Actinide Partition In Humic Colloidal Ternary Systems

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Rajiv Robert Kay
School of Chemistry
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Figure 4.22; Model 2 results for ternary humic acid/quartz sand system/²³⁹Pu(IV), 1.22 mBq ml⁻¹, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([ST].k_{MSf} = 5.5 x 10⁻⁶ s⁻¹; k_{MSb} = 1.83 x 10⁻⁶ s⁻¹; k_{f} = 1.1 x 10⁻⁸ s⁻¹; k_{b} = 1.0 x 10⁻⁷; [HA_{exch,T}].K_{exch} = 50)
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Figure 4.24; Model 1 results for ternary humic acid/quartz sand system Pu(V), 0.6125 mBq ml$^{-1}$, $I = 0.1$, pH = 6, as a function of total humic concentration and Model fit to data ($[S_T].k_{MSf} = 9.0x10^{-6}$ s$^{-1}$; $k_{MSb} = 3.0x10^{-6}$ s$^{-1}$; $k_f = 1.1x10^{-8}$ s$^{-1}$; $k_b = 1.0x10^{-7}$; $[HA_{exh,T}].K_{exch} = 10$)

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Figure 4.25; Model 2 results for ternary humic acid/quartz sand system Pu(V), 0.6125 mBq ml$^{-1}$, $I = 0.1$, pH = 6, as a function of total humic concentration and Model fit to data ($[S_T].k_{MSf} = 1.5x10^{-5}$ s$^{-1}$; $k_{MSb} = 3.75x10^{-6}$ s$^{-1}$; $k_f = 1.1x10^{-8}$ s$^{-1}$; $k_b = 1.0x10^{-7}$; $[HA_{exh,T}].K_{exch} = 50$)

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Figure 4.26; Model 3 results for ternary humic acid/quartz sand system $^{239}$Pu(V), 0.6125 mBq ml$^{-1}$, $I = 0.1$, pH = 6, as a function of total humic concentration and Model fit to data $k_{HA1S1f} = 1.40E-06$; $k_{HA1S1b} = 2.00E-05$; $k_{HA1S2f} = 2.00E-08$; $k_{HA1S2b} = 6.00E-07$; $k_{HA2S1f} = 1.40E-05$; $k_{HA2S1b} = 3.00E-06$; $k_{HA2S2f} = 2.00E-08$; $k_{HA2S2b} = 6.00E-07$

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Figure 4.27; Model 1 results for ternary humic acid/quartz sand system $^{239}$Pu (VI), 1.22 mBq ml$^{-1}$, $I = 0.1$, pH = 6, as a function of total humic concentration and Model fit to data ($[S_T].k_{MSf} = 9.0x10^{-5}$ s$^{-1}$; $k_{MSb} = 4x10^{-6}$ s$^{-1}$; $k_f = 1.1x10^{-8}$ s$^{-1}$; $k_b = 1.0x10^{-7}$ $[HA_{exh,T}].K_{exch} = 100$)

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Figure 4.28; Model 2 results for ternary humic acid/quartz sand system²³⁹Pu (VI), 1.22 mBq ml⁻¹, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S][k] = 1.60x10⁻⁵ s⁻¹; k = 8x10⁻⁷ s⁻¹; k_f = 1.1x10⁻⁸ s⁻¹; k_b = 1.0x10⁻⁷ [HAexch,T].Kexch. = 20)

Figure 4.29; Model 3 results for ternary humic acid/quartz sand system²³⁹Pu (VI), 1.22 mBq ml⁻¹, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data k_HA1S1f = 2.00E⁻⁶; k_HA1S1b = 7.00E⁻⁶; k_HA1S2f = 6.00E⁻⁷; k_HA1S2b = 1.40E⁻⁵; k_HA2S1f = 7.00E⁻⁶; k_HA2S1b = 1.40E⁻⁸; k_HA2S2b = 6.00E⁻⁷

Figure 4.30; Model 1, Eu³⁺ HA > 100 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S][k] = 3.4x10⁻⁶ s⁻¹; k = 2.4x10⁻⁷ s⁻¹; [HAexch,T].Kexch. = 100)

Figure 4.31; Model 1, Eu³⁺ 100 > HA > 10 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S][k] = 3.5x10⁻⁶ s⁻¹; k = 2.5x10⁻⁷ s⁻¹; [HAexch,T].Kexch. = 100)

Figure 4.32; Model 1, Eu³⁺ 10 > HA > 3 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S][k] = 3.5x10⁻⁶ s⁻¹; k = 2.5x10⁻⁷ s⁻¹; [HAexch,T].Kexch. = 50)

Figure 4.33; Model 1, Eu³⁺ HA < 3 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S][k] = 3.5x10⁻⁶ s⁻¹; k = 2.5x10⁻⁷ s⁻¹; [HAexch,T].Kexch. = 250)
Figure 4.34; Model 3, Eu$^{3+}$ HA > 100 kDa/quartz system, I = 0.1, pH = 6
$[\text{Eu}]_T = 133 \text{ mBq ml}^{-1}$
Model fit to data $k_{\text{HA1S1f}} = 1.00 \times 10^{-06}$; $k_{\text{HA1S1b}} = 2.00 \times 10^{-06}$; $k_{\text{HA1S2f}} = 2.50 \times 10^{-08}$; $k_{\text{HA1S2b}} = 6.00 \times 10^{-08}$; $k_{\text{HA2S1f}} = 1.00 \times 10^{-06}$; $k_{\text{HA2S1b}} = 2.00 \times 10^{-07}$; $k_{\text{HA2S2f}} = 2.00 \times 10^{-07}$; $k_{\text{HA2S2b}} = 6.00 \times 10^{-08}$

Figure 4.35; Model 3, Eu$^{3+}$ 100 < HA < 10 kDa/quartz system, I = 0.1, pH = 6
$[\text{Eu}]_T = 133 \text{ mBq ml}^{-1}$
Model fit to data $k_{\text{HA1S1f}} = 1.00 \times 10^{-06}$; $k_{\text{HA1S1b}} = 2.00 \times 10^{-06}$; $k_{\text{HA1S2f}} = 1.00 \times 10^{-07}$; $k_{\text{HA1S2b}} = 5.00 \times 10^{-08}$; $k_{\text{HA2S1f}} = 2.00 \times 10^{-06}$; $k_{\text{HA2S1b}} = 1.00 \times 10^{-06}$; $k_{\text{HA2S2f}} = 2.00 \times 10^{-07}$; $k_{\text{HA2S2b}} = 5.00 \times 10^{-08}$

Figure 4.36; Model 3, Eu$^{3+}$ 10 < HA < 3 kDa/quartz system, I = 0.1, pH = 6
$[\text{Eu}]_T = 133 \text{ mBq ml}^{-1}$
Model fit to data $k_{\text{HA1S1f}} = 1.00 \times 10^{-06}$; $k_{\text{HA1S1b}} = 1.00 \times 10^{-07}$; $k_{\text{HA1S2f}} = 3.00 \times 10^{-08}$; $k_{\text{HA1S2b}} = 5.00 \times 10^{-08}$; $k_{\text{HA2S1f}} = 1.00 \times 10^{-06}$; $k_{\text{HA2S1b}} = 5.00 \times 10^{-06}$; $k_{\text{HA2S2f}} = 1.00 \times 10^{-08}$; $k_{\text{HA2S2b}} = 1.00 \times 10^{-06}$

Figure 4.37; Model 3, Eu$^{3+}$ HA < 3 kDa/quartz system, I = 0.1, pH = 6
$[\text{Eu}]_T = 133 \text{ mBq ml}^{-1}$
Model fit to data $k_{\text{HA1S1f}} = 1.00 \times 10^{-06}$; $k_{\text{HA1S1b}} = 1.00 \times 10^{-07}$; $k_{\text{HA1S2f}} = 2.00 \times 10^{-07}$; $k_{\text{HA1S2b}} = 6.00 \times 10^{-08}$; $k_{\text{HA2S1f}} = 1.00 \times 10^{-06}$; $k_{\text{HA2S1b}} = 2.00 \times 10^{-07}$; $k_{\text{HA2S2f}} = 5.00 \times 10^{-05}$; $k_{\text{HA2S2b}} = 7.00 \times 10^{-04}$

Figure 4.38; Model 1, Uranyl HA > 100 kDa/quartz system, I = 0.1, pH = 6,
$[\text{Ur}]_T = 100 \text{ mBq ml}^{-1}$
$(k_{\text{MSf}} = 2.0 \times 10^{-07} \text{ s}^{-1}; k_{\text{MSb}} = 1.0 \times 10^{-07} \text{ s}^{-1}; [\text{HA}_{\text{exch,T}}].K_{\text{exch}} = 1000)$

Figure 4.39; Model 1, Uranyl 100 < HA < 10 kDa/quartz system, I = 0.1, pH = 6,
$[\text{Ur}]_T = 100 \text{ mBq ml}^{-1}$
$(k_{\text{MSf}} = 2.0 \times 10^{-07} \text{ s}^{-1}; k_{\text{MSb}} = 1.0 \times 10^{-07} \text{ s}^{-1}; [\text{HA}_{\text{exch,T}}].K_{\text{exch}} = 100)$
Figure 4.40; Model 1, Uranyl 10 > HA > 3 kDa/ quartz system, I = 0.1, pH = 6, [U\textsubscript{T}] = 100 mBq ml\textsuperscript{-1} ([S\textsubscript{T}].k\textsubscript{MSf} = 9.0x10\textsuperscript{-6} s\textsuperscript{-1}; k\textsubscript{MSb} = 3.0x10\textsuperscript{-7} s\textsuperscript{-1}; [HA\textsubscript{exch,T}].K\textsubscript{exch} = 1000)

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Figure 4.41; Model 1, Uranyl HA < 3 kDa / quartz system, I = 0.1, pH = 6, [U\textsubscript{T}] = 100 mBq ml\textsuperscript{-1} ([S\textsubscript{T}].k\textsubscript{MSf} = 7.0x10\textsuperscript{-6} s\textsuperscript{-1}; k\textsubscript{MSb} = 3.0x10\textsuperscript{-6} s\textsuperscript{-1}; [HA\textsubscript{exch,T}].K\textsubscript{exch} = 1)

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Figure 4.42; Model 1, Pu (VI) HA > 100 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\textsuperscript{-1}) ([S\textsubscript{T}].k\textsubscript{MSf} = 5.50x10\textsuperscript{-5} s\textsuperscript{-1}; k\textsubscript{MSb} = 4.0x10\textsuperscript{-6} s\textsuperscript{-1}; [HA\textsubscript{exch,T}].K\textsubscript{exch} = 12)

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Figure 4.43; Model 1, Pu (VI) 100 > HA > 10 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\textsuperscript{-1}) ([S\textsubscript{T}].k\textsubscript{MSf} = 7.00x10\textsuperscript{-5} s\textsuperscript{-1}; k\textsubscript{MSb} = 4.0x10\textsuperscript{-6} s\textsuperscript{-1}; [HA\textsubscript{exch,T}].K\textsubscript{exch} = 10)

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Figure 4.44; Model 1, Pu (VI) 10 > HA > 3 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\textsuperscript{-1}) ([S\textsubscript{T}].k\textsubscript{MSf} = 7.00x10\textsuperscript{-5} s\textsuperscript{-1}; k\textsubscript{MSb} = 4.0x10\textsuperscript{-6} s\textsuperscript{-1}; [HA\textsubscript{exch,T}].K\textsubscript{exch} = 1)

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Figure 4.45: Model 1, Pu (VI) 10 > HA > 10 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\textsuperscript{-1}) ([S\textsubscript{T}].k\textsubscript{MSf} = 6.00x10\textsuperscript{-5} s\textsuperscript{-1}; k\textsubscript{MSb} = 5.00x10\textsuperscript{5} s\textsuperscript{-1}; [HA\textsubscript{exch,T}].K\textsubscript{exch} = 1)

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Figure 4.46; Model 3, Pu (VI) 100 > HA kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\textsuperscript{-1}) Model fit to data k\textsubscript{HA1S1f} = 1.00E-06; k\textsubscript{HA1S1b} = 4.00E-06; k\textsubscript{HA1S2f} = 2.50E-08; k\textsubscript{HA1S2b} = 6.00E-08; k\textsubscript{HA2S1f} = 1.00E-07; k\textsubscript{HA2S1b} = 2.00E-07; k\textsubscript{HA2S2f} = 5.00E-05; k\textsubscript{HA2S2b} = 1.00E-08

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Figure 4.47; Model 3, Pu (VI) 100 > HA > 10 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\textsuperscript{-1}) Model fit to data k\textsubscript{HA1S1f} = 5.00E-06; k\textsubscript{HA1S1b} = 4.00E-06; k\textsubscript{HA1S2f} = 1.00E-07; k\textsubscript{HA1S2b} = 1.00E-07; k\textsubscript{HA2S1f} = 5.00E-06; k\textsubscript{HA2S1b} = 4.00E-07; k\textsubscript{HA2S2f} = 5.00E-05; k\textsubscript{HA2S2b} = 9.00E-07

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Figure 4.48; Model 3, Pu (VI) 10 > HA > 3 kDa/ quartz system, $I = 0.1$, pH = 6, (1.22 mBq ml$^{-1}$) Model fit to data $k_{HA1S1f} = 2.00E-07; k_{HA1S1b} = 2.00E-06; k_{HA1S2f} = 2.00E-08; k_{HA1S2b} = 6.00E-08; k_{HA2S1f} = 2.00E-07; k_{HA2S1b} = 5.00E-07; k_{HA2S2f} = 2.00E-07; k_{HA2S2b} = 6.00E-07$

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phase humic species; $\text{HA}_{\text{S1}}$ and $\text{HA}_{\text{S2}}$: are sorbed humic species;  
$k_{\text{exch}} \text{ dm}^3 \text{ mol}^{-1}$ is an equilibrium constant and $k_6$, $k_b$, $k_{\text{MS}b}$, $k_{\text{HAS1}b}$, $k_{\text{HAS2}b}$, $k_{\text{HA1}Sb}$, $k_{\text{HA2}Sb}$, $s^{-1}$;  
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Abstract

The University of Manchester by Rajiv Robert Kay for the Degree of Doctor of Philosophy, entitled

Actinide Partition in Humic Colloidal Ternary systems

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The partition of radionuclides between solid and solution phase has been studied in humic/quartz sand ternary systems. Data have been recorded under ambient (air) and inert (O₂ and CO₂ free) atmospheres. For Eu (III) and Th (IV), the systems show simple ternary behaviour, with sorption decreasing (and mobility increasing) in the presence of humic, whilst for U (VI), the behaviour is more complex, with the humic enhancing sorption and reducing mobility. There is also evidence that the sorbed humic has an enhanced affinity for the uranyl, which is probably due to fractionation of the humic. Further, the behaviour of plutonium has also been studied in these systems. Pu (IV) showed the simple ternary characteristics, which had been observed for Eu (III) and Th (IV). Pu (V) and Pu (VI) systems exhibited more complex behaviour, with low concentrations of humic actually enhancing sorption, probably due to ternary complex formation. A simple mathematical model has been developed to predict the behaviour of both metal ion and humic acid. The model performs well in predicting the partition of the humic and that of the metal ions in the systems that show simpler ternary behaviour.
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Chapter 1

Introduction
1.1 Introduction To Humic Substances

Humic substances can be described as polydisperse, heterogeneous mixtures of organic molecules that have a high attraction for most metal ions. As a result, they have the capacity to compete with mineral surfaces for radionuclides (RN), increasing RN solubility, and hence mobility (Bryan et al., 2007). Therefore, it is essential to understand the effects of humic substances on RN behaviour, for example in the safety case for a radioactive waste repository. Hence, various models have been developed to predict the effect of humics on RN behaviour and transport.

In recent years there has been a significant improvement in our understanding of humic/RN interactions, with experimental analysis focusing on metal ion uptake, by using techniques such as solvent extraction, ultra-filtration and resin / ligand exchange (Bryan et al., 1998, 2006) (Pitois et al., 2003).

Most recent studies have expanded the study of simple (metal ion-humic) binary systems to more complex ternary systems, where natural organic matter, metal ion and mineral phases are all present together (Lenhart & Honeyman, 1999), (Evans et al., 2007) (Weng et al., 2007b). In order to predict radionuclide movement through the sub-surface environment, it is essential that this ternary system behaviour be investigated. Ternary systems generally exhibit complex behaviour, since size and chemical fractionation accompanies sorption of humic species to mineral surfaces (Bryan et al., 2012).

Other aspects of radionuclides, that need to be taken into account, are as those factors that form part of Radiological Performance Assessment (RPA). The RPA is a method, which identifies processes, using models to evaluate containment, and possible impacts that may arise from a proposed nuclear waste repository. In general, RPA considers factors that go beyond handling difficulties associated with radioactive materials, these include:

Environmental scenario, which identifies specific regions in and around a disposal facility, where radionuclides might impact the surrounding environment, and where human contact is likely to occur:

Barrier performance, which evaluates the radionuclide waste is stored, and radionuclide migration through the sub-surface. (USNRC website):
Therefore, given the complexity of calculating these factors, and because humic substances account for a small part of RPA calculations, there is an inherent requirement to keep humic mathematical models as simple as possible. However given the presence of humic substances, which may affect metal ion transport, there a need to predict their effect on radionuclide speciation (Bryan et al., 2012).

Actinides show significant redox effects and are prone to hydrolysis. For example, plutonium exists in a variety of oxidation states: III; IV; V; and VI, and (depending upon the pH and Eh) these multiple oxidation states can co-exist. The equations for hydrolysis of Eu (III) Th (IV), U (IV), U (VI), Pu (IV), Pu (V) and Pu (VI) are shown below:-

Stepwise hydrolysis of Eu (III):-

\[
\begin{align*}
Eu_{aq}^{3+} + OH_{aq}^- & \iff [EuOH]_{aq}^{2+} \\
[EuOH]_{aq}^{2+} + OH_{aq}^- & \iff [Eu(OH)_2]_{aq}^+ \\
[Eu(OH)_2]_{aq}^+ + OH_{aq}^- & \iff [Eu(OH)_3]_{aq} \\
[Eu(OH)_3]_{aq} + OH_{aq}^- & \iff Eu(OH)_3(s)
\end{align*}
\]

Stepwise hydrolysis of Th (IV):-

\[
\begin{align*}
Th_{aq}^{4+} + OH^- & \iff [Th(OH)]_{aq}^{3+} \\
[Th(OH)]_{aq}^{3+} + OH^- & \iff [Th(OH)_2]_{aq}^{2+} \\
[Th(OH)_2]_{aq}^{2+} + OH^- & \iff [Th(OH)_3]_{aq}^+ \\
[Th(OH)_3]_{aq}^+ + OH^- & \iff Th(OH)_3(s)
\end{align*}
\]
Stepwise hydrolysis of U (IV):

\[ U^{4+}_{aq} + OH^- \Leftrightarrow [U(OH)]^{3+}_{aq} \]
\[ [U(OH)]^{3+}_{aq} + OH^- \Leftrightarrow [U(OH)]^{2+}_{aq} \]
\[ [U(OH)]^{2+}_{aq} + OH^- \Leftrightarrow [U(OH)]^{+}_{aq} \]
\[ [U(OH)]^{+}_{aq} + OH^- \Leftrightarrow U(OH)_{4(s)} \]

Stepwise hydrolysis of U (VI):

\[ UO_2^{2+}_{aq} + OH^- \Leftrightarrow [UO_2(OH)]^{+}_{aq} \]
\[ [UO_2(OH)]^{+}_{aq} + OH^- \Leftrightarrow UO_2(OH)_{2(s)} \]

Stepwise hydrolysis of Pu (IV):

\[ Pu^{4+}_{aq} + OH^- \Leftrightarrow [Pu(OH)]^{3+}_{aq} \]
\[ [Pu(OH)]^{3+}_{aq} + OH^- \Leftrightarrow [Pu(OH)]^{2+}_{aq} \]
\[ [Pu(OH)]^{2+}_{aq} + OH^- \Leftrightarrow [Pu(OH)]^{+}_{aq} \]
\[ [Pu(OH)]^{+}_{aq} + OH^- \Leftrightarrow Pu(OH)_{4(s)} \]
Stepwise hydrolysis of Pu (VI):

\[ PuO_2^{2+} \,_{\text{aq}} \, + \, OH^- \, \Leftrightarrow \, [PuO_2(OH)]_{aq}^+ \]

\[ [PuO_2(OH)]_{aq}^+ + OH^- \, \Leftrightarrow \, PuO_2(OH)_{2(s)} \]

Stepwise hydrolysis of Pu (V):

\[ PuO_2^+ \,_{\text{aq}} \, \Leftrightarrow \, PuO_2(OH)_{(s)} \]

Further, their chemistry can make data collection difficult. In particular, the actinide IV oxidation state is hard to study, as these ions are sparingly soluble, very prone to hydrolysis, and often sorb to vessel walls (Bryan et al., 2012).

One aspect of this project is to study the partition of radionuclides in humic ternary systems and develop models (suitable for inclusion in RPA calculations) to predict the solid/solution partition.

1.1.1 Humic Substances

Humic substances (HS) are a naturally occurring category of materials found in different media, such as soils, sediments and natural waters (Tanford 1961). Humic substances are ubiquitous in nature, existing in all terrestrial and aquatic environments (Gjessing, 1976; Thurman, 1985). They are large organic macromolecules formed as by-products from the decomposition of plants and animals. Around 60-70% of soil organic matter is comprised of humic material (Jones & Bryan, 1998). Humic substances are difficult to define, as they are not categorised as discrete materials, such as proteins, polysaccharides and nucleic acids. Hence, the standard definition of HS, “a category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow-to-black in colour, of high molecular weight (MW), and refractory” (Aiken et al., 1985), provides little information as to their chemical nature. Humic substances vary greatly in terms of molecular weight and functional groups, thus the probability of finding humic species of identical chemical and structural compositions in a given sample is low (Choppin 1988). This makes
characterisation difficult. However certain important characteristics include (Wood 1995):

- Physical appearance, such as colour and texture
- Solubility in aqueous media;
- Proton exchange capacity;
- Ability to bind to metal ions, pesticides and organic chemicals

1.1.2 Classification of Humic Substances

Humic substances are heterogeneous mixtures and as such are classified by their solubility, rather than by their chemical reactivity or chemical structure. HS exhibit similar macroscopic properties, but have differing microscopic structures (Livens, 1991; Buffle et al., 1990). Extraction of HS from soils produces three distinct fractions, humic acid (HA), fulvic acid (FA), and humin. Each fraction is defined in terms of its solubility in aqueous media as a function of pH;

- Humic acids are insoluble under acidic conditions, pH < 2, but soluble at pH >2.
- Fulvic acids are soluble at all pH values.
- Humins are insoluble at all pH values.
Further differences also exist between each fraction. Humic acids have higher molecular weights and greater aromaticity than fulvic acids, 40-60 % and 20-50 %, respectively (Choppin, 1988), though later studies suggest aromatic carbon content of humic acids to be as low as 20-40% (Benincasa et al., 2002). Figure 1.1 shows a scanning electron microscope image and the proposed structural building block of solid humic acid (Davies et al., 1997). Carbon and oxygen are the most abundant elements by weight in HS. All three fractions have similar structural properties but different molecular weights and functional group constituents. Humic acid contains 10% more carbon and 10% less oxygen than fulvic acids, and hence fulvic acids have more oxygen containing functional groups per unit weight than either humic or humin species (Schnitzer et al., 1978).

The solubility of HS increases with pH. At high pH there is high intra- & intermolecular repulsion, due to the increased negative charge on the humic molecules (Hayes et al., 1989; Hayes & Swift., 1990). Conversely at low pH and/or in the presence of metal ions, HS tend to aggregate, and form fibres. H-bonding, Van der Waals and adjacent ring electronic interactions are thought to be responsible for this aggregate binding (Swift, 1989 A & B). Humic species are typically highly charged, caused by presence of deprotonated carboxylate and/or phenolic groups, consequently an electrostatic double layer forms around the humic molecule (Tipping & Hurley 1992). This double layer is important when considering metal ion interactions, as it can enhance metal ion binding. This ability to bind metal ions readily, and their relative
abundance in nature, means it is important to understand the role of humic species in the environment.

1.1.3 Humic Substance Structure

Various authors have suggested the likely structure of humic species. Stevenson (1982) proposed long coiled chains, linked together forming a 3D macromolecule, with a randomly distributed electrical charge. Benedetti (1996) and Tombacz et al (1997) suggest a semi flexible humic structure penetrated by solvent molecules and ions. For example, Na\(^+\) may penetrate through the surface and into the interior of the humic molecule (Benedetti et al., 1996, Tombacz et al., 1997, Buffle et al., 1998, Chin et al., 1998). Humic substances undergo a small amount of expansion and contraction, with changes in ionic strength and pH. Changes in pH result in different humic charges, whilst increasing ionic strength results in a degree of shielding of the humic charge. (Benedetti et al., 1996; Schimpf & Petteys, 1997; Chin et al., 1998).

There are three theoretical models that attempt to explain humic structure, (Clapp & Hayes, 1999):

- The Random Coil Model;
- The Self Association model;
- Micelle/Pseudo-Micelle Model.

1.1.3.1 Random Coil Model

This model suggests humic structures are comprised of long, charged molecular strands that loop/coil randomly in solution, and have functional groups running along their length. It is assumed that each individual humic molecule is spherical, with a central Gaussian mass distribution, i.e., the greatest density is located in the centre, decreasing to zero at the outer edges of the humic molecule (Keepax et al., 2002). Deprotonation of the acidic functional groups, causes intramolecular repulsion, resulting in structural rearrangement of the humic molecule (Stevenson, 1982). Solvent molecules are able to
saturate the coil, and exchange with those in the bulk solution. This free exchange takes place at the edges of the coil.

Figure 1.2; Random coil model structure along with penetrating solvent molecules (Taken from Keepax et al., 2002)

The high density at the centre of the coil “traps” solvent molecules for an extended period of time (Swift, 1999). How tightly the coil is packed governs the amount of solvent molecules trapped (Hayes & Swift 1990). Various factors determine coil packing, and these include:

- The nature of the solvent;
- The degree of solvent penetration;
- Charge density on the humic;
- The ionic strength;
- pH of solution.

The presence of large numbers of carboxylate groups in humic substances (typically 4-8 carboxylate groups per 1000 Daltons, Swift., 1996) cause the high charge density found in humic molecules. Repulsion between these carboxylate groups occurs when they are deprotonated. This explains why a single humic coil molecule can exhibit different sizes with changing pH. Under alkaline conditions, deprotonation of carboxylate groups
results in increased intra-molecular electrostatic repulsion, producing less tightly packed coils, and hence larger molecular sizes (Swift et al., 1989b). For acidic conditions, the reverse is true. The carboxylate groups are neutralised, and the resultant decrease in electrostatic repulsion increases the coil packing, and thus a decrease in molecular size is observed. However, when the maximum level of neutralisation is reached, the coil cannot contract any further, and at this point all of the trapped solvent molecules are ejected, and the humic molecule is in its most collapsed state. This effect of decreasing pH is similar to that observed with increasing ionic strength. There, the contraction is due to cations from the electrolyte shielding the negative charges on the coil (Swift, 1999). Intermolecular forces between molecules are also affected by charge neutralisation and shielding. Poorly solvated humic molecules are prone to aggregation due to their hydrophobic nature, which results in precipitation, with only tightly bound water being retained. The presence of water allows some molecular flexibility, causing rapid ion exchange reactions and surface interactions. Schulton & Schnitzer (1993) found a high proportion of cross-linked chains in humic substances. Therefore, humic substances can be thought of as cross-linked, sponge like structures, able to expand and contract, allowing penetration of solvent molecules (Benedetti et al., 1996; Keepax et al., 2002). Figure 1.2 shows the sponge like structure, with penetrable solvent molecules.

1.1.3.2 Self association Model

In this model, humic substances are thought of as small heterogeneous molecular aggregates held together by weak forces (Wershaw, 1986, 1993, Piccolo et al., 1996; Piccolo, 1997; Conte & Piccolo, 1999). Aggregation is thought to occur randomly, with rapid binding and detachment of smaller species from their larger aggregates. The aggregation mechanism is complex, and heavily dependant on the charge of the smaller ‘monomer units’ (Keepax., 2002). For example, studies carried out by De Nobili & Chen, (1999), performing acid precipitations, washing, re-dissolution and dialysis on humic samples, proved ineffective in altering the weight distribution of humic substances. This is unexpected, as weakly bound humic agglomerates would be affected by these techniques (Swift, 1989a, 1989b). Further, how these smaller aggregates bind together in solution remains unclear, possible hydrogen bonding, π bonds, metal ion bridging and hydrophobic interactions have been all been suggested (Wershaw, 1986,
However, for aggregation to be maintained in solution, the strength of these interactions would have to be comparable to that of a covalent bond (Swift, 1999).

1.1.3.3 Micelle/Pseudo-Micelle Model

Again, the large humic substance species in solution are considered to be aggregates, but have characteristics based on micelle type chemistry. Micelles form from surfactants, and contain both hydrophilic and hydrophobic groups. The hydrophobic groups, form the inner part of the humic aggregate, while the hydrophilic groups are found on the external surfaces. However, direct comparison of surfactant micelle chemistry with humic structure is unlikely as humic species are heterogeneous mixtures, unlike surfactant micelles, which are highly ordered (Piccolo, 2001, 2002). Thus the pseudo micelle model, assumes that humic aggregates contain randomly distributed hydrophilic and hydrophobic regions (von Wandruszka, et al., 1997).

1.1.3.4 The Best Humic Structural Model

There are differing views about which model is the best able to describe the properties of humic structure. Authors such as Swift (1999) prefer the random coil model, whereas others, such as Piccolo (2001), favour of the self-association model for describing humic structure.

Certain properties of humic materials may provide a key to understanding their structure. Lignin molecules are known precursors of humic substances. Lignin structures expand and contract, rather like in the random coil model (Clapp & Hayes, 1999). Experiments using fractionated humic samples re-applied to a size exclusion column (SEC) showed no change in the humic elution peak in terms of its position and width after acid precipitation (Swift, 1999). Further, elution peaks from size exclusion columns of fractionated humic substances occurred between proteins and polysaccharides of the same mass (Benincasa et al., 2002). These results indicate the self-association model cannot entirely explain humic structure, as a change in the elution peaks should be observed. Further debate about the self-association model focuses on intermolecular hydrophobic interactions, and if they are strong enough to
hold aggregates together. Additionally, possible coulombic repulsions may prevent aggregate formation (Swift, 1999).

Size exclusion column experiments, carried out by Piccolo (2001, 2002a) reversibly shifted humic acid molecular size from high to low, using simple carboxylic acids. UV-visible spectrometry was used to record these changes in molecular size. The experiments suggested that the amphiphilic nature of the simple acids, caused the break up of humic aggregates. At near neutral pH it was concluded, humic species consist of small heterogeneous molecules held together by weak dispersive forces. However, similar experiments carried out using electrophoretic mobility measurements, showed no change in the size distribution of humic acid molecules (Farrelly 2007).

Diallo et al (2003) developed a conceptual model that produced fulvic acid type structures, which were consistent with experimental measurements of humic species, using mass spectrometry, NMR and IR. The isomers formed by the model may form supra-molecular associations via hydrogen bonds and van de Waals forces. However, this conceptual model depends on the accuracy of the ESI-MS technique, for example molecular weights generated by ESI-MS technique have to be accurate, if the proposed molecular structure is to be correct.

Even after various studies and countless experiments, humic structure cannot be completely described by just one conceptual model. Indeed, to understand and fully characterise humic structure, certain aspects from all three models should be incorporated (Diallo et al., 2003).

1.2 Metal Ion Interactions

1.2.1 Humic Interactions with Metal ions

Humic substances bind strongly to a range of metal ions. Interactions with transition metal, lanthanide and actinide ions are particularly favourable (Jones & Bryan., 1998; Illés & Tombácz., 2006). Generally, the solubility of the metal ions increases when they are bound to humic substances under conditions expected in the environment. However, at very high metal ion concentrations precipitation can occur. Also, in the presence of a solid surface, ternary complex formation could reduce metal ion concentration. However under conditions expected in the environment and at very high metal ion
1.2.2 Electrostatic double layer

Formation of an electrostatic double layer occurs when any charged substance is placed in a liquid, the resultant structure is comprised of two layers. The first layer is the surface charge, which is either positive or negative and is dependant on the substance itself. Deprotonation of carboxylate and phenolic groups results in a negative surface charge on the humic molecule. This charge attracts cations from the bulk solution, resulting in an adjacent second layer (K.H Tan., 1998). In this 2nd layer the cations are attracted to the negatively charged surface, while being able to exchange the bulk solution, this can be seen in Figure 1.3, which shows a simple pictorial representation of double layer around a humic molecule. The resulting double layer significantly affects interactions of humic substances with radionuclides (Jones & Bryan, 1998).
Figure 1.3; Pictorial representation of double layer around a humic molecule

Various theories have been put forward to explain the electrostatic double layer. The earliest and simplest of these was put forward by Helmholtz (1879). The negative charge is evenly distributed, over the surface of the humic molecule, with a charge density (\(\sigma\)) in the first layer. In the second layer the counter charge is most concentrated in the parallel plane closest to the surface at a distance, \(\chi\). If the medium has a dielectric constant (D), then the total potential of the system \(\Psi\) is given by:

\[
\psi = \frac{(4\pi\sigma\chi)}{D} \tag{Equation 1}
\]

In the Gouy-Chapman theory, again the negative charge is distributed over the humic surface. However the counter ion charge in the 2\(^{nd}\) layer is not localised in a single layer but it is dispersed over the entire layer. The concentration distribution of this layer follows a Boltzman equation:

\[
C_x = C_x^\circ \exp\left(\frac{-ze\psi}{kT}\right) \tag{Equation 2}
\]
Where $C_x$ is the cation concentration (mol/L) at distance $x$ from the surface, $C_x^0$ is the
cation concentration in bulk solution (mol/L), $z$ is the valence of the metal ion, $e$ is the
electronic charge, $\Psi$ is the electrical potential at distance $x$ from the surface, $k$ is the
Boltzman constant and $T$ is the absolute temperature. Hence the initial electric potential
decreases exponentially from the humic surface and is given by;

$$\Psi_x = \Psi_o e^{(-Kx)} \quad \text{(Equation 3)}$$

where $\Psi_x$ is the electric potential at a given distance $x$, $\Psi_o$ is the surface potential and $K$
is a constant based on concentration, ion valency, dielectric constant and temperature.

The maximum electrochemical potential is found at the humic surface, and decreases
with increasing distance, with the net charge density and potential reaching zero at the
double layer boundary Figure 1.4.

\[
\begin{align*}
\text{Potential (\Psi)} &\quad \text{Potential distribution as related to distance} \\
0 &\quad \frac{1}{K} \\
\text{Distance (x)} &\rightarrow
\end{align*}
\]

Figure 1.4; Distribution potential in the diffuse double layer (Taken from Tan, 1998)

Additional improvements to the diffuse double layer theory were added by Stern
(1924). The Stern theory takes into account ionic size, for example, at a certain point,
ions become too big to get any closer to the surface. The Stern layer is a sub-layer that
is found immediately adjacent to the humic surface; ions present in this layer can’t penetrate further. In the Stern layer, ions are essentially considered immobile.

Figure 1.5; Schematic illustration of distribution of potential in the Stern layer (Taken from Tan, 1998)

Figure 1.5 shows the change in potential from the humic surface ($\Psi_o$) through the Stern layer ($\Psi_d$) and into the diffuse layer. Using Poisson's equation, the potential surrounding the humic molecule can be determined (Tanford, 1961);

$$\nabla^2 \psi = -\rho / \varepsilon \quad \text{(Equation 4)}$$

where $\nabla^2$ is the Laplacian operator, $\rho$ is the charge density, and $\varepsilon$ is the permittivity. In the Stern layer, the charge density ($\rho$) is zero. The charge density $\rho$ varies with distance from the centre of the colloid, and depends upon both the humic and counter ion charges (Bartschat et al., 1992). Double layer theory is applicable to the study of adsorption, ion exchange and other surface reactions that occur between metal ions and humics.
1.3 Kinetics of metal ion-humic binding

Humic substances are unlike ordinary ligands, and have two binding modes, exchangeable and non-exchangeable (Cacheris & Choppin 1987; Choppin & Clark 1991; King et al., 2001). Metals ions initially bind in the exchangeable mode resulting in a strong interaction (Log\(_{10}\) K for Eu\(^{3+}\) = 8.27), and complex formation. (Tipping & Hurley 1992, Bryan et al., 2000). Metal ions can also dissociate rapidly from the complex, if they encounter a stronger binding site, such as other ligands or mineral surfaces (Warwick et al., 2000).

Metal ions bound non-exchangeably are more resistant to removal by a stronger sink. If the humic complex encounters a stronger binding site, the non-exchangeable metal ion would need to undergo a slow transfer to the exchangeable binding site, before it could dissociate from the complex.

Studies carried out by Schussler et al (1998), King et al (1999), Schussler et al (1999), Warwick et al (2000), have examined this kinetic effect, identifying the initial fast components such as exchangeable binding modes, however the focus has been the slower, long-lived components, as these are most significant for metal ion transport in the environment (Bryan et al., 2007). These studies show that metal ions in the slow component, present in all the humic samples, have similar rates of desorption, Table 1.1 (Bryan et al., 1998).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Desorption rate (s(^{-1}))</th>
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<tbody>
<tr>
<td>Eu(III) (pH 4.5, 20°C)</td>
<td>1.2 x 10(^{-6})</td>
</tr>
<tr>
<td>Eu(III) (pH 4.5, 40°C)</td>
<td>1.4 x 10(^{-6})</td>
</tr>
<tr>
<td>Eu(III) (pH 6.5, 40°C)</td>
<td>5.0 x 10(^{-7})</td>
</tr>
<tr>
<td>Co(II) (pH 6.5, 40°C)</td>
<td>1.3 x 10(^{-6})</td>
</tr>
<tr>
<td>Am(III) (pH 6.5, 40°C)</td>
<td>1.1 x 10(^{-6})</td>
</tr>
</tbody>
</table>

Table 1.1; First order desorption rate constants of various metal ions (Bryan et al., 1998)
The rate of desorption is slow and hence the metal ion remains attached to the humic for a longer time, thus increasing its mobility. When a metal ion bound non-exchangeably encounters a stronger binding site a slow rate of desorption is observed, and the rate is independent of the competing sink. The overall desorption rate is determined by the transfer rate of the metal ion from the non-exchangeable to the exchangeable, unlike the behaviour for exchangeable binding, where the metal type determines strength of the interaction (Tipping & Hurley, 1992; Read & Falck, 1996).

The process of metal ion movement to a non-exchangeable binding site, produces a kinetic resistance effect (Choppin et al., 1988). This movement of the metal to and from exchangeable and non-exchangeable is illustrated in the Figure 1.6, where M represents the metal ion (Warwick et al., 2000).

![Figure 1.6](image)

**Figure 1.6; Conceptual representation of metal ion movement in and out of a non-exchangeable binding site (Adapted from Warwick et al., 2000)**

An alternative to the ‘movement’ method is illustrated in Figure 1.7. After initial metal ion binding, the humic rearranges its structure over a period of time, resulting in complete coordination of the metal ion. Hence, the metal ion is isolated from any aqueous phase solution chemistry, rendering it non-exchangeable (Keepax, 2002).
The mechanisms, by which non-exchangeable metal binding occurs, are poorly understood. However the formation of hydrophobic zones within the humic structure when polyvalent metal ions bind may help to explain why complete coordination of the metal ion by the humic is often observed (Von Wandruszka et al., 1997).

1.3.1 Modelling exchangeable metal ion-humic binding

Attempts to predict speciation and metal binding behaviour using mathematical models has had varying degrees of success. One of the biggest challenges in terms of humic substances is the ability to predict and quantitatively describe metal ion binding to humic substances, while also accounting for electrostatic effects. Authors such as Reiller et al., (2005) treat humic substances as normal ligands, while others, Wang et al., (2007b) see humic substances as large polyelectrolytes.

Improvements in our understanding of humic structure and the behaviour of humic substances have enabled the development of complex mathematical models, which take into account heterogeneity and the electrostatic factors associated with large polyelectrolytes. Two such models, MODEL VI (Tipping, 1998) and NICA-Donnan (Non Ideal Competitive Adsorption), (Van Riemsdijk et al., Kinniburgh et al., 1996), have been widely applied to the speciation of metal ion/humic systems.

MODEL VI (Tipping, 1998) takes into account site heterogeneity by using a set of finite binding sites. In all, the model assumes that the humic has eight binding site types; four carboxylic, type A, and four phenolic, type B. Binding metal ions compete with each
other for either type A or type B sites, resulting in simple monodentate binding, according to the reaction:

\[ R^Z + M^z = RM^{Z+z} \quad \text{(Equation 5)} \]

The model allows further metal ion binding at bi-dentate and tri-dentate sites, each of which have a range of binding affinities.

Electrostatic effects are considered that also take into account counter-ion contributions. An advantage of using this type of model is its ability to estimate equilibrium constants from small data sets, allowing comparison between different binary systems. More recently Tipping et al (2011) have developed Model VII which addresses inadequacies encountered with Model VI. For example, when applying Model VI to systems involving lanthanide, Co and UO$_2$, binding to humic and fulvic acids, the model overestimated the pH dependence at higher pH. This overestimation was attributed to binding sites containing multiple weak type B-acid groups (e.g. phenolic) being present in the humic. In Model VII, multi-dentate binding sites that have more than one type B-acid group are excluded. This is important as the model now uses different combinations of monodentate sites to produce multi-dentate sites with fewer monodentate combinations (Tipping et al., 2011). Further, Tipping established a correlation between equilibrium constants for metal ion binding, at type A and type B sites ($\log K_{MA}$ and $\log K_{MB}$) respectively. Along with the spread factors $\Delta LK_{A1}$ and $\Delta LK_{B1}$ being linked the resultant humic ion-binding Model is much simpler. An example of how well Model VII performs is displayed in Figure 1.8, which shows a better correlation of Model VII prediction with an experimental data set than the Model VI prediction.
Figure 1.8; Comparison of experimental data for La\textsuperscript{III} binding by humic acid (open circles) and fulvic acid (closed circles), with Models VI (dashed lines) and VII (full lines) fits (Taken from Tipping et al 2011). Experimental data provided by Sonke, (2006)

Model VII improves on Model VI, in terms of its more simplistic approach to metal ion binding. Overall, most predictions between the two models do not differ significantly; hence calculations involving Model VI are unlikely to be changed greatly by Model VII (Tipping et al., 2011).

The NICA-Donnan model uses a continuum of binding site affinities, with two specific parameters characterizing the heterogeneity. The first parameter deals with the heterogeneity of the humic itself, while the second parameter deals with the heterogeneity associated with the metal ion. Use of the NICA-Donnan approach is two fold; initially the specific ion binding is described by the NICA (non-ideal competitive adsorption) part of the model, which assumes monodentate binding of the metal ion to proton binding sites; and the second non-specific binding (counterion accumulation) is described by the Donnan model. In order to describe proton binding at differing ionic strengths, the NICA-Donnan model uses seven or eight parameters, two for site densities, two for median equilibrium constants, two for distribution parameters, an electrostatic parameter, and a possible initial humic charge parameter (Tipping et al 1998).
Overall the NICA-Donnan model has been shown to fit a wide range of data, covering a range of free metal ion concentrations (Benedetti et al., 1995) and various detailed competition experiments (Kinniburgh et al., 1996).

Both of these models have been included in general speciation codes, WHAM (MODEL VII) and ECOSAT (NICA), allowing processes such as hydrolysis, ligand complexation and metal ion speciation to be simulated at the same time. For example, ECOSAT, has been used to calculate metal ion speciation in groundwaters, soils, soil solutions and surface waters (Fest et al., 2007; Lumsdon, 2004; Weng et al., 2002; Kalis et al., 2006). WHAM has been applied to lake and river waters (Cory et al., 2007; Guthrie et al., 2005) and soils (Almas et al., 2007). The need to keep RPA calculations simple, only allows for the inclusion of simple mathematical models. This is because of the need to find a balance between a simple model that gives an approximation but is not computationally intensive, and one that accounts for most of the complex interactions occurring in a system, which is very computationally intensive. However, as computing power increases the possibility to include more complex models would become possible, but would require a change in the attitude of waste management organisations.

The last 20 years has seen various authors propose a simplified approach to describing metal ion-humic binding. This approach has been termed either the “Charge Neutralisation Model” (CNM) or “Effective Humate Ligand Concentration Approach”. In either case, the humic is treated as a mixture of simple ligands, with a single equilibrium constant, $\beta_{\text{CNM}}$:

\[
\beta_{\text{CNM}} = \frac{[MHA]}{[M] \{ (\frac{PEC}{n} \alpha - [MHA]) \}}
\]

(Equation 6)

Where, [M] and [MHA] represent the free metal and complexed metal concentrations; the PEC is the total humate proton exchange capacity (determined by potentiometric titration); $\alpha$ represents the degree of ionisation; and, n is the number charge on the metal ion.
The model proposes that the humic is comprised of small species, with masses of the order of 500 Da or less and an average 3-4 charge units per molecule, and hence, electrostatic effects between species are considered negligible. ESI-MS studies of humic substances support this approach by showing that humic molecules could be smaller than originally thought (Plancque et al., 2001).

The CNM approach has proved successful in describing the behaviour of various actinides, such as Am$^{3+}$, Cm$^{3+}$, NpO$_2^+$ and UO$_2^{2+}$ (Reiller, 2005; Seibert et al., 2001; Mibus et al., 2007; Morgenstern et al., 2000).

The use of a single equilibrium constant $\beta_{\text{CNM}}$ to describe humic binding as a whole might seem surprising, given the complex and heterogeneous nature of humic substances. However it is thought that the largest free energy contribution occurs from the increased entropy associated with metal ion dehydration, with this value being the same for each ligand type present in the humic (Bryan et al., 2000). Further evidence supporting the single equilibrium constant suggests that the majority of metal ions involved in binding are coordinated to carboxylic and or similar functional groups (Boyd et al., 1981), thereby reducing the range of metal ion binding strengths. Authors such as Ivanova et al. (2008) and Reiller et al. (2007, 2008) have shown that a single equilibrium constant can be used across a wide range of metal ion concentrations. Reillier et al. (2007, 2008) predicted An (IV) binding with a single conditional equilibrium constant, and a consistent set of hydrolysis parameters (Figure 1.9).
The CNM is a simplistic approach, given the inherent complexity of humic substances is not being taken into account (Bryan et al., 2012). Regardless, there is still sufficient evidence to suggest that a single equilibrium constant could be used to predict metal-humic interactions, and one of the main advantages of using the CNM is its possible use in RPA calculations.

1.3.2 Modelling Non-exchangeable metal ion-humic interaction

Recently, both batch and column experiments have improved our knowledge of metal ion-humate systems, in particular the non-exchangeable interaction. Initially, metal ions bind in the exchangeable mode, however after a period of time, metal ions transfer to the non-exchangeable mode. Dissociation of this non-exchangeably bound metal ion is not instantaneous, but is kinetically controlled (Bryan et al., 2007).

Various column experiments have highlighted that non-exchangable binding significantly affects humic mediated metal ion transport in the environment (Artinger et al., 2002, Bryan et al., 2005, 2007, Schuessler et al., 2000, 2001, Warwick et al., 2000). By modelling these results, it has been shown that both the first order dissociation rate constants and the amount of metal ions bound non-exchangeably, along with the residence time, determine the amount of metal ions transported (Bryan et al., 2007).
Many techniques have been used to study the non-exchangeable binding mode, and these include; ligand competition (Cacheris & Choppin, 1987, Rate et al., 1993), isotopic exchange (Mezera et al., 2001) and the most common technique, the resin competition method. The methodology of this technique is as follows:-

- Metal ions are added to humic substances, forming complexes, which are left to mature, before being exposed to the resin;
- The resin has a very strong affinity for metal ions. Excess resin is used, to ensure the equilibrium favours metal ion dissociation;
- Any free metal ions in solution or those bound in the exchangeable sites, bind to the resin immediately. Only the non-exchangeable metal ions do not dissociate from the humic instantaneously. Therefore, the only metal ion remaining in solution is non-exchangeably bound.
- Over a period of time, the non-exchangeable metal ions will be transferred to the exchangeable, and rapid dissociation to the resin will ensue.
- By plotting the natural log of metal ion concentration remaining in solution against time, a first order dissociation rate constant for the non-exchangeable fraction can be determined.

The resin competition method has been widely applied to metal/humic systems. These systems show only a small variation in the dissociation rate constant of the non-exchangeable metal ions. King et al (2001) measured the first order dissociation rate constants in the range 1.5 - 3.3 x 10^{-7} \text{s}^{-1} for Eu^{3+} (pH 6.5, at 10 ppm HS), with Davis et al (2000) giving rates of 1.6 - 2.8 x 10^{-7} \text{s}^{-1} for Th^{4+} (pH 6.4 - 7.8, 30 ppm HS). Along with metal ion chemistry, the origin of the humic species, i.e. from soil, groundwater or surface water, also has little impact on the dissociation rate constant (Monsallier et al., 2003). The pH of these systems affects the amount of non-exchangeably bound metal ions. At high pH humic molecules experience a large degree of deprotonation, leading to structural expansion, allowing greater access to the non-exchangeable binding sites (King et al., 2001). Further studies involving both humic and fulvic acids show a
significantly greater amount of non-exchangeably bound metal ions for humic acids than for fulvic acids. It is thought that this is due to the presence of larger species found in humic acids (Keepax et al., 2002).

Humic-metal ion systems exhibit a continuous set of first order dissociation rate constants between the instantaneous (exchangeable) and most slowly dissociating (non-exchangeable) interactions (Bryan et al., 2007; King et al., 2001). To simulate transport in column experiments, it is necessary to incorporate the non-exchangeable effect. Most transport simulations have focussed on two primary components, the exchangeable and the slowest non-exchangeable fraction (Warwick et al., 2000; Schuessler et al., 2000, 2001; Bryan et al., 2005), with only Artinger et al., (2002) using an intermediate fraction (Bryan et al., 2007). Transport models such as NICA and MODEL VI/VII describe the exchangeable interactions, but do not take into account non-exchangeable interactions.

Bryan et al., (2005) used the k1-D transport code to model the effects of humic substances on the transport of Co$^{2+}$ and Eu$^{3+}$ in column experiments. For the Co$^{2+}$, unlike for Eu$^{3+}$, the columns were not pre-equilibrated with humic prior to the injection of the metal. In both cases in the absence of humic, no significant elution was observed. Retardation was seen for the Co$^{2+}$/humic complex, and with possible reversible sorption being observed, a single equilibrium constant was used to describe the behaviour. Similarly retardation occurred for the Eu$^{3+}$/humic complexes, but the interaction was more complex, requiring more kinetic equations and rate constants. Using the k1-D transport code Warwick et al (2000), predicted Eu$^{3+}$ transport in humic equilibrated columns in sand without considering the sorption of the metal/humic complex. Due to the high number surface sorption sites in this system, it was assumed that the only interaction that affects metal ion transport is the one between the surface and the metal ion.

Others modelling radionuclide behaviour in batch and column experiments have used the KICAM (kinetically controlled availability model) chemical model. The initial KICAM model comprised of two humic components, a fast dissociating (exchangeable) fraction and a slow component (non exchangeable). Later, an intermediate fraction was incorporated. This additional component was needed to account for a wider range of humic pre-equilibration and surface contact times (Schuessler et al., 2000, 2001;
Artinger et al., 2002). The initial fast dissociating fraction is similar to that of the Warwick et al (2000) and Bryan et al (2005) approach.

Application of the KICAM to predict transport requires a chemical transport/speciation code, which can simultaneously model both kinetic and equilibrium processes, and hence the k1-D transport code was developed. Schuessler et al (2001) verified the k1-D transport code and its applicability in modelling Am(III) transport using the KICAM model. This verification was accomplished in three stages. The first stage in verification was by comparison of the k1-D conservative tracer transport simulation with an analytical solution, (Appelo et al., 1996). Figure 1.10, taken from Schuessler et al., (2001) highlighted a close agreement between the k1-D simulation breakthrough curve and that of the analytical solution.

Figure 1.10; Comparison of analytical solution with an ideal tracer breakthrough curve for k1-D transport verification (Taken from Schuessler et al., 2001)

The second stage involves comparison of the transport code with calculated breakthrough curves using the verified PHREEQC code (Parkhurst et al., 1995). The PHREEQC code does not include an applicable transport module, therefore transport calculations were done by the use of a cascade model. Two experimental scenarios were then selected for comparison; the first was the injection of one pore volume solution containing Eu and Am at a concentration of $10^{-6}$ mol dm$^{-3}$ into a column with surface sorption sites of $6 \times 10^{-2}$ mol dm$^{-3}$; the second scenario involved injection of a humic
solution (1.2 x 10^{-5} \text{ mol dm}^{-3}) after the Eu/Am solution, the resultant breakthrough curves were different for the two elements, it was surmised this was a consequence of differing complexation constants with humic acid (Buckau et al., 1991; Rabung et al., 1998). Figure 1.11 shows the comparison of the breakthrough curves of the k1-D and the PHREEQC transport codes with respect to Eu and Am. In both cases, the predictions for the elements corresponded well.

Figure 1.11; Comparison of the K1D coupled transport/equilibrium model with the PHREEQC speciation code along with for the mobilization of sorbed Am and Eu by humic acid (Taken from Schuessler et al., 2001)

The k1-D model was then used to fit data from humic colloid borne Am (III) migration experiments (Artinger et al.,1998). The rate constants used in the k1-D calculations were determined using the KICAM model (Schuessler et al., 2001). In Figure 1.2 the resulting breakthrough curves gave a good agreement with the calculated simulations and experimental data.
Incorporation of the KICAM model in the k1-D transport code enables prediction of Am movement in the pulsed columns. During experimentation most of the Am applied to the start of the column did not elute (Schuessler et al., 2001). The majority of the Am/humic complex that did so appeared slightly ahead of one pore volume, and showed no retardation. A small amount of slower moving Am was present as a ‘tail’ on the elution peak. The slower moving fraction represented a small proportion of the total eluted metal (Artinger, 2002). Application of the KICAM in k1-D to further experimental data is shown in Figure 1.13, which shows good correlation between the predicted and the experimental data.
Figure 1.13; Application of the KICAM/ k1-D model to column experiments in the Gorleben groundwater system with varying migration times and column lengths (Taken from Schuessler et al., 2001)

Similar uranium pulsed column experiments again showed elution of the U/humic material before one pore volume. The main elution peaks had more significant ‘tails’. A possible explanation for these peaks is displacement of the surface bound metal-humic complex (Artinger, 2002).
1.4 Mineral Surfaces

Adsorption of humic substances on to inorganic surfaces has been well established (Jada et al., 2006). This is important when considering humic migration and any associated metal ion transport in the environment. If the humic is bound to a mineral surface, it is essentially immobile (while it remains sorbed) and any metal ion bonded to that humic species is also immobile. Additionally, metal ions can bind directly to mineral surfaces. Hence, understanding the surface properties of minerals, such as quartz, is essential for predicting metal ion migration.

The surface charges of mineral oxides are pH dependant, because the amphoteric nature of the surface results in either a positive or negative surface charge. A simple way to describe the surface reactions is:

\[
\equiv\text{SOH}_2^+ \leftrightarrow \equiv\text{SOH} + \text{H}^+ \quad \text{(Equation 7)}
\]

\[
\equiv\text{SOH} \leftrightarrow \equiv\text{SO}^- + \text{H}^+, \quad \text{(Equation 8)}
\]

Where \(\equiv\text{SOH}\) is a hydroxylated surface group and ‘S’ represents the cationic component of the inorganic solid, for example in the case of silica, \(\equiv\text{Si}\). At low pH, the surface equilibrium produces an overall positive surface charge, whilst at higher pH it will carry a net negative charge. At a certain pH, the net surface charge amounts to zero, and this is Point of Zero Charge (PZC). The PZC gives an indication of how surface charge varies with pH. The charge is positive below it and negative above it. Every mineral surface has its own PZC. Table 1.2 shows the Point of Zero Charge for some common minerals. At high pH a mineral surface has an overall negative charge, increasing cation attraction, resulting in stronger cation sorption.
<table>
<thead>
<tr>
<th>Material</th>
<th>pH (PZC)</th>
<th>Material</th>
<th>pH (PZC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃</td>
<td>5.0</td>
<td>SiO₂ Quartz</td>
<td>2.0</td>
</tr>
<tr>
<td>Magnetite</td>
<td>6.5</td>
<td>Feldspars</td>
<td>2 - 2.4</td>
</tr>
<tr>
<td>Fe-OOH</td>
<td>7.8</td>
<td>Kaolinite</td>
<td>4.6</td>
</tr>
<tr>
<td>Goethite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.5</td>
<td>Hydroxyapatite</td>
<td>7.6</td>
</tr>
<tr>
<td>Hematite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2.5</td>
<td>Albite</td>
<td>2.0</td>
</tr>
<tr>
<td>MgO</td>
<td>12.4</td>
<td>Chrysotile</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Calcite</td>
<td>9.5</td>
<td>TiO₂ Rutile</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 1.2; Point of Zero Charge for some common minerals
1.4.1 Quartz Sand Structure

Quartz occurs in all environments, and is an essential constituent of igneous rocks.

![Silicon dioxide atomic structure](image)

**Figure 1.14; Silicon dioxide atomic structure**

Structurally, quartz is comprised of helical chains of silicon tetrahedra that consist of four tetrahedra, rotated 120° relative to one another (Figure 1.14). Each chain is then connected to two other chains. The positive Coulomb field associated with the Si$^{4+}$ ion at the centre is shielded by this conformational arrangement. Substitution of Si$^{4+}$ with Al$^{3+}$ can occur, resulting in excess in negatively charged units, allowing the attachment of interstitial cations.

Fracturing of quartz crystals breaks the Si-O bond, creating active surface sites, where water molecules readily sorb, resulting in a surface coverage of hydroxyl groups. The surface can also have additional chemical groups including Si-O-Si, which is hydrophobic (Battery, 1972; Haung & Furstenau, 2001).
1.5 Modelling

1.5.1 Humic Transport Modelling

In most transport models, the main focus has been on the metal ion. However, McCarthy et al (1996) and Gu et al (1994) have modelled the humic substance itself. McCarthy et al (1996) used a two site modelling approach, whilst Gu et al (1994) adapted a Langmuir model, by including a hysteresis parameter. One of the most successful approaches to humic sorption/transport applied to batch, column and field tracer data was that of van de Weerd et al (1999, 2002). In this approach, the heterogeneity of the mineral surface is assumed to be small compared to that of the humic. Hence, a single site is defined for the mineral surface. Different humic sized fractions therefore compete for the single surface site. Each humic size fraction occupies a different surface area when sorbed to the mineral surface. Hence, the surface capacity varies with each fraction. The fractional surface coverage, $\theta_i$, for each fraction $i$, is defined as;

$$
\theta_i = \frac{Q_i}{Q_{i,max}} \quad \text{(Equation 9)}
$$

Where $Q_i$ is the amount of fraction $i$, sorbed at the surface and $Q_{i,max}$ represents the amount of the fraction that would be sorbed if the surface was saturated only with fraction $i$. The solution concentration of fraction $i$, expressed in terms of mg of carbon per dm$^3$, is denoted $[\text{HA}_i]$, and the rate of change of $Q_i$ is given by;

$$
\frac{dQ_i}{dt} = k_{a,\text{HA}_i}[\text{HA}_i](Q_{i,max} (1 - \theta_T)) - k_{d,\text{HA}_i}Q_i \quad \text{(Equation 10)}
$$

where $k_{a,\text{HA}_i}$ is the sorption rate constant (dm$^3$ mg C$^{-1}$ s$^{-1}$) and $k_{d,\text{HA}_i}$ is the first order desorption rate constant (s$^{-1}$). The equilibrium constant for the sorption of fraction $i$, at the surface, is given by the ratio of $k_{a,\text{HA}_i} / k_{d,\text{HA}_i}$. Use of this ‘NOMADS’ model was able to predict humic sorption by iron oxide successfully (van de Weerd et al., 1999).
Further, integration of the NOMADS model into a 1-D transport code, allowed modelling of lab based column and field tracer experiments (van de Weerd et al., 2002). When modelling humic sorption, either three or six fractions were used by van de Weerd et al (2002), Table 1.3 shows the model parameters used by the six-fraction humic sorption approach.

<table>
<thead>
<tr>
<th>Fraction Name</th>
<th>Abundance of fraction as a function of total humic concentration, $f$</th>
<th>Humic sorption forward rate constant, $k_{a,HAi} \text{ (dm}^3 \text{ mg C}^{-1} \text{ s}^{-1})$</th>
<th>Humic sorption backward rate constant, $k_{d,HAi} \text{ (S}^{-1})$</th>
<th>Humic sorption equilibrium constant, $K_{HAi} \text{ (dm}^3 \text{ mg C}^{-1})$</th>
<th>Sorption capacity of solid phase, $Q_{i,\text{max}} \text{ (mg C kg}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1: $M_w &lt; 3 \times 10^3$</td>
<td>0.19</td>
<td>$1.05 \times 10^{-5}$</td>
<td>$1 \times 10^{-4}$</td>
<td>0.105</td>
<td>106.86</td>
</tr>
<tr>
<td>Hb: $M_w &lt; 3 \times 10^3$</td>
<td>0.30</td>
<td>$1.49 \times 10^{-5}$</td>
<td>$7.08 \times 10^{-5}$</td>
<td>0.210</td>
<td>151.73</td>
</tr>
<tr>
<td>H1: $3 \times 10^3 &lt; M_w &lt; 10^5$</td>
<td>0.08</td>
<td>$1.82 \times 10^{-6}$</td>
<td>$5.19 \times 10^{-7}$</td>
<td>3.50</td>
<td>170.99</td>
</tr>
<tr>
<td>Hb: $3 \times 10^3 &lt; M_w &lt; 10^5$</td>
<td>0.36</td>
<td>$2.57 \times 10^{-6}$</td>
<td>$3.67 \times 10^{-7}$</td>
<td>7.02</td>
<td>242.78</td>
</tr>
<tr>
<td>H1: $M_w &gt; 10^5$</td>
<td>0.04</td>
<td>$5.75 \times 10^{-7}$</td>
<td>$1.64 \times 10^{-8}$</td>
<td>35.0</td>
<td>172.46</td>
</tr>
<tr>
<td>Hb: $M_w &gt; 10^5$</td>
<td>0.03</td>
<td>$8.14 \times 10^{-7}$</td>
<td>$1.16 \times 10^{-8}$</td>
<td>70.1</td>
<td>244.86</td>
</tr>
</tbody>
</table>

Table 1.3; Model parameters of the six fraction approach to model humic sorption (Taken from van de Weerd et al., 2002)
Table 3 shows that as the size of the humic species increases, both the forward and backward rate constants decrease. Hence, when competition for fresh surfaces sites occurs, smaller humic fractions initially coat these sites, due to their faster kinetics. Over time, displacement of these smaller fractions may occur, as the humic concentration and competition increases (van de Weerd et al., 2002). Although small species bind more rapidly, larger species have a stronger interaction. More recent large-scale migration experiments with C-14 tracers, have modelled humic substance migration in Boom Clays. The authors used a similar kinetic modelling approach to the NOMADS model; they concluded that although more complex transport models could be applied to better describe humic migration in Boom Clays, the more simplistic kinetic sorption approach performed reasonably well in describing experimental data (Martens et al., 2010).

1.5.2 Environmental Implications of Humic metal ion Transport

Humic substances play a key role in metal transport in the natural environment (Bryan et al., 1998; Piccolo et al., 2001; Piccolo et al., 2002b). Livens and Singleton (1991), highlighted the importance of metal-humic interactions with respect to radionuclides, by the study of soil samples from Cumbria. They found soil samples containing Pu - 239,240 had a specific activity of 2860 Bqkg⁻¹ but analysis of the humic fractions revealed a specific activity of 27,400 Bqkg⁻¹, nearly 10 times higher than that found in the soil sample. At the Oak Ridge site in the US, rapid mobilisation of transuranic (TRU) radionuclides (²⁴¹Am and ²⁴⁴Cm) has been observed especially during periods of intense rain fall, despite the fact that both radionuclides have high affinities for mineral surfaces (Kₐ 1 x 10⁵ to 1 x 10⁷ dm³ kg⁻¹). Migration of these radionuclides was shown to be 80 m away from the source (McCarthy et al., 1998a). Analysis of the activity over a period of weeks produced a linear velocity between 8.7-1.2 x 10⁻⁵ ms⁻¹, indicating little retardation of TRU radionuclides in the subsurface. A field scale trivalent lanthanide injection experiment was carried out to identify possible mechanisms responsible for this rapid migration over a period of 73 days (McCarthy et al., 1998). Nd³⁺ and Br⁻ tracers were found together over a period of 2-4 days, and a distance of 10 m from the injection point, and the linear velocity was calculated in the range of 5.8-2.9 x 10⁻⁵ ms⁻¹. At a further two sampling points, 50 m and 73 m from the injection site, Eu³⁺ and Br⁻ were also found together after a period of 18 days. Given that sorption isotherms for
Am and Eu\(^{3+}\) with the insitu sediment in the absence of humic showed a high sorption affinity (R > 50 000), the results show metal ion mobility to be much greater than this. A possible explanation for this high mobility could be due to the short residence times of the metal ions in the groundwater column (Bryan et al., 2007). McCarthy et al (1998) concluded that humic substances facilitated the transport of the lanthanide tracers and TRU. Humic substances are therefore thought to be responsible for the mobility and rapid migration of TRU radionuclides at the Oak Ridge site.

1.6 Fractionation

1.6.1 Humic Fractionation

One of the essential requirements needed for developing models to predict contaminant mobility, is the quantitative understanding of sorption of humic substances to mineral surfaces, however such an understanding has remained elusive due to the complex nature of humic substances. As discussed earlier, humic substances are thought of as polydisperse and heterogenous polyelectrolytes, which exhibit differing molecular weights (MW) and chemical compositions (Stevenson et al., 1994; Vermeer et al., 1998). Humic substances show similar sorption properties to those of polymers (for example; adsorption/desorption hysteresis and surface-area-to-volume ratio dependant isotherms which represent the amount of humic bound at the surface as a function of the humic present in the solution phase) and this provides an insight into humic fractionation (Koopal 1981; Vermeer et al., 1998; Pitois et al., 2008). For example in non-ionic polymer systems, higher molecular weight fractions (HMW) sorb preferentially to surfaces, as they are thermodynamically favoured over the lower molecular weight fractions (LMW) (Koopal 1981;). This is similar to humic systems, where various authors have reported preferential sorption of HMW fractions to mineral surfaces. Van de Weerd et al (1999) determined that at high humic concentrations, the initially fast sorbing LMW fractions would be displaced by the more thermodynamically favoured HMW fractions. In aquatic based humic systems, sorption of HMW fractions on to both kaolinte and haematite were observed, however for terrestrial based systems, the HMW fractions favoured sorption on to kaolinte, while LMW fractions sorbed to hematite. This contrasting sorption behaviour could be attributed to the differences in chemical structure between the aquatic and terrestrial
humic species (Hur & Schlautman et al., 2003). Further, chemical fractionation is revealed by preferential sorption of aliphatic fractions onto clay surfaces, while sorption of terrestrial aromatic fractions onto montmorillonite has been observed (Wang & Xing, 2005; Feng et al., 2006). Hysteresis is common for all these systems, and various authors have highlighted that sorption and desorption processes of certain fractions occur much slower than anticipated (Gu et al., 1994; van de Weerd et al., 1999, 2002). Field tracer studies carried out by McCarthy et al (1996) highlighted differences in transport behaviour of various molecular weight size fractions, ranging from 3000-10000 Da. Fractions of less than 3000 Da, showed little or no retardation, and behaved like the tracer, whereas higher molecular weight fractions were much more retarded. There also appeared to be a strong adsorption-desorption hysteresis effect, where weakly binding lower molecular weight fractions were replaced with heavier molecular weight fractions with a stronger binding affinity. This behaviour is important when considering humic transport, as different fractions can affect various transport processes. For example, large molecular weight fractions that are more hydrophobic have a greater binding affinity for organic contaminants, while the more hydrophilic fractions that have high oxygen to carbon ratios can affect complexation of metals and radionuclides (Perdue.,1989)

Various techniques have been used to characterise fractionated humic substances, and these include ultra filtration, ultracentrifugation and size exclusion chromatography. However, these techniques suffer from certain drawbacks, such as poor resolution and interaction of the humic with the separation medium. Hence, flow fractionation (FFF) techniques have been developed. Pitois et al (2008) used the FFF technique to study the sorption of fractionated humic acid onto quartz sand. Following the initial rapid uptake of humic acid, a much slower kinetic step was seen, indicating possible multi component behaviour. Additionally, preferential sorption of certain humic fractions as observed during the interaction. It was found that the molecular weight distribution of the residual humic acid was different to that of the original humic acid. Humic acid molecules with a weight average molecular weight ($M_w$) of 1450 Da were sorbed initially in the fast kinetic step, with subsequent sorption of humic molecules of ($M_w$) 3700 Da in the slower kinetic step.

Eventually understanding humic fractionation on sorption to a mineral surface, should enable more reliable predictions of radionuclide behaviour in the environment.
1.7 Ternary Systems

Humic ternary systems (HA + mineral + metal ion) are highly complex. Identifying the interactions taking place is the first step in trying to understand these systems.

![Diagram of ternary systems interactions](image)

**Figure 1.15; Basic overview of interactions occurring in ternary systems (Adapted from Bryan et al 2012)**

In Figure 1.15 labels A) – E) identify interactions occurring in ternary systems; A) represents simple binary interactions of humic with metal ion; B) interactions between the humic and mineral surface; C) interactions between metal ion and mineral surface; D) represents the formation of a ternary complex, where the humic acts as bridge between the metal ion and the mineral surface; E) a ternary complex, however in this case the metal ion acts as a bridge between the mineral surface and humic.

The interactions shown in the figure provide a simplistic view of the ternary systems. In reality the interactions are much more complex. For instance, many mineral surfaces show differing degrees of heterogeneity, complicating surface interactions. Further complexity arises from the polydisperse and heterogeneous nature of humic substances, with the resultant interactions having their own kinetic and thermodynamic parameters.
Recent developments made during the European union 6\textsuperscript{th} Framework Integrated Project FUNMIG have increased our understanding of the interactions of humic substances, mineral surfaces and radionuclides in ternary systems. One such development was the immobilisation of humic substances using silica (Szabo et al., 2006a). Using this technique, the immobilised humic displayed similar characteristics to that of normal solution phase humic substances. The use of these silica materials, avoids the need to separate solution phase humic complexes from any unbound metal ions. Results from these experiments provided various isotherms and conditional equilibrium constants for metal ions, such as $\text{Ag}^{+}$, $\text{Sr}^{2+}$ and $\text{Am}^{3+}$. An added benefit of the immobilised humic material was that it provides a model for humic substances sorbed to mineral phases around waste repositories (Szabo et al., 2007b).

FUNMIG also produced studies that provided some mechanistic understanding of humic-radionuclide redox processes. Such studies conducted by Marquardt and Seibert (2007) involved the reduction of Pu(VI) by fulvic acids and hydroquinone. After an initial rapid reduction to Pu(V), further reduction to Pu(IV/III) took much longer. Both the fulvic acid solution and hydroquinone reduced the Pu in the same way, hence any hydroquinone type structures present in the fulvic solution may account for this Pu reduction. Further studies conducted by Bruggeman et al (2006) used batch experiments to investigate the interaction of Se oxyanions, selenite ($\text{SeO}_3^{2-}$) and selenate ($\text{SeO}_4^{2-}$) with dissolved humic species present in Boom Clay and Gorleben groundwater. The $\text{SeO}_3^{2-}$ and $\text{SeO}_4^{2-}$ oxyanions were thought undergo reduction to Se$^0$ and subsequent precipitation in solution. However for $\text{SeO}_4^{2-}$, no change in speciation was observed, indicating the stability of the selenate oxyanion in the presence of humic rich ground water. Possible reduction of the selenate oxyanion may occur via biotic mechanisms. For selenite, a dramatic change in speciation was observed, along with a decrease in the total Se concentration after centrifugation. This change in speciation can be explained by formation of a newly formed Se species in the presence of humic, thus an abiotic mechanism for the $\text{SeO}_3^{2-}$ transformation is thought to occur.
1.7.1 Modelling Ternary systems

The modelling of humic systems so far has focussed upon simple binary systems, i.e. interactions between humic species and metal ions. Ternary systems are more complex but exist universally in the environment. Hence, it is important to try and model the behaviour of these systems.

The Linear Additive approach models ternary systems by using separate binary models, but this method is not always effective, as the humic may affect metal ion behaviour (Evans et al 2007). A critical factor when analysing these systems is the formation of ternary complexes. Generally, the metal ion interactions follow two paths; the first occurs if the metal-mineral interaction dominates, then the presence of humic will not significantly affect metal ion sorption, (assuming humic coating on the mineral surface does affect the binary surface metal-ion interaction) however, if the metal-humic interaction dominates, then metal sorption follows that of the humic, highlighting the importance of ternary complexes in metal ion behaviour (Warwick et al., 2006).

Using Cs⁺, Cd²⁺, Ni²⁺ and Eu³⁺ in contact with montmorillonite, kaolinite and goethite, Warwick et al (2006) showed increasing ternary complex importance in the order Cs⁺ ≈ Cd²⁺ < Ni²⁺ ≈ Eu³⁺.

Key to the success of the linear additive method is the metal ion/ humic stability constant. As it increases, the humic dominates the chemistry of the system (Evans et al., 2007), and metal ions start to behave like the humic, which is important when attempting to predict radionuclide transport.

The ligand charge distribution (LCD) model was developed to model humic and metal ion interactions at equilibrium, in ternary systems (Van Riemsdijk et al 1999, 2002). The LCD model incorporates both the CD-MUSIC model to describe metal ion surface binding, and the NICA-Donnan model for metal ion– humic interactions in solution (Filius et al., 2001, 2003). As an example, the LCD model was used to simulate behaviour in the calcium/goethite/fulvic acid ternary system. The results predicted the main interactions between the metal ion and the sorbed fulvic acid to be electrostatic, and showed direct binding of sorbed calcium to the mineral surface (Wang et al., 2005). The addition of the ADAPT model improved the LCD model, by determining the extent of humic sorption onto mineral surfaces. The extent of this sorption is predicted as follows;
\[ \mu_{\text{solution}} = \mu^o + \Delta F_{\text{solution}} + RT \ln C_{\text{solution}} \quad \text{(Equation 11)} \]

\[ \mu_{\text{sorbed}} = \mu^o + \Delta F_{\text{sorbed}} + RT \ln C_{\text{sorbed}} \quad \text{(Equation 12)} \]

Where \( \mu^o \) is the standard potential of the humic in its reference state; \( \Delta F_{\text{solution}} \) and \( \Delta F_{\text{sorbed}} \) represent the change in free energy of humic from its reference state to the solution and adsorbed states. The free energy change is comprised of two components; the first is the change in the free energy of the specifically bound ions in solution and on the surface \( \Delta F_{\text{solution}, sp} \) and \( \Delta F_{\text{sorbed}, sp} \) respectively, and the second is the change for the non-specifically bound ions \( \Delta F_{\text{solution}, nsp} \) and \( \Delta F_{\text{sorbed}, nsp} \);

\[ \Delta F_{\text{solution}} = \Delta F_{\text{solution}, sp} + \Delta F_{\text{solution}, nsp} \quad \text{(Equation 13)} \]

\[ \Delta F_{\text{sorbed}} = \Delta F_{\text{sorbed}, sp} + \Delta F_{\text{sorbed}, nsp} \quad \text{(Equation 14)} \]

\( C_{\text{solution}} \) and \( C_{\text{sorbed}} \) are the humic concentrations in the solution and adsorbed phases. The concentrations, \( C_{\text{solution}} \) and \( C_{\text{sorbed}} \), are related by the adsorption affinity of the humic \( (K_{\text{ads}}) \),

\[ K_{\text{ads}} = \frac{C_{\text{sorbed}}}{C_{\text{solution}}} \quad \text{(Equation 15)} \]

The size of the adsorption affinity is a function of the total free energy change, comprising the four components;
\[ C_{\text{solution}} \left( e^{\frac{\Delta F_{\text{solution,sp}} - \Delta F_{\text{solution,sp}}}{RT}} \right) \left( e^{\frac{\Delta F_{\text{solution,nsp}} - \Delta F_{\text{solution,nsp}}}{RT}} \right) = C_{\text{solution}} \] (Equation 16)

The LCD model has been successfully applied to predict the binding of anions (PO$_4^{3-}$ and AsO$_4^{3-}$) on mineral surfaces in the presence of humic substances (Weng et al., 2008). Further, the LCD approach has enabled differences in sorption behaviour between larger particle humic acids and smaller fulvic acids to be explained. Larger species spread further out from the mineral surface, experiencing variable electrical potentials (Weng et al., 2007b). The LCD model is able to predict sorption of humic onto a mineral surface with increasing ionic strength. As the ionic strength increases, the humic acid structure contracts, thereby changing the volume it occupies, resulting in changes in the electrical potential from the mineral surface that it experiences. Overall, the LCD model has proved fairly successful in predicting ternary system behaviour. However the LCD approach is still deemed too complex to be included in RPA calculations (Bryan et al., 2012).

1.7.2 Previous work on ternary system behaviour

The complex nature of ternary systems has made the task of predicting metal ion and humic behaviour very challenging. Initially the behaviour of binary systems was studied for example, metal ion-mineral surface systems, metal ion-humic systems and humic acid mineral surface systems. Binary data for these simple systems can be modelled, as shown in Figure 1.16 for a binary humic, mineral system.
For the binary system shown in Figure 1.16 there is a good degree of correlation between the experimental data and the predicted model line. Identifying individual binary systems is the first stage in developing a model to describe a ternary, metal ion/humic/sand system. Abrahamsen et al (2007), (2008) and Bryan et al (2005) used batch experiments to collect the experimental data for both binary and ternary systems. In order to simulate metal ion humic interactions and to keep the model as simple as possible, a fast and a slow reaction was used, along with a single equilibrium and a single pair of rate constants to describe the exchangeable and non-exchangeable interactions. In order to account for variations in mineral phases, two variants of the model were produced. The first variant (Model 1) used a single humic binding site and two mineral-binding sites for the sand and quartz. The second variant (Model 2) used a single mineral binding site and two types of humic. The chemical and mathematical equations used by model 1 are shown in Table 1.4;
Table 1.4: Chemical reactions and mathematical equations used in Model 1, HA\textsubscript{exch} humic exchangeable binding site, M\textsubscript{exch} and M\textsubscript{non-exch}, exchangeably and non-exchangeably humic bound metals; S\textsubscript{m}, surface metal binding site; M\textsubscript{s}, metal sorbed to surface; S\textsubscript{HA1} and S\textsubscript{HA2} surface humic binding sites; HA\textsubscript{free} is solution phase humic species; HA\textsubscript{S1} and HA\textsubscript{S2} are sorbed humic species; K\textsubscript{exch} dm\textsuperscript{3} mol\textsuperscript{-1} is an equilibrium constant and k\textsubscript{f}, k\textsubscript{b}, k\textsubscript{MSb}, k\textsubscript{HAS1b}, k\textsubscript{HAS2b}, k\textsubscript{HA1Sb}, k\textsubscript{HA2Sb}, ppm\textsuperscript{-1} s\textsuperscript{-1}; k\textsubscript{MSf} dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}; k\textsubscript{HAS1f}, k\textsubscript{HAS2f}, k\textsubscript{HA1Sf} and k\textsubscript{HA2Sf} ppm\textsuperscript{-1} s\textsuperscript{-1} are rate constants

Model 1 assumes any humic-metal complex will sorb to the mineral surface in the same way as the parent humic molecule. In Model 2, humic sorption is similar to that shown in the van de Weerds et al (2002) model, but this case, only 2 fractions are used to determine humic sorption. Overall, the models developed by Bryan et al (2005) and Abrahamsen et al (2007) (2008) provide an adequate fit for the experimental data in the humic/europium/sand system, as shown by Figure 1.17.

<table>
<thead>
<tr>
<th>Chemical Reactions</th>
<th>Mathematical Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_{\text{aq}} + HA_{\text{exch}} \leftrightarrow M_{\text{exch}})</td>
<td>(K_{\text{exch}} = \frac{[M_{\text{exch}}]}{[M_{\text{aq}}][HA_{\text{exch}}]})</td>
</tr>
<tr>
<td>(M_{\text{exch}} \leftrightarrow M_{\text{non-exch}})</td>
<td>(\frac{d[M_{\text{non-exch}}]}{dt} = k_f[M_{\text{exch}}] - k_b[M_{\text{non-exch}}])</td>
</tr>
<tr>
<td>(M_{\text{aq}} + S_M \leftrightarrow M_s)</td>
<td>(\frac{d[M_s]}{dt} = k_{ MSf} [M_{\text{aq}}][S_m] - k_{ MSb} [M_s])</td>
</tr>
<tr>
<td>(HA_{\text{free}} + S_{HA1} \leftrightarrow HA_{S1})</td>
<td>(\frac{d[HA_{S1}]}{dt} = k_{ HAS1f} [HA_{\text{free}}][S_{HA1}] - k_{ HAS1b} [HA_{S1}])</td>
</tr>
<tr>
<td>(HA_{\text{free}} + S_{HA2} \leftrightarrow HA_{S2})</td>
<td>(\frac{d[HA_{S2}]}{dt} = k_{ HAS2f} [HA_{\text{free}}][S_{HA2}] - k_{ HAS2b} [HA_{S2}])</td>
</tr>
</tbody>
</table>
Figure 1.17: Example results for ternary system model of Eu/humic acid/sand system (Abrahamsen et al., 2007): data plotted as Eu solution concentration ratios of (C/Co) vs time, range of humic concentration = 5, 50, 100 ppm: experimental data (points, error bars are ±2 σ) and Model 1 fits (lines) (Taken from Bryan et al (2006))

Further studies attempting to simulate environmental conditions using columns, were carried out by Mibus et al (2007), investigating uranium migration in a humic quartz sand system. Column experiments performed in the presence and absence of humic acid at pH 7.5 provided data showing the effect humic has on the migration of U(VI) and U(IV) in a complex ternary system. In each case, the migration of uranium was monitored, first in the absence, then in the presence of the humic acid. The migration of U(VI) through the column with no humic acid present showed significant retardation, which could be caused by precipitation or adsorption processes. In the presence of humic acid, transport of U(VI) is significantly increased. The breakthrough curves for the experiments highlight the effect humic has on the system, as shown Figure 1.18:
Figure 1.18; Breakthrough curves of U(VI) in the absence and presence of humic acid respectively (Taken from Mibus et al., 2007)

The presence of humic acid affects the migration behaviour of U (VI), increasing mobilization by the formation of a uranyl humate complex, which confirmed studies carried out by Artinger et al (2002a). Stockdale and Bryan (2012) used equilibrium dialysis to investigate U (VI) binding to humic acid over the pH range 10 to 13. The results suggest that uranyl does bind to dissolved organic matter in the presence of competing hydroxide ligands. However, a decrease in binding was observed as the pH of the system increased. Thus the presence of humic can affect the transport of U (VI), but that the effect is likely to decrease at very high pH. Hence, pH can have a large impact on the transport of metal ions in humic containing systems.

For the U(IV) system, similar breakthrough behaviour was observed. However, Mibus et al (2007) concluded that, attributing the mobilization of U(IV) to the humic was uncertain given the sparing soluble nature of the metal ion under reducing conditions. Also concurrently in both U(VI) and U(IV) systems, a slight tailing effect was observed, indicating partial immobilization of the humic metal ion complex on the surface of the quartz sand, thus producing a delaying effect (Mibus et al 2007).

Other studies into ternary systems have focused on the effect that humic acid has on the sorption of the metal ion onto the mineral surface. Lee et al (2011), investigated the influence of humic acid on the sorption of americium (III) onto kaolinite. Initial results in the absence of humic, showed increased sorption of the metal ion with increasing pH. The addition of humic to the system increases Am (III) sorption at low pH. This increased sorption was attributed to the greater sorption affinity of humic at low pH and the enhanced binding of the metal ion to the sorbed humic. Krepelová et al (2007)
experienced a similar result with U(VI). Two possible mechanisms were suggested for U(VI)/koalinite binding in the presence of humic acid; either the U(VI) binds to the koalinite surface via sorbed humic or binds directly to the mineral surface with additional humic molecules attached to the metal itself. Similar mechanisms may explain the binding in the Am(III)/koalinite/humic acid system (Krepelová., et al 2006 and Krepelová, et al 2007).

At higher pH the presence of humic reduced Am(III) sorption to kaolinite caused by increased dissociation of the humic functional groups resulting in greater metal ion-humate complex formation. Additionally a reduction in the amount of humic sorption on to the mineral surface occurs due to greater electronic repulsions between the kaolinite surface and the charged groups present on the humic.

In a comparative study, Lee et al (2011) investigated Am (III) kaolinite sorption using different molecular weight humic fractions. They observed that the higher molecular weight fractions resulted in retention of the metal ion under acidic conditions because of a greater sorption affinity for the kaolinite, while under alkaline conditions the lower molecular weight fractions resulted in greater Am(III) mobility. These findings show that under environmentally relevant conditions, the presence of humic increases Am (III) mobility, with lower molecular weight humic fractions enhancing the effect (Lee et al., 2010).

Schmeide et al (2010), used neptunium which is concerning from a radiological safety standpoint due to the long half life of Np-237 (2.14 million years) and relatively high mobility. In the study both Np (IV) and Np (V) were studied in the kaolinite/humic system. Np(V) is considered the more mobile of the two oxidation states, due to its weak interactions with mineral surfaces. Additionally in this study the effect of carbonate on this system was taken into account. In the non carbonate Np(V)/kaolinite system, the sorption of the metal ion increases with increasing pH. However, the presence of carbonate results in a reduction of sorption at higher pH, due to the presence of dissolved metal carbonate complexes in the system. The addition of humic to the system results in a reduction in sorption over a larger pH range, due to the formation of metal carbonate and/or metal humate complexes. The effect for Np (IV) is more pronounced, resulting in greater mobilization of the metal ion. One of the key aspects of this study is the effect carbonate has on the system, as it can affect sorption and overall mobility of metal ion, given the right geochemical conditions (Schmeide et al., 2010).
In a similar study, Buda et al (2008), investigated the migration behaviour of Pu (III) and Pu(IV) in a humic/kaolinite system under environmental conditions. Using plutonium is difficult as it exhibits complex redox chemistry and has a variety of oxidation states, which can co-exist, thus making it hard to produce a homogenized solution containing a single oxidation state. Both Pu (III)/(IV) were used in the study, as they are the most likely to occur under the conditions found at a nuclear waste repository site. Initially sorption of the metal ion species onto kaolinite was studied, with significant differences between the two Pu species observed. At acidic pH, the aluminium layer present in kaolinite is positively charged, repelling the Pu (III), which exists as the free Pu$^{3+}$ ion. This is why a 90% desorption of the metal ion was observed when re-suspension at lower pH was carried out.

At higher pH inner sphere complexation occurs between the silicon surface sites and the metal ion, with sorption of the Pu (III) predominately occurring at pH > 5.5, which is the same as the point of zero charge on kaolinite (Schroth et al., 1997).

Pu(IV) forms various hydroxide species with increasing pH. At pH > 8.5 carbonate species such as Pu(OH)$_4$(CO$_3$)$_2^{4-}$ and Pu(OH)$_2$(CO$_3$)$_2^{2-}$, dominate, and thus will affect sorption of the metal ion on to the negatively charged kaolinite surface (Banik et al., 2007). Similarly to the Pu(III)/kaolinite system, the sorption of Pu(IV) is strongly influenced by pH. At low pH, 80-90% sorption of the metal ion was observed, however a subsequent reduction in sorption was found at pH 4-6, as shown by Figure 1.19, which shows the sorption of Pu(IV) on to kaolinite at various pH and at different metal ion concentrations.
Figure 1.19; Sorption of Pu (IV) onto kaolinite (4.0 g/L) as a function of pH, at different plutonium concentrations (Taken from Banik et al., 2007)

Through the use of liquid-liquid extraction, the authors were able to suggest that the reduced sorption of the metal ion could be a result of the partial oxidation of Pu(IV) to Pu(V). At higher pH, carbonate species dominate, reducing sorption of the metal ion (Banik et al., 2007).

Much of the previous work on ternary systems has predominately focused on the use of kaolinite as the mineral surface. In this study, kaolinite will be replaced with quartz sand. Both the ionic strength and pH will be kept constant, so a direct comparison between the behaviour of different metal ions can be established. Changes to the ionic strength or pH will affect the amount of sorption to the mineral surface, thereby increasing the complexity of modelling these systems.
1.8 Aims and objectives

The overall aim of this research is to study the behaviour of radionuclides in ternary systems with quartz sand and humic acid. Europium behaviour has been studied extensively before (e.g., Li 2011). One of the aims of this work is to extend that to other radionuclides that are more likely to be present in the discharge from a Geological Disposal Facility, and which show more complex redox behaviour than Eu\(^{3+}\). Further, the effect of humic fraction size will be studied to determine whether the size fractionation that has been observed previously (Pitois et al 2008) is also responsible for chemical effects, i.e., preferential binding of radionuclides to sorbed or solution phase humic molecules. The results of the ternary system experiments will be analysed, and a mathematical model will be produced in an attempt to simulate the change in the concentrations of the humic and radionuclide with time. This model will include fractionation, which has not been included in previous kinetic ternary system models (e.g., Li 2011). The model will be kept as simple as possible in order that it would be most useful in radiological performance assessment (RPA) calculations.

The specific project objectives are:

- to measure humic acid sorption to quartz sand;
- to measure radionuclide sorption in ternary systems of quartz sand, humic acid and Eu\(^{3+}\), Th(IV), U(VI), U(IV), Pu(IV), Pu(V), Pu(VI);
- to study desorption behaviour in selected systems;
- to produce size fractionated humic acid samples, and to study the sorption of those samples to quartz sand;
- to study Eu\(^{3+}\), U(VI) and Pu(VI) sorption in ternary systems of quartz sand and humic size fractions;
- to produce a kinetic model that includes fractionation effects, and to test it with the experimental data.

Note, because humic binding is so strong, and the sand binding is so weak, a large concentration of sand is required to provide a large surface site binding concentration to allow a distribution of the metal ion and sand, otherwise all the metal ion would bind to the humic.
Chapter 2

Experimental
2.1 Introduction to Techniques

Conventional techniques used to measure radioactivity focus upon decay processes. Radioactive species decay via the emission of alpha/beta particles or gamma radiation. Alpha and gamma emissions have discrete energies that are specific to each transition and it is these emissions that can be measured (Choppin & Ryberg, 1980). Similarly beta emissions can also be measured by liquid scintillation counting (LSC). Beta particles do not have discrete energies, hence characterisation is difficult, however they can be used to measure metal ion concentrations.

2.1.1 UV visible Spectroscopy

The energies of UV visible photons correspond to differences in the electronic energy levels of many molecules. Upon absorption of UV/visible radiation, electronic transitions occur promoting species from their ground state to an excited state. The electronic transitions correspond to certain characteristic wavelengths, shown by absorbance peaks in the UV visible spectrum. Comparison of the absorbed light intensity of a specific wavelength with that of the incident intensity enables the transmittance, \( T \), to be determined,

\[
T = \frac{I}{I_0}
\]

(Equation 17)

Where \( I \) is the intensity of the transmitted light and \( I_0 \) is the incident intensity

From this, the absorbance \( (A) \) of a sample can be ascertained,

\[
A = -\log_{10} T = -\log_{10} \frac{I}{I_0}
\]

(Equation 18)
The concentration of a sample is related to the absorbance by the Beer-Lambert equation,

\[ A = \varepsilon cl \]  \hspace{1cm} (Equation 19)

Where, \( c \) is the sample concentration, \( l \) is the path length, and \( \varepsilon \) is the extinction coefficient. When using the Beer Lambert law to measure concentrations, assumptions such as, monochromatic incident radiation, no light scattering and a homogeneous sample, are made.

For the purposes of this work UV visible spectroscopy was used to determine humic concentrations. Humic species absorb light strongly in the UV-visible region of the electromagnetic spectrum (Gu et al., 1996). When using UV visible spectroscopy to determine concentration it is important that the measured absorbance is within the correct range. A low absorbance, \( A < 0.05 \), or high absorbance \( A > 1 \), produces large errors for the measured concentrations. In this study 400 nm was deemed the ideal wavelength at which the overall error was minimised given the range of concentrations needed to be measured. Figure 2.1 shows the basic outline of the UV visible spectrometer used for these experimental measurements.

![Figure 2.1; Schematic representation of a simple UV-Visible spectrometer](image)

A PG instrument T-60 UV-visible spectrometer was used for experiments in this project. The spectrometer has two lamps providing the light source, a deuterium lamp
for UV absorbance and a simple tungsten lamp for absorbance in the visible region. The wavelength range is from 190-1100 nm, with a manually set changeover point at 349 nm. The deuterium lamp is used below 349 nm and the tungsten lamp used above 349 nm. The spectrometer is a split beam instrument, with one beam passing through the sample solution and detected, while the other is monitored directly acting as a reference. Comparison of the transmitted beam and reference beams enables an absorbance versus wavelength spectrum to be plotted.

2.1.2 Gamma Counting

Semi conductor detectors are used to analyse gamma-emitting samples. Isotopes emit gamma rays with well-defined, discrete energies. There are numerous ways in which gamma radiation can interact with matter.

Photoelectric Effect

Interaction between a gamma photon and an atom results in the transfer of gamma photon energy to a single electron. The binding energy is overcome, and an electron with a high kinetic energy (a photoelectron) is ejected from the atom, hence;

\[ E_\gamma = B.E + K.E \]  

(Equation 20)

Where \( E_\gamma \) is the energy of gamma photon, with \( B.E \) and \( K.E \) the binding and kinetic energies of the ejected electron. In gamma spectrometry the binding energy of the electron is effectively constant as the source of atoms used for gamma interactions come from high purity germanium crystals. Identical gamma energies produce electrons with kinetic energies that are the same, causing a single peak in the gamma spectrum. The ejected photoelectron experiences a loss of kinetic energy upon collisions with atoms in the germanium crystal. Low energy valence band electrons are promoted to a high energy conduction band, producing a charge-pair. The total charge produced is directly proportional to the energy of the photoelectron. An electric field applied across the
crystal causes charge migration. This current is then converted to a voltage pulse by an amplifier, the height of which correlates with the energy of the initial interacting gamma photon. The voltage pulse is allocated a specific channel based on its height and is counted by a multi-channel analyser. A histogram of the number of counts vs channel number is produced, resulting in a γ-ray spectrum.

**Compton Effect**

The Compton effect differs from the photoelectric effect, because only part of the gamma photon’s energy is passed to an electron. In the Compton effect, the atom does not absorb the gamma photon; instead a lower energy gamma photon occurs. The amount of energy passed from the gamma photon to the electron differs with each interaction, producing a continuum in the gamma spectrum.

**Pair Production**

The conversion of a gamma photon to an electron and a positron occurs as it passes through the Coulomb field of an atomic nucleus. This process is dependant on the incoming gamma photon possessing a minimum energy of at least 1.022 MeV. Any excess energy that the gamma photon possesses will result in electron and positron kinetic energy.

**X-ray Production**

X-rays can be produced inside a gamma spectrometry system by the absorption of gamma photons in the shielding material. Lead is used in the majority of gamma spectrometry systems. The absorbance of gamma photons causes excitation of electrons in the shielding material. Subsequent de-excitation results in x-ray photon production. A fraction of the resultant x-rays are then absorbed by the detector. The absorbed x-ray energies appear as well defined, low energy peaks in the spectrum.
2.1.3 Efficiency of Gamma Detection

Detection efficiency is dependant on a variety of parameters, such as distance between the sample and detector, along with the size and shape of the sample. By using identical containers and volumes of samples all positioned in same location to that of previous gamma measurements, these parameters will have a constant effect, thus producing a consistent set of results. The following all reduce counting efficiency: the photon missing the detector, absorption of the photon by detector casing and, the photon passing through the detector without being absorbed, all lower detector efficiency. Figure 2.2 illustrates these effects;

Figure 2.2; Three possible events where the gamma photon remains undetected; A) The gamma photon misses the detector; B) The gamma photon does not interact and passes through the detector; C) the gamma photon is absorbed by the detector casing (Adapted from Farrell 2007)

Overall, the gamma detector efficiency varies depending on the type of detector, but on average, the efficiency is less than 5%. Throughout this study, small aliquots of sample solution were used and counted on either a Canberra high purity germanium (HP-Ge) detector or a EG&G HP-Ge lo-ax low energy gamma detector, both connected to a Model 919 analogue to digital converter and multi-channel analyser.
2.2 Liquid Scintillation Counting

2.2.1 Theory of Liquid Scintillation Counting

Liquid scintillation counting is an analytical technique used to measure the concentration of radioactive species. The process of scintillation occurs when radioactive species are mixed with a liquid chemical medium (scintillation cocktail) that emits light when it interacts with ionizing radiation. A liquid scintillation cocktail comprises of scintillant, solute and solvent, all of which play a part in the scintillation process. The scintillant converts the energy from the ionizing radiation into the emitted flash of light. The solvent dissolves the components and aids the mixing of the radioactive sample with the scintillant (Dyer, 1989). For the purposes of this study an aqueous liquid scintillant cocktail was used; Perkin-Elmer© Optiphase Hisafe 3.

2.2.2 Scintillation Process

Liquid scintillation relies on the principle that alpha and beta emissions lose energy by excitation of surrounding species. This process is predominately used for radioactive species that decay via beta emissions, although species that decay by alpha emissions can also be analysed.

The scintillation process occurs via the exchange of kinetic energy from an alpha or β particle, to the surrounding solvent molecules, causing excitation. The energy from these excited solvent molecules can be emitted as UV light as they return to the ground state. Alternatively, these excited solvent molecules transfer energy to the scintillant causing excitation. Upon returning to the ground state, visible photons are produced that are detected with a photo-multiplier tube.

The patterns of light emitted by alpha and beta particles differ. Alpha particles are more ionising, producing more triplet-excited states, while beta particles yield more singlet-excited states. The resulting fluorescence for each alpha and beta scintillation event produces a fast (prompt) and delayed component (Brooks 1979). This delayed component stems from the combination of two triplet states forming a singlet-excited state,

\[ ^3X^- + ^3X^- \Rightarrow ^1X^+ + X + \text{photons} \]  

(Equation 21)
where; $^3X^*$ is a triplet excited state; $^1X^*$ is a excited singlet state; $^1X$ is a ground state singlet. Light produced in a beta scintillation event occurs via the fast component and is derived from singlet-excited states, with typical lifetimes of 2-8 nanoseconds. Emissions due to triplet excited states occur in the delayed component and have lifetimes of hundreds of nanoseconds. Figure 2.3 shows a typical scintillation event decay curve in scintillant cocktail.

![Scintillation decay curve](image)

**Figure 2.3; Typical luminescence decay curve for a beta scintillation event showing both fast and slow components (Taken from Passo & Cook., 1994)**

Alpha and beta particles exhibit differing degrees of ionisation with variable amounts of the fast and slow components, giving specific scintillation events resulting in distinct pulse shapes. For example, the delayed component of an alpha scintillation event is much more significant than the corresponding beta event. This difference in timescale between alpha and particles is the basis for pulse shape analysis (PSA).
2.2.3 Pulse Shape Analysis

Pulse shape analysis enables the simultaneous recording of alpha and beta scintillation events (Tomè et al., 2001). During these events, the scintillation counter allocates a count to either an alpha or beta channel. To minimise alpha and beta events being assigned to the wrong channel, an ideal ‘PSA level’ is determined. At high PSA levels, alpha scintillation events can be directed to the beta channel, conversely at low PSA levels, beta events may be assigned to the alpha channel. By monitoring the total number of counts of a natural uranium stock solution with an activity of $1.24 \times 10^4$ Bq\(^{-1}\) over a range of PSA values, an ideal PSA of 75 was established. Figure 2.4 shows the PSA calibration plot for the uranium solution on the same detector that was used for this work.

![PSA calibration plot](image)

**Figure 2.4; PSA calibration plot for natural uranium stock solution, counted for 250 minutes (Taken from A.Heydon 2008)**

At PSA level of 75 the number of alpha and beta counts occurring in each channel remained constant, hence, this PSA level was used for all batch experimental counting in this study.

Much of the experimental work undertaken in this project involved low concentrations of radioactive species. For these samples a Quantulus 1220 (Wallac, Turku, Finland) liquid scintillation counter was used, which is designed specifically for low radioactive level counting. The Quantulus has two photomultiplier tubes that simultaneously detect light emissions from the sample vial, resulting in separate and simultaneous electrical pulse detections in the respective photomultiplier tubes. Then, following pre-
amplification, the electrical pulses enter a coincidence circuit, which allows only simultaneous electrical pulses to be detected by multi-channel amplifiers. Additionally, coupled to the two photo-multiplier tubes is an active guard that sends anti-coincidence signals to the two multi-channel amplifiers. This enables one of the multi-channel amplifiers to monitor sample counts, and the other to monitor the active shield performance. Figure 2.5 gives a basic overview of the coincidence circuit used by the Quantulus 1220.

![Coincidence Circuit Diagram]( Taken from Makinen, 1995)

A second, Packard 1900 TR liquid scintillation counter was used to count higher activity samples in this study. Although both scintillation counters are similar, the Packard 1900 does not possess an active guard counter or an asymmetric passive shield, (Kojola et al., 1984) resulting in higher background counts, thus increasing the limit of detection.
2.2.4 Background Effects

Contributions from background can have an effect on the counting efficiency of the detector. There are two types of background effects; one is referred to as the quenchable effect and originates from the sample and scintillation cocktail, while the other is referred to as unquenchable, and is a result of natural external phenomena (Horrocks, 1985). The quenchable effect will be discussed in more detail in the next section. The unquenchable background effect is caused by the interaction of high-energy cosmic radiation with the sample vial or photomultiplier tubes, resulting in the production of Cherenkov radiation, secondary electrons and gamma rays. Cherenkov events are found principally in the $^{14}$C and $^3$H energy regions, but have an effect over a broad range of energies. To minimise contributions from the unquenchable effects, lead shielding is used to reduce external gamma radiation. Figure 2.6 shows a typical pulse pattern due to unquenchable background effects.

![Typical pulse pattern decay curve for a beta scintillation event with unquenchable background effects. Note after pulses not to scale (Taken from Passo & Cook., 1994)](image)

2.2.5 Quenchable Effects

There are three types of quenchable effects caused by contamination of the sample or the scintillation cocktail: the type (I) effect is photon quenching and occurs from incomplete energy transfer to solvent molecules; the type (II) effect is chemical...
quenching and is caused by the loss of energy from solvent molecules but not scintillant molecules, usually due to the presence of an impurity; Type (III) quenching (optical/colour) is caused by the sample colour, which attenuates the photons. In each case a reduction in the number of photons reaching the photomultiplier tube occurs, decreasing the counting efficiency. The best way to reduce the effects of quenching is to produce a calibration curve using a set of radioactive standards in the same sample matrix. The sample measurements can then be adjusted according to the calibration curve, and comparisons between different samples can be made (Keepax 2004).

2.2.6 Limits of Detection

The limit of detection that will be used in this study was defined by Currie (1968). Currie outlined two limits. The first identifies if an observed signal is in fact a “real” signal, caused by an actual radio-chemical event. This aspect of detection is qualitative and based on two conditional errors, Type (I) and Type (II). Type (I) errors describe “non-real” signals, while Type (II) errors account for “real” signal events. Type (I) errors introduce the critical level parameter, $L_c$, which is mathematically defined by;

$$L_c = 2.33B^{\frac{1}{2}}$$

(Equation 22)

Where B is the total count number of an appropriate blank sample. For LSC, a 5% error is acceptable, implying that 5% of observed signals are due to “non-real” radio-chemical events. For Type (II) errors, a 5% value is an acceptable probability that a “real” radio-chemical event will not be detected. Combination of Type (II) errors with the established critical level parameter, gives a true detection limit ($L_d$) for a signal, given by;

$$L_d = 4.65B^{\frac{1}{2}}$$

(Equation 23)
where $B$ is the total number of counts of an appropriate blank sample and 4.65 is a statistical value that accounts for both Type (I) and Type (II) errors. Additionally $[(4.65 \times 2.71) \times \sqrt{B}]$ is added to the $L_d$ parameter to account for a false negative detected signal.

The lower limit of detection (LLD) is the minimum concentration of sample that yields a total count of above background. Modification of the LLD expression to account for total background of less than 70 counts (Prichard et al., 1992) is given by;

\[
LLD = 1.1L_d/K \\
L_d = 0.1B + 4.65B^{1/2} + 2.71
\]

(Equation 24)

where $K$ can be affected by a range of parameters such as efficiency, aliquot size, decay correction. LLD is especially relevant for the samples used in this study, given their relatively low activities.

2.3 Ultra filtration Technique

Ultra filtration is a separation technique that uses hydrostatic pressure, usually in the form of a pressurised gas cylinder to force liquid through a filter. The filter used in this study was a cellulose based semi permeable membrane that allows molecules of a specific size to pass through, with the retentate solution containing molecules of higher molecular weights. Three filter sizes of 3 kDa, 10 kDa and 100 kDa were used to produce four fractionated humic solutions. For example, a humic stock solution was passed through a 100 kDa membrane, producing a retentate humic fraction of HA > 100 kDa. The resulting filtrate was then passed through a 10 kDa membrane, giving a humic fraction of 10 < HA < 100 kDa, with the final filtrate going through a 3 kDa membrane, producing two humic fractions of 10 < HA < 3 kDa and HA < 3 kDa. Figure 2.7 shows the components of the ultra-filtration system used in this study.
Figure 2.7: Components of ultra-filtration equipment; (1) Pressure source, (2) Millipore Amicon 8200 ultra filtration cell, (3) Millipore ultra-filtration membrane, (4) Magnetic stirrer, (5) Filtrate (Taken from Ignacio Moreno-Villoslada et al., 2004)
2.4 Methodology

2.4.1 Experimental methods

One of the principal objectives of this study is to provide a ternary system model that can be applied to RPA studies. The simple binary interaction of humic acid / quartz sand was investigated first, followed by the addition of different metal ions to make a ‘ternary’ system. The metal ions Eu\(^{3+}\), Th\(^{4+}\), UO\(_2\)\(^{2+}\), U\(^{4+}\), Pu\(^{4+}\), PuO\(_2\)\(^{+}\), PuO\(_2\)\(^{2+}\) were all used in these ternary systems. The decay data for the isotopes used are as described below.

\[ \frac{\text{Eu}^{152}}{\text{Eu}^{63}} \]

Eu-152 can decay by electron capture (72.1 %) and positron emission (0.027 %) to Sm-152.

\[ \text{Eu}^{152} \xrightarrow{E.C., \beta^+} \text{Sm}^{152} \]

The electron capture (E.C.), positron \( \beta^+ \) and \( \gamma \) transition energies for Eu-152 to Sm-152 are shown in Tables 2.1, 2.2 and 2.3.

<table>
<thead>
<tr>
<th>E.C Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.C ( _{0,2} )</td>
<td>1507.8</td>
</tr>
<tr>
<td>E.C ( _{0,1} )</td>
<td>1752.5</td>
</tr>
</tbody>
</table>

Table 2.1; Electron capture (E.C) transition energies for Eu-152 decay to Sm-152
<table>
<thead>
<tr>
<th>β⁺ Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β⁺₀,₂</td>
<td>485.8</td>
</tr>
<tr>
<td>β⁺₀,₁</td>
<td>730.5</td>
</tr>
</tbody>
</table>

Table 2.2; Positron β⁺ transition energies for Eu-152 decay to Sm-152

<table>
<thead>
<tr>
<th>γ Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ₁₀,₀</td>
<td>121,7818</td>
</tr>
<tr>
<td>γ₂₁</td>
<td>244,6976</td>
</tr>
<tr>
<td>γ₁₃₁₀</td>
<td>295,9390</td>
</tr>
<tr>
<td>γ₁₂₂</td>
<td>1005,276</td>
</tr>
<tr>
<td>γ₉₀</td>
<td>1085,841</td>
</tr>
<tr>
<td>γ₁₀₁</td>
<td>1112,080</td>
</tr>
<tr>
<td>γ₁₂₁</td>
<td>1249,994</td>
</tr>
<tr>
<td>γ₁₁₀</td>
<td>1292,784</td>
</tr>
<tr>
<td>γ₁₃₁</td>
<td>1408,013</td>
</tr>
<tr>
<td>γ₁₄₁</td>
<td>1457,651</td>
</tr>
<tr>
<td>γ₁₆₁</td>
<td>1528,111</td>
</tr>
</tbody>
</table>

Table 2.3; γ transitions with the highest energies in keV for Eu-152 decay to Sm-152
The electron capture (E.C.) positron $\beta^+$ and $\gamma$ emission energies for Eu-152 to Sm-152 are shown in Tables 2.4, 2.5 and 2.6.

<table>
<thead>
<tr>
<th>E.C Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.C$_{0,2}$</td>
<td>1507.8</td>
</tr>
<tr>
<td>E.C$_{0,1}$</td>
<td>1752.5</td>
</tr>
</tbody>
</table>

**Table 2.4; Electron capture emission energies for Eu-152 decay to Sm-152**

<table>
<thead>
<tr>
<th>$\beta^+$ Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta^+_{0,2 \text{ max}}$</td>
<td>485.8</td>
</tr>
<tr>
<td>$\beta^+_{0,2 \text{ avg}}$</td>
<td>230.7</td>
</tr>
<tr>
<td>$\beta^+_{0,1 \text{ max}}$</td>
<td>730.5</td>
</tr>
<tr>
<td>$\beta^+_{0,1 \text{ avg}}$</td>
<td>338.1</td>
</tr>
</tbody>
</table>

**Table 2.5; $\beta^+$ emissions emission energies for Eu-152 decay to Sm-152**
Table 2.6; \( \gamma \) emissions with the highest energies for Eu-152 decay to Sm-152

<table>
<thead>
<tr>
<th>( \gamma ) Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_{1,0} )</td>
<td>121,7817</td>
</tr>
<tr>
<td>( \gamma_{2,1} )</td>
<td>244,6974</td>
</tr>
<tr>
<td>( \gamma_{13,10} )</td>
<td>295,9387</td>
</tr>
<tr>
<td>( \gamma_{12,2} )</td>
<td>1005,272</td>
</tr>
<tr>
<td>( \gamma_{9,0} )</td>
<td>1085,837</td>
</tr>
<tr>
<td>( \gamma_{10,1} )</td>
<td>1112,076</td>
</tr>
<tr>
<td>( \gamma_{12,1} )</td>
<td>1249,994</td>
</tr>
<tr>
<td>( \gamma_{11,0} )</td>
<td>1292,778</td>
</tr>
<tr>
<td>( \gamma_{13,1} )</td>
<td>1408,013</td>
</tr>
<tr>
<td>( \gamma_{14,1} )</td>
<td>1457,643</td>
</tr>
<tr>
<td>( \gamma_{16,1} )</td>
<td>1528,103</td>
</tr>
</tbody>
</table>

\(^{152}\text{Eu} \) can also decay via negatron emission (27.9 %) to Gd-152

\[ ^{152}\text{Eu} \xrightarrow{\beta^-} ^{152}\text{Gd} \]

The \( \beta^- \) and \( \gamma \) transition energies for Eu-152 decay to Gd-152 are shown in Table 2.7 and 2.8.
<table>
<thead>
<tr>
<th>( \beta^- ) Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta^-_{0,3} )</td>
<td>1063.4</td>
</tr>
<tr>
<td>( \beta^-_{0,1} )</td>
<td>1474.5</td>
</tr>
</tbody>
</table>

**Table 2.7; \( \beta^- \) transition energies for Eu-152 decay to Gd-152**

<table>
<thead>
<tr>
<th>( \gamma ) Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_{1,0} )</td>
<td>344,2789</td>
</tr>
<tr>
<td>( \gamma_{7,3} )</td>
<td>367,7896</td>
</tr>
<tr>
<td>( \gamma_{3,1} )</td>
<td>411,1171</td>
</tr>
<tr>
<td>( \gamma_{7,1} )</td>
<td>778,9066</td>
</tr>
<tr>
<td>( \gamma_{6,0} )</td>
<td>1109,178</td>
</tr>
<tr>
<td>( \gamma_{13,1} )</td>
<td>1261,349</td>
</tr>
<tr>
<td>( \gamma_{14,1} )</td>
<td>1298,148</td>
</tr>
</tbody>
</table>

**Table 2.8; \( \gamma \) emissions with the highest energies for Eu-152 decay to Gd-152**

The \( \beta^- \) emission energies for Eu-152 to Gd-152 are shown in Table 2.9 and 2.10.
### Table 2.9: \( \beta^- \) emission energies for \( \text{Eu-152} \) decay to \( \text{Gd-152} \)

<table>
<thead>
<tr>
<th>( \beta^- ) Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta^- \ 0, 3 \text{ max} )</td>
<td>1063.4</td>
</tr>
<tr>
<td>( \beta^- \ 0, 3 \text{ avg} )</td>
<td>364.6</td>
</tr>
<tr>
<td>( \beta^- \ 0, 1 \text{ max} )</td>
<td>1474.5</td>
</tr>
<tr>
<td>( \beta^- \ 0, 1 \text{ avg} )</td>
<td>535.4</td>
</tr>
</tbody>
</table>

### Table 2.10: \( \gamma \) emissions with the highest energies for \( \text{Eu-152} \) decay to \( \text{Gd-152} \)

<table>
<thead>
<tr>
<th>( \gamma ) Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma \ 1, 0 )</td>
<td>344,2785</td>
</tr>
<tr>
<td>( \gamma \ 7, 3 )</td>
<td>367,7891</td>
</tr>
<tr>
<td>( \gamma \ 3, 1 )</td>
<td>411,1165</td>
</tr>
<tr>
<td>( \gamma \ 7, 1 )</td>
<td>778,9045</td>
</tr>
<tr>
<td>( \gamma \ 6, 0 )</td>
<td>1109,174</td>
</tr>
<tr>
<td>( \gamma \ 13, 1 )</td>
<td>1261,343</td>
</tr>
<tr>
<td>( \gamma \ 14, 1 )</td>
<td>1298,142</td>
</tr>
</tbody>
</table>
\[ {^{232}_{90}}Th^{142} \]

Th-232 decays by alpha emission to Ra-228

\[ Th - 232 \xrightarrow{\alpha} Ra - 228 \]

The \( \alpha \) and \( \gamma \) transition energies for Th-232 are shown in Tables 2.11 and 2.12.

<table>
<thead>
<tr>
<th>( \alpha ) Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{0,2} )</td>
<td>3876.9</td>
</tr>
<tr>
<td>( \alpha_{0,1} )</td>
<td>40178.8</td>
</tr>
<tr>
<td>( \alpha_{0,0} )</td>
<td>4081.6</td>
</tr>
</tbody>
</table>

Table 2.11; \( \alpha \) transition energies for Th-232

<table>
<thead>
<tr>
<th>Gamma Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_{1,0} ) (Ra)</td>
<td>63.811</td>
</tr>
<tr>
<td>( \gamma_{2,1} ) (Ra)</td>
<td>140.88</td>
</tr>
</tbody>
</table>

Table 2.12; \( \gamma \) transition energies for Th-232

The \( \alpha \) and \( \gamma \) emission energies for Th-232 are shown in Tables 2.13 and 2.14.
Table 2.13; \( \alpha \) emission energies for Th-232

<table>
<thead>
<tr>
<th>( \alpha ) Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{0,2} )</td>
<td>3810.0</td>
</tr>
<tr>
<td>( \alpha_{0,1} )</td>
<td>3948.5</td>
</tr>
<tr>
<td>( \alpha_{0,0} )</td>
<td>4011.2</td>
</tr>
</tbody>
</table>

Table 2.14; \( \gamma \) emission energies for Th-232

<table>
<thead>
<tr>
<th>Gamma Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_{1,0} )</td>
<td>63.811</td>
</tr>
<tr>
<td>( \gamma_{2,1} )</td>
<td>140.88</td>
</tr>
</tbody>
</table>

The \( \alpha \) and \( \gamma \) transition energies for U-238 are shown in Tables 2.15 and 2.16.
### Table 2.15; α transition energies for U-238

<table>
<thead>
<tr>
<th>α Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α(_{0,2})</td>
<td>4106.7</td>
</tr>
<tr>
<td>α(_{0,1})</td>
<td>4220.2</td>
</tr>
<tr>
<td>α(_{0,0})</td>
<td>4269.7</td>
</tr>
</tbody>
</table>

### Table 2.16; γ transition energies for U-238

<table>
<thead>
<tr>
<th>Gamma Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ(_{1,0}) (Th)</td>
<td>49.55</td>
</tr>
<tr>
<td>γ(_{2,1}) (Th)</td>
<td>113.5</td>
</tr>
</tbody>
</table>

### Table 2.17; α emission energies for U-238

<table>
<thead>
<tr>
<th>α Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α(_{0,2})</td>
<td>4038</td>
</tr>
<tr>
<td>α(_{0,1})</td>
<td>4151</td>
</tr>
<tr>
<td>α(_{0,0})</td>
<td>4198</td>
</tr>
</tbody>
</table>

The α and γ emission energies for U-238 are shown in Tables 2.17 and 2.18.
Pu-239 disintegrates principally by alpha emission to give excited U-235, with populated energy levels of 51.7, 13.0 and 0.07 keV. This is followed by further alpha and beta emissions, resulting, in the stable Pb-207 isotope. The full decay scheme is shown below,

\[
\text{Pu} \rightarrow \text{U} \rightarrow \text{Th} \rightarrow \text{Pa} \rightarrow \text{Ac} \rightarrow \text{Th} \rightarrow \text{Ra} \rightarrow \text{Rn} \rightarrow \text{Po} \rightarrow \text{Pb} \rightarrow \text{Bi} \rightarrow \text{Tl} \rightarrow \text{Pb}
\]

The \( \alpha \) and \( \gamma \) transition energies for Pu-239 are shown in Tables 2.19 and 2.20.

<table>
<thead>
<tr>
<th>( \alpha ) Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{0,2} )</td>
<td>5231.47</td>
</tr>
<tr>
<td>( \alpha_{0,1} )</td>
<td>5244.43</td>
</tr>
<tr>
<td>( \alpha_{0,0} )</td>
<td>5244.51</td>
</tr>
</tbody>
</table>

Table 2.19; \( \alpha \) transition energies for Pu-239
<table>
<thead>
<tr>
<th>Gamma Transitions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{1,0}$ (U)</td>
<td>0.0765</td>
</tr>
<tr>
<td>$\gamma_{2,1}$ (U)</td>
<td>12.975</td>
</tr>
</tbody>
</table>

Table 2.20; $\gamma$ transition energies for Pu-239

The $\alpha$ and $\gamma$ emission energies for Pu-239 are shown in Tables 2.21 and 2.22.

<table>
<thead>
<tr>
<th>$\alpha$ Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{0,2}$</td>
<td>5143.82</td>
</tr>
<tr>
<td>$\alpha_{0,1}$</td>
<td>5156.59</td>
</tr>
<tr>
<td>$\alpha_{0,0}$</td>
<td>5156.65</td>
</tr>
</tbody>
</table>

Table 2.21; $\alpha$ and $\gamma$ emission energies for Pu-239

<table>
<thead>
<tr>
<th>Gamma Emissions</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{1,0}$ (U)</td>
<td>0.0765</td>
</tr>
<tr>
<td>$\gamma_{2,1}$ (U)</td>
<td>12.975</td>
</tr>
</tbody>
</table>

Table 2.22; $\gamma$ emission energies for Pu-239

Sorption batch experiments provided the bulk of the experimental data. Each type of batch experiment was performed using a range of humic acid concentrations. The
The lowest concentration used was 10 ppm, as this approaches UV analysis detection limits. 200 ppm was the highest concentration used, which represents the upper limits of humic concentration in the environment. In each case, a control experiment with no humic (0 ppm) was also performed.

In the environment, humic molecules or humic/metal ion complexes are likely to encounter ‘fresh’ mineral surfaces/humic during transport. In an attempt to simulate this experimentally, a series of replacement experiments were undertaken, where the solid and solution phases were separated at the end of a simple batch experiment, with the humic solution added to a fresh mineral sample, while a new humic solution was added to the old mineral phase.

To test the mathematical models, a range of metal ion concentrations were used. All experiments are performed at pH 6 ± 0.1, with the ionic strength (I) maintained at 0.1 M.

Every experiment used commercially available Aldrich Chemical Company humic acid, and untreated quartz sand (surface area, 0.125 m² g⁻², measured by BET) Analytical grade NaOH and HCl were used in all experiments, with all solution preparations being carried out using fresh milli-pore de-ionized water (18 MΩ).

### 2.4.2 Humic Acid Quartz Sand Batch Experiments

This first series of batch experiments were set up to study simple humic acid sorption on quartz sand. Each experiment was carried out at ambient room temperature and pressure. Humic acid solutions (Each of total volume 10 ml) with concentrations of 0 ppm 10 ppm, 50 ppm, 100 ppm and 200 ppm were made up, and placed in 12 ml screw capped polysulphone tubes. Each sample was pH 6.0 ± 0.1 adjusted using appropriate quantities of NaOH (1M, 0.1M, 0.01M) or HCl (1M, 0.1M). An Orion model 720 pH meter and a BDH glass combination electrode monitored the pH of each solution. The ionic strength was kept constant by the addition of 0.1 M NaClO₄. The samples were allowed to equilibrate for 24 hours prior to analysis. Approximately 2 ml aliquots of solution were pipetted into a 1 cm glass cuvette and analysed using the T-60 UV-visible spectrometer. Subsequent addition of 5 g of quartz sand was followed by pH re-adjustment (6.0 ± 0.1). The samples were laid on their side and left to shake in an
automatic water bath/shaker at room temperature. After 24 hours, the samples were removed from the shaker, allowed to rest for 15 minutes and centrifuged twice for 10 minutes at 3500 rpm before further UV-visible analysis. After the spectra had been recorded the solution was returned to the sample tube. The sand was then re-suspended and the tube returned to the shaker. This analysis procedure was repeated at intervals over a period of 16 days.

2.4.3 Europium/Humic/Quartz batch experiments

Europium was added to the binary system, of humic acid and quartz sand. The five humic solutions were prepared as before, to which an appropriate measure of europium nitrate (7.91x10^{-10} M) was added containing radiotracer quantities of 133 Bq ml^{-1} of $^{152}$Eu (Total solution volume of 10 ml and pH 6.0 ± 0.1, I = 0.1 M (NaClO$_4$)). A 1.5 ml aliquot was taken and the gamma ray spectrum recorded, prior to the addition of the quartz sand. The sample solutions were left to shake for 24 hours, before being centrifuged as in section 2.4.2 and the γ ray spectrum recorded. Further 1.5 ml aliquots of the centrifuged sample solution were taken every 24 hours and their gamma spectra recorded. The characteristic $^{152}$Eu absorption peak, at 121.8 keV was used for determining the europium concentration. After each analysis, the aliquots were returned to the sample tube, the sand re-suspended and the tube was returned to the shaker.

2.4.4 U (VI)/Humic/Quartz batch experiments

Liquid scintillation counting was the analytical technique used for this series of batch experiments. Prior to sample preparation a set of humic/uranium standard solutions with activities of 100 mBq ml$^{-1}$, 75 mBq ml$^{-1}$, 50 mBq ml$^{-1}$ and 25 mBq ml$^{-1}$, were prepared. An initial, 100 Bq ml$^{-1}$ uranium solution, was made by dissolving 0.848 g uranyl nitrate in 0.1 M HCl (100 ml). Acidic conditions were used to minimise any uranyl sorbing to the glassware. Dilutions of this stock solution were used to make the remaining standards. Each standard was added to humic solutions of concentrations 200 ppm, 100 ppm, 50 ppm and 10 ppm. The 16 humic/uranium standards were all adjusted to pH 6.0 ± 0.1. 0.5 ml aliquots were removed and added to 5 ml Perkin-Elmer Opti-phase safe 3 scintillation cocktail, and counted using the Quantulus 1220 low-level scintillation
counter. The counting time for each sample was set at 30 minutes. Note, given the dark colour of the 200 ppm sample one would usually expect a reduction in the detector response compared to the other samples. For most uranium concentrations, there is no significant difference between the various concentrations. For the highest uranium concentration, the 200 ppm appears higher, but the error bars do overlap and this apparent difference may just be experimental error. Figure 2.8 shows the resultant calibration plot.

![Figure 2.8](image)

**Figure 2.8; Liquid scintillation calibration curve. Standard Solutions of (25 mBqml⁻¹, 50 mBqml⁻¹, 75 mBqml⁻¹ and 100 mBqml⁻¹) 0.5 ml aliquots added to 5ml scintillant cocktail**

For all humic concentrations it was found that the count rate was independent of humic concentration, therefore the humic acid will not prevent uranium measurements in any of these experiments. Due to the destructive sampling nature of LSC, the volumes of the solutions used in the experiments were scaled up to account for this. Solutions of humic acid (10, 50, 100 and 200 ppm) and uranyl nitrate (100 mBqml⁻¹) were made up with a total volume of 100 ml (pH 6 ± 0.1, I = 0.1 M NaClO₄), in 125 ml screw capped polypropylene containers. These were sealed and left to equilibrate on the automated shaker for 24 hours, with a small amount being taken for LSC prior to the addition of 50
g of sand. At intervals of 24 hours, 5 ml samples were removed from the experimental solution using a micropipette and placed in a 12 ml screw capped polysulphone tube and centrifuged as before. 0.5 ml aliquots of the centrifuged solution were mixed with scintillation cocktail (5 ml) and taken for LSC on the. The count time for each sample was set at 300 minutes. Note due to the operating system of the Quantulus 1220 counter, only count times could be specified when analysing samples, rather than the number of counts.

This sampling procedure was repeated over a period of several weeks. In these experiments the aliquots were not returned to the sample tubes.

Concurrently, another set of uranyl experiments were carried out under an inert atmosphere. These experiments took place in a Perspex glove box that was flushed with nitrogen to exclude oxygen. E₉₅ measurements in the glove box were used confirm the absence of O₂. The nitrogen gas was passed through two dreschel bottles with sintered frits containing 17 M NaOH to remove any traces of CO₂. A third dreschel bottle full of water was connected to remove any aerosols from the NaOH solutions. The glove box was flushed for 24 hours before each new batch experiment. All solutions used for experiments in the inert atmosphere were degassed for 24 hours prior to use, using a Schlenk line. All uranyl experiments in the glovebox were prepared as for those performed in air, with a Hanna portable pH meter to monitor pH inside the glove box. All sample tubes were sealed with parafilm to prevent air exposure, during shaking.
2.4.5 U (VI)/Humic/Quartz Replacement Experiments

Figure 2.9; Replacement method, with removal and replacement of the supernatant from the mineral phase with fresh humic solution, along with the addition of a fresh mineral phase to the supernatant solution

A series of replacement studies were undertaken to simulate the presence of a constant supply of fresh humic that may occur in the environment. Figure 2.9 illustrates the method once the U(VI)/humic/quartz samples had reached equilibrium, the supernatant solution was removed and replaced with fresh humic solution of the same pH, ionic strength and initial concentration, with the remaining supernatant solution added to fresh sand of equivalent mass. After the change, the solutions were analysed regularly to establish what effect this fresh humic and new quartz sand would have on the metal ion.
2.4.6 Thorium/Humic/Quartz batch experiments

Both high (188 mBq ml$^{-1}$) and low (47 mBq ml$^{-1}$) activity $^{232}$Th solutions were prepared. 100 ml sample solutions were prepared as before with appropriate amounts of thorium nitrate to give thorium concentrations of 188 mBq ml$^{-1}$ and 47 mBq ml$^{-1}$ in humic acid. A second set of samples, were produced for use in the inert atmosphere glovebox. As before subsequent addition of the quartz sand was followed by pH re-adjustment (6.0 ± 0.1). The samples were laid on their side and left to shake in an automatic water bath/shaker at room temperature. After 24 hours, the samples were removed from the shaker, allowed to rest for 15 minutes and centrifuged twice for 10 minutes at 3500 rpm.

0.5 ml aliquots of sample solution were taken before and after the addition of 50 g of sand. The high activity thorium samples were counted for 30 minutes using a Packard 1900 TR liquid scintillation counter, while the lower activity samples were counted for 240 minutes using the Quantulus 1220 counter. 5 ml samples were taken every 24 hours and centrifuged as before, with 0.5 ml aliquots mixed with the scintillation cocktail and counted.

2.5 U (IV) preparation

Prior to any U (IV) batch experiments, synthesis of UCl$_4$ was carried out. The reaction is done under an inert atmosphere, as the product is moisture and air sensitive. 10 g of UO$_3$ and 45 ml of hexo-chloropropene were added to a two necked round bottomed flask fitted with a reflux condenser, and heated to 158°C. Once the exothermic reaction had finished, the mixture was refluxed for approximately 7 hours. The trichloroaryloyl chloride-by product was removed by distillation. The contents were filtered using a dry filter stick and the product washed with dry CCl$_4$. The excess solvent was removed under vacuum, and the product was dried over heat and under a vacuum for another 6 hours. The resultant green solid was kept under nitrogen. The UCl$_4$ was stored and used in the inert atmosphere glove box.
2.5.1 U (IV)/Humic/Quartz Batch Experiments

Following the preparation, 1.283 g of UCl₄ was dissolved in 100 ml of 0.1 M HCl. Solutions (Each of total volume 45 ml, pH 6.0 ± 0.1, I = 0.1) of Aldrich humic acid to make a stock solution (0, 10, 50, 100 and 200 ppm), and uranium tetrachloride (100 mBqml⁻¹ and 50 mBqml⁻¹) were prepared and placed in 50 ml centrifuge tubes and equilibrated for 24 hours, before 22.5 g of quartz sand was added to each system. As before, 0.5 ml aliquots of centrifuged sample solution were removed before and after addition of the sand every 24 hours. Note, all U (IV) experimentation was conducted in a glove box.

2.6 Pu (IV) Preparation

A relatively straightforward method for Pu (IV) synthesis was developed. 2 ml of a 98 kBqml⁻¹ Pu-239 stock solution was diluted 160 times using 8 M HNO₃, along with a small amount of solid sodium nitrite, NaNO₂ (1 g). The resultant mixture was placed under a heat lamp for 45 minutes. The role of NO₂⁻ in solution during synthesis is two fold; it oxidises any Pu (III) to Pu (IV) is as well as reducing Pu (V) and Pu (VI) to Pu(IV). After heating to establish whether the correct oxidation state had been produced, a solvent extraction test was performed. Due to the acidic nature of the Pu (IV) synthesis, a thenoyltrifluoroacetone (TTA) solvent extractions was chosen.

A 0.5ml aliquot of the Pu (IV) stock solution was added to 0.5 ml 0.5 M sodium acetate at pH 4, and 1 ml of 0.5 M TTA solution in xylene and the mixture was shaken for 5 minutes. The resulting phases were separated for counting. The Pu (IV) was extracted with TTA in the organic phase. Figure 2.10 shows the separation scheme for the solvent extraction;
2.6.1 Pu (IV)/Humic/Quartz Batch and Replacement Experiments

Degassed solutions, (total volume 40 ml, pH 6.0 ± 0.1, I = 0.1 M) of Aldrich humic acid and Pu (IV) (100 mBq ml\(^{-1}\) and 50 mBq ml\(^{-1}\)) solutions were prepared. The solutions were left to equilibrate and aliquots taken for liquid scintillation counting prior to the addition of 20 g of quartz sand. The samples were left to shake on a water/bath shaker at room temperature. Every 24 hours, 0.5 ml aliquots of centrifuged sample were taken and analysed using liquid scintillation counting over a period of 30 days. Once the all of the Pu (IV) experiments had reached equilibrium, the supernatant was separated and replaced with fresh humic solution, while fresh quartz sand was added to the discarded supernatant solution. For both new experiments, 0.5 ml aliquots were taken for further liquid scintillation counting at regular periods of 10 days.

Figure 2.10; Schematic representation of solvent extraction using TTA (Adapted from Xia et al., 2000)
Concurrently, another set of Pu (IV) batch experiments were set up to establish what effect oxidation of Pu (IV) would have on sorption. This was done in two ways: The 1st set of solutions containing 20g of sand were allowed equilibrate for 24 hours, at which point 0.5 g of sodium chlorate was added; the 2nd set of solid/solutions were again left for 24 hours after which CO₂ free O₂ was directly bubbled into the sample solution, using an O₂ gas cylinder fitted with a regulator and a syringe line. The oxygen was pumped into sample at a flow rate of 30 ml per minute, for a total of 30 minutes. Oxygen was bubbled into the samples every 24 hours. To prevent exposure to the atmosphere the sample tubes were fitted with airtight rubber suba seals and para film. 0.5 ml aliquots were taken for counting over a period of 30 days.

2.7 Pu (VI) Preparation

An initial Pu (IV) solution was oxidised to Pu (VI) using 0.5 g of NaClO₃. The resulting Pu (VI) stock solution was used for both high (1.22 mBq ml⁻¹) and low (0.6125 mBq ml⁻¹) activity sample solutions. A solvent extraction was performed to determine whether oxidation had occurred. Alternative methods, such as UV spectroscopy were unsuitable given the low concentrations.

2.7.1 Pu (VI)/Humic/Quartz Batch Experiments

Humic with high and low activity Pu (VI) solutions were prepared as before (total volume 40 ml, pH 6.0 ± 0.1, I= 0.1). 0.5 ml aliquots were taken at relevant intervals for scintillation counting (Packard 1900 TR or Quantulus 1220). A further set of replacement experiments were performed.

2.8 Pu (V) Preparation

A previously prepared 10 ml Pu (VI) stock solution was reduced to Pu (V), by the addition of 0.1 ml 1 M of hydroxylamine hydrochloride. A similar solvent extraction to the one used for the tetravalent oxidation state, using 0.5 M TTA in xylene was carried
out. In this case the extracted organic phase contained both the Pu (IV) and Pu (VI) oxidation states, with the pentavalent state remaining in the aqueous phase.

2.8.1 Pu (V)/Humic/Quartz Batch Experiments

Humic and Pu (V) (50 mBq ml\(^{-1}\)) solutions of total volume 40 ml (pH 6.0 ± 0.1, I = 0.1) were left to equilibrate prior to addition of 20 g of quartz sand. 0.5 ml aliquots of centrifuged sample solution were taken before and after the addition of sand. A further set of replacement experiments were undertaken once equilibrium had been established.

2.9 Quartz sand /Humic Size Fraction Experiments

Stock solutions of 1000 ppm, 200 ppm, 100 ppm, 50 ppm and 10 ppm were fractionated by passing them through ultra filtration membranes, of pore sizes ranging from 100 kDa, 10 kDa and 3 kDa. 4 fractions for each humic concentration were collected, HA > 100 kDa, 100 > HA > 10 kDa, 10 > HA > 3 kDa and HA < 3 kDa.

As in section 2.4.2, solutions (Each of total volume: 10 ml, pH 6.0 ± 0.1, I = 0.1) of Aldrich Humic acid (10, 50, 100, 200 and 1000 ppm of each size fraction), were equilibrated for 24 hours with 5 g of sand. This was followed with regular removal of 1.5 ml centrifuged aliquots for UV analysis, over a period of 9 days. These aliquots were returned to the experiments.

2.9.1 Quartz /Metal Ion /Humic Size Fraction Experiments

In the final set of ternary experiments, Eu\(^{3+}\), UO\(_2^{2+}\) and PuO\(_2^{2+}\) (all 100 mBqml\(^{-1}\)) were added to fractionated Aldrich humic acid solutions (10, 50, 100, 200 and 1000 ppm), each of total volume 10 ml (pH 6.0 ± 0.1, I= 0.1). The europium samples were prepared and analysed using the procedure described in section 2.4.3, while the uranyl and plutonium samples followed the method described in sections 2.4.4 and 2.5.5, respectively.
2.10 Speciation Calculations

Furthermore, the inorganic speciation of metal ions studied in this thesis was calculated using PHREEQCi using the European Union SIT database. All concentrations are expressed in terms of percentage composition. Note, the speciation model is not able to calculate the amount of metal ion bound by the humics. The calculations also do not take into account any sorption in the ternary (or binary) systems. Therefore, the speciation data below are the percentage contributions to the solution phase chemistry of the ions, but excluding any metal ion bound to humic substances.

2.10.1 Europium Speciation

The speciation of europium in the pH range 4 - 8 is shown in Figure 2.11. At pH 6 the speciation is dominated by the free Eu\(^{3+}\) ion, so even though the experiments were conducted in the air, carbonate complexation should not be significant in these experiments.

![Inorganic europium speciation in the pH range 4 - 8 (I = 0.1)](image)

Figure 2.11; Inorganic europium speciation in the pH range 4 - 8 (I = 0.1)
2.10.2 Uranyl Speciation

Uranyl speciation, with and without atmospheric CO$_2$, in the pH range 4 – 8, is shown by Figures 2.12 and 2.13. In both cases, the speciation is more complex, with a number of species making a contribution > 0.1%. Equilibrium with atmospheric CO$_2$ does change the speciation significantly, although the major species is still (UO$_2$)$_3$(OH)$_5^+$.

Figure 2.12; Inorganic uranyl in air speciation in the pH range 4 – 8 (I = 0.1)
2.10.3 Thorium Speciation

Inorganic Th (IV) speciation, with and without atmospheric CO$_2$ in the pH range 4 – 8, is shown by Figures 2.14 and 2.15. Like Eu (III), the presence of carbonate is not predicted to make any significant difference to the speciation. However, unlike Eu, the speciation is dominated by hydrolysis species.
Figure 2.14; Th (IV) in air speciation in the pH range 4 - 8 (I = 0.1)

Figure 2.15; Th (IV) CO₂ free speciation in the pH range 4 - 8 (I = 0.1)
2.10.4 Plutonium Speciation

The speciation results for Pu (IV), Pu (V) and Pu (VI) are shown by Figures 2.16, 2.17 and 2.18 respectively. Hydrolysis increases in the order Pu (V) < Pu (VI) < Pu (IV).

Figure 2.16; Pu (IV) CO$_2$ free speciation in the pH range 4 - 7 (I = 0.1)
Figure 2.17; Pu (V) speciation in the pH range 4 - 8 (I = 0.1)

Figure 2.18; Pu (VI) speciation in the pH range 4 – 8 (I = 0.1)
2.10.5 Uranium (IV) Speciation

The uranium (IV) speciation is shown in Figure 2.19. As for Th (IV) and Pu (IV), hydrolysis species dominate the speciation.

![Figure 2.19; U (IV) speciation in the pH range 4 – 8 (I = 0.1)]
Chapter 3

Results and Discussion
3.1 Sorption Behaviour of Binary and Ternary Whole Humic Systems

All concentrations of HA and metal ions presented in this chapter are expressed in terms of the function \( (C/C_0) \), where \( C \) is the humic/metal ion concentration in solution at time \( t \), \( C_0 \) is the humic/metal ion concentration in solution at time \( t = 0 \) (prior to addition of sand). For some figures the data are expressed as the natural log of \( C/C_0 \), where this is clearer. All error bars are expressed as ‘2\( \sigma \)’, i.e., they represent 2 standard deviations. Additionally for clarity, all humic acid concentrations are assigned a specific colour and marker: 200 ppm ♦; 100 ppm ■; 50 ppm △; 10 ppm ●; 0 ppm ●, which are used throughout.

3.1.1 Humic Acid Sorption onto Quartz Sand

![Graph](image)

**Figure 3.1; Percentage concentration of humic acid in solution at 200, 100, 50 and 10 ppm following sorption onto 500 gL\(^{-1}\) quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M**

Figure 3.1 shows the humic acid concentration onto quartz sand as function of time. The 10 and 50 ppm solutions experience the biggest decrease in humic concentration of 60 -
65 % in the first 24 hours, followed by a steady reduction in the concentration for the remaining 15 days. The 200 and 100 ppm solutions by contrast show a small decrease in humic concentration over the first 24 hours, and with a reduction of 15 - 20 % over the final 15 day period. The sorption of humic acid onto a quartz sand surface can be characterised by two steps; an initial fast step, when the majority of humic sorbs onto the quartz sand surface, followed by a 2nd slower step, where the humic sorption takes place at a slower rate. The relative uptake of humic in both the fast and slow steps increases as the concentration of humic acid decreases.

Figure 3.2; Natural log plot of humic- quartz sand system (pH 6 ± 0.1, I = 0.1 M NaClO₄) as a fraction of humic concentration.

Figure 3.2 shows a natural log plot based on the data from Figure 3.1. The presence of linear regions indicates possible first order processes, especially for the 200 and 100 ppm solutions between days 2 to 14. These linear regions can be characterised by adsorption isotherm plot in Figure 3.3;
Figure 3.3; Adsorption isotherm of HA sorbing to sand. Data shown derived from 10 ml solutions (pH 6, I = 0.1 M, quartz sand concentration 500 g L\(^{-1}\)).

The adsorption isotherm plot, Figure 3.3 shows the amount of humic acid bound to the mineral surface versus the humic free concentration as a function of time. As the free humic acid concentration increases, the amount of surface bound humic acid increases, until a saturation point is reached (around 80 mg) i.e. the saturation point is the point at which no more humic can bind to the surface. Hence, the quartz sand has a finite capacity for humic binding. Similarly, Abrahamsen (2009) observed that above a humic concentration of 200 ppm, a plateaux was reached, where the amount of humic sorbed was no longer dependant on the humic concentration in solution. Given the very low surface area of quartz sand, 0.125 m\(^2\) g\(^{-1}\) (measured by BET), the number of surface sorption sites for the humic will be limited (surface site density 1.28 mg m\(^{-2}\)) and hence the saturation of the surface will occur quicker compared to other mineral surfaces, such as goethite (58 m\(^2\) g\(^{-1}\)) and montmorillonite (267 m\(^2\) g\(^{-1}\)) (Meier et al 1999), especially at higher humic concentrations. This may have implications for ternary systems of metal ions and humic. Sorption of humic acid to the sand surface results in an organic surface coating that could significantly alter the sorption capacity of the mineral phase (Warwick et al 2005) i.e. monolayer coverage of the sand surface with humic acid.
Overall in the humic/quartz system, typical binary system behaviour is observed, with the relative uptake decreasing with increasing humic concentration as the free binding site concentration on the sand surface decreases.

3.1.2 Humic/Europium/Quartz Sand

Figure 3.4; Concentration of Eu (III) in solution as a function of the total humic acid concentration following sorption onto 500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0. 1 M ([Eu]$T$ = 133 mBq ml$^{-1}$) (Molar concentration 7.9 x 10$^{-10}$ moles/litre)

Figure 3.4 shows the concentration on Eu$^{3+}$ in solution after sorption onto quartz sand, over a 13-day period. Simple ternary behaviour is observed, with all the humic containing solutions experiencing a rapid decrease in Eu$^{3+}$ concentration in the first 24 hours, with the 10 and 50 ppm solutions showing 80 % and 60 % drop in metal ion concentration respectively. While the 200 and 100 ppm solutions show a 25 % and 35 % decrease. Between days 1 to 3 all solutions experience a decrease in metal ion concentration, while for days 6 – 13, a plateau is reached where little or no change in the metal ion concentration is observed, this could indicate a saturation point where no more metal will bind either directly to the mineral surface or via any surface bound humic species. The concentration of humic does have a large effect on the amount of Eu$^{3+}$ left in solution, as the 56 % difference in the final concentrations between the
200 ppm and 10 ppm solutions demonstrates. The no humic (0 ppm) containing solution displays the lowest metal ion concentration, with 84 – 97 % of the Eu $^{3+}$ sorbing to the mineral surface.

For this system, the 200 and 100 ppm solutions, show a greater amount of Eu $^{3+}$ present in solution than for either the 50 or 10 ppm solutions. The Eu $^{3+}$ binds to the humic, thus the humic is acting as a competing solution phase ligand, thereby retaining the metal ion in solution and reducing sorption. These results suggest the presence of humic could increase Eu $^{3+}$ solubility, hence increasing metal ion mobility even at low humic concentrations (10 ppm), which may be found at real environmental sites. Additionally, the behaviour shown at different humic concentrations in the ternary system is very similar to that shown in the simple humic binary system, with highest humic acid concentrations (200 ppm) experiencing the lowest amount of relative sorption to the mineral surface, while the 10 ppm solution exhibits the highest relative sorption.

![Figure 3.5; Comparison between C/Co for humic acid and C/Co for Eu $^{3+}$. Data derived from Figure 3.1 and 3.4 (a). (500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M) ([Eu]$T$ = 133 mBq ml$^{-1}$) (Molar concentration 7.9 x 10$^{-10}$ moles/litre)
Figure 3.5 shows the metal values of C/Co plotted versus the corresponding humic C/Co values. The figure shows a strong dependency of the metal C/Co on the humic C/Co. As more humic is bound to the surface, more metal ion is too. This is expected since the surface and humic compete, and if most of the humic is located on the surface, then one would expect metal ion sorption to be high, regardless of the state of competition between the sand and humic. Comparison between the distribution coefficient, (Rd) of the Eu $^{3+}$ with that of the HA will show whether the humic is dominating metal ion binding; the comparison for the Eu (III) systems is shown in Figure 3.6.

![Figure 3.6: Rd values for Eu $^{3+}$ and HA. (500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M). Note the Rd values are plotted on a Log scale to produce a more clearly defined trend.](image)

In Figure 3.6, the Rd values for the metal closely follow those of the humic, for the 200 and 100 ppm systems, where the data are within error of the equivalent humic values. This shows the humic is dominating the metal binding, and is typical of simple ternary system behaviour. At low humic concentrations, the humic and metal Rd values are very different (note the log scale). This is because the surface is able to compete with the low concentration of the humic and os the metal ion Rd value is higher. As the humic concentration increases, the two plots converge as the humic dominates the system and so the metal ion ‘follows’ the humic.
Figure 3.7; Schematic diagram of binding interactions between Eu$^{3+}$, humic acid and quartz sand in a simple ternary system

Figure 3.7 shows complex formation occurring between the Eu$^{3+}$ and the humic in solution, with the metal ion acting as a bridge between humic molecules. Additional interactions between the surface and metal ion occur either as surface bound Eu$^{3+}$ humic complex with either Eu of humic acting as the bridge between the surface and the other components, or a simple Eu$^{3+}$ surface bound metal ions.

Abrahamsen (2009) conducted similar europium experiments, using humic concentrations of 5 ppm, 20 ppm, 50 ppm and 100 ppm, the results of which showed similar metal ion behaviour as above, i.e. at higher humic concentrations more of the metal ion is present in solution. Further, ternary system studies carried out by Singh et al., (2009), using magnetite in the presence of humic acid, observed a strong sorption of trivalent Eu. It was suggested that this was a result of a combination of both complexation and direct electrostatic interactions with a magnetite surface. The
presence of HA was found to have had a minimal effect on the sorption of the metal ion, due to a strong sorption affinity of the metal ion for the mineral surface.

3.1.3 Humic/Thorium/Quartz Sand

![Graph showing Th (IV) Concentration in solution as a function of the total humic acid concentration following sorption onto 500 gL⁻¹ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M ([Th⁴⁺] = 47 mBqm⁻¹) in air (with CO₂) (Molar concentration 4.99 x 10⁻⁵ moles/litre)](image)

Figure 3.8; Th (IV) Concentration in solution as a function of the total humic acid concentration following sorption onto 500 gL⁻¹ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M ([Th⁴⁺] = 47 mBqm⁻¹) in air (with CO₂) (Molar concentration 4.99 x 10⁻⁵ moles/litre)

Figure 3.8 shows the results for a Th (IV) system under ambient atmospheric conditions. The data are more scattered than for the Eu system, probably due to the different detection method used for Th. It seems unlikely that the day to day variation in the data are significant, and do not reveal any mechanistic information. It is the general trends that are important. As with the Eu³⁺ system, simple ternary behaviour is observed, i.e. as the humic concentration increases, the Th (IV) concentration in solution increases, hence greater metal ion solubility and thus mobility. An initial rapid decrease in the Th (IV) concentration in solution occurs on day 1, with the 0 ppm solution showing a 50 % drop in metal ion concentration. After day 1, a high degree of data scatter is observed, especially for the 0, 10 and 100 ppm solutions where Th (IV) concentration varies by around 30 - 35 % over a three-day period. The 200 ppm
solution, shows a 28% decrease in Th (IV) concentration during the first day, this is followed by small fluctuations in the concentration for the remaining experimental period. The 50 ppm solution, shows a similar distribution during day 1, however a 14% decrease metal ion concentration from day 2 - 20. In order to rule out experimental error a 2nd Th (IV) in air experiment was carried out (not shown here) and this also, produced a large degree of data scatter. Comparison with the Eu $^{3+}$ system shows that, at higher humic concentrations a decrease in metal ion sorption is observed.

![Figure 3.9; Comparison between C/Co for HA and C/Co for Eu $^{3+}$ and Th (IV) in air with HA. Data derived from Figure 3.1, 3.4 and 3.8 (a). (500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M)](image)

Figure 3.9 shows again that there is a dependency of the C/Co values for the Th (IV) in air system with those of the humic. The Th C/Co values are closer to those of the humic than for the Eu. This suggests that the relative strength of the interaction of the Th with the humic compared to that of the surface is higher than for Eu.

Previous studies by Reiller et al (2002, 2003) who performed sorption studies using haematite and silica reported a similar reduction in Th (IV) sorption at higher humic concentrations. The presence of humic has a large effect on sorption behaviour and is thought to be a consequence of metal ion humate complex formation. Furthermore,
because this system was conducted in air, the presence of carbonate could affect the interaction between the humic and metal ion, which could result in possible mixed metal ion humic-carbonate complexes. Figure 3.10 shows the various species that could be present in this system.

**Figure 3.10; Schematic diagram of the binding interactions between Th (IV), humic acid, carbonate and mineral surface in the in air system**

Figure 3.10 shows complex formation occurring between the humic, Th (IV) and carbonate in solution with the metal ion again acting as a bridge. Other Th (IV)/humic species may also be present. On the mineral surface, simple Th (IV) interactions occur, along with either (humic/Th (IV)/carbonate) and (Th (IV)/carbonate) bound complexes. The extent to which carbonate affects the Th (IV) system is unknown, previous authors such as Reiller et al (1992) have eluded to possible ternary complexes such as (Th/humic/CO$_3^{2-}$) occurring or even possible colloid formation, which could account for the high degree of data scatter observed in Figure 3.8. However, the speciation calculations in Table 2.2, suggest that carbonate will not be an effective ligand for Th (IV) at the pH of these experiments. Unfortunately, there is no way to test whether this is the case here.
Figure 3.11; Concentration of Th (IV) in solution as a function of the total humic acid concentration following sorption onto 500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M ([Th$_T$] = 47 mBqm$^{-1}$) in CO$_2$ free conditions (Molar concentration 4.99 x 10$^{-5}$ moles/litre)

Figure 3.11 shows sorption data for a Th (IV) system in CO$_2$ free conditions. The system displays simple ternary behaviour, i.e. at higher humic concentrations there is a reduction in metal ion sorption, however there are obvious differences between this system and the previous Th (IV) system exposed to air. Under CO$_2$ free conditions, the 50, 10 and 0 ppm solutions show a 70 -75 % reduction, in the relative metal ion concentration in solution, a drop of almost 35 % when compared with the corresponding solutions in the in air system. Both the 200 and 100 ppm CO$_2$ free and in air solutions, show similar metal ion concentrations throughout the experiment. However, one of the key differences is that the in the air system data are more scattered.
Figure 3.12; Comparison between C/Co for HA and C/Co for Eu $^{3+}$, Th (IV) in air and Th (IV) CO$_2$ free with HA. Data derived from Figures 3.1, 3.4, 3.8 and 3.11 (a).

(500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M)

Figure 3.12, shows that Eu$^{3+}$ and Th (IV) CO$_2$ free systems show similar relationships between the metal and humic C/Co values, with gradients of 1.3 and 1.1 respectively. The Th (IV) in air system shows different behaviour, with a gradient of 0.7. Hence, there is a definite difference between the behaviour of the metal in the presence and absence of CO$_2$. 
Figure 3.13; Rd values for Eu$^{3+}$, Th (IV) in air/ CO$_2$ free conditions and HA bound to the mineral surface. (500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M).

Note the Rd values are plotted on a Log scale to produce a more clearly defined trend.

Figure 3.13 shows the comparison of Rd values between Eu$^{3+}$, Th (IV) in air/ and Th (IV) CO$_2$ free conditions. All systems show a general trend of convergence with the humic acid, with all three systems within error of HA, at concentrations above 100 ppm. The humic dominates the binding in all three systems, especially at higher humic concentrations. In all three systems the metal eventually follows the humic. The presence of the CO$_3^{2-}$, also appears to affect the behaviour of the Th (IV) system.
3.1.4 Humic/Uranium/Quartz Sand

Figure 3.14; Concentration of U (VI) in solution as a function of the total humic acid concentration following sorption onto 500 gL⁻¹ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M ([U₁] = 100 mBqml⁻¹) (Molar concentration 3.38 x 10⁻⁵ moles/litre)

Figure 3.14 shows sorption results for a uranyl system in the presence of air. In this system, all solutions containing humic show similar reductions in the metal ion concentrations, of between 80 – 95 % during the first 5 days. The concentration of humic seems to have only a small effect on the amount of uranyl that binds to the mineral surface, for example there is only a 15 % difference in the final sorbed amounts between the 10 – 200 ppm solutions. This would suggest that the interaction between the uranyl species and the mineral surface is weaker than it is with the humic, and the presence of humic, regardless of concentration actually increases uranyl sorption. Therefore the metal ion seems to preferentially bind to the surface bound humic, rather than directly binding to the surface itself.
Comparing of Rd values for U (VI) in air system (Figure 3.15) shows a different trend to those in previous systems. The metal Rd values do not follow those of the humic, which could be the result of possible fractionation and subsequent formation of ternary complexes. It seems that the ternary complexes are favourable for uranyl and thus, the presence of humic enhances metal ion sorption. These results shown here are consistent with those of both Lenhart and Honeyman, (1999), who investigated the sorption of U (VI) on to haematite in the presence humic acid, and of Payne et al., (1996) who examined the sorption of uranium on hydrous ferric oxide in the presence of natural organic matter.

The significance of the humic on the uranium distribution is shown by a replacement experiment, where the initial humic solution was removed and replaced with a fresh humic solution (Figure 3.16).
In Figure 3.16, the data plotted at day 0, represents the uranium concentration in solution prior to supernatant removal and subsequent replacement with fresh humic solution of the same concentration. For the non-humic (0 ppm) solution, there is no significant change in the metal ion concentration after the addition of fresh humic. However, the humic containing solutions all show large increases in metal ion concentration, of around 65 %, with the 200 ppm solution experiencing the highest increase of 85 %, once the fresh humic solution is added. This suggests re-suspension of the uranyl from the quartz sand surface by the fresh humic. Following this re-suspension, the metal ion concentration starts to decrease gradually, this may be the result of a slow exchange between the solution and sorbed humic species, which in turn promotes uranium return to the surface as a ternary complex. Note the last 200 ppm point is not visible on the chart because it is so close to the final concentration values of the other solutions.

Figures 3.17 to 3.20, provide a schematic representation of the likely binding interactions that occur in the uranyl system following a sorption and replacement experiment. Note the blue HA\textsubscript{1} refers to the original humic acid solution and red HA\textsubscript{2} refers to the fresh humic acid solution following replacement of the supernatant solution.
Figure 3.17; Initial binding interactions between the uranyl, humic and mineral surface prior to fresh humic addition

Figure 3.18; Binding interactions between uranyl, humic and the mineral surface following the addition of fresh humic
Upon addition of the fresh humic (HA$_2$) surface bound HA$_1$ complexes could dissociate back into solution, Figure 3.18. This explains the increase in metal ion concentration shown in Figure 3.16, for all humic containing solutions in the first day after replacement. Figure 3.19 shows the HA$_1$ complex in solution prior to metal ion dissociation from the original humic.

**Figure 3.19; Schematic of the surface bound HA$_2$ and HA$_1$ metal ion complex in solution**

**Figure 3.20; Dissociation of the metal ion from the HA$_1$ complex in solution, binding to the fresh surface HA$_2$ forming a ternary surface complex**
In Figure 3.20, the metal ion dissociates from the complex and subsequently binds with the fresh surface humic HA₂, this accounts for the resulting decrease in metal ion concentration with time following initial spike in concentration that is observed in Figure 3.16. The final diagram, Figure 3.21, shows the final metal ion / humic HA₂ / mineral surface ternary complex.

Overall the results suggest that in a system where a dynamic flow is present, for example groundwater in the sub-surface, then if fresh humic is introduced, it could result in the re-suspension of uranium. Whether this would cause an increase in uranium mobility would depend on the rate of the re-adsorption, which seems to take several days and the residence time of the groundwater in the contaminated area.
Further uranyl experiments were conducted under CO$_2$ free conditions to assess the effect of carbonate. Figure 3.22 shows the metal ion concentration before and after addition of fresh humic. The 200 ppm solution, shows a greater percentage of the metal ion present in solution than observed in the equivalent in air system. Around 35-40 % of the uranyl remains in solution, during the first 14 days. The remaining humic containing solutions, all show a slight increase in metal ion concentration under CO$_2$ free conditions. Subsequent replacement of the supernatant produces a decrease in metal ion concentration after day 1, across the whole humic solution range. The 200 ppm solution shows the highest relative decrease in metal ion concentration of 26 %, 24 hours after humic replacement, while the 50 and 10 ppm solutions experience a 4 % and 8 % decrease, respectively. This decrease in metal ion concentration is slightly different to the in air uranyl system, where all the humic solutions experienced a rapid increase in metal ion concentration 48 hours following humic replacement (Figure 3.16). However in Figure 3.22 the 200, 100 and 50 ppm solutions show only a slight increase in metal ion concentration, which could be indicative of metal ion re-suspension from humic bound surface species. After humic replacement, the results show that initially the
uranyl stays sorbed to the surface, however after a 17 day period, a small amount of metal desorption is observed, especially for the 200 ppm solution.

Figure 3.23; U (VI) concentration in the 200 ppm humic solution onto 500 g·L⁻¹ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M ([U₁] = 100 mBqml⁻¹) (Molar concentration 3.38 x 10⁻⁵ moles/litre) as a function of total humic concentration in both CO₂ free and in air conditions.

Comparison between equivalent 200 ppm solutions under in air and CO₂ free conditions in Figure 3.23, shows the relative metal ion concentration in solution is 30 %, greater in the CO₂ free system. This trend is also observed for the 100, 50 and 10 ppm solutions, although the differences between the relative metal ion concentrations between the air and CO₂ free conditions are slightly smaller. For the in air system, (Figure 3.23) approximately 95 % of the uranyl sorbs to the surface. Overall in humic containing solutions, metal ion solubility and hence mobility appear greater when CO₃²⁻ is removed.
Figure 3.24; U (VI) concentration in the 0 ppm humic solution onto 500 $g \cdot L^{-1}$ quartz sand at pH $= 6.0 \pm 0.1$ and I $= 0.1 \ M ([U_{T}] = 100 \ mBqml^{-1})$ (Molar concentration $3.38 \times 10^{-5}$ moles/litre) as a function of total humic concentration in both CO$_2$ free and in air conditions

Figure 3.24 shows the data for the humic free systems. Uranyl concentration in solution is lower in the CO$_2$ free system than in air, hence in the absence of carbonate the metal ion appears to sorb more strongly to the mineral surface. Krepelova et al (2006) also found a similar trend for U (VI) sorbing onto kaolinite. Unlike the Th (IV) system, the speciation calculations indicate that carbonate may have an effect on uranyl speciation, although the major inorganic species is unaffected. Given the speciation, it seems unlikely that simple direct competition by carbonate has produced the differences between the air and CO$_2$ free data here. Mixed humic/CO$_3^{2-}$ complexes seem to be a more likely cause. Previous studies carried out by Moulin et al (1999) confirmed the presence of mixed HA-Eu-CO$_3^{2-}$ complexes using time-resolved laser-induced fluorescence (TRLIF).

Table 2.1 shows that the speciation is very complex in these systems (with or without CO$_3^{2-}$) even in solutions without humic. Hence, it is probable that multiple species are present in the solution phase and on the surface, and these may include mixed OH$^-$ and/or CO$_3^{2-}$/humic complexes. Steudtner et al (2011) verified the formation of ternary U (VI) humate complexes by in situ spectroscopic measurements, with complex
formation for both the ternary U (VI) mono hydroxo humate complex, (UO₂(OH)
HA(I)) and U (VI) dicarbonato humate complex (UO₂(CO₃)₂ HA(II)⁴⁺). This would suggest the presence of mixed multiple species. A revised U (VI) speciation diagram was produced (Figure 3.25), which showed that at pH > 6.5, speciation was dominated by the U (VI) carbonato humate complex.

Figure 3.25; Revised speciation of U (VI) in the presence of humic acid of HA ([U (VI)] =1mM, [HA] = 1 g L⁻¹, I = 0.1 M (NaCl), pCO₂ = 10⁻³.⁵ atm) taken from Steudtner et al 2011
3.1.5 Humic / Uranium (IV) / Quartz Sand

Figure 3.26; U (IV) concentration in solution following sorption onto 500 gL$^{-1}$ quartz sand pH= 6.0 ± 0.1 and I = 0. 1 M as a function of humic acid concentration under CO$_2$ free conditions ([U$_T$]= 100 mBqml$^{-1}$) (Molar concentration 3.38 x 10$^{-5}$ moles/litre)

Figure 3.26 shows the concentration of U (IV) left in solution following sorption onto the quartz surface. The data are plotted as the ($C/C_o$) / mass of quartz sand in kg where C is the concentration of the metal ion solution at any point, and $C_o$ is the concentration of metal in solution before exposure to the mineral surface.

The data has three distinct sections. The first shows a decrease in metal ion concentration as the U (IV) binds to the sand in the first 2 days. Both the 50 and 10 ppm humic solutions experience the greatest reduction in metal ion concentration in solution, during this period. The second section occurs between days 5 – 16, where a rapid increase in metal ion concentration occurs, caused by apparent desorption of U (IV) species back into solution. The third section, days 16 – 30 shows a steady increase in metal ion concentration as all systems appear to approach equilibrium. As in the previous U (VI) in air system, Figure 3.14, humic concentration appears to have little impact on the distribution of uranium (IV) in this system.
Figure 3.27; Comparison between C/Co for HA and C/Co for U (IV). Data derived from Figure 3.1 and 3.26 (500 gL⁻¹ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M)

From Figure 3.27, it is clear the metal C/Co values are not dependant of those of the humic. Hence, the presence of humic does not directly affect the metal ion concentration in solution, unlike in the previous Eu³⁺ and Th (IV) systems.
Figure 3.28; Rd’s for the U (IV) and humic acid systems bound to the mineral surface. All Rd values are in litres per kilo. Note the Rd values are plotted on a Log scale to produce a more clearly defined trend.

Analysis of the distribution coefficient values, Figure 3.28, shows that the metal Rd values do not converge with those of the humic at high humic concentrations again unlike the behaviour in the Eu and Th systems. In the previous U (VI) in air system, fractionation and ternary complex formation were thought to be responsible for the lack of correlation between metal ion and humic behaviour. The highly insoluble nature of U (IV) in aqueous solution, due to hydrolysis, may be responsible for the behaviour shown in Figure 3.28.
Figure 3.29; U (IV) concentration in solution before and after humic replacement (pH= 6.0 ± 0.1 and I = 0. 1 M) as a function of humic acid concentration under CO₂ free conditions. ([U₁]= 100 mBqm⁻¹) (Molar concentration 3.38 x 10⁻⁵ moles/litre)

Figure 3.29 is a plot showing the change in metal ion concentration over a period of 50 days before and after a replacement of the humic solution. The red line represents the metal ion concentration before removal and subsequent addition of fresh humic. The 0 ppm solution, experiences a drop in metal ion concentration, following humic replacement, however much of the U (IV) appears not to be in solution given the actual concentration of metal ion prior to humic addition. At equilibrium, one would expect the concentration, to be virtually the same before and after humic replacement, however this does not happen here, which is probably due to non-instantaneously-reversible association with the solid phase. This would be consistent with extensive hydrolysis and possible colloid formation.

The 200 and 100 ppm solutions, show a minimal change in metal ion concentration before and after humic replacement. This is expected since the surface will be saturated with respect to humic at these concentrations. Hence, when more humic is added, that amount on the surface hardly changes as does the concentration left in solution. This
accounts for the minimal changes in metal ion concentration observed in both of these solutions after humic replacement. However, surface saturation has not happened at lower humic concentrations. Hence, in the 50 and 10 ppm solutions, when fresh humic is added, the amount of humic coating the sand surface increases. Additionally, after humic replacement, the 50 and 10 ppm solutions follow a similar trend to that of the 0 ppm solution, this indicates that at lower humic concentrations, the effect of humic on metal ion behaviour is less important.

A second set of sorption experiments using a lower concentration of U (IV) (Figure 3.30) found the lowest metal ion concentration in the 0 ppm solution, with 98 % of the metal sorbing to the mineral surface. The humic containing solutions, (10 – 200 ppm), showed similarly high metal sorption behaviour, typically 92 – 95 %.

Figure 3.30; Sorption of U (IV) onto 500 gL⁻¹ quartz sand pH= 6.0 ± 0.1 and I = 0.
1 M ([U₄] = 50 mBqml⁻¹) (Molar concentration 1.69 x 10⁻⁵ moles/litre) as a function of humic acid concentration in CO₂ free conditions

Unlike the previous, U (VI) in air system (Figure 3.14) where ternary complex formation was thought to be occurring, the data from both the U (IV) high and low concentration systems suggests a different type of mechanism. Additionally, speciation calculations showed that in the absence of humic complexation, the solutions in Figure
3.29 and 3.30 are predicted to be supersaturated with respect to U (OH)$_4$. Hence discrete and/or colloidal U (OH)$_4$ species could have formed in these solutions. The behaviour in these systems is very different to that in other (Eu, Th) experiments. Hence, in these systems the humic may actually be competing with U(OH)$_4$ solubility, rather than direct sorption to the mineral surface. Further, there is some evidence that the presence of organic ligands in supersaturated actinide (IV) systems can stabilise An(OH)$_4$ colloids in solution, (Reference) and this may be occurring here. Figures 3.31 and 3.32 show the possible mechanism occurring in the U (IV) system.

Figure 3.31; Diagram of U (IV) solutions with no humic acid present

In the 0 ppm solutions with no humic acid present (Figure 3.31) the U (IV) can either bind directly to the sand surface, or form a solid U (OH)$_4$ precipitate. In the solution U (IV) is likely to exist as U (OH)$_4$ colloid species. In humic acid containing solutions Figure 3.32, the HA surrounds the U (OH)$_4$ colloids, resulting in larger colloidal U (OH)$_4$/ humic species.
Figure 3.32; Diagram of U (IV) humic acid containing solutions with the formation of U (OH)$_4$ humic colloidal species in solution
3.1.6 Humic/ Plutonium (IV) / Quartz Sand

Figure 3.33 shows the sorption data for the uptake of Pu (IV). Here, the data are presented in terms of the solution phase concentration, expressed as a percentage of the total Pu added to the system at the start of the experiment. Note prior to the start of each Pu experiment, a solvent extraction was carried out to determine the oxidation state of plutonium in solution.

![Sorption of $^{239}$Pu (IV) (0.6125 mBq ml$^{-1}$) (Molar concentration $1.12 \times 10^{-12}$ moles/litre) onto 500 gL$^{-1}$ quartz sand pH= 6.0 ± 0.1 and I = 0. 1 M as a function of humic acid concentration](image)

Figure 3.33; Sorption of $^{239}$Pu (IV) (0.6125 mBq ml$^{-1}$) (Molar concentration $1.12 \times 10^{-12}$ moles/litre) onto 500 gL$^{-1}$ quartz sand pH= 6.0 ± 0.1 and I = 0. 1 M as a function of humic acid concentration

The Pu (IV) system shows fairly simple, ‘classical’ ternary behaviour. As the humic concentration increases, the amount of Pu sorbed to the mineral surface decreases. The 200 ppm solution shows a comparatively higher metal ion concentration in solution than the equivalent U (IV) and Th (IV) systems. The 10 and 0 ppm solutions show the greatest amount of metal ion sorption. Therefore, the main effect of the humic is to act a competing solution phase ligand. Further evidence to suggest simple ternary system behaviour is shown by the Rd values of both the Pu (IV) and humic, Figure 3.34
Figure 3.34; Rd’s for the Pu (IV) and humic acid systems bound to the mineral surface. All Rd values are in litres per kilo. Note the Rd values are plotted on a Log scale to produce a more clearly defined trend.

As in previous systems that displayed simple ternary system behaviour, a converging trend is observed, where the humic dominates the metal binding at humic values and hence the Pu (IV) Rd values follow those of the humic. As for the other systems, the Pu and humic values converge at 100 ppm.

Figure 3.35 A, shows the results of a sorption and solid replacement experiment, where a higher concentration Pu (IV) solution (1.22 mBq ml\(^{-1}\)) was used. The data points on red line represent the last day before replacement of either the quartz sand or humic. After solid replacement, the solution phase concentration is calculated based on the Co value at day 0 (note the same procedure was used to calculate the solution phase concentration in the humic replacement experiment). After 18 days, the solid phase was removed and replaced with fresh quartz sand. Following this replacement, all the humic acid solutions show further removal of Pu from the solution, Figure 3.35 B shows the release of Pu back into solution when fresh humic (containing no Pu) is added to the original solid phase.
Figure 3.35; Sorption of $^{239}$Pu (IV) (1.22 mBq ml$^{-1}$) (Molar concentration $2.2 \times 10^{-12}$ moles/litre) onto 500 gL$^{-1}$ quartz sand pH= 6.0 ± 0.1 and I = 0.1 M as a function of humic acid concentration A: Pu concentration in solution following exposure to 2 successive samples of mineral. B: Pu concentration in solution before and after replacement of the solution for the same sample of mineral
Prior to any humic/quartz sand replacement, the Pu (IV) system in Figure 3.35 displays simple ternary behaviour, with both the 200 and 100 ppm solutions showing the least amount of metal ion sorption, while approximately 95% of the metal ion sorbs to the mineral surface in the 50, 10 and 0 ppm solutions. The solid replacement experiment (Figure 3.35 A) was designed to try and simulate the processes that take place when a plutonium containing solution encounters fresh mineral surfaces as it migrates. After solid replacement, there is little or no change in the relative metal ion concentrations in the 50, 10 ppm and 0 ppm solutions. However, at the higher humic concentrations (100 and 200 ppm), further sorption of plutonium is observed. For example, the 200 ppm solution, experiences a rapid 21% drop after solid replacement, whilst the 100 ppm solution shows a 29% reduction in the metal ion concentration.

Further a notable result from Figure 3.35A is that there is no significant difference in the sorption of Pu (IV) between the 10 ppm and 0 ppm solutions. The typical humic substance concentration observed in the environment is less than 10 ppm, and so the results suggest that for the quartz sand system, the presence of humic at realistic concentrations would not affect the metal ion concentration in solution if a fresh mineral surface were encountered. For the higher concentration systems (100 and 200 ppm), exposure to a second sample of mineral results in further sorption of Pu: for the 100 ppm system, the amount of Pu removed in the second step is approximately the same as that in the first, whilst for the 50 ppm system the amount is slightly less.

The data in Figure 3.35 B suggests sorption at certain humic acid concentrations could be reversible. The plutonium concentrations in both the 10 and 0 ppm solutions appear to be same as before fresh humic was added. This is the expected behaviour for a reversible system, where most of the metal ion sorbs to the mineral surface and upon addition of fresh humic there is virtually no change in the amount of metal ion present in solution. Figure 3.36 shows a schematic representation of the reversibility in this system.
Figure 3.36; Demonstration of reversibility in a plutonium system following humic replacement. Note HA$_1$ represents the old humic in solution and HA$_2$ represents the fresh humic.
For the 200 and 100 ppm humic concentrations, if the sorption is fully reversible, after the replacement of the humic solution, the expected solution phase concentrations would be 22 % and 23 %, respectively. This explains why the two systems appear coincident after 23 days, with the final values for both solutions occurring at $22 \pm 0.5$ %. Therefore, the data suggest that this system is fully reversible, although it takes approximately 4 days after humic replacement for equilibrium to be established.

3.1.7 Humic/ Plutonium (V) / Quartz Sand
Figure 3.37; Sorption of $^{239}$Pu (V) (0.6125 mBq ml$^{-1}$) (Molar concentration 1.12 x $10^{-12}$ moles/litre) onto 500 gL$^{-1}$ quartz sand pH= 6.0 ± 0.1 and I = 0. 1 M as a function of humic acid concentration. A: Pu concentration in solution following exposure to 2 successive samples of mineral. B: Pu concentration in solution before and after replacement of the solution for the same sample of mineral.

Figure 3.37 shows a set of similar ‘replacement experiments’ to those shown in Figure 3.35, but using Pu (V) (0.6125 Bq ml$^{-1}$). The behaviour of the Pu (V) system is much more complex than for the Pu (IV) system. In that system, the presence of humic increased the amount of Pu in solution. However, for the Pu (V) system, the 0 ppm solution has a higher metal ion concentration before solid replacement, than either the 10 or 50 ppm solutions (Figure 3.37 A). This behaviour is typically observed when the interaction of the metal ion with humic is particularly strong, and the resultant ternary metal ion complexes that form are stronger than the direct interaction with the mineral surface. In the 10 and 50 ppm solutions, the majority of the humic is sorbed to the mineral surface during the experiment, whilst for 100 and 200 ppm, most is left in solution. Therefore, ternary complexes are especially important for the 10 and 50 ppm solutions, and the Pu (V) data are consistent with the humic behaviour, qualitatively at least.

The data in Figure 3.37 B show evidence of some reversibility, since some plutonium has been brought back into solution. In a fully reversible system, the expected Pu
concentrations, following addition of humic, are 20, 24, 12 and 8 % for the 200, 100, 50 and 10 ppm solutions, respectively, while the values at the end of experiment are 25, 36, 26 and 8%. Therefore, although there is clearly some reversibility, the Pu (V) system is much harder to predict, possibly due to significant ternary complex formation.

3.1.8 Humic/ Plutonium (VI) / Quartz Sand
Figure 3.38; Sorption of $^{239}$Pu (VI) (1.22 mBq ml$^{-1}$) (Molar concentration $2.2 \times 10^{-12}$ moles/litre) onto 500 gL$^{-1}$ quartz sand pH= 6.0 ± 0.1 and I = 0. 1 M as a function of humic acid concentration results for A: Pu concentration in solution following exposure to 2 successive samples of mineral. B: Pu concentration in solution before and after replacement of the solution for the same sample of mineral

Figure 3.38 shows the data for the Pu (VI) system. Replacement of solid phase in Figure 3.38 A shows similar behaviour to that seen in the equivalent Pu (IV) system, Figure 3.35 A, where any changes in sorption in both the 10 and 0 ppm solutions after addition of fresh solid are minimal, and similarly for the 200 and 100 ppm solutions further sorption of metal ion takes place following solid replacement. Note, the final metal ion concentrations, for the 100 50 10 and 0 ppm solutions in Figure 3.38 A have different concentrations, but plot in the same place because of the way C/Co is calculated.

Overall the data suggest that at typical humic concentrations found in the environment, the solid/solution partition for both Pu (VI) and Pu (IV) systems would not be affected.
Comparison between 200 ppm and 10 ppm solutions, (typical of the concentrations found in the environment) shows the effect that high humic concentrations have on the solid/solution partition in both the Pu (IV) and Pu (VI) systems. For example, from Figure 3.39, following solid replacement, the metal ion concentration for the 200 ppm solution drops by 21 % and 13 % for the Pu (IV) and Pu (VI) systems, respectively. However, there is no change in the metal ion concentration at 10 ppm.

Figure 3.28 B shows the replacement data for the Pu (VI) system (1.22 mBq ml⁻¹). In this system, if sorption were reversible, then the expected concentrations following humic replacement would be estimated at 18, 25, 8 and 5 % for the 200, 100, 50 and 10 ppm solutions, respectively, while the actual experimental values are 22, 25, 25 and 6 %. The experimental values for 200, 100 and 10 ppm solutions are similar to those predicted. However, the origin of the discrepancy in the 50 ppm system is unclear, but it seems unlikely that this system would not be reversible, given that the other solutions containing higher and lower humic acid concentrations are.
Figure 3.40; Comparison between C/Co for HA and C/Co for Pu (IV), (V), (VI) with HA. Data derived from Figures 3.1, 3.35, 3.37 and 3.38 (a) (500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M)

As in the Eu and Th systems, Figure 3.40 shows there is a strong dependency of the C/Co values for the plutonium upon those for the humic. The gradients for the Pu (IV), (V) and (VI) are all greater than 1, and are similar to those shown by other metal ions that exhibit simple ternary behaviour, such as Eu$^{3+}$ and CO$_2$ free Th (IV) systems.
Figure 3.41; Rd’s for the Pu (IV), (V) (VI) and humic acid. All Rd values are in litres per kilo. Note the Rd values are plotted on a Log scale to produce a more clearly defined trend.

The Rd values for the Pu (IV), (V) and (VI), Figure 3.41 all show a converging trend. An increase in humic acid concentration results in a decrease of the metal Rd value, and hence the humic dominates the metal ion binding at high humic concentration.

Due to the changeable nature of plutonium oxidation states in solution, two further experiments were attempted where Pu (IV) (0.6125 mBq ml\(^{-1}\)) was allowed to sorb to the quartz surface before the system was ‘oxidised’ in order to account for possible changes of Eh values in the vicinity of a radioactive waste repository. The initial attempt used the addition of sodium chlorate (Figure 3.42).
Figure 3.42: Sorption of $^{239}$Pu (IV) (0.6125 mBq ml$^{-1}$) (Molar concentration $1.12 \times 10^{-12}$ moles/litre) onto 500 gL$^{-1}$ quartz sand pH = 6.0 ± 0.1 and I = 0.1 M as a function of humic acid concentration. Samples exposed to sodium chlorate (0.5 g) during experiment.

However, the concentration of chlorate required to raise the Eh, also increased the ionic strength significantly, and this could affect the humic Pu interactions because at high ionic strength values, cations in the electrolyte shield the negative charge on the humic, resulting in contraction of the double layer (Swift R.S 1998B), thus rendering the humic ineffective as a ligand. Therefore, a second attempt involved bubbling CO$_2$ free O$_2$ through the solutions to raise the Eh, which did not change the ionic strength significantly. The results of this experiment are shown in Figure 3.43.
Figure 3.43; Sorption of $^{239}$Pu (IV) (0.6125 mBq ml$^{-1}$) (Molar concentration $1.12 \times 10^{-12}$ moles/litre) onto 500 gL$^{-1}$ quartz sand pH = 6.0 ± 0.1 and I = 0.1 M as a function of humic acid concentration. Samples exposed to O$_2$ during the experiment

Following the exposure to the oxygen, the system experiences a small change in behaviour. At the end of experiment, the approximate metal ion concentrations left in solution are 70, 46, 12, 4 % for the 200, 100, 50 and 10 ppm systems, respectively. Following O$_2$ exposure one would expect to see a similar sorption pattern to that of either the Pu (V) or Pu (VI) systems. There does appear to be a close match to the Pu (VI) system, which shows 75, 46, 9 and 5 % approximate metal ion concentrations left in solution, although given the relatively small differences between the concentrations in Figure 3.43 before and after O$_2$ exposure, it is difficult to establish whether the Pu (IV) ion has been oxidized or not. Certainly, a change in Eh results in very little change to the solid/solution partition.
3.2 Sorption of Binary and Ternary Fractionated Humic Systems

4 size fractions were studied, HA > 100 kDa, 100 > HA > 10kDa, 10 > HA > 3kDa and HA < 3kDa. The concentrations of HA and metal ions are presented in terms of the solution phase concentration, expressed as a percentage of the total metal or humic added to the system at the start of the experiment. All size fractions have been assigned a specific colour and marker: HA > 100 kDa ♦; 100 > HA > 10 kDa ■; 10 > HA > 3 kDa ▲; HA < 3 kDa ●; Whole humic *, which are used throughout. In this section, ‘whole humic’ refers to the unfractionated humic sample.

3.2.1 Size Fraction Comparison of Whole Humic

Ultra filtration was used to determine the amount of each fraction present at whole humic concentrations of 200, 100, 50 and 10 ppm. Figure 3.44 shows the average amount of each size fraction present at each concentration.
100 ppm Humic Faction

- 100 > HA kDa: 24.68%
- 10 > HA > 10 kDa: 43.50%
- 10 > HA > 3 kDa: 9.05%
- 10 > HA < 3 kDa: 22.77%

50 ppm Humic Fraction

- 100 > HA kDa: 14.34%
- 10 > HA > 10 kDa: 66.09%
- 10 > HA > 3 kDa: 7.48%
- 10 > HA < 3 kDa: 12.09%
Figure 3.44; weighted average of each fraction as a function of the total humic concentration, following ultra filtration at pH = 6.0 ± 0.1 and I = 0.1 M

At 200 ppm, Figure 3.44 A, the two largest size fractions, when combined, make up 87% of the whole humic, with the HA > 100 kDa fraction dominating. At 100, 50 and 10 ppm concentrations the 100 > HA > 10 kDa is the dominant component fraction, and accounts for 66% of the total humic at 50 ppm, Figure 3.47 C. Additionally for all four concentrations, the smallest size fraction, HA < 3 kDa is the least significant and on average it only accounts for 6.5% of the whole humic concentration. The data can help to explain the behaviour of the whole humic in terms of the individual fractions for both binary and ternary systems.
3.2.2 Sorption of Humic Acid Fractions on Quartz Sand

Figure 3.45; Sorption of humic fractions onto 500 gL\(^{-1}\) quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M as a function of the total (sorbed plus free) humic concentration. A: sorption of the 200 ppm humic fraction B: sorption of the 100 ppm humic fraction.
Figure 3.45A shows the sorption data for the uptake of humic fractions at 200 ppm. The largest size fractions, HA > 100 and 100 > HA > 10 kDa, show the least amount of sorption, with the HA > 100 kDa closely following the trend of the whole humic in solution, this behaviour is unsurprising given that over half of the total humic at 200 ppm is comprised of the HA > 100 kDa fraction, (Figure 3.44 A).

Similarly at 100 ppm (Figure 3.45B) shows the largest size fractions to be the least sorbing, with both the HA > 100 kDa and 100 > HA > 10 kDa fractions following the whole humic, this makes sense, since the HA > 100 and 100 > HA > 10 kDa fractions together account for 68 % of the total humic, as shown in Figure 3.44B. For both the 200 and 100 ppm solutions, the larger fractions show an initial rapid binding, followed by a slower uptake from day 2- 9, with only a small difference in sorption between fractions at the end of experiment. The HA > 3 kDa fraction for both the 200 and 100 ppm concentrations, show 60 % sorption to the mineral surface. Given that both the humic and quartz sand surface are both negatively charged, the smaller sized fractions have a lower surface potential than larger species, and so they will be repelled by the surface less than the larger fractions and thus show greater sorption.
Figure 3.46; Sorption of humic fractions onto 500 gL^{-1} quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M as a function of the total (sorbed plus free) humic concentration. A: sorption of the 50 ppm humic fraction B: sorption of the 10 ppm humic fraction

Similarly for the equivalent 50 and 10 ppm concentrations, Figure 3.46, the smallest humic fractions, (10 > HA > 3 and HA > 3 kDa) show a higher relative amount of sorption than at the equivalent 200 and 100 ppm concentrations. For example at 50 ppm (Figure 3.45 A), sorption of the HA > 3 kDa size fraction is around 80 %, compared with 60 % for 100 ppm (Figure 3.45 B). At 10 ppm (Figure 3.46 B), the relative sorption of all humic fractions is greater than at higher humic concentrations. This result is not surprising, since in any surface sorption experiment with a fixed surface area, as sorbent concentration is increased, the fraction of material sorbed can only decrease or remain the same as concentration increases. Finally, in both 50 and 10 ppm systems (Figure 3.46 A & B), the whole humic follows a similar sorption trend to that of the HA > 100 kDa fraction. However comparison with the data in Figure 3.44 (C & D) suggests that, the total humic is principally composed of the 100 > HA > 10 kDa fraction. From these results it seems that the behaviour of the whole humic follows that of the largest size humic fraction and not that of the component fraction which accounts for the greatest percentage of the total humic.
Figure 3.47: Rd values for humic acid fractions bound to the mineral surface. All Rd values are in litres per kilo. Note the Rd values are plotted on a Log scale to produce a more clearly defined trend.

The Rd values, for the humic fractions (Figure 3.47) show the HA > 100, 100 > HA >10 and 10 > HA > 3 kDa fractions tend to follow that of the whole humic, which is unsurprising given that the larger size fractions makeup most of the whole humic. The smallest HA > 3 kDa fraction at both 50 and 10 ppm concentrations does not.

Similar studies in this area have also suggested that smaller size fractions sorb more readily to the mineral surface, i.e, the binding strength increases with a decrease in fraction size. From the humic fraction data, it appears the radionuclides attached to larger humic fractions are more likely to be mobile in a sand system.

Illes and Tombacz (2004), reported results from size distribution experiments of HA solutions following sorption on to magnetite using size exclusion chromatography, which showed preferential sorption of small humic fractions. Likewise Reillier et al (2006), using haematite, also found preferential sorption of low molecular weight fractions. However, other studies such as those conducted by Li (2011) and Pitois et al., (2008), have found evidence to suggest that larger HA fractions sorbed more strongly to the mineral surface. Indeed, van de Weerd et al., (1999, 2002) have suggested that larger fractions should show stronger binding, because surface coverage by small sized
fractions results in a higher entropy loss than that with larger sized fractions. The results shown here do not follow this trend, however one key point to note is the studies carried out by, Li (2011) and van de Weerd et al., (1999), used iron oxides as the mineral surface. For the humic quartz sand fraction results, greater electrostatic repulsion between neighbouring high molecular weight humic molecules may account for preferential sorption of the low molecular weight humic species (Zhou et al., 2001). Studies with fulvic acid have revealed a close correlation between elemental composition and the relative amount of sorption. Li et al (2007) suggested that adsorption density was proportional to the carbon content, and fulvic fractions that had a high ratio of alkyl carbon to carboxyl and carbonyl carbon displayed greater surface sorption.

There are clear differences between the fraction data at 200 ppm and those of lower humic concentrations, which suggest that aggregation is taking place due to the high humic concentration. This will complicate interpretation of ternary system data, because the humic species that are present at 200 ppm are different to those at lower concentrations.
3.2.3 Europium Sorption In The Presence of Humic Acid Fractions

![Graph A](image)

![Graph B](image)
Figure 3.48; Sorption of Eu$^{3+}$ using humic fractions onto 500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M as a function of the total (sorbed plus free) humic concentration, $[\text{Eu}]_{T} = 133$ mBq ml$^{-1}$ (Molar concentration $7.9 \times 10^{-10}$ moles/litre)

A: 200 ppm humic fraction B: 100 ppm humic fraction C: 50 ppm humic fraction D: 10 ppm humic fraction
Eu$^{3+}$ sorption in the presence of the different humic size fractions at 200, 100, 50 and 10 ppm concentrations are shown by Figures 3.48 A, B, C and D. At 200 ppm, Figure 3.31A, the HA > 100 and 100 > HA > 10 kDa fractions show a relatively low sorption of 10 – 15 %, hence most of the Eu$^{3+}$ remains in solution. The 10 > HA > 3 and HA > 3 kDa fractions experience a 50 – 60 %, with more of the metal sorbing to the mineral surface, with the no humic solution experiencing a 90 % drop in metal ion concentration. Additionally, the sorption of the whole humic lies between, the HA > 100 kDa and HA > 3 kDa fractions. This behaviour is somewhat unexpected given that at 200 ppm, the HA > 100 and 100 > HA > 10 kDa fractions, make up 87 % whole humic, see figure 3.47 A. At 100 ppm, Figure 3.48 B, the 100 > HA > 10 kDa fraction, follow a similar trend to the whole humic, this is expected as this size fractions makes up 43 % of the whole humic. The fractions experience a 65 % and 90 % sorption, respectively. This high sorption observed for the smallest fractions, continues at 50 ppm, Figure 3.48 C, where sorption for 10 > HA > 3 and HA > 3 kDa fractions is around 90 %. At 10 ppm, Figure 3.48 D all fractions show the greatest metal ion sorption, with only a 7 % difference in the final sorbed amounts between the HA > 3 and HA > 100 kDa. This trend is expected, since as the humic concentration decreases, it will become a less effective competitor for the Eu$^{3+}$ thus sorption differences between the size fractions reduces.

Overall the data shows that the largest size fractions are more effective at holding the metal ion in solution, while the smallest show the most strongly sorbing behaviour, especially at lower humic concentrations. Interpreting this behaviour is difficult, given the complexity of the system, however the surface sorption capacity at lower humic concentrations is higher and therefore more total binding sites (humic plus quartz) are available, and hence a greater amount of sorption would occur.
The Rd values of the Eu$^{3+}$ (Figure 3.49) as in the humic system, show that the HA > 100, 10 > HA > 10 and 10 > HA > 3 kDa fractions tend to follow that of the whole humic. However, both the 10 > HA > 3 and HA > 3 kDa fractions show very high Rd values at 50 ppm. Normally this is expected given the fraction size, however the large degree of uncertainty shown by the error bars, suggests experimental error.
Figure 3.50; Comparison of the Rd values for the humic and Eu\textsuperscript{3+} fractions bound to the mineral surface. All Rd values are in litres per kilo. Note the Rd values are plotted on a Log scale to produce a more clearly defined trend

Figure 3.50 shows a convergence of the Eu\textsuperscript{3+} fractions with those of the humic. This suggests the behaviour of the metal fractions is tending towards that of the humic, especially at concentrations greater than 100 ppm.

Further comparison between the behaviour of the Eu\textsuperscript{3+} HA > 100 kDa fraction and that of the equivalent humic acid fraction (Figure 3.51), shows that both the metal and humic display decreasing sorption with increasing concentration. However there is no direct correlation between the two data sets, despite the fact that at 200 ppm the humic acid and Eu\textsuperscript{3+} data are close. This is where the humic would be expected to dominate the Eu\textsuperscript{3+} speciation the most.
Likewise, similar behaviour is observed for the remaining fractions. For all fractions both the metal and the humic showed a reduction in sorption at higher humic concentrations, but the humic sorption data may not be used to predict the behaviour of the humic.

Recent europium studies carried out by Li (2011) using the same humic size fractions, but using magnetite as the mineral surface, found that systems with the smallest humic fractions, irrespective of concentration, generally showed the highest amount of Eu$^{3+}$ sorption. This type of behaviour is also exhibited in the quartz sand systems in Figure 3.48, where the smallest fractions showed the largest amount of Eu$^{3+}$ sorption. Li (2011), measured the relative binding strength of the metal ions with each of the fractions and found significantly stronger binding by larger fractions. This, combined with the lower uptake of the larger fractions onto the quartz sand explains the observations made here.

One of the most unexpected results presented here, is that for certain systems, the whole humic behaves outside the range of its component fractions. Hence, in these cases, it seems that the different sized species must be interacting together, thus affecting Eu$^{3+}$
behaviour. Again, studies by Li (2011), indicated that the whole humic system showed the lowest amount of sorption when compared to its component fractions.

3.2.4 Sorption of Uranyl In The Presence of Humic Acid Fractions
Figure 3.52; Sorption of U (VI) using humic fractions onto 500 gL$^{-1}$ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M as a function of the total (sorbed plus free) humic concentration ($[U_T]$ = 100 mBqml$^{-1}$) (Molar concentration $3.38 \times 10^{-5}$ moles/litre).

A: 200 ppm humic concentration  
B: 100 ppm humic concentration  
C: 50 ppm humic concentration  
D: 10 ppm humic concentration
Figure 3.52 shows the humic size fraction results for a uranyl system in the absence of carbonate. As in the europium system, the HA > 3 kDa fraction experiences the highest amount of sorption to the surface, thus the lowest concentration in solution, hence are less able to compete for the metal ion. The HA > 100 and 100 > HA > 10 kDa fractions again show lower sorption, and appear better at holding the metal ion in solution. At higher concentrations, as was the case for europium, the whole humic tends to follow the largest size fractions which is unsurprising given the whole humic is comprised largely of HA > 100 and 100 > HA > 10 kDa species, (Figure 3.44). At lower humic concentrations (50 and 10 ppm), much higher sorption behaviour is observed. Most notably at 10 ppm  (Figure 3.52 D), the sorption for the whole humic system and that of the HA < 3 kDa fraction, are very similar. At first sight it is tempting to assign this similarity to the fact that the metal ion is strongly complexing to the HA < 3 kDa humic fraction and thus follows the same trend. However, given the amount of quartz sand remains constant, and that in the europium system, the metal ion does not follow the humic at higher concentration (where one might expect the humic to dominate the speciation), Figure 3.48, it is difficult to ascertain why this would happen in the fraction with the smallest amount of humic present. It seems more likely that the uranyl behaviour is tending towards that of the system with no humic and the apparent match between the HA < 3 kDa and the metal ion at 10 ppm is a coincidence.
Figure 3.53; Rd values for U (IV) fractions bound to the mineral surface. All Rd values are in litres per kilo. Note the Rd values are plotted on a Log scale to produce a more clearly defined trend

The Rd values for the uranyl system (Figure 3.53) again show the HA > 100, 100 > HA > 10 and 10 > HA > 3 kDa fractions tend to follow that of the whole humic. The HA < 3 kDa fraction shows the highest Rd values which is unsurprising given that the smallest humic species show the highest sorption to the surface, and hence the lowest concentration in solution.
Figure 3.54: U (VI) sorption data and humic sorption data for the Ha > 100 kDa fraction at different humic acid concentrations. Solid lines represent the humic acid data and the symbols represent the metal data.

Figure 3.54 compares the values for U (VI) in the presence of humic fractions and those of the fractions themselves. The metal ion data in the HA > 100 kDa fraction follows the equivalent humic, at 200 and 100 ppm (Figure 3.54). At high concentration, the HA > 100 kDa fraction seems to be dominating the speciation, and so the uranyl follows the humic.
3.2.5 Sorption of Pu (VI) in the Presence of Humic Acid Fractions

Figure 3.55; Sorption of Pu (VI) 1.22 mBq ml⁻¹ (Molar concentration 2.2 x 10⁻¹² moles/litre) using humic fractions onto 500 gL⁻¹ quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M as a function of the total (sorbed plus free) humic concentration. A: 200 ppm humic fraction B: 100 ppm humic fraction
The 200 and 100 ppm Pu (VI) sorption data are shown in Figure 3.55. At 200 ppm, figure 3.55A, both the whole humic and the HA > 100 kDa fraction are the best retaining at the metal ion in solution, is this expected since the largest fraction makes up 51.67% of the total whole humic, also larger fractions have stronger binding effects. The 100 > HA > 10 kDa fraction shows a relatively high amount sorption around 54%, much higher than in the equivalent europium or uranyl system. Similarly the 10 > HA > 3 and HA < 3 kDa fractions show on average 80% to 90% sorption, much greater than for the previous metal ion systems. Further, the smallest size fractions follow a similar trend to the no humic system, where the majority of the metal ion sorbs to the mineral surface, within the first 48 hours. Likewise at 100 ppm Figure 3.55B, the smallest size fractions, show the highest sorption, and again follow the no humic system, whilst the HA > 100 kDa fraction experiences an increase in sorption of 35% between 200 and 100 ppm. However, the most notable characteristic is that the whole humic shows the least amount of sorption of Pu, compared to its the component fractions.
Figure 3.56; Sorption of Pu (VI) 1.22 mBq ml\(^{-1}\) (Molar concentration \(2.2 \times 10^{-12}\) moles/litre) using humic fractions onto 500 gL\(^{-1}\) quartz sand at pH = 6.0 ± 0.1 and I = 0.1 M as a function of the total (sorbed plus free) humic concentration. A: 50 ppm humic fraction B: 10 ppm humic fraction

The equivalent results for the 50 and 10 ppm systems are shown in Figure 3.56. At these lower concentrations, all the fractions experience an initial rapid sorption in the first 24 hours followed by a slower sorption period that lasts up to 4 days. Again at both 50 and 10 ppm, Figures 3.56 A and Figure 3.56B, the HA > 100 and 100 > HA > 10 kDa fractions show a further increase in sorption, with the HA > 3 kDa fraction exhibiting approximately 98 % sorption and following trend of the no humic system. As is the case for the 200 and 100 ppm systems, the whole humic exhibits much lower sorption than the component fractions. The reason for this difference is not certain, but of the three metal ions studied with the humic size fractions, Pu (VI) is by far the most redox sensitive. The complex interaction of the redox sensitive Pu (VI) metal ion, with the humic could account for this difference. For example, it is possible that the size fractionation process has separated the species responsible for redox interactions from those that control the complexation.
Figure 3.57; Rd values for Pu (VI) fractions bound to the mineral surface. All Rd values are in litres per kilo. Note the Rd values are plotted on a Log scale to produce a more clearly defined trend.

The Rd values for the Pu (VI), Figure 3.57, show that for the HA > 100 and 100 > HA > 10 kDa fractions follow that of the whole humic, yet both the 10 > HA > 3 and HA > 3 kDa fractions do not follow this trend. The contribution of both the 10 > HA > 3 and HA > 3 kDa fractions to the whole humic is so small, that inevitably the behaviour will be different. Similarly, the high Rd values of both 10 > HA > 3 and HA > 3 kDa fractions are not surprising because they show the highest amount of humic bound to the surface.
The Rd values for the Pu (VI) fractions and that of the humic (Figure 3.58) converge with the humic for the HA > 100 and 100 > HA > 10 kDa fractions. However, while the smaller size 10 > HA > 3 and HA > 3 kDa metal fractions show no convergence.

The fact that the smaller fraction plots do not converge in these experiments suggests that the metal is not following the humic in these systems. This suggest the smaller fractions show weaker binding than the larger humic species.

Further comparison of the Pu fractions with that of the humic fractions shows much higher sorption of the metal fractions than the equivalent humic. The 10 > Ha > 3 kDa fraction Figure 3.59, gives the best example of this comparison.
Figure 3.59; Pu (VI) sorption data and humic sorption data for the 10 > Ha > 3 kDa fraction at different humic acid concentrations. Solid lines represent the humic acid data and the symbols represent the metal data

Figure 3.59 shows no correlation between metal fraction sorption data and those of the fraction. Both the metal and humic display decreasing sorption with increasing concentration. The undulations displayed by the humic data, are not real given the size of the overlapping error bars.

The overall behaviour suggests the larger size fractions are much more effective at holding, not only for the Pu (VI), but also the Eu$^{3+}$ and uranyl ions, which strongly suggests stronger complexation of the metal ions by larger species.
Chapter 4

Modelling and Discussion
4.1 Introduction to Modelling

A simple mathematical model was developed to predict the interactions between metal ions, humic acid and mineral surfaces. Initially the model was applied to simple binary systems (See Figure 2.4) before being modified to account for the more complex ternary behaviour.

In this model, the interaction of aqueous metal ion $M_{(aq)}^{n+}$, with the humic (HA) is described using two components, with initial uptake to an exchangeable fraction, $M_{exch}$, assumed to be instantaneous.

\[
M_{(so \ln)}^{n+} + HA_{exch} \leftrightarrow M_{exch} \quad \text{(Equation 24)}
\]

\[
K_{exch} = \frac{[M_{exch}]}{[M_{(so \ln)}^{n+}][HA_{exch}]} \quad \text{(Equation 25)}
\]

where $HA_{exch}$ is the humic exchangeable binding site, $K_{exch}$ an equilibrium constant for the process.

\[
M_{(exch)} \leftrightarrow M_{non-exch} \quad \text{(Equation 26)}
\]

\[
\frac{d[M_{non-exch}]}{dt} = k_f[M_{exch}] - k_b[M_{non-exch}] \quad \text{(Equation 27)}
\]

Subsequent transfer to and from the non-exchangeable fraction, $M_{non-exch}$, is a first-order kinetic (slow) process, where $k_f$ and $k_b$ are first order rate constants. Figure 4.1 represents the model interaction between the metal ion and humic molecule.
Figure 4.1: Schematic of interaction between metal ion and humic molecule

Prior to the desorption experiments conducted by Abrahamsen (2009), the interaction of the metal ion with the quartz surface was considered using an equilibrium process. However, slow desorption of the sorbed metal requires a kinetic reaction.

\[
M^{n+}(\text{aq}) + S_M \leftrightarrow M_S \quad \text{(Equation 26)}
\]

\[
\frac{d[M_S]}{dt} = k_{MSf} [M^{n+}(\text{soln})][S_M] - k_{MSb} [M_S] \quad \text{(Equation 27)}
\]

where \( S_M \) is a metal binding site on the quartz sand surface, \( M_S \) is M sorbed to the surface and \( k_{MSf} \) and \( k_{MSb} \) are the forward and backward rate constants, respectively. This means that the inorganic speciation described in tables 2.1-2.6 are not explicitly included in the calculations. However, because all of the experiments in this work were performed at the same pH and ionic strength, the constants \( k_{MSf} \) and \( k_{exch} \) may be corrected for background speciation by multiplying each by the fraction of free metal in the speciation tables. \( M_{(\text{soln})} \) is the total solution concentration of the metal ion, i.e., the constants involving \( M_{(\text{soln})} \) are conditional (\( k_{MSf}, K_{exch} \)).

Note various metal-humic and metal-surface interactions are thought to have a combination of complex electrostatic components. However inclusion of these extra
complex components would negate the applicability of the model for RPA studies, hence these effects are not included in the model.

4.1.1 Modelling Humic Acid and Quartz Sand Systems

The interactions between humic acid and quartz sand systems are complex and are comprised of multiple kinetic components. The humic uptake data showed evidence of both fast and slow types of kinetic behaviour, and hence each is assigned a general reaction and a pair of forward and backward rate constants. This heterogeneity could be due to the presence of either, more than one type of HA molecule or surface binding site, or both. In the first instance, the modelling work described here assumed that the sand surface was the source of the heterogeneity. This approach will be referred to as Model 1. The Model 1 interactions are shown schematically in Figure 4.2.

![Diagram of Model 1 interactions of HA and metal ions with two mineral surface binding sites](image)

Figure 4.2; Model 1 interactions of HA and metal ions with two mineral surface binding sites
The model assumes a single type of humic species in solution with two surface sites. The humic sorption equations for model 1 are given by:

\[ HA_{\text{free}} + S_{HA1} \rightleftharpoons HA_{S1} \]  

(Equation 28)

\[ \frac{d[HA_{S1}]}{dt} = k_{HAS1}[HA_{\text{free}}][S_{HA1}] - k_{HAS1b}[HA_{S1}] \]  

(Equation 29)

\[ HA_{\text{free}} + S_{HA2} \rightleftharpoons HA_{S2} \]  

(Equation 30)

\[ \frac{d[HA_{S2}]}{dt} = k_{HAS2f}[HA_{\text{free}}][S_{HA2}] - k_{HAS2b}[HA_{S2}] \]  

(Equation 31)

where: \( S_{HA1} \) and \( S_{HA2} \) are surface binding sites, type 1 and 2, respectively; \( HA_{S1} \) and \( HA_{S2} \) are humic bound to surface sites, type 1 and 2, respectively; and \( k_{HAS1f} \), \( k_{HAS1b} \), \( k_{HAS2f} \) and \( k_{HAS2b} \) are rate constants.

Figure 4.3; Model 1 results for binary humic acid/quartz sand system, \( I = 0.1 \), \( \text{pH} = 6 \), total \([HA] = 10, 50, 100, 200 \text{ ppm}\): experimental data (points) and model fits (lines)

Figure 4.3 shows the Model 1 predicted uptake of HA onto the quartz sand surface compared with the experimental data. As discussed in section 3.1.1, the reaction is
comprised of two steps, an initial, relatively fast step (sorption complete within 24 hours), followed by a slower, second step (sorption takes place over a number of weeks).

Model fitting was done manually, by adjusting the rate constants and binding site parameters, until a good fit between the model output and experimental data was achieved, i.e. an iterative process was used throughout when fitting the models to the experimental data. A number of different humic concentrations were used in each experiment, but a general set of best-fit parameters were used for each system. Table 4.1 shows the values of the parameters used in Model 1 to obtain the best overall fits for the experimental data in the HA / sand system.

For the 200, 100 and 10 ppm systems the model slightly underestimates the amount of HA sorbing onto the sand surface. However given the humic solutions contain a mixture of heterogeneous species, all of which have different physical and chemical properties, the model produces an adequate fit to the data. As with previous sand/humic Model 1 fits produced by Abrahamsen (2009), though not perfect, the fit is acceptable, given the relative complexity of the system.

<table>
<thead>
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<th>Parameters</th>
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<tr>
<td>$k_{HAS1f}$</td>
<td>$1.40 \times 10^{-6} \text{ ppm}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_{HAS1b}$</td>
<td>$7.00 \times 10^{-6} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_{HAS2f}$</td>
<td>$1.00 \times 10^{-8} \text{ ppm}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_{HAS2b}$</td>
<td>$6.00 \times 10^{-7} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$[S_1]_o$</td>
<td>20 µg HA per g of sand</td>
</tr>
<tr>
<td>$[S_2]_o$</td>
<td>30 µg HA per g of sand</td>
</tr>
</tbody>
</table>

Table 4.1; best fit parameters for Model 1 for HA / quartz sand system
A second model was developed based on one developed for humic / Fe oxide interactions by Van De Weerd et al (1999). That model has up to 6 fractions, but for simplicity, and to make the model more applicable for RPA studies, the model developed here has only two HA fractions, (here referred to as HA1 and HA2) and a single binding site. This model will be referred to as Model 2. Figure 4.4 shows schematically the interactions occurring in Model 2. Significantly, the calculations using Model 2 assume that 2 types of humic have different interactions with the sand surface, but the same interactions with the metal ion. Hence, in Model 2, for each metal ion there is a single set of $K_{\text{exch}}, k_f, k_b$ constants.

Figure 4.4; Model 2 interactions of two HA fractions with a single mineral surface binding site

An alternative set of humic sorption equations is required by Model 2;

\[ HA_{1\text{free}} + S_{HA} \rightarrow HA_{1s} \]  

(Equation 32)
\[
\frac{d[H_{A1s}]}{dt} = k_{HA1sf}[H_{A1,free}][S_{HA}] - k_{HA1sb}[H_{A1s}]
\]  
(Equation 33)

where \(\text{HA}_{1\text{free}}\) is humic type HA1 in the solution phase and \(\text{HA}_{1s}\) refers to the HA1 in the sorbed phase. \(S_{HA}\) is the surface-binding site, with \(k_{HA1sf}\) and \(k_{HA1sb}\) representing the forward and backward rate constants for the 1st HA fraction surface binding reaction. Equations for the 2nd HA fraction are given by;

\[
\text{HA}_{2\text{free}} + S_{HA} \xrightarrow{HA_{2s}}
\]

(Equation 34)

\[
\frac{d[H_{A2s}]}{dt} = k_{HA2sf}[H_{A2,free}][S_{HA}] - k_{HA2sb}[H_{A2s}]
\]  
(Equation 35)

As for Model 1, a similar humic/sand binary system fit was achieved using Model 2, as shown by Figure 4.5

Figure 4.5; Model 2 results for binary humic acid/quartz sand system, \(I = 0.1\), \(\text{pH} = 6\), total \([\text{HA}] = 10, 50, 100, 200\ \text{ppm}\): experimental data (points) and model fits (lines)
The model 2 fit for the experimental data, again slightly underestimates the amount of HA sorption on the surface of the sand. Table 4.2 shows the best fit parameters values used in model 2 for experimental data in the HA / sand system (unless stated otherwise).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{HAS1f} )</td>
<td>1.50x10^{-7} \text{ ppm}^{-1} \text{s}^{-1}</td>
</tr>
<tr>
<td>( k_{HAS1b} )</td>
<td>2.00 \times 10^{-8} \text{s}^{-1}</td>
</tr>
<tr>
<td>( k_{HAS2f} )</td>
<td>2.00 \times 10^{-6} \text{ ppm}^{-1} \text{s}^{-1}</td>
</tr>
<tr>
<td>( k_{HAS2b} )</td>
<td>3.00 \times 10^{-5} \text{s}^{-1}</td>
</tr>
<tr>
<td>([S_0])</td>
<td>30 \text{ g HA per g of sand}</td>
</tr>
</tbody>
</table>

Table 4.2; best-fit parameters for Model 2 for HA / quartz sand system

Recently a third, denoted Model 3, was developed using aspects of both Model 1 and Model 2. In Model 3, two HA fractions, designated HA1 and HA2, are coupled with two surface binding sites, denoted S1 and S2. Both of the humic species act independently of one another, and can have different binding strengths, unlike in the previous models, where the binding strength of all humics are the same. One of the main aspects that Model 3 addresses is that different types of humic can have different interactions with the metal ion. The inclusion of an extra HA fraction with different metal ion parameters and a 2\textsuperscript{nd} surface binding site, will hopefully tackle some of the shortcomings associated with the linear additive approach, providing a more comprehensive model of ternary system behaviour. Figure 4.6 shows the interactions involved in Model 3.
Figure 4.6: Model 3 interactions of two HA fractions with two mineral surface sites

There are various ways in which the metal ion $M^{n+}$ can interact with the humic and the mineral surface, Model 3 accounts for these interactions. For example, in solution the metal can bind either exchangably or non-exchangably to the humic fractions HA1 or HA2. Conversely, the $M^{n+}$ can bind directly to surface bound humic species, such as HA1S1, HA2S1, HA1S2 or HA2S2. Significantly, the calculations using Model 3 assume that 2 types of humic have different interactions with the sand surface and different interactions with the metal ion.

Hence Model 3 should be able to account for the more complex behaviour associated with ternary systems.
The equivalent set of Model 3 equations are shown below;

\[
\text{HA1}_{\text{free}} + S_{1\text{HA}} \xrightleftharpoons[k_{\text{HAIS1f}}]{k_{\text{HAIS1b}}} \text{HA1}_{S1} \quad \text{(Equation 31)}
\]

\[
\frac{d[\text{HA1}_{S1}]}{dt} = k_{\text{HAIS1f}}[\text{HA1}_{\text{free}}][S_{1\text{HA}}] - k_{\text{HAIS1b}}[\text{HA1}_{S1}] \quad \text{(Equation 32)}
\]

HA1$_{S1}$ and S$_{1\text{HA}}$ are the first type 1, humic bound and surface binding sites respectively. HA1$_{\text{free}}$ is the first humic fraction in the solution phase. HA$_{S1}$ is the type 1 humic bound to surface site S$_{1\text{HA}}$, with $k_{\text{HAIS1b}}$ and $k_{\text{HAIS1f}}$ the rate constants. The equations for the first type of humic interacting with the second surface site are;

\[
\text{HA1}_{\text{free}} + S_{2\text{HA}} \xrightleftharpoons[k_{\text{HAIS2b}}]{k_{\text{HAIS2f}}} \text{HA1}_{S2} \quad \text{(Equation 33)}
\]

\[
\frac{d[\text{HA1}_{S2}]}{dt} = k_{\text{HAIS2f}}[\text{HA1}_{\text{free}}][S_{2\text{HA}}] - k_{\text{HAIS2b}}[\text{HA1}_{S2}] \quad \text{(Equation 34)}
\]

where S$_{2\text{HA}}$ is the surface binding site, HA1$_{S2}$ is the type 1 humic bound to surface site 2, $k_{\text{HAIS2f}}$ and $k_{\text{HAIS2b}}$ are rate constants.

The equivalent equations for the second type of humic are;

\[
\text{HA2}_{\text{free}} + S_{1\text{HA}} \xrightleftharpoons[k_{\text{HA2S1f}}]{k_{\text{HA2S1b}}} \text{HA2}_{S1} \quad \text{(Equation 35)}
\]

\[
\frac{d[\text{HA2}_{S1}]}{dt} = k_{\text{HA2S1f}}[\text{HA2}_{\text{free}}][S_{1\text{HA}}] - k_{\text{HA2S1b}}[\text{HA2}_{S1}] \quad \text{(Equation 36)}
\]

\[
\text{HA2}_{\text{free}} + S_{2\text{HA}} \xrightleftharpoons[k_{\text{HA2S2b}}]{k_{\text{HA2S2f}}} \text{HA2}_{S2} \quad \text{(Equation 37)}
\]

\[
\frac{d[\text{HA2}_{S2}]}{dt} = k_{\text{HA2S2f}}[\text{HA2}_{\text{free}}][S_{2\text{HA}}] - k_{\text{HA2S2b}}[\text{HA2}_{S2}] \quad \text{(Equation 38)}
\]
Figure 4.7; Model 3 results for binary humic acid/quartz sand system, I = 0.1, pH = 6, total [HA] = 10, 50, 100, 200 ppm: experimental data (points) and model fits (lines).

The equivalent model 3 fit for the simple humic acid/sand system, Figure 4.7, again slightly underestimates humic acid sorption for the 10 ppm system, however the 50 100 and 200 ppm systems show an overall better fit than for models 1 and 2. Table 4.3 shows the best-fit parameters for in the HA/sand system in Model 3.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{HA1S1f}$</td>
<td>$1.00 \times 10^{-5}$ ppm$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{HA1S1b}$</td>
<td>$7.00 \times 10^{-6}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{HA1S2f}$</td>
<td>$7.00 \times 10^{-9}$ ppm$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{HA1S2b}$</td>
<td>$5.00 \times 10^{-8}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{HA2S1f}$</td>
<td>$1.00 \times 10^{-8}$ ppm$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{HA2S1b}$</td>
<td>$3.00 \times 10^{-6}$ s$^{-1}$</td>
</tr>
<tr>
<td>$K_{HA2S2f}$</td>
<td>$7.00 \times 10^{-5}$ ppm$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{HA2S2b}$</td>
<td>$7.00 \times 10^{-4}$ s$^{-1}$</td>
</tr>
<tr>
<td>$[S_1]_o$</td>
<td>$20$ µg HA per g of sand</td>
</tr>
<tr>
<td>$[S_2]_o$</td>
<td>$30$ µg HA per g of sand</td>
</tr>
</tbody>
</table>

Table 4.3; Best-fit parameters for Model 3 for HA / quartz sand system
4.2 Ternary System Modelling

The metal ion data presented in the model comparison plots are expressed as natural log $C/C_0$, where $C$ is the metal ion concentration at any time, $t$, and $C_0$ is the metal ion concentration in solution before exposure to the mineral surface at time $= 0$. As in the previous chapters, all humic acid concentrations use the same specific colour and marker. In addition, the corresponding solid coloured lines represent the model fits for the data.

4.2.1 Europium Modelling

Figure 4.8: Model 1 results for Eu sorption the in the ternary humic acid/quartz sand system, $[\text{Eu}]_T = 133 \text{ mBq ml}^{-1}$ (Molar concentration $7.9 \times 10^{-10}$ moles/litre), $I = 0.1$, pH = 6, in air, as a function of humic acid concentration: experimental data (points) and model fits (lines) - $[\text{S}_T].k_{sf} = 6.5 \times 10^{-5} \text{ s}^{-1}$; $k_{sb} = 4.64 \times 10^{-6} \text{ s}^{-1}$; $k_f = 1.1 \times 10^{-8} \text{ s}^{-1}$; $k_b = 1.0 \times 10^{-7} \text{ s}^{-1}$; $[\text{HA}_{\text{exch,T}}].K_{\text{exch}} = 20$
Figure 4.9; Model 2 results for Eu sorption in ternary humic acid/quartz sand system, $[\text{Eu}]_T = 133 \text{ mBq ml}^{-1}$ (Molar concentration $7.9 \times 10^{-10} \text{ moles/litre}$), $I = 0.1$, $\text{pH} = 6$, in air, as a function of humic acid concentration: experimental data (points) and model fits (lines) - $[S_T].k_{Sf} = 1.6 \times 10^{-5} \text{ s}^{-1}$; $k_{Sb} = 1.143 \times 10^{-6} \text{ s}^{-1}$; $k_f = 1.1 \times 10^{-8} \text{ s}^{-1}$; $k_b = 1.0 \times 10^{-7} \text{ s}^{-1}$; $[\text{HA}_{\text{exch,T}}].K_{\text{exch,T}} = 0.99$

Figures 4.8 and 4.9 show the Model 1 and 2 results for the uptake of Eu $^{3+}$ onto the sand surface in the presence of HA. The Eu $^{3+}$ system displays fairly classical ternary behaviour. Model 1, (Figure 4.8) performs relatively well, over the range of humic concentrations, although for the 10 ppm solution it underestimates the Eu $^{3+}$ concentration in the first 3 days, followed by a slight overestimation for the remainder of the experiment. Similarly in the 0 ppm solution, the model underestimates metal ion concentration for the first 3 days, but performs relatively well after this point.

Model 2 (Figure 4.9) generally gives an adequate fit to the data. However, it overestimates the Eu$^{3+}$ concentration in the 100 ppm solution when compared to the equivalent model 1 prediction, as shown in Figure 4.10. The model 1 fit occurs within error of the experimental data points.
Figure 4.10; Model 1 and 2 fits for the 100 ppm solution \([\text{Eu}]_1 = 133 \text{ mBq ml}^{-1}\), (Molar concentration \(7.9 \times 10^{-10}\) moles/litre), \(I = 0.1\), pH = 6, in air, as a function of humic acid concentration: experimental data (points) and model fits (lines)

However, the Model 2 fit for the 10 ppm solution more accurately predicts the behaviour of the metal ion, as shown in Figure 4.11,

Figure 4.11; Model 1 and 2 fits for the 10 ppm solution \([\text{Eu}]_1 = 133 \text{ mBq ml}^{-1}\), (Molar concentration \(7.9 \times 10^{-10}\) moles/litre), \(I = 0.1\), pH = 6, in air, as a function of humic acid concentration: experimental data (points) and model fits (lines)
Given the complexity of the system, the quality of fits for both models is encouraging, with Model 2 giving a better fit for the 10 ppm solutions, while Model 1 is better at fitting the 200, 100 and 50 ppm solutions.

Figure 4.12; Model 3 results for Eu$^{3+}$ sorption in ternary humic acid/quartz sand system, [Eu]$\text{T} = 133$ mBq ml$^{-1}$, (Molar concentration $7.9 \times 10^{-10}$ moles/litre), $I = 0.1$, pH = 6, in air, as a function of humic acid concentration: experimental data (points) and model fits (lines) $k_{\text{HA1S1f}} = 1.00 \times 10^{-5}$; $k_{\text{HA1S1b}} = 7.00 \times 10^{-6}$; $k_{\text{HA1S2f}} = 7.00 \times 10^{-9}$; $k_{\text{HA1S2b}} = 5.00 \times 10^{-8}$; $k_{\text{HA2S1f}} = 1.00 \times 10^{-8}$; $k_{\text{HA2S1b}} = 3.00 \times 10^{-6}$; $k_{\text{HA2S2f}} = 7.00 \times 10^{-5}$; $k_{\text{HA2S2b}} = 7.00 \times 10^{-4}$

Figure 4.12 shows the Model 3 results for the Eu$^{3+}$ system. The model can predict the europium behaviour in the ternary system relatively well. However, it still overestimates and underestimates the metal ion concentration in the 100 and 10 ppm solutions, respectively. Figure 4.13, compares the fits for all three models for both the 100 and 10 ppm solutions. Models 1 and 3 predict metal ion behaviour quite well for the 100 ppm solution, with most of the trend lines falling within error of the experimental data. Conversely, for the 10 ppm solution, model 2 shows a better correlation with the experimental data than either Models 1.
Figure 4.13; Model 1, 2 and 3 fits for the 10 and 100 ppm solutions [Eu]$_T$ = 133 mBq ml$^{-1}$, (Molar concentration 7.9 x 10$^{-10}$ moles/litre), I = 0.1, pH = 6, in air, as a function of humic acid concentration: experimental data (points) and model fits (lines)

Overall, there seems to no additional benefit to using the more complex model 3, when trying to predict the sorption behaviour of the metal ion, especially considering the need for mathematical simplicity in RPA speciation calculations. Further, the extra parameters associated with Model 3, may not address the fundamental problems associated with Model 1 and Model 2, for example Models 1, 2 and 3 assume all uptake follows a langmuir type trend, however if this is not the case, then irrespective of any additional parameters, Model 3 would offer no additional benefit in modelling the data.
4.2.2 Thorium Modelling

Figure 4.14; Model 1 results for Th sorption in ternary humic acid/quartz sand system, ([Th] = 47 mBqml⁻¹, (Molar concentration 4.99 x 10⁻⁵ moles/litre), I = 0.1, pH = 6, in air, as a function of humic acid concentration: experimental data (points) and model fits (lines) - [S₄].K_MSf = 7.5x10⁻⁶ s⁻¹; k_MSb = 2.5x10⁻⁶ s⁻¹; k_f = 1.1x10⁻⁸ s⁻¹; k_b = 1.0x10⁻⁷ s⁻¹; [HA_exch,T].K_exch = 10

Figure 4.14 shows the results for a Th (IV) ‘in air’ system. Qualitatively, the behaviour between europium, (Figure 4.8) and thorium, (Figure 4.14) is similar, given that systems show simple ternary behaviour (solution phase metal ion concentration increasing with [HA]). In Figure 4.14, the model is able to simulate metal ion behaviour, though the goodness of fit is harder to judge than the Eu system, because there is much more scatter in the experimental data (due to the greater difficulty in measuring relatively low concentrations of Th) than in the europium experiment. Likewise, there are quantitative differences between the two metal ion systems: Th (IV) sorption to the surface is somewhat slower and weaker, as is the apparent binding strength of the metal ion for the humic. At first sight, this might seem surprising, given that we would expect stronger binding to both by the Th⁴⁺ ion. However, this is due to the competition with the OH⁻ ions (Figures 4.8 and 4.14 show data recorded in the presence of air), which forms very strong complexes with Th⁴⁺. The Eu speciation calculations shown in Figure 2.11 show that hydroxide complexation is not significant for Eu³⁺ at pH 6, and so a significant fraction of the metal ion exists as free Eu³⁺(aq), available for humic or surface
complexation. However, in case of Th\(^{4+}\), hydrolysis is significant, with the dominant species being Th\(_4\)(OH)\(_{12}\)\(^{4+}\) and free Th\(_{4}^{+}(aq)\), accounting for only 1.1 \(\times\) 10\(^{-5}\)% of the Th. Hence, the apparent weaker binding for Th\(^{4+}\) must be due to competition by OH\(^-\) ions for the metal. Given, the higher charge of the Th\(^{4+}\), the intrinsic surface complexation constant must be higher than that for Eu\(^{3+}\).

---

**Figure 4.15:** Model 1 results for Th sorption in ternary humic acid/quartz sand system, [Th\(_T\)] = 47 mBqml\(^{-1}\)(Molar concentration 4.99 \(\times\) 10\(^{-5}\) moles/litre), I = 0.1, pH = 6, in inert atmosphere, as a function of humic acid concentration: experimental data (points) and model fits (lines) - [S\(_T\)].k\(_{MSf}\) = 2.5 \(\times\) 10\(^{-5}\) s\(^{-1}\); k\(_{MSb}\) = 4.17 \(\times\) 10\(^{-6}\) s\(^{-1}\); k\(_f\) = 1.1 \(\times\) 10\(^{-8}\) s\(^{-1}\); k\(_b\) = 1.0 \(\times\) 10\(^{-7}\) s\(^{-1}\); [HA\(_{exch,T}\)].K\(_{exch}\) = 3

The Model 1 results for Th (IV) sorption in the absence of air are displayed in Figure 4.15. The data show that excluding air does affect the results, even for redox insensitive ions, such as Th\(^{4+}\). The stronger sorption in the absence of air is due the removal of CO\(_3^{2-}\) as a competing ligand and hence the behaviour of the system is an intermediate between the simple behaviour of the Eu\(^{3+}\) and the more complex uranyl system. The most significant point to note is that the 50 ppm data lies below the 0 ppm data. As the degree of scatter has been reduced, the apparent overall quality of the model fit is better, but this may just be a result of the fact that it is easier to compare the fit with the experimental data, because of the lower degree of scatter. For instance, at 200 ppm the
data closely match the model fit. Likewise at 10 and 0 ppm, although the model slightly overestimates Th$^{4+}$ concentration, the model fit is within error of the experimental data. At 50 ppm, the sorption is high, and the model adequately predicts the low metal ion concentration.

Figure 4.16; Model 3 results for Th sorption in ternary humic acid/quartz sand system, [Th$_T$] = 47 mBqml$^{-1}$, (Molar concentration 4.99 x 10$^{-5}$ moles/litre), I = 0.1, pH = 6, in inert atmosphere, as a function of humic acid concentration: experimental data (points) and model fits (lines) $k_{HA1S1f} = 2.00E-06$; $k_{HA1S1b} = 1.50E-05$; $k_{HA1S2f} = 1.00E-08$; $k_{HA1S2b} = 6.00E-07$; $k_{HA2S1f} = 2.00E-05$; $k_{HA2S1b} = 1.50E-09$; $k_{HA2S2f} = 1.00E-08$; $k_{HA2S2b} = 6.00E-07$

Figure 4.16, shows the corresponding Model 3 results for Th (IV) in the absence of CO$_2$. In contrast to the Model 1 fit for the 50 ppm solution, Model 3 is able to account for the high sorption behaviour, producing an adequate fit to the experimental data, especially during the early stages (up to 4 days /354600 s) of the experiment. Models 1 and 2 are unable to fit the 50 ppm data because not only does it fall below the 0 ppm data, but it shows greater sorption than the humic itself. In a model that does not take into account chemical fractionation of the humic (i.e. it does not allow the sorbed humic
to have a larger equilibrium constant than humic in solution), the two limiting behaviours are:

1. The surface binding strength is greater than that of the humic in this case, the maximum binding is observed in the 0 ppm solution, provided that the fraction of humic bound in the system is less than that of the metal in the 0 ppm solution, here the presence of humic can only decrease sorption.

2. The humic binding strength dominates, hence the behaviour of the metal will tend to follow that of the humic, as the humic concentration increases. For these systems, the fraction of metal bound has to be between that of the 0 ppm solution and the humic itself.

For either of these two scenarios, a model without fractionation cannot simulate the behaviour in the 50 ppm solution, where the sorption of the metal ion is stronger than that of both the 0 ppm solution and that of the humic.

Model 3 is able to simulate this data (see 50 ppm data fit, Figure 4.16), because it allows humic sorbed to the mineral surface to have stronger binding than if left in solution. However, the Model 3 fit is by no means perfect.

For the 100 ppm solution, Model 3 underestimates the metal ion concentration, compared to the equivalent Model 1 and Model 2 predictions, as shown in Figure 4.17. Although not perfect, Models 1 and 2 provide a better correlation with the data.
Figure 4.17; Model 1, 2 and 3 fits for the 100 ppm solution Th sorption in ternary humic acid/quartz sand system, [Th\textsubscript{T}] = 47 mBq/ml\textsuperscript{-1}, (Molar concentration 4.99 x 10\textsuperscript{-5} moles/litre), I = 0.1, pH = 6, in inert atmosphere, as a function of humic acid concentration: experimental data (points) and model fits (lines)

Hence overall Model 3 does not provide an improvement in the global fit to the data. However, it does allow a particular type of behaviour to be simulated that is not possible with Models 1 and 2.

The fact that excluding CO\textsubscript{2} produced a change in sorption is surprising given that carbonate complexes are not predicted to be significant in the inorganic speciation (Table 2.2). There are two possible explanations for this. The first is that there is mixed complex formation involving Th\textsuperscript{4+}/CO\textsubscript{3}\textsuperscript{2-} and humic in solution and/or at the surface. Secondly, there may be thermodynamic data missing from the PHREEQC database, and in fact there are no Th/ carbonate complexes in the database. Hence it is possible that carbonate complexes are important, but that they have not been considered for inclusion in the PHREEQC database.
Figure 4.18; Model 1 results for uranyl sorption in ternary humic acid/quartz sand system, ([U] = 100 mBqml$^{-1}$), (Molar concentration $3.38 \times 10^{-5}$ moles/litre), I = 0.1, pH = 6, in inert atmosphere, as a function of humic acid concentration: experimental data (points) and model fits (lines) - $[S]_f$, $k_{Sf} = 1 \times 10^{-5}$ s$^{-1}$; $k_{Sb} = 3.33 \times 10^{-6}$ s$^{-1}$; $k_f = 1.1 \times 10^{-8}$ s$^{-1}$; $k_b = 1.0 \times 10^{-7}$ s$^{-1}$; $[HA_{exch,T}]$, $K_{exch} = 1$
Figure 4.19; Model 2 results for Uranyl sorption in ternary humic acid/quartz sand system, ([U\textsubscript{T}] = 100 mBqml\textsuperscript{-1}), (Molar concentration 3.38 x 10\textsuperscript{-5} moles/litre), I = 0.1, pH = 6, in inert atmosphere, as a function of humic acid concentration:

experimental data (points) and model fits (lines) - [S\textsubscript{T}].k\textsubscript{Sf} = 2.0x10\textsuperscript{-5} s\textsuperscript{-1}; k\textsubscript{Sb} = 6.67x10\textsuperscript{-6} s\textsuperscript{-1}; k\textsubscript{f} = 1.1x10\textsuperscript{-8} s\textsuperscript{-1}; k\textsubscript{b} = 1.0x10\textsuperscript{-7} s\textsuperscript{-1}; [HA\textsubscript{exch,T}].K\textsubscript{exch} = 200

Figures 4.18 and 4.19 show the Model 1 and 2 results for the uptake of uranyl onto the sand surface under an inert atmosphere. In this case, the effect of humic on the behaviour of the system is very different to previous metal ions: the presence of humic increases the sorption of uranyl. This happens when the interaction between the metal ion and the surface is weak compared to that with the humic. The data show that ternary surface complexation is particularly favourable for this metal ion. Hence, attempting to model these types of systems is difficult, because the problem with both Models 1 and 2 is they have the same binding constant for all humic species. Hence, when the distribution of the metal in the system does not follow that of the humic, it is hard to predict metal ion behaviour using Models 1 and 2. For example Model 1 (Figure 4.18) provides a poor fit for the experimental data at each humic concentration. Generally, the model overestimates the uranyl concentration, especially in the 100, 50 and 10 ppm solutions. Clearly for the CO\textsubscript{2} free uranyl system, the behaviour of the metal is different to that in the previous Eu\textsuperscript{3+} and Th (IV) systems. Similarly Model 2, Figure 4.19, shows a poor correlation between the predicted metal ion behaviour and that of the
experimental data, although in the 10 ppm solution the model is able simulate the high sorption behaviour of the metal.

Figure 4.20; Model 3 results for Uranyl sorption in ternary humic acid/quartz sand system, ([U$_T$] = 100 mBqml$^{-1}$), (Molar concentration 3.38 x 10$^{-5}$ moles/litre) $I$ = 0.1, pH = 6, in inert atmosphere, as a function of humic acid concentration: experimental data (points) and model fits (lines) $k_{HA1S1f}$ = 3.00E-06; $k_{HA1S1b}$ = 9.00E-05; $k_{HA1S2f}$ = 9.00E-08; $k_{HA1S2b}$ = 3.50E-07; $k_{HA2S1f}$ = 1.00E-06; $k_{HA2S1b}$ = 1.00E-05; $k_{HA2S2f}$ = 1.00E-06; $k_{HA2S2b}$ = 4.00E-07

The Model 3 fit, Figure 4.20, shows a better correlation between the model prediction and the experimental data. In the 200 ppm solution, during the first 3 days (259200s) the model slightly overestimates metal ion sorption, but following this, the model fit closely follows the experimental data points. Likewise in the 100 ppm solution, for the first 4 days (345600s) of the experiment, the uranyl concentration is slightly underestimated, but this is followed by a good correlation between the model and experimental data. Therefore Model 3 gives a more comprehensive fit for the uranyl behaviour.
4.2.4 Plutonium Modelling

Figure 4.21; Model 1 results for ternary humic acid/quartz sand system/²³⁹Pu(IV), 1.22 mBq ml⁻¹, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([Sₜ].kₘₛₕ = 4.0x10⁻⁵ s⁻¹; kₘₛₜ = 1.5x10⁻⁶ s⁻¹; k₉ = 1.1x10⁻⁸ s⁻¹; k₈ = 1.0x10⁻⁷; [HAₑₓch,T].Kₑₓch = 42)

Figure 4.22; Model 2 results for ternary humic acid/quartz sand system/²³⁹Pu(IV), 1.22 mBq ml⁻¹, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([Sₜ].kₘₛₕ = 5.5x10⁻⁶ s⁻¹; kₘₛₜ = 1.83x10⁻⁶ s⁻¹; k₉ = 1.1x10⁻⁸ s⁻¹; k₈ = 1.0x10⁻⁷; [HAₑₓch,T].Kₑₓch = 50)
Figures 4.21 and 4.22 show the modelled sorption behaviour of the Pu (IV)/quartz sand ternary system, by speciation Models 1 and 2. The Model 1 results, Figure 4.21, show the best fit occurs for the 200 and 100 ppm solutions. For the 200 ppm solution, the model slightly overestimates the metal ion concentration for the first 5 days, (432000s), but then closely matches the experimental data after this point. Similarly, the 100 ppm solution exhibits a poor initial fit (up to 5 days 432000s), however this is followed by a good correlation between the experimental data and the model. The remaining 50 and 10 ppm humic solutions in Model 1 show poor correlation at all time points. Overall the Model 2 (Figure 4.22) fit is as good as Model 1.

For Model 3, the fit to the 10, 100 and 200 ppm data are quite good, but the model overestimates the concentration in the 50 ppm solutions.

Figure 4.23; Model 3 results for ternary humic acid/quartz sand system/\(^{239}\)Pu(IV), 1.22 mBq ml\(^{-1}\), \(I = 0.1\), \(pH = 6\), as a function of total humic concentration and Model fit to data; \(k_{HA1S1f} = 2.00E-06\); \(k_{HA1S1b} = 1.50E-05\); \(k_{HA1S2f} = 1.00E-08\); \(k_{HA1S2b} = 6.00E-07\); \(k_{HA2S1f} = 2.00E-05\); \(k_{HA2S1b} = 1.50E-09\); \(k_{HA2S2f} = 1.00E-08\); \(k_{HA2S2b} = 6.00E-07\)
The behaviour in the Pu (IV)/quartz sand ternary system appears simple, with the humic appearing to act largely as a competing solution phase ligand, and Pu sorption decreases with increasing HIA concentration for all systems. All three models fit the data equally well, hence the extra parameters and greater flexibility in Model 3 do not improve the fit. Note, the prediction of the metal ion concentration in the 50 ppm solution is poor for all three models because there is a large difference in the experimental data for the 100 and 10 ppm solutions. Hence, it is difficult to fit such a big change between these two concentrations. It is possible to achieve a better 50 ppm fit, however this would be at the detriment of the 200 and 100 ppm solutions. Hence accepting a bad fit for the 50 ppm system is the best available result.

Consequently, although Model 3 represents an improvement for some systems, it is not able to produce perfect fits for all systems, and in some instances does not always show a significant improvement over the simpler models, 1 and 2.

**Figure 4.24; Model 1 results for ternary humic acid/quartz sand system Pu(V), 0.6125 mBq ml\(^{-1}\), I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S\(_T\)].k\(_{MSF}\) = 9.0x10\(^{-6}\) s\(^{-1}\); k\(_{MSb}\) = 3.0x10\(^{-6}\) s\(^{-1}\); k\(_f\) = 1.1x10\(^{-8}\) s\(^{-1}\); k\(_b\) = 1.0x10\(^{-7}\); [H\(_{A \text{exch,T}}\)].K\(_{\text{exch}}\) = 10)**
Figure 4.25; Model 2 results for ternary humic acid/quartz sand system Pu(V), 0.6125 mBq ml\(^{-1}\), \(I = 0.1\), \(pH = 6\), as a function of total humic concentration and Model fit to data \((|S_T| \cdot k_{MSf} = 1.5 \times 10^{-5} s\(^{-1}\); k_{MSb} = 3.75 \times 10^{-6} s\(^{-1}\); kf = 1.1 \times 10^{-8} s\(^{-1}\); kb = 1.0 \times 10^{-7}; [HA_\text{exch,T}] \cdot \kappa_{\text{exch}} = 50)\)

Figures 4.24 and 4.25 show the Model 1 and 2 results for the equivalent Pu (V) ternary system. The Model 1 fit for the metal in the 200 ppm solution correlates well with the experimental data (Figure 4.24). For the other humic containing systems, the model overestimates the metal ion concentration, especially for the 50 and 10 ppm solutions, where the predicted metal ion concentrations are approximately twice the experimental values. However, in the non-humic system, the predicted metal ion behaviour is similar to that of the experimental data.

For Model 2 (Figure 4.24) the predicted metal ion concentrations are closer to the experimental data, particularly for the 50 and 10 ppm solutions. For example, while the 10 ppm fit in Model 1 (Figure 4.25) overestimates the metal ion concentration by a factor of 2, the equivalent model 2 fit is within error of most of the experimental data points. Furthermore, the model is unable to predict the sorption behaviour in the 200 solution very closely.
However, Model 3 (Figure 4.24) is better able to predict the sorption behaviour of the metal ion, giving a good correlation with the experimental data, in particular for the 100 and 10 ppm solutions. Furthermore, the fit to the 200 ppm data, although not perfect is close, and for the 50 ppm solution, the model fit is better than for the simpler approaches.

**Figure 4.26; Model 3 results for ternary humic acid/quartz sand system/\(^{239}\)Pu(V), 0.6125 mBq ml\(^{-1}\), I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data** $k_{HA1S1f} = 1.40E-06$; $k_{HA1S1b} = 2.00E-05$; $k_{HA1S2f} = 2.00E-08$; $k_{HA1S2b} = 6.00E-07$; $k_{HA2S1f} = 1.40E-05$; $k_{HA2S1b} = 3.00E-06$; $k_{HA2S2f} = 2.00E-08$; $k_{HA2S2b} = 6.00E-07$

For the Pu (V) ternary system, although not perfect, Model 3 provides the best fit for the experimental data.

The behaviour in the Pu (IV) and Pu (V) systems is complex. Although Model 1 provides an adequate fit for the 200, 100 and 0 ppm solutions, the match to the 50 and 10 ppm solution is not as good. This is particularly evident for the Pu (V) system, where the data shows an increase in sorption in the presence of low humic concentrations, compared to the 0 ppm solution. The reason for the poor fit is that the solution phase and sorbed humic species have different binding strengths, because of fractionation. As a result, Model 1 is unable to provide a good fit to the data, since it assumes a single
binding strength for all of the humic molecules. Therefore, the poor quality of the low concentration Model 1 fit is unsurprising. Model 3 performs better in this respect because it has 2 binding site parameters for the humic, but of course the fit is still not perfect. When considering the quality of the fit, it is important to consider that van de weerd et al (2002) needed a minimum of 6 humic fractions and associated reactions and parameters just to predict the behaviour of the humic itself. Therefore Model 3 still represents a significant simplification of the real system. However, if models such as these are to be useful, they must provide an adequate fit, but with the minimum complexity, and the balance between quality of fit and number of parameters is hard to judge.

Figure 4.27; Model 1 results for ternary humic acid/quartz sand system/\(^{239}\)Pu (VI), 1.22 mBq ml\(^{-1}\), I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([Si], \(k_{MSf} = 9.0 \times 10^{-5} \text{ s}^{-1}\); \(k_{MSb} = 4 \times 10^{-6} \text{ s}^{-1}\); \(k_f = 1.1 \times 10^{-8} \text{ s}^{-1}\); \(k_b = 1.0 \times 10^{-7} [HA_{exch,T}] \cdot K_{exch} = 100\))
Figure 4.28; Model 2 results for ternary humic acid/quartz sand system/$^{239}$Pu (VI), 1.22 mBq ml$^{-1}$, $I = 0.1$, pH = 6, as a function of total humic concentration and Model fit to data ($[S_{T}], k_{MSf} = 1.60 \times 10^{-5}$ s$^{-1}$; $k_{MSb} = 8 \times 10^{-7}$ s$^{-1}$; $k_f = 1.1 \times 10^{-8}$ s$^{-1}$; $k_b = 1.0 \times 10^{-7}$ [HA$_{exch,T}$].K$_{exch,T}$ = 20)

Figure 4.29; Model 3 results for ternary humic acid/quartz sand system/$^{239}$Pu (VI), 1.22 mBq ml$^{-1}$, $I = 0.1$, pH = 6, as a function of total humic concentration and Model fit to data $k_{HA1S1f} = 2.00 \times 10^{-6}$; $k_{HA1S1b} = 7.00 \times 10^{-6}$; $k_{HA1S2f} = 2.00 \times 10^{-7}$; $k_{HA1S2b} = 6.00 \times 10^{-7}$; $k_{HA2S1f} = 1.40 \times 10^{-5}$; $k_{HA2S1b} = 7.00 \times 10^{-6}$; $k_{HA2S2f} = 1.40 \times 10^{-8}$; $k_{HA2S2b} = 6.00 \times 10^{-7}$
The Model 1, 2 and 3 results for the ternary Pu (VI), humic/quartz sand systems are shown in Figures 4.27, 4.28 and 4.29. In Model 1, Figure 4.27, the fits for both the 200 and 100 ppm solutions are adequate. The model fit closely matches the experimental data in the first 2 days, (172800s), followed by a slight underestimation in metal ion concentration for the 200 ppm solution. For 100 ppm solution the initial fit (first 2 days) is poor, however for the remainder of the experiment a better correlation with the data is observed. However, in the 50 and 10 ppm solutions, the model significantly overestimates the metal ion concentrations, this trend was also found in the Model 1 fits for Pu (IV) and Pu (V).

Model 2, Figure 4.28, shows a better correlation with the 50 and 10 ppm solutions, giving a good fit with the experimental data. Similarly, in the 0 ppm solution, though the model slightly underestimates metal ion concentration in the first 11 days (950400s), after this period a good fit is established. For both the 200 and 100 ppm solutions, the model fit is quite poor and underestimates the metal ion concentrations.

Model 3 (Figure 4.29) as for the previous Pu (IV) and Pu (V) systems, gives a more accurate prediction of metal ion behaviour across the whole range of humic concentrations. For example, Model 3 gives a better correlation with the data for the 200 and 100 ppm solutions, than shown by model 2, while also providing a fit that is within error for the 10 and 0 ppm systems: the fit to the 50 ppm solution is only just outside of the error bars.

4.2.5 Approach to Surface Complexation Modelling

The approach presented in this section is a ‘Kinetic Surface Complexation Modelling’ approach. In standard Thermodynamic Surface Complexation Modelling (SCM), all reactions are defined as instantaneously reversible reactions that are represented with equilibrium constants. The distinction between ‘kinetic’ and ‘equilibrium’ approaches to modelling a reaction or process is artificial, since it depends upon the timescale of the observation. For any reaction, the equilibrium constant is given by the ratio of the forward and backward rate constants. Therefore, in order to obtain a thermodynamic SCM for these systems, the same chemical reactions in the kinetic models should be used, with the stability constants given by the ratio of the rate constants defined above. The fit that would be obtained by such a model can be judged by comparing the final
data points in the modelling plots with the appropriate experimental data points, when the system is at (or near) to equilibrium.

The kinetic SCM has shown that multiple reactions are required in order to explain the behaviour in the system. In a thermodynamic approach, only the final, equilibrium position is modelled. Given the smaller dataset, it might be possible to define a simpler set of equations that might produce a prediction, particularly if the model were only required to model the metal data (and not the humic sorption simultaneously). However, such a model would be purely empirical and would not take into account the processes that the kinetic data have shown to be important.
4.3 Modelling of Fractionated Humic Acid Experiments

The previous fraction studies conducted by Li (2011) investigated the sorption behaviour in the Eu$^{3+}$/magnetite ternary system, using approaches equivalent to Models 1 and 2 described in this thesis. This proved relatively unsuccessful, and the author suggested that this was due to chemical fractionation and differences in binding strength between surface and solution phase humic species.

4.3.1 Europium Behaviour with Fractionated Humic

![Graph showing Europium behaviour with Fractionated Humic](image)

Figure 4.30; Model 1, Eu$^{3+}$ HA > 100 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S$_T$].k$_{MSf} = 3.4 \times 10^{-6}$ s$^{-1}$; k$_{MSb} = 2.4 \times 10^{-7}$ s$^{-1}$; [HA$_{exch,T}$].K$_{exch} = 100$)
Figure 4.31; Model 1, Eu\(^{3+}\) 100 > HA > 10 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S\(_T\]).k\(_{MSf}\) = 3.5x10\(^{-6}\) s\(^{-1}\); k\(_{MSb}\) = 2.5x10\(^{-7}\) s\(^{-1}\); k\(_f\) [HA\(_{exch,T}\)].K\(_{exch}\) = 100)

Figure 4.32; Model 1, Eu\(^{3+}\) 10 > HA > 3 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S\(_T\]).k\(_{MSf}\) = 3.5x10\(^{-6}\) s\(^{-1}\); k\(_{MSb}\) = 2.5x10\(^{-7}\) s\(^{-1}\); [HA\(_{exch,T}\)].K\(_{exch}\) = 50)
Figure 4.33; Model 1, Eu$^{3+}$ HA < 3 kDa/quartz system, I = 0.1, pH = 6, as a function of total humic concentration and Model fit to data ([S]).$k_{MSf} = 3.5 \times 10^{-6}$ s$^{-1}$; $k_{MSb} = 2.5 \times 10^{-7}$ s$^{-1}$; [HA$_{exch,T}$].$K_{exch}$ = 250

The Model 1 fits for the sorption behaviour of Eu$^{3+}$ for the 4 humic fractions, HA > 100 kDa, 100 > HA > 10 kDa, 10 > HA > 3 kDa and HA < 3 kDa are shown in Figures 4.30, 4.31, 4.32 and 4.33, respectively. The Model 1 fits for the HA > 100 kDa fraction, Figure 4.30 provide an adequate prediction for metal ion behaviour at the various humic concentrations for the ternary system. The fits for the remaining fractions, are overall relatively poor, with the model generally overestimating the metal ion concentrations, especially for the smaller size fractions, 10 < HA < 3 and HA < 3 kDa.
Figure 4.34; Model 3, Eu$^{3+}$ HA > 100 kDa/quartz system, I = 0.1, pH = 6 \[\text{[Eu]}_T = 133 \text{ mBq ml}^{-1}\] Model fit to data $k_{HA1S1f} = 1.00E-06$; $k_{HA1S1b} = 2.00E-06$; $k_{HA1S2f} = 2.50E-08$; $k_{HA1S2b} = 6.00E-08$; $k_{HA2S1f} = 1.00E-06$; $k_{HA2S1b} = 2.00E-07$; $k_{HA2S2f} = 2.00E-07$; $k_{HA2S2b} = 6.00E-08$

Figure 4.35; Model 3, Eu$^{3+}$ 100 < HA < 10 kDa/quartz system, I = 0.1, pH = 6 \[\text{[Eu]}_T = 133 \text{ mBq ml}^{-1}\] Model fit to data $k_{HA1S1f} = 1.00E-06$; $k_{HA1S1b} = 1.00E-06$; $k_{HA1S2f} = 1.00E-07$; $k_{HA1S2b} = 5.00E-06$; $k_{HA2S1f} = 2.00E-06$; $k_{HA2S1b} = 1.00E-06$; $k_{HA2S2f} = 2.00E-07$; $k_{HA2S2b} = 5.00E-06$
Figure 4.36; Model 3, Eu$^{3+}$ 10 < HA < 3 kDa/quartz system, I = 0.1, pH = 6  [Eu]$_T$ = 133 mBq ml$^{-1}$ Model fit to data $k_{HA1S1f} = 1.00E-06$; $k_{HA1S1b} = 7.00E-06$; $k_{HA1S2f} = 3.00E-08$; $k_{HA1S2b} = 5.00E-08$; $k_{HA2S1f} = 1.00E-06$; $k_{HA2S1b} = 5.00E-05$; $k_{HA2S2f} = 1.00E-08$; $k_{HA2S2b} = 1.00E-06$

Figure 4.37; Model 3, Eu$^{3+}$ HA < 3 kDa/quartz system, I = 0.1, pH = 6  [Eu]$_T$ = 133 mBq ml$^{-1}$ Model fit to data $k_{HA1S1f} = 1.00E-06$; $k_{HA1S1b} = 7.00E-07$; $k_{HA1S2f} = 2.00E-07$; $k_{HA1S2b} = 6.00E-08$; $k_{HA2S1f} = 1.00E-06$; $k_{HA2S1b} = 2.00E-07$; $k_{HA2S2f} = 5.00E-05$; $k_{HA2S2b} = 7.00E-04$
The equivalent Model 3 fits for the fractionated humic Eu$^{3+}$ ternary system are shown in Figures 4.34, 4.35, 4.36 and 4.37. There is an improvement in the modelling of the data, especially for the smallest size fractions, HA < 3 kDa and 10 < HA < 3 kDa (Figures 4.35 & 4.36). For example, the fit for the 200 ppm HA < 3 kDa fraction is much improved over that from Model 1. However, overall the model shows a poor correlation with the experimental data.

4.3.2 Uranyl Behaviour with Fractionated Humic

![Figure 4.38; Model 1, Uranyl HA > 100 kDa/ quartz system, I = 0.1, pH = 6, $[U_T] = 100$ mBq ml$^{-1}$ ($[S_T].k_{MSf} = 7.0 \times 10^{-6}$ s$^{-1}$; $k_{MSb} = 3.0 \times 10^{-7}$ s$^{-1}$; $[HA_{exch,T}].K_{exch} = 1000$)]
Figure 4.39; Model 1, Uranyl 100 < HA < 10 kDa/ quartz system, I = 0.1, pH = 6, [U\textsubscript{T}] = 100 mBq ml\(^{-1}\) ([S\textsubscript{T}].k\textsubscript{MSf} = 7.0x10\(^{-6}\) s\(^{-1}\); k\textsubscript{MSb} = 3.0x10\(^{-6}\) s\(^{-1}\); [HA\textsubscript{exch,T}].K\textsubscript{exch} = 100)

Figure 4.40; Model 1, Uranyl 10 > HA > 3 kDa/ quartz system, I = 0.1, pH = 6, [U\textsubscript{T}] = 100 mBq ml\(^{-1}\) ([S\textsubscript{T}].k\textsubscript{MSf} = 9.0x10\(^{-6}\) s\(^{-1}\); k\textsubscript{MSb} = 3.0x10\(^{-7}\) s\(^{-1}\); [HA\textsubscript{exch,T}].K\textsubscript{exch} = 1000)
Figure 4.41; Model 1, Uranyl HA < 3 kDa / quartz system, I = 0.1, pH = 6, \([U_T] = 100 \text{ mBqml}^{-1}\) ([ST].kMSf = 7.0x10^{-6} s\(^{-1}\); kMSb = 3.0x10^{-6} s\(^{-1}\);[HAexch,T].Kexch.= 1)

Figures 4.38, 4.39, 4.40 and 4.41 show the Model 1 fits for the uranyl fractionated humic ternary systems. For all four humic fractions, the model shows is unable to simulate metal ion behaviour. For the HA > 100 and 10 < Ha < 100 kDa fractions, the data show the majority of the metal remains in solution, with little separation between each humic concentration. Overall the Model shows very poor correlation with the experimental data. In this case, the poor performance of the model cannot be explained by chemical fractionation, and so Model 3 is unable to improve on the fits in Figures 4.38, 4.39, 4.40 and 4.41. Therefore, although introducing chemical fractionation can improve the fit in some systems, there are other effects that can complicate the behaviour, which are not included in Model 3.
4.3.3 Pu (VI) Behaviour with Fractionated Humic

Figure 4.42: Model 1, Pu (VI) HA > 100 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml$^{-1}$) ([S$_T$].$k_{MSf}$ = 5.50x10$^{-5}$ s$^{-1}$; $k_{MSb}$ = 4.0x10$^{-6}$ s$^{-1}$; [HA$_{exch,T}$].$K_{exch}$ = 12)

Figure 4.43: Model 1, Pu (VI) 100 > HA > 10 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml$^{-1}$) ([S$_T$].$k_{MSf}$ = 7.00x10$^{-5}$ s$^{-1}$; $k_{MSb}$ = 4.0x10$^{-6}$ s$^{-1}$; [HA$_{exch,T}$].$K_{exch}$ = 10)
The Model 1 fits for the fractionated humic Pu (VI) ternary systems are given by Figures, 4.42, 4.43, 4.44 and 4.45. The model provides the best fit for the HA > 100 ppm system, where the overall fit with the data is relatively good. Furthermore, the fit to the 50 ppm system is good after the first 3
days (259200s). For the 100 > HA > 10 kDa fraction (Figure 4.43), the closeness of the fit with the data is relatively poor. For the smallest size fractions, 10 > HA>3 kDa and HA > 3 kDa (Figures 4.44 and 4.45), there is quite poor correlation between the experimental data and the model. The higher sorption, compared to the 0 ppm systems, suggests the presence of strong humic ternary surface complexes and chemical fractionation.

Figure 4.46; Model 3, Pu (VI) 100 > HA kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml$^{-1}$) Model fit to data $k_{HA1S1f} = 1.00E-06; k_{HA1S1b} = 4.00E-06; k_{HA1S2f} = 2.50E-08; k_{HA1S2b} = 6.00E-08; k_{HA2S1f} = 1.00E-07; k_{HA2S1b} = 2.00E-07; k_{HA2S2f} = 5.00E-05; k_{HA2S2b} = 1.00E-08
Figure 4.47; Model 3, Pu (VI) 100 > HA > 10 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\(^{-1}\)) Model fit to data: 
\[
\begin{align*}
  k_{HA1S1f} &= 5.00 \times 10^{-6}; \\
  k_{HA1S1b} &= 4.00 \times 10^{-6}; \\
  k_{HA1S2f} &= 1.00 \times 10^{-7}; \\
  k_{HA1S2b} &= 1.00 \times 10^{-7}; \\
  k_{HA2S1f} &= 5.00 \times 10^{-6}; \\
  k_{HA2S1b} &= 4.00 \times 10^{-7}; \\
  k_{HA2S2f} &= 5.00 \times 10^{-5}; \\
  k_{HA2S2b} &= 9.00 \times 10^{-7}
\end{align*}
\]

Figure 4.48; Model 3, Pu (VI) 10 > HA > 3 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml\(^{-1}\)) Model fit to data: 
\[
\begin{align*}
  k_{HA1S1f} &= 2.00 \times 10^{-7}; \\
  k_{HA1S1b} &= 2.00 \times 10^{-6}; \\
  k_{HA1S2f} &= 2.00 \times 10^{-8}; \\
  k_{HA1S2b} &= 6.00 \times 10^{-8}; \\
  k_{HA2S1f} &= 2.00 \times 10^{-7}; \\
  k_{HA2S1b} &= 5.00 \times 10^{-7}; \\
  k_{HA2S2f} &= 2.00 \times 10^{-7}; \\
  k_{HA2S2b} &= 6.00 \times 10^{-7}
\end{align*}
\]
Figure 4.49; Model 3, Pu (VI) HA < 3 kDa/ quartz system, I = 0.1, pH = 6, (1.22 mBq ml⁻¹) Model fit to data \( k_{HA1S1f} = 2.00 \times 10^{-8}; k_{HA1S1b} = 4.00 \times 10^{-6}; k_{HA1S2f} = 2.00 \times 10^{-6}; k_{HA1S2b} = 6.00 \times 10^{-6}; k_{HA2S1f} = 1.00 \times 10^{-5}; k_{HA2S1b} = 5.00 \times 10^{-10}; k_{HA2S2f} = 2.00 \times 10^{-8}; k_{HA2S2b} = 6.00 \times 10^{-8} \)

Figures 4.46, 4.47, 4.48 and 4.49 show the Model 3 fits for the Pu (VI) humic fractionated system. The fits of the HA > 100 kDa and 100 > HA > 10 kDa fractions are similar to the equivalent Model 1 fits discussed earlier. For the 10 > HA > 3 kDa fraction, the model shows no correlation with the data in the first 3 days, however following this, there is an adequate fit with the 100, 50 and 10 ppm systems. Finally for the HA < 3 kDa fraction, the model provides an adequate fit for the data in the 100 and 10 ppm systems. Again, the Model 3 fit is far from perfect, but it is able to provide a better fit than Model 1. Further, it is able to simulate the behaviour in ternary systems qualitatively, which is not possible with the simpler model.
Chapter 5

Conclusions and Future Work
5.1 Conclusions For whole humic Systems

Europium shows simple ‘classical’ ternary system behaviour with the humic mostly acting as a competing solution phase ligand reducing sorption, retaining the metal ion solution. As a result, Model 1, which excludes fractionation parameters, is able to predict metal ion behaviour quite well. The corresponding Model 2 prediction although provides an adequate fit, cannot simulate the close correlation observed in Model 1. The addition of extra reactions and parameters to account for the chemical fractionation in the more complex, Model 3, does not significantly improve the fit.

For Th, the metal ion again seems to show simple ternary behaviour, but in this case, the model including chemical fractionation did improve on the fit for systems where carbonate was excluded. Different sorption was observed with or without carbonate which, was unexpected, given the insignificance of carbonate complexes in the predicted aqueous speciation values. It is possible that mixed carbonate Th/ humic complexes are forming in solution or on the sand surface, but these are currently too complex to be included in the model parameters.

In the Uranyl systems, again there is a significant difference with or without carbonate, and so mixed complexes, maybe important here too, though the uranyl speciation is affected significantly by the presence of carbonate. In carbonate containing system, there is direct evidence for ternary complexes and chemical fractionation, since the sorption increases on addition of the humic, and the fraction of uranium bound is higher than that of the whole humic itself. This is only possible when the affinity of the uranyl for the humic is greater than that for the bare mineral surface and when the humic sorbed on the surface has the higher binding strength than that left in solution. Both Models 1 and 2 were unable to account for this more complex behaviour, with Model 3 proving more successful, in accounting for the high uranyl affinity for the humic.

Further, there is evidence of re-suspension of sorbed uranyl when fresh humic is added to the system, before equilibrium is established. It seems that fresh humic molecules could displace humic/uranyl complexes from the mineral surface, before the metal ion returns forming a new ternary surface complex, presumably with the fresh sorbed humic.

For U (IV) very strong sorption is observed with or without humic and the presence of humic only reduces sorption very slightly. In this system the solution is supersaturated
with respect to U(OH)$_4$ and it maybe that this system is controlled by precipitation rather than sorption.

Experimental data has been measured for the sorption of Pu (IV), (V) and (VI) in quartz sand/humic acid ternary systems. In all cases, higher concentrations of humic substances were found to reduce sorption. The Pu sorption in all systems is reversible to some extent, and in the Pu (IV) system, it seems fully reversible. Again, the humic acts as competing solution phase ligand, holding the metal in solution.

The Pu(V) system is complex, and there is direct evidence from the experimental data that ternary complexes are very significant here. Although they are less obvious in the Pu(IV) and Pu(VI) systems, the modelling suggests that they are present.

However in spite of the fact that some of the models can fit the 100 ppm and humic free system data, the match to the other humic concentrations is not as good. The reason for the poor fit is that the ions have different affinities for solution phase and sorbed humic species, because of fractionation. In both cases, the surface humic ternary complexes are stronger than the simple binary complexes in solution, and this is responsible for the poor fits. Consequently further work will concentrate on developing a model that has different binding strengths for sorbed and solution phase humic species.
5.1.1 Fractionated Humic Systems

Contrary to previous work with iron oxides, it was found smaller sized fractions where preferentially sorbed to the quartz sand surface. For ternary systems involving Eu(III), Pu(VI) and Uranyl, with fraction sizes HA > 100, 100 > HA > 10, 10 > HA > 3 and HA < 3 kDa, it was found that the lowest sorption, occurred for the systems with largest size fractions. This result was unsurprising given that, the larger size fractions, were more likely to remain in solution which would tend to reduce sorption. Previous work with the same size fractions (Li 2011) had found that the larger humic fractions showed the strongest binding of metal ions. Although, the simpler model were able to fit the Eu(III) – humic fraction data, for the Pu (VI) the more complex model including fractionation was required, even though, the humic had been size fractionated in these experiments. Therefore, it seems that preferential binding observed for sorbed humic in the whole humic experiments cannot solely be due preferential binding of certain fractions, and even within narrow sized fractions, there must be distinct chemical differences between the humic species.

The more complex speciation model, Model 3, was developed to account of chemical fractionation and preferential binding of metal ions by either sorbed or solution phase humic molecules. However, in all the systems studied here it was always necessary for the sorbed humic to show stronger binding than that in solution, regardless of metal ion chemistry. Therefore it seems that in the quartz sand system, the surface attracts humic species that provide the best metal ion binding sites.
5.2 Suggestions for Future Work

All of the experiments in this thesis have been conducted at a fixed pH and ionic strength. However, in the far-field of a Geological Disposal Facility, there will be variations in pH and ionic strength. In particular, around a cementitious repository, high pH would be expected. Therefore, experiments should be performed at different ionic strengths and pH.

It would be useful to study the nature of the chemical differences that have been found in this work between the interactions between solution phase and sorbed humics. At the concentrations used in this work, there is almost certainly insufficient radionuclide to use X-ray absorption techniques. However, uranyl (which does show extensive chemical fractionation effects) does lend itself to luminescence spectroscopy. Therefore, luminescence could be used to detect any differences between uranyl coordination to sorbed and solution phase humic species.

Only static, batch experiments have been used in this work. Flow effects are very important, and so it would be interesting to conduct column experiments using the radionuclides studied here. Such experiments would provide a more rigorous test of the model developed here.

Although the new ternary system model has been able to model behaviour that was not previously possible, there were some experiments here that it could not fit. The model could be adapted to see if this improved the fit. For example, more fractions could be added to make it similar to the 6 fraction approach of van de Weerd et al (2002). Such a model would not be directly applicable to Radiological Performance Assessment Studies, but it would be of academic interest, and it could provide some mechanistic understanding.

The uranium and thorium experiments could be repeated using $^{232}\text{U}$ and $^{228}\text{Th}$, which would allow lower radionuclide concentrations to be studied. These isotopes were not available when this project started.
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