Current knowledge on transport and reactivity of technology-critical elements (TCEs) in soil and aquifer environments

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Environmental context. Technology-critical elements, widely used in modern industry, are found in the environment as a result of both anthropogenic usage and natural sources. This review describes current knowledge on the transport of technology-critical elements in sand, soils and aquifer environments. The chemical compositions of the soils and groundwaters influence the transport of technology-critical elements, and natural colloids increase their mobility.

Abstract. Technology-critical elements (TCEs) are now present in soil and aquifer environments, as a result not only of the geogenic origin but also of the recent anthropogenic activities and release. TCEs can interact with all components of the soil and water, which include inorganic and organic ligands (natural organic matter), clays, mineral surfaces and microorganisms. The literature regarding the transport and fate of TCEs in subsurface porous media (e.g. soil and aquifers) is limited and highly diverse. This review offers a detailed analysis of the existing literature on the transport and fate of TCEs in porous media, and emphasises what is still needed to fully understand their behaviour in the environment. Different modes of TCE transport are presented. First, the mobility of TCEs following interaction with colloids (e.g. natural organic matter, clays) is described. For these cases, an increase in the ionic strength and pH of aqueous solutions shows stronger retention or sorption of TCEs on porous matrices. The transport of nanoparticles (NPs) that contain TCEs is presented as a second mode of mobility. The ionic strength of the solution is the key parameter that controls the transport of cerium nanoparticles in porous media; natural organic matter also increases the mobility of nanoparticles. The third part of this review describes sorption and dissolution processes during transport. Finally, results from the field experiments are reported, which show that rare earth elements and indium are transported in the presence of natural organic matter. We conclude this review with suggested directions for future research.

Additional keywords: column experiments, field transport studies, gallium, indium, platinum, rare earth elements.

Introduction

Metals are essential elements for human activity. From the Bronze Age to modern times, humans have been using metals to create tools, and metals have since become an important part of industrial production. Over the past two decades, some trace metal elements – called technology-critical elements (TCEs) – which have received little attention by the scientific community until recently, have been introduced in a wide range of new technologies.

The European Union (EC 2010) identifies TCEs as including rare earth elements (REEs; yttrium and all the lanthanides from lanthanum to ytterbium), platinum group elements (PGEs; ruthenium, rhodium, palladium, osmium, iridium and platinum), and other elements such as gallium, germanium, niobium, indium, tellurium, tantalum and thallium. The mining of TCEs has increased rapidly in recent years. For example, the production of rare earth oxides grew from 80 Gg in 1995 to ~130 Gg in 2017 (Du and Graedel 2011; USGS 2018) and for some of the less abundant REEs (Sm, Gd, Dy, Er, Yb), their use has at least tripled during a 12-year interval (Zaimes et al. 2015). The criticality of these elements arises from their low abundance in the crust as well as their supply and environmental risks (Graedel et al. 2012).

The release of TCEs during mining, production and applications in industry has changed their natural cycles at the Earth’s surface. TCEs can be released to the atmosphere, soils and water, and their possible toxicity and fate in the environment need to be studied to understand their effects on human and animal health, as well as for recycling (Binnemans et al. 2013) and remediation purposes. Moreover, mining exploitation and poor recycling of the metals from technological products can lead to environmental damage (atmospheric, water and soil pollution, vegetation degradation).

The presence of REEs (Elderfield et al. 1990; Gaillardet et al. 2003), PGEs (Dubiella-Jackowska and Namieśnik 2008; Lesniewska et al. 2004), and gallium, indium and other elements (Reimann et al. 2018) in waters and soils has been reported. TCEs were found in natural waters at concentrations of a few nanograms per litre (Table 1). However, the origin – natural
versus anthropogenic – of these TCEs is often unknown. For instance, gadolinium, which is used heavily in medical imaging, has been shown to be mobile in surface water resources (Bau and Dulski 1996; Kulakowski and Bau 2007; Kulakowski and Bau 2013) along with other REEs. Platinum group elements have been found in soils owing to their use in the automobile industry (Whiteley and Murray 2003; Zereini et al. 2000), and anthropogenic indium was also found in rivers (Nozaki et al. 2000). However, the transport paths and mechanisms are not well known.

Technology-critical elements are metals and metalloids, and they can therefore interact with all of the components of soils and waters: inorganic ligands, such as phosphate and sulfates, organic ligands, such as small organic molecules, and natural organic matter, clays, mineral surfaces, such as iron oxides and aluminium oxides, and microorganisms. The redox state of TCEs also influences their fate. Complex chemical interactions can occur among TCEs and soil and water components, which make it more difficult to characterise the TCE behaviour in natural systems. However, most of these elements have been studied very little in the past. Many studies have reported the presence of TCEs in the environment, but fewer have investigated their speciation, even fewer have examined their toxicity, and only a handful of studies have focussed on their transport in porous media. Hydrological processes, such as advection, dispersion and diffusion, can affect the mobility of elements in soil and aquifer environments. Chemical processes will also influence the transport of TCEs. Among them, some chemical processes may have a significant influence:

- Groundwater often contains inorganic complexing ligands, such as carbonates, phosphates or sulfates, which can influence TCE mobility
- Colloids (natural organic matter, clays, minerals, microorganisms) can facilitate TCE transport on porous media
- pH variations can lead to hydrolysis and precipitation of TCEs in the porous medium and therefore limit the TCE transport
- Sorption onto minerals can immobilise TCEs in porous media

### Table 1. Concentrations of TCEs in natural freshwaters

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ng L⁻¹)</th>
<th>Reference</th>
<th>Element</th>
<th>Concentration (µg L⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>&lt;2–160</td>
<td>Filella and Rodushkin (2018)</td>
<td>REEs:</td>
<td></td>
<td>He et al. (2004); Zhou et al. (2012)</td>
</tr>
<tr>
<td>Ge</td>
<td>&lt;5–120</td>
<td></td>
<td>La</td>
<td>0.065–988</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>&lt;2–96</td>
<td></td>
<td>Ce</td>
<td>0.135–1149</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>&lt;2–15</td>
<td></td>
<td>Pr</td>
<td>0.014–294</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>&lt;2–32</td>
<td></td>
<td>Nd</td>
<td>0.065–193</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>&lt;2–14</td>
<td></td>
<td>Sm</td>
<td>0.014–62.35</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>0.005</td>
<td>Ruchter et al. (2015)</td>
<td>Eu</td>
<td>0.016–5.59</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>1–2</td>
<td></td>
<td>Gd</td>
<td>0.011–67.33</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>1300</td>
<td></td>
<td>Tb</td>
<td>0.002–5.58</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.08–0.6</td>
<td></td>
<td>Dy</td>
<td>0.00–9.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ho</td>
<td>0.003–1.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Er</td>
<td>0.03–9.79</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yb</td>
<td>0.013–1.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lu</td>
<td>0.006–0.22</td>
<td></td>
</tr>
</tbody>
</table>
Redox variations can affect the redox state of the TCEs themselves or disturb redox-sensitive minerals that can sorb TCEs on their surface.

The literature regarding the transport in porous media of TCEs is limited, in terms of the number of TCEs studied and the conditions under which their transport and fate have been examined, and highly diverse, in the sense that TCE fate has been investigated for different forms of TCEs (as ions or complexes in solution and as nanoparticles) and for different media (sand, soils, aquifer materials). This review offers a detailed analysis of the existing literature on the transport of TCEs in sand, soils and aquifer materials, and emphasises what is still needed to fully understand their behaviour in these environments.

Owing to the limited number and diversity of existing studies dealing with TCE transport in soil and aquifer environments, a coherent synthesis of the current state-of-the-art is organised as follows. In the section titled Colloid-facilitated transport, the colloid-facilitated transport of TCEs is investigated. Colloids are known to be very mobile in porous media and, therefore, are significant in the transport of trace metal elements (Kretzschmar and Schäfer 2005; Kretzschmar et al. 1999; Ryan and Elimelech 1996; McCarthy and Zachara 1989). In batch experiments, natural organic matter is known to affect the sorption of TCEs onto minerals (Abrahamsen et al. 2006; Armstrong and Wood 2012; Tang and Johannesson 2010; Ledin et al. 1994) and can therefore play a role in their transport in porous media. Here we review papers that focus mostly on the impact of natural organic matter on TCE transport. First, we examine how natural organic matter influences the transport of europium in simple media, such as quartz sand, and in aquifer materials. The influence of organic matter and clays on the transport of cerium salt in aquifer materials is then considered. We also review studies that focus on simultaneous transport and competition of REEs in laboratory soil leaching experiments. The transport of other TCEs that have received recent, limited attention – indium and gallium – is then surveyed in quartz sand in the presence of different organic colloids. The transport of nanoparticle TCEs is examined in Nanoparticle transport. Sorption processes focuses on sorption processes in porous media, as REEs are known to sorb onto minerals in batch experiments (Tang and Johannesson 2003; Coppin et al. 2002). Here, we examine papers regarding the transport of europium in a granite fracture, the transport of cerium in a carbonate fracture, and the transport of gadolinium in soil using laboratory-controlled experiments. Field and lysimeter studies investigates TCE transport in field studies. The transport of neodymium and europium in a radioactive waste disposal site, as well as the transport of indium in field lysimeters are examined. The last section concludes with suggestions for future research.

**Colloid-facilitated transport**

Natural and engineered colloids are known to impact the mobility of metals in porous media (Kretzschmar et al. 1999), and, therefore, the majority of studies in porous media have focussed on the impact of colloids on TCE transport. Attention has been concentrated on the behaviour of REEs in soils, with the fate of REEs being investigated mostly in the context of nuclear energy.

**Rare earth elements**

Rare earth elements have the same chemistry as americium, curium and plutonium in their trivalent state, with the advantage of being non-radioactive. As a consequence, REEs have been widely used as surrogates to investigate the transport of these actinides in soils (Randall et al. 1994; Warwick et al. 2000; Kim et al. 1994). Trivalent REEs are also fission products of the nuclear cycle and are found in nuclear wastes that can be released accidentally to the environment. Europium has thus received particular attention from the radiochemistry community, as a representative of REE chemistry.

Several studies have focussed on the transport of Eu(III) in the Gorleben site (Lower Saxony, Germany), which was proposed by the German government to become a long-term repository for nuclear waste. The aquifer is rich in organic matter, composed mainly of humic and fulvic acids (Kim et al. 1994).

Kim et al. (1994) focussed on understanding the mobility of trivalent europium associated with humic acid colloids. Laboratory column experiments were performed under anaerobic conditions using sand collected at the Gorleben site together with groundwater collected under the same anaerobic conditions. Europium was introduced in the groundwater in its trivalent form at a concentration of 0.5 µM; 98% of Eu was expected to complex to the humic substances. After 7 days, the recoveries of Eu(III) were 64.3%, 71.2% and 91.6% for flow velocities of 16.4, 66.2 and 378 m year⁻¹ respectively (the flow velocity in the Gorleben aquifer varies between 1 and 48 m year⁻¹). Thus the flow rate has a strong impact on the total recovery of europium, with more colloids being retained in the column at lower flow rates. However, the retardation factor (ratio of the number of pore volumes required for the metal to reach half of its final outlet concentration, as compared with that of the tracer), R°, is not impacted by the flow rate and was ~1 in all cases (respectively, 0.90, 0.98 and 1.2). These results suggested that trivalent Eu cations were stabilised in groundwater with humic colloids, and that the complexes essentially did not interact with quartz sand. However, in some experiments, while as much as 30% of Eu(III) was not recovered, the mechanisms of retention remain unknown. It is important to note also that the concentration of dissolved organic carbon in the Gorleben aquifer was high and not representative of natural systems (0.5–1 mg L⁻¹ for groundwater, 1–10 mg L⁻¹ for lakes and rivers, 10–50 mg L⁻¹ for wetlands; Thurman 1985, Chapter 10, ‘Aquatic humic substances’; Tipping 2002). It can be speculated that experiments with lower concentrations of humic may show different behaviours of Eu(III).

In this study performed under anaerobic conditions, europium was only in its trivalent state and not reduced to its (+II) state. Two rare earth elements, Eu and Ce, can exist in an oxidation state different than the (+III) state in natural systems. Europium can be found as (+III) and (+II) and Ce as (+III) and (+IV). Therefore, focusing only on Eu as a representative of all REEs should be done with caution in anaerobic experiments, because the reduction of Eu(III) to Eu(II) can alter the retention dynamics. Pourbaix diagrams can be used to estimate the redox state of the metal; redox speciation can be studied as shown by Artinger et al. (2000) in the case of neptunium speciation.

Some studies have focussed on the transport of europium in sand (Randall et al. 1994; Yoshida and Suzuki 2006; Nagao et al. 1998); a summary of three experiments is given in Table 2. All of the experiments were performed in sand with different compositions. Inorganic species of europium were shown not to be eluted in quartz sand, as evidenced by Kim et al. (1994) and Randall et al. (1994). Europium was either complexed to the surface sites of sand or precipitated owing to the low solubility of the Eu and the high concentrations of the metal and pH.
Transport of TCEs in porous media

Table 2. Parameters investigated in the studies of europium transport in sand

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Column length</td>
<td>length 15 cm, diameter not given</td>
<td>length 31 cm, diameter 1.5 cm</td>
<td>length 2.5 cm, diameter not given</td>
</tr>
<tr>
<td>Flow rate</td>
<td>0.16 mL min⁻¹</td>
<td>0.17 mL min⁻¹</td>
<td>0.85–0.96 mL min⁻¹</td>
</tr>
<tr>
<td>Effective porosity</td>
<td>not given</td>
<td>0.5</td>
<td>not given</td>
</tr>
<tr>
<td>Composition of the sand</td>
<td>quartz sand, clay (mica, kaolinite and chlorite)</td>
<td>quartz sand (75–200 μm), surface area 0.1 m² g⁻¹</td>
<td>sandy soil (quartz and feldspar)</td>
</tr>
<tr>
<td>Eu concentration</td>
<td>152Eu 24 800 cpm mL⁻¹</td>
<td>Eu 40 μM</td>
<td>510 cpm mL⁻¹</td>
</tr>
<tr>
<td>Humic substances</td>
<td>36 mg L⁻¹</td>
<td>40 mg L⁻¹ of purified Aldrich HA filtered at 0.45 μm</td>
<td>20 mg L⁻¹</td>
</tr>
<tr>
<td>pH</td>
<td>6.55</td>
<td>6</td>
<td>5.2–5.5</td>
</tr>
<tr>
<td>IS</td>
<td>5.83 mM</td>
<td>1–100 mM</td>
<td>10 mM</td>
</tr>
</tbody>
</table>

(∼7–8) used in the experiments. Europium mobility is therefore the outcome of complication of the metal with humic substances. Randall et al. (1994) performed tests in the presence of humic acid, and showed by speciation experiments that only 20% of the Eu was bound to humic substances. Therefore, the recovery of Eu was very low (11%), which indicated that Eu ions have a high affinity to sand. Kim et al. (1994) reported that 98% of Eu was bound to the humic acids. The different observations of the two studies can be explained by the speciation of Eu in solution.

Yoshida and Suzuki (2006) focussed on understanding the influence of the ionic strength and the presence of organic matter on the transport of europium in quartz sand. The experimental conditions (Table 2) were very similar to those of Randall et al. (1994) except for the length of the columns. At ionic strengths of 1 and 10 mM, Eu was not eluted after 6 pore volumes in the absence of humic acid; the authors concluded that europium is not mobile in quartz sand at these ionic strengths. Note, though, the experiments were of very short duration and that inorganic europium may be transported on longer time scales. However, at a NaClO₄ concentration of 100 mM, inorganic Eu was highly mobile and its recovery reached 61%. This was the first experiment showing significant europium mobility in a simple quartz sand medium. An increase in ionic strength led to the screening of quartz sand sorption sites by sodium ions, and prevented europium sorption. In saline systems, the mobility of rare earth elements can therefore be relatively high. In the presence of humic substances, the ionic strength appeared to have little influence on Eu recovery, as shown in Fig. 1 (9%, 13% and 10% for ionic strengths of 1, 10 and 100 mM respectively), although humic acid recovery varied (100%, 74% and 37% for ionic strengths of 1, 10 and 100 mM respectively). At 1 mM, 100% of the humic acid was recovered while only 9% of Eu was recovered. Speciation calculations using Visual MInteq, under these experimental conditions, showed that all of the Eu was expected to be bound to humic acid in solution. At the highest ionic strength, humic acid recovery was only 37% and Eu was 10%, and Eu was still eluted after the end of humic acid elution. Europium was therefore also eluted as inorganic substances. It is noted that the experiments of Yoshida and Suzuki (2006) were performed at a similar flow rate to the studies of Kim et al. (1994) and Randall et al. (1994); however, the experiment durations were much shorter (2 pore volumes), thus explaining the lower recoveries of Eu.

The influence of different types of organic matter was investigated by Nagao et al. (1998): a commercial humic acid (Aldrich HA), an aquatic humic acid (Suwannee River, SRHA), an aquatic fulvic acid (Suwannee River, SRFA), and a groundwater-dissolved organic matter (gDOM) sampled from the Glass Block site at the Chalk River Laboratories, Ontario, Canada. Europium was shown to be very mobile in the presence of Aldrich HA and SRHA with a relative concentration (C/C₀) reaching 0.62 (similar to Kim et al. (1994)), and was less mobile in the presence of SFRA with a C/C₀ of 0.21. In the presence of gDOM, C/C₀ reached 0.4 with a rapid increase compared with the experiments on other organic matter extracts. In addition, the mobility of the different organic matter extracts was studied in the absence and presence of europium. The authors found that dissolved organic matter was more mobile in the presence of europium for the commercial Aldrich HA, SRHA and SRFA extracts, while gDOM mobility was very similar in the presence or absence of europium (C/C₀ = 0.99). The mobility of dissolved organic matter followed the molecular weight of the extract: gDOM had the lowest molecular weight and was more mobile, followed by SRFA, SRHA and Aldrich HA. The origin of the dissolved organic matter extract was also shown to influence strongly the mobility of europium, but not according to the molecular weight or the proton exchange capacity. Nagao et al. (1998) showed that dissolved organic matter extracts with different characteristics affected europium mobility, but further studies are needed to identify the controlling factors.

In summary, europium migration in the presence of humic acid has been shown to depend on the ionic strength (Yoshida and Suzuki 2006) and on the presence of organic matter (Kim et al. 1994; Nagao et al. 1998). At high ionic strength, Eu and humic acid were sorbed on quartz as binary or ternary complexes while
at low ionic strength, Eu-humic acid complexes in solution were dissociated and Eu was adsorbed on quartz. The transport of Eu in the presence of colloids – in media other than quartz sand – was examined for a sandstone (Bryan et al. 2005) in the presence of humic acid. A known volume of Eu solution was injected into a column that was previously equilibrated with humic acid, and the inlet solution was then switched to a humic acid solution. Europium was shown to be retarded in the column as compared with the tracer. However, Eu was found to exhibit a rapid breakthrough, as did humic acid. Bryan et al. (2005) analysed the data using a coupled equilibrium and kinetic model with chemical transport. Europium was considered to be complexed with humic acid as exchangeable or non-exchangeable fractions, and two types of sites (for humic) were used to model the data. The authors showed that equilibrium and kinetic dynamics are needed to describe both the Eu and humic acid mobility in the sandstone.

Cerium has been studied because of its analogy to trivalent actinides. Tran et al. (2015, 2016) investigated the transport of cerium in fractured carbonate rocks, focusing mostly on how the intrinsic formation of cerium carbonate colloids, and the presence of humic acid and bentonite, can affect cerium mobility (the influence of carbonates is discussed in Sorption processes). Tran et al. (2016) used a chalk core to study the impact of bentonite and humic acid on the transport of cerium. The migration of cerium depends on the colloids present in the system; for example, with bentonite, cerium migration was similar to that of a bromide tracer. Cerium was transported mostly as a result of sorption on bentonite colloids. Cerium recovery was lower in the presence of organic matter than in the presence of bentonite (14.85 % versus 20.30 %) but the migration velocity was greater than that of the bromide tracer. Cerium organic matter complexes in solution migrated faster than cerium sorbed on bentonite colloids. In the presence of bentonite and humic acid, cerium recovery was higher than in Cebentonite and Ce-humic acid systems. The presence of humic acid with bentonite colloids led to higher electrostatic repulsions between the colloids, which prevented aggregation and deposition in the fractured rock. The ternary colloids were therefore more stable in solution and migrated in a fracture, which led to the increased recovery of cerium.

Two studies focussed on the leaching column experiments of various trace metal elements, which included REEs already present in the soil. Pédrot et al. (2008) investigated the influence of natural colloids on the transport of trace metal elements, which included REEs, in a wetland organic-rich soil collected in the Kervidy/Coët-Dan catchment, Brittany, France. A percolating solution consisting of 1.88 mM NaCl (ionic strength of the wetland water) was pumped continuously to columns, under aerobic conditions, and samples were collected at the column outlets. Filtration and ultrafiltration at 0.2 μm, 30, 5 and 2 kDa were performed to determine the fractions in which the trace elements were found. REEs were shown to be strongly mobilised by the natural colloids, as expected by the studies on europium. More than 60 % of the REEs were mobilised by the high molecular fractions, between 5 and 30 kDa, where humic acids are found. Significant fractionation was not found to depend on the weight of the REEs. The REEs can associate to humic acids, to iron oxides or can be in ternary complexes of REEs-humic acid-iron oxides, but the humic acids associating with iron nanoparticles and thus the mechanisms of REE leaching are not known.

Hodson (2002) performed a Soxhlet extraction experiment with a cellulose sock filled with 3 cm of quartz, 4 cm of sieved B horizon soil and 1 cm of sieved A horizon soil from a granitic podzol collected from the Allt a’Mharcaidh catchment in Scotland. The two horizons had a similar composition – mostly quartz, plagioclase, K-feldspar – with REEs present. The two horizons differed in their organic matter content (20 % and 5 % for horizons A and B respectively).

The concentration of the majority of REEs was not correlated with time (Table 3), except for Nd, Sm, Gd and Dy. The evolution of REE concentrations with time can reflect different processes occurring in the column, which include dissolution of mineral-releasing REEs, reprecipitation of REE phases, or sorption onto the different soil layers. With a soil pH of ~4, it can be hypothesised that dissolved organic carbon will precipitate on the soil surface with some REEs. The A and B horizons were also rich in Al and Fe, which can, in their oxide form, act as bearing phases for REEs. Nevertheless, the mechanisms in the column are not understood. Hodson (2002) suggested that light REEs were enriched preferentially in the extraction solution, mid REEs were

<table>
<thead>
<tr>
<th>pH</th>
<th>6</th>
<th>9</th>
<th>14</th>
<th>19</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Sm</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Gd</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Dy</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Er</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Tm</td>
<td>0.3</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Yb</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Lu</td>
<td>0.2</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 3. pH, concentrations of dissolved organic and inorganic carbon (mg L⁻¹) and concentrations of REEs (µg L⁻¹) in soil samples from granitic podzol after 6, 9, 14, 19 and 27 days

Y and Tb concentrations were below the limit of detection. Modified from Hodson (2002) with permission from Elsevier.
enriched mostly in the soil, while heavy REEs did not show a specific trend (when fractionation was observed by Pédrot et al. 2008). Release rates calculated by Hodson (2002) suggested that light REEs were released preferentially from the soil compared with other REEs. From this study, it was concluded that investigating the transport of one REE as a proxy for the mobility of all REEs is insufficient, given that they behave differently. Moreover, competition reactions for sorption on soil components that can occur among all of the REEs remain to be elucidated.

The studies of Pédrot et al. (2008) and Hodson (2002) suggested that the role of organic matter and iron and aluminium oxides as REE-bearing phases need to be investigated under different redox conditions, because they can affect REE speciation. In particular, reduction can dissolve the oxides and release the sorbed REEs.

**Indium and gallium**

A recent study focussed on indium and gallium transport (Ringering et al. 2019), which, as REEs, are expected to be more mobile in the presence of organic matter. The effect of humic acid – as a representative molecular weight organic molecule present in soils and water – on the transport of indium-citrate and gallium-citrate complexes in quartz sand was investigated. Trisodium citrate was used to complex and stabilise indium and gallium, at near neutral pH conditions.

Breakthrough curves showed that while indium and gallium lie in the same column of the periodic table, and are therefore expected to have similar chemistry, their mobilities are different. Indium transport was shown to be slower than that of gallium, with \( C/C_0 \approx 0.8 \) after ~75 pore volumes for indium versus \( C/C_0 = 0.95 \) after ~30 pore volumes for gallium, and with retardation factors of \( R_T = 3.2 \) for indium and \( R_T = 6.0 \) for gallium. The gallium breakthrough curve displayed a longer tailing after the inlet solution was switched to a deionised water solution, which indicated the release of gallium during flushing. This pattern was not observed for indium. The authors suggested that the behaviour of indium and gallium was explained by the presence of citrate. The Ga-citrate complexes were more stable than In-citrate complexes in solution; there was thus a weaker binding of gallium onto the quartz sand. The weaker indium citrate complexes were broken up, which led to the formation of other indium species in solution.

The presence of humic acid influenced the retention of indium and gallium in sand. Binding of indium on quartz sand decreased in the presence of humic acid, which caused indium to be more mobile. However, for gallium, retention in the column was slightly higher in the presence of humic acid. The authors suggested that indium and gallium formed different types of complexes with organic molecules, with gallium complexes more stable than indium complexes. Indium and gallium were both shown to be very mobile in the presence of organic ligands (humic acid or citrate), with indium being mobilised by humic acid, while gallium seemed to be less affected by the presence of humic acid owing to the strength of the gallium citrate complexes in solution.

**Platinum**

Two studies focussed on the transport of platinum compounds used in pharmaceuticals, by using laboratory saturated column experiments (Goykhman et al. 2018; Goykhman et al. 2019). These compounds were found in hospital wastewaters and surface waters (Kümmner and Helmers 1997; Vyas et al. 2014).

Goykhman et al. (2018) studied the transport of oxaliplatin (and its derivative species) in sand and in soil at various redox conditions – oxic, nitrate reducing, iron reducing and methanogenic conditions – and the influence of trisodium citrate and humic acid on the transport. In quartz sand, for oxic conditions, oxaliplatin species were mobile and eluted just slightly after the bromide tracer used in the experiments. Oxaliplatin transport in sand was influenced by the presence of humic acid, but not by the presence of trisodium citrate. Experiments performed at pH 9.8 showed that 4–11 % of oxaliplatin was retained by the sand (Table 4). The sorption of oxaliplatin on sand was shown to be weaker in the humic acid experiments compared with the oxic and oxic-citrate experiments.

Oxaliplatin is less mobile in soil than in sand, and the retardation factors are higher owing to different sorption mechanisms. Oxaliplatin retention was higher in iron-reducing conditions than in oxic conditions owing to the presence of goethite in the inlet solution, which can sorb on quartz and provide additional surface sites for oxaliplatin sorption. Methanogenic conditions and nitrate-reducing conditions did not exhibit significant differences; the amount of oxaliplatin species retained was similar under both conditions, although the

<table>
<thead>
<tr>
<th>Compound</th>
<th>Porous media</th>
<th>Redox conditions</th>
<th>( R_T )</th>
<th>( C/C_0 )</th>
<th>Released/Retained (%)</th>
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<tr>
<td><strong>Oxaliplatin</strong></td>
<td>Quartz sand</td>
<td>Oxic</td>
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<td>3</td>
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<td>0.40</td>
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<td>Nitrate reducing</td>
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<td>Soil</td>
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<td>0.55</td>
<td>7</td>
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<td>0.81</td>
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<td><strong>Cisplatin</strong></td>
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<td>Oxic</td>
<td>1</td>
<td>0.92</td>
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</table>

Transport of TCEs in porous media

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sorption strength was higher under methanogenic conditions. The authors hypothesised that some organic functions of the soil were reduced under methanogenic conditions, which led to more favourable sorption sites, although fewer sites were available.

Goykhman et al. (2019) studied the transport in sand and soil of cisplatin and carboplatin, which are other platinum chemical compounds used in cancer treatment. Carboplatin is highly mobile, has a low affinity with sand and soil, and redox conditions do not affect its retention in soils. Carboplatin retention in sand and soil was shown to be lower than the retention of oxaliplatin and cisplatin; transport in sand and soils was very similar, independent of redox conditions. In the sand experiments, the retardation factors were the same for the three pharmaceutical compounds, but the retention of cisplatin was higher than that of carboplatin and oxaliplatin. The released-to-retained ratio for cisplatin in sand was 7–12%, which indicated weak sorption of cisplatin on the sand surface (Table 4). In soil, the retardation factor of cisplatin was higher, and cisplatin retention under different redox conditions was similar. The released-to-retained ratio was lower in soil than in sand (0.81% and 0.51% versus 7% and 12%, for oxic and methanogenic conditions respectively); these values were comparable to those obtained for oxaliplatin.

In summary, the three platinum-based pharmaceuticals studied in Goykhman et al. (2018, 2019) were shown to exhibit different transport behaviours, although they have very similar structures. Carboplatin displays tracer-like behaviour in sand and soil. Oxaliplatin has tracer-like behaviour in sand but exhibits stronger sorption on soil components. Cisplatin transport behaviour is very different, with higher sorption on sand and soil. These pharmaceuticals undergo transformations in solution with time, and the different speciations of platinum affect interactions with soil components and can explain these different behaviours. Therefore, one platinum-based drug cannot be studied to predict the fate of all platinum-based drugs. Each pharmaceutical should be studied to understand its particular fate in porous media.

General comments and future directions

The transport of TCEs arising from the presence of natural colloids (humic substances) has been studied only for europium, cerium, indium, gallium and platinum. In the case of the rare earth element studies reviewed here, speciation in solution was predicted on the basis of available thermodynamic constants. The predicted speciation was used to explain the retention behaviour of europium and cerium in porous media. However, the redox conditions were not considered to be important parameters in the studies, and no mention was made regarding the redox state of europium and cerium arising from aerobic or anaerobic conditions. Redox conditions are known to impact the mobility of metals in porous media and future studies should focus on this aspect, as was done for the platinum studies.

With regard to indium and gallium, citrate was used to bind the metals owing to their low solubility at neutral pH (Ringering et al. 2019); thus, this study focussed on the impact of humic substances on the transport of indium and gallium citrate complexes, and not only on the transport of indium and gallium (as the presence of citrate alters the retention of the metals in the sand). The use of citrate in this study was relevant regarding gallium because gallium citrate is used in medical imaging (Anderson and Welch 1999) and can therefore reach the environment in this form.

The paucity of speciation studies and the lack of thermodynamic data on indium and gallium prevent a fuller understanding of their mobility in porous media. Most of the existing studies were performed in clean sand, which does not represent the complexity of natural environments. Future studies should focus on experiments that employ real soils, with lower metal concentrations that are more relevant to environmental conditions; indium and gallium are not expected to precipitate at environmental concentrations of 1–100 ng L\(^{-1}\) and neutral pH, and therefore their mobility in soil will be very different as no complexing agents will be needed to keep the metals in solution. Moreover, coupling transport and speciation techniques to understand TCE retention mechanisms would improve the ability to predict TCE mobility in porous media.

Nanoparticle transport

Cerium nanoparticles

Cerium dioxide (CeO\(_2\)) is used widely in industry – mainly as a catalyst (Montini et al. 2016) – and in medical applications to transport drugs in cells (Xu et al. 2013). CeO\(_2\) nanoparticles (NPs) are released to the environment mostly from diesel car catalytic converters and can thus reach surface waters and groundwater. Because of these applications, anthropogenic cerium is released to the environment (Powell et al. 2002). The behaviour of CeO\(_2\) NPs in the environment has become a major concern because these particles can be toxic for humans and fish (Gaiser et al. 2012). In terms of ecotoxicology, CeO\(_2\) NPs were shown to affect the lungs of rats after inhalation (Morimoto et al. 2015). There is thus a need to understand CeO\(_2\) NP behaviour in the environment, by considering water and soils that represent other paths for exposure.

Existing studies have focussed on CeO\(_2\) NP transport in water-saturated, sand column experiments. The influences of physicochemical parameters, such as pH and ionic strength (Li et al. 2011; Liu et al. 2012; Lv et al. 2014; Petosa et al. 2013), the type of sand (quartz or loamy sand), the coating of the NPs (Petosa et al. 2013), and the presence of humic acids (Lv et al. 2014), were investigated (Table 5). The insights obtained from these studies are discussed below.

Ionic strength

Li et al. (2011) studied the impact of pH and ionic strength on the transport of CeO\(_2\) NPs in quartz sand column experiments. To investigate CeO\(_2\) NP deposition, transport and retention, three stages were examined: a deposition stage, where CeO\(_2\) NPs in a background solution with fixed pH and ionic strength were introduced during 6 pore volumes, followed by a desorption stage, where 4 pore volumes of the background solution were introduced, and a re-entainment stage, where milli-Q water was introduced to lower the ionic strength and re-entrain weakly sorbed CeO\(_2\) NPs. At pH 3, no breakthrough of CeO\(_2\) NPs was observed for any of the studied ionic strengths, which indicated aggregation of CeO\(_2\) NPs. At pH 6 and 9, and ionic strength of 10 and 100 mM, there was also no breakthrough of CeO\(_2\) NPs during the deposition stage, but a sharp peak was observed during the re-entainment stage. The decrease in ionic strength during this last stage allowed for the detachment of CeO\(_2\) NPs that were bound weakly to the sand. At 1 mM, complete breakthrough of CeO\(_2\) NPs was observed after 1 pore volume, and a plateau was reached at C/C\(_0\) = 0.9 during the deposition stage, followed by a sharp decrease in CeO\(_2\) NP concentration during the desorption stage, which indicated that the NPs retained in the sand were not released.
The ionic strength of the solution was shown to control, more than pH, the transport of CeO₂ NPs in sand; the authors therefore studied the influence of NaCl concentration at pH 6. A rapid and complete breakthrough was observed at 1 and 2 mM of NaCl during the deposition stage with no significant differences with ionic strength, while at 3 and 5 mM, only partial breakthroughs were observed with a slow increase in C/C₀. The water chemistry therefore controls the transport and retention of CeO₂ NPs. They are less mobile when the ionic strength increases, owing to the compression of the electrostatic double layer of the sand and the NPs, which reduces electrostatic repulsions.

Petosa et al. (2013) studied the transport of CeO₂ NPs coated with polyacrylic acid, in quartz and loamy sand, by altering the ionic strength by the addition of mono and divalent salts. The polyacrylic acid was used to stabilise the NPs; its presence can affect NP mobility. With increasing ionic strength, the NP apparent size increased owing to the lower repulsion between the polyacrylic acid chains, and the surface potential of the quartz sand decreased owing to the screening of the charge and compression of the double layer. Therefore, at high ionic strength, CeO₂ NP aggregation was expected in this case. In addition, experiments using a natural groundwater were performed by Petosa et al. (2013); retention was higher in loamy sand (60 %) than in quartz sand (20 %).

Table 5. Parameters investigated in CeO₂ NP transport studies

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<tr>
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<tbody>
<tr>
<td>Column length (cm)</td>
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<td>14</td>
<td>15</td>
</tr>
<tr>
<td>Column diameter (cm)</td>
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<td>2.5</td>
<td>1.6</td>
<td>2</td>
</tr>
<tr>
<td>Type of sand</td>
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<td>Ottawa sand 50–60 mesh size</td>
<td>quartz sand 50–70 mesh size</td>
<td>loamy sand quartz sand 40–50 mesh size</td>
</tr>
<tr>
<td>Bed porosity</td>
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<td>0.387</td>
<td>0.37</td>
<td>0.4</td>
</tr>
<tr>
<td>Flow rate (mL min⁻¹)</td>
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<td>1.5</td>
<td>4.6</td>
<td>10</td>
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<tr>
<td>Hydrodynamic radius (nm)</td>
<td>152.7 in 1 mM NaCl</td>
<td>172</td>
<td>54–712 depending on ionic strength</td>
<td>234–538.2</td>
</tr>
<tr>
<td>Size by other techniques (nm)</td>
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<td>TEM</td>
<td>TEM</td>
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</tr>
<tr>
<td>pH</td>
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<td>4, 6, 8, 5</td>
<td>8</td>
<td>7, 8, 10</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>1, 2, 3, 5, 10, 100 mM NaCl</td>
<td>10 mM NaCl</td>
<td>0.1–1 M NaNO₃, 0.33–10 mM CaCl₂, 0.33–12 mM MgCl₂</td>
<td>5 and 10 mg L⁻¹ Aldrich HA</td>
</tr>
<tr>
<td>Organic matter</td>
<td>1–6 mg L⁻¹ of SRHA, SRFA, citric acid, alginic acid sodium salt, sodium carboxymethyl cellulose</td>
<td>polyacrylic acid</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Coating of the NPs

The presence of divalent salts (CaCl₂, MgCl₂) strongly influences the retention of CeO₂ NPs. Breakthrough curves for ionic strengths of 0.33 and 3.3 mM CaCl₂, and 0.33 mM MgCl₂, were similar to those for ionic strengths of 100 and 200 mM NaNO₃. Retention in loamy sand was stronger than in quartz sand, which was attributed to CeO₂ NP sorption on clays and iron oxides present in the loamy sand. It was also shown that NP retention was higher in loamy sand when the ionic strength increased owing to screening of Na⁺ or Ca²⁺ ions. When sorption sites on the loamy sand were occupied by the NPs, fewer sites were available for the incoming NPs from the inlet solution. Inorganic NPs were electrostatically repulsed by the NPs already sorbed on the sand, which led to a blocking effect. In addition, experiments using a natural groundwater were performed by Petosa et al. (2013); retention was higher in loamy sand (60 %) than in quartz sand (20 %).

Organic matter

Liu et al. (2012) studied the influence of organic matter of various origins on the transport of CeO₂ NPs. The influence of humic substances (Suwannee River humic and fulvic acids), citric acid, alginic acid and sodium carboxymethyl cellulose on CeO₂ NP transport was studied for various concentrations (1–6 mg L⁻¹). Sand column experiments were performed at pH 4–8 without organic matter (ionic strength 10 mM NaCl). No breakthrough was observed for pH 4 and 6 owing to aggregation, in accord with Li et al. (2011), and CeO₂ NPs were deposited in the first centimetre of sand from the inlet. CeO₂ NP mobility increased with increasing concentration of organic matter. However, the authors noted that the mechanisms controlling this behaviour were unknown because organic matter was sorbed on the sand and also on the NPs. The different functional groups of the organic matter seemed also to affect NP retention, as the breakthrough curves showed similar shapes – but various retentions, with C/C₀ values from 0.7 to 1 – for the same concentration of organic matter.
The effect of humic acid on the transport of CeO$_2$ NPs was also investigated by Lv et al. (2014) at various ionic strengths. Without humic acid, CeO$_2$ NP retention was strong, with only 9.9% eluting after 1 pore volume at pH 7 and an ionic strength of 1 mM owing to particle aggregation within the column. When adding humic acid at concentrations of 5 and 10 mg L$^{-1}$, 65–70% of the CeO$_2$ NPs were eluted with very similar breakthrough curves. The concentration of organic matter did not have a strong impact on the transport of cerium NPs. The effect of pH was minimal on the mobility of CeO$_2$ NPs in the presence of humic acid at 5 mg L$^{-1}$, with very similar breakthrough curves and recoveries, as shown in Fig. 2 (68.6% at pH 7, 71.5% at pH 8, 74.8% at pH 10, at an ionic strength of 1 mM). However, in the presence of 5 mg L$^{-1}$ of humic acid at pH 7, the ionic strength affected the mobility of CeO$_2$ NPs, with Ce recoveries of 68.6% at an ionic strength of 1 mM, 65.3% at 10 mM, 45.6% at 50 mM and 23.3% at 100 mM (Fig. 2). The retention of NPs increased at higher ionic strength owing to screening of Na$^+$ ions that decreased the electrostatic repulsions between the sand and the NPs, and therefore favoured the deposition of CeO$_2$ NPs onto sand.

**Mobility**

Cerium oxide NP mobility depends strongly on ionic strength and on the presence of divalent salts in solution. The presence of a coating alters the NP mobility, as is seen by comparing the studies of Petosa et al. (2013) and Liu et al. (2012). For similar ionic strength, column dimensions, porosity, flow rate and sand size range, CeO$_2$ NPs were fully retained (Liu et al. 2012) at pH 6 and 9; in the presence of a polyacrylic acid coating (Petosa et al. 2013), the CeO$_2$ NPs were completely eluted from the quartz sand column at pH 8. Therefore, the presence of organic molecules that coated CeO$_2$ NPs increased the mobility of cerium in sand.

**General comments and future directions**

From the studies discussed in the section Cerium nanoparticles, it can be concluded that pH has a minor effect on the transport of CeO$_2$ NPs in sand. However, while small local variations of pH in groundwater will not influence the NPs directly, pH variations will affect the soil components (organic matter and minerals) and therefore impact the mobility of CeO$_2$ NPs. An increase in ionic strength will lead to stronger retention of CeO$_2$ NPs mostly when the electrolyte consists of divalent ions, while organic molecules will increase the mobility of NPs. In comparison to cerium ions, cerium nanoparticles have a limited mobility in the presence of organic material.

With regard to colloid facilitated transport, we note that existing studies on cerium nanoparticle transport have been performed only in sand; experiments in soils would improve the understanding of their mobility in natural environments. Redox conditions are not taken into account, although cerium is known to have two oxidation states. Therefore, future studies should investigate the effect of redox on the transport of cerium nanoparticles. Moreover, the presence of a coating—and its nature—on nanoparticles will have an impact on the retention of the NPs (dissolution of the coating or interactions of the coating with humic substances) and should be investigated in future studies.

The use of isotopically labelled nanoparticles was shown to be promising to study the behaviour of nanoparticles at relevant environmental concentrations of a few parts per trillion (Supiandi et al. 2019). This technique could be helpful in measurements of TCE transport in porous media, and in avoiding aggregation that arises only from the high NP concentrations applied to date in transport studies.

**Sorption processes**

**Rare earth elements**

Missana et al. (2008) studied the transport of europium in a granite fracture in the framework of nuclear waste disposal. Clays are known to be a good barrier in the event of nuclear waste release in the environment, because they limit the transport of water to the waste and, therefore, the mobility of radionuclides. The impact of bentonite colloids on the transport of radionuclides in a granite fracture was studied in the laboratory using environmentally-relevant flow rates. Breakthrough curves of Eu showed that it was not retarded compared with tritiated water tracer, owing to the presence of bentonite colloids, but europium recovery was very small (<7%). In solution, 80% of the Eu was expected to be sorbed on bentonite, based on sorption experiments performed by the authors; column experiments with bentonite and no europium showed a bentonite recovery of 25–40%. Therefore, the recovery of europium sorbed onto colloids should be at least 20%. The lower europium recovery observed in the experiments was explained by the reversibility of Eu-bentonite sorption. In a granite fracture, europium was sorbed on granite walls as Eu-bentonite complexes or as the Eu ionic form. Kinetic sorption and desorption play a major role in the transport of Eu in the environment, and in these experiments, Eu was shown to not be mobile, which supported the use of clay barriers for nuclear waste storage.

Cerium can precipitate with carbonates that are ubiquitous in the environment to form carbonated colloids that can be mobile in fractured rocks. Tran et al. (2015) performed cerium transport experiments in a chalk core containing a natural fracture, with a CeCl$_3$ salt dissolved in artificial rainwater similar to that in the Negev Desert of Israel. The solution contained carbonates, so that Ce-carbonate complexes were expected to form in solution and/or to precipitate. The cerium was found to migrate faster than the bromide tracer in all of the experiments, with a maximum relative concentration for cerium lower than that for bromide.

Recovery of cerium colloids was very low for all experiments, with recovery of small colloids (<0.45 μm) being negligible. These smaller colloids were easily sorbed in the...
Gadolinium is used commonly in the medical field, because of its magnetic properties, as the basis for contrast media for magnetic resonance imaging (Caravan et al. 1999). In the ionic form, gadolinium can replace calcium in proteins because of its similar ionic radius (Lansman 1990) and is toxic to humans. However, gadolinium can be employed as a contrast agent for magnetic resonance imaging (MRI) scans in humans when \( \text{Gd}^{3+} \) is chelated by an organic ligand (e.g. diethylenetriamine pentaaacetic acid, DTPA). These complexes are very stable in the human body and are thought to be excreted without transformation after injection. Anthropogenic gadolinium has been shown to be released in natural waters (Bau and Dulski 1996; Klaver et al. 2014).

Wastewater treatment plants are not efficient in removing gadolinium complexes because they are highly soluble and stable. About 10% of gadolinium MRI complexes were shown to be removed from sewage treatment (Telgmann et al. 2012), and three species of gadolinium that were not MRI complexes and not present in the influent were found at the wastewater treatment plant outlet. This indicated that gadolinium complexes underwent transformations in the wastewater treatment plants. Moreover, when present in water and soils, gadolinium complexes can be broken down because of water chemistry and the presence of other ligands that can compete for binding gadolinium. The toxicity of other complexes has not been assessed, and the fate of gadolinium complexes in the environment requires investigation.

Gadolinium-DTPA transport in saturated soil column laboratory experiments was studied by Menahem et al. (2016), for various soil redox conditions, in quartz and in a red sandy clay soil. The authors found no transport of the \( \text{GdNO}_3 \) salt in soil and sand after 6 pore volumes, because gadolinium was sorbed on the soil or sand, or was precipitated with hydroxides and carbonates owing to the high concentration of \( \text{Gd} \) (5 ppm) used in the experiments. The authors calculated that \( \text{Gd}^{3+} \) was likely to precipitate as \( \text{Gd}_2(\text{CO}_3)_3 \) in their experimental conditions, which was then deposited on the soil surface. In contrast, \( \text{Gd-DTPA} \) complexes were shown to be highly mobile in sand and soil for all redox conditions, and migrated together with the conservative bromide tracer used in the experiments. Complete breakthrough was observed after 2 pore volumes, with a larger chemical dispersion of \( \text{Gd-DTPA} \) in soil than in sand owing to the heterogeneity of the soil. It can thus be concluded that \( \text{Gd-DTPA} \) is highly mobile and can be transported over long distances in soil-water environments. Because competition reactions can occur between DTPA and natural organic matter to bind gadolinium, further studies should focus on assessing the impact of soil organic colloids on the transport of \( \text{Gd-DTPA} \).

General comments and future directions

There are very few studies that report on the retention of TCEs arising from sorption processes in porous media, with data available only for europium and cerium. Bentonite was shown to impact strongly the retention of europium in porous media; however, even for this case, future studies should focus on the kinetics of europium–bentonite interactions because the recovery of europium was not comparable to that expected from the batch experiments. The importance of speciation here is again crucial and should be investigated to understand if the retention of europium arises only from bentonite, or arises from the formation of ternary complexes between europium, bentonite and, in this case, the granite walls of the fracture. For the cerium carbonate complex retardation experiments, lower concentrations of cerium and lower flow rates would be more relevant to understand cerium mobility under realistic conditions. However, in the case of nuclear waste storage, it can be expected that cerium will be present in high concentrations in the rock and therefore, the use of the different and high concentrations of cerium in this study was relevant. However, the presence of other radionuclides would change the proportion of cerium carbonate complexes and, therefore, the transport of cerium can be affected. Studies using cerium in the presence of other trivalent and tetravalent elements would help to elucidate cerium retention under relevant conditions.

Field and lysimeter studies

Rare earth elements

Americium and curium were found in groundwater near the burial site of radioactive waste at the Waste Area Group 5-North (WAG-5N) of the Oak Ridge National Laboratory, Tennessee, USA. Transuranic wastes were buried in trenches in this site between 1970 and 1981. The actinides were hypothesised to migrate with natural organic matter. Therefore, europium and neodymium were used as field tracers to understand the transport of actinides in groundwater (McCarthy et al. 1998). Non-reactive tracers (\( \text{MgBr}_2 \), sulfur hexafluoride) were also injected to investigate REE retardation and the effects of meteorological events (rain and storms). Soil at the site was composed mostly of clays minerals and iron and manganese oxides; groundwater was composed mostly of \( \text{CaCO}_3 \) at near neutral pH.

Europium and neodymium were injected for 73 days in 2 adjacent wells, 5 m downgradient from the trenches (McCarthy et al. 1998). In the first well, \( \text{MgBr}_2 \), sulfur hexafluoride and \( \text{EuCl}_3 \) were injected; in the second well, \( \text{MgBr}_2 \) and \( \text{NdCl}_3 \) were injected. Samples taken 10 m and 60 m downgradient in other wells were analysed by inductively coupled plasma spectroscopy to measure concentrations, and by chromatography for speciation information. At 10 m downgradient, \( \text{Eu} \) and sulfur hexafluoride were not detected. However, they were detected 60 m downgradient after 18 days. Neodymium and bromide were detected 10 m downgradient after 2 days of injection.
Bromide arrived after 2 days and reached a plateau after 20 days, then decreased after 60 days. Neodymium arrived together with the bromide (no retardation); however, the breakthrough curve was different and no plateau was reached. Up to 45% of the Nd injected was detected. Samples were filtered at 0.05 μm and Nd was not retained on the filters. Therefore, the authors concluded that Nd was not sorbed on inorganic colloids, but most likely remained in solution. Anion exchange chromatography showed that Nd was present as natural organic matter complexes in solution. The observed decrease in the bromide concentration was likely on account of the large storms during days 22 to 29, i.e. hydraulic gradients increased owing to the storm, which led to a decrease in bromide concentration by dilution. However, Nd was not diluted. The authors hypothesised that Nd precipitated or was deposited in the well. The increase of the hydraulic gradient might have detached Nd aggregates from the well that were subsequently transported, which explained the continuous inflow of neodymium. To conclude, REEs were shown to be very mobile in soil after a few days to a few weeks, owing to the presence of natural organic matter colloids in the groundwater, and hydrological conditions were shown to remobilise Nd that was sorbed in the soil.

Transport of europium colloids in nuclear waste storage was studied by Liu et al. (2013). The Hanford site in Washington State has been the largest nuclear waste storage site in the USA since 1944. Before then, Hanford was a production site of plutonium, and radioactive waste was accidentally released to the subsurface environment from 1944 to 1990, which included radioactive europium. Field lysimeters were used at the site to study the transport of Eu-hydroxy-carbonate colloids when exposed to precipitation and irrigation. Colloid solutions were sprayed at the surface of 4 lysimeters filled with sandy sediment from the Hanford site. One lysimeter (1.35-m diameter) was not covered and received natural precipitation while the other three (0.3-m diameter) were covered and irrigated (124, 248 and 348 mm year\(^{-1}\)) were covered and received natural precipitation while the other three from the Hanford site. One lysimeter (1.35-m diameter) was not sprayed at the surface of 4 lysimeters filled with sandy sediment exposed to precipitation and irrigation. Colloid solutions were injected was detected. Samples were filtered at 0.05

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**Indium**

Three studies focussed on investigating the transport of indium and other metals (Ag, Sn, Sb and Bi) in soils using laboratory column experiments and field lysimeters (Hou et al. 2005; Wen et al. 2013; Murata et al. 2018). In Hou et al. (2005), columns were filled with four types of soils (Andosol, Cambisol, Fluviosol and Regosol) collected in rural areas in Japan. The columns were then placed in grass-covered fields where they were exposed to natural precipitation. The metal solutions were sprayed on the soil surface and small amounts of EDTA and citric acid were also sprayed to ensure that the metals were present in their dissolved form and not as precipitates. The metals were therefore present as complexes of M-EDTA and M-citrate. The columns were covered for two weeks before being exposed to weathering for 18 months, with 1790 mm of precipitation and pH 4.2–6.1. The recoveries of indium in the soils were 100% in the Andosol column, 60% in the Cambisol column, 79% in the Fluviosol column and 66% in the Regosol column. Indium concentrations were higher in the upper two centimetres (~10 mg kg\(^{-1}\) in the upper 2 cm versus 0.1 mg kg\(^{-1}\) at 30 cm) and represented 62% to 95% of the In\(^{3+}\). In the Andosol, In\(^{3+}\) was completely retained in the column, probably because of its affinity to aluminium minerals and Al-humate structures present in Andosol soils. The authors suggested that repetitive sorption or desorption processes of indium onto the Andosol was able to explain the distribution of indium with depth. In the other soils, 21% to 40% of the indium migrated outside of the columns. The mechanisms of migration are not known but ion exchange onto the sorption sites of the soil, and the formation of In-organic matter colloids in solution, might have contributed to the transport of indium. Therefore, in soils with high contents of organic matter, indium is expected to be mobile and can reach groundwater.

Murata et al. (2018) studied the fate of indium, silver, tin and antimony in a lysimeter filled with a contaminated Andosol for 8 years. Hou et al. (2005) applied metals, EDTA and citric acid to the soil surface. Deionised water was applied each day to account for precipitation of 1700 mm year\(^{-1}\). Soil solutions were sampled at various depths from 17.5 cm to 122.5 cm, and the soil core was sampled after 3 months, 1, 2, 5 and 8 years. After one year, more than 80% of the indium was present in the first 2 cm of soil. However, after 2 and 8 years, only 30% and 40% respectively of the indium contents were present in the first 4 cm. Indium is therefore highly mobile in surface soils. The mechanisms of indium transport and retention or release are not known, but the authors suggest that indium is repeatedly sorbed and desorbed from soil and migrates as In(OH)\(_3\)(aq) and In(OH)\(_3\)\(^2+\). The presence of humic acid in the Andosol and the citric acid that was added to the soil can affect indium mobility. As observed by Ringerig et al. (2019) and in the section Colloid-facilitated transport, indium probably also migrated as indium-citrate and indium-humic acid complexes. More studies on the speciation and transport of indium are needed to understand its behaviour in the environment.

The use of EDTA and citric acid to ensure the stability of the metal solutions (and avoid metal precipitation at the soil surface) alters the mobility and retention of the metals and might not be relevant to understand the mobility of TCEs in natural environments. However, the speciation of anthropogenic TCEs in the environment is currently unknown becase field campaigns reported to date have focussed solely on the determination of the total element concentrations and not on TCE speciation. TCEs are probably not transported in the environment in their cationic or anionic forms, but most likely as complexes or nanoparticles. Therefore, field studies should investigate the speciation of TCEs that are released to the environment and changes that occur following their exposure to subsurface components. Transport studies should emphasise the mobility of these TCE species. In some extreme environments (e.g. acid mine drainage sites with very low pH or high concentration industrial effluents), TCEs can be present in their ionic form, and their mobility in the environment will depend on the composition of the soil and groundwater in which they are transported.

Wen et al. (2013) investigated the mobility of indium in laboratory column experiments, and particularly the influence...
of EDTA and acid rainwater on metal mobility. Vertical glass columns were filled from the bottom with 2 cm of quartz sand, 30 cm of unpolluted soil (20.4 % sand, 30.5 % silt, 49.1 % clay and 0.713 % organic matter) and 5 cm of the same soil spiked with metals (In concentration of 50 mg kg$^{-1}$ of soil). The columns were leached for 42 days with 84 mL day$^{-1}$ of inlet solution at a flow rate of 14 mL h$^{-1}$ during 6 h per day. Column experiments were performed with different inlet solutions to examine the influence of acid rainwater on the transport of metals: a leaching solution of deionised water (DW), a leaching solution of artificial acid rainwater (AARW) at pH 4.75, a leaching solution of EDTA in DW (EDTA), and a leaching solution of EDTA in artificial acid rainwater (EDTA-AARW).

Soil solutions were collected at various depths and the concentrations of metal were measured (Table 6). The standard deviations are calculated on six experiments.

Table 6. Recovery of indium in the soil columns and concentrations of indium in soil solutions at different depths (data from Wen et al. 2013)

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>DW 90%</th>
<th>EDTA 73%</th>
<th>AARW 96%</th>
<th>EDTA-AARW 69%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of In ($\mu$g L$^{-1}$) in soil solutions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DW</td>
<td>EDTA</td>
<td>AARW</td>
<td>EDTA-AARW</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.27 ± 0.43</td>
<td>4454 ± 5654</td>
<td>96.3 ± 159</td>
<td>4694 ± 11039</td>
</tr>
<tr>
<td>6.5</td>
<td>0.89 ± 0.17</td>
<td>6456 ± 5223</td>
<td>0.32 ± 0.35</td>
<td>7707 ± 11039</td>
</tr>
<tr>
<td>10.5</td>
<td>1.11 ± 0.91</td>
<td>8038 ± 5011</td>
<td>0.31 ± 0.42</td>
<td>3271 ± 4137</td>
</tr>
<tr>
<td>16.5</td>
<td>0.74 ± 0.22</td>
<td>3641 ± 5285</td>
<td>0.12 ± 0.13</td>
<td>1653 ± 2862</td>
</tr>
<tr>
<td>23.5</td>
<td>0.55 ± 0.11</td>
<td>5.19 ± 1.44</td>
<td>0.25 ± 0.29</td>
<td>587 ± 1436</td>
</tr>
</tbody>
</table>

Regarding indium, owing to the high concentrations used in the studies, citrate and EDTA were used to ensure that indium would remain in solution and not precipitate at the soil surface. Future studies should identify stable TCE species that can reach the environment from anthropogenic uses, and investigate the speciation and transport of these species in porous media.

**Conclusions**

Limited studies of transport of TCEs in sand, soils and aquifer materials of different compositions have been reported. Physicochemical parameters, such as pH and ionic strength, influence the TCE transport. It can be concluded that even if small pH variations have a minor effect on the TCEs themselves, local pH variations in soil water and groundwater will still affect the soil components and therefore impact the mobility of TCEs. An increase in ionic strength will lead to higher retention of TCEs mostly when the electrolyte consists of divalent ions.

In the absence of organic molecules, TCEs precipitate as inorganic complexes or are sorbed onto the sites available on soil, sand and aquifer materials, and so are not mobile. Owing to the limitations of the analytical techniques, all of the transport studies reported to date have involved relatively high concentrations of TCEs (~0.5–5 mg L$^{-1}$ in transport experiments versus ~1–100 ng L$^{-1}$ in natural waters) that are not representative of the concentrations found in the environment, even in contaminated sites. Therefore, in the absence of organic substances, TCEs precipitate owing to their concentrations (higher than their solubility products), thus impacting the retention and mobility of these elements. For this reason, these experiments cannot be considered to represent the real behaviour of TCEs in the environment.

Natural colloids, and mostly natural organic matter, have been shown to increase TCE mobility in soils. The origin of organic matter appears to influence strongly the mobility of TCEs, but further studies are needed to understand how different origins of organic matter influence TCE behaviour. Most studies to date have been performed in sand; experiments in real soils should be investigated to understand TCE behaviour in natural environments.

Natural organic matter has also been shown to influence the TCE mobility in porous media. However, many other colloids are known to influence the fate of TCEs, as seen in batch studies: clays (Tertre et al. 2006), iron and aluminium oxides (Janot et al. 2013), oxide coated organic matter colloids (Tessier et al. 1996), engineered nanoparticles (Stepka et al. 2018), and biocolloids, bacteria and mineral aggregates with bacteria or fungi (Morley 2013).
and Gadd 1995; Zengotita et al. 2017). The influence of these colloids on TCE transport should be investigated in controlled laboratory column experiments, to understand their respective influences and to determine how changes in physicochemical parameters (e.g. pH, pE, ionic strength) affect the fate of colloids and, therefore, the fate of TCEs in soils and aquifer materials. However, laboratory experiments cannot fully describe the fate of TCEs in the environment. Therefore, in future studies, a focus should also be placed on field experiments. The monitoring of TCE mobility in natural porous media is more relevant from an environmental point of view. The impact of precipitation and various water flow rates and compositions should also be studied.

TCEs that are expected to have the same chemistry behave differently in soils. For example, indium and gallium do not behave similarly in the presence of organic matter (Ringer et al. 2019), three similar platinum pharmaceuticals exhibit different transport behaviours (Goykhman et al. 2018, 2019), and REEs can be fractionated into light REEs and heavy REEs (Pédrot et al. 2008). Therefore, studying the behaviour of one TCE as a representative of other TCEs is not sufficient. Competition reactions among TCEs for complexation with natural colloids also need to be investigated.

Future studies should also focus on trying to understand the retention mechanisms of TCEs, their sorption or desorption onto soil and aquifer materials, and their kinetics. A combination of transport experiments and spectroscopic techniques (e.g. XANES, EXAFS, XAS, XRF) may enable a better understanding of the fate of TCEs in soils.

Regarding the transport of other TCEs in soils and aquifer materials, the current lack of speciation data in solution has hindered the scientific community from investigating TCE migration. However, the interest in TCEs by the geochemical community is increasing, and it can be expected that future studies will be performed to understand the fate of TCEs in the environment. A focus should be placed on the understanding of their speciation, to enable better understanding of transport phenomena in the environment. A multiscale approach combining transport experiments and spectroscopy techniques will enable the acquisition of relevant information on TCE fate in the environment that can then be used in geochemical models to predict TCE mobility.

Conflicts of interest
The authors declare no conflicts of interest.

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Y. Kouhaul et al.


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