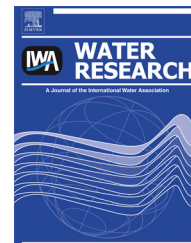


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# Humic substances interfere with phosphate removal by lanthanum modified clay in controlling eutrophication

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## ABSTRACT

The lanthanum (La) modified bentonite Phoslock<sup>®</sup> has been proposed as dephosphatisation technique aiming at removing Filterable Reactive Phosphorus (FRP) from the water and blocking the release of FRP from the sediment. In the modified clay La is expected the active ingredient. We conducted controlled laboratory experiments to measure the FRP removal by Phoslock<sup>®</sup> in the presence and absence of humic substances, as La complexation with humic substances might lower the effectiveness of La (Phoslock<sup>®</sup>) to bind FRP. The results of our study support the hypothesis that the presence of humic substances can interfere with the FRP removal by the La-modified bentonite. Both a short-term (1 d) and long-term (42 d) experiment were in agreement with predictions derived from chemical equilibrium modelling and showed lower FRP removal in presence of humic substances. This implies that in DOC-rich inland waters the applicability of exclusively Phoslock<sup>®</sup> as FRP binder should be met critically. In addition, we observed a strong increase of filterable La in presence of humic substances reaching in a week more than 270  $\mu\text{g La l}^{-1}$  that would infer a violation of the Dutch La standard for surface water, which is 10.1  $\mu\text{g La l}^{-1}$ . Hence, humic substances are an important factor that should be given attention when considering chemical FRP inactivation as they might play a substantial role in lowering the efficacy of metal-based FRP-sorbents, which makes measurements of humic substances (DOC) as well as controlled experiments vital.

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## 1. Introduction

Eutrophication through excessive nutrient enrichment is considered the most important water quality problem in

freshwater and coastal ecosystems (Conley et al., 2009; Smith and Schindler, 2009). Water blooms of potentially toxic cyanobacteria (blue-green algae) – the most obvious symptoms of eutrophication, are a threat to human and animal health

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(Codd et al., 2005; Dittmann and Wiegand, 2006), e.g. they cause swimming bans, and have caused drinking water shortages (Lürling and Van Oosterhout, 2013a; Yang and Liu, 2010). The attainment of a good water quality is required by European legislation (EU, 2000) and the ‘good ecological state’ or ‘potential’ of lakes by 2015, as required from the EU WFD (European Union, 2000), makes eutrophication control an important challenge to water authorities.

It is widely accepted that excessive loadings with both nitrogen and phosphorus, are the major causes of blooms of cyanobacteria (Smith et al., 1999; Cooke et al., 2005), which would indicate that mitigation should focus on dual reductions (Paerl, 2009). For practical purposes only phosphorus can be lowered effectively to limiting concentrations, hence eutrophication control has primarily focused on phosphorus control (Schindler et al., 2008). Phosphorus control implies both strong reduction of the external phosphorus inputs as well as phosphorus present within the system (Klapper, 2003; Cooke et al., 2005; Mehner et al., 2008). In-lake phosphorus control requires both water column dephosphatisation as well as blocking phosphorus release from the sediment (Cooke et al., 1993, 2005; Spears et al., 2013a). Traditionally, aluminium-, calcium- and iron salts have been applied for in-lake restoration (e.g. Cooke et al., 1993; Cooke et al., 2005), while more recently solid-phase phosphorus sorbents have gained interest (Spears et al., 2013a). Solid-phase phosphorus sorbents are mainly clays enriched with aluminium (Al) (Gibbs et al., 2011), iron (Fe) (Zamparas et al., 2012) or lanthanum (La) (Haghseresht et al., 2009; Yuan et al., 2009).

Most information exists on the La modified bentonite Phoslock® (Douglas, 2002). Phoslock® was developed by the Australian CSIRO, as dephosphatisation technique aiming at removing Filterable Reactive Phosphorus (FRP) from the water and blocking the release of FRP from the sediment. Several studies reported Phoslock® as promising technique to control eutrophication (Robb et al., 2003; Akhurst et al., 2004; Ross et al., 2008; Haghseresht et al., 2009; Van Oosterhout and Lürling, 2013). Under favourable conditions La and FRP bind to rhabdophane (LaPO<sub>4</sub>), a mineral with an extreme low solubility ( $K_{sp} = 10^{-24.7}$  to  $10^{-25.7} \text{ mol}^2 \text{ l}^{-2}$ ) (Johannesson and Lyons, 1994; Liu and Byrne, 1997). The La-FRP bond is less affected by non-neutral pH as compared with Al- and Fe-based FRP binders (Douglas et al., 2004). The FRP binding capacity of La is not affected by altered redox conditions such as those in anoxic waters (Ross et al., 2008). However, the efficacy of this La modified clay in controlling phosphorus in an enclosure experiment (Lürling and Faassen, 2012) and in the first application in The Netherlands (Het Groene Eiland) did not meet the expectations (Lürling and Van Oosterhout, 2013a). Recent experiments showed that the dose of 100:1 Phoslock®:P as recommended by the manufacturers was too low (Reitzel et al., 2013a,b).

The effectiveness of La to bind FRP is hindered by naturally occurring compounds such as humic substances. Although it is plausible that naturally occurring oxyanions (in particular carbonates) hinder this effectiveness as well (Johannesson and Lyons, 1994), we focus on humic substances because the actual DOC concentrations in many (Dutch) lakes (e.g. 2–20 mg l<sup>-1</sup>; De Lange, 2000) are in the range where a reduction of the effectiveness might be expected. Complex-formation of La with humic substances was predicted at 5 mg l<sup>-1</sup> DOC (Tang and

Johannesson, 2003) and experimentally demonstrated for example at 10 mg l<sup>-1</sup> Aldrich humic acids, natural organic matter and Suwannee River fulvic acids (Sonke and Salters, 2006; Tang and Johannesson, 2010a,b). Chemical equilibrium modelling suggested that La complexation with humic substances is dominated by humic complexes from pH 4 upward (Sonke, 2006). It is suggested that humic substances may have caused the La-modified bentonite clay (LMB) to be less effective than theoretically expected (Lürling and Faassen, 2012; Lürling and Van Oosterhout, 2013a; Reitzel et al., 2013b), i.e. through the formation of complexes, the humic substances physically hinder the precipitation of La with FRP. Humic substances are known to form complexes with metals (Van Dijk, 1971; Rashid, 1974) and as such could potentially reduce the P-removal capacity of the LMB. This is an important notion as eutrophic/dystrophic lakes tend to have higher DOC concentrations (on average 10–30 mg l<sup>-1</sup>) than oligo/mesotrophic ones (on average 2–3 mg l<sup>-1</sup>) (Thurman, 1985). Furthermore, climate change is predicted to increase leakage of terrestrial humic substances to surface waters leading to “brownification” (Monteith et al., 2007; Ekvall et al., 2013). Hence, the potential effect of humic substances on the efficacy of La modified clay for eutrophication control should be taken into consideration. To our knowledge no controlled experiments testing the effect of humic substances on the FRP removal by the LMB have been reported in the scientific literature. As we suspected humic substances to interfere with the FRP binding capacity of LMB, we conducted controlled laboratory experiments to measure the FRP removal by the LMB in the presence and absence of humic substances. We tested the hypotheses that the presence of humic substances influences the FRP removal of the LMB and that this influence depends on humic substance concentration.

## 2. Materials and methods

### 2.1. Chemicals

The lanthanum modified bentonite, LMB, (Phoslock®, alleged 5% La) was supplied by Phoslock Europe GmbH (Ottersberg, Germany). Humic substance was obtained from Sigma–Aldrich® Chemie GmbH (Steinheim, Germany) as humic acid sodium salt, technical grade (CAS: 68131-04-4). Dipotassium hydrogen phosphate (CAS: 7758-11-4) was obtained from Merck KGaA (product no. 1.05104.1000, Darmstadt, Germany).

### 2.2. Chemical equilibrium modelling

The effect of humic substances on the P-removal efficiency of Phoslock® was evaluated by chemical equilibrium modelling using the program CHEAQS Pro (release P2013.1; Verweij, 2013). In this program Model V/WHAM-W (Tipping and Hurley, 1992; Tipping, 1994) was chosen to evaluate the formation of complexes of lanthanum with humic acids. Model V/WHAM-W is a discrete site model for humic-ion complexation using carboxylic and phenolic groups as two main types of functional groups (Sonke, 2006). The model was run with: 2182 µg l<sup>-1</sup> La (based on 50 mg l<sup>-1</sup> Phoslock® containing 4.37% La that was determined by ICP-MS in five different batches of

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