5.

lagoon has been documented by Ambastian *et al.* (1997) and Fernandez *et al.* (2002, 2006).

Table 5 and Figure 8 present dissolved metal concentrations collected from selected locations to illustrate the variety of existing environmental condi-

tions present in a highly sensitive tropical marine environment such as New Caledonia's lagoon:

- Port Moselle, the main commercial port of Noumea: High concentrations of Cu were observed ($1.6 \mu\text{g l}^{-1}$) likely due to the use of copper-based anti-

fouling paints. With the exception of around Noumea, elsewhere Cu concentrations were extremely low ($< 0.1 \mu\text{g l}^{-1}$). The explanation has to be found in the fact that Cu, present in natural rock composition, is restricted to sites in the northern part of New Caledonia.

The high Mn concentrations ($2.5 \mu\text{g l}^{-1}$) present around Noumea, and particularly in Port Moselle, were as a result of solubilisation of manganese oxide in the reducing parts of the sediment.

- Grande Rade, a juxtaposed bay to the SLN nickel refinery: This area showed amongst the highest Ni concentrations measured in New Caledonia. The existence of a strong concentration gradient from the end ($3.98 \pm 0.43 \mu\text{g l}^{-1}$) to the mouth of the bay ($0.57 \pm 0.13 \mu\text{g l}^{-1}$) was easily identifiable and can be linked to the industrial activities present at the end of the bay. The other metals equally followed a similar gradient to Ni.

- Three bays corresponding to three different catchment basins were sampled: (i) Boulari Bay ($1.7 \pm 0.80 \mu\text{g l}^{-1}$ Ni), an area exposed to runoff from an abandoned mining catchment area, (ii) Dumbea Bay ($2.9 \pm 1.2 \mu\text{g l}^{-1}$ Ni), which is exposed to a natural runoff from an undisturbed catchment basin; (iii) Saint Vincent Bay ($4.7 \pm 1.5 \mu\text{g l}^{-1}$ Ni), a bay still subject to active mining with the current exploitation of La Tontouta nickel mine.

- Prony Bay, a bay subjected to terrestrial inputs from numerous rivers: In the southern part of New Caledonia the influence of lateritic soils is evident in the bay where Ni concentrations ranged from 0.44 - $0.55 \mu\text{g l}^{-1}$.

- Havannah Channel, area dominated by oceanic waters: Relatively pristine coastal waters were observed in the south west and south lagoons of New Caledonia due to an oceanic influence. The concentrations in Ni were in the order of 0.18 - $0.26 \mu\text{g l}^{-1}$ along the Southern coast.

- The Reserve Merlet (Canal de la Havannah) was almost entirely dominated by oceanic waters scarce in dissolved metals. The lowest concentrations of dissolved Ni (0.09 - $0.10 \mu\text{g l}^{-1}$) were recorded within the reserve.

In addition to the seawater measurements, this technique was applied to determine the metal concen-

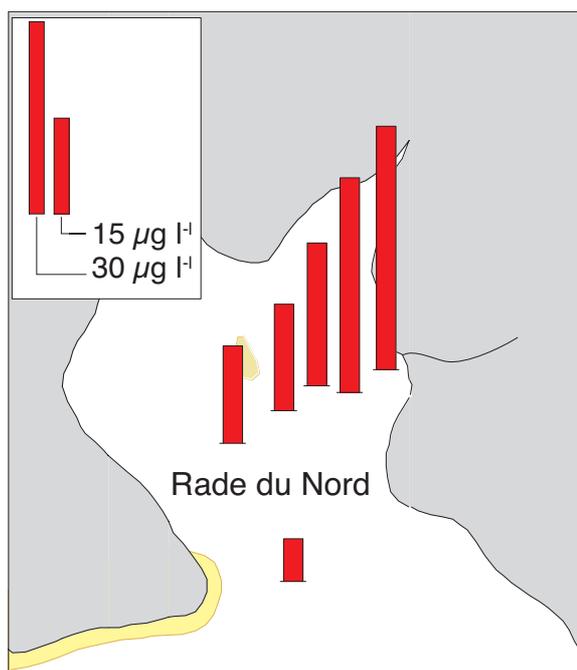


Figure 9. Dissolved Ni concentrations determined in interstitial waters from sediment of the Rade Nord of Prony Bay.

trations in interstitial sediment seawaters and in river waters.

The higher expected dissolved metal concentration in the sediment meant that only about 50 ml of interstitial water was pre-concentrated. The concentrations of dissolved Ni taken from a transect collected from close to the mouth of a creek going out to the centre of Prony Bay varied significantly from 37.4 - $6.6 \mu\text{g l}^{-1}$ (Table 5 and Figure 9).

Dissolved metal concentrations in river water samples were measured after pre-concentrating 900 ml of water. Under normal hydrological conditions the three rivers showed clear differences in dissolved metal concentrations. Dissolved Ni concentrations were $2.01 \pm 0.10 \mu\text{g l}^{-1}$, $6.3 \pm 0.72 \mu\text{g l}^{-1}$ and $9.80 \pm 0.86 \mu\text{g l}^{-1}$, for the Tontouta River, the Dumbea River and the Coulée river, respectively. (Table 5, Figures 8 and 9).

Conclusions

The preconcentration technique presented here has been successfully used to routinely determine hundreds of dissolved metal concentrations in seawater for a number of projects, including environmental baseline studies and impact assessments around New Caledonia.

This technology, based on the use of readily available IDA cartridges (OnGuard II M, Dionex) and analysis by the ubiquitous ICP-OES, offers the following advantages:

- The dissolved metals are retained on the resin at natural pH conditions of seawater. This ability to retain metals at higher pHs (> 6) allowed the simultaneous determination of Mn with the other metals, which would not otherwise be possible with traditional buffering at pH < 6. In addition, the elimination of a buffer reduces considerably the risk of sample contamination.
- The use of high capacity resins with high kinetic exchange rates allowed greater preconcentration flow rates to be used (> 15 ml min⁻¹) making it possible to obtain preconcentration factors of over 250 in under one hour.
- The cartridge's form and Luer fittings allowed for both easy manipulation and airtight connection both during preconcentration and storage.
- The cartridges can be reused a number of times which significantly reduced the analytical (operating) cost.
- The development of the preconcentration unit allowing the simultaneous treatment of up to fourteen samples considerably increased sample throughput.
- Standardising the conditioning and elution steps through the use of an automated unit minimised any potential contamination.

The complete system has a pack size of approximately 0.1 m³ making it easily transportable and that allowed immediate treatment of the sample after collection. Moreover, this technique has been applied to a range of waters making comparison of the results easier.

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