# Environment Canada Water Science and Technology Directorate

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# Direction générale des sciences et de la technologie, eau Environnement Canada



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# Water analysis: Particle characterization

Gary G. Leppard

# Abstract

Ultra-small particles in aquatic ecosystems are responsible for much of the transport and transformations of contaminants. These colloidal particles (0.001 to 1.0 um least diameter) are physically unstable, by virtue of their being ultra-small, thus causing electrical phenomena to dominate their aggregation/disaggregation behaviour. They tend to aggregate spontaneously when perturbed by physico-chemical changes in nature, thus altering their own settling properties and chemical activities. It is generally accepted that ultra-small particles must be characterized better than they have been, for an improved understanding of their important roles in aquatic ecosystems. The state-of-the-art technology for characterizing these particles has just been established, much of it by NWRI. This article reviews the new technology, and its "tunable" nature for use in a great variety of water types.

# Analyse de l'eau : caractérisation des particules

Gary G. Leppard

# Résumé

Dans les écosystèmes aquatiques, les particules ultra-fines sont largement responsables du transport et de la transformation des contaminants. Ces particules colloïdales (de 0,001 à 1,0  $\mu$ m de diamètre) sont physiquement instables, en raison de leur taille ultra-fine, et sont donc à l'origine des phénomènes électriques qui régissent leur agrégation et leur désagrégation. Dans la nature, elles ont tendance à s'agréger spontanément lorsqu'elles sont perturbées par des changements physicochimiques, ce qui modifie leurs propriétés sédimentaires et leurs activités chimiques. Si l'on veut mieux comprendre l'importance de leur rôle dans les écosystèmes aquatiques, il convient de mieux les caractériser. La technologie de pointe en matière de caractérisation des particules vient juste d'être établie, en grande partie par l'INRE. Cet article se penche sur la nouvelle technologie et sur le fait qu'elle s'adapte à une grande variété d'écosystèmes aquatiques.

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### NWRI RESEARCH SUMMARY

#### Plain language title

Chacterization of ultra-small particles in water

#### What is the problem and what do sicentists already know about it?

Nanoparticles and microparticles in aquatic ecosystems are responsible for much of the transport and transformation of both contaminants and substances of importance

to biogeochemical cycles. These colloidal particles (0.001 to 1.0 µm diameter) are physically unstable, by virtue of being ultra-small, and tend to aggregate spontaneously when perturbed in nature, thus altering their own settling properties and chemical activities. It is generally accepted that such particles must be characterized better than they have been, for a better understanding of their important roles. The state-of-the-art technology for characterizing these particles has just been established, much of it by NWRI, and is currently being "tuned" for use globally with a wide variety of aquatic ecosystems.

#### Why did NWRI do this study?

The author was invited by the Encyclopedia of Analytical Science to write this stateof-the-art review.

#### What were the results?

The Editors have already accepted the preliminary version of the review, without revision, thus short-circuiting the process which was established to yield a final version for submission to the Editors after management approval. The "results" indicate a high interest and demand for the information.

#### How will these results be used?

The results, in the form of a synthesis, will be used by anyone (government, university, private) who consults the "Encyclopedia" for this kind of information.

#### Who were our main partners in the study?

I have co-published the basis for this review with more than eighty different scientists over the past dozen years; these many scientists and their organizations and granting agencies are all partners.

## Sommaire des recherches de l'INRE

#### Titre en langage clair

Caractérisation de particules ultra-fines dans l'eau.

#### Quel est le problème et que savent les chercheurs à ce sujet?

Dans les écosystèmes aquatiques, les nanoparticules et les microparticules sont largement responsables du transport et de la transformation des contaminants et des principales substances dans les cycles biogéochimiques. Ces particules colloïdales (de 0,001 à 1,0 µm de diamètre) sont physiquement instables, en raison de leur taille ultra-fine; dans la nature, elles ont tendance à s'agréger spontanément lorsqu'elles sont perturbées, ce qui modifie leurs propriétés sédimentaires et leurs activités chimiques. Si l'on veut mieux comprendre l'importance du rôle de ces particules, il convient de mieux les caractériser. La technologie de pointe en matière de caractérisation des particules vient juste d'être établie, en grande partie par l'INRE, et s'adapte à une grande variété d'écosystèmes aquatiques dans le monde.

#### Pourquoi l'INRE a-t-il effectué cette étude?

L'Encyclopedia of Analytical Science a invité l'auteur à rédiger cet article sur la technologie de pointe.

#### Quels sont les résultats?

Les directeurs de publication ont déjà accepté la version préliminaire de l'article, sans révision, et court-circuité ainsi le processus établi pour produire une version finale à présenter aux directeurs de publication après l'approbation des gestionnaires. Il existe un grand intérêt et une forte demande de renseignements à l'égard des résultats.

#### Comment ces résultats seront-ils utilisés?

Les membres du gouvernement, les universitaires et les institutions privées pourront consulter la synthèse des résultats dans l'encyclopédie.

#### Quels étaient nos principaux partenaires dans cette étude?

En collaboration avec plus de quatre-vingts scientifiques, j'ai publié la base de cet article au cours des douze dernières années; ces nombreux scientifiques, les organisations pour lesquels ils travaillent et les organismes subventionnaires sont des partenaires du projet. Marine Geology, 37 (1980) 231—240 Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

# GEOCHEMISTRY OF A SUBARCTIC SALT MARSH ENVIRONMENT

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(Received May 25, 1979; revised and accepted December 12, 1979)

ABSTRACT

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ic: 975. Glooschenko, W.A. and Capobianco, J.A., 1980. Geochemistry of a subarctic salt marsh environment. Mar. Geol., 37: 231-240.

Sediment and soil samples were collected along three transects located in a subartic salt marsh at North Point on the southwest coast of James Bay, Ont, Canada. Samples were analysed for major elements (Ti, Mg, Ca, K, Na, Fe, Mn, Si, Al, P and S) and trace metals (Cu, Pb, Ni, Co, Cd, Cr, Hg and Zn). In addition, inorganic and organic carbon, clay mineralogy, and particle size were determined. Results were subjected to a geological factor-analysis program.

In general, the elemental composition of sediments reflected the contributions from major sources of bedrock in the area, Paleozoic carbonates, and Canadian Shield igneous and metamorphic rocks. Important factors controlling elemental composition appear to be: (1) the composition of parent material, (2) chemical/physical changes which occur during erosion and transportation, and (3) chemical/physical changes which occur in situ, either during sedimentation or diagenesis.

#### INTRODUCTION

In geochemical studies of marine environments, the nearshore or "nonpelagic" environment has been relatively neglected. Nearshore environments have mainly been subjected to sedimentological studies of a more textural, structural and mineralogical nature (Calvert, 1976). However, there is much current interest in nearshore sedimentary environments, especially in terms of the geochemistry of potentially toxic trace metals (Loring, 1975, 1976; Windom, 1976; Grieve and Fletcher, 1976; Jaffe and Walters, 1977). Little geochemical research has been done in the salt marsh environment.

Salt marshes are of particular geochemical interest as they are a transitional zone from marine or brackish water intertidal flats across a supratidal zone terminating in either fresh-water wetlands or terrestrial upland ecosystems. This salinity gradient is paralleled by a vegetation gradient (Glooschenko, 1978), thus offering the geochemist an opportunity to determine the influence of vegetation development upon sediment geochemistry. In the case

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of the present study carried out on the James Bay coast, which is experiencing uplift due to isostatic rebound (Webber et al., 1970; Hunter, 1970), the influence of time upon diagenesis can also possibly be studied.

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In order to study these potential interactions of vegetation growth and time upon sediment chemistry, this study of major and trace-element distributions was begun on a subarctic salt marsh located on James Bay.

#### ENVIRONMENTAL SETTING

The present study was carried out in a coastal salt marsh located at North Point, Ontario, Canada (51°29N, 80°27W), which is on the southwestern shore of James Bay, approximately 27 km NE of the town of Moosonee (Fig.1). The climate of the area is subarctic with a dominant upland vegetation of northern boreal forest and large inland areas of bog and fen peatlands.



Fig.1. Map of Hudson Bay Lowlands. Arrow north of Moosonee points to North Point salt marsh site.

The study site is in the Hudson Bay Lowlands, a vast peatland located on the area originally under the marine waters of the Tyrrell Sea, which existed in the Hudson Bay basin during and following deglaciation (Lee, 1968). After deglaciation, upwarping of the land took place leading to a recession of the sea to the present Hudson/James Bay system. The present coastline is characterized by intensive salt marsh development (Glooschenko and Martini, 1978).

The area is underlain by Paleozoic rocks of Ordovician, Silurian and Devonian age. Rock types present are mainly sandstones, shales, limestones, dolomites and evaporites. Outcrops are sparse. The lowlands are surrounded by the Precambrian Superior Province of the Canadian Shield, characterized by large areas of granites and gneisses, along with inliers of highly deformed metamorphosed rocks which are remnants of ancient sedimentary and volcanic sequences. Small intrusions of alkali and ultrabasic intrusive rocks may occur (Whitmore and Liberty, 1968).

In terms of marine geology, little research has been done in James Bay, with most work having been done in Hudson Bay (Pelletier, 1968; Pelletier et al., 1968). Research here has emphasized bathymetry and sediment description in terms of texture and color; geochemical parameters measured have been limited to organic and  $CaCO_3$  content. James Bay was not included in the survey.

The North Point shoreline is flat with slopes of approximately 0.6 m/km. Extensive silty tidal flats are present, which are reworked by ice scouring during periods of thaw. Ice rafting of rock materials was observed to be an important depositional process. Coastal beach ridges are present at North Point, both transverse and longitudinal types. The former type forms a major, wide headland with bedrock near the surface. The latter type is roughly parallel to the coastline, composed of gravels and sands piled up by storm waves with some wind and ice modification. These ridges serve to trap sediments and form protected areas where salt marshes can develop. This area is described in more detail by Glooschenko and Martini (1978), while Glooschenko (1978) has described the vegetation zonation and plant biomass distribution at one site.

#### FIELD AND ANALYTICAL METHODS

#### Sampling

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During May 1976, three transects of approximately 1 km distance were surveyed using a transit and stadia rod. The lines began in the intertidal flats, seaward of the zone where vegetation colonisation started, and were run to the edge of willow thickets on old beach ridges. Due to the lack of nearby bench marks, all elevations are relative. During August 1976, a vegetation study was conducted in the area by one of the authors (Glooschenko, 1978) and along each transect six distinct zones of vegetation were found (Table I). In each of these zones, ten randomly selected sediment samples were collected

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#### TABLE I

-t-time of compling sites

Site number	Description of vegetation zone				
NP/A-1	high intertidal zone of vegetative colonization by grass, Puccinellia				
-9	high intertidal—supratidal flats with salt marsh vegetation				
-3	zone between beach ridges characterized by salt marsh vegetation				
-4	salt marsh vegetation complex				
-5	salt marsh zone of brackish/salt water ponds and salt pans				
-6	transitional zone of poorly drained gleysol soils with fresh-water vegetation				
NP/B-1. 2. 3. 4	same as NP/A 1-4, respectively				
-5	brackish water ponds dominated by sedges (Carex spp.)				
-6	same as NP/A-6				
NP/C-1	same as NP/A, B-1				
-2	same as NP/A-5				
-3	same as NP/A, B-6, site is located on low gravelly ridge				
-4	same as NP/B-5				
-5	mildly brackish water ponds dominated by fresh-water vegetation				
-6	old beach ridge with willow thickets				

to a depth of 10 cm by use of a hand trowel. This depth was chosen as it represented the root zone of plant species. The samples were mixed together in the field, i.e., an integrated random stratified sampling procedure was used. Some in situ pH's were measured in the field by use of a calibrated pH meter and were in the range of 7.2-8.8, the highest measurements being found in pans where salts accumulate, and lowest pH's in fresh-water areas. However, problems were encountered with the pH meter in the field, and only a limited number of sites were available for pH measurements. For the same reason, Eh measurements were not taken. The root zone was characterized by oxidizing conditions near living plant roots; however, all samples indicated localized reducing conditions within a few centimetres of the surface visually by either brown or gray mottling or black, H<sub>2</sub>S-rich layers as indicated by odor.

#### Sample preparation and analysis

Samples were preliminarily air-dried in the field. Upon return to the laboratory, the samples were freeze-dried and sieved through a 20-mesh screen (0.84 mm) to remove larger plant fragments, shells, pebbles, etc. The samples were then ground to approximately 200-mesh size (0.74 mm) for XRF analysis.

The elements Ti, Mg, Ca, K, Na, Fe, Mn, Si, Al, P and S were determined by X-ray fluorescence using a Phillips P.W. 1220C automatic spectrometer, thus representing a total elemental analysis. The trace elements Cu, Pb, Ni, Co, Cd, Cr and Zn were run by digesting 2.5 g of sediment with a mixture of  $HCl/HNO_3(1 + 1)$ , and using a Techtron AA-5 atomic absorption spectrophotometer. Analytical results were subjected to the factor-analysis computer program of Cameron (1967) developed for geochemical data, and a linearcorrelation coefficient matrix was produced between variables.

Particle-size analysis was done before grinding by the short pipette analysis procedure (Rukavina and Duncan, 1970). X-ray diffraction analyses were carried out with a Phillips X-ray diffractometer ( $CuK_{\alpha}$  radiation) using ground samples (200 mesh-size). The samples were analysed using a powderpack technique.

Mercury was determined by use of flameless atomic absorption (Capobianco, 1976). Carbon, both inorganic and organic, was determined by a Leco induction furnace carbon analyser (Capobianco, 1974).

**RESULTS AND DISCUSSION** 

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# Elemental composition of North Point samples

The results of elemental composition of samples are summarized in Table II along with results of particle-size analysis. Several points are obvious. In terms of "average" oceanic sediments (El Wakeel and Riley, 1961), North Point sediments are higher in Ca and Mg and lower in Si, Al, Fe and Mn, while Na, K, Ti and P are quite similar. This, probably, is in part due to the influence of Paleozoic carbonates in the area as a source material for sediment formation. The beach ridge gravels from the site are enriched in Si and Ca compared to sediments and soils, but contain less Al, Na, K, Mn and Ti, Thus, it appears that weathering processes of such gravels tend to remove Ca by dissolution, and Si either by weathering of quartz and/or clay-mineral genesis. The latter would be supported by the increase of Al, Na, K, Mn and Ti in the sediments or soils compared to the beach ridge material which acts as a parent material for soil development along with nearshore sediments.

Little data are available on chemical composition of rocks in the area, except for the Superior Province rocks described by Eade et al. (1966) and Shaw et al. (1976). Using these data in conjunction with geochemical data of Turekian and Wedepohl (1961), it appears that the major elemental composition of sediments and soils in the present study is closely approximated by assuming a roughly equal mixture of limestone and either Superior Province rocks or "average" shale, except that Na and Ti appear to be somewhat lower in our samples. The lower values of Ti may be due to lack of basaltic debris in the area (Chester and Aston, 1976).

Trace elements can be compared with those of nearshore muds (Wedepohl, 1960), marine argillaceous sediments (Potter et al., 1963) and southeastern U.S. salt marshes (Windom, 1976). Trace-metal values are based upon a  $HCl/HNO_3$  digestion, and are not a total elemental analysis, and as such, results are not directly compared to these published references. Trace-element compositions are roughly of the same order of magnitude except for Cr, Co and Ni, which are somewhat higher than the other authors' data.

#### TABLE II

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Summary of elemental composition of samples (dry-weight basis)

	Mean	Range	Std. dev.	
	70.0	4.72-82.6	9.46	
Clev(%)	21.2	11.10 - 42.3	7.69	
Sand (%)	8.9	2.60-33.4	8.40	
Inorganic carbon (%)	4.0	2.80-5.0	0.47	
Organic carbon (%)	2.8	0.80-9.7	2.22	
Ti (%)	0.30	0.20-0.44	0.09	
Mr (%)	3.10	2.63-3.83	0.27	
$C_{0}(\%)$	15.23	8.99-33.40	6.63	
$\mathbf{K}(\mathbf{K})$	1.63	1.19-1.96	0.17	
$N_{0}(\%)$	0.67	0.01 - 1.27	0.44	
$\mathbf{F}_{\alpha}(\mathcal{K})$	1.63	0.98-3.55	0.61	
Mn(%)	0.07	0.03-0.18	0.04	
Si (%)	14.05	11.24-19.59	2.12	
A1(%)	4.36	3.18-5.91	0.98	
P(%)	0.07	0.02-0.11	0.04	
S (%)	0.05	0.01-0.07	0.02	
	13.3	7.70-22.9	4.3	
$Dh \left( \frac{\mu g}{kg} \right)$	22.7	11.90-28.5	5.2	
Ni (ua/ka)	23.4	13.70-44.1	9.1	
$\dot{\Gamma}_{0} \left( \mu g / kg \right)$	11.9	7.50-20.5	2.9	
Cd (#8/#8)	1.4	0.60-2.0	0.4	
$\nabla u (\mu g/\kappa g)$	36.0	22.40-58.2	8.8	
$C_{2} (mallea)$	16.2	8.50-29.2	6.9	
Ur (με/με) Ur (με/με)	0.052	0.041-0.093	0.014	

### Factors controlling element distribution

The results of elemental analyses were subjected to a multiple correlation analysis. Due to its complexity, a copy of these results is available from the authors. However, these data are not easy to interpret due to the larger amount of data, possible lack of causal relationships between two variables that are significantly correlated with each other, and masking of negative correlation coefficients by dominant positive correlations (Spencer et al., 1968). For interpretation of such geochemical data, the use of factor analysis has been used by many investigators (see Spencer et al., 1968; Loring, 1975; Calvert, 1976; Dean and Gorham, 1976; Grieve and Fletcher, 1976). Our results based upon a varimax rotation, are presented in Table III. Loadings below 0.468 (P < 0.05) are omitted.

The factor loadings do give an indication of factors controlling elemental associations. Factor 1 appears to separate basic clay alumino-silicates and carbonate minerals (+loading) from quartz and acidic feldspars (-loading). Factor 2 has no significant +loadings and the -loadings suggest Fe-organic carbon-P-trace-metal interaction. This does not appear to be strictly due to organic-matter-trace-metal complexes. In terms of the trace-metal associa-

#### Varimax rotation Parameter bcs Silt Clay Inorganic carbon Organic carbon Ti Mg Ĉa ĸ Na Fe Mn Si A) P s Cu РЪ Ni Co Cđ Zn Cr Hg Elevation Distance % Variance explain

Cumulative % vari Note: factors <

by factor

tion, significa Cu and Ni, w significant ne associated mo dominant coi but Fe-hydra positive corre adsorbed to s oxides to be i: et al., 1968;C to oceanic sy this role, as in

Factor 3 is appears to be diffraction. ( 1962). The n tance from t as a combina fresh-water i

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TABLE III

#### TABLE III

Varimax rotation-North Point geochemistry

Parameter	Factor					_		
·	1	2	3	4	5	6	7	8
Silt	-	_	·			0 904		·····
Clay	<u> </u>	_	0.524	_	_	-0.516	_	_
Inorganic carbon	—			0.832	_	_		_
Organic carbon	-	-0.469	0.676	_				_
Ti	0.947	<u> </u>			_	<u> </u>		
Mg	0.657		<del></del>	<del></del>	_	-0.331		_
Ca	0.844	_	<del></del>			_	_	
ĸ	·		0.542	_		_	_	0 520
Na	-0.794	_					_	
Fe	-0.578	-0.540	_	_		_		
Mn	0.895	_	_	سنت	_	·	_	
Si	-0.707	_	_	_		0.316		0.549
Al	0.855		_		<u> </u>		_	0.043
P		-0.654	-	-0.480	_		_	_
S		-	-	-	_	· <u> </u>		-0 672
Cú	¥	-0.939		_	_	_	_	
Pb				_	0.905	·		_
Ni		-0.923	<u> </u>		_			
Co	_		_		_	0 544	0 479	
Cd	_	<u></u>			<u> </u>	-	0.412	
Zn	·	0.771	_	_			0.004	-
Cr	_		0.659	_	-0 650	_	_	_
Hg	-			-0.485		_		_
Elevation	_	-	-0.939		_		<u> </u>	_
Distance	_	_	-0.778		_		_	_
% Variance explained by factor	31.7	25,8	15.0	6.4	5.3	3.9	3.1	2.9
Cumulative % variance	31.7	57.5	72.5	78.9	84.2	88.1	91.2	94.1

Note: factors < 0.468 omitted.

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tion, significant positive correlations with organic carbon were found with Cu and Ni, which is similar to the results of Calvert and Price (1970). A significant negative correlation was exhibited by Cr which appears to be associated more with clay fractions. Thus, organic matter may not be the dominant controlling factor affecting distribution of these trace metals, but Fe-hydrated oxides could be important also as evidenced by significant positive correlations between Fe and Cu, Ni and Zn. Phosphorus could be adsorbed to such iron oxides (Hirst, 1962). Other studies have shown Mn oxides to be important in controlling trace-metal concentrations (see Spencer et al., 1968; Calvert, 1976). However, our Mn values were quite low compared to oceanic systems (Table III) and, therefore, Mn may not be important in this role, as in more oceanic sedimentary environments.

Factor 3 is of interest. The positive loading component, Cr, K and clay, appears to be related to clays, perhaps illite, which was detected by X-ray diffraction. Chromium also tends to be associated with clay fractions (Hirst, 1962). The negative loading of factor 3 is a combination of elevation, distance from the tidal flats, and organic carbon. This factor can be interpreted as a combination of two controls: (1) the contrast between marine and fresh-water influences pedogenesis as soil formation is proceeding on sedi-

ments that become exposed to increased drainage, and (2) terrestrial vegetation development.

These first three factors account for 72.5% of the variance. The other five factors account for 21.6% of the variance and tend to give little added information. Factor 4 appears to be a positive carbonate factor vs. organic carbon, P and Hg. Factor 5 is most likely Pb vs. Cr as host minerals. The factor-6 loading appears to be a silt vs. clay factor. Factor 7 has only a positive component in which the metals Cd and Co could be associated with sulfides based upon a significant positive correlation, while factor 8 is unclear. These observations are supported by mineralogical analyses of pebbles and light and heavy minerals of sands from North Point (Martini and Protz, 1978). Pebbles are composed mainly of mafic volcanics, limestones and dolostones, with less than 10% of granitoid pebbles, hematitic rocks and mollusc shell fragments. Dominant particles in the sand fraction were homblende, magnetite, ilmenite, igneous and metamorphic rock fragments and amphiboles.

X-ray diffraction analyses showed that all the sediments had a similar mineralogy containing such light minerals as quartz, feldspars and plagioclase (Na, Ca), and biotite. Also abundant are dolomite and calcite. The major clay minerals found in the samples were chlorite, illite and kaolinite. Montmorillonite was not present, but is found in older soils in the interior of the Hudson Bay Lowlands where longer time periods are available for genesis of this clay mineral (Martini and Protz, 1978).

In terms of the influence of distance from the tidal flats, i.e., the length of time, the only significant factors found were clay (r = -0.469, p < 0.05), organic carbon (r = 0.695, p < 0.01), and mercury (r = -0.716, p < 0.01). Thus, organic carbon is increasing probably by plant growth and incorporation of organic matter into the sediments. No major effect of time can be observed in our data, but these marshes are young, probably less than 200-300 years based on uplift rates, so not enough time for geochemical changes to be observed as influenced by vegetation development.

#### CONCLUSIONS

Studies on the geochemistry of sediments from the North Point salt marshes indicate that the parent material from which the sediments were derived, i.e., Paleozoic carbonates vs. Canadian Shield igneous and metamorphic rocks, is the major controlling factor determining elemental composition of these materials. Other factors, such as acid vs. basic nature of alumino-silicates, hydrated iron oxides, clay and sand content, sulfides and organic matter influence sediment composition within the salt marsh in terms of total elemental composition. However, since the marsh sediments and soil represent a system changing through time, exposure to saline vs. fresh water, and thus varying redox potential, one would expect such sediments to change in terms of soluble and exchangeable cations and anions. Studies are in progress subjecting these sediments and soils to soil chemical methods to further interpret these changes.

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