



# Fractionation and size-distribution of metal and metalloid contaminants in a polluted groundwater rich in dissolved organic matter



Ivan Kozyatnyk\*, Sylvain Bouchet<sup>1</sup>, Erik Björn, Peter Haglund

Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

## HIGHLIGHTS

- DOM is mainly present as acidic and neutral hydrophobic compounds.
- Metals are primarily found within the acidic hydrophobic and hydrophilic fractions.
- Most metals are associated with high molecular weight DOM (40–100 kDa).
- Few metals exist as “free” ions or complexed by low molecular weight DOM.
- Reference FA bind many metals while reference HA bind only a few.

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## ABSTRACT

We investigated the concentration levels, fractionation and molecular weight distribution (MWD) of dissolved organic matter (DOM) and metals (V, Cr, Co, Ni, Cu, Zn, As, Cd, Sn, Ba, Hg and Pb) in a polluted groundwater from an industrial area in Northern Sweden. DOM was mainly recovered in the hydrophobic acidic and hydrophobic neutral sub-fractions (45 and 35%, respectively) while most metals were found in the acidic sub-fractions (46–93%) except for V, Fe and As, which were predominant in the basic sub-fractions (74–93%) and Cd in the neutral ones (50%). DOM exhibited a broad MWD in groundwaters, usually from 5 to 200 kDa and was dominated by high molecular weight hydrophobic acids, low molecular weight hydrophilic acids and hydrophilic neutral compounds. Most of the studied metals (Fe, Cr, Co, Sn, Ba, Hg) were associated with the high molecular weight DOM fraction (ca. 40–100 kDa). Cu, Pb, Zn, Cd and Ni interacted with a broad range of DOM size fractions but were still most abundant in the high molecular weight fraction. Few metal/metalloids (As, V and Cr in some cases) presented a very weak affinity for DOM and presumably existed predominantly as “free” inorganic ions in solution.

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## 1. Introduction

Discharges from chemical industries are local sources of contamination that often need to be treated because organic and inorganic pollutants degrade soil and water quality, affect living organisms and eventually human health [1]. Various remediation techniques have been developed to address these problems,

including excavation, soil washing, thermal treatment, pump and treat approaches, phytoremediation and permeable reactive barriers (PRBs) [2,3]. PRBs have gained in popularity because they are passive systems, installed downstream of the pollution source to prevent the contamination plume to spread [4,5] but are only cost-effective in long-term use because of high installation costs. However, designing efficient treatments requires a deep knowledge of the physico-chemical characteristics of pollutants. Metals (hereafter used in this manuscript as a generic term for major or trace metals and metalloids) are often strongly bound to dissolved organic matter (DOM), which is a polydisperse mixture of macromolecules with different structures and molecular weights [6] that originates from various organic compounds (lignin, proteins, polysaccharides, lipids, low molecular weight organic acids, etc.),

\* Corresponding author.

E-mail address: [kozyatnik@gmail.com](mailto:kozyatnik@gmail.com) (I. Kozyatnyk).

<sup>1</sup> Present address: IPREM-LCABIE, CNRS UMR 5254, Université de Pau et des Pays de l'Adour, Technopole Helioparc, 2, avenue du Président Angot 64053 PAU cedex 09.

The structure of the macromolecules involved and their properties, such as apparent charge and molecular weight, remain relatively unknown; although it is a crucial information when implementing remediation strategies, for example to select effective materials for PRBs.

In early studies, DOM was operationally defined in terms of its relative contents of fulvic and humic substances [7]. Humic substances usually comprise about 50% of DOM but may account for up to 90% in strongly colored surface waters [8], whereas low-molecular weight acids can dominate in groundwater (up to 50%) [9]. However, this operationally defined separation does not provide enough information when designing treatments since the behavior of DOM and its binding capacities for contaminants depend on its physico-chemical properties [10]. DOM contains diverse reactive functional groups, such as carboxyl, phenol, amine or thiols, acting as ligands with various affinity for metals [11,12]. Complexation of metals by DOM strongly alters their fate, i.e. mobility, bioavailability and toxicity in the environment [13–16] and the responsible molecules and/or functional groups have therefore been investigated in both natural [17] and engineered systems.

The molecular weight distribution (MWD) of DOM is also an important parameter to understand its behavior in natural environments [6,18] and during industrial processes such as water treatment [19,20]. Size exclusion chromatography (SEC) is widely used to determine MWD, due to its ease of operation and coupling with several detectors [19,21,22] although the separation may not solely be based on molecular weight. Molecules eluting from size exclusion columns are usually detected based on their UV absorbance at 254 nm [23] while complementary information can be obtained with fluorescence detection [24,25], total organic carbon determination [26], or mass spectrometry [27]. Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most powerful techniques to measure metals, especially when used on-line after a chromatographic separation since it is a fast multi-element technique with high sensitivity, selectivity and robustness [17,28–30]. Therefore, the hyphenation of SEC with ICP-MS is very suitable to study the MWD of metals associated to organic molecules and it has been applied to e.g. compost leachates [31], groundwater [32], natural stream [17,31] and marine waters [33]. Despite recent instrumental improvements, the extreme heterogeneity and complexity of DOM make direct analyses still difficult and fractionations based on chemical and/or physical properties are often performed before the above mentioned separation and detection techniques are applied.

There are very few studies that combined fractionation and MWD to look at metals and DOM associations, especially in ground-

waters and, to the best of our knowledge, none for polluted sites located in subarctic boreal regions (including Canada, northern USA, Scandinavia and Russia). Soils in these areas are supplied with organic matter, mostly decomposing coniferous material from natural sources and industrial activities. Groundwaters are therefore very rich in DOM, which may increase the fraction of metals bound to DOM but also present specific MWD of metals complexes. In this work, we investigated the concentrations, MWD and fractionation of DOM and metals in a polluted groundwater from an industrial area in Northern Sweden, which is likely representative of other industrial sites located in boreal regions, in order to expand the limited knowledge in this area. For MWD, we briefly evaluated the best SEC separation conditions for such samples considering both UV absorbance spectrometry and ICP-MS detection and then investigated the MWD of DOM and metals in raw samples and six fractions of a composite sample (hydrophilic acidic, basic and neutral, and hydrophobic acidic, basic and neutral). The findings presented in this study will be of great value in future work to select suitable material(s) for use in PRBs for groundwater remediation [34].

## 2. Materials and methods

### 2.1. Sampling of groundwater

Groundwater samples were extracted in March 2013 from 9 representative wells distributed over a 10 ha industrial area in Västerbotten County in Northern Sweden located on the coast of the Gulf of Bothnia (Fig. 1). This site has long been used for various industrial purposes including production of pulp and viscose, chlorine and other fine chemicals, storage of fuel oil and timber that released various metals and organic pollutants to the adjacent soil and groundwater. These wells were selected for investigations based on differences in their pedological profiles, groundwater chemistry and the expected location of a PRB for groundwater treatment. Only wells showing oxic conditions were considered for sampling, which was carried out in March during snow melt (high level of water) as this is the period of the year that should give the highest load on the future permeable barrier. Half a liter of groundwater was sampled at about 1.2 m (whole depths of the wells given in Table S2) and transferred to acid washed PE bottles after discarding the first 2–3 L from each well. Each bottle was preconditioned with ca. 200 mL sample before sample collection. Both electrical conductance and pH were measured directly in the wells. Samples were kept in a cooler within a few hours until arrival at the laboratory, where they were immediately filtered through 0.45  $\mu\text{m}$  filters (Sartorius, Minisart) and pH was measured with a 691 pH

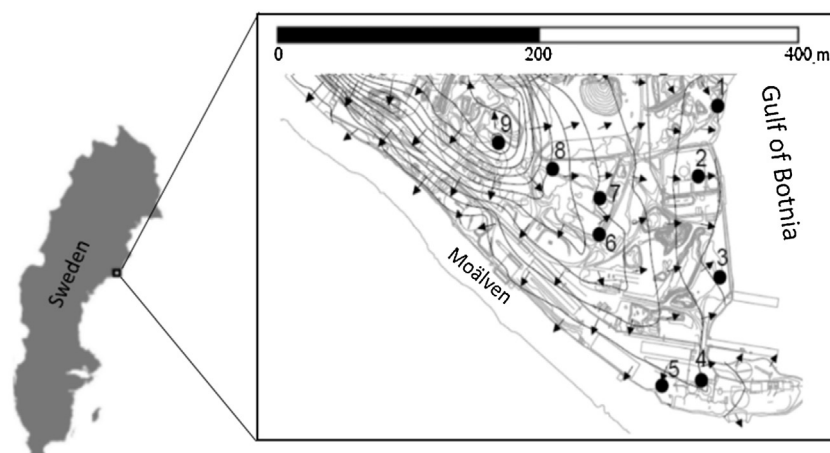


Fig. 1. Location of the sampling wells on the study site.

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