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# Measurement and recovery of rare earth elements from hypersaline fluids

Clint Noack

2015 November 4

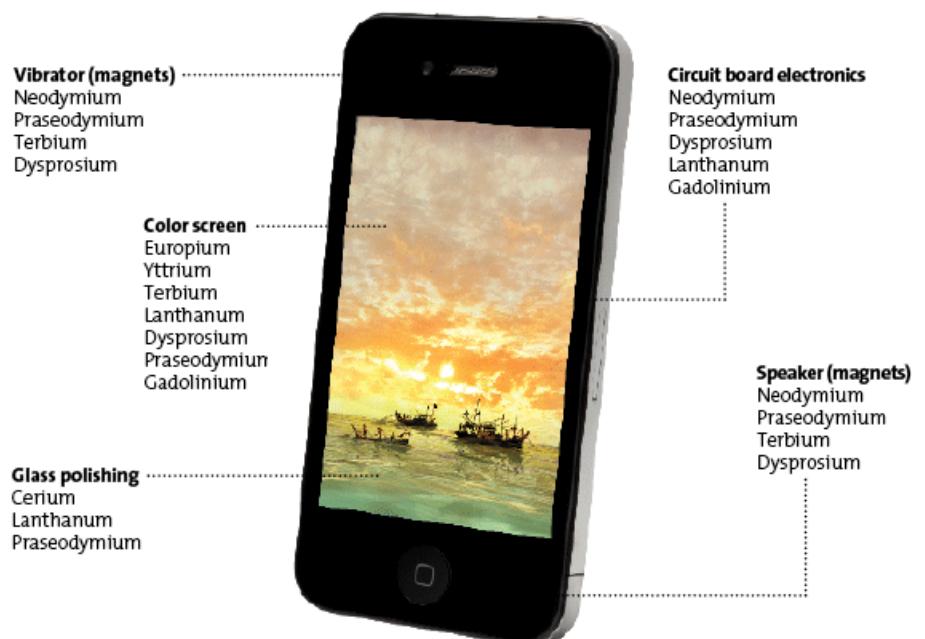
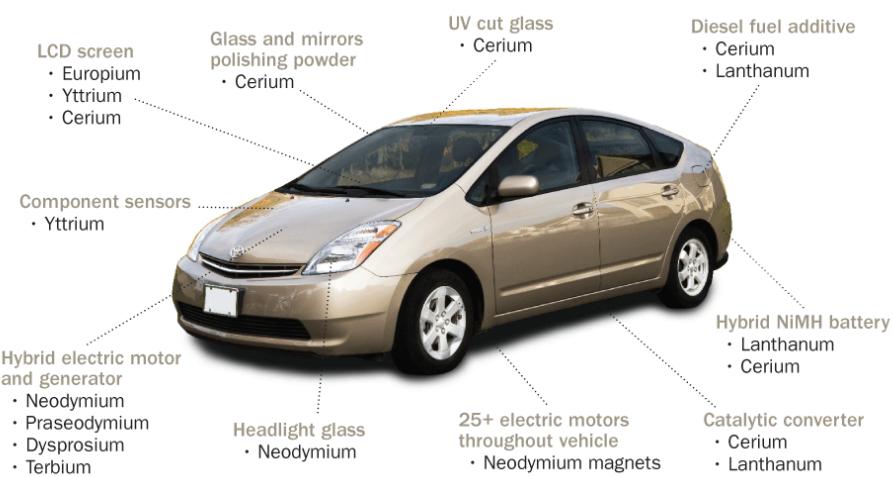
Carnegie Mellon University

Civil and Environmental Engineering

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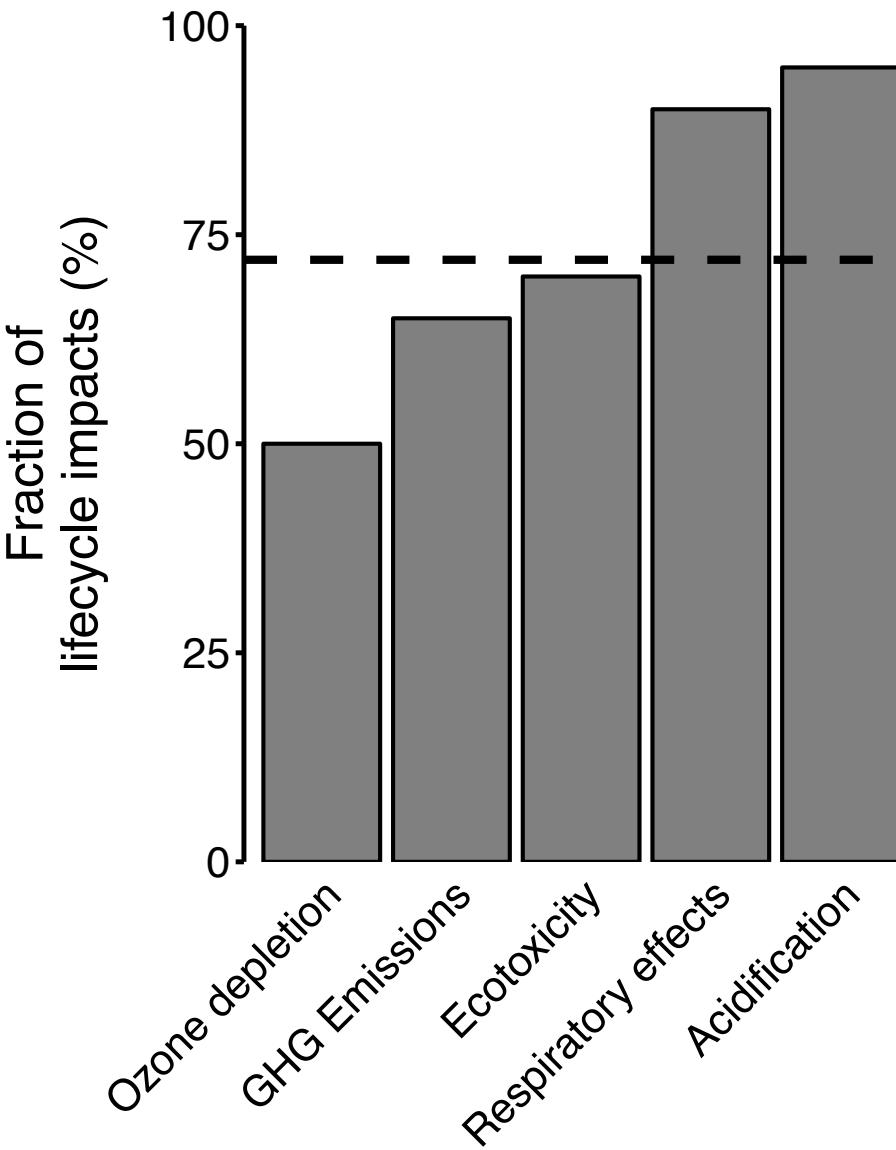
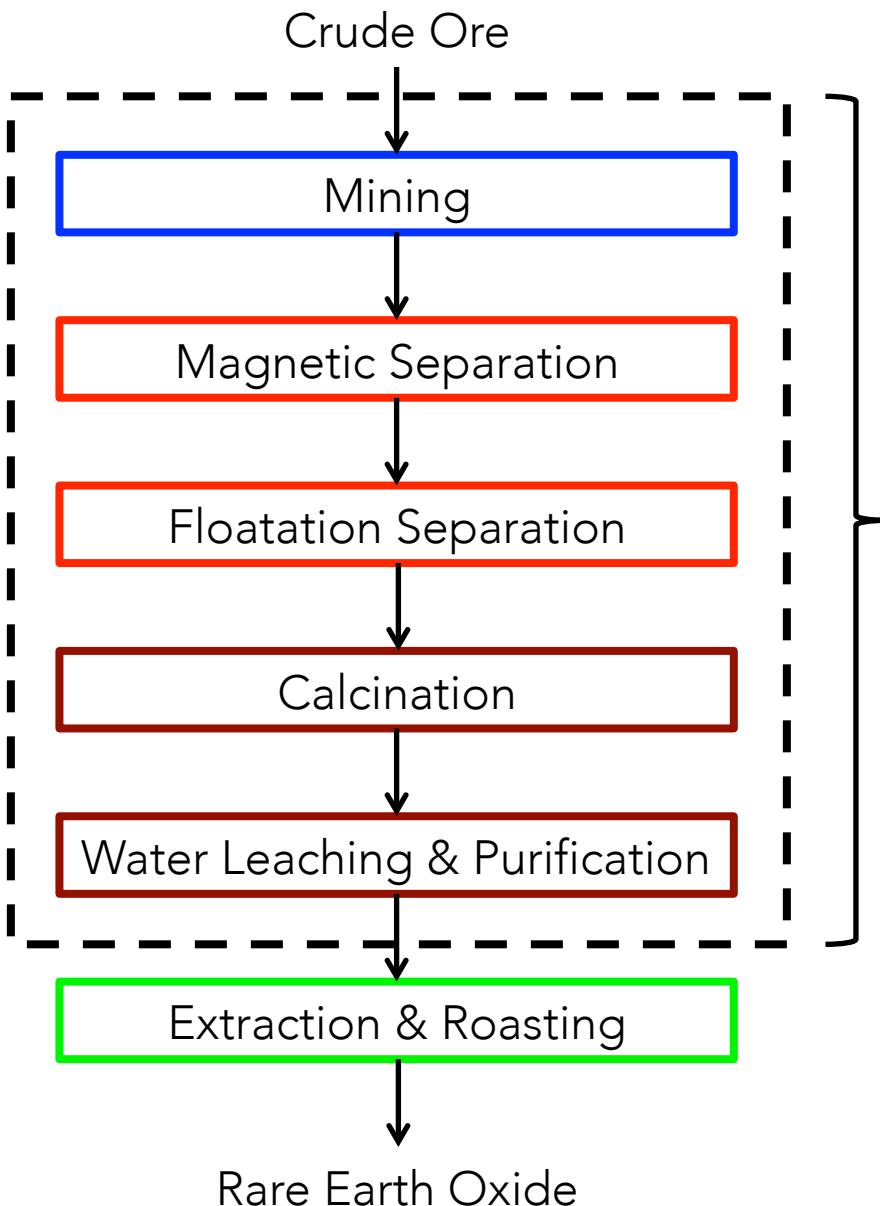
**REE are a chemically  
coherent group of  
elements ubiquitous to  
modern consumer  
and industrial products**



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# Mining

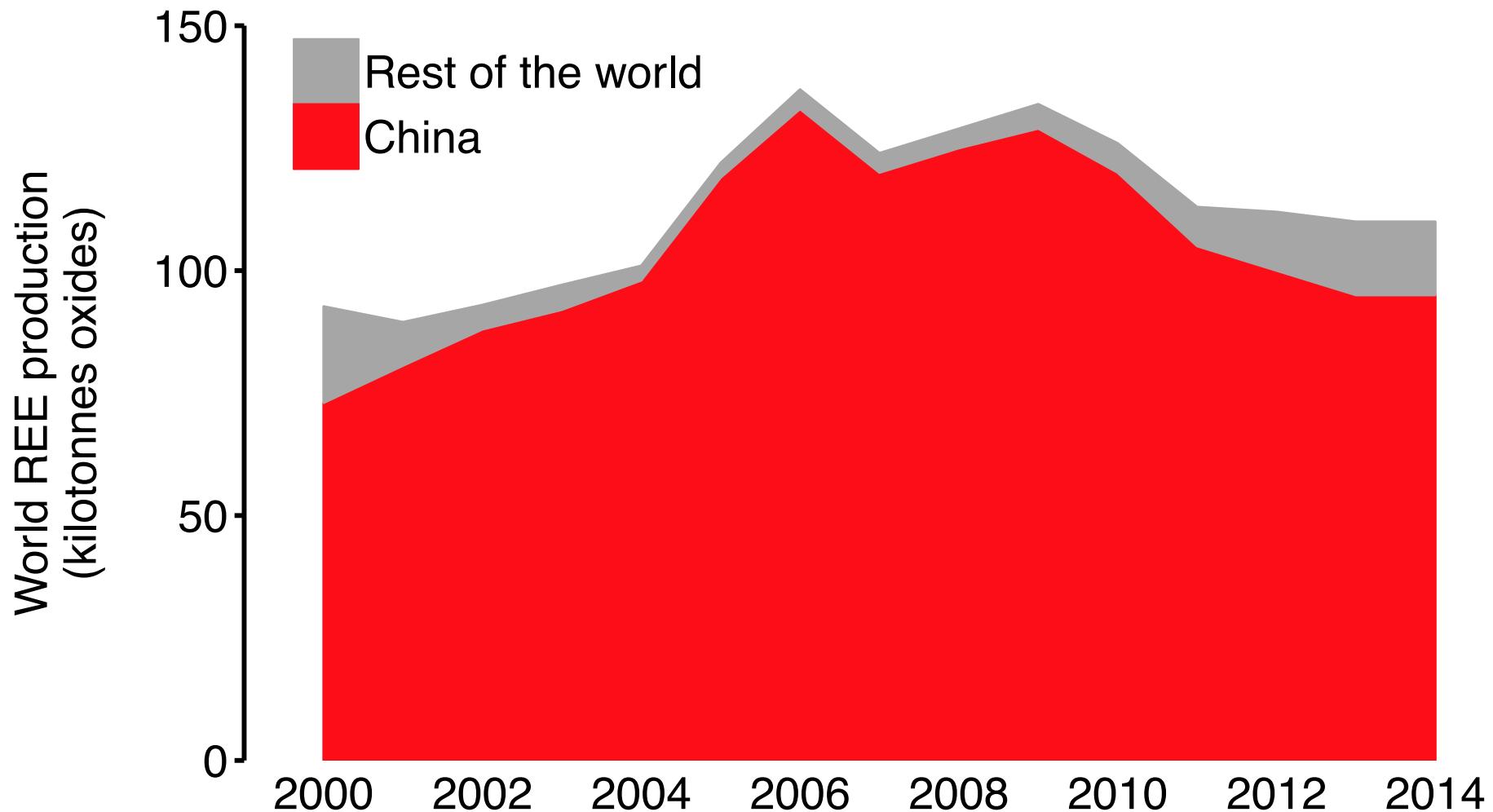
## Environmental impacts



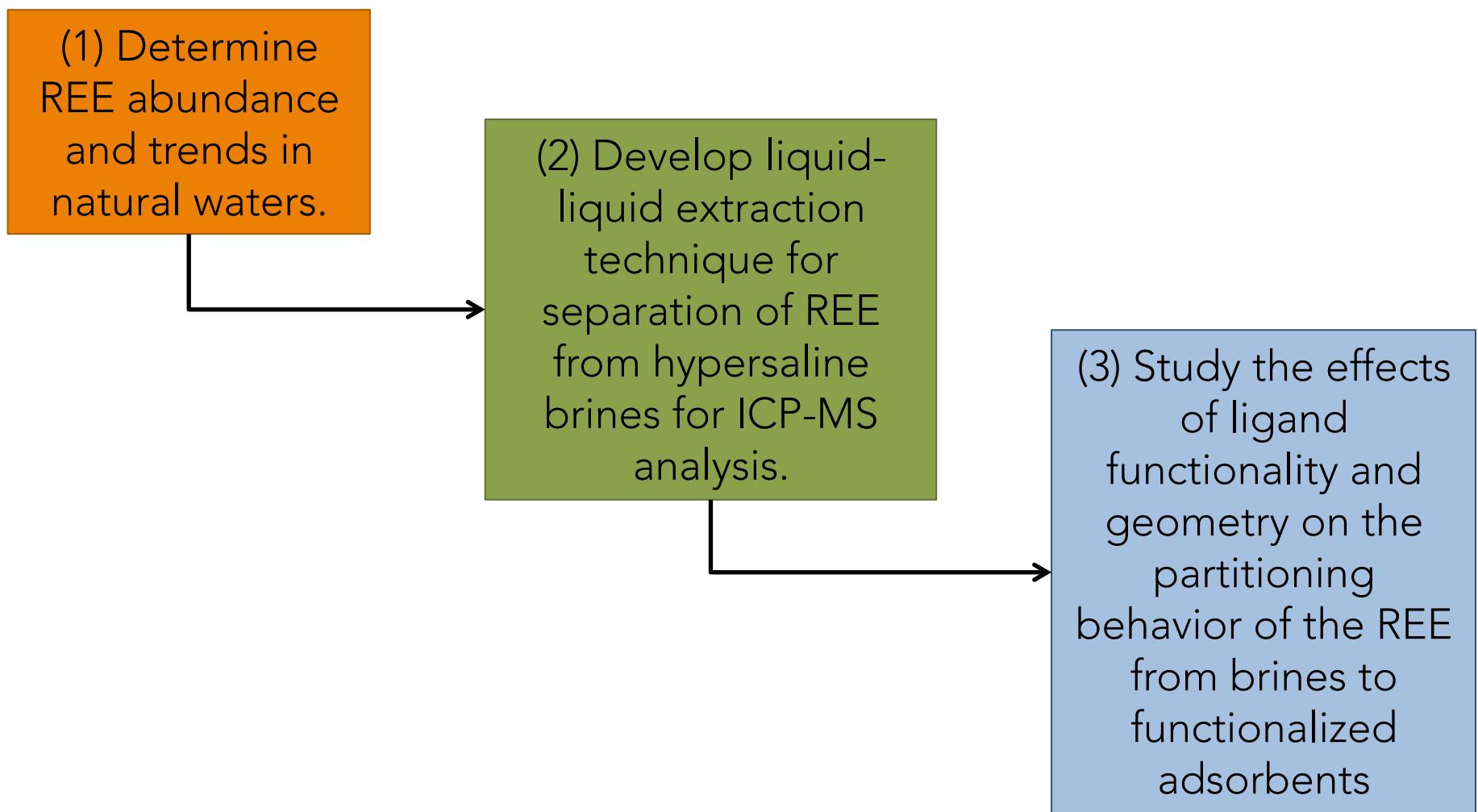
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# China

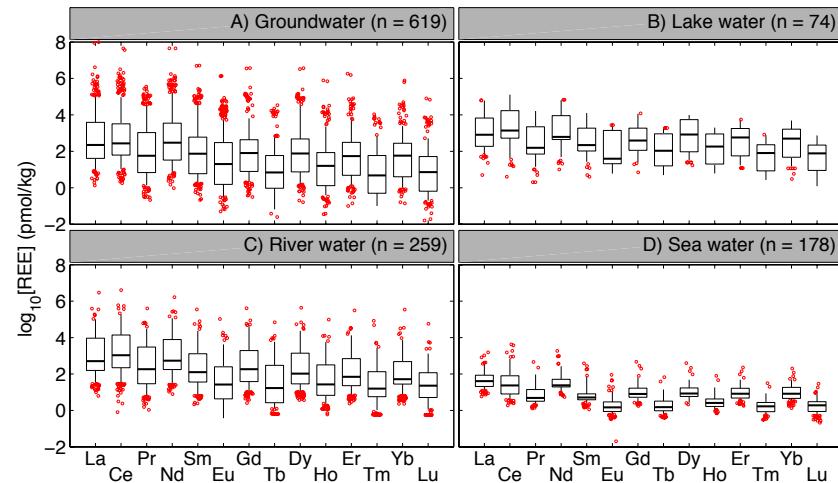
## Near supply monopoly



# Project objectives & structure



# Objective 1



## Rare Earth Element Distributions and Trends in Natural Waters with a Focus on Groundwater

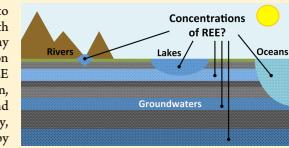
Clinton W. Noack,<sup>†,‡</sup> David A. Dzombak,<sup>‡</sup> and Athanasios K. Karimalidis<sup>\*§,†,‡</sup>

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<sup>§</sup> Supporting Information

**ABSTRACT:** Systematically varying properties and reactivities have led to focused research of the environmental forensic capabilities of rare earth elements (REE). Increasing anthropogenic inputs to natural systems may permanently alter the natural signatures of REE, motivating characterization of natural REE variability. We compiled and analyzed reported dissolved REE concentration data over a wide range of natural water types (ground-, ocean, river, and lake water) and groundwater chemistries (e.g., fresh, brine, and acidic) with the goal of quantifying the extent of natural REE variability, especially for groundwater systems. Quantitative challenges presented by censored data were addressed with nonparametric distributions and regressions. Reported measurements of REE in natural waters range over nearly 10 orders of magnitude, though the majority of measurements are within 2–4 orders of magnitude, and are highly correlated with one another. Few global correlations exist among dissolved abundance and bulk solution properties in groundwater, indicating the complex nature of source-sink terms and the need for care when comparing results between studies. This collection, homogenization, and analysis of a disparate literature facilitates interstudy comparison and provides insight into the wide range of variables that influence REE geochemistry.



## INTRODUCTION

In the natural sciences, predictable thermodynamic differences between the rare earth elements (REE) allow for interpretation of natural geologic and chemical processes.<sup>1,2</sup> Rare earth lithochemistry have long been used to infer depositional environments of geologic strata.<sup>1,3,4</sup> Similarly, REE serve as benign analogues to the transuranic actinides for nuclear waste disposal studies<sup>5,6</sup> and for studying mixing and metal cycling in the oceans.<sup>7,8</sup> These characteristics make REE attractive tools for environmental forensic applications such as pollutant source identification and apportionment.<sup>9,10</sup>

On the basis of atomic number, the REE are segregated into light and heavy REE (LREE and HREE, respectively) with the division occurring between Eu and Gd.<sup>11</sup> Some studies also distinguish middle REE (MREE), though the specific elements are inconsistently defined among authors.<sup>12–14</sup> These "weight" distinctions allow for simplified description and quantification of the interelement relationships, typically ratios of normalized concentrations, which are exploited in REE analysis. Similarly, anomalies of certain REE (due to redox lability for Ce and Eu<sup>15</sup> and large anthropogenic emissions for Gd<sup>16</sup>) are used to interpret geochemical processes. Y and Sc exhibit similar properties to the lanthanides and are thus included in the suite of REE; Y is most similar to HREE, and Sc is most similar to LREE in solution.<sup>15</sup>

Aquatic geochemists apply the same principles used by geologists (the interelement ratios and anomalies described previously) to infer water–rock interactions, hydrologic connectivity between geologic units, and groundwater mixing

members.<sup>17–20</sup> Interactions with different mineral phases have been shown to alter REE patterns predictably. For example, an MREE enrichment is observed for freshwater in contact with phosphate-rich minerals,<sup>12</sup> while HREE enrichment is found in carbonate-rich waters.<sup>21</sup> Tesmer et al.<sup>22</sup> showed that groundwater end-members, especially at shallow depths, could be established by interpretation of REE patterns. Similarly, REE concentrations have been used to calculate end-member contributions to groundwater.<sup>17,19</sup>

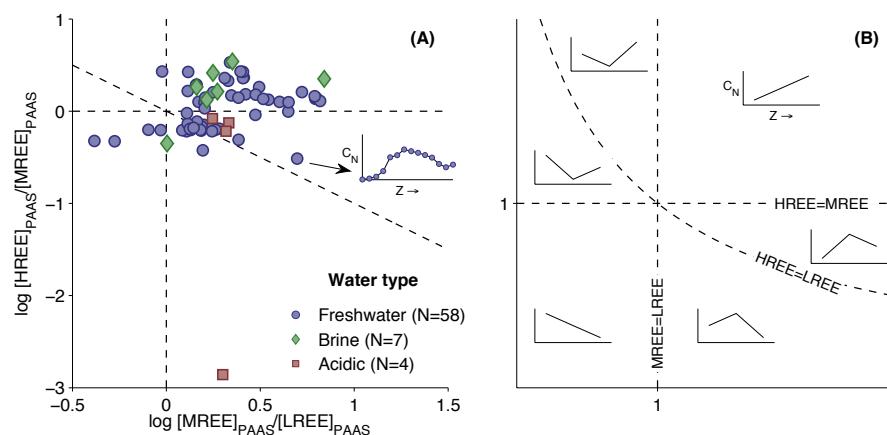
The capabilities of REE to serve as tracers of groundwater migration and mixing have potential applications to the study of hydrology and geochemistry of shale gas development or the capture and sequestration of carbon dioxide ( $\text{CO}_2$ ) gas in geologic formations. For example, characteristic REE profiles could possibly enable detection of brines displaced from shale or  $\text{CO}_2$  storage zones and into overlying groundwater aquifers.<sup>23–26</sup> Capable tools for contaminant detection, as well as contaminant source apportionment, are critical to the long-term environmental feasibility of these technologies. Increasing anthropogenic input of REE into the environment threatens to obfuscate natural signals, which would complicate these applications.<sup>27,28</sup>

A primary challenge in analyzing REE data, like other geochemical compositional data,<sup>29</sup> is the prevalence of censored

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# Objective 2



Article  
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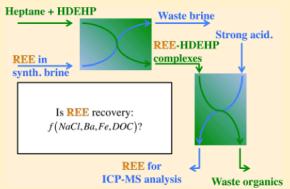
## Determination of Rare Earth Elements in Hypersaline Solutions Using Low-Volume, Liquid–Liquid Extraction

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### Supporting Information

**ABSTRACT:** Complex, hypersaline brines—including those coproduced with oil and gas, rejected from desalination technologies, or used as working fluids for geothermal electricity generation—could contain critical materials such as the rare earth elements (REE) in valuable concentrations. Accurate quantitation of these analytes in complex, aqueous matrices is necessary for evaluation and implementation of systems aimed at recovering those critical materials. However, most analytical methods for measuring trace metals have not been validated for highly saline and/or chemically complex brines. Here we modified and optimized previously published liquid–liquid extraction (LLE) techniques using bis(2-ethylhexyl) phosphate as the extractant in a heptane diluent, and studied its efficacy for REE recovery as a function of three primary variables: background salinity (as NaCl), concentration of a competing species (here Fe), and concentration of dissolved organic carbon (DOC). Results showed that the modified LLE was robust to a range of salinity, Fe, and DOC concentrations studied as well as constant, elevated Ba concentrations. With proper characterization of the natural samples of interest, this method could be deployed for accurate analysis of REE in small volumes of hyper-saline and chemically complex brines.



### INTRODUCTION

The rare earth elements (REE) are among the most frequently cited critical materials for clean energy and high-tech manufacturing.<sup>1,2</sup> The unique and varied properties of REE have led to their application in many consumer products than nearly any other element group.<sup>3</sup> REE are mostly obtained from mining and processing of REE-enriched ores.<sup>2</sup> While economically preferred, mining is laborious with a significant environmental burden, and inexpensive alternative sources of critical materials are sought after resources.

Aqueous byproduct or waste streams, both natural and industrial, are potential sources of the REE and other critical materials. With increasing global interest in geothermal energy,<sup>4</sup> development of unconventional oil and gas resources (e.g., hydraulic fracturing of organic rich shales),<sup>5</sup> and desalination technologies,<sup>6,7</sup> large volumes of waste brines are being managed and processed at great expense. Development of technologies for recovery of valuable byproducts, such as the REE, from these waste streams could improve the economics of these technologies while diversifying available critical material resources. Development of such technologies requires accurate determination of the source REE concentration in order to develop and implement recovery systems. However, precise quantitation of REE in complex matrices like brines is a significant challenge for conventional instrumentation such as inductively coupled plasma mass spectrometry (ICP-MS).<sup>8</sup>

There exists a dearth of methodologies in the analytical literature for quantitation of REE in brines by ICP-MS. Many approaches have been applied for separation and concentration of REE from aqueous media including solid-phase extraction (SPE),<sup>9–25</sup> coprecipitation (coppt),<sup>26–28</sup> and liquid–liquid extraction (LLE).<sup>29–32</sup> However, nearly all studies in the analytical chemistry literature have focused on fresh water or seawater matrices, neglecting hypersaline waters (i.e., more concentrated than ~0.7 M NaCl or seawater). Despite this deficiency, approximately 14% of published measurements of REE in groundwater constitute brine samples (greater than 1 eq/kg ionic strength),<sup>33</sup> with these analyses utilizing methodologies not explicitly validated for extreme salinities.

Commonly applied separation techniques such as SPE and coppt may lack the robustness necessary to analyze REE in hypersaline brines. For example, high dissolved organic carbon may lead to fouling of column-based SPE while high dissolved metal loads may lead to saturation of the surface sites responsible for REE binding. Oliveira et al.<sup>34</sup> ascribed diminished Zn recovery in 166‰ salinity produced water to competitive sorption of matrix cations on their iminodiacetate

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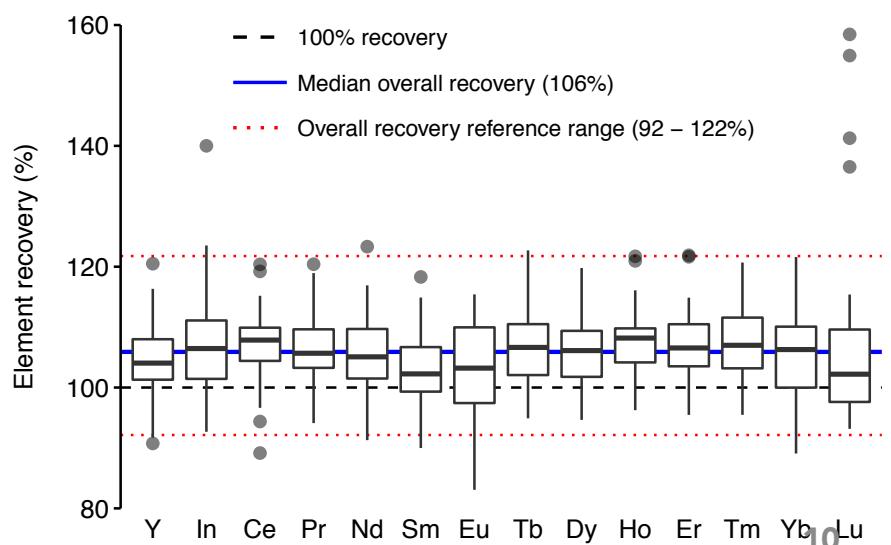
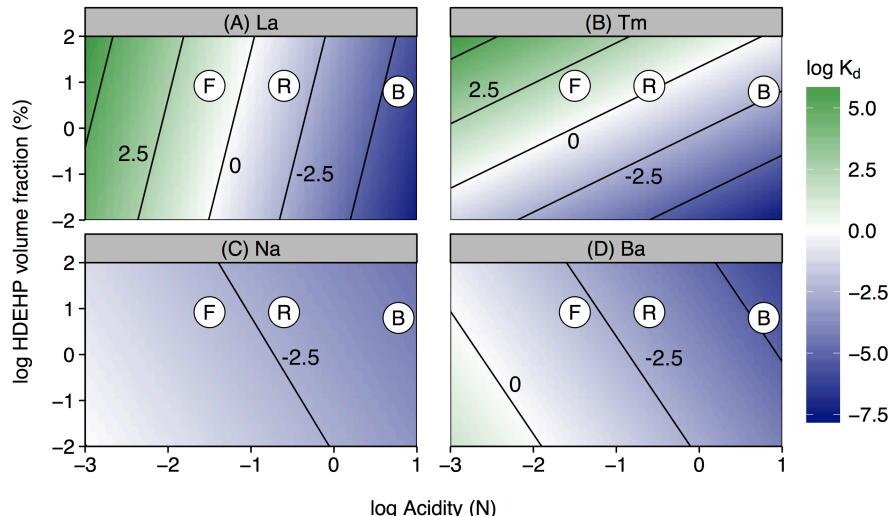
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Environ. Sci. Technol. 2015, 49, 9423–9430



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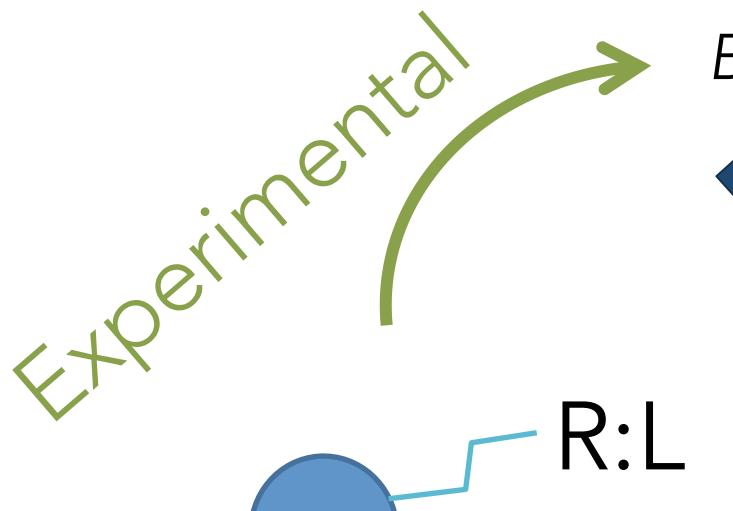
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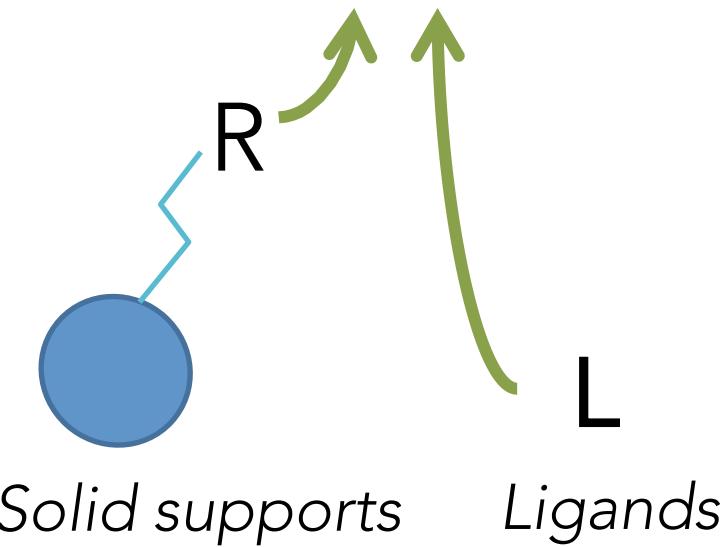
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# Objective 3

- Study the reactivity of REE-selective ligands grafted onto a model support
- Are those ligands with greatest aqueous affinity the same when attached to a surface?
- Do surface attached ligands retain their selectivity?
- Use classical set of adsorption experiments: pH edge, constant-pH isotherm, kinetics

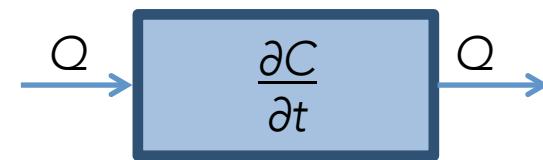


Functionalized adsorbents

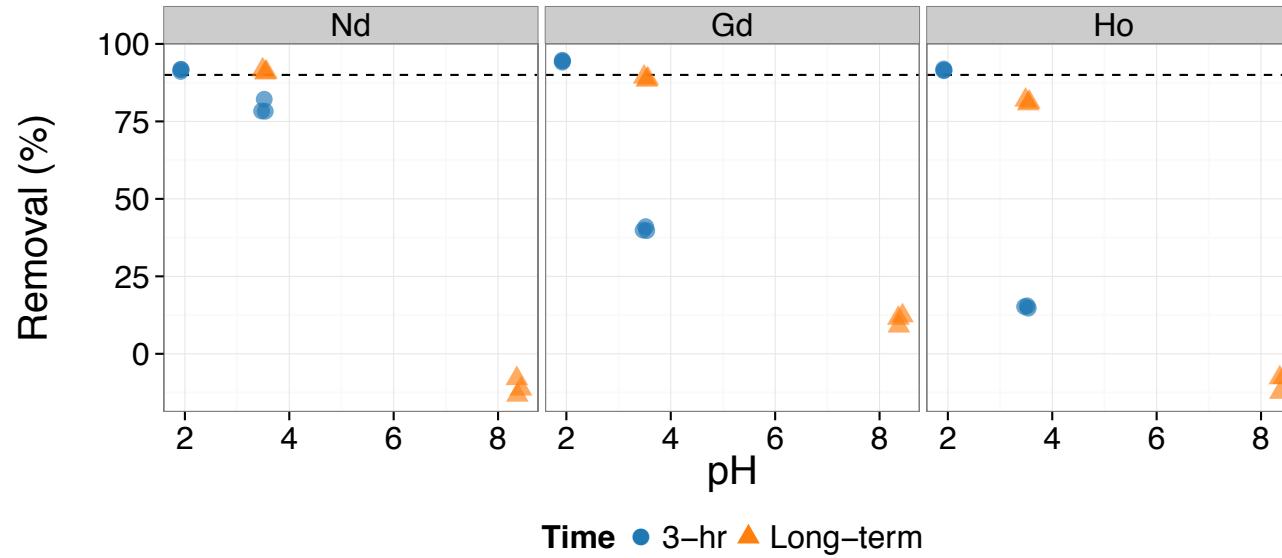
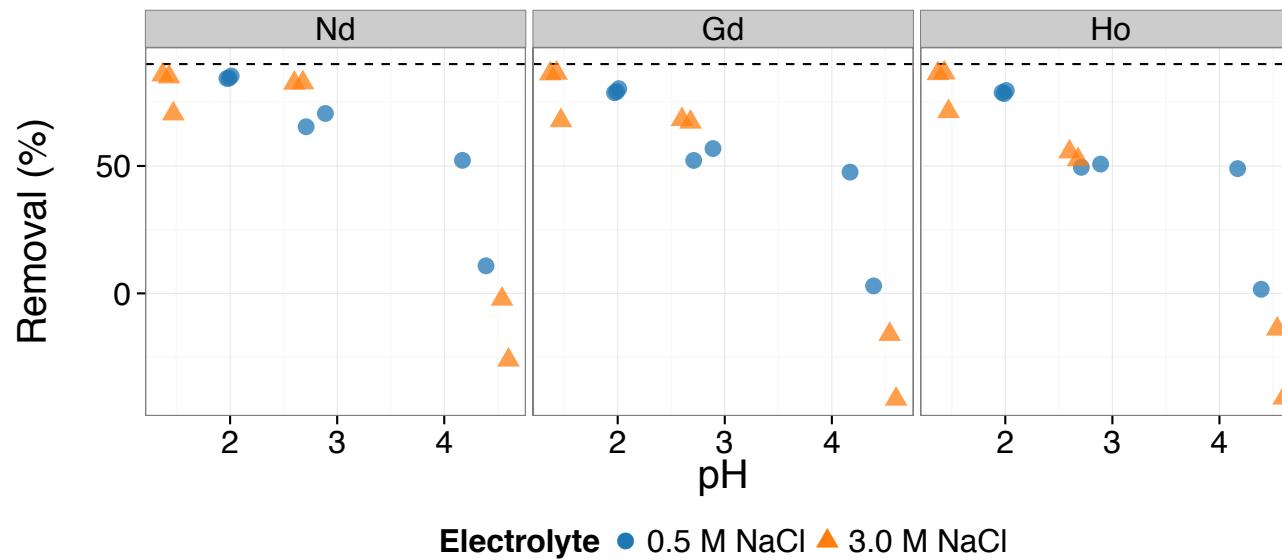


Batch testing

Continuous flow



Integration  
with  
geothermal  
power plant



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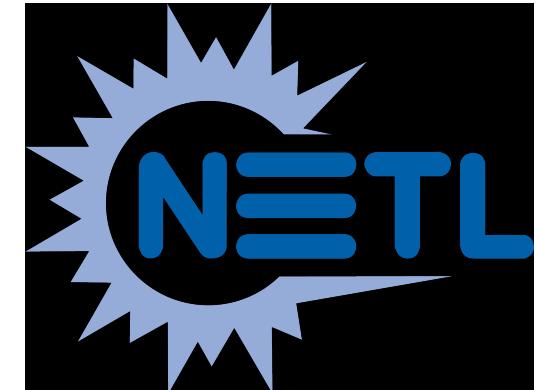
# Contributions / broader impacts

- Research proposed here will contribute significantly to:
  - Understanding of trace-metal geochemistry in high salinity systems
  - Development of alternative resources for critical material extraction and recovery
- Impacts for general brine management:
  - Oil & gas produced waters
  - Carbon capture, utilization, and storage
  - Seawater desalination

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# Acknowledgements

- Oak Ridge Institute for Science and Education
- The National Energy Technology Laboratory (U.S. DOE NETL)
- U.S. DOE Office of Energy Efficiency and Renewable Energy
- My committee for going through this again!



U.S. DEPARTMENT OF  
**ENERGY**

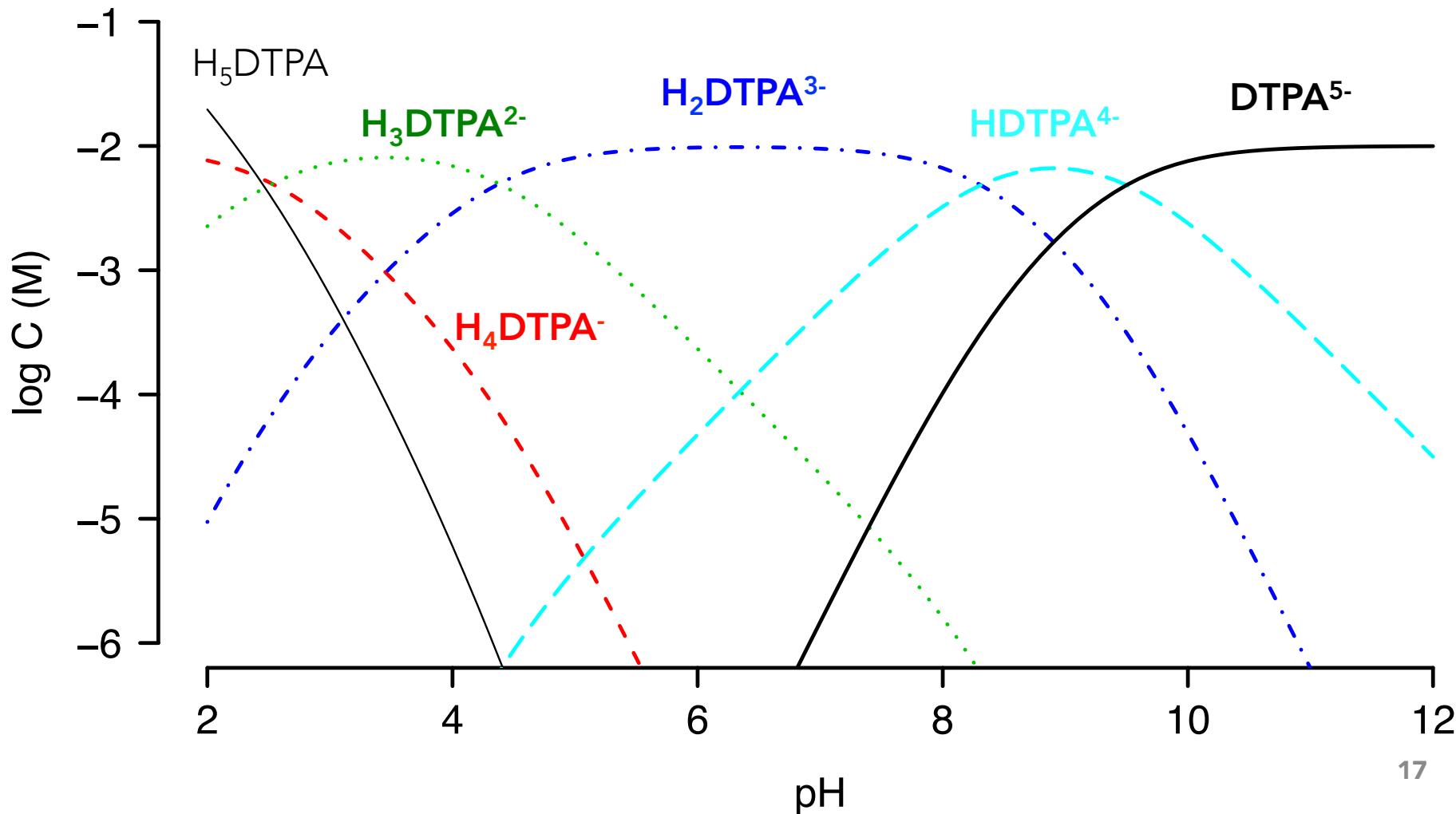
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Energy Efficiency &  
Renewable Energy

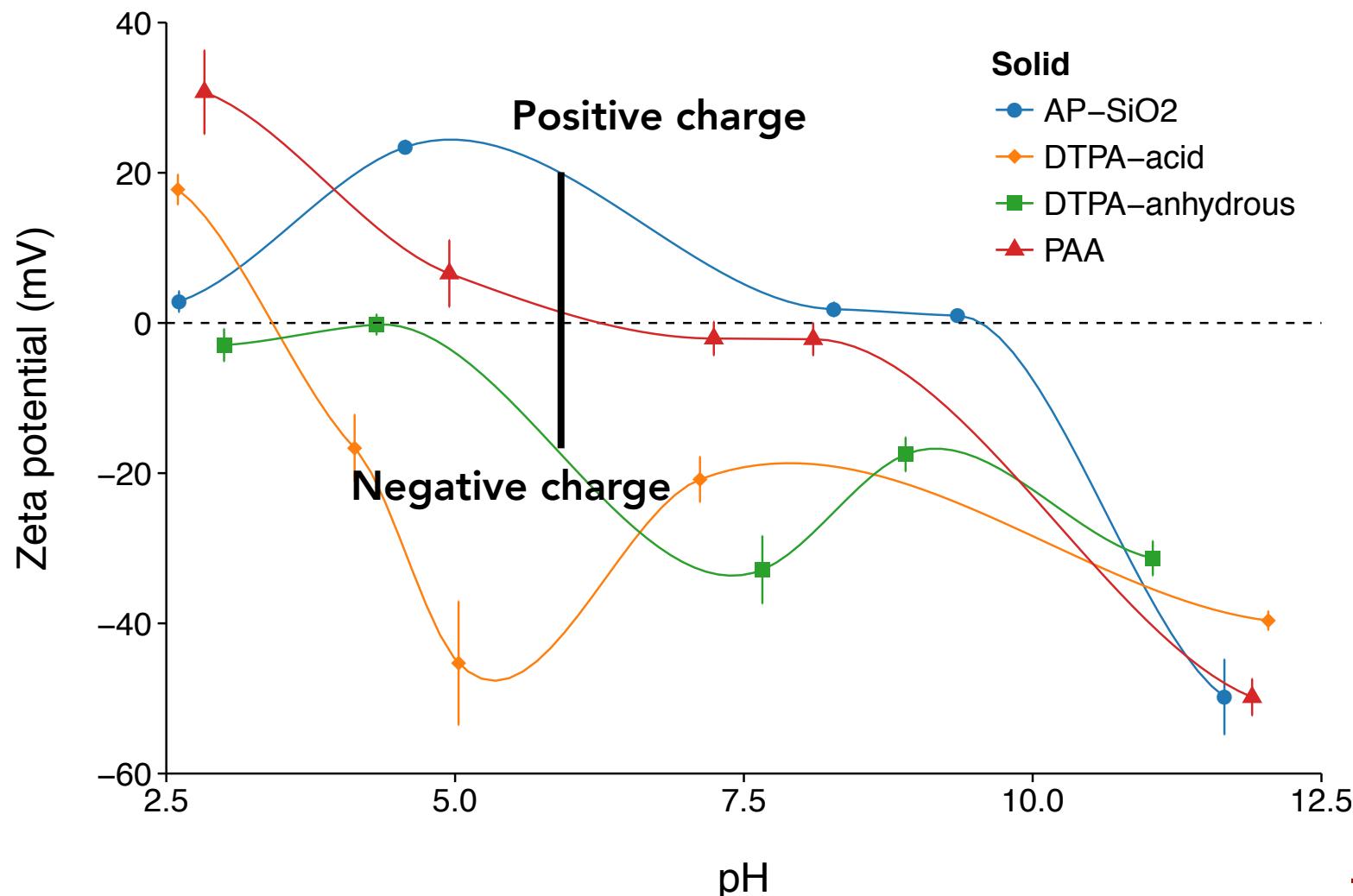
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# Etc.

At low pH, DTPA has a mixture of protonation states. At higher pH, 3- or higher charges predominate



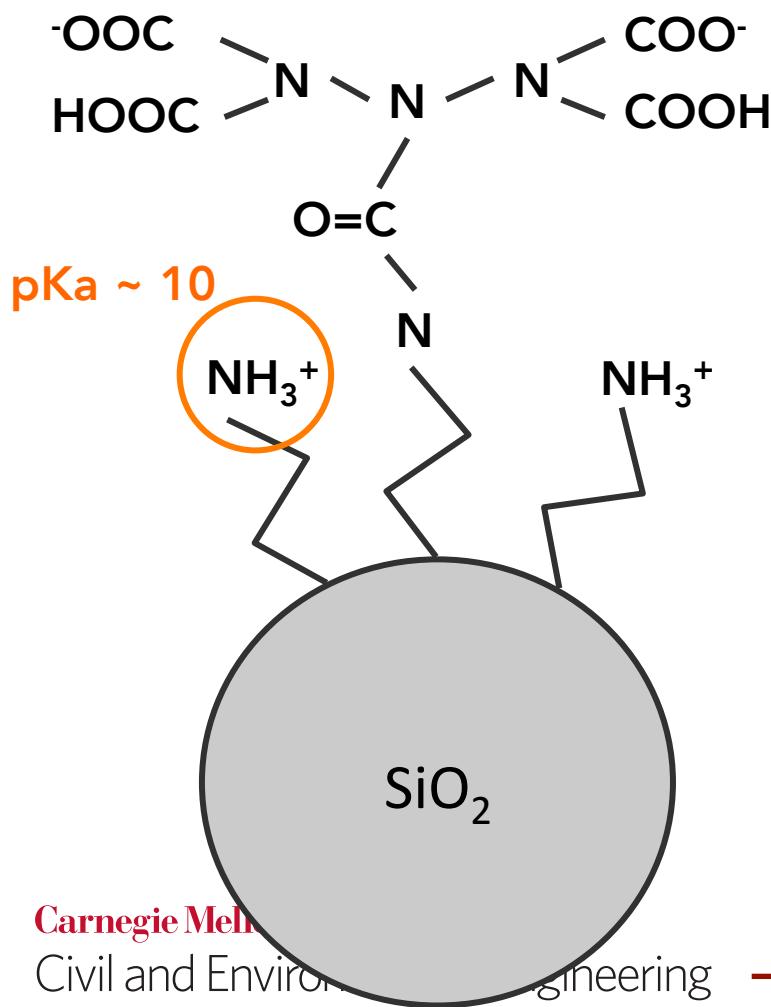
At mid-range pH, there is a large disparity between the surface charges of the anhydrous DTPA and the bare AP-SiO<sub>2</sub>



# Unreacted amines could interfere with DTPA functionality

## Low pH ( $\leq 4$ )

## Neutral pH (5-8)



Electro-static interactions diminish functionality?

