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Phosphate adsorption to iron sludge from waterworks, ochre precipitation basins and commercial ferrihydrite at ambient freshwater phosphate concentrations

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ABSTRACT
Measures such as storm water ponds, constructed wetlands and buffer strips along streams are used to reduce diffuse phosphorus (P) loading to surface waters. These systems often retain particulate P well, whereas the retention of dissolved P is less efficient and might require addition of P adsorbents. In this study, we screened waterwork ochre sludge (WWS) originating from groundwater treatment and ochre sludge from ochre precipitation basins along streams for their applicability as P adsorbents at ambient P concentrations. We compared with a commercial ferric hydroxide (CFH™) for which adsorption properties is well described. The adsorption capacity of 9 products was measured over 24 h at different P concentrations (5–2000 µg L⁻¹), a range that covers Danish drainage water and stormwater. WWS desorbed phosphate at concentrations below 50–200 µg P L⁻¹ and should only be considered for use in systems with a constantly high load of dissolved P. High affinity combined with little or no desorption characterized the commercial product and the ochre sludge from the precipitation basins, rendering these useful for treating drainage water and storm water. The study underlines that waste products may act as potentially effective P adsorbers at environmentally relevant P levels.

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KEYWORDS
Run-off; ochre; P removal; reuse; Fe products

1. Introduction
Phosphorus (P) plays a major role in the eutrophication of freshwater ecosystems [1]. In Europe, reduction of the nutrient discharge to the aquatic environment has been obtained through implementation of several actions plans focused on decreasing P loading from point sources, such as sewage treatment plants, as well as by stricter regulation of agricultural practices [1]. Despite these efforts, P loading often remains too high to obtain good water quality [1]. Today, the input of P to the aquatic environment in northwest Europe mainly originates from diffusive run-off from farmland and urban areas [2]. In order to obtain good water quality and thereby fulfil the objectives of the European Water Framework Directive, implementation of and improvement in different techniques to lower diffusive nutrient loading are essential. Especially methods to target dissolved inorganic P are needed since this is assumed to be readily bioavailable. Several techniques to reduce P run-off already exist and are in use, for instance buffer strips along streams, constructed wetlands and storm water ponds with and without P-adsorbing filter systems. These systems are highly dependent on trapping the particulate P by settling of particles, plant uptake of phosphate and/or free adsorption capacity for P. Most of the existing systems are efficient at retaining particulate P and less effective at retaining dissolved P [3]. Thus, attention is currently paid to low-cost phosphate-sorbing materials, such as blast furnace slag, crushed concrete, red mud, fly ash, Al and Fe water treatment residuals (WTR) and ochre sludge from different sources [4–6]. The products will typically adsorb phosphate due to a high content of Ca (high pH products) or a high content of Fe or Al oxy-hydroxides that adsorb phosphate at lower pH than the Ca-rich products [6]. In engineered systems that discharge water directly into natural ecosystems, Al- and Fe-rich products seem preferable since Ca-rich products may require pH neutralization of the discharged water [5,6].

Several studies have examined the adsorption capacity for phosphate of Al- and Fe-rich WTR [7–11]. It is often waste products from the first step in drinking water production from surface water in which Al- or Fe-rich flocculants are added to precipitate suspended solids and phytoplankton. Similar adsorption studies have been performed on ochre sludge from groundwater treatment plants (where iron is precipitated during oxygenation of the groundwater) [12,13] and on iron sludge from wastewater from coal and metal mining activities [14–18].
studies, the adsorption capacity varies from 3 [9] to 32 mg P g\(^{-1}\) [11]. Although all the studies demonstrate effective phosphate adsorption by iron products, only few of them have tested the adsorption capacity at phosphate concentrations below 1 mg P L\(^{-1}\) [11,16].

For some type of ochre sludge, there is a risk of high content of heavy metals in the products which may cause environmental concern. For instance, Fenton et al. [14,15] found that acidic ochre sludge from abandoned mines can leach heavy metals, whereas Habibian-dehkordi et al. [16] and Heal et al. [19] only observed limited leaching especially when the products were mixed in soils. Although ochre sludge from groundwater oxygenation generally has a low content of most heavy metals, there is a risk of a high content of Arsenic (As) [20,21]. Hence, the assessment of the content of heavy metals in the products is inevitable when different waste products are screened for their applicability as P adsorbents in treatment facilities treating storm water and drainage water.

In some parts of Europe, drainage water discharged from specific soil types may have P concentrations above 1 mg L\(^{-1}\) [12]. In Denmark and other low-land countries with intensive agriculture, however, drainage water typically exhibits much lower P concentrations albeit run-off from specific soils or first flush during rain events may increase total phosphorus (TP) levels [22–24]. Nielsen et al. [23] measured TP concentrations in 10 drains from fertilized agricultural fields during the wettest season and found these to vary between 0.013 and 0.063 mg P L\(^{-1}\). In a large-scale study including 254 drains distributed across Denmark, the median concentration of phosphate was found to be 0.035 mg L\(^{-1}\), and only 15–20% of the drains had concentrations above 0.1 mg L\(^{-1}\) [24]. Only two of the drains exhibited concentrations as high as 2.2 and 4.7 mg L\(^{-1}\) P. These two drains received water from an old marine sediment bed or from humic-rich soil. [24] Also, inlets to storm water ponds receiving water from industrial areas, urban areas or rural areas had median flow-weighted TP concentration of 0.060 mg L\(^{-1}\) in the 66 investigated ponds, although the TP concentration could reach a level of 1 mg P L\(^{-1}\) or higher during first flush [22,25]. Only run-off consisting of nutrient-enriched storm water because of the presence of companies selling and handling fertilizers, or similar point sources in the catchment, demonstrated a median concentration of 0.372 mg L\(^{-1}\) of which dissolved P constituted about one-third [25]. Most often, TP is evenly distributed between dissolved and particulate P [22,24,25]. In catchments with sensitive recipients, it may be required that both particulate P and dissolved P are retained to very low concentrations in the recipient inlet. Thus, phosphate adsorption onto P-adsorbing materials should be investigated at low phosphate concentrations in order to test the potential of these for use as the filter materials in, for instance, storm water ponds or as a soil amendment in vegetated buffer strips along streams. In this study, we test if ochre sludge from groundwater treatment plants for drinking water and ochre sludge from ochre precipitation basins can be used to retain P at environmentally relevant low P levels and we compare it with a commercial ferric hydroxide product (CFH 12\(^{\text{TM}}\)) for which P sorption characteristics have been reported previously [13]. Thus, two quick 24 h adsorption/desorption experiments combined with IOS–ICP measurement of heavy metals in the products are used to screen the products for their applicability as the filter materials in, for instance, buffer strips. The ochre sludge products are tested because it would provide a double benefit if they are suitable. At present, they represent a waste problem in Denmark.

2. Methods

2.1. Sampling and characterization of iron products

The iron products used in this study were derived from five waterworks and two ochre precipitation basins in Denmark together with the commercial product CFH 12\(^{\text{TM}}\), consisting of dried amorphous iron hydroxide manufactured by Kemira. This product is normally used in waterworks to adsorb arsenate and phosphate. CFH 12\(^{\text{TM}}\) has been tested by Lyngsie et al. [13], who, based on X-ray diffraction and Raman extraction, characterized it as a poorly ordered Fe-oxide. In our study, we used the product in its original form and in a crushed and screened form (<180 µm).

Ochre sludge from waterworks originates from oxygenation of iron-rich groundwater and should not be confused with WTR, which are waste products from the first step in drinking water production from surface water. The ochre sludge samples were collected from waterworks in different regions of Denmark and were selected based on a map from the Danish Geological Survey showing different P concentrations in the groundwater [26]. We aimed at obtaining sludge from groundwater with low (<0.05 mg P L\(^{-1}\)), medium (0.05–0.1 P mg L\(^{-1}\)) and high (>0.3 mg L\(^{-1}\)) concentrations of TP. Due to low ochre production in sites with low P, we ended up with one sample from a high P site (Hjørring WW), three from medium to high P sites (0.1–0.3 mg P L\(^{-1}\), Lybæk Mose, Holmsland and Slagelse WW) and one from a low to medium P site (Farversmølle 0.12 mg P L\(^{-1}\)).
Both ochre precipitation basins are situated in the western part of Denmark. Their purpose is to increase Fe$^{2+}$ oxidation and precipitate ochre before it reaches natural streams. Hence, ochre sludge from both watersheds and precipitation basins is considered waste products.

Total concentrations of Fe, P, aluminium (Al), manganese (Mn), magnesium (Mg), calcium (Ca), arsenic (As), copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), lead (Pb) and zinc (Zn) were determined by inductively coupled plasma optical emission spectroscopy (ICP–OES, Perkin Elmer Optima 2100 DV) on a 0.2–0.5 g dried sample digested in 10 mL concentrated HNO$_3$ at 400 W, 200°C and 800 psi for 15 min in a MarsXpress microwave from CEM Corporation. Particle size was determined on a Mastersizer 3000 from Malvern and divided into pre-selected intervals. Due to the large particle size of CFH 12$^{TM}$, size separation was performed manually. Oxalate–oxalic acid extractable iron was extracted in 0.2 M oxalate–oxalic acid (pH 3) for 2 h in darkness according to Schwertmann [27].

Wet sludge was used for the extraction. Oxalate extractable iron was determined spectrophotometrically using Ferrozin [28].

### 2.2. Adsorption experiments

Adsorption experiments were conducted on fresh iron sludge samples. Wet iron sludge with a dry weight (DW) of 12–13 mg was mixed at low speed for 24 h in 50 mL 2 mM sodium bicarbonate solutions with PO$_4^{3-}$ concentrations of 0, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2 mg P L$^{-1}$. Due to the 4–5 times lower content of Fe in the ochre sludge from Hvirlå basin, 47 mg DW was used for this material. For each concentration of PO$_4^{3-}$ also a blank sample without iron sludge was included to correct for PO$_4^{3-}$ adsorption onto container walls. pH was adjusted to 7 by HCl or NaOH and remained neutral during the adsorption experiment. pH 7 and bicarbonate was used to mimic natural conditions. Afterwards, the samples were centrifuged for 10 min at 2000g and the supernatant was filtered. Soluble molybdate reactive P (SRP) was measured in the filtrates according to Koroleff [29]. It was tested if SRP differed between filtrates filtered on a 0.2 or 0.45 μm cellulose membrane filter. No difference was observed and 0.45 μm filters were subsequently chosen for the main experiment.

Another 24 h adsorption experiment was performed with agricultural drainage water from three different locations using the same method used for artificial water except that the P concentrations and the pH in the drainage water were not adjusted. The soil at the three locations ranged from clayey to sandy. The drainage water from the three different locations differed only slightly in SRP concentrations, from below the detection limit in the Egeskov drainage water to 1 μg P L$^{-1}$ in the Spjald drainage water to 10 μg P L$^{-1}$ in the drainage water from Odder. Alkalinity was 0.6 meqV L$^{-1}$ in the Spjald sample, 3.4 meqV L$^{-1}$ in the Odder sample and 5.3 meqV L$^{-1}$ in the Egeskov sample.

### 3. Results

#### 3.1. General characteristics

Iron contents in the various samples ranged from 43 to 547 mg Fe g$^{-1}$ DW; however, the samples also contained small amounts of Ca (2–90 mg Ca g$^{-1}$ DW) and Mn (up to 72 mg Mn g$^{-1}$ DW) (Table 1). The main part of the iron was oxalate extractable and most samples exhibited very low contents of Al and Mg (Table 1). The heavy metals content varied between samples, but in several cases the content of at least one heavy metal (As, Cd and Ni) was above the Danish limit for application of waste products on farmland (Table 1). Only Holmsland waterwork ochre sludge (WWS) and iron sludge from the Hvirlå precipitation basin fulfilled all the criteria thresholds regarding heavy metals. The waterwork samples of iron sludge had P contents between 15 and 38 mg g$^{-1}$ DW (Table 1). In contrast, the samples from the iron precipitation basins and the commercial iron hydroxide CFH 12$^{TM}$ had very low P contents (<1 mg P g$^{-1}$ DW). The weight ratio of Fe to P varied from 10.4 to 14.6 in the waterwork sludge, but was 47 in the sludge from the Hvirlå precipitation basin (Table 1), whereas the ratio could not be calculated for Spåbæk and CFH-12$^{TM}$ due to P contents below detection limits.

The five WWS samples demonstrated a relatively similar particle size distribution (Table 2). The main particle fractions were in the 2–10 μm and the 10–100 μm size class, but the Slagelse and Holmsland WWS also contained a significant fraction below 2 μm (26–35% of total). The iron sludge from Spåbæk basin showed a similar size distribution as that of the WWS, whereas the sludge from Hvirlå mainly contained particles larger than 100 μm. The crushed CHF 12$^{TM}$ was sieved on a 180 μm mesh net, and the remaining particles varied in size mainly from 10 to 180 μm. In comparison, 88.6% of the original CFH 12$^{TM}$ was larger than 500 μm, 7% ranged within 125–500 μm and 1.6% was below 125 μm.

#### 3.2. Adsorption experiments

The 24 h adsorption experiment performed in 2 mM bicarbonate solution spiked with phosphate revealed that phosphate was desorbed from all the WWS at
concentrations up to 0.050–0.200 mg P L\(^{-1}\). The Slagelse WWS desorbed phosphate until 0.050 mg P L\(^{-1}\), whereas the Lybæk WWS and Farversmølle WWS desorbed phosphate at concentrations up to 0.200 mg L\(^{-1}\) (Figure 1). Above these concentrations, the WWS adsorbed phosphate more effectively as the initial phosphate concentrations increased (Figure 1). Hence, at an initial concentration of 1–2 mg P L\(^{-1}\), 51–82% of the phosphate in the solution was adsorbed. In contrast, the iron sludge from the Spåbæk basin and the CFH 12™ product adsorbed phosphate efficiently (up to 100%), even at an initial concentration as low as 5 µg P L\(^{-1}\).

The crushed CFH 12™ had a higher affinity for phosphate than the original product when applied in the same amount. The sludge from the Hvirlå basin only desorbed phosphate at 0 µg P L\(^{-1}\) and began to adsorb phosphate from a start concentration of 20 µg P L\(^{-1}\), adsorbing only between 11% and 39% of the phosphate at the different start concentrations, though (Figure 1).

When the iron sludge and CFH 12™ were incubated in natural drainage water with SRP concentrations varying from below the detection limit to 10 µg P L\(^{-1}\), desorption of phosphate also occurred. The largest desorption was recorded in drainage water from Egeskov and the smallest desorption in drainage water from Odder. In all cases, less SRP was desorbed in the drainage water than in pure 2 mM sodium bicarbonate solution (Figure 2).

### Table 1. General characteristics of sludge samples from five waterworks (Hjørring, Farversmølle, Slagelse, Holmsland and Lybæk), two ochre precipitation basins (Hvirlå and Spåbæk) and a commercial ferric hydroxide product (CFH-12™).

<table>
<thead>
<tr>
<th>ID</th>
<th>Unit</th>
<th>Hjørring WW</th>
<th>Farversmølle WW</th>
<th>Slagelse WW</th>
<th>Holmsland WW</th>
<th>Lybæk WW</th>
<th>Spåbæk basin</th>
<th>Hvirlå basin</th>
<th>CFH 12™</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>mg g(^{-1}) DW</td>
<td>26</td>
<td>15</td>
<td>38</td>
<td>30</td>
<td>38</td>
<td>BDL</td>
<td>1</td>
<td>BDL</td>
</tr>
<tr>
<td>Fe</td>
<td>mg g(^{-1}) DW</td>
<td>301</td>
<td>207</td>
<td>405</td>
<td>437</td>
<td>397</td>
<td>257</td>
<td>47</td>
<td>547</td>
</tr>
<tr>
<td>Fe/P Weight ratio</td>
<td>11.6</td>
<td>13.8</td>
<td>10.7</td>
<td>14.6</td>
<td>10.4</td>
<td>–</td>
<td>47</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>mg g(^{-1}) DW</td>
<td>1</td>
<td>5</td>
<td>BDL</td>
<td>BDL</td>
<td>1</td>
<td>46</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Mn</td>
<td>mg g(^{-1}) DW</td>
<td>72</td>
<td>14</td>
<td>2</td>
<td>6</td>
<td>11</td>
<td>2</td>
<td>20</td>
<td>BDL</td>
</tr>
<tr>
<td>Mg</td>
<td>mg g(^{-1}) DW</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Ca</td>
<td>mg g(^{-1}) DW</td>
<td>47</td>
<td>65</td>
<td>49</td>
<td>48</td>
<td>51</td>
<td>90</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>Fe ox</td>
<td>mg g(^{-1}) DW</td>
<td>204</td>
<td>234</td>
<td>277</td>
<td>294</td>
<td>245</td>
<td>172</td>
<td>38</td>
<td>282</td>
</tr>
<tr>
<td>As*</td>
<td>ng g(^{-1}) DW</td>
<td>200</td>
<td>170</td>
<td>640</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>6</td>
<td>BDL</td>
</tr>
<tr>
<td>Cu*</td>
<td>ng g(^{-1}) DW</td>
<td>37</td>
<td>6</td>
<td>BDL</td>
<td>1</td>
<td>1</td>
<td>7</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Cr*</td>
<td>ng g(^{-1}) DW</td>
<td>69</td>
<td>23</td>
<td>13</td>
<td>32</td>
<td>34</td>
<td>23</td>
<td>8</td>
<td>21</td>
</tr>
<tr>
<td>Cd*</td>
<td>ng g(^{-1}) DW</td>
<td>6</td>
<td>6</td>
<td>20</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Ni*</td>
<td>ng g(^{-1}) DW</td>
<td>34</td>
<td>4</td>
<td>BDL</td>
<td>4</td>
<td>51</td>
<td>220</td>
<td>13</td>
<td>55</td>
</tr>
<tr>
<td>Pb*</td>
<td>ng g(^{-1}) DW</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Zn*</td>
<td>ng g(^{-1}) DW</td>
<td>70</td>
<td>18</td>
<td>134</td>
<td>41</td>
<td>164</td>
<td>602</td>
<td>41</td>
<td>286</td>
</tr>
</tbody>
</table>

Notes: If the P content was below the detection limit (BDL), it was not possible to calculate the Fe/P ratio. Values written in bold exceed the thresholds for application of waste products to agricultural fields.

*The criteria thresholds for application of waste products such as ochre sludge to agricultural fields are: 25 ng As g\(^{-1}\), 1000 ng Cu g\(^{-1}\), 100 ng Cr g\(^{-1}\), 0.8 ng Cd g\(^{-1}\), 30 ng Ni g\(^{-1}\), 120 ng Pb g\(^{-1}\) and 4000 ng Zn g\(^{-1}\) (implementation of a EU directive from 2006 on sewage sludge [30].

### Table 2. Size distribution of particle size (%) in different types of ochre sludge.

<table>
<thead>
<tr>
<th>Size classes (µm)</th>
<th>ID</th>
<th>Hjørring WW</th>
<th>Farversmølle WW</th>
<th>Slagelse WW</th>
<th>Holmsland WW</th>
<th>Lybæk WW</th>
<th>Spåbæk basin</th>
<th>Hvirlå basin</th>
<th>CFH 12™ &lt;180 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;2</td>
<td>9</td>
<td>9</td>
<td>26</td>
<td>35</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2–10</td>
<td>39</td>
<td>37</td>
<td>28</td>
<td>34</td>
<td>41</td>
<td>29</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>10–100</td>
<td>49</td>
<td>45</td>
<td>30</td>
<td>26</td>
<td>41</td>
<td>65</td>
<td>19</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>100–500</td>
<td>3</td>
<td>9</td>
<td>16</td>
<td>5</td>
<td>5</td>
<td>6</td>
<td>49</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>&gt;500</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
All five types of WWS used in our experiment contained considerable amounts of P (15–38 mg P g\(^{-1}\) DW); in comparison, Chardon et al. [12] worked with WWS with 2.6 mg P g\(^{-1}\) DW. When the five types of WWS were incubated in water with different phosphate concentrations, they therefore desorbed phosphate up to initial concentrations of 0.050–0.200 mg P L\(^{-1}\) depending on the specific product. The originally adsorbed P originates from groundwater that can have P concentrations in the range of 0.1–0.3 mg L\(^{-1}\) in some areas [26]. This corresponds to the concentration range where the WWS types in this study shifted from desorption of P to adsorption of P. Other studies of various iron sludge products have demonstrated that desorption occurs from sludge that is partly to fully saturated with P. For example, Chardon et al. [12] found that saturated WWS desorbed P until the P content declined to approximately 32 mg P g\(^{-1}\) Fe corresponding to a Fe/P ratio of 31 by weight. Ochre sludge from metal and coal mining areas typically saturates at 19–31 mg P g\(^{-1}\) DW [14,15,17]. Hence, an explanation for the observed desorption of phosphate in our study could be that the WWS forms were close to P saturation, possibly resulting in partial desorption of phosphate until a steady state between desorption and re-adsorption was reached.

Adsorption of phosphate to ferric hydroxides occurs in two phases: (1) an initial rapid low-energy phase with adsorption to surface reactive groups and (2) a slow phase controlled by diffusion into micropores [32]. Other adsorption studies found that most of the initial sorption of phosphate to ochre sludge took place within the first few minutes of the study [16,17], especially when initial phosphate concentrations were low [16]. On contrary, diffusion-controlled adsorption can take weeks to months depending on the pore size [33]. In constructed systems such as buffer strips, wetlands or storm water ponds, the contact time might be longer than 24 h (days to weeks) [34] but can also be much less [34,35]. Thus, it is likely that we did not reach a true adsorption/desorption equilibrium within the 24-h exposure; nevertheless, the 24 h adsorption experiment works well as a first-step screening/selection tool for P adsorbents. Furthermore, we expect that the longer contact time will mainly affect the maximum adsorption capacity.

Figure 1. Adsorption of phosphate (mg g\(^{-1}\) DW) during 24 h by nine iron products at varying start concentrations of phosphate. The numbers above the columns show the retention in per cent of the initial amount of PO\(_4^{3-}\).
sorption capacity and not the release of phosphate at low ambient phosphate concentrations since this release seems to be related to the P which is already linked with a product-specific equilibrium phosphate concentration.

Contrary to the WWS, iron sludge from the precipitation basins, especially from Spåbæk, effectively adsorbed phosphate even at low phosphate concentrations, being even more effective than the original CFH 12™ product (not crushed). The higher affinity for phosphate of iron sludge from the Spåbæk and Hvirål precipitation basins compared to the WWS probably reflects the low content of P (<1 mg P g⁻¹ DW) in the initial material. Also the grain size of the material can affect the adsorption. The WWS, the Spåbæk sludge and the crushed CFH 12™ product adsorbed P more effectively at high P concentrations than the large grain-sized CHF 12™ product and the Hvirål sludge at similar total Fe contents. In general, smaller particle sizes may promote a more rapid sorption of phosphate [13] due to the smaller particles constituting a larger specific surface area to which the phosphate can be adsorbed [6]. Over time, the adsorption of P to the larger grain-sized CFH 12™ may increase due to adsorption into micropores [6]. Adsorption of phosphate into micropores makes CFH 12™ effective under both low- and high-flow conditions at an ambient phosphate concentration of 0.3 mg L⁻¹ and makes sure that desorption is limited even under phosphate-free conditions [36]. The major part of the drainage water in Denmark has TP levels below 100 µg P L⁻¹ [24] and storm water often exhibits dissolved P levels of 22–108 µg P L⁻¹ [25]. Due to the high affinity for phosphate even at low ambient concentrations of phosphate, the CFH 12™ as well as the iron sludge from the ochre precipitation basins showed promising properties for utilization in treatment facilities for drainage water and storm water. Because of the larger particle size, the CFH 12™ and the iron sludge from the Hvirål basin are best fitted for use in filter materials since the low particle size of the iron sludge from the Spåbæk basin decreases the hydraulic conductivity of the filter [12]. Chardon et al. [12] suggest a maximum content of fine-grained iron sludge of 10% in a sand matrix in order to achieve acceptable conductivity, whereas the higher conductivity of iron-coated sand allows direct application. Contrary to the CFH 12™ and the ochre sludge from the precipitation basins, the WWS forms tested in this study are only recommended for use as the adsorbent material in buffer strips, storm water treatment ponds or constructed wetlands in sites that are fed with water with constantly high concentrations of phosphate. A good alternative would be to use the products in sewage treatment plants as suggested by Sharma et al. [21]. Alternatively, they could be used as the filter material in simple filter basins to treat rural wastewater from private sewage systems, in which SRP concentrations can vary between 0.3 and 10.6 mg P L⁻¹ [37].

Besides the P adsorption potential, it is also important to screen the ochre sludge for heavy metals since sludge, at least in Denmark, is considered a waste product and
thus is regulated by the stipulations governing management of waste products. Specific threshold values prevail for the different heavy metals in waste products applied on agricultural land. Our screening of the products showed that several had a content of As, Cd and/or Ni exceeding the Danish criteria thresholds. Only two of the products (Holmsland WWS and Hvirlå sludge) completely fulfilled the criteria for waste application on farmland. The leaching of heavy metals from ochre sludge with comparable amounts of heavy metals has previously been tested and found to be product specific [14–16]. Hence, some types of ochre sludge are safe to use [16], whereas others leach heavy metals, probably due to a low pH in the ochre sludge [14,15]. In soils with high anion retention capacity As mobilization is induced by P adsorption due to competition on adsorption sites which is not the case for Cd [38,39]. Adsorption of Cd increases with increasing pH due to an increase in negative surface charge of soil [39]. Hence, for the ochre sludge, it is likely that P adsorption will mobilize As, whereas low pH may play a more important role on release of Cd and other heavy metals. Hence, when a location for remediation options, such as buffer strips, storm water ponds or constructed wetlands, has been chosen, it should be tested if mixtures of soil or sediment with iron products release heavy metals under site-specific conditions.

The present study demonstrated that the adsorption properties of different types of ochre sludge vary with their native P concentrations. Based on a relatively quick and simple screening for P adsorption properties, we can recommend the ochre sludge from the ochre basins and CHF 12™ as the potential P adsorbents for use in facilities treating drainage and storm water. Hence, the iron sludge from Hvirlå seems to be the optimal choice among the waste products tested in this study also due to low heavy metal content. Although CFH 12™ is less cost effective than the waste products, it provides a good alternative in remediation projects where testing of adsorption capacity and measurement of heavy metal content are not possible.

The five WWS products cannot be recommended for use as the P adsorbents in systems treating drainage and storm water seen in the light of the common Danish concentrations of dissolved P, but their application may be considered in wastewater treatment systems where rapid phosphate adsorption at high concentrations of dissolved P are needed and where ‘dilution’ with sewage sludge likely leads to a final product meeting the criteria for heavy metal concentrations in sewage sludge [21]. In conclusion, reutilization of WWS products is preferable to the current disposal strategies of landfill and combustion as long as the use is restricted to P-rich systems in which the additional load of heavy metals is tolerated. Finally, CHF 12™ is very effectively adsorbing phosphate and if waste Fe products cannot be used, this product could be considered for application in filter systems for P removal.

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