BACKGROUND LEVELS OF Cr, Cu AND Ni IN ST. LAWRENCE RIVER SEDIMENTS: IMPLICATIONS FOR SEDIMENT QUALITY CRITERIA AND ENVIRONMENTAL MANAGEMENT

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ABSTRACT
Pre-industrial sediments dredged from the St. Lawrence Seaway are often considered potentially toxic with respect to the interim sediment quality criteria, and their management is a concern. The St. Lawrence Centre undertook a research project to document the background levels of trace metals in these sediments. Three extractions were performed to evaluate the distribution and potential bioavailability of contaminants: a total extraction with HF, a total recoverable extraction with concentrated nitric and HCl acids, and a 1N HCl digestion. Results show that although the background levels established for the interim criteria are representative of contaminant concentrations in pre-industrial sediments, this is not the case for the post-glacial marine clays underlying these sediments. Chromium (Cr), nickel (Ni) and copper (Cu) concentrations in marine clays exceed the Minimal Effect Threshold, whereas Cr and Ni also frequently exceed the Toxic Effect Threshold. These trace metals, however, are mostly associated with inert silicates in marine clays and are therefore not bioavailable.

RÉSUMÉ
Les sédiments préindustriels dragués dans le fleuve Saint-Laurent sont souvent considérés potentiellement toxiques selon les critères intérimaires pour l'évaluation de la qualité des sédiments et représentent une défi pour la gestion environnementale. Un projet de recherche fut initié au Centre Saint-Laurent, afin de documenter les concentrations naturelles de métaux traces dans ces sédiments. La distribution et la biodisponibilité potentielle des contaminants ont été évaluées selon trois digestions: une extraction totale, avec acide fluorhydrique, une attaque par acides nitrique et chlorhydrique concentrées et une digestion à l'acide chlorhydrique 1N. Les résultats révèlent que bien que les teneurs naturelles ayant servi à l'élaboration du seuil de base des critères intérimaires sont représentatives de concentrations dans les sédiments préindustriels, il en est autrement pour les argiles marines postglaciaires présentes sous ces sédiments. Les concentrations de Cr, Ni et de Cu dans ces sédiments excèdent, dans une forte proportion, le Seuil d'effet mineur des critères intérimaires, alors que les teneurs de Cr et de Ni dépassent fréquemment le Seuil d'effet néfaste. Cependant, ces métaux traces sont principalement associés à des silicates inertes dans les argiles marines et donc peu biodisponibles.

1. INTRODUCTION

Interim criteria for assessing the quality of St. Lawrence River sediments were established in 1992 (St. Lawrence Centre and MENV, 1992). These criteria consist of three levels of evaluation defined for targeted metals (arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc). The first level of assessment was named the No Effect Threshold (NET) and referred to background or natural concentrations of contaminants based on the available literature (Loring, 1978; Loring et al., 1978; Serodes, 1978; Barbeau et al., 1981; Gobeil et al., 1987; Pelletier et al., 1988, 1989; Procéan, 1991; St. Lawrence Centre, 1992). These characterizations involved very diverse sampling and analytical methods and, with the exception of the report by Sérodes (1978), all referred to the marine portion of the St. Lawrence. The following levels were determined using the screening level concentration approach and referred to the Minimal Effect Threshold (MET) and the Toxic Effect Threshold (TET), for which the contaminants were tolerated by a proportion of 85% and 10% of benthic fauna, respectively (St. Lawrence Centre and MENV, 1992). This approach was also applied by the Ontario Ministry of the Environment (Persaud et al., 1992) for the Great Lakes.

Local and regional background concentrations of several contaminants in the St. Lawrence river, however, had yet to be assessed and were therefore problematic for the application of the criteria. As a result, pre-industrial sediments dredged in the Seaway were often considered potentially toxic relative to the interim sediment quality criteria and subject to unnecessary and costly containment (St. Lawrence Centre and MENV, 1992).

To address this issue, a research project was carried out to better document the local and regional background noise of trace metals and their chemical associations in St. Lawrence River sediments.

2. METHODS

Sediment core samples were taken by means of a percussion hammer corer for chemical and physical parameters analysis. Sediment sampling was performed as prescribed in the Methods Manual for the characterization of sediments (Environment Canada and MENV, 1992). Over a three-year period, a total of about 50 sediment cores and almost 200 samples were taken from the freshwater stretch of the St. Lawrence River (Figure 1).

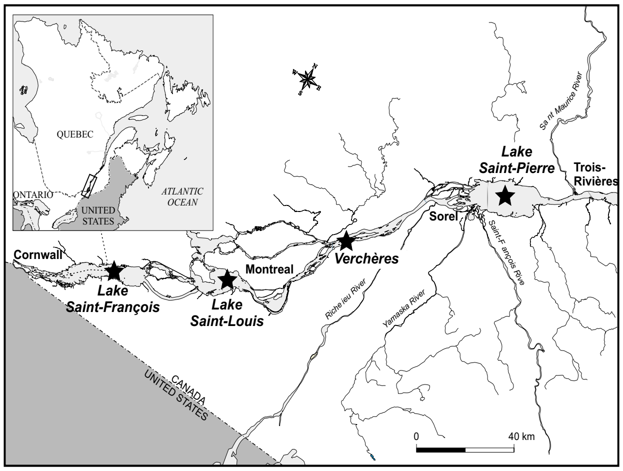


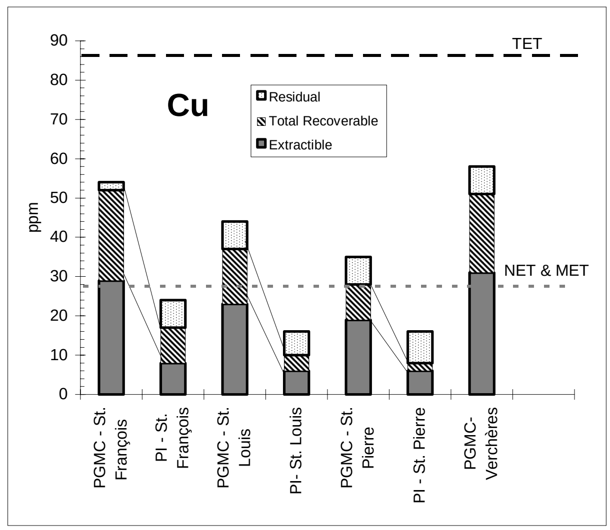
Figure 1. Location map of sampling area.

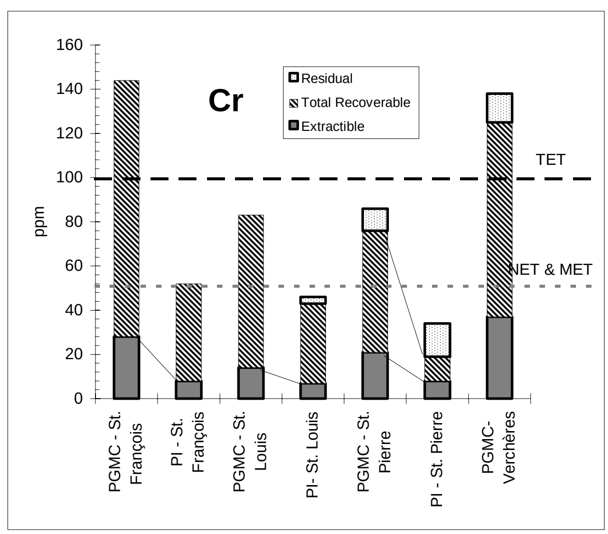
From each sediment core, only sediments deposited prior to the industrial period were sampled. Pre-industrial sediment horizons were determined using data available in the literature (Procean, 1992; Carignan and Lorain, 2000) and from geochronological dating in areas where information was sparse and incomplete. Most of these sediments overlie thick deposits of silty blue-grey clays from the Champlain Sea, which covered the entire St. Lawrence Valley during the last deglaciation period some 12 000 years ago (Cremer, 1979).

Trace-metal concentrations were analysed using three different leaching procedures designed to define trace-metal distribution within the sedimentary material and potential bioavailability. A first digestion, referred to as the total extraction, was performed with a mixture of perchloric, nitric, hydrochloric and hydrofluoric acids, which dissolved all the phases present in the sediments (Rantala and Loring, 1975; Gobeil, 1987). A second chemical attack, known as total recoverable extraction, involved *aqua regia*, with the addition of perchloric acid, thereby solubilizing all the nondetritic phases in the sediments (Lord, 1982; Sturgeon et al., 1982; Canfield, 1989; Krantzberg, 1994). Lastly, a weaker 1N HCl extraction was performed in order to solubilize the trace metals associated with the most reactive phases of the sediments, such as labile organic matter, Fe and Mn oxyhydroxides, carbonates, and hydrous alumino-silicates (Huerta-Diaz and Morse, 1990, 1992; Kostka and Luther, 1994; Bono, 1997). Sample preparation and characterization are described in the complete paper on this study (Saulnier and Gagnon, submitted).

3. RESULTS AND DISCUSSION

The median chromium (Cr), copper (Cu) and nickel (Ni) concentrations obtained with the leaching procedures are consistently more elevated in post-glacial marine clays (PGMC) than in the overlying St. Lawrence River pre-industrial sediments (PI) (Figure 2). The total and total recoverable Cr, Cu and Ni concentrations detected in nearly all the sediment samples taken in each sampling area exceed the NET and MET. Furthermore, total and total recoverable Cr and Ni concentrations were frequently above the TET, in proportions as high as 95% and 78%, respectively, in the Vercheres area and in Lake Saint-François. These trace-metal levels in pre-industrial sediments in the St. Lawrence River respect the background levels established for the interim criteria (Figure 2).





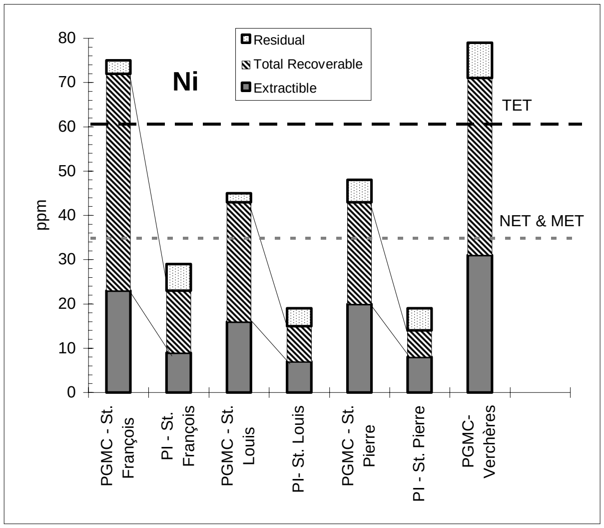


Figure 2. Median Cu, Cr and Ni concentrations and distribution for each leaching procedure.

The proportion of Cr, Ni and Cu in total recoverable phases, as well as extractable phases for Cu, are greater in post-glacial marine clays (PGMC) than in pre-industrial sediments (PI), to the detriment of the HF-solubilized portion (Figure 2). The same observation can be made for a number of other elements, including Al. These observations most likely reflect the increased abundance of clay minerals, mostly chlorite as well as carbonates and sulfide minerals, in the post-glacial marine clays (Table 1).

Table 1. Composition of post-glacial marine clays and St. Lawrence River sediments (X-ray diffraction analysis).

Mineral phases (% weight)	Post-glacial marine clay[1]	St. Lawrence River sediments[2]
Quartz	13.5	50–70
Feldspar	24	20–30
Mica	17	< 1
Clay minerals	24	trace
Amphiboles	6.5	2–3
Pyroxene	< 1	< 1
Carbonates	7	-
Oxides	1.5	1–3
Sulfides	2.25	trace
Accessory minerals	trace	trace
Organic matter	0.1–2.0	0.01–2.6[3]

[1](Lepage and Richard, unpublished)
[2](Loring, 1976)
[3] Saulnier and Gagnon (submitted)

Clay minerals, and sulfide and oxide minerals may be considerably enriched with trace metals such as Cr, Ni and Cu (Loring, 1976). Both chlorite (Snäll and Liljefors, 2000) and Fe sulfides such as pyrite (Huerta-Diaz and Morse, 1990), are entirely soluble in *aqua regia*, whereas carbonates and probably acid-volatile sulfides (FeS) are soluble in 1N HCl (Raiswell et al., 1994; Brumbaugh and Arms, 1996; Mikac et al., 2000). This hypothesis is further discussed in the paper presenting all the results generated by this research project (Saulnier and Gagnon, submitted).

The results of this study were used to normalize background levels of metals with conservative elements such as Al (Figure 3). Normalization with natural sediments is frequently used to evaluate anthropogenic inputs in recent sediments, while compensating for their mineralogical and textural variability (Loring, 1990 ; Aloupi and Angelidis, 2001). The relationship observed between total recoverable Al and trace metals further supports the hypothesis that trace metals would mostly be associated with reactive alluminosilicate mineral phases in both types of sediment, and could thereby be considered inert or non-reactive relative to early diagenetic processes (Saulnier and Gagnon, submitted).

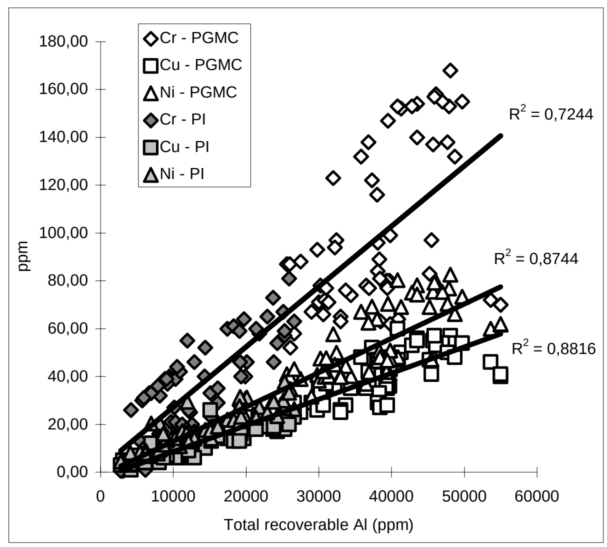


Figure 3. Total recoverable Cr, Cu and Ni normalization with total recoverable Al (from Saulnier and Gagnon, submitted).

Statistical comparison coupled with a discriminating analysis revealed that aluminum (Al), with a success rate of 98%, is an excellent tool for differentiating post-glacial marine clays from St. Lawrence River pre-industrial sediments. Accordingly, sediment samples presenting total recoverable Al concentrations above 26 800 µg/g would be post-glacial marine clays, whereas total recoverable Al concentrations in St. Lawrence River pre-industrial sediments should be below this value.

4. CONCLUSION

Due to their elevated Cr and Ni concentrations, post-glacial marine clays are problematic in terms of applying sediment quality assessment criteria. The results of this study, however, demonstrate that these metals are unlikely to be bioavailable to aquatic organisms. Accordingly, the use of tools to identify post-glacial marine clay may become necessary, if a particular management disposition should be established for this sedimentary material, upon confirmation of its nontoxicity by ecotoxicological assay. Total recoverable Al would be a useful tool if used in conjunction with other physical and visual characteristics of these marine clays. The information gathered in this study will contribute to the more judicious use, and eventual improvement of, the interim sediment quality criteria.

5. ACKNOWLEDGMENTS

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