



Partitioning of organic matter in Boom Clay: Leachable vs mobile organic matter



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ABSTRACT

Boom Clay (BC) is considered in Belgium as a potential host rock for nuclear waste disposal. The formation contains up to 5 wt% of natural organic matter and the presence of dissolved organic matter (DOM) may have a strong impact on radionuclide mobility. However, due to physical constraints, only a fraction of DOM is mobile through the BC layer and the extent of DOM-facilitated radionuclide transport is controlled by the distribution of OM over the mobile and immobile pools. In this work, we investigate 1/the concentration and the size distribution of leachable organic matter in BC, 2/the variability along the BC layer of the concentration and the size distribution of mobile DOM, 3/the parameters controlling the concentration and the size distribution of the leachable OM pool and of the mobile OM pool. Size exclusion chromatography with UV detection at 280 nm is chosen as the reference technique. The UV response of BC DOM is investigated as a function of MW. In pore waters, *i.e.* for mobile DOM, the $SUVA_{280}$ is dependent on the OM size/MW with the lowest value measured for low MW species (<1 kDa). The use of dynamic light scattering permits to also estimate the hydrodynamic radius (R_H) distribution of BC DOM. In the investigated part of BC, the concentration of mobile DOM represents only $0.15 \pm 0.8\%$ of the total organic matter content (TOC) and is mostly <20 kDa ($R_H < 2.8$ nm). In contrast, the OM leached from solid samples is dominated by species with MW > 50 kDa and $R_H > 5.3$ nm and accounts for about 12 TOC %. While the concentration of the leachable OM pool is mostly controlled by the TOC content of the rock and to a lower extent by the hydrogen index of the kerogen, the mineralogy plays a significant role in the concentration and the size distribution of the mobile DOM. Filtration and sorption are promoted by clay minerals that preferentially preserves large organic species and leave only small species mobile in pore waters. Inversely, coarser minerals like silt and/or sand facilitate the transport of DOM and increase both the concentration and the MW/ R_H of the mobile species. The threshold of 20 kDa ($R_H = 2.8$ nm) is considered as a cut-off over which DOM species are hardly mobile in BC. A large part of OM is showed insoluble or immobile but the distribution of OM over the mobile and immobile/insoluble pools, characterised by an average K_d of 140 L kg^{-1} is found to rather favour the transport of radionuclides than to act as an additive sorbent phase.

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1. Introduction

Organic matter (OM) is a ubiquitous component of soils and sediments and its distribution over the solid and the solution is known to control the fate of trace metals and contaminants in the environment. Solid or particulate organic matter immobilizes the contaminants acting as a sorption phase while dissolved organic matter was shown to transport several contaminants and notably

to enhance the migration of radionuclides in porous media (Maes et al., 2011, 2006; Mibus et al., 2007; Warwick et al., 2000).

Boom Clay (BC) is under study in Belgium as a potential host rock for deep geological repository of nuclear waste. It contains a significant amount of NOM (1–5 wt%) with up to 250 mgC L^{-1} collected in pore water (De Craen et al., 2004b). In soils, the concentration of DOM is mainly controlled by the combination of OM solubility and sorption/desorption equilibrium on mineral phases. Kaiser et al. (1996) showed that the amount of dissolved organic matter (DOM) released from various soils and expressed as dissolved organic carbon (DOC) was dependent on the soil organic

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carbon (OC) content. [Vandenbruwane et al. \(2007\)](#) were able to estimate the concentration of DOM, expressed as DOC, in different horizons of podsoils with the sole consideration of sorption processes. [Qualls \(2000\)](#) reported that adsorption was buffering the DOM concentration and this even in organic-rich horizons. However, in low-permeability media, such as BC or more generally the clay-rich rocks intended as potential host rocks for nuclear waste geological disposal, the concentration of organic matter transported in pore water is not only governed by chemical processes but also by physical constraints. These constraints partitioned the DOM into two fractions: a mobile and an immobile fraction. Accounting for these two fractions, the distribution of OM in low porous media might be sketched as presented in [Fig. 1](#). In this figure, OM is divided into three pools: the solid/particulate pool, the leachable pool and the dissolved pool. Each pool might interact with each other in a dynamic way. The mobile DOM is present in pore waters and can be retrieved by means of piezometers. The leachable OM pool accounts for potentially soluble and dissolved OM that is trapped in the rock either by chemical (sorption, i.e sorbed OM) or physical processes (filtration, i.e immobile DOM). This fraction of OM can be leached from the powdered rock. Besides sorption, the phenomenon of natural filtration was already mentioned by authors who investigated DOM in deep clay formations such as Boom Clay ([Bruggeman et al., 2010](#); [Put et al., 1998](#); [Van Geet et al., 2003](#)) or Callovo-Oxfordian argillite ([Courdouan et al., 2007](#)). However, a deeper investigation on the parameters controlling the distribution of OM over the leachable and mobile pools is, to the author's knowledge, still missing. Yet, the understanding of the distribution of OM over the different fractions is essential to assess the DOM-induced environmental impact.

The objective of this work is to give more insight into 1/the concentration and the size distribution of the leachable OM in BC, 2/the variability along the BC layer of the concentration and the size distribution of mobile DOM, 3/the parameters controlling the concentration and the size distribution of the leachable OM pool and of the mobile DOM pool.

The leachable OM is extracted by leaching from a series of BC samples. Several pore water samples are collected in parallel by means of piezometers to quantify and qualify the mobile DOM. The concentration and the size distributions of both extracted and mobile OM is discussed with regards to the composition and the porosity of BC. Size exclusion chromatography with UV detection at 280 nm is chosen as the reference technique. The UV response of BC OM is also investigated as a function of molecular weight (MW).

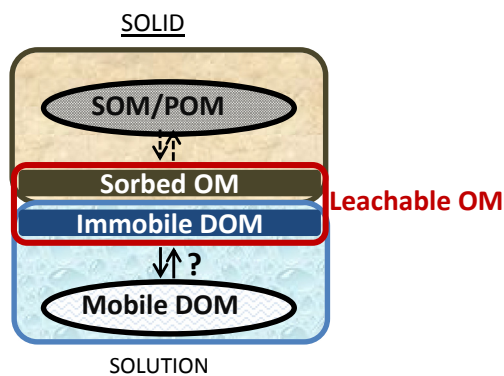


Fig. 1. Schematic distribution of organic matter (OM) in low-porous media such as BC. SOM = solid OM, DOM = dissolved OM, POM = particulate OM.

2. Materials and methods

2.1. OM samples

The concentration of OM solid or in solution is quantified by measuring the concentration of organic carbon. The term TOC (wt %) defines the total amount of organic carbon in a sample, here a rock sample, and is assumed to correspond to the total amount of OM in this sample. The term DOC (mgC L^{-1} or gC L^{-1}) defines the concentration of OC measured in solution after filtration at $0.45 \mu\text{m}$ ([Zsolnay, 1996](#)). DOC is used to quantify the concentration of OM in the liquid samples (pore waters or leached OM solutions). DOC and DOM should not be confused. The term DOM stands for the OM dissolved in BC pore waters (mobile and/or immobile but not leached).

2.1.1. Piezometer samples

The Boom Formation can be subdivided into four main stratigraphic units which are, from the basis to the top: the Belsele-Waas Member, the Terhagen Member, the Putte Member and the Boeretang Member. It is assumed that the piezometers installed in the Boom Formation around the HADES underground research facility collect mobile DOM. In order to evaluate the variation of mobile DOM size distribution in the formation both vertically and horizontally, pore waters were sampled using several of these piezometers. A schematic view of the different piezometers used in this work is presented in [Fig. 2](#) and the depth of the sampled filters is reported in [Fig. 3](#). To avoid air contact, the sampling was performed using vessels initially flushed with Ar/CO_2 0.4 ppm. The samples were then kept at room temperature in vessel overpressurized with Ar/CO_2 0.4 ppm or in a glovebox saturated with Ar/CO_2 0.4 ppm.

2.1.1.1. Horizontal piezometer: SPRING (TD-116E). Pore water samples were taken from a horizontally-oriented piezometer, SPRING, installed at the level of HADES laboratory (-196.6 m TAW (Tweede Algemene Waterpassing)). It is entirely made of stainless steel and contains 4 filters of 1.5 m length directly in contact with Boom Clay and with a pore size distribution from 7 to $16 \mu\text{m}$. Pore water was collected from each filter. The samples of filter 1, 2, 3 and 4 will be referred to as S1, S2, S3 and S4, respectively. Neither the granulometry nor the porosity of the sediments surrounding each filter was measured. However, we will refer to the data obtained on a core sample taken at the level of the HADES laboratory that is named EZE55.

2.1.1.2. Vertical piezometers: MORPHEUS (TD-11D) and CG-13U. Pore water samples were taken from the vertically-oriented piezometers MORPHEUS and CG-13U. The MORPHEUS piezometer consists of a PVC hollow pipe and contains 12 ceramic filters of 10 cm length and $60 \mu\text{m}$ pores in direct contact with BC. This set-up allows pore water sampling at distinct stratigraphic levels from -217.1 to -234.2 m TAW . Two filters are situated in the Terhagen Member. The other 10 belong to the Putte Member with one situated at the level of the Double Band (M8). The Double Band corresponds to two thin, relatively sandy layers at the bottom of the Putte Member which display significantly higher hydraulic conductivity compared to the surrounding layers. Samples from 11 of the 12 filters were taken as one filter did no longer provide pore water. The samples will be referred to according to the filter they were taken from: M2, M4, M6, M8, M9, M10, M12, M13, M18, M20 and M23.

The CG-13U piezometer contains 13 stainless steel filters of 9 cm length (pores from 7 to $16 \mu\text{m}$) which cover the upper part of the

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