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Characterization of the Natural Organic Matter (NOM) in groundwater contaminated with ^{60}Co and ^{137}Cs using ultrafiltration, Solid Phase Extraction and fluorescence analysis

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ABSTRACT

Spot samples of shallow groundwaters have been taken between the years 2004 and 2010 near a site formerly used for the dispersal of radioactive liquid wastes. Three sampling points, one clean (upstream), and two downstream of the contamination source, were processed by ultrafiltration (5000 Da cut-off) and Solid Phase Extraction (SPE) to determine the association of selected artificial radionuclides (^{60}Co, ^{137}Cs) with Natural Organic Matter (NOM). The last two sampling episodes (2008 and 2010) also benefited from fluorescence analysis to determine the major character of the NOM. The fluorescence signals are reported as humic-like, fulvic-like and protein-like, which are used to characterize the different NOM types. The NOM from the clean site comprised mostly fine material, whereas the colloidal content (retained by ultrafiltration) was higher (e.g., 15–40% of the Total Organic Carbon – TOC). Most of the 137Cs was present in the colloidal fraction, whereas ^{60}Co was found in the filtered fraction. Fluorescence analysis, on the other hand, indicated a contrasting behavior between the clean and contaminated sites, with a dominance of protein-like material, a feature usually associated with human impacts. Finally, SPE removed almost quantitatively the protein-like material (>90%), whereas it removed a much smaller fraction of the ^{137}Cs (<28%). This finding indicates that the ^{137}Cs preferential binding occurs with a fraction other than the protein-like NOM, likely the fulvic-like or humic-like portion.

1. Introduction

Natural Organic Matter (NOM) is a constituent of all types of natural waters, such as rain, rivers, lakes, other types of surface waters, groundwaters, estuarine and marine waters. Living organisms are the ultimate source of aquatic organic materials through the build-up and breakdown of complex molecules including cellulose, lignin, other plant residues, lipids, fats, and proteins. This material commonly accumulates in peat bogs, sediments and soils, and it is almost ubiquitous in natural terrestrial waters. Its slow decomposition produces large and refractory macromolecules, as the biodegradable portion containing readily available sugars is readily assimilated. The typical designation of the NOM from these origins is terrestrial (terrigenous) or allochtonous (Leenheer and Croué, 2003; Morel and Hering, 1993).

Secondary NOM is also produced in water systems from the biogeochemical assimilation and breakdown of allochtonous NOM. Large molecules can be assimilated and produce secondary NOM such as metabolites, exudates, degraded proteins, excreta, and decomposition of fresh biomass. This NOM is often called secondary or autochtonous (Leenheer and Croué, 2003; Morel and Hering, 1993). The secondary NOM is potentially dominant in carbon-deprived environments, such as open marine waters (Coble, 1996; (Fellman et al., 2010), in old deep groundwaters (Caron et al., 2010) and in human-impacted waters (Holbrook et al., 2006a, b; Riopel, 2013). Specifically, human impacts affecting the water directly such as waste water plants (Caron and Smith, 2011; Holbrook et al., 2006a, b; Riopel, 2013) and indirectly through land utilization, such as agriculture, landfilling, or urban development can generate a mixture of primary (allochtonous) and secondary (autochtonous) NOM (Caron and Smith, 2011; Holbrook et al., 2006).

NOM consists of a vast array of molecules of different sizes, which contain functional groups and acid–base properties (Morel and Hering, 1993; Stumm and Morgan, 1996; Frimmel, 1998; Litaor and Thurman, 1988). NOM plays an important environmental role, such as changes in speciation and transport of metals

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and radiocontaminants (Killey et al., 1984; Caron and Mankarios, 2004; Caron et al., 2007; Schmitt et al., 2003; Marley et al., 1993; Penrose et al., 1990; Akaighe et al., 2013), acid-base buffering of natural waters (Litaor and Thurman, 1988; Chapman et al., 2008; Ritchie and Perdue, 2003), changes in toxicity and contaminant or nutrient uptake to biota (Qiao and Farrell, 2002; Vigneault et al., 2000; Galvez et al., 2008), formation and transport of metal-nanoparticles (Akaighe et al., 2013), and the formation of toxic halocarbons in drinking waters (Pifer and Fairey, 2012; Nikolaou and Lekkas, 2001; Leenheer and Croué, 2003; Ahmad et al., 2002).

Analyses of natural waters to elucidate the composition of NOM have been used for years. For example, Leenheer and colleagues have used wet column separations (Leenheer, 1981), but this approach is tedious and time-consuming. It has the advantage to provide the composition of some of the major classes of NOM constituents. Alternatively, fluorescence spectroscopy has emerged as a leading analysis technique (Coble, 1996; Stedmon and Markager, 2005; Holbrook et al., 2006a, b). Fluorescence has the advantage that it is fast, non-destructive and requires only small amounts of sample. Analysis of the fluorescence signal, however, still suffers from the absence of certified reference materials for NOM. Nonetheless, digital resolution techniques exist to make a reasonable spectral interpretation. A leading digital tool is Parallel Factor Analysis (PARAFAC; Andersen and Bro, 2003), which is used to spectrally isolate and resolve individual components of the fluorescence signals.

The current investigation focuses on the NOM analysis and fractionation of samples taken from a shallow groundwater flowing in overburden sitting on granitic rocks of the Canadian Shield. The specific site is in the vicinity of a liquid dispersal area (LDA) which was formerly used for the dispersal of low-level radioactive liquid wastes. The NOM has been partially characterized for its potential role in the migration of selected radionuclides, especially ^{60}Co and ^{137}Cs (Caron and Mankarios, 2004; Caron et al., 2007; Caron and Smith, 2011). These past investigations have focused on developing methods to characterize the NOM-radionuclide associations based on ion exchange, size characterization by ultrafiltration, and hydrophobic character of the NOM using Solid-Phase Extraction (SPE). The current investigation is a continuation of the past works, with the following specific objectives, to:

i. Test and confirm the colloidal character and differences of NOM between an uncontaminated reference site and two contaminated sites, near the LDA;
ii. Characterize the differences in NOM between these reference and contaminated sites, using fluorescence spectroscopy; and
iii. Further test the major character of the NOM and selected radiocontaminants (^{60}Co and ^{137}Cs), using a combination of ultrafiltration, SPE and fluorescence.

2. Experimental

2.1. Sampling site

The sampling location was approximately 200 km West of Ottawa (Canada), on the Ontario side of the Ottawa River. The climate is humid continental with distinct seasons, with a snow cover from early to mid-December until early April. The sampling site consists largely of Aeolian sand deposits, up to 15 m thick, over the Canadian Shield bedrock (Jackson and Inch, 1980). The LDA is a coarse gravel trench excavated in a sand dune. The bottom sits ~1–2 m above the water table, and it does not have a protective cover or liner against the weather. An estimated volume of 3.3×10^5 m^3 was discarded in this trench from ~1956 to 1992, containing a total of ~230 TBq of beta (β) and ~0.31 TBq of alpha (α) emitters, until its permanent closure in 1995 (Caron et al., 2002; Caron and Mankarios, 2004). Radionuclides are still readily detected in the groundwater after interception of seepage water through the LDA. Station LDA-3 is located ~50 m upstream from the LDA; it is undisturbed and uncontaminated. Stations LDA-22 and -23 are located ~20 m in the flowpath downstream from the LDA. The flow rate is approximately 10–20 cm/day at the sampling point.

2.2. Sample handling and processing

Approximately 20 L of water were taken at each station for the sampling years reported (2004, 2005, 2007, 2008 and 2010). The water was collected using a submersible pump, lowered into pre-existing boreholes. The pump delivered the water through a polyethylene tube directly into collapsible plastic containers at the surface. The sampling set-up (e.g., tubing, collecting containers, etc.) were always covered with a dark plastic sheet to protect against direct sunlight to avoid photobleaching (Cooper and McHugh, 1983). After collection, the samples were filtered through a 0.45 μm hollow fiber cartridge (A/G Technologies) in the laboratory, under subdued light, either locally or in our laboratory in Sudbury, ON. The samples and fractions were kept in a refrigerator at ~4 °C in the dark until further processing or analysis.

The rest of the processing scheme is shown in Fig. 1 (modified from Caron and Mankarios, 2004). Aliquots of the 0.45 μm filtrate were taken: 1 L was spared in an HDPE bottle for gamma analysis, another ~40 mL was transferred into an amber glass bottle (I-Chem, Fisher Scientific; pre-soaked with de-ionized water) for TOC and fluorescence analysis, and a 250 mL aliquot was reserved for SPE. The aqueous extract (i.e., after passing through the SPE cartridge) was spared for gamma analysis (~210 mL) and fluorescence spectroscopy (~40 mL, in an amber glass bottle). All these operations were performed within 48 h of sampling.

The SPE was performed using a C_{18} sorbent cartridge (Millipore, Sep-Pak Plus, Milford, MA), to determine the hydrophobic or hydrophilic character of the NOM (Caron and Mankarios, 2004). Since the C_{18} sorbent on the cartridge is hydrophobic, the NOM in the aqueous solution retained on the cartridge has a dominant hydrophobic character, whereas the NOM contained in the aqueous extract (after passing through the cartridge) is operationally defined as hydrophilic. The spent SPE cartridge was also analyzed for gamma emitters, and for mass balance.

Approximately 18 L of the 0.45 μm original filtrates were further processed using a filtration cartridge (5000 Da MWCO[1]; A/G Technologies). The filtrate (~15–16 L) contained the NOM material smaller than the filter cut-off value, and is called "fines" henceforth. The rententate (~1.5 L) contained the NOM material larger than the cut-off value of the membrane, in addition to some fines, which we define as NOM material smaller than the cut-off value of the membrane. The reported colloidal NOM content was corrected for the fines contained in the retentate using our previously published protocols (Caron and Mankarios, 2004; Caron et al., 2007). Intentional losses from the initial volume were necessary for rinsing and wetting the filtration cartridges. As for the original filtrate, aliquots were spared for gamma analysis (1 L for the filtrate, 0.5 L for the retentate), TOC and fluorescence analysis. It should be noted that TOC analyses after SPE were intentionally omitted (because of the methanol preconditioning of the cartridge), and fluorescence

[1] Molecular Weight Cut-Off; the Dalton units (Da) are loosely used as equivalent of atomic weights for macromolecules, for which an absolute molar mass cannot be rigorously determined.

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