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Pascal E. Reiller

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Université Denis Diderot (Paris VII)

Dossier scientifique et administratif présenté à la commission des thèses et habilitations de l'UFR de Science de la Terre de l'Environnement des Planètes en vue de la soutenance d'une

Habilitation à diriger des recherches

**Relations entre structure et réactivité dans  
l'interaction entre les substances humiques,  
les polluants métalliques du cycle du nucléaire  
et les surfaces minérales.**

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*Soyez toujours prêt à être surpris*

*Swâmi Prajnânpad*

A Valérie, Emmanuel, Angèle et Maxime



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## 1. COMMUNICATIONS

### 1.1. PUBLICATIONS

#### 1.1.1. Peer reviewed publications

##### 1.1.1.1. Directly related to the thematic

1. Moreau P, Colette-Maatouk S, Vitorge P, Gareil P, and Reiller PE (2015) Complexation of europium(III) by hydroxybenzoic acids: a time-resolved luminescence spectroscopy study. *Inorg. Chim. Acta.* **432**, 81. [doi: 10.1016/j.ica.2015.03.036](https://doi.org/10.1016/j.ica.2015.03.036)
2. Janot N, Benedetti MF, and Reiller PE (2013) Influence of ionic strength and humic acid concentration on europium(III),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and humic acid interactions: macroscopic and time-resolved laser-induced luminescence data. *Geochim. Cosmochim. Acta.* **123**, 35. [doi: 10.1016/j.gca.2013.08.038](https://doi.org/10.1016/j.gca.2013.08.038).
3. Janot N, Reiller PE, and Benedetti MF (2013) Modeling Eu(III) speciation in a Eu(III)/PAHA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ternary system. *Colloids Surf. A.* **435**, 9. [doi: 10.1016/j.colsurfa.2013.02.052](https://doi.org/10.1016/j.colsurfa.2013.02.052).
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5. Reiller PE (2012) Modelling the metal-organic-surface systems: reasons for relative success, failure, and possible routes for peace of mind, *Miner. Mag.* **76**, 2643. [doi: 10.1180/minmag.2012.076.7.02](https://doi.org/10.1180/minmag.2012.076.7.02).
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27. Vercouter T, Reiller PE, Ansoborlo E, Février L, Gilbin R, Lomenech C, and Philippini V (2015) On the importance of ternary alkaline earth carbonate species of uranium(VI) in the speciation of natural waters : a round-robin modelling exercise, *Appl. Geochem.* **55**, 192. doi: [10.1016/j.apgeochem.2014.11.016](https://doi.org/10.1016/j.apgeochem.2014.11.016).
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33. Pointeau I, Hainos D, Coreau N, and Reiller P (2006) Effect of organics on selenite uptake by cementitious materials. *Waste Manage.* **26**, 733. [doi: 10.1016/j.wasman.2006.01.026](https://doi.org/10.1016/j.wasman.2006.01.026).
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### 1.1.1.3. Publications during PhD Thesis

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43. Moulin C, Reiller P, Beaucaire C, and Lemordant D (1993) Time-resolved laser-induced spectrofluorometry studies of uranium/sodium dodecyl sulfate interactions. *Appl. Spectrosc.* **47**, 2172. [doi: 10.1366/0003702934066569](https://doi.org/10.1366/0003702934066569).
44. Moulin C, Reiller P, Beaucaire C, and Lemordant D (1993) Time-resolved laser-induced spectrofluorometry for the study of uranium-anionic surfactant micelle interactions. *J. Colloid Interface Sci.* **157**, 411. [doi: 10.1006/jcis.1993.1203](https://doi.org/10.1006/jcis.1993.1203).

### 1.1.1.4. Publications submitted or in writing

45. Kouhail Y, Benedetti MF, and Reiller PE (in writing): Time-resolved luminescence spectroscopy study of Eu(III)-fulvate complexation: influence of pH, ionic strength, and fulvic acid concentration
46. Moreau P, Colette-Maatouk S, Gareil P, and Reiller PE (in writing) Influence of phenolic acids on the adsorption of Eu(III) onto alumina: a macroscopic and spectroscopic study.
47. Reiller PE, Testard F, Brevet J, Jestin J, Guenoun P, and Daillant J (in writing) Aggregation properties in concentrated humic acid solutions, observed by liquid Atomic Force Microscopy and Small Angle Neutron Scattering, *Langmuir*.

### 1.1.2. Edited works, contributions in monographies

48. Reiller PE and Buckau G (2012) Impacts of humic substances on the geochemical behaviour of radionuclides. In *Radionuclide Behaviour in the Natural Environment: Science, Impacts and Lessons for the Nuclear Industry* (Geickeis H, Poinssot C, Eds.) p. 103-160. Woodhead Publishing, Cambridge, UK. [Lien](#)
49. Reiller PE, Marang L, Jouvain D and Benedetti MF (2011) Uranium (VI) binding to humic substances: speciation, estimation of competition, and application to independent data. In *The New Uranium Mining Boom: Challenge and Lessons Learned* (Merkel B, Schipek M, Eds.) p. 565-572. Springer, Berlin, Germany. [doi: 10.1007/978-3-642-22122-4](https://doi.org/10.1007/978-3-642-22122-4).
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### 1.1.3. PhD

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### 1.1.4. Contributions in open reports and in the framework of European projects

52. Reiller P (2010) Bilan prospectif sur l'influence de la complexation par la matière organique sur l'effet accélérateur ou retard du transport des radionucléides: cas de la rétention des substances humiques. Rapport CEA-R-6255 (ISSN 0429-3460) pp. 72. Gif-sur-Yvette, France. In French. <http://dx.doi.org/10.13140/RG.2.1.4293.5202>
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### 1.1.5. Communications in congress and workshops\*

- I. Kouhail Y, Benedetti MF, and Reiller PE: Spectroscopic study of Eu(III)-fulvate complexation: influence of pH and fulvic acid concentration, Goldschmidt 2014, 8-13 June 2014, Sacramento, USA.
- II. Reiller PE, Janot N, and Benedetti MF: Adsorption of Eu(III) onto minerals in the presence of humic acids: effects of various solution parameters and sorptive fractionation on modelling and spectroscopy, Goldschmidt 2013, 25-30 August 2013, Florence, Italy.
- III. Reiller PE, Janot N, Moreau P, Colette-Maatouk S, Auriault C, Gareil P, and Benedetti MF: Commonalities and dissimilarities of Eu(III) interactions by simple organic acids and humic substances: complexation and sorption on Al<sub>2</sub>O<sub>3</sub>. International Workshop on Advanced Techniques in Actinide Spectroscopy, 5-7 November 2012, Dresden, Germany.
- IV. Moreau P, Colette-Maatouk S, Reiller PE, Gibert-Brunet E, and Gareil P: Interaction between Eu(III), phenolic acids and Al<sub>2</sub>O<sub>3</sub> nanoparticles, 21<sup>st</sup> Goldschmidt Conference, 24-29 June 2012, Montréal, Canada.
- V. Janot N, Reiller PE, Zheng X, Croué J-P, and Benedetti MF: Characterization of humic acid reactivity modifications due to adsorption onto  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Interfaces Against Pollution 2012, 10-14 June 2012, Nancy, France.
- VI. Moreau P, Collette-Maatouk S, Auriault C, Vitorge P, Gareil P, and Reiller PE: Interactions between Eu(III), phenolic acids and Al<sub>2</sub>O<sub>3</sub> nanoparticles, Interfaces Against Pollution 2012, 10-14 June 2012, Nancy, France.
- VII. Janot N, Benedetti MF, and Reiller PE: The ternary metal-natural organic matter-surface systems: comparing sorption and spectroscopic data, Geological Disposal of Radioactive Waste: Underpinning Science and Technology, 18-20 October 2011, Loughborough University, Loughborough, UK.
- VIII. Reiller PE, Marang L, Jouvin D, and Benedetti MF: Uranium (VI) Binding to humic substances: speciation, estimation of competition, and application to independent data, Uranium Mining and Hydrogeology VI, 18-21 September 2011, Technische Universität Bergakademie Freiberg, Freiberg, Germany.
- IX. Reiller PE: Modelling the metal-organic-surface systems: reasons of relative success, failure, and possible routes for peace of mind, frontiers in environmental geochemistry, The Mineralogical Society, 21-23 June 2011, Aberystwyth University, Aberystwyth, Wales, UK.
- X. Moreau P, Colette-Maatouk S, Reiller P, Varenne A, Gareil P, and Lucas-Lamouroux C: Etude des interactions entre les lanthanides trivalents et des nanoparticules d'alumine en présence d'acides phénoliques, SEP '11, 23-25 March 2011, Toulouse, France.
- XI. Reiller PE: Sorption of natural and anthropogenic organic molecules on mineral surfaces: implication of the structure and aggregation properties, Workshop on Organic Matter in Clay Rock, ANDRA-Subatech, Ecoles des Mines de Nantes, 27-28 September 2010, Nantes, France.
- XII. Reiller PE: Composition and structure of natural organic matter in relation with its reactivity, Workshop on Organic Matter in Clay Rock, ANDRA-Subatech, Ecoles des Mines de Nantes, 27-28 September 2010, Nantes, France.
- XIII. d'Orlyé F and Reiller PE: Potential of capillary electrophoresis for estimation of humic substances physico-chemical properties, 28<sup>th</sup> International Symposium on Chromatography, 12-16 September 2010, Valencia, Spain.

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\* The talks were given by the underlined author.

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- XIV. Janot N., Benedetti MF, and Reiller PE: Surface and organic speciation of europium(III) in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> - humic acid system: macroscopic and spectroscopic investigations. American Chemical Society Spring Meeting, 21-25 March 2010, San Francisco, CA, USA.
- XV. Janot N., Reiller P, Korshin G.V, and Benedetti MF: American Chemical Society Spring Meeting, 21-25 March, 2010, San Francisco, CA, USA.
- XVI. Janot N., Reiller P, Korshin G.V, and Benedetti MF: Effects of organic matter - Aluminium oxide interactions on Eu(III) speciation. *Geochim. Cosmochim. Acta* **73**, A585. 19<sup>th</sup> Annual VM Goldschmidt Conference, 21-26 June 2009, Davos, Switzerland.
- XVII. Marang L, Eidner S, Kumke MU, Benedetti MF, and Reiller PE: Characterization of competitive binding of Eu(III)/Cu(II) and Eu(III)/Ca(II) to Gorleben humic acid. *Geochim. Cosmochim. Acta* **73**, A831. 19<sup>th</sup> Annual VM Goldschmidt Conference, 21-26 June 2009, Davos, Switzerland.
- XVIII. Altmann S., Tournassat C, Goutelard F, Parneix J-C, Gimmi T, Maes N, and Reiller P: Radionuclide migration in clay-rich host formations: process understanding, integration and up-scaling for safety case. In *Euradwaste '08. 7<sup>th</sup> European Commission Conference on the Management and Disposal of Radioactive Waste*, 20-22 October 2008 - EUR 24040 (Davies C, Ed.), p. 309-325. European Communities, 2009, Luxembourg, Luxembourg.
- XIX. Schwyn B., Scheider J, Rüdi J, Alonso J, Altmann S, Brassines S, Cormenzana Lopez J.L, Hautojärvi A, Marivoet J, Puigdomenech I, Ruebel A, Tweed C, Missana T, Noseck U, Reiller P, and Schäfer T: Radionuclide migration in the far field: the use of research results in safety case. In *Euradwaste '08. 7<sup>th</sup> European Commission Conference on the Management and Disposal of Radioactive Waste*, 20-22 October 2008 - EUR 24040 (Davies C, Ed.), p. 353-359. European Communities, 2009, Luxembourg, Luxembourg.
- XX. Reiller P: Colloïdes du stockage et décontamination, Journée Colloïdes du Projet PARIS, 25 June 2008, ENSCP, Paris, France.
- XXI. Claret F, Schäfer T, Brevet J, Amekraz B, Moulin C, and Reiller P: Fractionnement des substances humiques sur une surface minérale, Séminaire CETAMA Spéciation, 8-9 January 2008, Montpellier, France.
- XXII. Reiller P: Avancée du projet intégré européen FUNMIG: fundamental processes of radionuclide migration, Séminaire CETAMA Spéciation, 8-9 January 2008, Montpellier, France.
- XXIII. Guétat P., Moulin V, Reiller P, Vercouter T, Bion L, Fritsch P, Monfort M, Flury-Hérard A, Comte A, Ménétrier F, Ansoborlo E, Jourdain F, Boucher L, and Vandorpe F: 5<sup>th</sup> Conference on Plutonium Futures "The Science", 7-11 July 2008, Dijon, France.
- XXIV. Marang L., Reiller P, and Benedetti MF: Measuring and modeling uranium (VI) binding by humic acid, 11<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 26-31 August 2007, Munich, Germany.
- XXV. Reiller P, Evans N.D.M, and Szabó G: Complexation parameters for the actinides (IV)-humic acid system: a search for consistency. 11<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 26-31 August 2007, Munich, Germany.
- XXVI. Marang L., Reiller P, and Benedetti MF: Measuring and modeling cobalt (II) and uranium (VI) binding by humic acid, 9<sup>th</sup> International Conference on the Biogeochemistry of Trace Elements (ICOBTE 2007), 15-19 July 2007, Beijing, China.
- XXVII. Reiller P and Schlegel M: Reactivity of iodine with natural organic matter: some spectroscopic evidence. Workshop on mobile fission and activation products in nuclear waste disposal (MOFAP), 16-19 January 2007, La Baule, France.
- XXVIII. Reiller P: Difficulties in modelling the sorption of ternary systems metal-natural organic matter-minerals: experimental inputs. Workshop on Organic Matter Modelling 2005, 16-18 November 2005, Université du Sud Toulon Var, La Londe lès Maures, France.

- XXIX. Pointeau I, Hainos D, Coreau N, and Reiller P: Effect of organics on selenite behaviour in cementitious media, International Workshop Mechanisms and Modelling of Waste/Cement Interactions - 2005; 8-12 May 2005, Meiringen, Switzerland.
- XXX. Reiller P, Amekraz B, and Moulin C: Fractionnement des acides humiques lors de la sorption sur l'hématite par spectrophotométrie UV et spectrométrie de masse à ionisation par électrospray, 6<sup>ème</sup> Colloque du Groupe Français de l'IHSS, 13-15 October 2004, Reims, France.
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- XXXII. Reiller P, Plancque G, Amekraz B, and Moulin C: Direct insight of the association of radiotoxic elements with fulvic acid provided by electrospray ionisation mass spectrometry, ICOBTE 7, 15-19 June 2003, Uppsalla, Sweden.
- XXXIII. Reiller P, Moulin V, Labonne-Wall N, Dautel C, Casanova F, and Mercier F: Retention behaviour of humic substances onto mineral surfaces : case of silica and iron oxides, IHSS Groupe France, 1999, Versailles, France.
- XXXIV. Reiller P, Moulin C, Lemordant D, and Beaucaire C: Dual use of micellar-enhanced ultrafiltration and time-resolved laser-induced spectrofluorimetry for uranium determination in solution, Euroanalysis VIII, 5-11 September 1993, Edimbourg, UK.
- XXXV. Reiller P, Moulin C, Beaucaire C, and Lemordant D: Utilisation couplée de l'ultrafiltration assistée par micelles et de la spectrofluorimétrie laser à résolution temporelle pour la détermination de l'uranium en solution, Symposium on Analytical Science, 4-6 May 1993, Deauville, France.

### 1.1.6. Posters\*

- i. Kouhail Y, Benedetti MF, and Reiller PE: Time resolved luminescence spectroscopy study of Eu(III)-fulvate complexation: influence of pH, ionic strength, and fulvic acid concentration, International Workshop on Advanced Techniques in Actinide Spectroscopy, 3-7 November 2014, Dresden, Germany.
- ii. Reiller PE, Influence of aromatics and substituents on the time-resolved luminescence spectroscopy of Eu(III)-complexes, International Workshop on Advanced Techniques in Actinide Spectroscopy, 3-7 November 2014, Dresden, Germany.
- iii. Vercouter T, Reiller PE, Ansoborlo E, Février L, Gilbin R, Lomenech C, and Philippini V: On the importance of ternary alkaline earth carbonate complexes of uranium(VI) in natural waters : a round-robin modelling test, Goldschmidt 2013, 25-30 August 2013, Florence, Italie.
- iv. Janot N, Reiller PE, and Benedetti MF: Influence of solution parameters on europium(III),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and humic acid interactions, Interfaces Against Pollution 2012, 10-14 June 2012, Nancy, France.
- v. Lebeau D, Fournier J-B, Leblanc C, Reiller P. E, Pourcher T, and Doizi D: Spéciation de l'iode en milieu biologique par desorption/ionisation par électrospray (DESI), Congrès Français de Spectrométrie de Masse et d'Analyse Protéomique (SMAP 2011), 19-22 September 2011, Avignon, France.
- vi. Janot N, Benedetti MF, and Reiller PE: Europium(III): colloidal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and humic acid interactions, 13-17 December 2010, AGU Fall Meeting, San Francisco, CA, USA.
- vii. Vercouter T, Reiller P, Duro L, and Ekberg C: Thermodynamic data of inorganic complexes of actinides: impact of data sets on speciation in underground waters, NEA Symposium - From Thermodynamics to the Safety Case, 17-19 May 2010, Karlsruhe, Germany.
- viii. Reiller P: FUNMIG - Research on well-defined processes. In Euradwaste '08. 7<sup>th</sup> European Commission Conference on the Management and Disposal of Radioactive Waste, 20-22 October 2008, Luxembourg - EUR 24040 (Davies C, Ed.), p. 497-501. European Communities, 2009, Luxembourg, Luxembourg.

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- ix. Reiller, P: FUNMIG RTDC-1: Well defined processes, 11<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 26-31 August 2007, Munich, Germany.
- x. Claret F, Schäfer T, and Reiller P: Natural organic matter fractionation on mineral surfaces: a spectroscopic approach, Clays in natural and engineered barriers for radioactive waste confinement - 3<sup>rd</sup> International Conference, 17-20 September 2007, Lille, France.
- xi. Claret F, Schäfer T, Amekraz B, Moulin C, and Reiller P: Fractionation of natural organic matter (NOM) on alpha alumina, 13<sup>th</sup> International Meeting of the International Humic Substances Society (IHSS 13), 30<sup>th</sup> July – 4<sup>th</sup> August 2006, Karlsruhe, Germany.
- xii. Marang L, Reiller P, and Benedetti M: Kinetic approach of the Donnan membrane technique, 13<sup>th</sup> International Meeting of the International Humic Substances Society (IHSS 13), 30<sup>th</sup> July – 4<sup>th</sup> August 2006, Karlsruhe, Germany.
- xiii. Pointeau I, Reiller P, Macé N, Landesman C, and Coreau N: Study of the surface potential evolution of hydrated cement paste vs. leaching, NUCPERF - 2006, 27-29 March 2006, Cadarache, France.
- xiv. Reiller P, Mercier-Bion F, Gimenez N, Barré N, and Miserque F: 10<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 18-23 September 2005, Avignon, France.
- xv. Szabó G, Guzzi J, Reiller P, Geckeis H, and Bulman R.A: Investigation of complexation of thorium by humic acid using chemically immobilised humic acid on silica gel, 10<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 18-23 September 2005, Avignon, France.
- xvi. Schlegel MS, Mercier F, Barré N, and Reiller P: Iodine speciation in iodine-rich humic substances by X-ray absorption spectroscopy, *Geochim. Cosmochim. Acta* **68**, A362. 14<sup>th</sup> Annual V.M. Goldschmidt Conference, 5-11 June 2004, Copenhagen, Denmark.
- xvii. Reiller P and Moulin V: Influence of organic matter in the prediction of iodine migration in natural environment, 26<sup>th</sup> Symposium on the Scientific Basis for Nuclear Waste Management held at the 2002 MRS Fall Meeting, 2-5 December 2002, Boston, MA, USA.
- xviii. Reiller P, Casanova F, Dautel C, and Moulin V: On the study of Th(IV)–humic acids interactions by competition towards sorption onto silica. 8<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 16-21 September 2001, Bregenz, Austria.
- xix. Reiller P, Casanova F, Dautel C, and Moulin V: Implication of the presence of humic acids on the retention of Th(IV) onto hematite colloids. 8<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 16-21 September 2001, Bregenz, Austria.
- xx. Reiller P, Casanova F, Spicq A, and Moulin V: Study of iodine-humic acids interactions by ultrafiltration and spectrophotometry. 8<sup>th</sup> International Conference on Chemistry and Migration of Actinides and Fission Products, 16-21 September 2001, Bregenz, Austria.
- xxi. Reiller P, Moulin V, Labonne-Wall N, Dautel C, and Casanova F: Retention behaviour of humic substances onto mineral surfaces and consequences upon radionuclide mobility: case of silica and iron oxides, 10<sup>th</sup> International Meeting of the International Humic Substances Society (IHSS 10), 24-28 July 2000, Toulouse, France.
- xxii. Moulin C, Reiller P, Beaucaire C, and Lemordant D: Uranium speciation in solution by micellar-enhanced ultrafiltration and time-resolved laser-induced fluorescence, Actinides-93, 19-24 September 1993, Santa Fe, USA.

## 1.2. SUPERVISION OF RESEARCH

### 1.2.1. Undergraduates

Siroux B (2014) Adsorption du strontium sur les argiles de type smectite, Stage de Recherche de 3<sup>ème</sup> année, Ecole Nationale Supérieure de Chimie de Paris, Chimie ParisTech.

Lagouvardos N (2014) Etude de complexation de l'euporium par des produits de dégradation hydrosolubles (PDH) des polymères PUR, EPR et PVC industriels, stage Master Pro 1, Université de Bourgogne.

79. Sorrya V (2014) Etude de complexation de l'euporium par des acides carboxyliques simples, Licence Professionnelle, IUT Orsay.

Léonço D (2013) Etude de complexation de l'euporium par des complexants organiques modèles de produits de dégradation hydrosolubles (PDH) réels du PVC, stage Master Pro 1, Université de Bourgogne.

Gimenez N (2004) Étude de l'iodation des substances humiques naturelles, stage DEA (Master2), Université d'Evry-Val d'Essonne.

### 1.2.2. PhD Theses

Siroux B (on-going) Interactions dans les systèmes césium/matière organique/argiles des sols : application à la décontamination et à la remédiation, Université Denis Diderot (Paris VII).

Fromentin E (on-going) Lixiviation des polymères irradiés : caractérisation de la solution et complexation des actinides, Université Pierre et Marie Curie (Paris VI).

Kouhail Y (on-going) Influence de la compétition des anions (hydroxydes, carbonates) sur la complexation des lanthanides trivalents par la matière organique naturelle : cas des substances humiques. Université Denis Diderot (Paris VII).

80. Moreau P (2012) Etude des interactions entre les lanthanides trivalents et des nanoparticules d'alumine en présence d'acides phénoliques. Université Pierre et Marie Curie (Paris VI) – ENSCP/ParisTech. <http://tel.archives-ouvertes.fr/tel-00789479>. Permanent position at BRGM, Orléans, France.

81. Janot N (2011) Influence de la matière organique naturelle et des surfaces minérales sur la spéciation des radionucléides en contexte environnemental. Thèse, Université Denis Diderot (Paris VII) <http://tel.archives-ouvertes.fr/tel-00643374/fr/>. Post-doctoral position (2012-2014) at SLAC National Accelerator Laboratory, Stanford, Palo Alto, CA, USA, and Post-doctoral position (from 2015) at Ecole Nationale Supérieure de Géologie, Nancy, France.

82. Marang L (2007) Influence de la matière organique naturelle sur la spéciation des radionucléides en contexte géochimique. Thèse, Université Denis Diderot (Paris VII) & CEA-R-6187. <http://tel.archives-ouvertes.fr/tel-00418723/fr/>, Paris, France. Permanent position at EDF, Chatou, France.

### 1.2.3. Post-doctorals

d'Orlyé F (2009-2011) Polychlorobenzènes-sédiment interactions, and natural organic matter structure by capillary electrophoresis. CEA and BRGM reports, and a publication (permanent position at ENSCP – ParisTech, Paris, France)

Brevet J (2007-2009) Europium(III)/natural organic matter interactions. CEA reports and publications (Engineering)

Claret F (2005-2007) Natural organic matter fractionation. CEA reports, EC reports, and publications (Head of the Storage and Deep Geological Settings Unit at BRGM – Orléans, France)

Pointeau I (2000-2002) Radionucléides/cementitious phases interactions. CEA and Andra reports, and publications (Permanent position at CEA – Cadarache, France)



## 2. INTRODUCTION AND SUMMARY ON THE ORIGINALITY OF THE RESEARCH ACTIVITIES

### 2.1. PRELIMINARY REMARKS

Conducting research works in organization like the French “Commissariat à l’Energie Atomique et aux énergies alternatives” (CEA) is for sure an enjoyable situation. A substantial amount of public expenses is devoted to develop the ability for France to have a marking position *in the “domain of research concerning atomic energy”*.<sup>\*</sup> But as it is happening now more and more in the academic research, the necessity to develop several axes of research is since long a reality in CEA. Moreover, some research cannot be the subject of publications, at least as long as confidentiality is required. This is the reason why some CEA researchers have non-linear career and are conducting rather “orthogonal” research projects, either because of funding issues, or of the necessity to develop specific competences. This was the case for me several times as I was hired in 1998 originally to develop a thematic linked to radionuclide-colloid interactions – metallic and non-metallic radionuclides and either inorganic or natural organic colloids –, then a couple of years later I was asked to adapt this competence to the cementitious systems in the presence of anthropogenic organic molecules. As I developed an expertise on complexation phenomena, some years later I was timely implied in high saline media generated by sludges, and more recently on complexation phenomena in radiolytic products of polymers. These different thematic generally helped me in building a wide vision of the different aspects of the nuclear fuel cycle, but may not help in constructing a specialized and in-depth expertise.

During all these 17 years, I had the chance to *keep* an on-going thematic related to the interactions of natural organic matter and the radionuclides that are involved with the nuclear fuel cycle. I had the possibility to build a personal view on some aspects related to this thematic, of the particular and sometimes peculiar comportment of these media. In order to keep an certain coherence, I will focus this document on the

#### **Structure-reactivity relationships in the interactions between humic substances, metallic pollutants from the nuclear cycle, and mineral surfaces,**

and only mention, or sometimes just evade, the works on other thematics.

### 2.2. GENERAL CONTEXT

The majority of pollutants issued from nuclear activities are radionuclides. These nuclei are unstable and undergo disintegrations inducing ionising radiations. These disintegrations involve the

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\* [http://www-centre-saclay.cea.fr/var/czwebin\\_site/storage/original/application/389ab9d7a1c3798062cb160a06b4bd2d](http://www-centre-saclay.cea.fr/var/czwebin_site/storage/original/application/389ab9d7a1c3798062cb160a06b4bd2d)

formation of fission (FP) and activation (AP) products. The massive electricity production in the French nuclear power plants implies that the chemical and radiotoxic risks of these elements are accounted. Even if the proportion of these FPs and APs are low regarding the initial mass of actinides, the dose and chemical toxicity of these elements justify this risk assessment.

Interactions of pollutants with natural organic molecules can be envisaged under different point of views: as a pollution vector, or as enhancement for detection. The different research programs that I have been involved in cover these aspects. I have been involved in the chemical risk assessment of the presence of radionuclides in an environment, and more particularly to the thematic linked to their interactions with natural organic matter (NOM); this comprises the interaction phenomena between radionuclides and NOM, between NOM and mineral surfaces, as well as the ternary systems, *i.e.*, radionuclides/NOM/surfaces. As it will be developed through this document, the NOM structure is very sensitive to the modification of physico-chemical conditions.

The complexation and migration issue of pollutants in the presence of NOM, particularly humic substances, which represents the alkaline extractible fraction, has been the subject of a vast literature from decades if not centuries. Actually, the first alkaline extraction of NOM goes back to the end of 18<sup>th</sup> century by ACHARD (1786), and the first use of “humus” term was introduced by SAUSSURE (1804). A historical background can be found in STEVENSON (1985).

The more marking examples of the influence of NOM on the migration of radionuclides are:

- migration of plutonium in the soils from Nagasaki (MAHARA & MIYAHARA, 1984; MAHARA *et al.*, 1988; MAHARA & KUDO, 1995; FUJIKAWA *et al.*, 1999), from the Rocky Flats site (SANTSCHI *et al.*, 2002), or from Chernobyl (AGAPKINA *et al.*, 1995; OLLUI MBOULOU *et al.*, 1998; MATSUNAGA *et al.*, 2004; BONDAR'KOV *et al.*, 2006; BRUDECKI *et al.*, 2009);
- presence of plutonium in humic substances extracted from lakes (ERIKSSON *et al.*, 2001);
- migration of americium and curium in soils after surface disposal at the Oak Ridge or Savannah River National Laboratories (ALBERTS *et al.*, 1986; MCCARTHY *et al.*, 1998a; MCCARTHY *et al.*, 1998b), or mobilisation of americium or plutonium at Rocky Flats (LITAOR *et al.*, 1998; SANTSCHI *et al.*, 2002);
- migration of actinides in an aquifer after a forced injection of an NOM-amended natural groundwater (MARLEY *et al.*, 1993; MCCARTHY *et al.*, 1993);
- migration of radionuclides after the formation of NOM in flooded technical galleries from the Nevada Test Site (ZHAO *et al.*, 2011);
- strong interaction between uranium and NOM but weak migration of uranium in an acidic podzol from the Landes, Gasconny, France (CRANCON, 2001; CRANCON & VAN DER LEE, 2003; CRANCON *et al.*, 2010), or in depleted uranium contaminated sites (DONG *et al.*, 2006; GRAHAM *et al.*, 2008).

In the following paragraph I will present the general framework and will make a brief summary of the works that are more developed in the rest of the document

### 2.3. STUDY ON THE STRUCTURE OF HUMIC SUBSTANCES

The complexity and heterogeneity of these substrates, as well as the numerous possible interactions with a surrounding environment, imply a difficulty to obtain a clear and global vision of these mechanisms. As an example, the determination of the NOM structure has still not come to a general consensus. The structural models were, and are still, abundant. Up to recent times, the major part of these models proposed polymeric structures, when no repetition motif has been identified. Based on experimental evidence, some called for a *new* paradigm consisting of an aggregate vision of NOM and HS ([WERSHAW, 1993, 2000](#); [PICCOLO, 2001](#)).

I have been involved in structural studies mainly through electrospray ionisation mass spectrometry (ESI-MS) where we were able to propose early stages of analyses of different molecules constituting HS, mainly after iodination [[20](#)], after the work from [PLANCQUE \*et al.\* \(2001\)](#). Based on this work, we applied this strategy to the analysis of the modification of the composition of HS after adsorptive fractionation on mineral surface [[26](#)]. I have also participated in the promotion of the use of Taylor-Aris dispersion analysis (TDA) for the determination of the size of HS constituting entities [[6](#)]. I have also participated in the use of small-angle scattering, atomic force microscopy and surface tension for the determination of size range and organization of HS aggregates. This very promising work does not end-up under a published form yet, but provide quite an interesting piece of information [[47](#)].

### 2.4. COMPLEXATION

The situation is intricate as well for the complexation of cations, interaction with halogens [[26,35,36,40](#)], interaction with organic pollutants [[29](#)]. It is worthy to notice that all these reactions do have an influence on the changing structure of NOM. The modelling of the complexation of metallic radionuclides by humic substances has been the subject of a vast literature, and no less than five different types of modelling, mostly operational, have been proposed, notwithstanding the kinetic control ([WARWICK \*et al.\*, 2000](#); [BRYAN \*et al.\*, 2005](#)) and redox properties ([AESCHBACHER \*et al.\*, 2011](#)) [[53](#)]. Surprisingly enough, even if the intimate structure of NOM is still mostly unknown and submitted to variations imposed by the chemical environment, these operational modelling provide an overall satisfying description of simple binary systems, *i.e.*, metal/NOM. On the other hand, only a few models can satisfactorily describe competition between cations, especially between multi-charged radionuclides and alkaline-earths. Out of the radionuclides, actinides and lanthanides (Sm, Eu, Am, Cm) do have a prevalent chemistry at the +III redox state in water – under the form of a trivalent cations,  $M^{3+}$ . Quite an extensive literature exists on the subject. Considering the strong analogy of the chemistry of these cations – particularly considering oxygen containing function ([PEARSON, 1963](#)) – the use of lanthanides to mimic the actinides(III)/NOM interactions were considered. In addition the extensive use of lanthanides, as part of the rare-earths family, in the modern industry ([BINNEMANS \*et al.\*, 2013a](#)), and the need for recycling ([BINNEMANS \*et al.\*, 2013b](#)), will lead the scientific community to address the outcome of increasing presence of lanthanides in the environment ([MOERMOND \*et al.\*](#),

[2001](#); [CENSI \*et al.\*, 2010](#); [CENSI \*et al.\*, 2013](#)). The reversibility of these interactions is also difficult to manage, particularly for the elements at the +IV redox state – under the form of a tetravalent cation,  $M^{4+}$  – that are particularly important for the redox sensitive actinides U, Np, and Pu.

Humic substances *non solum* have an influence on the chemistry of cations, *sed etiam* the aromatic and oxido-reductive character of the constitutive entities gives them an important role on the more general environmental chemistry ([SPOKES & LISS, 1995, 1996](#); [ANDERSEN \*et al.\*, 2002](#)), on halogen biochemistry, and more particularly on iodine ([HUANG \*et al.\*, 1994](#); [SPOKES & LISS, 1996](#); [HERZIG \*et al.\*, 2001](#); [ANDERSEN \*et al.\*, 2002](#)) [[35,36,40,26](#)]. Humic substances are implied in inhibition of enzymatic reaction in the liver or thyroid ([HUANG \*et al.\*, 1995](#); [FRÉCHOU \*et al.\*, 2002a](#); [FRÉCHOU \*et al.\*, 2002b](#); [YANG \*et al.\*, 2002](#)). The reactivity of humic substances towards iodine is certainly at stake. Association of halogens with soil NOM is strong ([LEE \*et al.\*, 2001](#); [ASHWORTH & SHAW, 2006a](#)), whereas iodide adsorption on minerals is relatively weak ([CROMIÈRES, 1996](#); [JOHANSON, 2000](#)). Halogenation of humic substances can be viewed as the halogenation of phenolic moieties ([LEE, 1967](#); [JOHANSON, 2000](#); [WARNER \*et al.\*, 2000](#)) [[26,35,36,40](#)]. This halogenation is also enzymatically catalysed ([MORRISON & BAYSE, 1970](#); [POMMIER \*et al.\*, 1973](#); [VAN PEE & UNVERSUCHT, 2003](#)) by peroxidases, which are implied in the elimination of  $H_2O_2$  from living organisms ([WAGENKNECHT & WOGGON, 1997](#)).

This constitutes the main part of this document. I have been involved in the quantification of the interactions between humic substances and radionuclides, mainly Th(IV) as an analogue of other actinides(IV) [[12,18,21,24](#)], and Eu(III) as an analogue of actinides(III) [[3,9,17](#)]. Different modelling concepts were used that allowed me to propose different reviews [[18,22,53](#)]. The quantification were done either through separation techniques – ultrafiltration, competitive adsorption – or using spectroscopic techniques like time-resolved luminescence spectroscopy (TRLS) that also allows apprehending the chemical surrounding of the metals [[9,11,13,15](#)] – mainly lanthanides.

## **2.5. ADSORPTION PHENOMENA**

In a natural medium, complexation phenomena are in direct competition with retention/adsorption/incorporation of radionuclides onto/into mineral phases. As NOM shows a strong affinity for cations, it also has a strong affinity for mineral surfaces. This can lead, as a function of medium conditions, either to an increase of mobility or to an immobilisation. Retention or adsorption properties of NOM influences the surface properties of minerals as the structure of NOM itself as well, and has numerous implications ([VON LÜTZOW \*et al.\*, 2006](#)): preservation of NOM from mineralization ([KAISER & GUGGENBERGER, 2000](#)) or from bacterial degradation ([CHENU & STOTZKY, 2002](#)), and inhibition of crystallite growth ([SUESS, 1970, 1973](#)).

The modelling of adsorption phenomena onto mineral surfaces has also given rise to a lot of models. From a general point of view, adsorption surface sites are either described as exchangers ([GAINES & THOMAS, 1953](#); [MOTELLIER \*et al.\*, 2003](#); [BRADBURY & BAEYENS, 2005](#); [BEAUCAIRE \*et al.\*, 2008](#); [BRADBURY & BAEYENS, 2009](#); [TERTRE \*et al.\*, 2009](#); [TERTRE \*et al.\*, 2010](#)) considering that the

mineral is a neutral phases in equilibrium with aqueous solution, or that adsorption sites are amphoteric sites that are giving rise to surface charges, which induces the explicit account of the electrostatic description of the interface ([DAVIS \*et al.\*, 1978](#); [DAVIS & LECKIE, 1978b, 1980](#); [DZOMBAK & MOREL, 1990](#); [LYKLEMA, 1995a, 1995b](#); [HIEMSTRA & VAN RIEMSDIJK, 1996](#); [LÜTZENKIRCHEN, 1999a, 1999b](#)). The efficiency of models in modelling either adsorption of cations [3] or simple anions as organic acids [4,52] has been shown.

Humic substances can sometimes be considered as mixtures of organic complexants, or as polyelectrolyte of an oligomeric character.\* This interaction can be sometimes modelled with a relative success, but it is most of the time confronted to the problems linked with the competition between cations, or more importantly to the particular evolution with ionic strength and to the fractionation of constitutive entities of NOM at the mineral surface [52]. Actually, the interaction of NOM with a charged and reactive surface has a great influence on their structural properties and functionality.

I have been involved in the qualification as well as quantification of adsorption phenomena of HS onto minerals, mainly oxide, with the aim to understand their role in the ternary systems metal/HS/mineral [2,4,7-10,15,16,20,23,25]. Different approaches and techniques were used to characterize the different modification of the structure and composition of HS, from very simple, as UV-Visible spectroscopy and total organic carbon analysis [15], to much more advanced ESI-MS [20] – modification of composition –, scanning transmission X-ray microscopy [15] – STXM, modification of functionality –, or TRLS [2,4,7-9,10,15,16] – modification of the chemical surrounding of a luminescent lanthanides in ternary system.

## 2.6. RATIONALE

As a rationale, the NOM related subjects are highly intricate. It appears that the reactivity of NOM is strongly linked to its origin, composition, structure, and organisation in the environment where it stands or flows. A lot of models and a lot of hypotheses have been proposed to give an *image* of both their reactivity and structure. All these models often contradict each other and as “*you cannot prove a vague theory wrong*” ([FEYNMAN, 1965, p. 158](#)), and as there is no available analytical tool that can provide a definitive answer to the on-going questions on structure and reactivity of NOM, yet, a lot of problems are still under high controversy. Nevertheless, there are some possible routes that, to my humble opinion, would permit to get closer to, if not satisfying, an operational description of the *difficult animal*† that are still humic substances. Then, it could seem vain to propose a description of the NOM reactivity in real systems, *i.e.* interaction with radionuclides and minerals, without a previous consideration on their structural properties. This will be the link that I will try follow throughout this document.

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\* Polymers of low polymerization degree

† Thanks to Gunnar Buckau for this suggestion





### 3. HUMIC SUBSTANCES: DEFINITIONS AND STRUCTURAL STUDIES TO BETTER COMPREHEND STRUCTURE-PROPERTIES RELATIONSHIPS

Following the introduction, one can understand that a thorough description of humic substances' structure is up to now awkward. Not only the heterogeneity of these substrates renders this task very difficult, but the continuing arguing between the different defenders of the different paradigms makes it even more difficult. I will only recall what is absolutely necessary to follow the rest of the text and invite the reader to the reference documents ([STEVENSON, 1982](#); [AIKEN \*et al.\*, 1985](#); [WERSHAW, 2000](#); [MACCARTHY, 2001a, 2001b](#)).

Humic substances can be extracted from almost every type of environment and are one of the most abundant form of organic matter in soils ([WOODWELL & HOUGHTON, 1977](#); [THURMAN, 1985](#)). From aquatic surface to deep geological formation, the concentration of humic substances essentially depends on the evolution of the physico-chemical conditions of the medium, and of the maturation of organic molecules. Humic substances being the result of the degradation of living organisms, they are mainly composed of carbon ( $\approx 40\text{-}60\%$ ), oxygen ( $\approx 35\text{-}45\%$ ), hydrogen ( $\approx 5\%$ ), nitrogen (1-5%) and sulphur ( $\leq 2\%$ ) ([RICE & MACCARTHY, 1991](#)). These abundances are representative of the historical evolution of the mixtures. The ratio H/C and O/C can help in retrieving information on the origin (aquatic, marine, sedimentary...) and on the aromatic character of humic substances ([RICE & MACCARTHY, 1991](#); [KIM \*et al.\*, 2003](#)).

#### 3.1. DEFINITIONS

Humic substances are showing oxido-reductive and pH-buffer properties, they contain a large amount of water, they are fixing metals and organic molecules, and catalyse photo-induced reactions ([DAVIES \*et al.\*, 2001](#)) [48]. This group of molecules are extracted from natural waters or from soils, sediments and rocks by acidic "precipitation" or after alkaline extraction from soils, sediments or rocks. They represent a class of substances that are operationally defined, and do not follow any kind of "standard" definition of molecules such as polysaccharides, proteins or lipids. Humic substances can be defined either as: (i) "*a series of relatively high-MW, brown to black colored substances, formed by secondary synthesis reactions*" ([STEVENSON, 1982](#)); or (ii) as "*a general class of biogenic, refractory, yellow-black organic substances that are ubiquitous, occurring in all terrestrial and aquatic environments*" ([AIKEN \*et al.\*, 1985](#)).

Since the latter definitions are extremely vague, one can rely on the operational definition from their extraction procedure, which permits to obtain three fractions ([THURMAN & MALCOLM, 1981](#); [AIKEN \*et al.\*, 1985](#); [THURMAN, 1985](#)):

- fulvic acids (FA), which are soluble at whatever pH;
- humic acids (HA), which are insoluble at acidic pH;
- humine, which is the insoluble fraction at whatever pH; humine is actually composed of a mixture of humic and non-humic matter ([BANERJEE \*et al.\*, 1971](#); [RICE & MACCARTHY, 1990](#)).

Based on this operational procedure, MACCARTHY (2001b) proposes the following definitions:

- *“humic substances comprise an extraordinary complex amorphous mixture of highly heterogeneous, chemically reactive yet refractory molecules,\* produced during early diagenesis in the decay of biomatter, and formed ubiquitously in the environment via processes involving chemical reaction of species randomly chosen from a pool of diverse molecules and through random chemical alteration of precursor molecules.”*
- *“The molecular heterogeneity inherent in humic substances renders the humic material highly refractory, thereby serving a role in Earth’s ecological system.”*

It is evident that these operational criteria involve other groups of molecules that are not extracted from flowing rivers, soils, or even from natural environments; the most extreme situation being the humic like substances (HULIS), present in atmospheric aerosols or in rain water – clouds, fog... (GRABER & RUDICH, 2006). Humic substances extracted from a particular environment can therefore be viewed as the *signature* of the NOM evolution. One can then ask oneself if these extracts do really exist, as they are extracted through non-natural processes. However, humic substances can be viewed as an analogue of the compartment of NOM (BENEDETTI *et al.*, 1996b; SANTSCI *et al.*, 1997; ALLARD *et al.*, 2002; HAMILTON-TAYLOR *et al.*, 2002; AUCOUR *et al.*, 2003; CANCES *et al.*, 2003).

Concentration of humic substances depends on the history of the physico-chemical conditions, and from the maturation of the constituting organic molecules. As an example, surface-extracted humic substances, in rivers or soils, are directly issued from the decay of living organisms. Whereas in deeper environments, such as in the aquifer above the Gorleben salt dome (Germany), oxidative alteration of sedimentary organic matter by intrusion of surface waters, has led to the formation of humic substances (ARTINGER *et al.*, 2000; BUCKAU *et al.*, 2000a; BUCKAU *et al.*, 2000b). One can also note the alkaline alteration of the NOM associated to the argillite from Bure (France) or Mont-Terri (Switzerland), lead to the extraction of humic substances (CLARET *et al.*, 2002; CLARET *et al.*, 2003; SCHÄFER *et al.*, 2003a; SCHÄFER *et al.*, 2003b; CLARET *et al.*, 2005), when they are absent in the original pore water (COURDOUAN *et al.*, 2007a; COURDOUAN *et al.*, 2007b; COURDOUAN *et al.*, 2008), or difficult to extract under acidic conditions (GRASSET *et al.*, 2010) [66].

### 3.2. STRUCTURAL STUDIES

As we will see, there is a strong correlation between structure and reactivity of humic substances; complexation is not easily described through usual thermodynamic models, and the adsorption compartment is rather comparable to the polyelectrolyte one. It is thus useful to keep a structural point of view when one tries to interpret complexation or adsorption experiments: (i) what is the size of the complexing entity?; (ii) what is the symmetry of the complexation site, and is it intra- or inter-molecular?; (iii) what is the conformation at the mineral surface?; (iv) what size or conformation variation can one await vs. pH, ionic strength, metal concentration or mineral phase?

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\* The use of this term denotes here that macroscopically the properties do not seem to change. Very often the authors do not define relative to which property HS are refractory. Nevertheless MacCarthy (2001b) precises that it is the resistance to microbial degradation which is at stake.

Almost all techniques for size or molecular mass determinations, hydrodynamic or gyration radii have been applied to the particular case of humic substances. But each technique is limited by its own *observation volume*, which is not necessarily compatible with the others:

- scanning or transmission electronic microscopy, required very low ambient pressure which induced dehydration of the sample ([TAN, 1985](#)), and an environmental scanning electron microscope is desirable ([DOUCET et al., 2005](#); [REDWOOD et al., 2005](#));
- size exclusion chromatography is linked to a standardization with real polymers ([CHIN & GSCHWEND 1991](#); [PEURAVUORI & PIHLAJA, 1997](#); [ZHOU et al., 2000](#)), which humic substances are not ([PICCOLO et al., 2001](#)), and the measured size are often out of the calibration curves ([CHIN & GSCHWEND 1991](#); [CHIN et al., 1994](#));
- mass spectrometry techniques require ionisation that can induce destructureation, and rely on the ionisation efficiency of the different constitutive molecules ([PLANCQUE et al., 2001](#); [THESE et al., 2004](#); [BONHOMMEAU & GAIGEOT, 2013](#)) [[20,26](#)];
- vapour pressure osmometry ([AIKEN & MALCOLM, 1987](#); [CHIN & GSCHWEND 1991](#); [CHIN et al., 1994](#); [PEURAVUORI & PIHLAJA, 1997](#)) depends on the number of particles in solution and not on their nature, but is strongly influenced by the lowest fraction in molecular mass;
- Taylor-Aris dispersion analysis requires a laminar flow in a capillary ([TAYLOR, 1953](#); [ARIS, 1956](#)), which can have interactions with humic substances [[6](#)];
- dynamic light scattering, from its  $R_{\text{H}}^6$  dependence is more sensitive to bigger particles ([RICE et al., 1999](#)) [[6](#)];
- small angle neutrons or X ray scattering require rather high concentrations ([RICE et al., 1999](#)) [[47](#)];
- atomic force microscopy required the presence of an underlying surface ([LEAD et al., 2005](#)) [[47](#)]...

These differences in *observation volumes* seem to be at the origin of the differences in the interpretation of the raw data by *supporters* of the different paradigms.

The structure of humic substances has long been considered as the result of secondary polymerisation reactions during the degradation of living matter ([STEVENSON, 1982](#)): (i) reactions between amines by micro-organisms with lignin or degradation products; (ii) reactions between polyphenols oxidised in quinones and in amines; and (iii) reactions between reductive saccharides and amines. A review is proposed by CLAPP & HAYES ([1999](#)). These molecules can thereafter undergo series of degradation, either microbial or thermal, in soils and sediments. Humic substances are then considered as complex polyelectrolytes ([GHOSH & SCHNITZER, 1980](#)).

Other complementary description propose that humic substances are aggregates of smaller molecules ([WERSHAW, 1993](#); [PICCOLO et al., 1996](#); [WERSHAW, 1999](#); [SIMPSON et al., 2001](#)), the cohesion of which are being assured by weak forces and/or hydrogen bonds ([CONTE & PICCOLO, 1999](#)), and structure being essentially fractal ([WERSHAW et al., 1967](#); [ÖSTERBERG & MORTENSEN, 1992](#); [RICE & LIN, 1993](#); [ÖSTERBERG et al., 1995](#); [REN et al., 1996](#); [RICE et al., 1999](#); [REDWOOD et al.,](#)

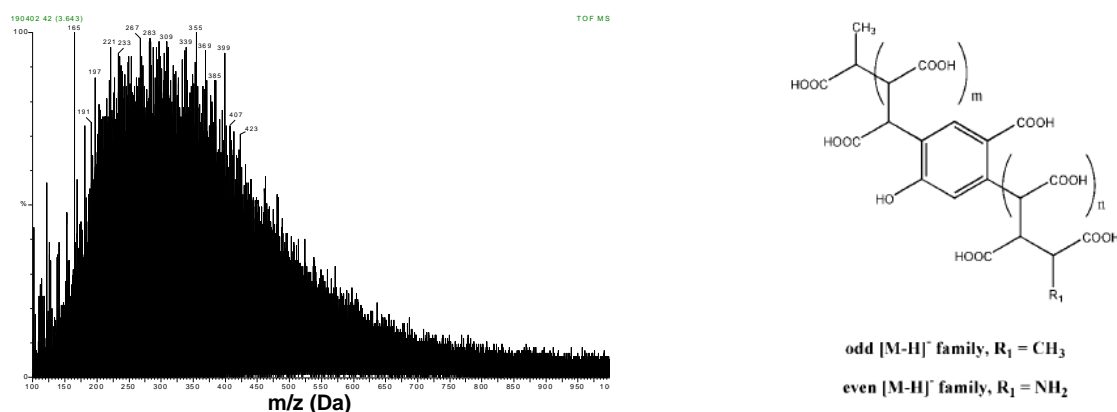
2005) [47]. As noted by RICE *et al.* (1999), humic substances could represent “*the ultimate in molecular disorder*”, but this must not prevent one from trying to understand its behaviour [48].

In the following, I will remind the results that were obtained using different techniques and I will propose an integrated vision before approaching complexation and adsorption phenomena in the next chapters.

### 3.2.1. Electrospray ionisation mass spectrometry (ESI-MS)

After the ESI-MS development for the analysis of proteins, many works have been reported on the application to the structure of humic substances during the last decade. After a systematic study of different fulvic extracts from different origin, we have proposed a generic structure of fulvic acid from MS-MS analyses (PLANCQUE *et al.*, 2001) [26]. As it was explicitly written in the original paper from PLANCQUE *et al.* (2001), this proposition was based on the hypothesis that the majority of the extracted ions during the MS-MS fractionation were mono-charged ions, and that each mass peak represented a single molecule. If the first hypothesis seems to be well admitted (PICCOLO *et al.*, 2010), it has been demonstrated that the mass peaks are in fact the sum of several unresolved peaks (KUJAWINSKI *et al.*, 2002a; KUJAWINSKI *et al.*, 2002b). The humic substances’ mass spectra always show a bell-like repartition (Figure 3-1) with  $m/z$  between 100 and 1000 Da for fulvic acids and 100 and 3000 Da for humic acids. The number-averaged value of  $\overline{M}_n = 873 \text{ g mol}^{-1}$  and  $\overline{M}_w = 1228 \text{ g mol}^{-1}$  for Aldrich humic acid (cf. Figure 5-9a, page 79) [20].

The problem in comparing different molecular mass determination techniques is often linked to their inherent hypotheses. For instance HPSEC were calibrated either with proteins or with polymers (polystyrene sulfonate, PSS), which can induce a five-fold difference between the calculated molecular masses (BECKETT *et al.*, 1987). Recent development seem to show that some correlation between the intensity of the ESI signal and of PSS-calibrated HP-SEC (PEURAVUORI *et al.*, 2007). Furthermore, these molecular mass ranges are also in general agreement with the values obtained in vapour pressure osmometry (AIKEN & MALCOLM, 1987; CHIN *et al.*, 1994; PEURAVUORI & PIHLAJA, 1997; PEURAVUORI *et al.*, 2007), even slightly lower. Nevertheless, the description of several ten thousands atomic mass units (a.m.u) entities is clearly linked to the packed structure of proteins and is not at stake for humic substances.



**Figure 3-1. ESI-MS Mass spectrum in negative mode (120° C, 30 V) of a 150 mg L<sup>-1</sup> fulvic acid solution (Mol, Belgium), and proposed generic structure – from [26] © 2001 Wiley and Sons].**

### 3.2.2. Surface tension

In a general manner, the presence of humic substances in aqueous suspension induces the decrease of the surface tension ( $\gamma$ ), which is linked to the hydrophobic expulsion of molecules and to their repartition at the water-air interface (TANFORD, 1980; LYKLEMA, 1995a). The analysis of the variation of  $\gamma$  with concentration through the Gibbs equation,

$$\Gamma_{\max} = \frac{1}{n} \frac{d\gamma}{RT \ln C} \quad (3-1)$$

which allows estimating the minimal area  $A_{\min}$  occupied by a molecule at the interface.

$$A_{\min} = \frac{1}{\Gamma_{\max} N_a} \quad (3-2)$$

From the available values in the literature, one can see that  $A_{\min}$  values do share the same order of magnitude (Figure 3-3).

Table 3-1 presents a compilation of the  $A_{\min}$  values on Figure 3-3 and from the slopes of Figure 3-2. The concentrations of humic substances in mol L<sup>-1</sup> are obtained from the molecular mass of 873 g mol<sup>-1</sup> determined in ESI-MS for Aldrich extract [Supp. Info. of 20]. One can note that the value of the molecular mass does not have any influence on the value of the slope. Actually, for the low values of  $\gamma$ , the values of  $d\gamma/d\ln C$  are far too weak and are not considered in the linear regressions (CHEN & SCHNITZER, 1978; TERASHIMA *et al.*, 2004). Experiments at pH 6 on Aldrich, Suwannee River (IHSS), Leonardite (IHSS), and Gorleben (WOLF *et al.*, 2004) humic acids show a satisfactory correlation with the literature values [47]. The obtained diameter values from the areas of the nanometric dimension. These sizes are in general agreement with radii of gyration determination in small angle X-ray scattering (THURMAN *et al.*, 1982; AIKEN & MALCOLM, 1987).

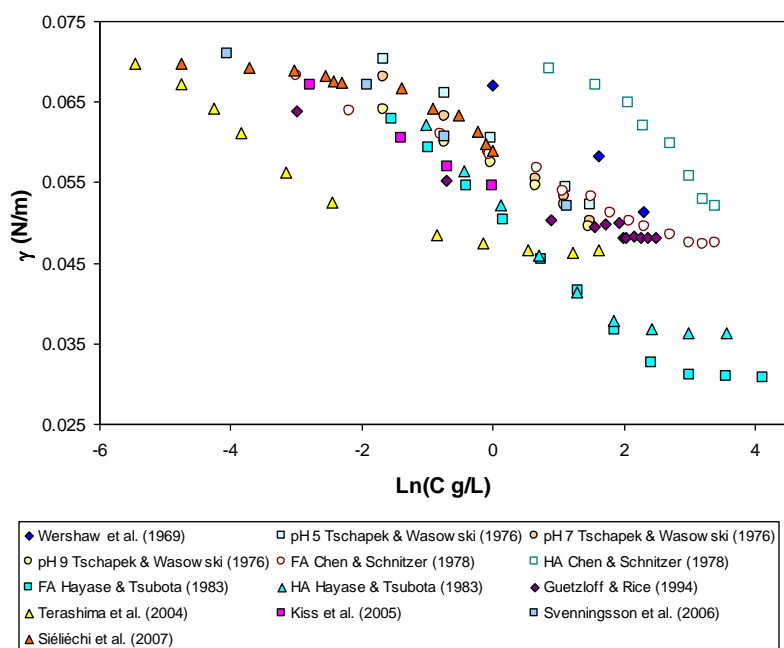


Figure 3-3: Compilation of surface tension values – adapted and completed from [53].

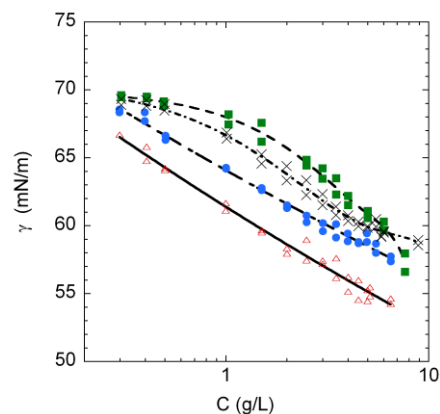


Figure 3-2. Surface tension (water-air) of aqueous HA solution: pH 6,  $[\text{NaNO}_3] = 0.1 \text{ mol L}^{-1}$ :  $\Delta$  PAHA,  $\bullet$  Gorleben,  $\times$  Leonardite,  $\blacksquare$  Suwannee River [47].

Table 3-1: Comparison of  $A_{\min}$  from the slope of  $\gamma = f(\text{Ln } c_{\text{HA}} \text{ g L}^{-1})$ .

Authors		pH	$A_{\min} \pm \sigma$ ( $\text{\AA}^2/\text{molecule}$ )	d (nm)
WERSHAW <i>et al.</i> (1969)	HA ?	?	$62.9 \pm 9.6$	
TSCHAPEK & WASOWSKI (1976)	HA brown coal	5	$70.4 \pm 3.2$	$0.95 \pm 0.04$
		7	$74.5 \pm 2.0$	$0.97 \pm 0.03$
		9	$92.3 \pm 4.4$	$1.08 \pm 0.05$
CHEN & SCHNITZER (1978)	FA sol	12.7	$96.5 (121 \pm 5)$	$1.24 \pm 0.04$
	HA sol	12.7	$40.4 (41.6 \pm 2.9)$	$0.73 \pm 0.14$
HAYASE & TSUBOTA (1983)	HA sediment	8	$47.8 \pm 1.7$	$0.78 \pm 0.03$
	FA sediment	8	$52.6 \pm 0.6$	$0.82 \pm 0.01$
GUETZLOFF & RICE (1994)	HA Aldrich	12.3	$126.9 \pm 10.8$	$1.27 \pm 0.11$
TUCKERMANN & CAMMENGA (2004)	HA Merck	?	$74.1 \pm 3.1$	
TERASHIMA <i>et al.</i> (2004)	HA	6	$63.1 \pm 2.0$	$0.90 \pm 0.08$
SVENNINGSSON <i>et al.</i> (2006)	SRFA (?)	?	$140 \pm 45$	
Purified Aldrich HA [47]		6	$103.3 \pm 3.0$	$1.15 \pm 0.03$
Leonardite HA [47]		6	$101.0 \pm 3.9$	$1.13 \pm 0.04$
Gorleben HA [47]		6	$115.1 \pm 2.5$	$1.21 \pm 0.03$
Suwannee River HA [47]		6	$80.9 \pm 0.4$	$1.01 \pm 0.06$

### 3.2.3. Atomic force microscopy (AFM)

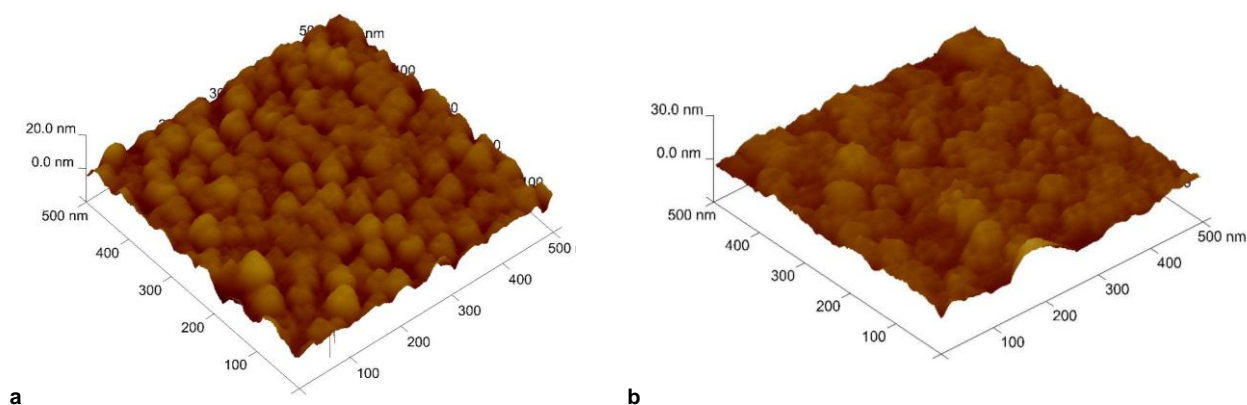
Atomic force microscopy allows the observation of height differences on a surface at the atomic level. In our case, it is necessary to observe the sample on an underlying surface, and to take care of the artefacts which may come from the pollution of the tip. Most of the time humic substances are deposited on the surface as a drop of solution, or adsorbed by soaking in a solution, rinsed and dried afterwards.



This can induce some biases:

- i. the deionised water rinsing, which implies an ionic strength shock that can desorb humic substances ([WENG \*et al.\*, 2007](#)) [[52](#)];
- ii. the entities which stay on the surface after rinsing are the more strongly adsorbed (chemisorbed), and the ones in weaker interactions are most probably carried away with the deionised water, when the lateral interactions are important in adsorption of humic substances ([OCHS \*et al.\*, 1994](#));
- iii. drying provokes a modification of the organisation of humic substances ([TAN, 1985](#); [REDWOOD \*et al.\*, 2005](#)). For all these reasons, an observation in liquid cell is desirable ([LEAD \*et al.\*, 2005](#)), even if it implies a high concentration and a high covering of the surface; heights can be then very difficult to interpret if the tip cannot have access to the underlying surface, and nanometric entities have been reported after deposition from diluted solution and drying ([BAALOUSHA & LEAD, 2007](#)), as well as greater objects in liquid cell ([PLASCHKE \*et al.\*, 1999](#)).

In order to have information on different type of objects, we have sampled humic substances solutions deposited on silicon wafer before and after rinsing with deionised water [[47](#)]. This allowed us to evidence different types of objects under different types of conditions. AFM images show non regular objects being composed of sub-entities. All the extracts do not show the same morphologies. The compactness of the objects seems to vary as a function of their origin since HA from Gorleben and Suwannee River, extracted from purely aquatic environment, are visually less compact compared to Aldrich and Leonardite HA, extracted from a peat and from soil, respectively. In either case, the smaller aggregates are nanometric and the larger ones are 50-100 nm (Figure 3-4). For Suwannee River fulvic acid, the AFM images show nanometric objects but no bigger aggregates. It seems that fulvic acids are composed of a heterogeneous mixture of small aggregates with no interactions between these aggregates. This is in accordance with the intermediate adsorption compartment of FA, relative to ionic strength, between simple organic molecules and humic acids [[52](#), and references therein].



**Figure 3-4. AFM images of Purified Aldrich (a) and Gorleben (b) humic acids samples – from [[47](#)].**



### 3.2.4. Small angle neutron and X-ray scattering (SANS, SAXS)

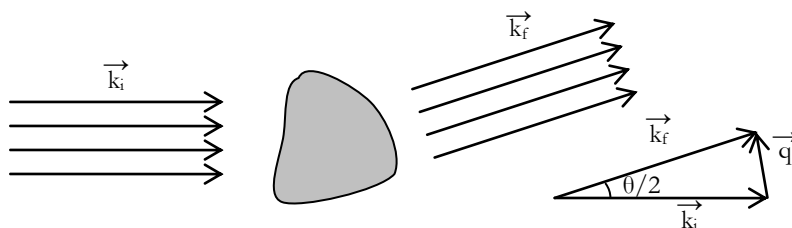
Small angle diffusion of neutrons (SANS) or X-rays (SAXS), allows estimating the organisation in a material or in solution. Briefly, when a material is exposed to a beam of incident vector  $\vec{k}_i$  and of wavelength  $\lambda$ , the scattered beam of vector  $\vec{k}_f$  is observed at angle  $\theta/2$  (COTTON, 1991). The diffusion vector  $\vec{q}$  is the sum of the incident and scattered vector and  $q$  is (Figure 3-5),

$$q = |\vec{q}| = |\vec{k}_i + \vec{k}_f| = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (3-3)$$

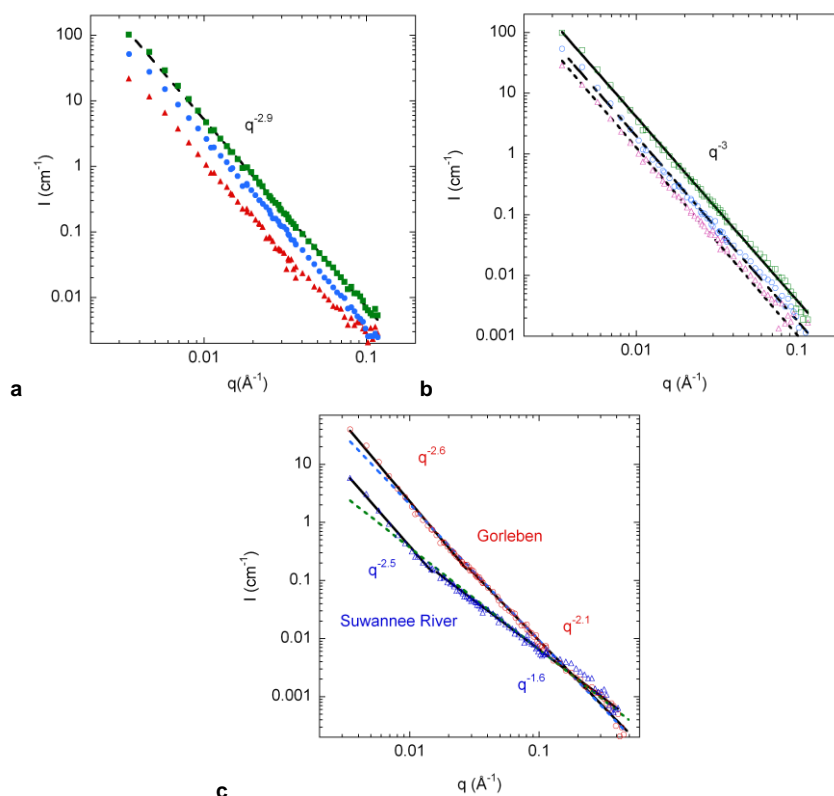
where  $n \approx 1$  in the case of neutrons. The unity of  $q$  is an inverse of a distance. From the Bragg's law, the relationship between the wavelength  $\lambda$  and angle  $\theta/2$  is,

$$\lambda = 2d \sin\left(\frac{\theta}{2}\right) \quad (3-4)$$

The characteristic distance range of the colloidal particles, *i.e.*, 2-200 nm, corresponds to  $q$  values of 0.3 to 0.003  $\text{\AA}^{-1}$ , and *small* angles from  $7^\circ$  to  $0.14^\circ$ .



**Figure 3-5. Schematic representation of the beam scattering by a particle.**



**Figure 3-6. SANS patterns of PAHA (a), LHA (b), SRHA and Gorleben HA (c) in  $\text{D}_2\text{O}$ , pH 5,  $I = 5 \text{ mM NaNO}_3$ . (a) and (b) for three different initial concentrations (squares)  $8 \text{ g L}^{-1}$  (circles)  $3 \text{ g L}^{-1}$  (triangles)  $1 \text{ g L}^{-1}$ , and (c) ( $\Delta$ ) SRHA and ( $\circ$ ) GoHyHA at  $8 \text{ g L}^{-1}$  [47]. Black lines are the fits obtained with the function  $A \cdot q^{-n}$  with two  $q$  range domain (i.e. a  $q_{\text{cut off}}$ ), the obtained value  $q^{-n}$  are indicated on the graph. The dashed lines are the fits obtained with only one  $q$  range domain for the function  $A \cdot q^{-n}$ .**

In the case of humic substances, the use of  $\text{D}_2\text{O}$  is mandatory to have a sufficiently high contrast compared to protons. Under our conditions (Laboratoire Léon Brillouin, Saclay, France), the relatively low neutron flux induces the necessity to use relatively high concentration of humic substances ( $C \geq 1 \text{ g/L}$ ), which are not quite representative of environmental conditions. All the works from the literature showed a linear dependence of  $\log_{10} I(q) = f(\log_{10} q)$ , with a slope  $n < 3$ , which exhibits a fractal organisation. From the low number of works, disparity of experimental conditions, and disparity of slopes it was not possible to propose a generic compartment. Henceforth, we proposed the complementary analyses of the SANS patterns of the samples which were already observed in surface tension and AFM [47]. As for the other works ([WERSHAW \*et al.\*, 1967](#); [LINDQVIST, 1970](#); [ÖSTERBERG & MORTENSEN, 1992, 1994](#); [ÖSTERBERG \*et al.\*, 1995](#); [TOMBÁ CZ \*et al.\*, 1997](#); [RICE \*et al.\*, 1999](#); [PRANZAS \*et al.\*, 2003](#); [DIALLO \*et al.\*, 2005](#)), representations of  $\log_{10} I(q) = f(\log_{10} q)$  showed a linear dependence, and evidenced a fractal organisation in suspension. In the  $q$  range – from  $3.44 \cdot 10^{-3}$  to  $4.92 \cdot 10^{-1} \text{ \AA}^{-1}$  in the reciprocal space, and *approx.*  $0.2\text{-}30 \text{ nm}$  in the real space –, the scattering objects are randomly organised. The awaited inflexion at low  $q$  value is not sufficient to have an estimation of the objects' limits. The random organisation can then be at place at larger scales.

From Figure 3-6, the origin of the humic extract does have an influence on the SANS signal. Two samples from terrestrial origin, *i.e.* extracted after alkaline extraction – Aldrich and Leonardite HA – the slopes are close to 3 (Figure 3-6a,b). The size of the aggregates is larger than 18 nm and the size of the smallest units is below 0.12 nm. The larger dimension is in agreement with dynamic light scattering results ([CACECI & BILLON, 1990](#); [CACECI & MOULIN, 1991](#); [SHINOZUKA & NIHEI, 1994](#); [PINHEIRO \*et al.\*, 1996](#); [WAGONER & CHRISTMAN, 1998](#); [RICE \*et al.\*, 1999](#); [MANNING & BENNETT, 2000](#); [PALMER & VON WANDRUSZKA, 2001](#)) [6] where objects between 60 and 500 nm are evidenced. The smaller dimension is in agreement with previous determination (*e.g.* cf. Table 3-1) with various techniques ([AIKEN & MALCOLM, 1987](#); [CHIN & GSCHWEND 1991](#); [CHIN \*et al.\*, 1994](#); [PEURAVUORI & PIHLAJA, 1997](#); [BOUBY \*et al.\*, 2002](#); [BAALOUSHA & LEAD, 2007](#)) [6,47]. The intensity being related to both concentration and contrast with solvent, the high scattering power of these two HA means that the formed aggregates are compact in agreement with the obtained scattering power law dimensions.

For two other samples from a more aquatic origin – Suwannee River (USA) and Gorleben (Germany) HA –, less intensity, much lower slopes, and change in slopes (Figure 3-6c) are indicating that the objects are smaller and less dense than the previous ones. For Gorleben HA, the scattering behaviour is modified for a typical length in real space around 25 nm while for SRHA the typical dimension is larger (*ca.* 42 nm). These dimensions are close to the typical values obtained by AFM for the smallest aggregates [47]. These two samples could be representative of mass fractal dimensions, which is in agreement with previous determinations ([ÖSTERBERG \*et al.\*, 1994](#); [ÖSTERBERG \*et al.\*, 1995](#); [RICE \*et al.\*, 1999](#)). One can also note that organic-containing sediment did not show either of these patterns ([JARVIE & KING, 2007](#))..

### 3.2.5. Dynamic light scattering (DLS)

DLS is based on the analysis of the intensity variation of the light scattered by a particle in motion.

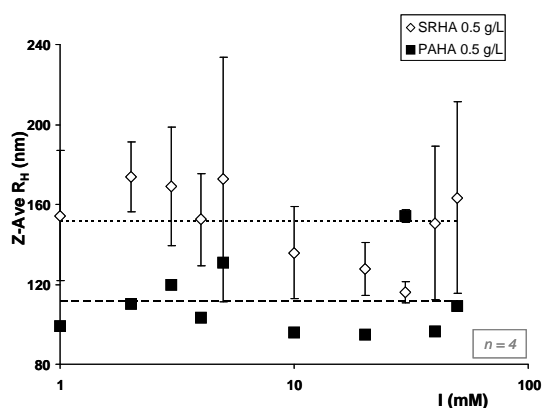
$$I = I_0 \frac{1 + \cos^2\theta}{2 r^2} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \left(\frac{D_H}{2}\right)^6 \quad (3-5)$$

with

$$D_H = 2R_H = 2 \frac{\kappa_B T}{6\pi\eta D}$$

The dependence in  $D_H^6$  implies that in a heterogeneous mixture the larger particles will scatter more intensely than the smaller ones. In the case of humic substances the range of observed sizes is from 60 to 500 nm ([CACECI & BILLON, 1990](#); [CACECI & MOULIN, 1991](#); [REID \*et al.\*, 1991](#); [SHINOZUKA & NIHEI, 1994](#); [PINHEIRO \*et al.\*, 1996](#); [WAGONER & CHRISTMAN, 1998](#); [RICE \*et al.\*, 1999](#); [MANNING & BENNETT, 2000](#); [PALMER & VON WANDRUSZKA, 2001](#)). In the same way, the size of the scattering entities of Aldrich and Suwannee River humic acids are about 100-200 nm [6]. The good quality data

for Aldrich HA indicate strongly cohesive entities, but the weak scattered intensity in the case of Suwannee River HA suggest poorly cohesive aggregates, as for SANS.



**Figure 3-7.** DLS-derived z-average  $R_H$  values for the HS samples (■ PAHA; ◇ SRHA II) as a function of ionic strength (1–50 mmol L<sup>-1</sup>) in sodium carbonate buffers, pH 10 [6 © 2012 Elsevier Ltd].

### 3.2.6. Capillary electrophoresis

Capillary electromigration techniques have been used to have access to size and mass distribution of humic substances from the analyses of the electropherograms (DUNKELOG *et al.*, 1997; SCHMITT *et al.*, 1997; SCHMITT-KOPPLIN & JUNKERS, 2003). Capillary electrophoresis allows using a large range of environmentally relevant physico-chemical conditions such as pH or ionic strength. Buffering of the medium is then mandatory. Characterisation are performed in silica capillary to minimize the electro-osmotic flow (CIAVATTA *et al.*, 1997). Adsorption properties of humic substances on silica [24] have to be taken into account nevertheless (FETSCH & HAVEL, 1998; FETSCH *et al.*, 1998), an buffering the solution at pH 10 with carbonate buffer – Na<sub>2</sub>CO<sub>3</sub>/CO<sub>2</sub>(g) – seem to be an adequate solution to minimize this possible bias (POKORNÁ *et al.*, 1999). The experimental set-up also allows evaluating diffusion coefficient through the TDA (TAYLOR, 1953; ARIS, 1956), which is relying on the detection of the dispersion of an analyte in a laminar flow (BELLO *et al.*, 1994; BELONGIA & BAYGENTS, 1997; D'ORLYÉ *et al.*, 2008); the Stokes radius  $R_H$  is then estimated.

Considering a mono-modal distribution, Aldrich humic acid, Suwannee River HA and FA are composed of 1.3, 1.2, and 0.9 nm objects, respectively (Figure 3-8), in agreement with other data (*vide ante*). But a closer inspection of the Taylor dispersion profiles indicates that one can account for a second population of a larger size. This is particularly marking in the case of Aldrich HA (Figure 3-8a), as a second larger size distribution ( $R_H \approx 10$  nm) accounts for about 10%; the smaller size distribution (90%) should be around 1 nm. For Suwannee River FA and HA, the bimodal distributions also show a better fit, but the correlation between parameters is much too high. The ionic strength influence, the value of which is supposed to strongly influence the size of the humic substances' aggregates, do not show any influence on  $R_H$  values (Figure 3-10). The nanometric size of the entities is once again confirmed.

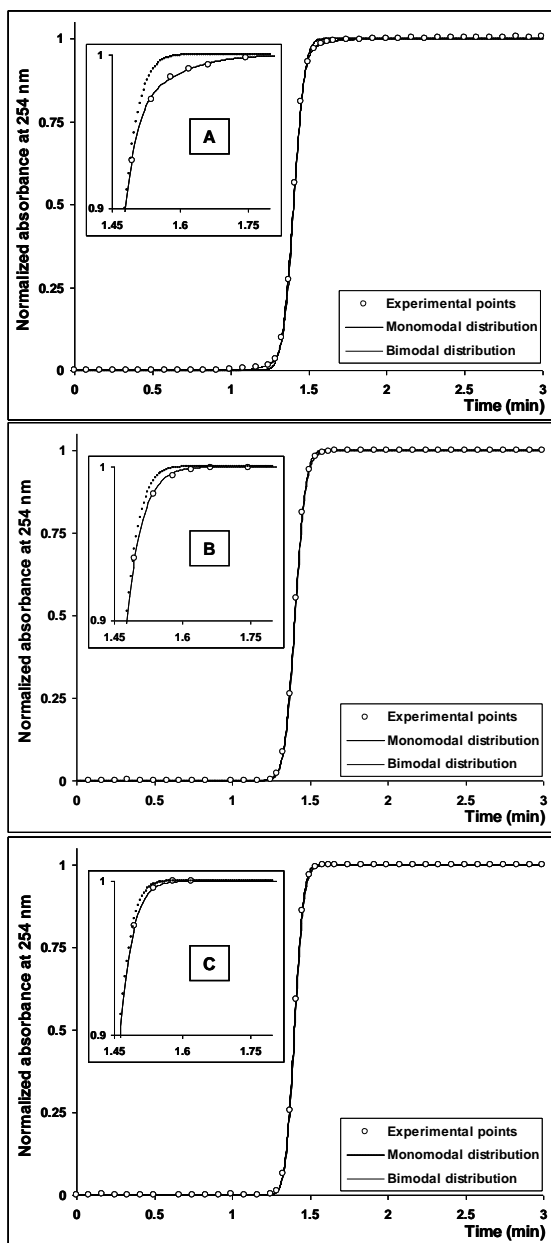


Figure 3-8. Experimental front concentration profiles (open circle; one tenth of the experimental points are represented for the sake of clarity) of HS samples (A- PAHA; B- SRHA II; C- SRFA II) at 0.5 g/L in a 20 mM Na<sub>2</sub>CO<sub>3</sub>/CO<sub>2</sub>(g) buffer (*I* = 50 mM), pH 10. Dotted and solid black lines are curves fitted to the analytical solution to the convection-diffusion equation assuming a mono-modal or bi-modal *D* distribution, respectively – from [6 © 2012 Elsevier Ltd.].

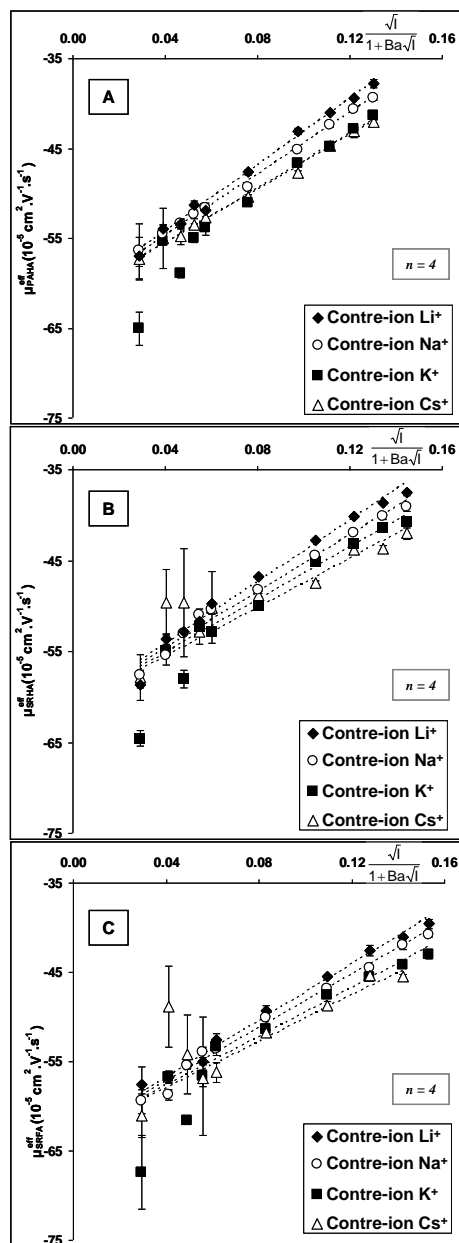
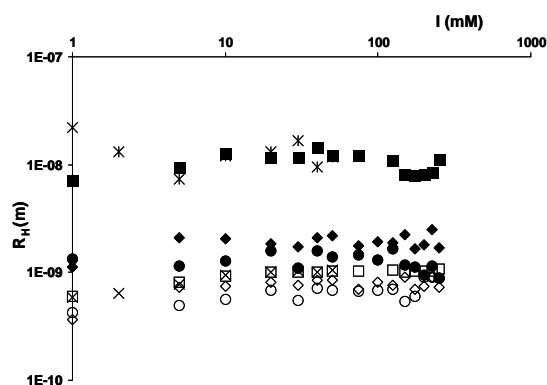


Figure 3-9. Electrophoretic mobilities of HS samples (7.A- PAHA; 7.B- SRHA II; 7.C- SRFA II) as a function of  $\sqrt{I}/(1 + Ba\sqrt{I})$  in carbonate buffers, pH 10, prepared with a variety of mono-valent cations chosen within the alkali-metal series ( $\blacklozenge$ Li<sup>+</sup>;  $\circ$ Na<sup>+</sup>;  $\blacksquare$ K<sup>+</sup>;  $\triangle$ Cs<sup>+</sup>) – from [6 © 2012 Elsevier Ltd.].



**Figure 3-10. Taylor dispersion analysis derived  $R_H$  values and distributions for the humic substances samples as a function of ionic strength in (i) 1–250 mmol L<sup>-1</sup> sodium carbonate buffers, pH 10 ( $\square$  PAHA;  $\diamond$  SRHA II;  $\circ$  SRFA II); (ii) 1–50 mmol L<sup>-1</sup> caesium carbonate buffers, pH 10 ( $\times$  PAHA). Full and open symbols represent the largest and smallest entities characterized in each bimodal distribution, respectively –from [6] © 2012 Elsevier Ltd].**

### 3.3. INTEGRATED VISION ON THE STRUCTURAL STUDIES

Confrontation between these different data, and with literature data, allows proposing an integrated vision of the humic substances' structure.

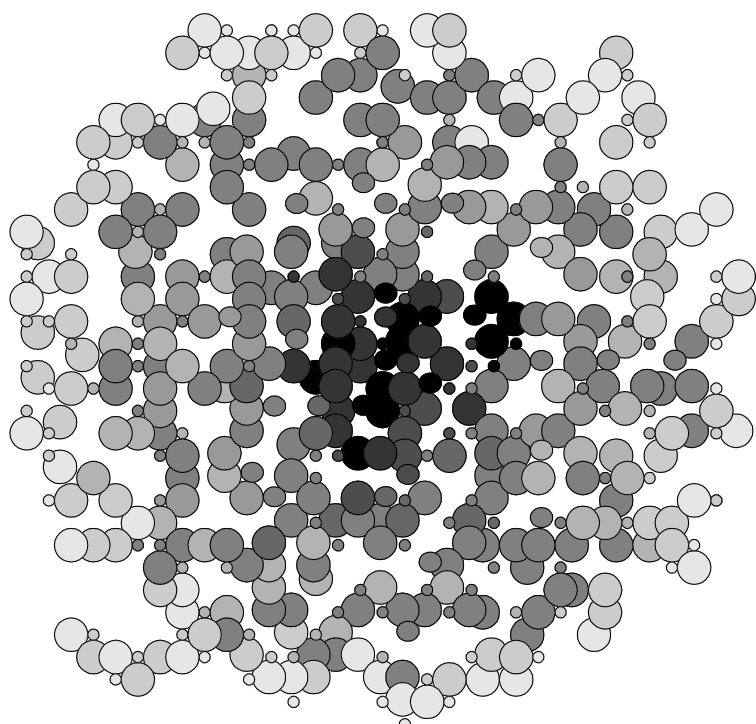
It seems clearly now that fulvic acids do not form aggregates bigger than a nanometric dimension. All the size determinations seem to be in accordance with this order of magnitude. Interactions between aggregates seem to be weak, but, as we will see it later on, sufficiently important to be weakly influenced by ionic strength when adsorbed on a mineral surface ([FILIUS \*et al.\*, 2000](#); [FILIUS \*et al.\*, 2003](#)) [[52](#) and references therein].

Humic acids show a different comportment. The measured sizes vary with the different techniques: from some nanometres in surface tension, AFM, SANS, and TDA – in accordance with osmometry –, up to some tens or hundreds of nanometres in AFM, and DLS. It seems then that HA are composed of heterogeneous mixtures of nanometric entities randomly organized, which are in turn randomly organized in larger entities.

It would be tempting to make a direct link between the compositions of the molecules analysed in ESI-MS and size determination. We must nevertheless not forget that mass spectroscopy techniques are closely linked to their ionisation mode, and to their ionisation efficiency. Moreover, as written earlier on, the MS-MS analyses were done on mass peaks [[26](#)], which were actually composed of several molecules ([KUJAWINSKI \*et al.\*, 2002a](#); [KUJAWINSKI \*et al.\*, 2002b](#); [THESE \*et al.\*, 2004](#)). Nevertheless, the combination of all these techniques should form the basis for a more advance analyses of the humic substances entities.

One can also remind that the size of about 1 nm does not stand for the simple molecules evidenced in [[26](#)] nor in [THESE \*et al.\* \(2004\)](#). As an example one can remind that a polyacrylic acid of  $\overline{M}_w = 1200$  Da shows a  $R_H$  of  $0.8 \pm 0.3$  nm ([BAIGORRI \*et al.\*, 2007](#)); this  $R_H$  is on accordance with the size of fulvic acid we have shown in TDA and with fractal “scale” reported in SAXS ([THURMAN \*et al.\*,](#)

[1982; AIKEN & MALCOLM, 1987](#)). Hence, even for the apparently simpler fulvic acid, the formation of aggregates of low molecular weight molecules seems to be a sound description. Figure 3-5 is an attempt to schematically visualize the general shape and organization of a humic acid aggregate, with the more hydrophobic entities regrouped inside the aggregate, creating hydrophobic cores, and the hydrophilic and amphiphilic entities regrouped on the outer rim of the aggregates.



**Figure 3-11. Schematic representation of a humic acid aggregate. The darker entities are the more hydrophobic – from [5].**

## 4. COMPLEXATION OF CATIONIC RADIONUCLIDES

The knowledge of the speciation of cationic radionuclides in solution is a prerequisite for an accurate modelling of their migration in natural systems. Speciation is partly controlled by natural organic matter, the structure of which is important to define a “thermodynamic standard state” of the fulvic acid, humic acid, and eventually natural organic matter entities. As we will see it through the chapter, the current knowledge on the structure of natural organic matter is far from being sufficiently sound to provide univocal answer(s). From all the cations of interest in the nuclear cycle are caesium(I), cobalt(II), strontium(II), lanthanides, as radionuclides –  $^{150}\text{Sm}$ ,  $^{152}\text{Eu}$ ... – as well as analogues of actinides(III) – plutonium, americium, and curium –, actinides(IV) – thorium, protactinium, uranium, neptunium, and plutonium –, actinides(V) – protactinium, neptunium, and plutonium –, and actinides(VI) – uranium, neptunium, and plutonium. Apart protactinium ([KIM et al., 1994](#); [MAES et al., 2011](#)), humic complexation of these elements has been widely studied during the last five decades. As we will see, the metal complexation by humic substances has been described through many models. I have proposed a compilation in an open CEA report [[53](#)], so I will only focus on the models that I have used, and will only mention the other models without entering into the details of their advantages and drawbacks. Amongst the different cations, particular emphasis will be given on alkaline metals [[6](#)], Co(II) [[19,82](#)], Eu(III) [[9,11,13,14,17,81](#)], Th,U,Pu(IV) [[12,18,21,22,24](#)], and U(VI) [[49,82](#)].

### 4.1. DIFFICULTIES IN THE ESTABLISHMENT OF A MODEL

There are several difficulties in establishing a model describing the complexation of cations by humic substances: heterogeneity of composition and operational definition of their extraction are one of the most evident ones. It comes out that a lot of models have been proposed, mostly strongly empiric and using extra-thermodynamic functions. From this a series of questions can be addressed.

#### 4.1.1. Is there a standard state?

One can argue that the definition of a standard state is currently out of reach. Humic substances are composed of a mixture(s) of thousands of molecules submitted to random aggregation mode(s). From this obstacle, the most usual way to represent humic complexation is through empirical models, based on more or less sound hypotheses. As noted by HUMMEL ([1997](#)) it ends with “*a véritable jungle*” of models, where the interaction constants are deeply linked to the basic foundations of the model and are sometimes difficult, or even impossible, to use outside the scope of their models. This statement is only an image of the reality that each and every scientist that works in this area of science has to deal with. Hence, to describe the experimental results within the analytical window of the method used, one has to use extra-thermodynamic concepts or functions to represent the inherent properties and heterogeneity of humic substances.



### 4.1.2. How to deal with the variation of properties?

The first problem that one has to face is the apparent increasing strength with pH of the metals complexation by humic substances, which can be related to an increasing ionization ([SCHNITZER & SKINNER, 1966, 1967](#)). The proton consumption, and thus the progressive ionization, can be monitored on different titration curves from the literature but no clear  $pK$  can be defined. Different strategies were used to address this point. When one uses the assumption that humic substances are an indiscernible mixture of complexing sites, the easiest one is to define an extra-thermodynamic function which represents this increasing interaction strength with pH. One has to define either an apparent complexation constant which 'varies' with pH and a finite number of sites, or a progressive ionization function with a constant interaction parameter. From the applicative point of view these two approaches are equivalent and can be classified as discrete site approaches. Another way to deal with this problem is to define different  $pK$ 's, or distribution of  $pK$ 's. Using these kinds of models, the complexing sites are not indiscernible but either belongs to families of sites part of a 'distribution of sites'. Extra-thermodynamic functions are still used at different degrees.

Another problem is the variation of apparent constants with the total concentration of metals. This is particularly sensitive in the case of actinides since their concentrations in solution are supposed to be low in the environment. This was shown by MOULIN *et al.* ([1992](#)) for Cm(III), CACECI ([1985](#)), HUMMEL *et al.* ([2000](#)), and MARSAC *et al.* ([2010](#)) – using a different modelling strategies – on other lanthanides and actinides. When total metal(III) concentration is of the micromolar order,  $\log_{10}\beta$  is of the order of 5-6; for lower concentration,  $\log_{10}\beta$  can be of the order of 9-10. This implies the account of another extra-thermodynamic function, or the use of more advanced models.

The influence of ionic strength on  $\log_{10}\beta$  is also an issue to address. Several authors noted a typical evolution of  $\log_{10}\beta$  as seen in Figure 4-1. We will discuss later about the evolution of the size of humic substances with ionic strength, the evolution of which is not straightforward to explain.

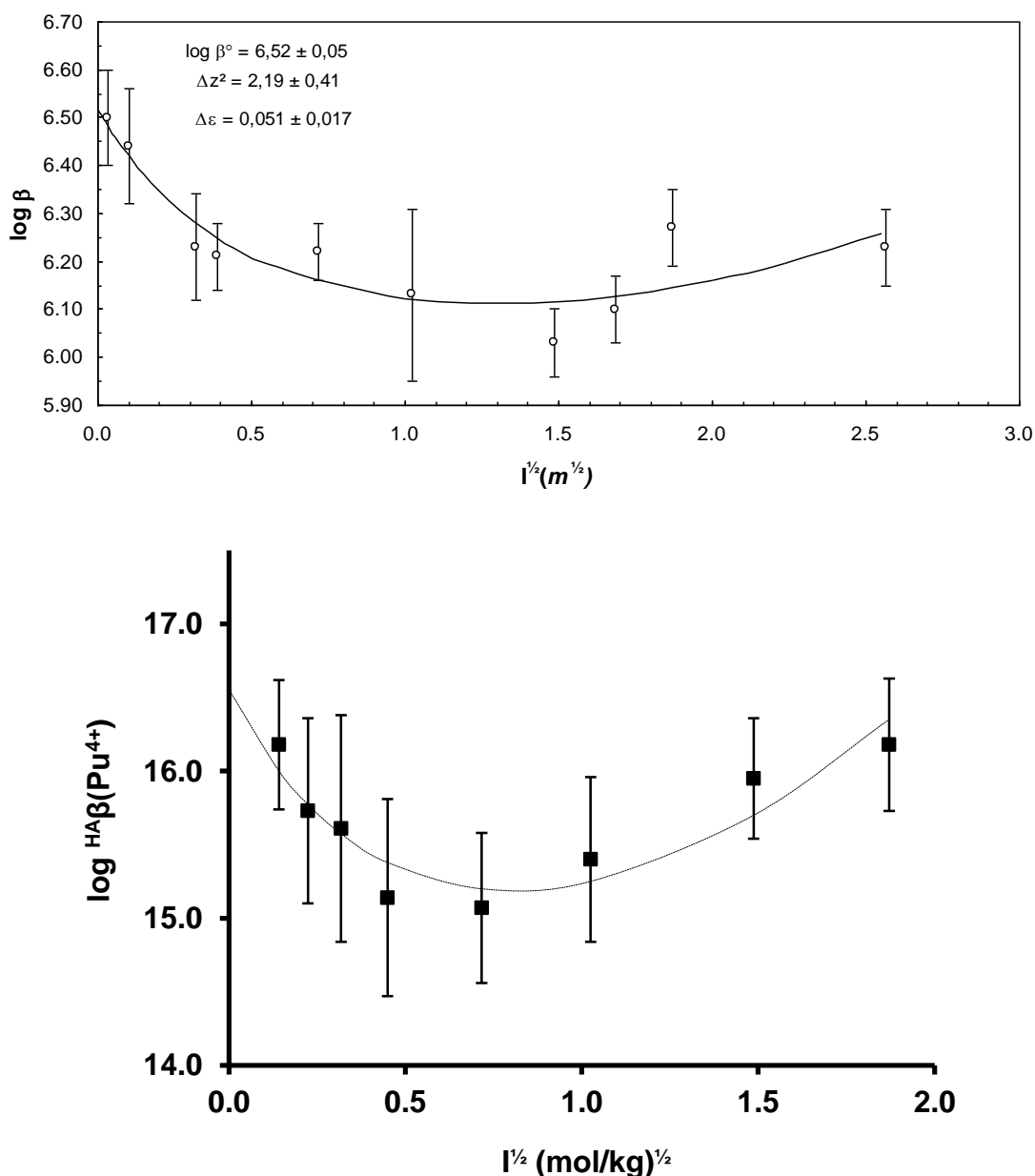


Figure 4-1. Evolution of formation constant of humic complexes vs. ionic strength for (a) Am,Cm(III) ([digitized from CZERWINSKI et al., 1996](#)), and (b) Pu(IV) [[12](#) © 2010 de Gruyter].

#### 4.1.3. How to deal with the charges?

As there is several experimental evidence of the formation of particles by humic substances, the establishment of a potential, either at the surface or inside the particles, has been proposed. This is another major difficulty. The description of a double or a triple layer is intimately linked to the definition of a surface of a hard sphere of a finite size ([DAVIS et al., 1978](#); [DAVIS & LECKIE, 1978b](#); [DZOMBAK & MOREL, 1990](#)): these descriptions have given satisfying fitting [[4](#)], even if the outer limits of the humic substances aggregates are not easily evidenced [[47](#)], and strongly depend on the analytical technique [[4](#)]. Some indications suggest that these particles are soft and permeable ([JONES & BRYAN, 1998](#); [DUVAL et al., 2005](#)). In the framework of these models, the description of the potential

is approximated by a square function, which gives a constant potential inside the particles: a DONNAN (1924) potential. Thus, a satisfactory fitting on either model could be deceiving and hide other biases.

#### 4.1.4. How to deal with units?

Another problem is the definition of the concentration of the humic substances, which is also an echo of the standard state definition. As seen previously, the definition of a molecular mass of these substrates is not univocal, and thus a molar concentration is very tricky to define. One of the most common ways is through size exclusion chromatography or mass spectrometry (SCHNITZER & SKINNER, 1966, 1967; RYAN *et al.*, 1983), which can induce biases (DE NOBILI & CHEN, 1999; PERMINOVA, 1999). Another way is to define through the titration and defining a molar concentration of reactive sites. Here again biases can take place as the analytical window –  $3 \leq \text{pH} \leq 9-10$  – may appear too narrow for some functionality that are supposed to be present in humic substances, as phenolic moieties, which also bears carboxylic functions. Unfortunately, this definition is not always used in the literature and a lot of authors have either defined their  $K$  values using mass concentration ( $\text{g L}^{-1}$ ), or  $K$  or  $\beta$  using a molar scale ( $\text{mol L}^{-1}$ ) but defined after a molecular mass defined in chromatography or mass spectrometry or even based on titration results.

#### 4.1.5. How to deal with competition?

Different types of models can be proposed:

- i. discrete models where sites are considered indistinguishable and can be activated as a function of a parameter – pH for instance –;
- ii. continuous models where distribution of sites possess acid-base properties.

Discrete models show the advantage of being simple and fast to implement. On the other hand, they are limited in their application. In natural systems, metals are always in competition with major cations –  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  – and other trace elements –  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ . Competition phenomena are often difficult to deal with using discrete models: some metals are in effective competition (KERNDORFF & SCHNITZER, 1980; ALBERTS & FILIP, 1998; PINHEIRO *et al.*, 1999; LIPPOLD *et al.*, 2007; LIPPOLD *et al.*, 2012), whereas others are not (HERING & MOREL, 1988; 1988; TIPPING *et al.*, 1988; BIDOGLIO *et al.*, 1991; PINHEIRO *et al.*, 2000; LIPPOLD *et al.*, 2007). These competition phenomena are occurring for higher concentrations than the ones awaited from the independent systems, and seem to depend on the concentration ratio between metals (MOULIN *et al.*, 1992; HELAL *et al.*, 1998; MANDAL *et al.*, 1999a; MANDAL *et al.*, 1999b; TIPPING *et al.*, 2002; KAUTENBURGER, 2009).

#### 4.1.6. Particular case of lanthanides and actinides

Speciation of actinides has been the subject of a particular attention and of advanced critical reviews. The most recognized ones are the ones commissioned by the Nuclear Energy Agency from the Organisation for Economic Cooperation and Development (GRENTHE *et al.*, 1992; SILVA *et al.*,

1995; RARD *et al.*, 1999; LEMIRE *et al.*, 2001; GUILLAUMONT *et al.*, 2003; BROWN *et al.*, 2005; GAMSJÄGER *et al.*, 2005; HUMMEL *et al.*, 2005; OLIN *et al.*, 2005; RAND *et al.*, 2009). From the very reason of their excellence, these data bases are necessarily incomplete [30,37,27], because they are contributing to the identification of unreliable and missing data. From the large number of data on actinides and lanthanides complexation by humic substances, I have proposed compilations of data to be used with different modelling strategies [9,12,18,21,22,24,53].

#### 4.1.7. Objectives of a modelling strategy

As it is difficult, and even impossible, to define a “humic object” which satisfies the definition of a species, the building of a model that describes the humic complexation must answer to a limited number of question, the formulation of which were the preceding sections heads, plus another one: are the answers to all these points really necessary to answer the question in the timeframe? The answer to this last question is not always easy as it enforces the scientific to “lock up doors”. Nevertheless, there doors must be locked up from sound scientific arguments that validates the use of simpler, or even operational, solutions. This implies the full understanding of the limits of application of these simpler models, their advantages and drawbacks.

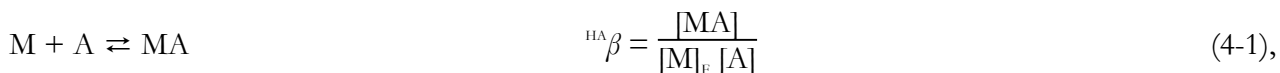
### 4.2. DISCRETE MODELS

Complexation properties of humic substances towards metals are known for long from a qualitative point of view, but the necessity to quantify these interactions could not rely on one established structure(s) or stoichiometry(ies) from the structural complexity and heterogeneity. A lot of authors have tried to adapt the law of mass action without making formal hypotheses on the charge of the complex. Given the wide variety of carboxylic, phenolic, or even enolic functions, the univocal interpretation of acid-base titration is very difficult as was the determination of formal thermodynamic constant for this functionality. This implied the proposition of apparent complexation constants between metals and humic substances, which can vary as a function of pH or as a function of metal concentration.

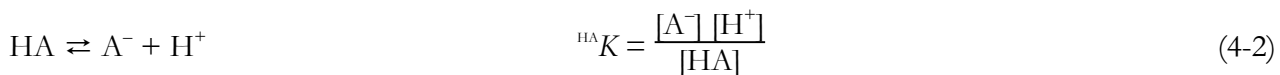
#### 4.2.1. General description

These kinds of models has been applied to a large number of cases, including d-transition elements – Ca(II), Pb(II), Cd(II) – or f-block elements. As a microscopic description of metal-HS interactions is not straightforward, a macroscopic description based on operational hypotheses is necessary. The most accepted approach is to consider that the association of complexation is achieved *via* a certain amount of available sites: the acid-base functions of the humic substances. Actually, under these hypotheses, humic substances are not considered as a ligand, but as a number of available sites that can participate in the complexation of a cation. The underlying paradigm is that humic substances are a mixture of independent “ligands”. The total number of sites is determined by potentiometric

titration. Under these hypotheses an adaptation of the law of mass action can be written, with an interaction *constant*,  ${}^{\text{HA}}\beta$ , which describes the following equilibrium (4-1):



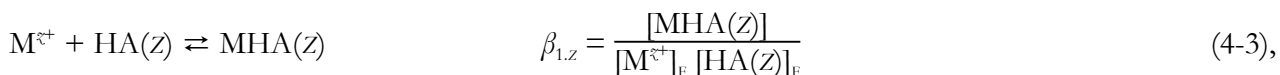
where charges are omitted and A is a site. Ionisation can be also described by a deprotonation constant.



From the preceding equations, it comes that *conditional constants* can be easily integrated in any modelling strategy, by analytical resolution or by integrating the *conditional constants* in software data bases. Nevertheless, as these parameters are operational and conditional, one must be cautious about their applicability outside of their parametric domain.

#### 4.2.2. The charge neutralization model (CNM)

The charge neutralization model (CNM) was proposed by KIM & CZERWINSKI (1996). The advantages, drawbacks, weaknesses and insufficiencies were discussed elsewhere (TIPPING, 2002) [53]. The complexation equilibrium between a cation  $\text{M}^{\text{c}+}$  and the available sites of natural organic matter supposes the maximum consumption of  $\text{z}$  sites to neutralize the charge of the metal. The equilibrium comes,



where  $[\text{HA}(\text{Z})]_{\text{F}}$  is the free concentration of humic sites in solution,  $[\text{MHA}(\text{Z})]$  the concentration of metal-humic complex, and  $[\text{M}^{\text{c}+}]_{\text{F}}$  is the concentration of free  $\text{M}^{\text{c}+}$  in solution. The concentration in free humic sites in solution  $[\text{HA}(\text{Z})]_{\text{F}}$  is not straightforward to calculate. Besides, the total concentration of humic sites can be estimated from the proton exchange capacity (PEC eq[mol]  $\text{g}_{\text{HA}}^{-1}$ ) by potentiometric titration. Under this formalism, the humic sites that are participating in the complexation exactly neutralize the charge of the metal  $\text{M}^{\text{c}+}$ . The total concentration of humic sites  $[\text{HA}(\text{Z})]_{\text{T}}$ , can be defined as,

$$[\text{HA}(\text{Z})]_{\text{T}} (\text{mol}_{\text{site}} \text{L}^{-1}) = \frac{C_{\text{HA}} (\text{g} \text{L}^{-1}) \times \text{PEC} (\text{mol}_{\text{site}} \text{g}^{-1})}{\text{z}} \quad (4-4),$$

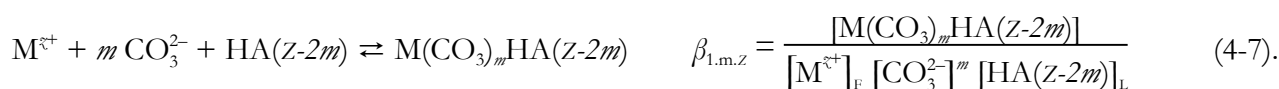
where  $C_{\text{HA}}$  is the total mass concentration of humic acid ( $\text{g} \text{L}^{-1}$ ). The concentration  $[\text{HA}(\text{Z})]_{\text{T}}$  can be presented as the maximum concentration in metal of charge  $\text{z}$  that can be neutralised by the introduced humic acid.

Actually, this maximum concentration is never attained. As in other more simplistic cases, the hypothesis of a maximum loading capacity (LC) for the metal cation  $M^{\kappa+}$  is used. This  $LC(Z)$  is defined as the available fraction of humic sites that can be effectively engaged in the complexation reaction,

$$LC(Z) = \frac{[MHA(Z)]}{[HA^*(Z)]_T} = \frac{\varkappa [M^{\kappa+}]^*}{PEC \times C_{HA}} \quad (4-5)$$

where  $[MHA(Z)] = \varkappa [M^{\kappa+}]^*$ , represents the maximum concentration of cation  $M^{\kappa+}$  which can be implied in the complexation reaction for a humic substance sample.

In order to monitor the fact that humic complexation keeps on increasing when hydrolysis of metals is taking place, the formation of mixed complexes has been included. The cumulative reactions are written as following.



One must also note that  $LC(Z)$  is not accessible under these hypotheses as determinations are performed as a function of  $\log_{10}[OH^-]$  or of  $\log_{10}[CO_3^{2-}]$ . Authors consider either that  $LC(\varkappa) = 1$ , from the pH values characteristic of these mixed complexes for lanthanides and actinides(III), or use an hypothetical ionisation of  $HA(II)$  in the case of uranium(VI) (ZEH *et al.*, 1997). Another possibility is to use  $LC(II)$  for  $AnOHAH(II)$ , or  $LC(I)$  from MARQUARDT & KIM (1998) on  $NpO_2^+$  for  $MOHHA(I)$ . This analogy seems to be justified in the case of Pu(IV) at pH 4 when  $Pu(OH)_3^+$  is major in solution [12].

### 4.2.3. Alkaline metals

The interactions of alkaline metals and humic substances is relatively weak compared to other cations, in particular caesium (SHABAN & MACÁŠEK, 1998). It seems that the inhibition of  $Cs^+$  adsorption on minerals in the presence of natural organic matter is more a consequence of a masking of adsorption sites that to a direct interaction with humic substances (VIDAL & RAURET, 1993; DUMAT & STAUNTON, 1999; RAJEC *et al.*, 1999; RIGOL *et al.*, 2002), which seems weak and non-specific. The interaction seems also to occur with the fraction of low molecular mass (RAJEC *et al.*, 1999). Nevertheless, as for other organic ligands, there is a possible interaction; only few reliable data are available. We have shown that there is a significant evolution of the electrophoretic mobility within the alkaline series, the value of which increases from  $Li^+$  to  $Cs^+$  – see Figure 3 from [6]. The inverse effect was expected because the alkaline cation mobilities are increasing from  $Li^+$  to  $Cs^+$ . The relaxation effect should be more important and decrease the mobility of humic substances entities

([NIELEN, 1991](#)). The solvent flux induces the counter-ions electromigration in the opposite direction to humic substances. This induces a retardation force, the intensity of which will depend on the nature of the counter-ion. As was described by MAUERHOFER *et al.* ([2003](#)), the low charge density alkaline cations ( $\text{Cs}^+$ ,  $\text{K}^+$ ), have a less organized hydration sphere than the high charge density alkaline metals ( $\text{Li}^+$ ,  $\text{Na}^+$ ). The friction effect on the hydration spheres should be less important for the former than for the latter. Low charge density cations are described as “structure breakers”, whereas high charge density cations are described as “structure makers” ([BÉRUBÉ & DE BRUYN, 1968](#)). If the friction effect is more important than the retardation effect, the electrophoretic mobility is then increasing from  $\text{Li}^+$  to  $\text{Cs}^+$ . We have seen that the humic substances entities can be considered, as a first approximation, as hard sphere, on the size of which ionic strength does not have any influence. One can also think the electrophoretic mobility increase is directly linked to a decrease of the association between the alkaline counter-ion and the humic substances entities. In natural water,  $\text{Na}^+$  and  $\text{K}^+$  concentrations are far more important than  $\text{Cs}^+$ .

The  $\log_{10}^{\text{HA}}\beta$  determined from the electrophoretic mobilities – see Table 3 in [[6](#)] – are of the same order of magnitude, but are decreasing from  $\text{Li}^+$  to  $\text{Cs}^+$ . Hence, for a radioactive isotope of  $\text{Cs}^+$  ( $^{134,137}\text{Cs}$ ), the competition with  $\text{Na}^+$  and  $\text{K}^+$  is not favourable from every point of view of the law of mass action, *i.e.*  $\log_{10}^{\text{HA}}\beta$  and the concentration ratio between cations. Interestingly,  $\log_{10}\beta(\text{Li}^+)$  for polyacrylic acid ([GREGOR & FREDERICK, 1957](#)) is directly comparable to the humic substances values.

#### 4.2.4. Europium(III)

Europium is a lanthanide that is often considered as a chemical analogue of the actinides(III), as Pu,Am,Cm(III). It is particularly justified in the case of oxygenated ligands. The first hydrolysis of these cations is occurring for pH values close to neutrality ([FANGHÄNEL \*et al.\*, 1994](#); [HUMMEL \*et al.\*, 2002](#); [GUILLAUMONT \*et al.\*, 2003](#)).<sup>\*</sup> I proposed a compilation of  $\log_{10}\beta$  values for these elements [[53](#)]. As noted earlier (cf. § 4.1.2, page 34), the  $\log_{10}\beta$  value, in the case of undistinguishable discrete sites, is strongly dependant on the concentration of metals ([CACECI, 1985](#); [MOULIN \*et al.\*, 1992](#)):  $10 \leq \log_{10}\beta \leq 6$  when  $-9 \leq \log_{10}([\text{M(III)}] \text{ mol L}^{-1}) \leq -5$ . Using this kind of simplistic, but fast, models we have proposed a value of  $\log_{10}^{\text{HA}}\beta = 6.7 \pm 0.7$  at pH 5, and  $[\text{Eu(III)}]_{\text{T}} = 10^{-5} \text{ mol L}^{-1}$ , for a vertisol humic acid [[9](#)], perfectly in agreement with other data [[53](#)].

#### 4.2.5. Actinides(IV)

These works have been done during the 4<sup>th</sup> [[75,77](#)],<sup>†</sup> 5<sup>th</sup> [[73](#)],<sup>‡</sup> and 6<sup>th</sup> [[62-64,67,70](#)]<sup>§</sup> research and development FrameWork Program from the European Economic Community.

<sup>\*</sup>  $\text{M}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{MOH}^{2+} + \text{H}^+$ ,  $\log_{10}^*\beta^{\circ}_1(\text{Eu}^{3+}) = -7.64$ ,  $\log_{10}^*\beta^{\circ}_1(\text{Pu}^{3+}) = -6.9$ ,  $\log_{10}^*\beta^{\circ}_1(\text{Am}^{3+}) = -7.2$ ,  $\log_{10}^*\beta^{\circ}_1(\text{Cm}^{3+}) = -7.6$

<sup>†</sup> Effect of humic substances in the migration of radionuclides: complexation and transport of actinides (HUMICS)

<sup>‡</sup> Humic substances in performance assessment of nuclear waste disposal: actinide and iodine migration in the far-field (HUPA)

<sup>§</sup> Fundamental processes of Radionuclide Migration (FUNMIG)



Under the conditions of a deep geological disposal of radioactive wastes, the redox potential is awaited to be highly reductive ([DE CRAEN \*et al.\*, 2004](#); [GAUCHER \*et al.\*, 2006](#); [GAUCHER \*et al.\*, 2009](#)). Redox sensitive actinides should be mainly under the +IV state. In more oxidant media, humic substances are known to promote the reduction of these sensitive elements. If the reduction of plutonium(VI) and (V) in plutonium(IV) and (III) in the presence of humic substances is rather fast ([NASH \*et al.\*, 1981](#); [SANCHEZ \*et al.\*, 1985](#); [ANDRÉ & CHOPPIN, 2000](#)), it is sufficiently slow in the case of reduction of neptunium(V) to neptunium(IV) ([KIM \*et al.\*, 1994](#); [ZEH \*et al.\*, 1999](#)) to permit the study of  $\text{NpO}_2^+$  complexation by humic substances [[53](#) and references therein]. No spontaneous reduction has been observed for uranium(VI) under laboratory conditions. Only the use of synthetic extracts containing catechol ([SACHS \*et al.\*, 2004](#)), the hydrothermal degradation products of wood in flooded mines ([ABRAHAM \*et al.\*, 1999a](#); [ABRAHAM \*et al.\*, 1999b](#); [BARANIAK \*et al.\*, 1999](#); [ABRAHAM, 2002](#)), or bacterial reduction ([GU \*et al.\*, 2005](#)), have been shown to induce the reduction to uranium(IV).

It is difficult to obtain data on actinides(IV) knowing the very low solubility of  $\text{An}(\text{OH})_4(\text{s})$  or  $\text{AnO}_2$  solids ([GUILLAUMONT \*et al.\*, 2003](#); [RAND \*et al.\*, 2009](#)), the propension to form colloidal particles ([ALTMAIER \*et al.\*, 2004](#)), and the very important adsorption properties on a large selection of materials ([RYDBERG & RYDBERG, 1952](#)). Hydrolysis of  $\text{An}^{4+}$  cations is extensive and occurs from pH lower than 3 for  $\text{Th}(\text{IV})^*$  ([RAND \*et al.\*, 2009](#)), and lower than 1 for  $\text{U/Np/Pu}(\text{IV})^\dagger$  ([GUILLAUMONT \*et al.\*, 2003](#)).

#### 4.2.5.1. Thorium(IV)

Even if thorium(IV) has no f-electrons, the chemical analogy with the other actinides(IV) complexation by oxygenated functions has not been contradicted. Some preliminary precautions are nevertheless needed when complexation constants are estimated, particularly concerning the differences between thermodynamic data, particularly the hydrolysis constants.

The oldest data on humic complexation of  $\text{Th}(\text{IV})$  are going back in the late seventies ([IBARRA \*et al.\*, 1979a](#); [NASH, 1979](#); [NASH & CHOPPIN, 1980](#)), in the mid-nineties ([TAO & GAO, 1994](#)) and more recently [[18,21,24,64](#)], [HELAL \(2007\)](#) and [BENEŠ \(2009\)](#). The experiments from [MURPHY \*et al.\* \(1999\)](#) on a marine natural organic matter extract can be compared from an informative point of view. On the other hand, the data from [HELAL \*et al.\* \(2005\)](#) are difficult to use as they are presented on unreadable graphs. The major part of these studies are regrouped in a pH range lower than 6.

We had obtained data on three different systems in a pH range between 3 and 9.2:

- i. a competitive system  $\text{Th}/\text{HA}/\text{SiO}_2$ , where the non-adsorption of HA on  $\text{SiO}_2$  is checked [[24](#)];

---

\*  $\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ThOH}^{3+} + \text{H}^+$   $\log_{10}^* \beta^{\circ}_1 = -2,5$

†  $\text{An}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{AnOH}^{3+} + \text{H}^+$   $-0,6 \leq \log_{10}^* \beta^{\circ}_1 \leq 0,6$



- ii. a colloidal SiO<sub>2</sub>-grafted humic acid [[18,21,64](#)]\*, the synthesis of which is described in SZABÓ *et al.* ([1990](#));
- iii. by ultrafiltration of a humic acid suspension [[18](#)].

All these independent studies can from the basis of a compilation to establish an operational relationship describing humic complexation of Th(IV) in a wide parametric space, including the available raw data from IBARRA *et al.* ([1979a](#)) and BENEŠ ([2009](#)). The data from the Nash's PhD thesis ([NASH, 1979](#); [NASH & CHOPPIN, 1980](#)) are included for comparison but are not directly included.† In the same way, the data from HELAL ([2007](#)), the log<sub>10</sub><sup>HA</sup>β values of which are available but not the raw data, are not included and used as comparison. One can propose a linear relationship (Figure 4-2),

$$\log_{10}^{\text{HA}}\beta = (2.69 \pm 0.13) \text{pH} - (2.23 \pm 0.95) \quad (4-8)$$

with a 95% uncertainty of 2.1 on log<sub>10</sub><sup>HA</sup>β at the centre of the regression. The other data from literature are satisfactorily distributed within the confidence hyperbole, with the exception of some data from NASH & CHOPPIN ([1980](#)).

A deeper analysis can evidence changes of slopes, particularly for pH values higher than 6.5. Actually, as log<sub>10</sub><sup>HA</sup>β values were corrected from the Th(IV) hydrolysis, the changes of slopes are imposed by the numerical treatment. This corresponds to the following equilibrium, using the hydrolysis data from NECK & KIM ([2001](#)).

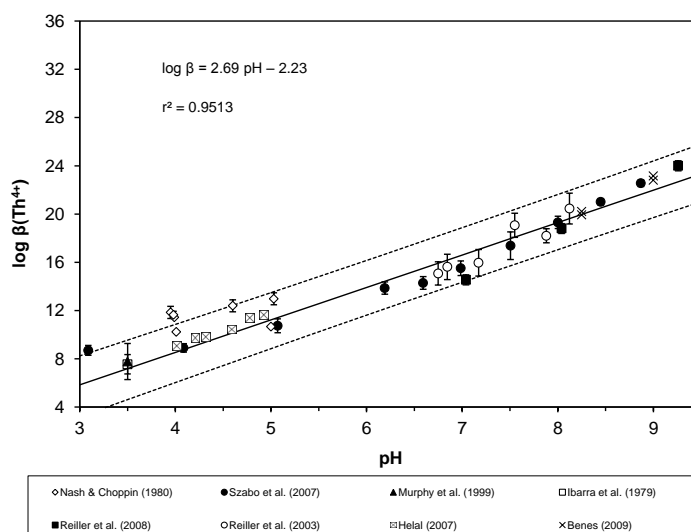


BENEŠ ([2009](#)) proposed other data at pH 10-11. They are fairly well aligned with a slope of +4 with other data above pH 6.5, but were obtained for pH values where alkaline hydrolysis of humic substances could occur ([KUMKE \*et al.\*, 2001](#)).

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\* In collaboration with the National Research Institute for Radiobiology and Radiohygiene « Frédéric Joliot-Curie » from Budapest, OSSKI, [http://www.osski.hu/index\\_en.php](http://www.osski.hu/index_en.php)

† These data were obtained in liquid-liquid extraction in 1 M acetate media which complexes dominates the Th(IV) speciation. The authors have adjusted their 1 M data to 0.1 M using a modified Debye-Hückel expression, which is not directly comparable to the Davies expression— see discussion in [[18](#)]



**Figure 4-2. Compilation of humic complexation data of thorium(IV) following a discrete model. The regression is done on data from IBARRA *et al.* (1979a), REILLER *et al.* [18,24], SZABÓ *et al.* [21], and BENEŠ (2009), using hydrolysis data from NECK & KIM (2001). Other data are given for comparison.**

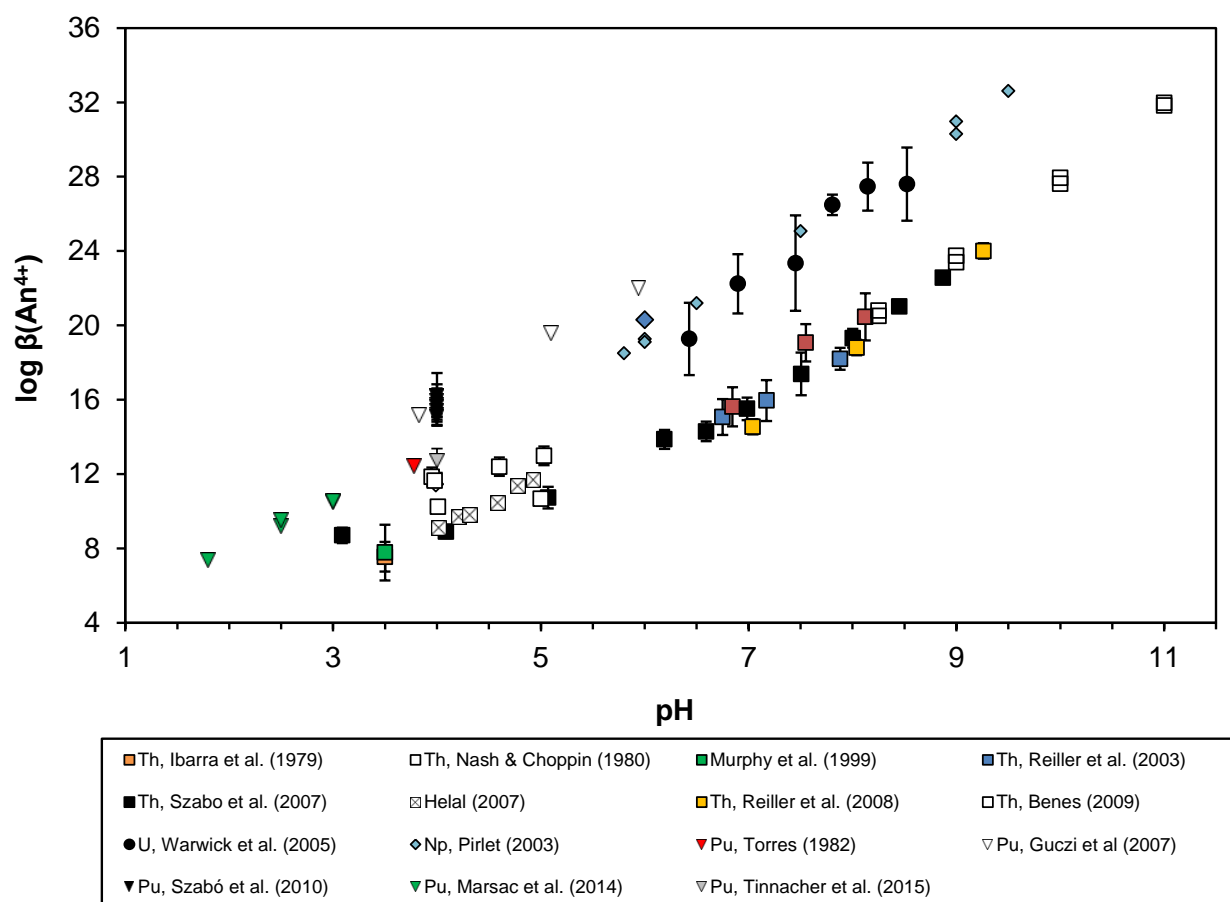
#### 4.2.5.2. Uranium(IV), neptunium(IV), and plutonium(IV)

Experimental data on uranium(IV) complexation by humic substances are even more difficult to obtain. The only available data are from LI *et al.* (1980) and WARWICK *et al.* (2005). The former are biased from over saturation respective to uranium(IV) at pH 6:  $0.1 \leq [U]_{\text{total}} \text{ mg L}^{-1} \leq 10$  being  $0.42 \leq [U]_{\text{total}} \mu\text{mol L}^{-1} \leq 42$  when the maximum solubility is  $3.16 \text{ nmol L}^{-1}$ : they can only be considered as comparison. We have corrected the data from WARWICK *et al.* (2005) in REILLER *et al.* [18].

Neptunium shows four oxidation states in water. If KIM *et al.* (1994) and ZEH *et al.* (1999) observed the slow reduction from Np(V) to Np(IV), the only quantitative study on neptunium(IV) is available in the PhD thesis of PIRLET (2003), which has not been published elsewhere, except a communication in Migration 2003 conference (PIRLET & DELÉCAUT, 2003). These data can be treated following a simple discrete model Figure 4-3. The difference with the Th(IV) data mainly comes from the difference between the hydrolysis and solubility constants. Coherence between these data and the ones on uranium(IV) is worthy to notice as the thermodynamic constants are comparable (GUILLAUMONT *et al.*, 2003).

Plutonium also shows a rich solution chemistry with four stable oxidation states in water [31,54] (GUILLAUMONT *et al.*, 2003). The humic complexation of plutonium in general (ERIKSSON *et al.*, 2001), and of Pu(IV) in particular has often been considered important, even if there were only few data available. Some data were available in the Richard Torres' PhD (TORRES, 1982) that permit an estimation of  $\log_{10} {}^{\text{HA}}\beta(\text{Pu}^{4+}) = 12.5$  at pH = 3.78. CZERWINSKI & KIM (1997) estimated in the framework of the CNM that  $\text{Pu}(\text{OH})_3\text{HA}(t)$  should have of value of  $\log_{10} \beta_{1.3,t} \approx 56.4$  – which gives

$\log_{10} {}^{\text{HA}}\beta(\text{Pu}^{4+}) \approx 38.6$  in a discrete site model,\* under the hypothesis that 90% of Pu(IV) were under the form of humic complex in natural waters. Dedicated experiments with SiO<sub>2</sub>-grafted humic acids gave values of  $15.2 \leq \log_{10} {}^{\text{HA}}\beta(\text{Pu}^{4+}) \leq 22$  in the interval  $3.8 \leq \text{pH} \leq 5.9$  (Figure 4-3) [12,67]. The very recent results from MARSAC *et al.* (2014) and TINNACHER *et al.* (2015) are also in excellent agreement with our previous estimation. The linear extrapolation of these data to pH 8 gives  $\log_{10} {}^{\text{HA}}\beta(\text{Pu}^{4+}) = 28.8 \pm 0.2$  and  $\log_{10} {}^{\text{HA}}\beta_{1,4,I} = 52.4$ , which is in fair agreement with the estimation of CZERWINSKI & KIM (1997). Coherence with data on U(IV) and Np(IV) is fair as the hydrolysis and solubility data are also comparable.



**Figure 4-3. Compilation of humic complexation data of actinides(IV) following a discrete model. Thermodynamic data from RAND *et al.* (2009) for Th(IV) and GUILLAUMONT *et al.* (2003) for U/Np/Pu(IV).**

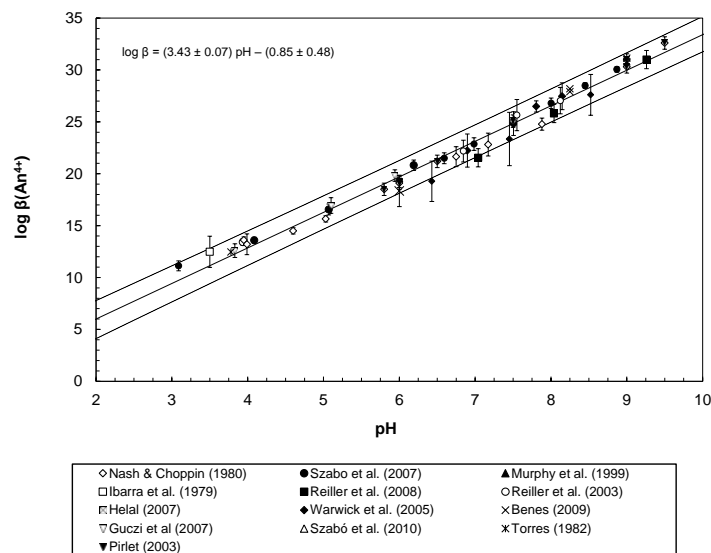
#### 4.2.5.3. Generalisation of analogy between actinides(IV)

The establishment of the operational relationship on Th(IV) can also be done on U(IV) as in [18] (Figure 4-4). Data from HELAL (2007) for Th(IV), from PIRLET (2003) for Np(IV), and from MARSAC *et al.* (2014) and TINNACHER *et al.* (2015) for Pu(IV) were not available at the time when reference [18] was written, but can be integrated in the relationship. For the establishment of this relationship all the raw data are corrected using the U(IV) hydrolysis (NECK & KIM, 2001).

\*  $\log {}^{\text{HA}}\beta \approx 56,4 - 3 \log(\text{OH}^-) = 56,4 - 3 \log(1,28 \cdot 10^{-6})$  à pH 8 et 0,1 mol.L<sup>-1</sup>

$$\log_{10} {}^{\text{HA}}\beta(\text{An}^{4+}) \approx \left[ 3.43 + \log_{10} \left( \frac{\alpha_{\text{An(IV)}}}{\alpha_{\text{U(IV)}}} \right) \right] \text{pH} - \left[ 0.85 + \log_{10} \left( \frac{\alpha_{\text{An(IV)}}}{\alpha_{\text{U(IV)}}} \right) \right] \quad (4-10)$$

$$\alpha = 1 + \sum_n \beta_n [\text{L}]^n$$



**Figure 4-4.** Comparison of the  $\log_{10} {}^{\text{HA}}\beta(\text{An}^{4+})$  values for different actinides corrected from U(IV) hydrolysis (NECK & KIM, 2001): U-Aldrich HA, and U-Boom Clay HA (WARWICK *et al.*, 2005) corrected in [18]; Th-SiO<sub>2</sub>-Aldrich HA [24]; Th-SiO<sub>2</sub> [18,21,64]; Pu-SiO<sub>2</sub>-HA [18,67]; Th-Aldrich HA, Lake Bradford HA, and IHA (NASH & CHOPPIN, 1980); Th-SRHA (MURPHY *et al.*, 1999); Th-Aldrich HA [18]; Pu-Lake Bradford HA (TORRES, 1982); Np-Boom Clay HA (PIRLET, 2003); and Th-HA (BENEŠ, 2009).

The correlation is satisfactory regarding the varying origin of the data. This relationship can be easily transposed to Np(IV) and Pu(IV) using the *ad hoc* hydrolysis and solubility data, *via* the RINGBÖM (1963) coefficient  $\alpha$  at each pH value, with an increasing uncertainty. The recent data from SASAKI *et al.* (2012) on Th(IV) and Pu(IV), as well as MARSAC *et al.* (2014) on Pu(IV) also fall into this correlation.

It is worthy to notice anyway that above a critical concentration, the formation of colloids occurs within the HS' structure (MARSAC *et al.*, 2014), which could explain the lack of, or weak, influence on the solubility of M(IV) metals, including Th(OH)<sub>4</sub>, observed at pH ≤ 4 (ANTONIOU & PASHALIDIS, 2014; PRODROMOU *et al.*, 2014). As observed otherwise, HS act as inhibitors of crystallization (HOCH *et al.*, 2000), which reduces the size of *e.g.* Th(OH)<sub>4</sub> crystallites (PRODROMOU *et al.*, 2014). I would suggest that it is not directly linked to the complexation mechanism of M(IV), but rather to structural issues that we could discuss later.

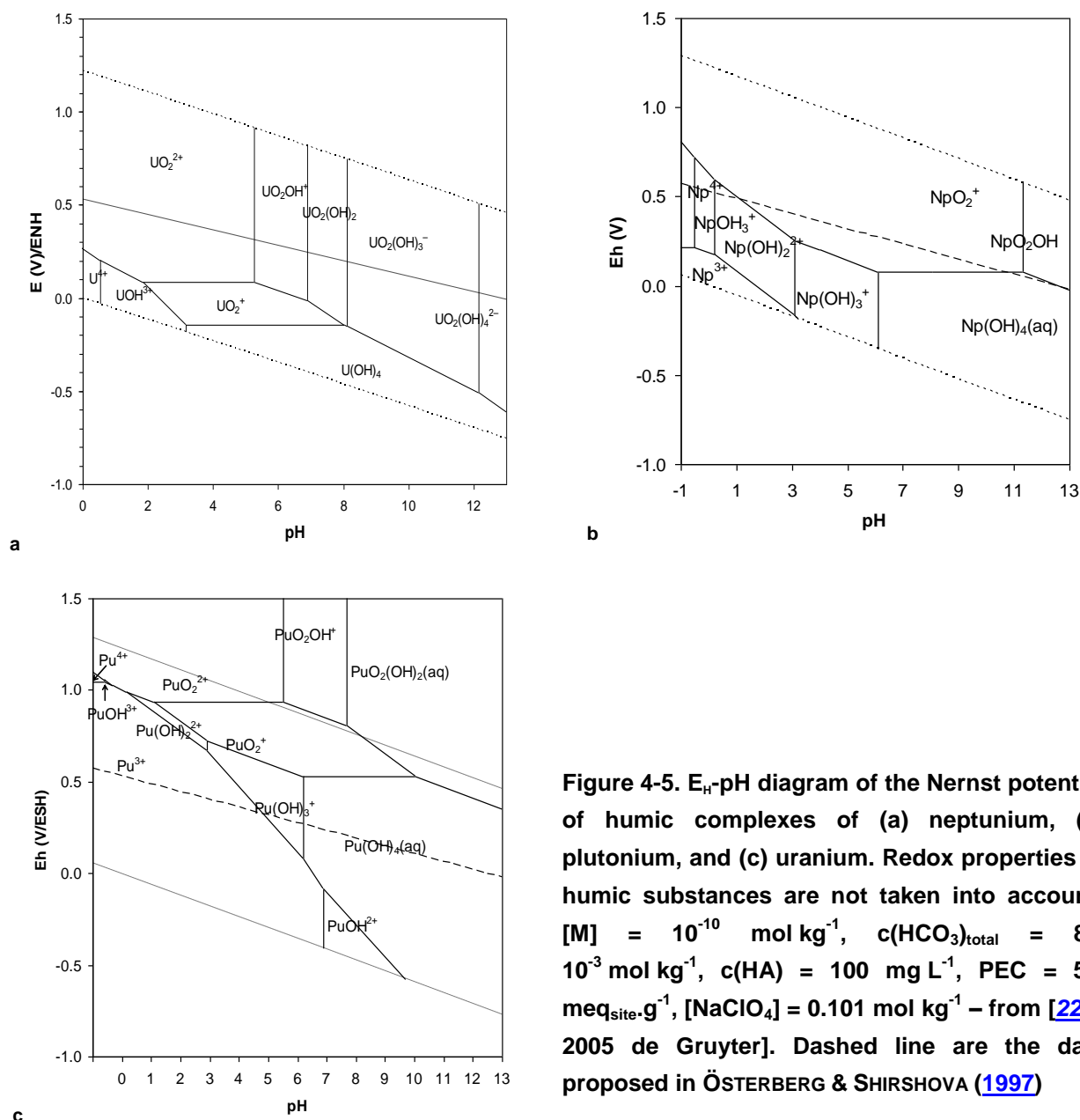
#### 4.2.5.4. Effect of humic complexation on the Nernst potentials

Even if the redox properties of humic substances are known (ÖSTERBERG *et al.*, 1995; ÖSTERBERG & SHIRSHOVA, 1997), the quantification of the humic complexes as a function of redox potential can

be estimated, and the Nernst potential of the complexes can be evaluated [22]. A Pourbaix diagram ( $E_h$ -pH) showing the predominance of hydrolysed species of uranium, neptunium, and plutonium can be proposed in Figure 4-5. The Eh-pH relationship for the redox potential of humic acids proposed by ÖSTERBERG & SHIRSHOVA (1997) is also reported. One can see that uranium(VI) can only be hardly reduced by humic substances as the Eh-pH relationship only crosses U(VI) complexes. On the contrary, in the case of neptunium(V) can be reduced under acidic pH conditions, but less easily in neutral media. Finally, plutonium(VI) and plutonium(V) should be readily reduced. It is also possible to propose the Eh-pH diagram of U, Np, and Pu, only considering the Nernst potentials induced by the humic complexation in carbonated media (Figure 4-5). At trace concentration, the predominance of humic complexes estimated in the framework of the CNM is rather clear.\*

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\* The difference between predominances of  $UO_2CO_3(aq)$  and  $PuO_2CO_3(aq)$  on Figure 4-5b,c should come from a systematic error (Vitorge, Pers. Comm.)



**Figure 4-5. Eh-pH diagram of the Nernst potential of humic complexes of (a) neptunium, (b) plutonium, and (c) uranium. Redox properties of humic substances are not taken into account:  $[M] = 10^{-10} \text{ mol kg}^{-1}$ ,  $c(\text{HCO}_3)_{\text{total}} = 8.2 \cdot 10^{-3} \text{ mol kg}^{-1}$ ,  $c(\text{HA}) = 100 \text{ mg L}^{-1}$ ,  $\text{PEC} = 5.4 \text{ meq}_{\text{site}} \cdot \text{g}^{-1}$ ,  $[\text{NaClO}_4] = 0.101 \text{ mol kg}^{-1}$  – from [22 © 2005 de Gruyter]. Dashed line are the data proposed in ÖSTERBERG & SHIRSHOVA (1997)**

#### 4.2.6. Repartition of humic complexes for the redox sensitive actinides: case of plutonium

One can draw an Eh-pH diagram in the particular case of plutonium accounting for the different constants available in the framework of the charge neutralization model (Figure 4-6), either from analogy with Am-Cm(III) for Pu(III), Np(V) for Pu(V), and U(VI) for Pu(VI), and after adaptation from Equation 4-8 for Pu(IV). One can see the extension of the domain of soluble Pu(III), Pu(IV) and Pu(VI). Species  $\text{Pu}(\text{OH})_4\text{HA}(I)$  is occurring at pH higher than 8 and is minor compared to total Pu, whereas major in solution (Figure 4-6c). The account of the atmospheric  $\text{CO}_2$  would lead to a decrease in  $\text{Pu}(\text{OH})_4\text{HA}(I)$  complex.

These diagrams do not account for the particular redox properties of HS. From the data in ÖSTERBERG & SHIRSHOVA (1997), it can be seen that in the presence of HS, Pu is a mixture of Pu(III) and Pu(IV) depending on pH. These estimations are in fair agreement with other data (MARQUARDT *et al.*, 2004; DARDENNE *et al.*, 2009).

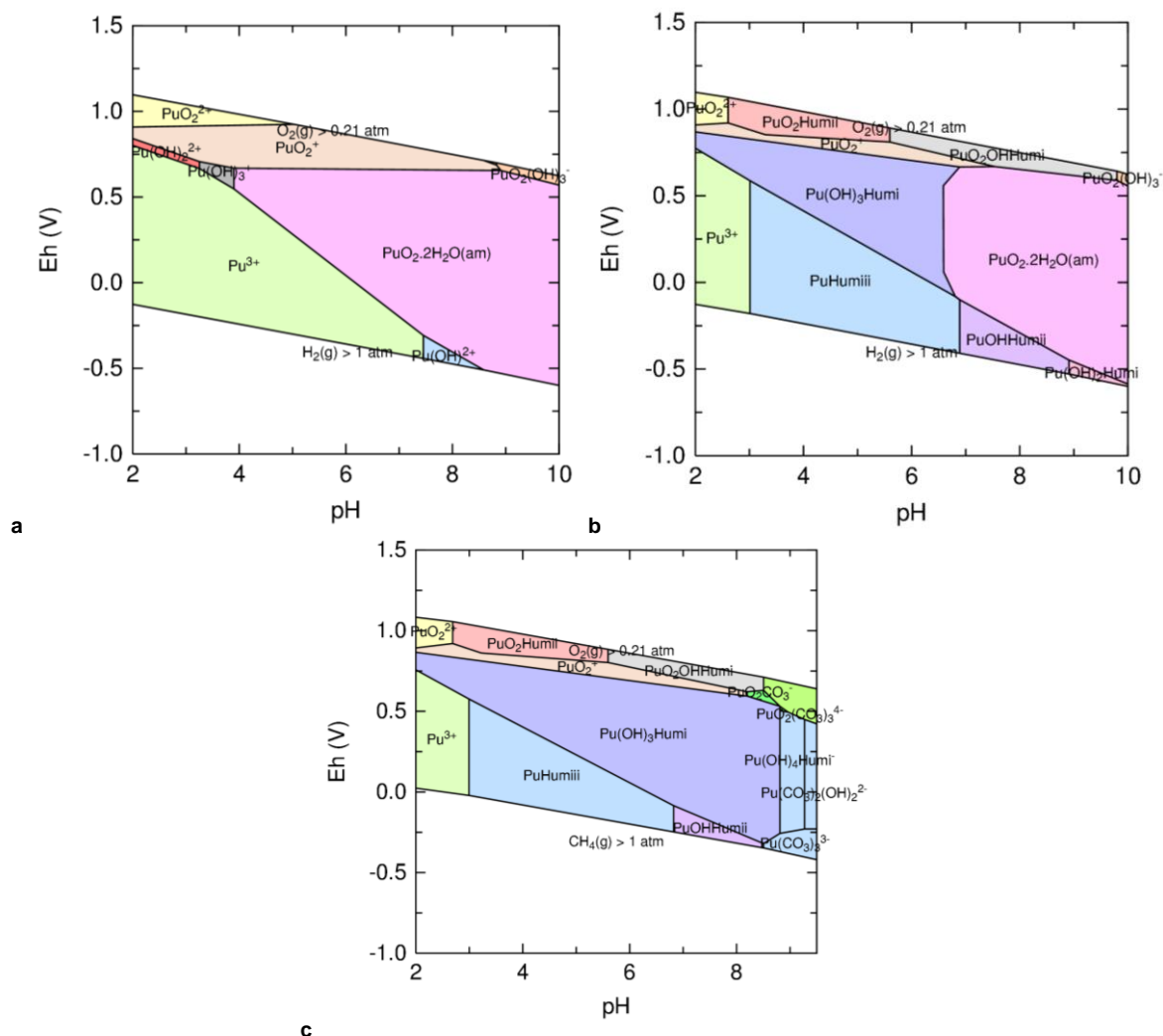


Figure 4-6. Comparison between  $E_h$ -pH diagram in 0.1 M NaCl of Pu ( $10^{-8}$  M) system calculated in the framework of the charge neutralization model, in the absence (a) and presence (b) of HS (160 mg/L), and Pu ( $10^{-12}$  M) and atmospheric  $\text{CO}_2$  (c); thermodynamic data from the ThermoChime data basis provided in the PhreeqC 3 software package\* (GIFFAUT *et al.*, 2014)

#### 4.2.7. Rationale of complexation constants for aquo-ions in the framework of discrete models

The stepwise complexation constants show two systematic trends. The first one is associated with the general trend to higher complexation constants with higher cation charge of the metal ions. In the case of the neptunyl and uranyl ions, the higher effective charge in the equatorial plane than the overall formal charge is also reflected in the elevated complexation constants. The final reflection is,

\* [http://www.brr.cr.usgs.gov/projects/GWC\\_coupled/phreeqc/](http://www.brr.cr.usgs.gov/projects/GWC_coupled/phreeqc/), and <http://www.thermochimie-tdb.com/>

as already discussed above, that the ternary complexes with hydroxyl ions have higher humic complexation constants than expected. The reason is not yet known but its resolution would be a great piece in the puzzle around the humic acid metal ion complexation. Nevertheless, a rationale can be proposed on Figure 4-7, which shows some consistency with increase charge of the free ion.

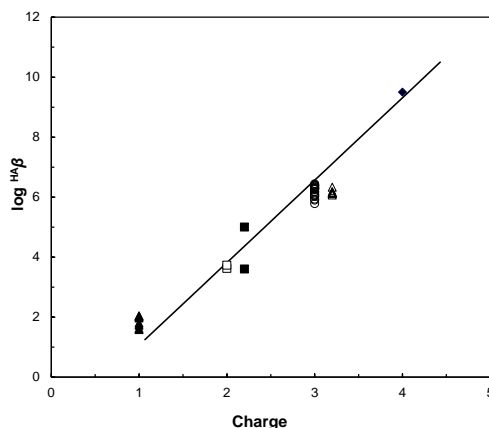


Figure 4-7. Rationale of the different constants obtained for free ions in the framework of the discrete models: ◆ Th<sup>4+</sup> [18], ■ NpO<sub>2</sub><sup>+</sup> (KIM & SEKINE, 1991), △ UO<sub>2</sub><sup>2+</sup> various authors [53], □ Co-Mn<sup>2+</sup> (RYAN *et al.*, 1983), ▲ Li-Na-K-Cs<sup>+</sup> [6], ○ Ln-An<sup>3+</sup> various authors [53]; the line is a guide to the eye – adapted from [48].

#### 4.3. CONTINUOUS MODELS – NICA-DONNAN

The Non-linear Isotherm Competitive Adsorption-Donnan model has been developed at the University of Wageningen (The Netherlands). This description supposes that an ion *i* interacts with a charge-bearing gel in non-specific coulombic interaction, and then can be in specific interaction with different groups of sites, as schematized in Figure 4-8.

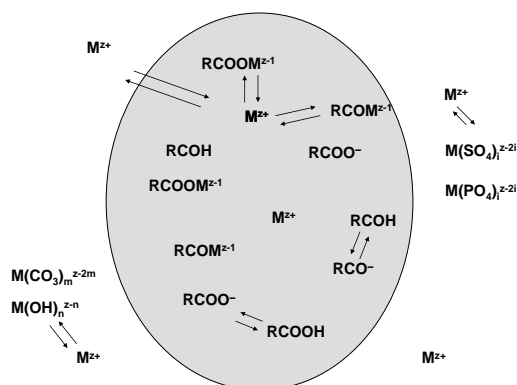


Figure 4-8. Schematic representation of the implied phenomena in the complexation of metallic cations by a humic substances in the framework of the NICA-Donnan model (KINNIBURGH *et al.*, 1999).

As we will see afterwards, the denomination of these sites, *i.e.*, « carboxylic » and « phenolic », can be viewed as a shortcut of the envisaged sites distribution, the  $\log_{10} K_{\max}$  values of which are compatible with the  $pK_a$  of carboxylic acids and phenols. These  $pK_a$  values can be strongly different



from the nominal values, *i.e.*  $pK_{\text{carb}} \approx 4.5$  and  $pK_{\text{phen}} \approx 8$ ; for instance phthalic acid\* has two carboxylic functions on a benzene cycle with  $pK_a$  being 2.95 and 5.41. Salicylic acid† has a carboxylic function ( $pK_a = 2.97$ ) and a phenolic function ( $pK_a = 13.74$ ). It can then be envisaged that other types of acid-base functions be included in the wider distribution as amine functions of aspartic acids‡ ( $pK_a = 9.82$ ), even if N-bearing functions are known to be minor.

In the Donnan approach, humic substances are considered as an electrostatically neutral gel phase with a constant electrostatic Donnan potential,  $\Psi_D$ . The “structural charges” of humic substances are compensated by the counter-ions. Outside the Donnan gel structure,  $\Psi_D = 0$ . The activities in the gel phase in the gel  $a_{iD}$  and in the bulk solution  $a_i$  are linked by a Boltzmann factor.

$$C_{i,\text{memb}} = C_i \exp\left(-\frac{z_i F \Psi_D}{R T}\right) \quad (4-11)$$

As the phase is electrically neutral:

$$\frac{q}{V_D} + \sum_i z_i (a_{iD} - a_i) = 0, \Rightarrow q = -V_D \sum_i z_i (a_{iD} - a_i) \quad (4-12)$$

where  $V_D$  is the volume of the Donnan phase,  $q$  is the charge of the humic substance extract and  $z_i$  the charge on the considered metal. For  $q$  values *vs.* pH for a known concentration of electrolyte,  $\Psi_D$  can be determined if  $V_D = f(\text{pH}, C_e)$  is known. Practically, this value can only be estimated by the Einstein law, with the approximation of a “simple” form. BENEDETTI *et al.* (1996a) showed a logarithmic dependence between  $V_D$  and ionic strength.

$$\log_{10} V_D = a + b \log_{10} I \quad (4-13)$$

Actually, the authors remarked that  $V_D$  tends to  $0.1 \text{ L kg}^{-1}$  for ionic strength higher than 10 mM.

$$\log_{10} V_D = b (1 - \log_{10} I) - 1 \quad (4-14)$$

It is noteworthy that even if a polyelectrolyte structure is evoked for humic substances in BENEDETTI *et al.* (1996a) – with a three dimensional structure –, there is no inclusion of a molecular mass definition in the definition of the Donnan gel and of its electrostatic potential, contrary to Model VI (TIPPING, 1998) for instance where the definition of the potential that spreads out of the hard-sphere humic particles requires the use of a molecular mass.

Within the Donnan phase, the cations complexation occurs with a distribution of sites. The quantity of fixed cations on the total number of sites  $\theta_{iT}$  is described by

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\* benzene-1,2-dicarboxylic acid

† 2-hydroxybenzoic acid

‡ (2S)-2-aminobutanedioic acid

$$\theta_{i,T} = \int_{\Delta \log K_i} \theta_{i,L} f(\log K_i) d(\log K_i) \quad (4-15)$$

where  $\theta_{i,L}$  is the fixed quantity on a site  $i$ ,  $f(\log_{10} K_i)$  is the continuous distribution function of sites.

From the Sips' equation (SIPS, 1948, 1950), KOOPAL *et al.* (1994) has applied an Henderson-Hasselbach treatment and proposed a general equation in the case of a cation  $i$  in competition with other species on a distribution of sites. As the model requires the electroneutrality of the phase, the complexation of an ion must be followed by the release of another cation. KINNIBURGH *et al.* (1999) have proposed the normalisation to the following expression for two distributions,

$$Q_{i,T} = \sum_j \left( \frac{n_{i,j}}{n_{H,j}} Q_{\max i,j} \right) \times \frac{(\tilde{K}_{i,j} C_{D,i})^{n_{i,j}}}{\sum_j (\tilde{K}_{i,j} C_{D,i})^{n_{i,j}}} \times \frac{\left[ \sum_j (\tilde{K}_{i,j} C_{D,i})^{n_{i,j}} \right]^{p_j}}{1 + \left[ \sum_j (\tilde{K}_{i,j} C_{D,i})^{n_{i,j}} \right]^{p_j}} \quad (4-16)$$

with  $Q_{i,T}$  the total quantity of a compound  $i$  fixed to humic substances ( $\text{mol kg}_{\text{HA}}^{-1}$ ),  $Q_{\max}$  the maximum number of available sites ( $\text{mol kg}_{\text{HA}}^{-1}$ ),  $C_{D,i}$  the concentration of  $i$  in the Donnan phase,  $\tilde{K}_i$  the median affinity value of species  $i$  in the distribution,  $p_j$  the width of the  $j^{\text{th}}$  distribution or its intrinsic heterogeneity (the same for all the cations) ( $0 \leq p_j \leq 1$ ), and  $n_{i,j}$  the heterogeneity or non-ideality of the ion  $i$  with the distribution  $j$  ( $0 \leq n_{i,j} \leq 1$ ). The parameter  $n_{i,j}$  can be viewed as an inverse of stoichiometry,  $n_{i,j} = 1$  stoichiometry 1:1 or mono-dentate, and  $n_{i,j} = 0.5$  stoichiometry 1:2 or bi-dentate (KOOPAL *et al.*, 2005). This expression is actually rather equivalent to a Langmuir-Freundlich isotherm. In the case of  $\text{H}^+$ , only the product  $m_{\text{H}^+,j} = n_{\text{H}^+,j} p_j$  can be experimentally obtained. Parameters  $n_{\text{H}^+,j}$ ,  $p_j$ , and  $n_{i,j}$  for other cations are determined from titration of the humic substance and from complexometric experiments.

#### 4.3.1. Cobalt(II) and the flux Donnan membrane technique.

Cobalt is a structural element of the nuclear reactors alloys. After its activation it gives a major part of the radiation exposition. The radionuclide  $^{60}\text{Co}$  is also greatly used in the medical domain. This part has been done during the Laura Marang's PhD thesis [19,82].

The flux Donnan membrane technique (FDM) is based in the Donnan Membrane Technique (DMT) (TEMMINGHOFF *et al.*, 2000), which allows measuring free metal concentration in solution. The separation between free positive cations and negative humic complexes is done with a negatively charged membrane. The interferences which are due to other species in solution are weak compared to other speciation techniques. Under equilibrium condition the concentrations of free metal are the same at each side of the membrane and can be calculated following the Donnan equilibrium

(DONNAN, 1924). The concentrations in the Donnan phase (membrane) and in the solution are linked by the Boltzmann relation

$$C_{i,\text{memb}} = C_i \exp\left(-\frac{F \Psi}{R T}\right) = C_i B \quad (4-17)$$

Knowing that the membrane is electrically neutral, the negative charge is neutralized by the counter-ions.

$$q + \sum_i z_i C_i \exp\left(-\frac{z_i F \Psi}{R T}\right) = q + \sum_i z_i C_i B^{z_i} = 0 \quad (4-18)$$

The counter-ion is generally a salt of a divalent cation to avoid the exchange between an alkaline cation and the studied metal. The Boltzmann coefficient  $B$  is calculated from the membrane parameters.\* The originality of the work resides in the study of the cation flux through the Donnan membrane. In order to accelerate, or enforce, this flux a ligand is introduced in the acceptor side to create a stronger concentration gradient which promotes the migration from the donor side. Under equilibrium conditions, the concentration of free metal in the donor can be calculated from the metal concentration measured in the acceptor using the analytical relationships in WENG *et al.* (2005). The cation fluxes in the DMT cell can be limited by diffusion in the membrane or at the membrane-solution interface – see. Figure S1 in ref. 19.† The ratio  $C_{i,\text{memb}}/C_i$  in Equation 4-17 gives the relative increase of cation concentration within the membrane (Table 4-1). This concentration increase has a great importance on the solubility of cations in the Donnan membrane as we will see it afterwards.

The FDM has been developed in order to obtain quantitative information on the complexation of radionuclides by humic substances in a shorter time scale than DMT, and to decrease the limit of detection. The FDM is also a dynamic approach of the DMT but it is based on an experimental calibration [19], which allows to get rid of theoretical parameters and analytical solution of the cation transport. The FDM also allows obtaining information on the lability of the studied complex. The study of the flux is done in the presence of a strong ligand of the free cation in the acceptor. The lability criterion defined by VAN LEEUVEN *et al.* (2005) allows estimating that Co(II) humic complexes are inert during the time of the separation.

The obtained NICA-Donnan parameters, *i.e.*  $\log_{10} \tilde{K}_{i,j}$ ,  $n_{i,j}$ , and  $p_j$  for this humic acids in reference [19] can be compared to the proposed generic values. In the generic data compilation from MILNE *et al.* (2001; 2003), the fixation on the “carboxylic sites” was awaited to be mainly non-specific ( $\log_{10} \tilde{K}_{\text{Co}^{2+},1} = -0.24$ ) whereas fixation on higher proton affinity sites was proposed and not adjusted ( $\log_{10} \tilde{K}_{\text{Co}^{2+},2} = 1.0$ ). In the dedicated study,  $\log_{10} \tilde{K}_{\text{Co}^{2+},1} = 2.5$  for the lower proton affinity sites, and

\*  $B = \sqrt{-\frac{q}{z_i C_i}} = 29.6$ , for  $C_i = 2$  mM,  $\text{CaCl}_2$   $z_i = 2$ ,  $\delta_m = 0.16$  mm,  $A = 7$  cm<sup>2</sup>, charge density  $-0.8$  mmol g<sup>-1</sup>, mass per surface  $0.014$  g cm<sup>-2</sup>, which gives  $q = -0.7$  mol.L<sup>-1</sup> for the effective surface. if only 20% is effective  $q = -3.5$  mol.L<sup>-1</sup>

† <http://pubs.acs.org/doi/suppl/10.1021/es060608t>

$\log_{10} \tilde{K}_{\text{Co}^{2+},1} = 3.5$ , for the higher proton affinity sites, imply a more specific character of the cobalt(II)/HA association [19]. MILNE *et al.* (2003) proposed also correlations between  $n_{ij}$  and  $n_i \times \log_{10} \tilde{K}_{ij}$  with first hydrolysis constants. From this correlation  $\text{Co}^{2+}$  was through to show a compartment which should be more comparable with alkaline-earth metals than with a d-transition element. The values from MARANG *et al.* [19] seem to show that the Co(II)/HA association is far more specific than anticipated. The reason behind this discrepancy is not easy to settle, but our data cover a wider parametric space.

**Table 4-1. Values of Boltzmann factors for different ionic strengths fixed by  $\text{CaCl}_2$  or  $\text{Mg}(\text{NO}_3)_2$  for different charges for a membrane such as the ones used in Weng *et al.* (2005) and [19,82].**

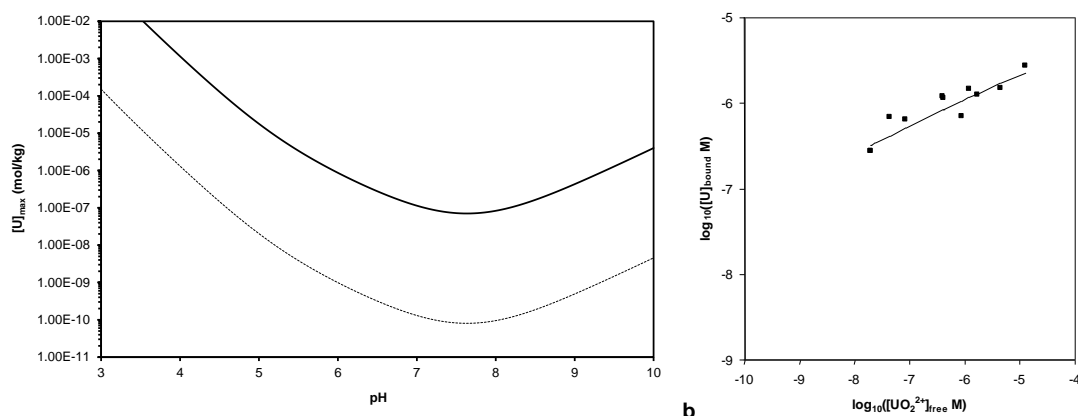
$I$ (mmol L <sup>-1</sup> )	M <sup>+</sup>	M <sup>2+</sup>	M <sup>3+</sup>	M <sup>4+</sup>	M <sup>-</sup>
2	29.6	876.2	25 934.3	767 656.3	0.034
20	9.4	88.4	830.6	7 807.5	0.106
100	4.2	17.6	74.1	311.2	0.238

### 4.3.2. Case of uranium(VI)

#### 4.3.2.1. Uranium(VI) and the limits of the FDM

As noted earlier, uranyl ion ( $\text{UO}_2^{2+}$ ) is the only actinyle VI ion that is stable in water which reduction has not been observed in the presence of humic acid (MOULIN *et al.*, 1992; CZERWINSKI *et al.*, 1994), contrary to  $\text{PuO}_2^{2+}$  (NASH *et al.*, 1981; SANCHEZ *et al.*, 1985; ANDRÉ & CHOPPIN, 2000). Only catechol-containing synthetic extracts (SACHS *et al.*, 2004), or hydrothermal alteration products of wood (ABRAHAM *et al.*, 1999a; ABRAHAM *et al.*, 1999b; BARANIAK *et al.*, 1999; ABRAHAM, 2002), or bacterial reduction (GU *et al.*, 2005), allow the reduction to U(IV). The major part of the authors agree on apparent humic complexation constant of  $\text{UO}_2^{2+}$ , the values of which are very close to the ones of actinides(III) – see compilation in [53].

Uranium(VI) has also been studied in FDM, under the same conditions than  $\text{Co}^{2+}$ ;  $\text{MgCl}_2$  was chosen instead of  $\text{CaCl}_2$  to limit the solubility of calcium uranates (GUILLAUMONT *et al.*, 2003). As already seen in Table 4-1, the increase of  $\text{UO}_2^{2+}$  concentration in the Donnan membrane is of 876.2. One can anticipate solubility problems of schoepite ( $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ), or other hydroxide from Figure 4-9. Nevertheless, the  $\text{UO}_2^{2+}$  adsorption isotherm at pH 4 is satisfactory [49,82]. The values  $\log_{10} \tilde{K}_{\text{UO}_2^{2+},1} = 4.6 \pm 0.05$  and  $n_{\text{UO}_2^{2+},1} = 0.3 \pm 0.1$  are obtained keeping the values of  $\log_{10} \tilde{K}_{\text{UO}_2^{2+},2}$  and  $n_{\text{UO}_2^{2+},2}$  from Saito *et al.* (2004).



**Figure 4-9.** Solubility diagram of  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$  at  $I = 6 \cdot 10^{-3} \text{ mol L}^{-1}$  (plain line) and apparent solubility in the Donnan membrane for  $z = 2$  (dotted line) (GUILLAUMONT *et al.*, 2003) (a), and uranium(VI) complexation isotherm at pH 4 with Gorleben HA in FDM [49,82] (b).

#### 4.3.2.2. Use of an insolubilized humic acid

In order to obtain fixation isotherm at high pH values the data on Gorleben humic acid were compared between FDM and an insolubilized humic acid (IHA) [49,82], used otherwise for Fe complexation (WEBER *et al.*, 2006a; WEBER *et al.*, 2006b). The fair agreement between FDM at pH 4 and the IHA and literature values (SAITO *et al.*, 2004) allows a reasonable level of confidence in the obtained NICA-Donnan data. The generic data proposed by MILNE *et al.* (2003) could be biased by high uranium concentration and low pH data under which HA may eventually not be soluble.\* It would then be necessary to implement the data bases with other inner consistent data which were not taken into account – see compilation in [53].

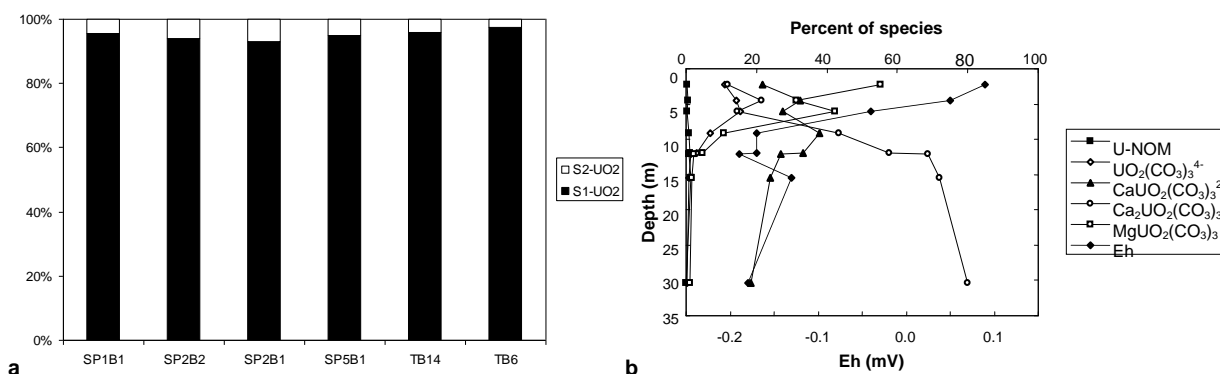
The data in IHA at pH 4, 5, and 6 give  $\log_{10} \tilde{K}_{\text{UO}_2^{2+},1} = 4.7 \pm 0.1$  and  $n_{\text{UO}_2^{2+},1} = 0.8 \pm 0.1$  [49], keeping the values of  $\log_{10} \tilde{K}_{\text{UO}_2^{2+},1}$  and  $n_{\text{UO}_2^{2+},1}$  from Saito *et al.* (2004). These data are greater than the generic data from MILNE *et al.* (2003), *i.e.*  $\log_{10} \tilde{K}_{\text{UO}_2^{2+},1} = 2.45$  and  $\log_{10} \tilde{K}_{\text{UO}_2^{2+},1} = 4.81$ , part from the atypical experiments – see compilation in [53] –, and part from the differences in the proton parameters;  $\log_{10} \tilde{K}_{\text{H}^+,1} = 2.93$  for generic humic acid from MILNE *et al.* (2001), and  $\log_{10} \tilde{K}_{\text{H}^+,2} = 4.11$ , and  $\log_{10} \tilde{K}_{\text{H}^+,1} = 4.5$  for Gorleben HA [19] and IHA (WEBER *et al.*, 2006a), respectively.

#### 4.3.2.3. Application to independent field data

These data allows modelling experimental field data [49]. In the case of the Savannah river Site (SC, USA, in JACKSON *et al.*, 2005), where pH varies in a range 4.5-5.96, and the organic carbon concentration varies between 44 and 199  $\text{mg L}^{-1}$ , more than 99.99% of uranium(VI) is complexed by natural organic matter (Figure 4-10a). Similarly, the data from CRANÇON *et al.* (2003; 2010) for an acidic podzol for Gascony (France) also ends in a complete humic complexation.

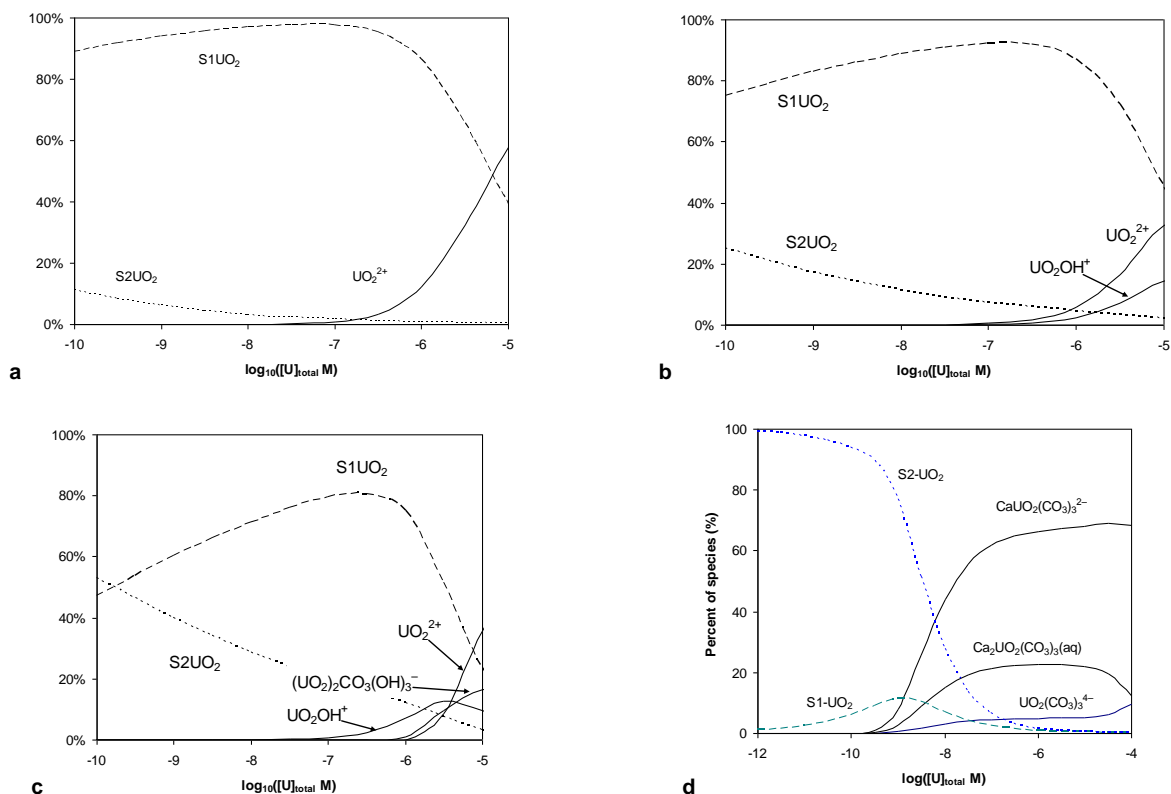
\* pH  $\leq 3$

On the other hand, for more basic media, which has a greater carbonate and alkaline-earth concentration, humic complexation is not relevant due to the competition of carbonate complexes –  $\text{UO}_2(\text{CO}_3)_n^{2-2n}$  (GUILLAUMONT *et al.*, 2003) – and of mixed calcium and magnesium carbonate complexes –  $(\text{Ca},\text{Mg})_n\text{UO}_2(\text{CO}_3)_3^{4+2n}$  (DONG & BROOKS, 2006). Noteworthy, it is the case for a Canadian site (RANVILLE *et al.*, 2007), and a Finnish site (PRAT *et al.*, 2009). In the former case, uranium(VI) is awaited under the form of ion pair complexes  $(\text{Ca},\text{Mg})_n\text{UO}_2(\text{CO}_3)_3^{4+2n}$  (Figure 4-10b), and in the latter case, with lower concentration of  $\text{Mg}^{2+}$ , under the form of  $\text{Ca}_n\text{UO}_2(\text{CO}_3)_3^{4+2n}$  and  $\text{UO}_2(\text{CO}_3)_3^+$  complexes.



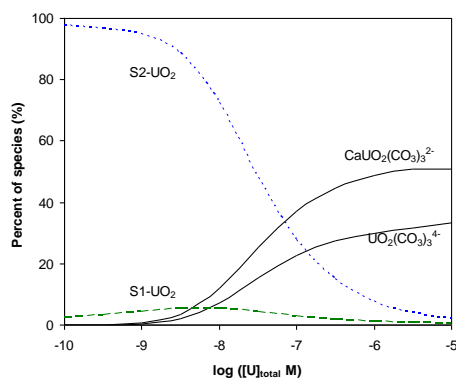
**Figure 4-10. Speciation of uranium in natural waters from Savannah River Test site (JACKSON *et al.*, 2005) (a) and in a Canadian site (RANVILLE *et al.*, 2007) (b) – from [49].**

In the case of uranium, humic complexation is important as long as pH and carbonate concentration do not imply an extensive competition. This competition is more important than for lanthanides and actinides(III) that forms a cationic complex  $\text{LnCO}_3^+$ , which can interact with the negative structure of humic substances. On the other hand, the total concentration effect, which we briefly evoked beforehand (cf. § 4.1.2, page 34, and § 4.2.4, page 40), shows clearly that the association is awaited to be stronger (HUMMEL *et al.*, 2000) for lower total uranium concentration. In Figure 4-11a,b,c is shown the theoretical calculation of humic-complexed uranium vs. total uranium concentration using the generic data from MILNE *et al.* (2001; 2003). One can then await a significant humic complexation of total uranium concentration lower than  $10 \text{ nmol L}^{-1}$ . If the calculation from PRAT *et al.* (2009) would permit to predict a significant humic complexation of uranium Figure 4-11d, it has not been verified by the authors.



**Figure 4-11. Speciation of uranium at pH 4 (a), pH 6 (b), and pH 8 (c),  $c(\text{HA}) = 10 \text{ mg L}^{-1}$  et  $P(\text{CO}_2) = 10^{-3.5} \text{ atm}$ , from the generic data from MILNE *et al.* (2001; 2003), and the same evolution under the condition of low uranium concentration Finnish water (d) (sample S10 from PRAT *et al.*, 2009).**

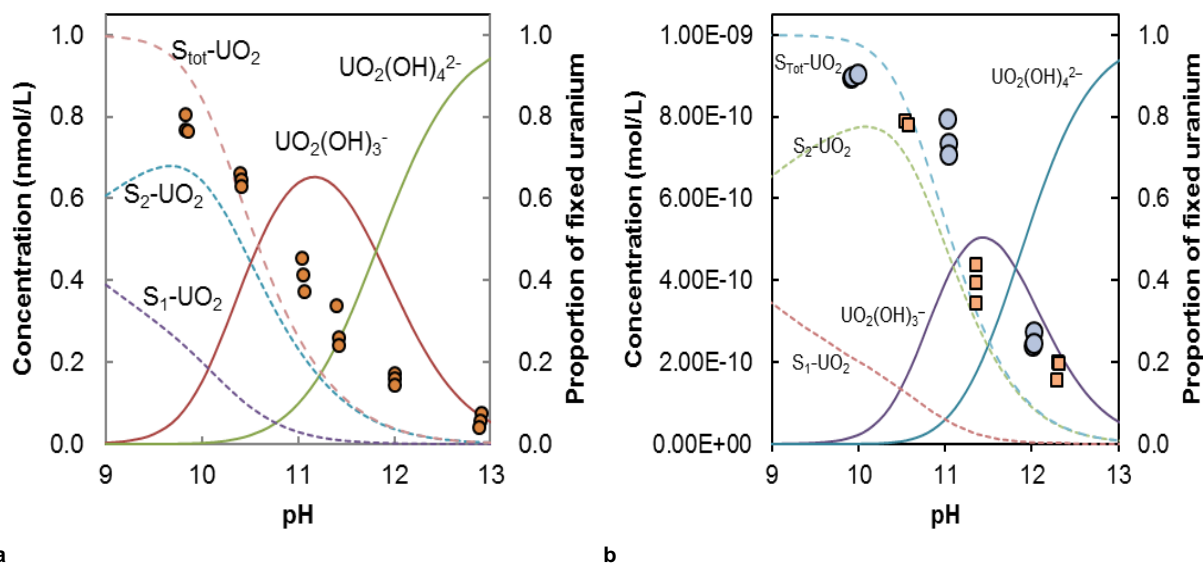
On the contrary, BRUGGEMAN & MAES (2010) have clearly showed this effect in the case of the Mol site (Belgium). For total uranium concentration of  $1 \mu\text{mol L}^{-1}$  no influence of HA on the adsorption of uranium on pyrite was neither observed nor awaited, whereas it decreases the adsorption for total uranium concentration lower than  $10^{-7} \text{ mol L}^{-1}$  (Figure 4-12a). The agreement between experimental data and predictive calculation is noteworthy. BRUGGEMAN & MAES (2010), assigned the significant decrease of uranium adsorption to the reduction from U(VI) to U(IV), but do not propose a mechanism. The use of NICA-Donnan data makes the representation of experimental data possible in a satisfactory manner without accounting for U(IV). Let's remark that under these conditions, the formation of a  $\text{UO}_{2+x}$  solid phase is possible;  $\text{U}_3\text{O}_8$  was proposed by BRUGGEMAN & MAES (2010) to control the solubility of uranium in this system.



**Figure 4-12.** Calculated speciation of uranium-HA in the argillaceous water from the Boom site (Mol, Belgium) (BRUGGEMAN & MAES, 2010) as a function of the total uranium concentration.

One would also to account for the recent determination (STEUDTNER *et al.*, 2011a; STEUDTNER *et al.*, 2011b) where a mixed  $\text{UO}_2\text{-CO}_3\text{-HA}$  complex at pH higher than 7 was evidenced.

Recently, experimental evidence of the complexation of uranyl under high pH conditions was given (STOCKDALE & BRYAN, 2012; STOCKDALE *et al.*, 2013). A comparison with the data from STOCKDALE *et al.* (2013) and the speciation of uranium obtained with the data from SAITO *et al.* (2004) leads to a slight underestimation. A higher value of  $\log_{10} \tilde{K}_{\text{UO}_2^{2+},2}$  would be necessary to properly fit the data.



**Figure 4-13.** Comparison of predicted speciation of uranium(VI) under high pH conditions from the parameters proposed by SAITO *et al.* (2004) and the experimental data digitized from (a) STOCKDALE *et al.* (2012), and (b) STOCKDALE *et al.* (2013).

### 4.3.3. Europium(III)

If the data on humic complexation of europium(III) are quite numerous – § 4.2.4, page 40, MILNE *et al.* (2003), and compilation in [53] –, the dedicated experiments of competition between lanthanide/actinides(III) and major cations were scarce. Overall, even if a difference of complexation sites, or types, between alkaline-earth and Ln/An(III) seemed to have reached a consensus, no



spectroscopic evidence was available. We have proposed dedicated experiments which combined the use of ion selective electrodes for  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  determinations and time-resolved laser-induced luminescence spectroscopy (TRLIS), in the framework of the Laura Marang's PhD thesis [82] in the framework of the European Integrated Project FUNMIG in collaboration with the Institute of Chemistry from the University of Potsdam [60]. The obtained data on the different systems were in agreement with the generic data from MILNE *et al.* (2003) [17], enhancing the highly specific character of the interaction between  $\text{Eu}^{3+}$  and humic substances.

#### 4.3.4. Consideration on the NICA-Donnan generic data for lanthanides and actinides

##### 4.3.4.1. Lanthanides/Actinides(III)

Data on Eu(III) compared to Am(III) and Cm(III) in MILNE *et al.* (2003) are giving rise to some comments. The authors proposed correlation between  $n_i$ ,  $\log_{10} \tilde{K}_i$  and the first hydrolysis constants of the metal. In Figure 1 of MILNE *et al.* (2003), it seems that the first hydrolysis of  $\text{Cm}^{3+}$  is not coherent with known thermodynamic data. The value is reported next to  $\log_{10} {}^*\beta_1(\text{UO}_2^{2+})$ , *i.e.* -5.25, whereas it should be more in agreement with  $\log_{10} {}^*\beta_1(\text{Am}^{3+}) = -7.2$ . This is the origin the difference between  $\log_{10} \tilde{K}_{\text{Am}^{3+},1} = 0.94$  and  $\log_{10} \tilde{K}_{\text{Cm}^{3+},1} = 2.7$  on the low proton affinity sites for the generic humic acid in MILNE *et al.* (2001). On the other hand, MILNE *et al.* (2003) did not propose an important difference for the high proton affinity sites, *i.e.*  $\log_{10} \tilde{K}_{\text{Am}^{3+},2} \approx 5.8$  and  $\log_{10} \tilde{K}_{\text{Cm}^{3+},2} \approx 6.0$ . These  $\log_{10} \tilde{K}_{\text{Cm}^{3+},1}$  values are from the following correlations:

$$\left. \begin{aligned} n_1 &= 0.14 - 0.0055 \log_{10} {}^*\beta_1^\rho, r^2 = 0.85 \\ n_2 &= 0.76 n_1 \\ n_1 \log_{10} \tilde{K}_{i,1} &= 0.26 \log_{10} {}^*\beta_1^\rho + 2.59, r^2 = 0.83 \\ n_2 \log_{10} \tilde{K}_{i,2} &= 0.41 \log_{10} {}^*\beta_1^\rho + 4.98, r^2 = 0.71 \end{aligned} \right\} \quad (4-19)$$

As americium(III) was included in the regression, this difference was not noticed by the authors. From my point of view, as there is a profound chemical analogy in the humic complexation of these two actinides – see compilation in [53] –, it would be reasonable to propose at least similar data for  $n_{\text{An}^{3+},j}$  and  $\log_{10} \tilde{K}_{\text{An}^{3+},j}$ .

The uncertainties of the correlations in Equations 4–19 can be estimated after digitizing the figures from Figure 1 in MILNE *et al.* (2003). First, one must note that when  $n_{i,j}$  is to be estimated from  $\log_{10} {}^*\beta_1^\rho$  the expression should be calculated as  $\log_{10} {}^*\beta_1^\rho = f(n_{i,j})$ . From the original data (Figure 1 in MILNE *et al.*, 2003), one can obtain a correlation which is very close to the one from MILNE *et al.* (2003), and the “correct” expression can be estimated as follows.

$$\log_{10} {}^*\beta_1^\rho = (3.1 \pm 1.1) - (19.0 \pm 1.8) n_{i,1}, r^2 = 0.9$$

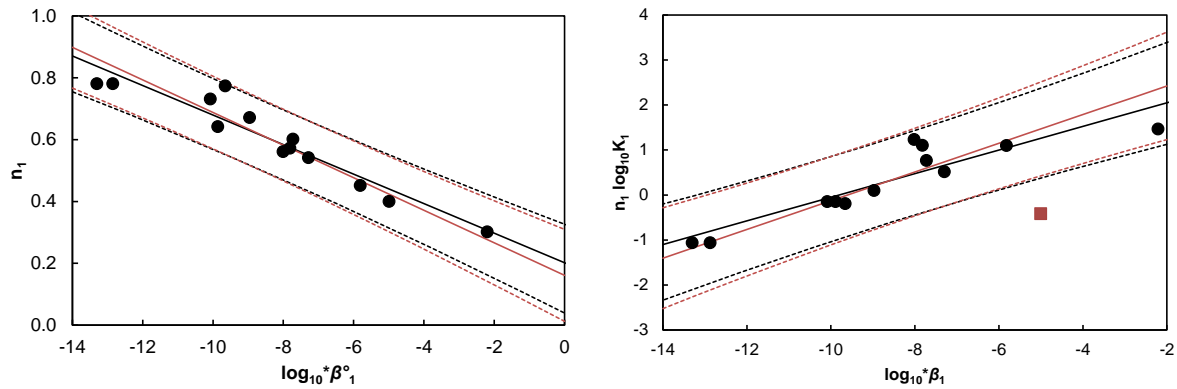
The differences can be seen in Figure 4-14a. The 95% confidence hyperboles ( $2\sigma$ ) give an indication of the uncertainties on the estimated  $n_{i,j}$  values; at the mean value of  $\log_{10}\beta_1^\circ$ , *i.e.*  $-8.3$ ,  $\sigma(n_{i,1}) = 0.05$ .

The same exercise can be done for the  $\log_{10}^*\beta_1^\circ = f(n_{i,1}, \log_{10}\tilde{K}_{i,1})$  relationship (Figure 4-14b). The obtained  $n_{i,1}\log_{10}\tilde{K}_{i,1} = f(\log_{10}^*\beta_1^\circ)$  is close from the relationship given in Equation 4-19, and the “correct” expression is,

$$\log_{10}^*\beta_1^\circ = (3.1_3 \pm 0.4_6) n_{i,1}\log_{10}\tilde{K}_{i,1} - (9.6 \pm 0.4), r^2 = 0.82$$

and for the mean  $\log_{10}\beta_1^\circ$ ,  $n_{i,1}\log_{10}\tilde{K}_{i,1} = 0.4$ , and  $\sigma(n_{i,1}\log_{10}\tilde{K}_{i,1}) = 0.44$ .

For  $\text{Sm}^{3+}$ ,  $\log_{10}^*\beta_1^\circ = -7.9$  (SPAHIU & BRUNO, 1995) gives  $n_{\text{Sm}^{3+},1} = 0.58 \pm 0.05$ , and  $n_{\text{Sm}^{3+},1} \log_{10}\tilde{K}_{\text{Sm}^{3+},1} = 0.54 \pm 0.44$ , and finally  $\log_{10}\tilde{K}_{\text{Sm}^{3+},1} = 0.9_6 \pm 0.7_6$ . As usual, these kinds of correlations are useful for estimating missing data but are giving highly uncertain parameters.



**Figure 4-14. Correlation between  $n_{i,1}$  and  $\log_{10}^*\beta_1^\circ$  (a) and  $n_{i,1} \log_{10}\tilde{K}_{i,1}$  (b) for the case of humic acids, digitized from MILNE *et al.* (2003). The black lines are the original correlations, and the red lines are estimated in the document. Confidence hyperboles are  $2\sigma$ .**

This is even more true for  $n_{i,2} = f(\log_{10}^*\beta_1^\circ)$  and  $n_{i,1} \log_{10}\tilde{K}_{i,1} = f(\log_{10}^*\beta_1^\circ)$  relationships. The very high dispersion of  $n_{i,2} = f(\log_{10}^*\beta_1^\circ)$  and apparent colinearity with  $n_{i,1} = f(\log_{10}^*\beta_1^\circ)$  drove MILNE *et al.* (2003) to propose  $n_{i,2} = 0.76 n_{i,1}$ ,\* which can be understood looking at the correlations in Figure 4-15a. calculating in the “correct” way,

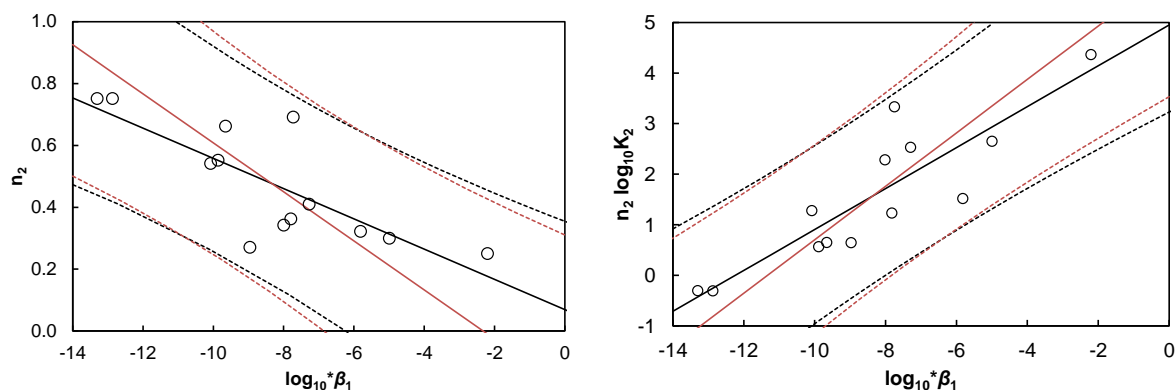
$$\log_{10}^*\beta_1^\circ = -(2.3 \pm 0.1) - (12.6 \pm 3.0) n_{i,2}$$

would give negative values of  $n_{i,2}$  for  $\log_{10}^*\beta_1^\circ \geq -2.3$ , *e.g.* for  $\text{Fe}^{3+}$  or for  $\text{An(IV)}$ . The  $n_{i,2} \log_{10}\tilde{K}_{i,2} = f(\log_{10}^*\beta_1^\circ)$  is,

$$\log_{10}^*\beta_1^\circ = (1.8_9 \pm 0.3_2) n_{i,2} \log_{10}\tilde{K}_{i,2} - (11.3_3 \pm 0.6_5)$$

\*  $0.76 \pm 0.16$  being the mean of  $n_{i,2}/n_{i,1}$  without  $\text{Pb}^{2+}$  considered as an outlier.

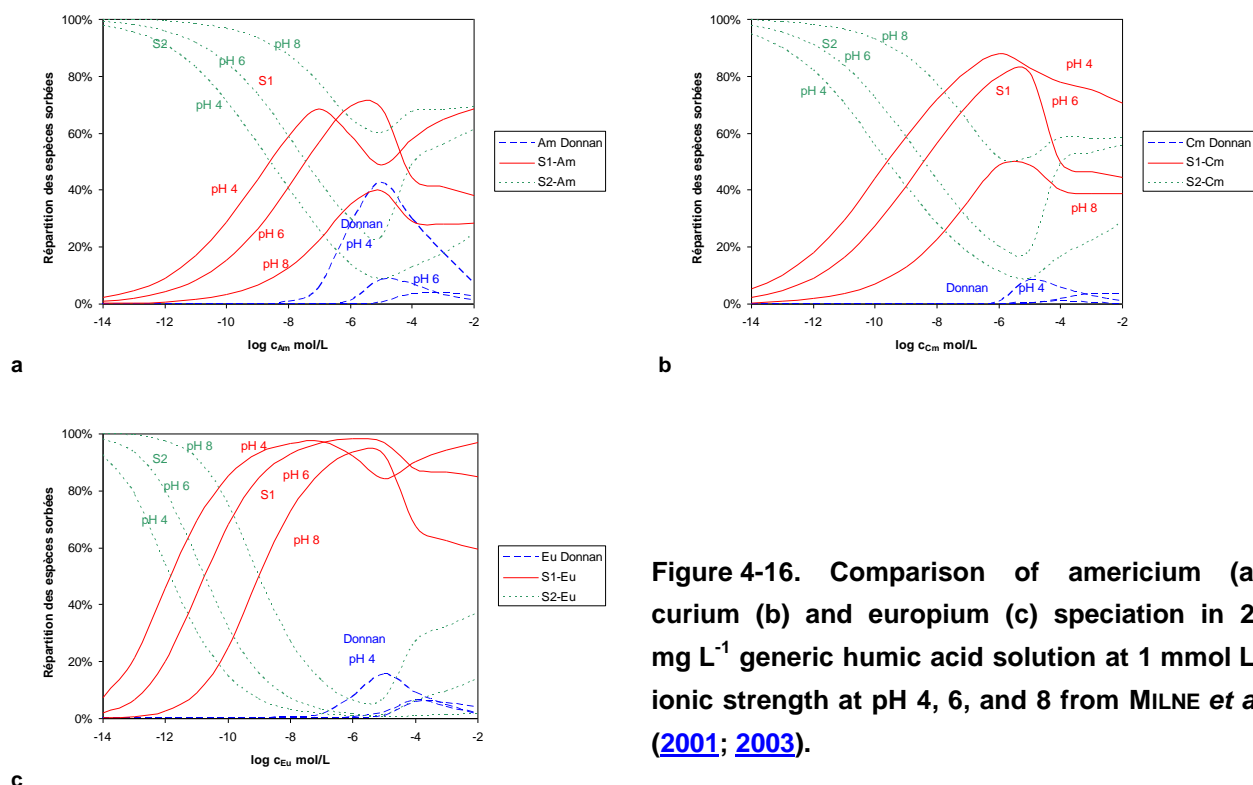
In the case of  $\text{Sm}^{3+}$ ,  $n_{\text{Sm}^{3+},2} = 0.44 \pm 0.18$ , and  $n_{\text{Sm}^{3+},2} \log_{10} \tilde{K}_{\text{Sm}^{3+},2} = 1.81 \pm 0.84$ , and finally  $\log_{10} \tilde{K}_{\text{Sm}^{3+},2} = 4.1_1 \pm 2.5_4$ .



**Figure 4-15. Correlation between  $n_{i,2}$  and  $\log_{10}^* \beta_1$  (a) and  $n_{i,2} \log_{10} \tilde{K}_{i,2}$  (b) for the case of humic acids, digitized from MILNE *et al.* (2003). The black lines are the original correlations, and the red lines are estimated in this document. Confidence hyperboles are  $2\sigma$ .**

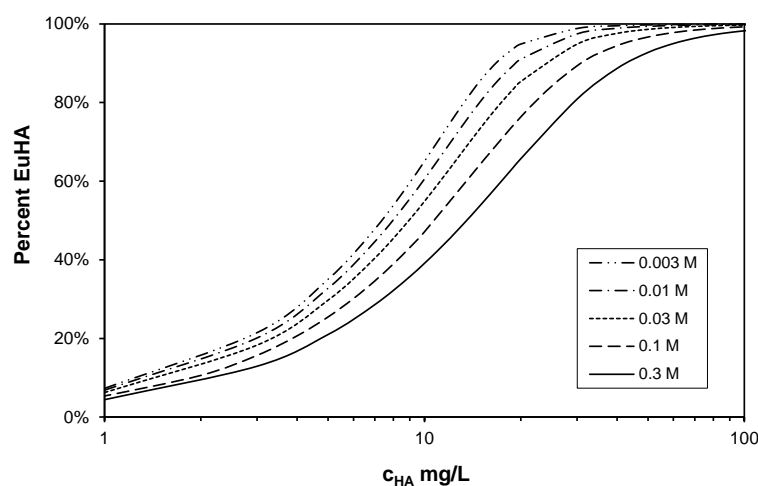
The values for  $\text{Eu}^{3+}$  from MARANG *et al.* [17] are in excellent agreement with the generic data from MILNE *et al.* (2003) and could form the basis for an implemented generic data for the actinides(III). One must not forget that each humic extract is particular. LUKMAN *et al.* (2012) and JANOT *et al.* [3,81] evidenced that some HA has a slightly lower  $\log_{10} \tilde{K}_{\text{Eu}^{3+},1}$ . Recently, within the Yasmine Kouhail's PhD we also obtained data on fulvic acid which are slightly different than the generic ones [45] :  $\log_{10} \tilde{K}_{\text{Eu}^{3+},1} = -3.2$  and  $\log_{10} \tilde{K}_{\text{Eu}^{3+},2} = 7.15$ , for  $\log_{10} \tilde{K}_{\text{Eu}^{3+},1} = -1.9$  and  $\log_{10} \tilde{K}_{\text{Eu}^{3+},2} = 5.8$  proposed in MILNE *et al.* (2003).

The best way to visualise the consequences of the different proposition is to perform the speciation calculation at low ionic strength, which favours the non-specific binding in the Donnan phase (Figure 4-16). For trace concentration almost no difference can be noted between the three different sets of data. It is noteworthy that the proportion of low proton affinity sites can be different, and that pH dependant complexation data are not numerous, and are absent from the compilation from MILNE *et al.* (2003). A thorough review of these data seem to be necessary, with the inclusion of not included or latter data (PANAK *et al.*, 1996; MORGENSTERN *et al.*, 2000; POURRET *et al.*, 2007a, 2007b, 2007c) [3,17,81,82].



**Figure 4-16. Comparison of americium (a), curium (b) and europium (c) speciation in 20 mg L<sup>-1</sup> generic humic acid solution at 1 mmol L<sup>-1</sup> ionic strength at pH 4, 6, and 8 from MILNE *et al.* (2001; 2003).**

Another proposition is to calculate the proportion of EuHA complex at different ionic strength vs. the concentration of HA using the generic data from MILNE *et al.* (2003) on Figure 4-17.



**Figure 4-17. Influence of ionic strength on the proportion of 10  $\mu\text{mol}_{\text{Eu}}$  L<sup>-1</sup> fixed to the generic humic acid defined by MILNE *et al.* (2003) at pH 4.**

#### 4.3.4.2. $M^{4+}$ cations and actinides(IV)

MILNE *et al.* (2003) proposed estimated data for  $\text{Th}^{4+}$  from Equations 4-19, *i.e.*  $\log_{10} \tilde{K}_{\text{Th}^{4+},1} \approx 7.4$  and  $\log_{10} \tilde{K}_{\text{Th}^{4+},2} \approx 20$ . The values obtained using our estimations are given in Table 4-2. From the data

dispersion, one can think that the uncertainties on  $\log_{10}\tilde{K}_{i,j}$  should be important and are to be used with great care in predictive calculations.

It is difficult to comment the rather important values, particularly for U,Np,Pu(IV) without dedicated experimental data. One could propose the reinterpretation of literature data in the framework of NICA-Donnan. One can also note that  $An^{4+}$  ions are extremely minor in the usual calibration of NICA-Donnan model (pH 4, 6, and 8). The use of mixed complexes would be envisaged as for  $Fe^{3+}$  ([WEBER et al., 2006a](#); [WEBER et al., 2006b](#)), but non-charged  $An(OH)_4(aq)$  species are more difficult to account for, and would be major from pH 6 ([NECK & KIM, 2001](#); [RAND et al., 2009](#))\*.

**Table 4-2: Estimation of  $n_{i,j}$  and  $\log_{10}\tilde{K}_{i,j}$  values for actinides(IV) using our estimations and the first hydrolysis constant for Zr(IV) ([BROWN et al., 2005](#)), Hf(IV) ([RAI et al., 2001](#)), Th(IV) ([RAND et al., 2009](#)), and U,Np,Pu(IV) ([GUILLAUMONT et al., 2003](#)).**

	$\log_{10}^*K_1^o$	$n_{An^{4+},1}$	$n_{An^{4+},1} \log_{10}\tilde{K}_{An^{4+},1}$	$n_{An^{4+},2} \pm 0.18$	$n_{An^{4+},2} \log_{10}\tilde{K}_{An^{4+},2}$	$\log_{10}\tilde{K}_{An^{4+},1}$	$\log_{10}\tilde{K}_{An^{4+},2}$
Zr(IV)	0.32	$0.14 \pm 0.07$	$3.2 \pm 0.6$	0.11	$6.2 \pm 1.1$	$22 \pm 12$	$58 \pm 98$
Hf(IV)	-0.2	$0.17 \pm 0.07$	$3.0 \pm 0.6$	0.11	$5.9 \pm 1.1$	$18 \pm 8$	$46 \pm 64$
Th(IV)	-2.5	$0.29 \pm 0.06$	$2.3 \pm 0.5$	0.22	$4.7 \pm 1.0$	$7.8 \pm 2.4$	$21 \pm 18$
U(IV)	-0.54	$0.19 \pm 0.07$	$2.9 \pm 0.6$	0.14	$2.9 \pm 0.6$	$15 \pm 6$	$39 \pm 50$
Np(IV)	-0.55	$0.13 \pm 0.07$	$3.2 \pm 0.6$	0.10	$6.3 \pm 1.1$	$25 \pm 14$	$64 \pm 116$
Pu(IV)	0.6	$0.13 \pm 0.07$	$3.2 \pm 0.6$	0.10	$6.3 \pm 1.1$	$25 \pm 14$	$64 \pm 117$

#### 4.3.4.3. Considerations on mixed complexes

Justification of mixed complexes is not straightforward. A certain number of these mixed complexes was proposed from slope analyses ([DIERCKX et al., 1994](#); [GLAUS et al., 1995](#); [PANAK et al., 1996](#); [MORGENSTERN et al., 2000](#)) [[12,18,22](#)], most of them in the framework of the CNM ([KIM & CZERWINSKI, 1996](#)), to counter balance the constraint of the limited number of available site when  $pH \geq 7-8$  ([PANAK et al., 1996](#)). [POURRET et al. \(2007c\)](#) seem to show that the mixed  $Eu(CO_3)_2HA$  complex proposed by [DIERCKX et al. \(1994\)](#) does not occur. Nevertheless, the analysis of the raw data from [POURRET et al. \(2007a, 2007c\)](#) seem to show that a complex like  $EuCO_3HA(I)$  proposed by [PANAK et al. \(1996\)](#) would help in interpreting the disagreement between awaited and obtained data [[53](#)], as long as the analogy between Cm(III) and Eu(III) can be done. The evidence of the mixed complexes were from slope and spectroscopic analysis by [PANAK et al. \(1996\)](#) and [MORGENSTERN et al. \(2000\)](#). To my opinion there is nevertheless a bias as for the mixed hydroxo complexes, one cannot discriminate an  $H^+$  that is freed from the hydrolysis of water by  $Cm^{3+}$  and the release of an  $H^+$  from complexation. As in the principles of CNM, no sites are explicitly activated and are limited to  $pH \approx 8$ , they can also be attributed to the hydrolysis of water by the metal to form  $Cm(OH)_nHA$ . This does not mean that these complexes do not occur, but that they must be evidenced clearly.

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$An(OH)_3^+ + H_2O \rightleftharpoons An(OH)_4^0 + H^+$   $\log_{10}K^o = -6.4$  for Th(IV),  $-6.6$  for U(IV),  $-6.1$  for Np(IV),  $-6.2$  for Pu(IV)

MORGENSTERN *et al.* (2000) noted that the luminescence spectra and decay time evolution were rather continuous, and did not allow to clearly define a species. We came to the same conclusion on Eu(III) [8,81]. These species were then defined by fitting the spectral evolution of Cm(III) between two extreme situations and looking for the lower number of species that can help in interpreting the spectral variation. Nevertheless, it seems difficult to obtain better results in this particular case. In the case of Eu(III) we also obtained a continuous evolution [8,81], which would be easier to interpret in the framework of a continuous distribution framework, like NICA-Donnan. We must nevertheless admit that fitting results, as satisfactory as they can be are not a direct evidence of the existence of a species.

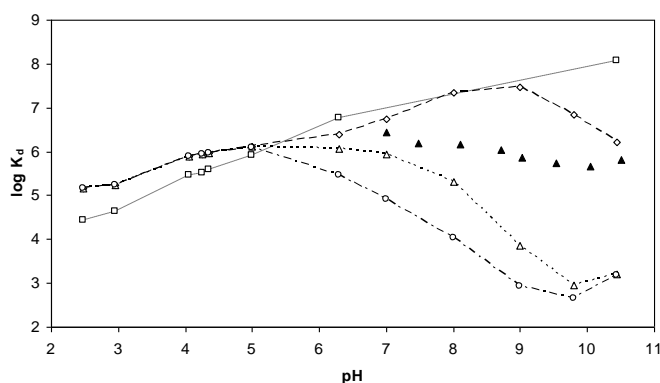


Figure 4-18. Comparison of data from POURRET *et al.* (2007a) without carbonate (□), from POURRET *et al.* (2007c)  $[\text{HCO}_3^-] = 0.01 \text{ mol L}^{-1}$  (▲) with the estimations from CNM on Cm(III) (PANAK *et al.*, 1996; MORGENSTERN *et al.*, 2000): complexes MHA(III) and  $\text{M}(\text{OH})_n\text{HA}(\text{III}-n)$  without carbonate (◇), MHA(III) and  $\text{M}(\text{OH})_n\text{HA}(\text{III}-n)$  with carbonates (○), MHA(III) +  $\text{M}(\text{OH})_n\text{HA}(\text{III}-n)$  +  $\text{MCO}_3\text{HA}(\text{I})$  with carbonate (△).

#### 4.4. SPECTROSCOPIC STUDIES ON EUROPIUM(III)

##### 4.4.1. Time-resolved laser-induced luminescence

The time-resolved laser-induced luminescence spectroscopy (TRLS) allows obtaining luminescence spectra as a function of excitation wavelength – obtained after the excitation of a pulsed laser –, as well as to the luminescence decay. It has been used for the detection of lanthanides/actinides(III) and uranium(IV) in various conditions (BERTHOUD *et al.*, 1989; MOULIN *et al.*, 1990; MOULIN *et al.*, 1995; MOULIN *et al.*, 1998), including micellar media (MOULIN *et al.*, 1991) [41-44,51]. The time resolution is particularly important in organic media, as humic substances, to get rid of their very intense and fast decaying luminescence –  $\tau < 100 \text{ ns}$ , see figure 3 from BERTHOUD *et al.* (1989). Europium(III), as other lanthanides(III)\* and actinides(III)†, shows luminescence properties. Its main transitions being from the  $^5\text{D}_{0,1}$  excited‡ to the fundamental  $^7\text{F}_j$  ( $0 \leq j \leq 5$ ) manifolds (BÜNZLI, 1989; BÜNZLI *et al.*,

\*  $\text{Ce}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Tm}^{3+}$

†  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$

‡  $\nu(^5\text{D}_0) = 17\,257 \text{ cm}^{-1}$

2007). The luminescence decay time of aquo-ion is *ca.* 110  $\mu\text{s}$  (HORROCKS & SUDNICK, 1979), weakly dependent of temperature (KUKKE *et al.*, 2010) contrary to  $\text{UO}_2^{2+}$  (MORIYASU *et al.*, 1977) [51].

In our case, only the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions were obtained (Figure 4-19). Evolutions of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_i$  manifold (ALBIN & HORROCKS, 1985; FREY & HORROCKS, 1995; GÖRLLER-WALRAND & BINNEMANS, 1996), and of the ratio between  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition ( ${}^7\text{F}_2 / {}^7\text{F}_1$ ) give information on the symmetry of the formed complex (JØRGENSEN & JUDD, 1964), and on the covalence of the Eu-ligand bond, respectively. The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition is not allowed by the selection rules, but can this can be partly allowed if the symmetry has no centre of inversion (GÖRLLER-WALRAND & BINNEMANS, 1996). In the case of europium(III), excitation is generally done by a tuneable laser source at  $\lambda_{\text{exc}} \approx 394 \text{ nm}$  (CARNALL *et al.*, 1968), the value of which corresponds to the transition  ${}^5\text{L}_6 \leftarrow {}^7\text{F}_0$ . After inner conversion, and thanks to the time-resolution of the signal, one can observe the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_i$  manifold. For the Eu(III)-HS complexes, the increase of luminescence, compared to  $\text{Eu}^{3+}$  is also due to an energy transfer from the excited chromophores of HS, from the triplet state  ${}^3\pi\pi^*$  to the  ${}^5\text{D}_i$  levels of Eu(III) (BÜNZLI *et al.*, 2007). In the case of simple organic molecules, this triplet state is of about 19 000-25 000  $\text{cm}^{-1}$  (KUMKE *et al.*, 2005); in the case of natural organic matter, it seems that these levels should be around 14 000-15 500 and 20 500  $\text{cm}^{-1}$  (ZEPP *et al.*, 1985; BRUCCOLERI *et al.*, 1993).

Even if luminescence data are existing on Eu(III)-HS (SHIN *et al.*, 1995; THOMASON *et al.*, 1996; MONSALLIER *et al.*, 2003; PLANCQUE *et al.*, 2003; KUMKE *et al.*, 2005; JAIN *et al.*, 2009), it is not always easy to have a general view on the luminescence properties of this system. We have undertaken a systematic exploration of the luminescence spectra and decay time of complexed-Eu(III) by the humic extracts that we are commonly using. Even if the humic substances show very similar complexation properties whatever the origin, it is noteworthy that there are slight differences in the chemical environments of our eight different samples [9,13,14],\* the spectra of seven of which are presented in Figure 4-19. The very close  ${}^7\text{F}_2 / {}^7\text{F}_1$  ratios indicate that very close types of bonds are in play within these complexes (LAVÍN *et al.*, 2001).

The luminescence decay is described by a sum of first order kinetics. For a fully integrative system as a photo diode array, the following relationship is obtained,

$$F = \sum_{i=1}^n \int_D^{D+W} F_i^0 \exp\left(-\frac{t}{\tau_i}\right) dt = \sum_{i=1}^n F_i^0 \tau_i \exp\left(-\frac{D}{\tau_i}\right) \left[1 - \exp\left(-\frac{W}{\tau_i}\right)\right] \quad (4-20)$$

where  $F$  is the total luminescence,  $F_i^0$  is the initial luminescence of the  $i^{\text{th}}$  decaying phenomenon,  $\tau_i$  is the decay time of the  $i^{\text{th}}$  decaying phenomenon,  $D$  is the observation delay after the laser flash, and  $W$  is the width of the observation gate.

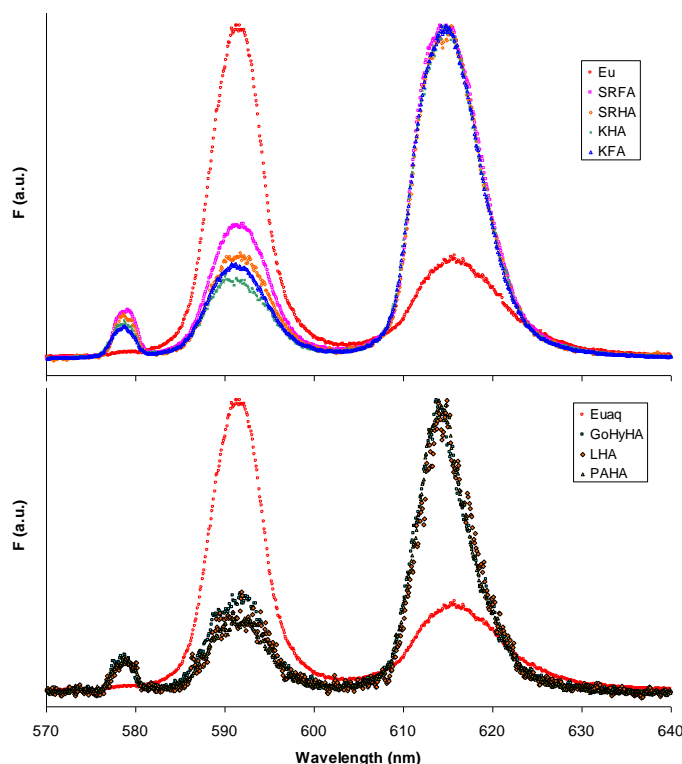
\* In the framework of european integrated project FUNMIG [56].



In the presence of humic substances, the luminescence decay of lanthanides, *i.e.*, Tb(III) and Eu(III), and actinides(III), *i.e.*, Cm, is systematically bi-exponential ([PANAK \*et al.\*, 1996](#); [MORGENSTERN \*et al.\*, 2000](#); [CHUNG \*et al.\*, 2005](#); [KUMKE \*et al.\*, 2005](#); [FREYER \*et al.\*, 2009](#)) [[8,9,11,13,14](#)].

$$F = F^{\circ} \left\{ x_1 \tau_1 \exp\left(-\frac{D}{\tau_1}\right) \left[ 1 - \exp\left(-\frac{W}{\tau_1}\right) \right] + (1 - x_1) \tau_2 \exp\left(-\frac{D}{\tau_2}\right) \left[ 1 - \exp\left(-\frac{W}{\tau_2}\right) \right] \right\} \quad (4-21)$$

where  $F^{\circ}$  is the overall initial luminescence, and  $x_1$  is the proportion of the first decay.



**Figure 4-19.** Normalised luminescence spectra of  $[\text{Eu(III)}] = 10 \mu\text{mol L}^{-1}$  in  $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ ,  $C_{\text{SH}} = 200 \text{ mg L}^{-1}$ ,  $\text{pH } 5$ ,  $\lambda_{\text{exc}} = 394 \text{ nm}$ ,  $\text{Delay} = 10 \mu\text{s}$ ,  $\text{gate width} = 300 \mu\text{s}$ ,  $\text{grating } 600 \text{ lines mm}^{-1}$ :  $\text{Eu}^{3+}$  (red circle), and Eu-HS complexes Suwannee River FA (SRFA, empty squares), Suwannee River HA (SRHA, empty diamonds), Kranishsee HA (KHA, crosses), Kranishsee FA (KFA, empty triangles), Gorleben HA (GoHyHA, filled squares), Leonardite HA (LHA, filled diamonds), Purified Aldrich HA (PAHA, filled triangles) [[13](#) © 2009 Elsevier Ltd].

#### 4.4.2. Luminescence spectra of Eu(III)-HS complexes

As seen earlier, the bands of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  manifold can be used to propose complex symmetry. The manifold is supposed to show at maximum 1 ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ), 3 ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) and 5 ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) lines. In aqueous solution these lines are not easily observed due to line broadening. The aquo-ion is mainly  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$ . YAMAGUCHI *et al.* ([1988](#)) proposed 8.6 water molecules with equivalent distances. The awaited ideal symmetry of the aquo-ion can be  $\text{D}_{4h}$  (8  $\text{H}_2\text{O}$ ) or  $\text{D}_{3h}$  (9  $\text{H}_2\text{O}$ ). MARMODÉE *et al.* ([2010](#)) proposed decay times of *ca.* 110  $\mu\text{s}$  for  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$  and *ca.* 120  $\mu\text{s}$  for  $\text{Eu}(\text{H}_2\text{O})_8^{3+}$ . From observation at 4-5 K it seems that aquo-ion shows a  $\text{C}_{2v}$  symmetry ([MARMODÉE \*et al.\*, 2010](#)), which means that the



H<sub>2</sub>O molecules are not equivalent for Eu(H<sub>2</sub>O)<sub>8</sub><sup>3+</sup> at 4-5 K, which also suggests that Eu(H<sub>2</sub>O)<sub>9</sub><sup>3+</sup> is major in solution at ambient temperature.

In every Eu(III)-HS complexes the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> transition – an induced electric dipole – is always apparent showing symmetry point group that have no centre of inversion [13] (GÖRLLER-WALRAND & BINNEMANS, 1996). The <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition – magnetic dipole – is generally showing larger full width at mid heights than the aquo ion [13], and more than two bands can be proposed (GÖRLLER-WALRAND & BINNEMANS, 1996; MARMODÉE *et al.*, 2009b). The <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition – electric dipole, which is hypersensitive to complexation (JØRGENSEN & JUDD, 1964) – is showing the major modifications of luminescence spectra. From the observation of spectra in Figure 4-19, it appears that differences are occurring in the shape of this <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition. The use of a more dispersive grating\* allows obtaining more detailed information. Generally, it seems that humic extracts from an aquatic environment are showing similar <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transitions with an important shoulder at 612 nm (Figure 4-20a) [13]. Concerning the extracts from a terrestrial environment, which are extracted after an alkaline treatment, the 612 nm shoulder is less apparent (Figure 4-20b,c) [2,13]. The origin of this difference in shape of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition is not formerly identified but could be connected to the maturation or humification of the natural organic matter. As a matter of fact, a humic acid extracted from an Ethiopian vertisol (Ghinch) seems showing an intermediate spectrum (Figure 4-20b) [2]. One can think that this surface extract has a lower maturation degree compared to deeper soils.

The use of dispersive grating allows distinguishing more than three lines in the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition of all the Eu(III)-HS complexes analysed so far (Figure 4-20b) [2,14]. Five lines were used to fit the shape of Eu(III)-SRFA(Figure 4-20d) [13]. This indicates that at the most the symmetry of Eu(III)-HS complexes are showing a C<sub>2v</sub> symmetry – 4 lines –, or even monoclinic (C<sub>2</sub>, C<sub>s</sub>) or triclinic (C<sub>1</sub>) symmetry – 5 lines – following GÖRLLER-WALRAND & BINNEMANS (1996) and as proposed by MARMODÉE *et al.* (2009b). One must not forget that a notable proportion of Eu(H<sub>2</sub>O)<sub>8</sub><sup>3+</sup> exists and that it can participate to the degeneracy of the transition. The relative intensities of the lines are different but the straightforward assignment remains difficult. The exact geometry cannot be proposed as the number of ligands is not formerly known, and the use of H<sub>2</sub>O-D<sub>2</sub>O mixtures could help (HORROCKS & SUDNICK, 1979; SUPKOWSKI & HORROCKS, 2002).

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\* 1800 lines mm<sup>-1</sup>

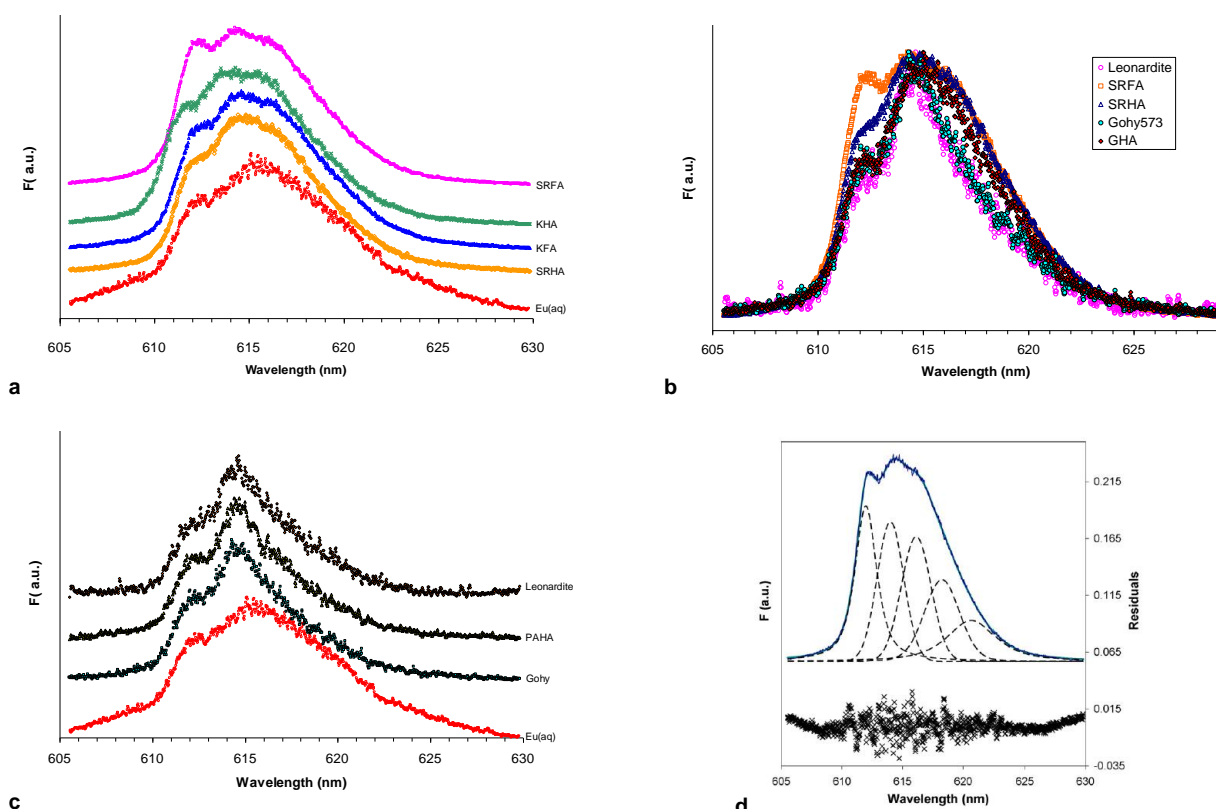


Figure 4-20. Comparison  ${}^5D_0 \rightarrow {}^7F_2$  transition of  $[Eu(III)] = 10 \mu\text{mol L}^{-1}$  in the presence of humic substances  $C_{SH} = 200 \text{ mg L}^{-1}$ ,  $I = 0.1 \text{ mol NaClO}_4 \text{ L}^{-1}$ , grating  $1800 \text{ lines mm}^{-1}$  [9] © 2009 Elsevier Ltd, [13] © 2011 Elsevier Ltd].

#### 4.4.3. Luminescence decay time of Eu(III)-HS complexes

From kinetics theory, bi-exponential decay necessarily implies two different excited states: ideally two different species. In the case of Eu(III)-HS complexes, the shorter decay time is shorter than  $\text{Eu}(\text{H}_2\text{O})_n^{3+}$ . The second decay process is slower than  $\text{Eu}(\text{H}_2\text{O})_n^{3+}$  (Figure 4-21).

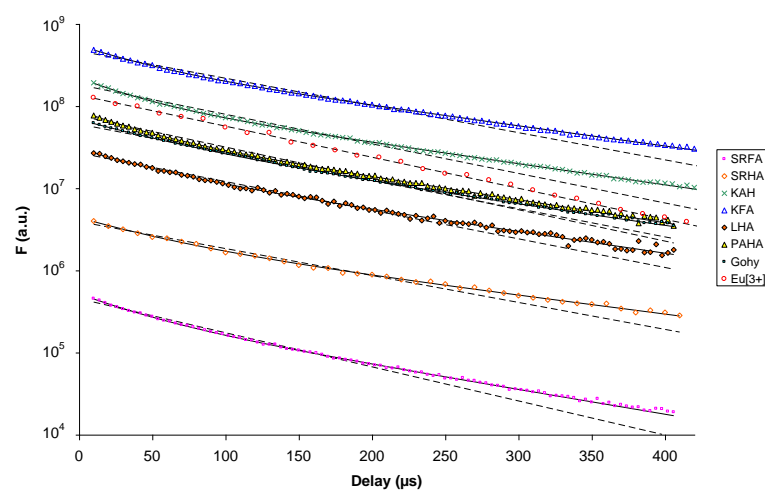
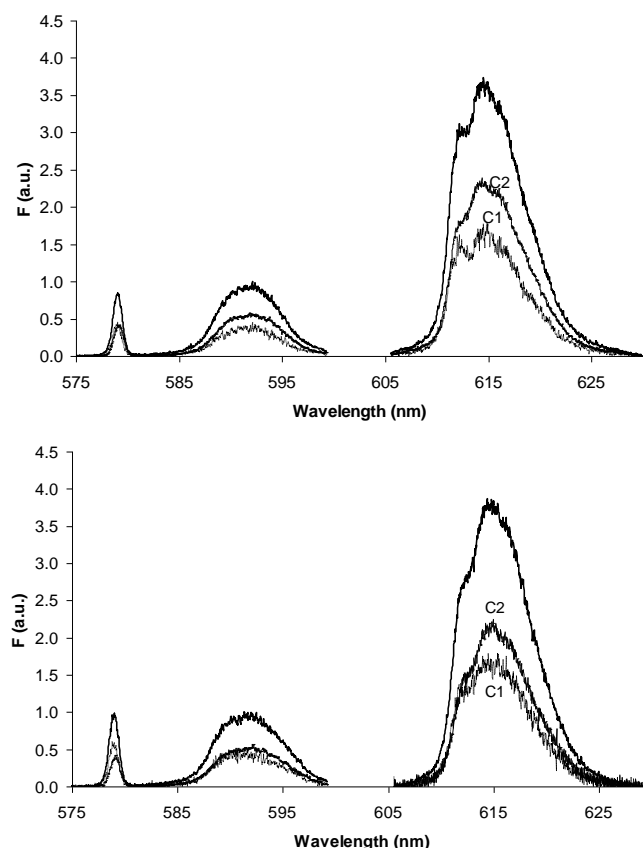


Figure 4-21. Comparison of luminescence decay time of free  $\text{Eu}^{3+}$  (red circles) and complexed by different humic extracts. The dashed lines are mono-exponential fitting and the plain lines are bi-exponential fitting – from [13] © 2009 Elsevier Ltd].

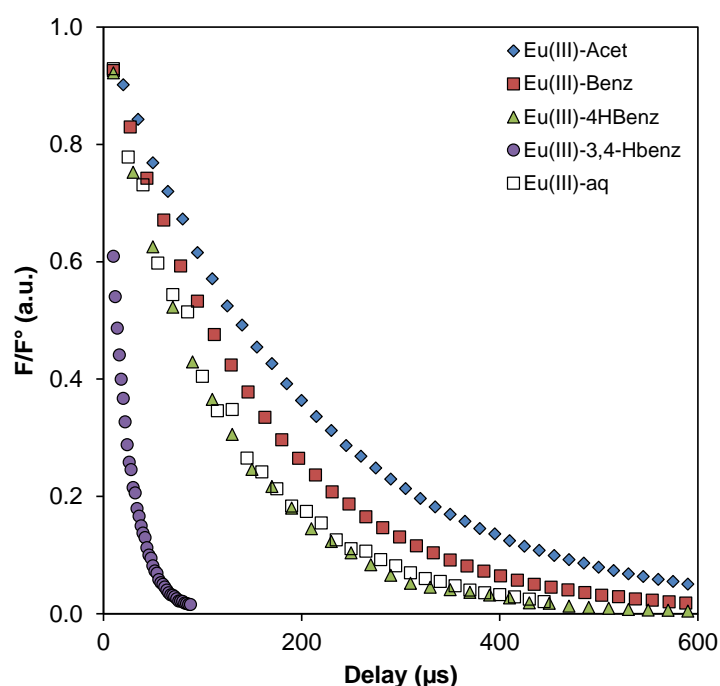
As a multiple decay process originates from multiple excited states, we have tried connecting the decay times to the modifications of spectra *vs.* delay [11]. The originality of the approach lied in the necessary normalisation of the spectra, which was not done in the classical manner applying a homothetic factor at different delay but increasing the integration time with delay such as spectra of comparable intensities could be obtained. Using an 1800 lines mm<sup>-1</sup> grating, significant differences in the  $^5D_0 \rightarrow ^7F_0$  and  $^5D_0 \rightarrow ^7F_2$  transitions can be observed as a function of delay, which allows proposing two different spectra for the two decay processes (Figure 4-22).



**Figure 4-22. Propositions of luminescence spectra for the fast (C1) and slow (C2) decays of Eu(III) complexed by Suwannee River fulvic (left) and humic (right) acids – from [11] © 2010 Elsevier Ltd].**

It is still difficult to formally assign a complex to these spectrum-decay time couples. Nevertheless, we have observed this type of phenomenon in various conditions, and it seems that the  $\tau_1$  values are rather insensitive to physico-chemical conditions. As we will see it further in the text, Eu(III) also shows bi-exponential luminescence decay in ternary system Eu/HA/surface; the faster decay time is fairly insensitive to pH conditions [7,8,81]. A possible interpretation could be a fast exchange between excited  $(Eu^{3+})^*$  and  $(Eu-HA)^*$  complexes as proposed otherwise (TSUKAHARA *et al.*, 2000; BILLARD & LÜTZENKIRCHEN, 2003; FREYER *et al.*, 2009). KUMKE *et al.* (2005) proposed the participation of an intramolecular energy back transfer in the case of Tb(III)-HS complexes, but they do not observed the same phenomenon on Eu(III)-HS as observed otherwise [2,7,8,11,13]. Nevertheless, there is a possibility that these bi-exponential decays come from different complexation environments. KUKE *et al.* (2010) and PLANCQUE *et al.* (2005) reported that the decay time of Eu(III) complexed by salicylic

acid (2-hydroxybenzoic acid) or phenylacetic acid are showing a lower than  $\tau(\text{Eu}^{3+})$  – *ca.* 90  $\mu\text{s}$  and 50  $\mu\text{s}$  for salicylic and phenylacetic acid, respectively –, whereas the decay time of, *e.g.* glycolic acid,<sup>\*</sup> was higher than  $\tau(\text{Eu}^{3+})$ . In the same manner, in the Pauline Moreau's PhD thesis [1,80] we also showed that the decay time of Eu(III) complexed by a series of hydroxybenzoic acids (4-hydroxybenzoic, 3,4-dihydroxybenzoic) are also either equal or lower than  $\tau(\text{Eu}^{3+})$  (Figure 4-23). Thus, it cannot be excluded that the fast component of the bi-exponential decay is due to the complexation environment provided by hydroxybenzoic acids. Conversely, we also recently showed that benzoic acid induces an increase of decay time, although lower than Eu(III) complexed by acetic acid [79]. The lowering of the decay time, relative to monocarboxylic acids seems to be due to the presence of aromatic moieties. An illustration is proposed on Figure 4-23. Nevertheless, no aromatic ligand shows a bi-exponential decay.



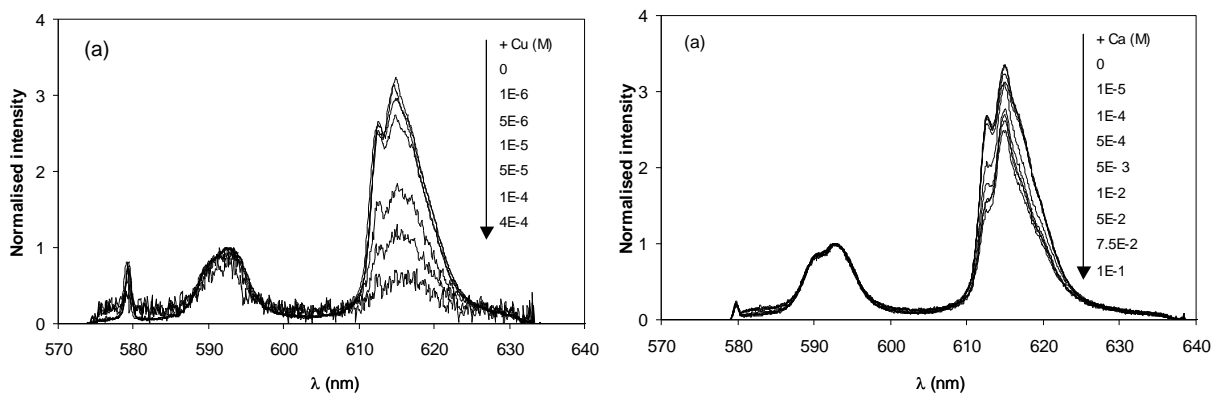
**Figure 4-23.** Comparison between the mono-exponential decay profiles of different Eu(III) complexes: aquo complex (empty squares) [13], acetate (blue diamonds) [79], benzoate (red squares) [79], 4-hydroxybenzoate (green triangles) [1,80], and 3,4-hydroxybenzoate (purple circles) [1,80].

#### 4.4.4. Competition Ln(III)-Ca(II) and Ln(III)-Cu(II)

The analyses of both luminescence spectra (Figure 4-24) and decay times of Eu(III) in different solutions [14], allows showing that in the competitive Eu(III)/Cu(II)/HA system, the competition between metal for the complexing sites is important. From the complexation data in Marang *et al.* [17], it can be calculated that Cu(II) expulses Eu(III) from the specific complexing sites to the non-specific Donnan volume, the nature of which is awaited to be close to the bulk aqueous solution. The

\* hydroxyacetic acid

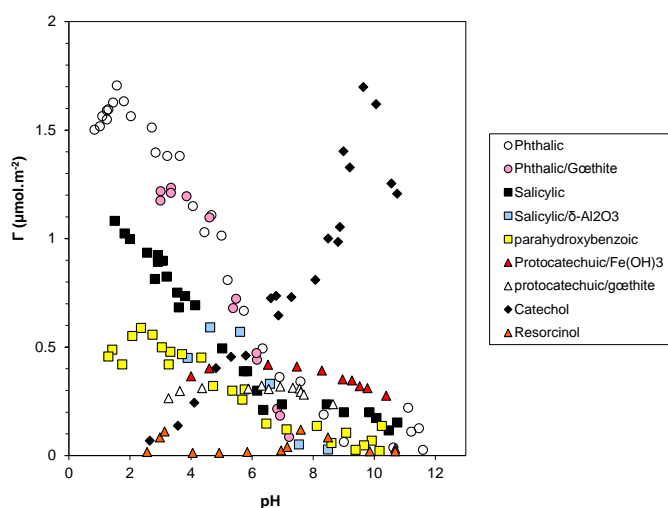
Eu(III) luminescence spectra are suggesting that the increase of Cu(II) changes the Eu(III) chemical environment to a less specific environment as the asymmetry ratio  ${}^7F_2/{}^7F_1$  is strongly decreasing (Figure 4-24a). In the Eu(III)/Ca(II)/HA system, the competition was awaited to be less important [17]. Effectively, the competition of Ca(II) implies a lesser important modification of the chemical environment of Eu(III), which stays in specific interaction with HS from the  ${}^7F_2/{}^7F_1$  ratio (Figure 4-24b).



**Figure 4-24. Luminescence spectra of [Eu(III)]  $5 \mu\text{mol L}^{-1}$  (left) and  $7 \mu\text{mol L}^{-1}$  (right) in the presence of Gorleben humic acid  $c(\text{HA}) = 15 \text{ mg L}^{-1}$  (left) and  $20 \text{ mg L}^{-1}$  (right), as a function of Cu(II) (left) and Ca(II) (right) concentration – from [14 © 2009 Elsevier Ltd,82].**

## 5. INFLUENCE OF NATURAL ORGANICS ON THE ADSORPTION OF LANTHANIDES AND ACTINIDES ONTO MINERAL SURFACES

Once the interactions between radionuclides and humic substances are quantified, modelling of real systems requires the account of adsorption onto mineral surfaces. As in the case of simple organics ([PARFITT \*et al.\*, 1977a](#)), it is clear that the main driving force of NOM adsorption is the ligand exchange that can be evidenced in Fourier transform infrared spectroscopy ([PARFITT \*et al.\*, 1977b](#); [GU \*et al.\*, 1994](#); [YOON \*et al.\*, 2004](#)). But, as said earlier, an important part comes from the formation of sitting particles on the surface, which held together through lateral interactions ([OCHS \*et al.\*, 1994](#)). The fact that there is an overcompensation of charges ([VERMEER, 1996](#); [AU \*et al.\*, 1999](#)) [25] during adsorption is a clear indication. Description of adsorption of simple ions onto surfaces ([GAINES & THOMAS, 1953](#); [DZOMBAK & MOREL, 1990](#); [LYKLEMA, 1995a, 1995b](#); [HIEMSTRA & VAN RIEMSDIJK, 1996](#); [BRADBURY & BAEYENS, 2005, 2009](#)) [4,80] allows modelling simple organic systems with the help of synergetic surface complexes ([ALI & DZOMBAK, 1996b](#); [ALLIOT \*et al.\*, 2005a](#); [ALLIOT \*et al.\*, 2005b](#); [ALLIOT \*et al.\*, 2006](#)). On the other hand, the case of humic substances is far more difficult to model. Several experimental evidence can be reminded, which are developed otherwise [52, and references therein]. As it has been seen in § 3.2, humic substances cannot be totally compared to simple organic molecules, nor to polyelectrolytes. In this case, the link between structure and reactivity is particularly important. The cohesion of the formed aggregates may appear weak, but the interactions with surfaces are particularly strong.



**Figure 5-1.** Adsorption of aromatic acids – phthalic, or 2-hydroxybenzoic (salicylic acid) – and polyphenols – 1,2-hydroxybenzene (catechol), or 1,3-dihydroxybenzene (resorcinol) – onto hematite ([GU \*et al.\*, 1995](#)), ferrihydrite (3,4-dihydroxybenzoic acid or Protocatechuic, [DAVIS & LECKIE, 1978a](#)), goethite ([Phthalic, ALI & DZOMBAK, 1996a](#); [protocatechuic, EVANKO & DZOMBAK, 1998](#)), and  $\delta$ -alumina ([Salicylic, KRAEMER \*et al.\*, 1998](#)), on the basis of number of moles adsorbed per  $\text{m}^2$  – from [52].

Some parameters can be steadily put forward: (i) pH, which fixes the surface potential of the mineral surface, the ionisation of the humic extract, and the specific interaction between both;

(ii) ionic strength, which governs the distance of closest approach between the surface and the humic extract, as well as the interactions between nanometric humic entities – c.f. § 3.2, and [4] –; and (iii) the different affinities of the functional groups of the humic entities for the mineral surfaces, an illustration of which is given in Figure 5-1 [52] for aromatic acids and phenolic derivatives. These three parameters allow describing, but not necessarily quantifying, the differences in reactivity between humic fractions, but also the fractionation of natural organic matter at the surface.

Indeed, using a linear additive model of the binary systems – *i.e.* metal/surface, metal/HS, and HS/surface – do not allow representing satisfactorily the ternary system in a wide parametric domain (ROBERTSON & LECKIE, 1994; ROBERTSON, 1996; VERMEER *et al.*, 1999; CHRISTL & KRETZSCHMAR, 2001; LUMSDON, 2004). This discrepancy is assigned mainly to the HS or NOM fractionation at the surface – also qualified as adsorptive fractionation – (HEIDMANN *et al.*, 2005; BANAITIS *et al.*, 2006). Even if the results may appear contradictory, the adsorptive fractionation has been evidence (DAVIS & GLOOR, 1981; GU *et al.*, 1994; MEIER *et al.*, 1999; ZHOU *et al.*, 2001; HUR & SCHLAUTMAN, 2003; KAISER, 2003; HUR & SCHLAUTMAN, 2004; BANAITIS *et al.*, 2006) [15,20]. A preferential adsorption of higher molecular weight fractions on oxides or clays was shown for lacustrine or aquatic NOM (DAVIS & GLOOR, 1981; GU *et al.*, 1994; MEIER *et al.*, 1999), whereas adsorption of low molecular weight fraction on iron oxides was proposed for commercial Aldrich HA (HUR & SCHLAUTMAN, 2003). However, HUR & SCHLAUTMAN (2004) have shown in HP-SEC that the apparent molecular weight of non-sorbed fractions of purified Aldrich HA onto hematite was depending on pH: before the point of zero charge (pH 8), the apparent molecular weight was higher than the original one, whereas at higher pH value the apparent molecular weight seemed lower suggesting the preferential adsorption of higher molecular weight fractions. These observations are in accord with our ESI-MS observation of purified Aldrich HA adsorptive fractionation on hematite at pH 7 [20]. Conversely, ZHOU *et al.* (2001) observed the inverse effect for an aquatic FA/göethite system with a preferential adsorption of higher molecular weight at low pH and intermediate molecular weight at high pH value. These latter results are in accord with MEIER *et al.* (1999) who noted a preferential adsorption of higher molecular weight fraction of HS on goethite and kaolinite at pH 4.

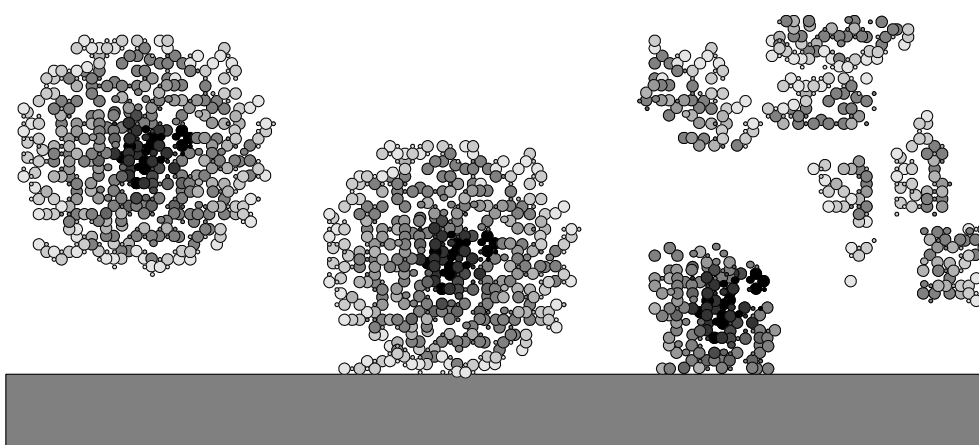


Figure 5-2. Schematic representation of adsorptive fractionation of NOM onto mineral surfaces – adapted from [5].



Another particular effect of NOM adsorption on mineral is the overcompensation of charges ([VERMEER, 1996](#); [AU \*et al.\*, 1999](#)) [25]. This can be interpreted by the adsorption of NOM aggregates that are fixed by ligand exchange but which cohesion is assured through a substantial amount of lateral interaction ([OCHS \*et al.\*, 1994](#)).

Thus, adsorptive fractionation of NOM onto mineral surfaces will be function of NOM origin, and of crystallo-chemistry of the surface. This modification of the composition of organic fractions at the surface and in solution necessarily has an influence on the functionality of these fractions, organisation of the nanometric entities, electrostatic interactions between entities, and complexation properties of the different entities. The link between reactivity and structure of humic substances, and of NOM in general, is here also at the centre of the problem.

### **5.1. QUANTIFICATION OF THE COMPLEXATION SITES AT LOW HUMIC SUBSTANCES CONCENTRATIONS**

One of the most reliable methods to quantify the number of acid-base functions of humic substances is potentiometric titration. The main drawback of this method is the high concentration in solution – generally in the range of  $1 \text{ g L}^{-1}$  – necessary to obtain a signal, which can be considered as significantly different from the background electrolyte ([RITCHIE & PERDUE, 2003](#)) [10,19]. These conditions are often unrealistic compared to natural concentrations which can occur in current natural media – *i.e.*  $0.1$  and  $100 \text{ mg L}^{-1}$  –, *a fortiori* in supernatant of adsorption experiment under laboratory conditions in NOM/surface or metal/NOM/surface. Furthermore, the variety of possible acid-base sites leads to an indetermination on the end point of the titration curve. As an example, one can remind the deprotonation constant of phenolic functions of dihydroxybenzoic acids, the values of  $\text{pK}$  is higher than  $12.5$  ([SILLÉN \*et al.\*, 1971](#)). This illustrates that acid-base data of humic substances are only valid within the limits of their determination domains, and carry an operational character ([PERDUE \*et al.\*, 1980](#)). Several possible strategies can be used to estimate the functionality modifications of humic extracts in binary or ternary systems. Recently, [WENG \*et al.\* \(2008\)](#) proposed a modelling strategy of  $\text{Cu(II)}$  adsorption onto goethite in the presence of fulvic acid at various pH values, metal and FA concentrations using the Ligand and Charge Distribution (LCD) model, which describes HS adsorption onto mineral surfaces ([FILIUS \*et al.\*, 2003](#); [WENG \*et al.\*, 2006a](#); [WENG \*et al.\*, 2006b](#)). The free energy of the FA during adsorption is adapted without considering any modification of the FA functionality. This implies that the FA adsorptive fractionation has mainly physical sources. From experimental fact the chemical part is evident during adsorption of both FA and HA ([YOON \*et al.\*, 2005](#)).

In the framework of the Noémie Janot's PhD [10,81], and following other previous works [15,20], we have evidenced the chemical origin of the adsorptive fractionation, and partly quantified the influence on functionality. We used the modification of UV/Visible absorbance of humic substances as a function of pH. Even if the spectrophometric properties of HS are thought to be of low use for the determination of functionality ([MACCARTHY & RICE, 1985](#)), its variation as a function of pH



seemed to be a valuable signal to study. However, it seems to be linked to more than a single phenomenon.

Following the works on differential absorption spectrometry during titration of fulvic acids ([DRYER \*et al.\*, 2008](#)), we have proposed an operational relationship between the evolution of absorbance of a humic acid on one hand, and the modification of its charge on the other hand. The probed functional groups in potentiometry are in close vicinity of the humic acids chromophores; the charge variations of the former influence the optical properties of the latter, but even also of all the structure. Ionic strength also influences the spectrophotometric properties of humic substances ([DEL VECCHIO & BLOUGH, 2004](#)), and chromism is also possible ([VEKSHIN, 1987](#)). Hence, the main objective was to evidence a relationship – even an operational one – between these phenomena.

The differential absorption spectra were obtained using

$$\Delta A_{\text{pH}}(\lambda) = \frac{1}{\ell_{\text{cell}}} \left[ \frac{A_{\text{pH}}(\lambda)}{\text{DOC}} - \frac{A_{\text{pH}_{\text{ref}}}(\lambda)}{\text{DOC}_{\text{ref}}} \right] \quad (5-1)$$

where  $\ell_{\text{cell}}$  is the cell length (cm),  $\text{DOC}$  and  $\text{DOC}_{\text{ref}}$  ( $\text{mg}_c \text{ L}^{-1}$ ) are the dissolved carbon concentrations in solution at the considered pH and at the reference pH, respectively.  $A_{\text{pH}}(\lambda)$  and  $A_{\text{pH}_{\text{ref}}}(\lambda)$  are the measured absorbance at the wavelength  $\lambda$  at the considered pH and the reference pH, respectively.

As the absorbance increase is more or less uniform *vs.* pH (Figure 5-3a), the ionic strength effect is minimised around 270 nm. The differential absorption spectra are analysed at 270 nm using an adapted NICA-Donnan equation ([KINNIBURGH \*et al.\*, 1999](#)), and compared to the potentiometric titrations.

Under the hypothesis of the minimisation of ionic strength on the UV/Visible signal at  $\lambda = 270$  nm, the increase of  $\Delta A$  can be related to the increase of the number of charges *vs.* pH. The proportion of  $A_1$  and  $A_2$  are mostly invariant whatever the ionic strength (51/49). It is thus possible to consider the sum of these absorbencies to obtain the operational relationship between the increase of charges and the increase of absorbance.

Surprisingly enough, this relationship is linear as a function of the logarithm of ionic strength (Figure 5-3a,b). The conversion factor can be established taking a high ionic strength, where the structure of the humic acid is more compressed, or the Debye length between the nanometric entities is minimal. Under these conditions, the  $\Delta A = f([\text{H}^+])$  curves can be transformed in an ionic strength independent master curve  $\Delta A = f([\text{H}^+]_0)$  (Figure 5-3c,d).

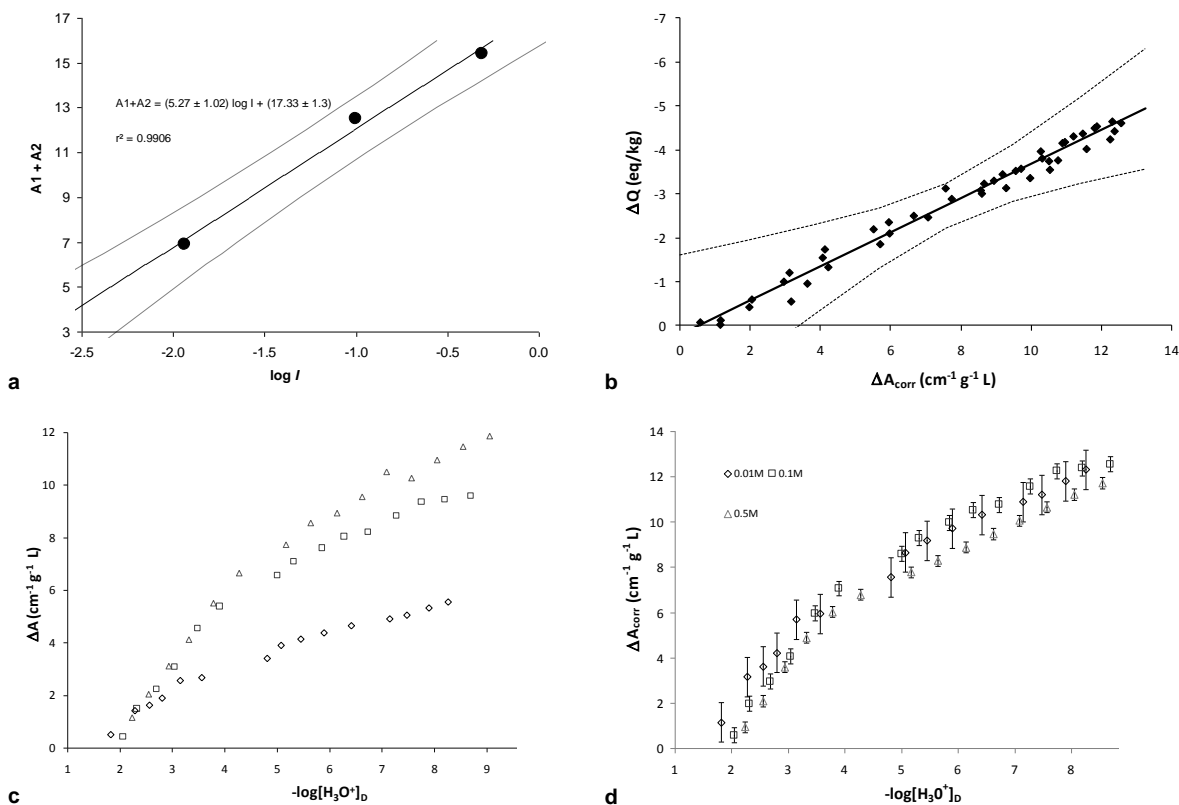
As all operational expression, it does not allow answering the fundamental problems hidden behind its relative success:

- i. for which reason does the relationship is following a linear behaviour with the logarithm of ionic strength?\*

---

\* One can also remind that the Debye-Hückel correction is not straightforwardly applicable in the case of metal complexation by HS [[18,53](#)].

- ii. what is the origin of the absorbance increase in the wavelength range 200-500 nm, when the absorbance of the aromatic compound is limited to a lower range ([ARAUJO \*et al.\*, 2005](#); [ANDRÉ \*et al.\*, 2007](#))?;
- iii. does this expression, or protocol, can be applied to other humic extracts?

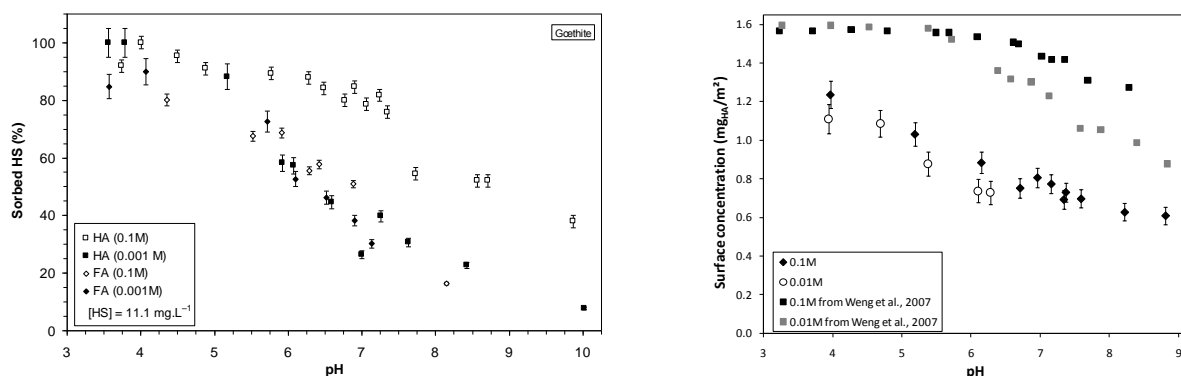


**Figure 5-3. Establishment of the operational relationship between the absorbance of the purified Aldrich humic acid and its functionality obtained through titration: a. relation between total absorbance and ionic strength, b. relation between differential absorbance and charge, c. UV-Visible titration, d. UV/Visible master curve [10 © 2010 American Chemical Society, 81].**

## 5.2. ADSORPTION OF HUMIC SUBSTANCES ONTO METAL OXIDES

The adsorption of humic substances is not comparable to the case of simple organic molecules. Indeed, the ionic strength effect on the adsorption of the latter tends to decrease the adsorption by competition effect ([SCHULTHESS & MCCARTHY, 1990](#); [MESUERE & FISH, 1992a, 1992b](#); [ALI & DZOMBAK, 1996a](#)). In the case of fulvic acids this effect is low or absent ([SCHLAUTMAN & MORGAN, 1994](#); [FILIUS \*et al.\*, 2000](#); [FILIUS \*et al.\*, 2003](#)) [25], whereas for humic acids the adsorption onto minerals is increasing with ionic strength ([MURPHY \*et al.\*, 1994](#); [SCHLAUTMAN & MORGAN, 1994](#); [KRETZSCHMAR \*et al.\*, 1997](#); [AU \*et al.\*, 1999](#); [TOMBÁČZ \*et al.\*, 2000](#); [WENG \*et al.\*, 2006a](#)) [25, 81] due to the concomitant effect of the decrease of the Debye length and the aggregation of HA. We have

verified this evolution on the particular cases of goëthite ( $\alpha$ -FeOOH, Figure 5-4) [25],\* and  $\alpha$ -alumina [3,81].



**Figure 5-4. Adsorption of humic substances as a function of pH (a)  $c = 11.1 \text{ mg L}^{-1}$  onto goëthite  $500 \text{ mg L}^{-1}$  – squares, Aldrich humic acid; diamonds, Fanay-Augères fulvic acid; open symbols,  $I = 0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ ; closed symbols,  $I = 10^{-3} \text{ mol L}^{-1} \text{ NaClO}_4$  [25 © 2002, Elsevier Ltd] – and of humic substances onto  $1 \text{ g L}^{-1}$  goëthite (b) – ■  $I = 0.1 \text{ mol L}^{-1} \text{ NaNO}_3$ ; grey squares,  $I = 10^{-3} \text{ mol L}^{-1} \text{ NaNO}_3$  (WENG *et al.*, 2006a; WENG *et al.*, 2007) –, and Aldrich humic acid onto  $1 \text{ g L}^{-1}$   $\alpha$ -alumina – ○  $I = 0.01 \text{ mol L}^{-1} \text{ NaClO}_4$ , ◆  $I = 0.1 \text{ mol L}^{-1} \text{ NaClO}_4$  [3 © 2012 Elsevier Ltd,81].**

In the case of NOM-assisted migration, it is possible to distinguish two extreme cases: (i) NOM migrates with a minimal interaction with the mineral phases, and fractionation is a second order phenomenon on the migration of a metal; and (ii) NOM suffers an important interaction with mineral phases, and fractionation noticeably modifies the composition of NOM. The former case can be symbolised by a HP-SEC immobile phase, which opposes a size based sorting out of the Eu(III)/NOM complexes [9]; the latter is approached through the different binary systems NOM/oxide [10,15,20,81].

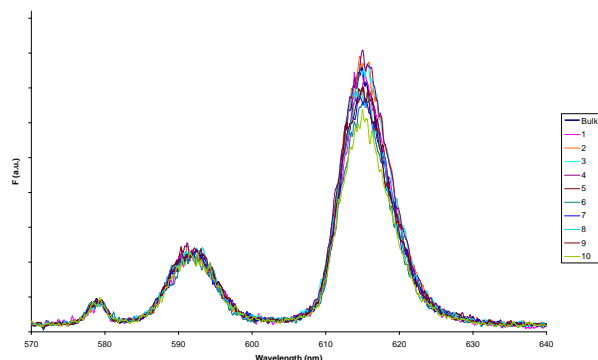
### 5.2.1. Case of an immobile phase with a weak interaction

The chemical environment of europium(III) complexed by HP-SEC fractions of a vertisol humic acid is only very weakly modified (Figure 5-5a); complexation constants are also very similar. Only the later eluted fractions, which are the smaller in relative size, seem to show a significant different symmetry, and a lower number of complexing sites (Figure 5-5b).

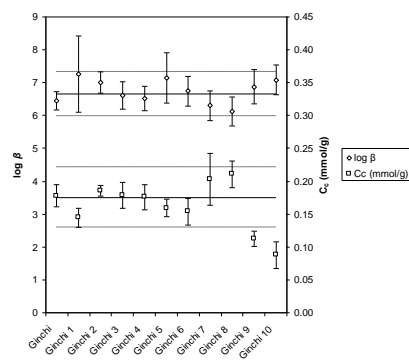
It is then evident that in case of a weak interaction between NOM and mineral surfaces the fractionation of NOM is not an important phenomenon; it could even be neglected, as a first approximation in an operational modelling. This can be directly related to radionuclide transport in sandy soils column experiments in the presence of HA, where the migration of Am(III) or U(VI) could be modelled without accounting for the fractionation (SCHÜBLER *et al.*, 2001; BRYAN *et al.*, 2005; ABRAHAMSEN *et al.*, 2007; BRYAN *et al.*, 2007); the sandy soils being mainly composed of silica are not

\* European project HUMICS [78]

strongly adsorbing NOM under near neutral pH conditions [24]. Column experiments with hematite as the mineral phases clearly required the account of fractionation (ABRAHAMSEN *et al.*, 2008).



**Figure 5-5. Normalised luminescence spectra of Eu(III) complexed by HP-SEC fractions of a vertisol humic acid, [Eu] =  $10^{-5}$  mol L $^{-1}$ ,  $I = 0.1$  mol L $^{-1}$  NaClO $_4$ ,  $C_{HA} = 200$  mg L $^{-1}$ ,  $D = 10$   $\mu$ s,  $W = 300$   $\mu$ s,  $\lambda_{exc} = 394$  nm – from the Supp. Info. of [9].**



**Figure 5-6. Comparison of parameters of Eu(III) complexation by different HPSEC fractions of a vertisol humic acid [9 © 2011 Elsevier Ltd].**

### 5.2.2. Case of mineral phases with a strong interaction and adsorptive fractionation

The fractionation of a humic acid on a mineral surface, and the physico-chemical modification of their composition and structure, can be the origin of the relative failure of linear additivity of ternary systems metal/HS/surface. Though the analyses of humic acids adsorbed on  $\alpha$ -alumina surface\* or in the supernatant of adsorption experiments ( $\alpha$ -Al $_2$ O $_3$  or  $\alpha$ -Fe $_2$ O $_3$ ), we showed that the proportion of different types of carbon evolved with the surface coverage, *i.e.* mass of humic substances over mass of oxide [15,20,81]. Commonly used techniques, such as spectrophotometry and total organic carbon analysis, allow showing the decrease of aromatic moieties that absorb in the UV region [10,15,20,81] (Figure 5-7 and Figure 5-8).

The repartition of the molecules, which build up the humic aggregate, are also strongly disturbed during the adsorption onto oxides. We observed these changes in the supernatant of adsorption experiments of a purified Aldrich humic acid onto  $\alpha$ -Fe $_2$ O $_3$  by ESI-MS [20] (Figure 5-9a-d). There is a shift in the centroid of masses, and an increase in the average “molecular mass”, in number and in weight, when the relative concentration of HA decreases, *i.e.* when the saturation of the surface sites is achieved (Figure 5-9e). This can be directly linked to the decrease of the relative permittivity of water ( $\epsilon_r$ ) under the effect of an electrostatic field of charged particles (BOOTH, 1951; OLSHOEFT, 1981; SHANNON, 1993). It clearly appears that important portions of mass spectra are not present in fractionated samples. Estimations of the number- and weight-averaged masses – or more precisely number- and weight-averaged intensities  $\bar{I}_n$  and  $\bar{I}_w$ , respectively – show an increase in mass (intensity)

\* European Integrated Project FUNMIG [59,63]

distribution for the weaker concentrations of humic acid in the supernatant. This is in agreement with the preferential adsorption of the smaller molecules onto the surface for short contact times (GU *et al.*, 1994; VAN DE WEERD *et al.*, 1999). Afterwards, a progressive decrease of the averaged masses (intensities) is observed when the surface is saturated (Figure 5-9e). From the mass spectra the fraction of intermediate masses ( $m/z \approx 900$  Da) would be more impacted by the fractionation process.

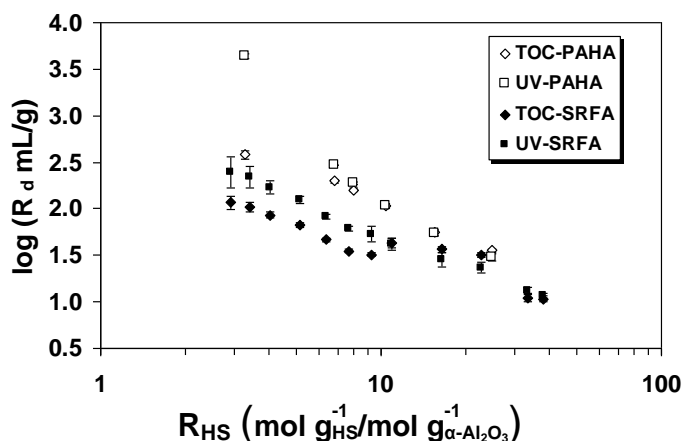


Figure 5-7. Partition coefficient  $R_d$  (mL/g) evolutions for the Suwannee River fulvic acid (SRFA, filled symbols) and purified Aldrich humic acid (PAHA, empty symbols) adsorbed on  $\alpha\text{-Al}_2\text{O}_3$  determined in UV-Visible (squares) and in TOC (diamonds) as a function of the ratio between the mole of HS and of surface reactive sites  $R_{\text{HS}}$  (a), pH 6,  $I = 0.1 \text{ mol kg}^{-1} \text{ NaClO}_4$  – [15] © 2008 American Chemical Society].

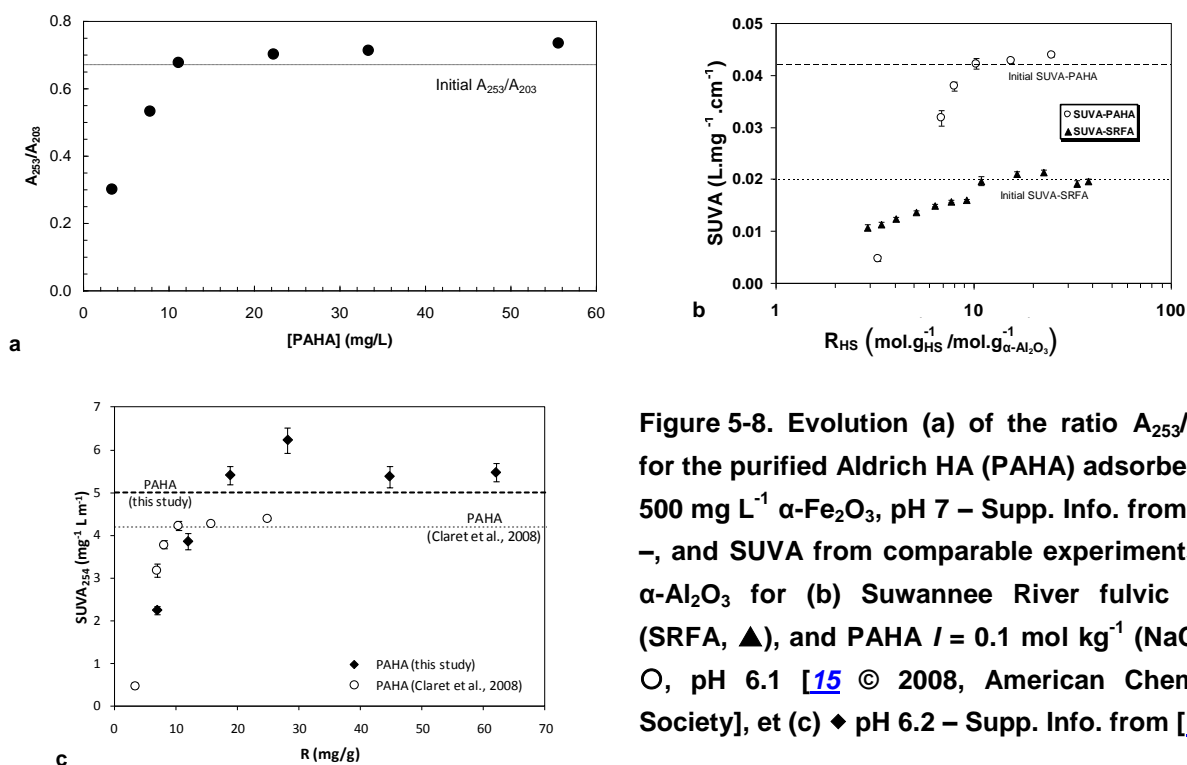
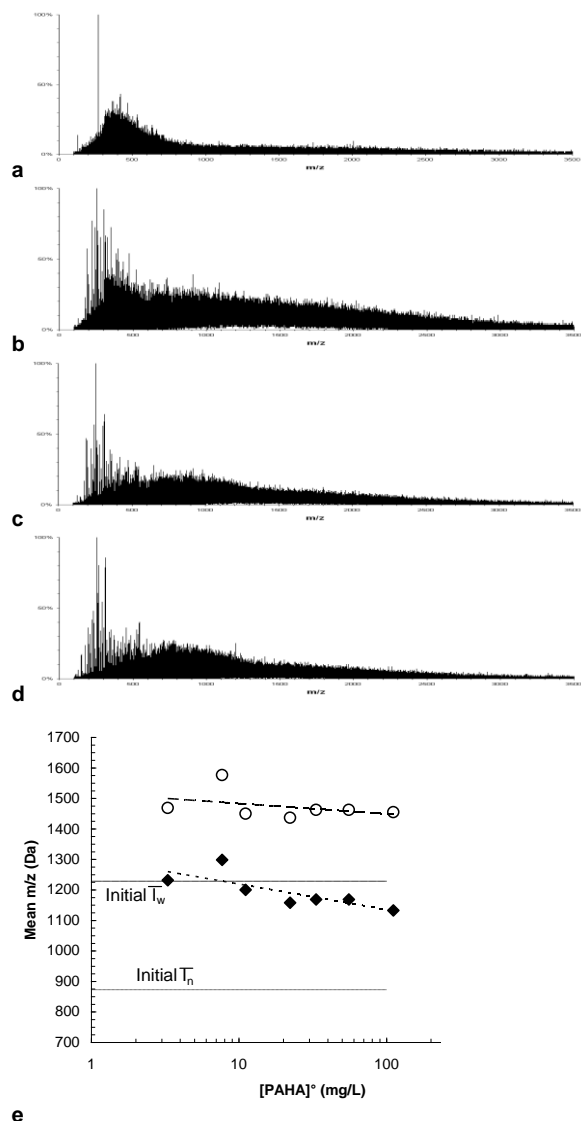
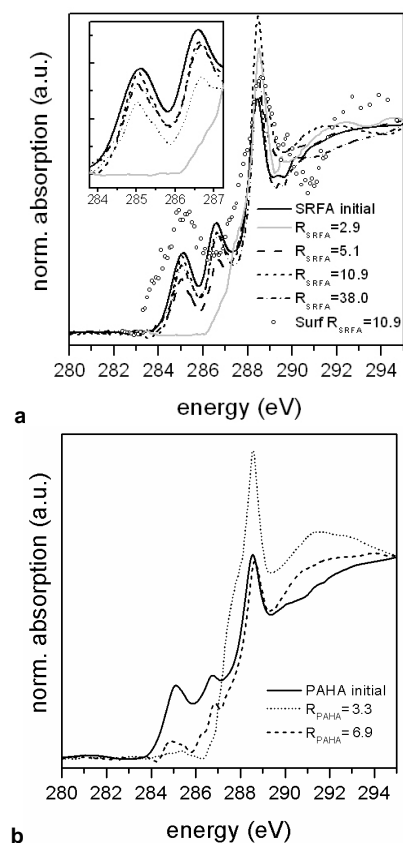


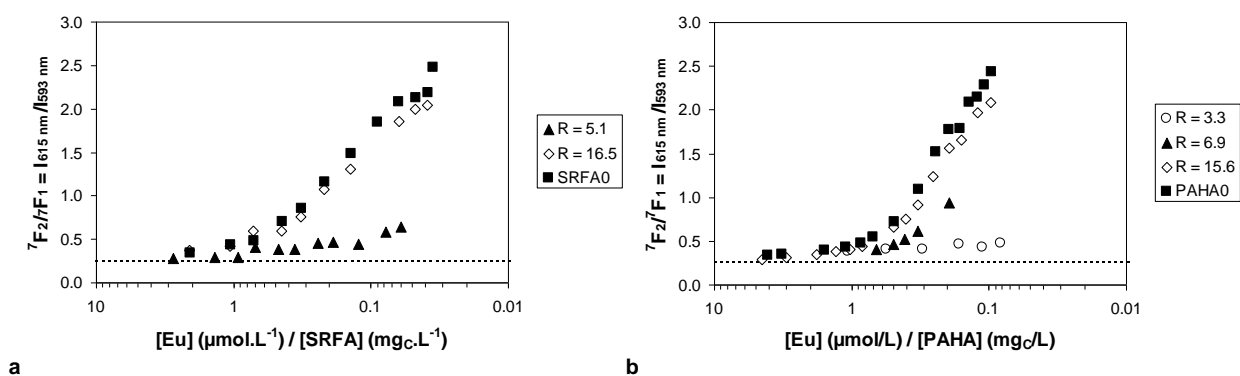
Figure 5-8. Evolution (a) of the ratio  $A_{253}/A_{203}$ , for the purified Aldrich HA (PAHA) adsorbed on  $500 \text{ mg L}^{-1} \alpha\text{-Fe}_2\text{O}_3$ , pH 7 – Supp. Info. from [20] –, and SUVA from comparable experiments on  $\alpha\text{-Al}_2\text{O}_3$  for (b) Suwannee River fulvic acid (SRFA,  $\blacktriangle$ ), and PAHA  $I = 0.1 \text{ mol kg}^{-1} (\text{NaClO}_4)$   $\circ$ , pH 6.1 [15] © 2008, American Chemical Society], et (c)  $\blacklozenge$  pH 6.2 – Supp. Info. from [7].



**Figure 5-9.** ESI Q-ToF Mass spectra of negative ions of purified Aldrich humic acid (PAHA) pH  $\approx$  7 (a) before adsorption:  $c(\text{HA}) = 11 \text{ mg L}^{-1}$ ; (b-d) in the supernatant experiment  $c(\alpha\text{-Fe}_2\text{O}_3) = 500 \text{ mg L}^{-1}$ , for different initial concentrations of PAHA:  $c(\text{HA}) = 33 \text{ mg L}^{-1}$  (b),  $11 \text{ mg L}^{-1}$  (c),  $3.3 \text{ mg L}^{-1}$  (d), and evolution of the number- and weight-averaged « molecular masses » – from [20] © 2006 American Chemical Society].



**Figure 5-10.** C(1s) NEXAFS Spectra obtained before adsorption (plain line), and in the supernatant of adsorption experiment onto  $\alpha\text{-Al}_2\text{O}_3$  for different  $R_{\text{HS}}$  ratios for SRFA (dashed and dotted line), and smoothed spectrum of the SRFA covered  $\alpha\text{-Al}_2\text{O}_3$  sample at  $R_{\text{SRFA}} = 10.9$  (circle) (a), and supernatant of PAHA (b), pH 6.1,  $I = 0.1 \text{ mol kg}^{-1}$  – from [15] © 2008 American Chemical Society].



**Figure 5-11.** Evolution of the  ${}^7F_2/{}^7F_1$  ratios as a function of  $[Eu(III)]/TOC$  ( $\mu\text{mol}_{Eu} \text{ L}^{-1}/\text{mg}_C \text{ L}^{-1}$ ) for the Suwannee River fulvic acid (SRFA, a) and purified Aldrich HA (PAHA, b), for different values of  $R_{HS}$ , pH 4,  $I = 0.1 \text{ mol kg}^{-1}$ : the dashed and dotted are the  ${}^7F_2/{}^7F_1$  ratios of  $Eu^{3+}$  at pH 4 – from [15] © 2008 American Chemical Society].

In the supernatant of adsorption experiment onto  $\alpha\text{-Al}_2\text{O}_3$ , as well as on the surface, the different types of carbon were observed in scanning transmission X-ray microscopy (STXM).<sup>\*</sup> The relative loss of aromatic (285.2 eV) and phenolic (286.6 eV) carbon in the supernatant seen in spectrophotometry is verified (Figure 5-10). A relative enrichment of aromatic carbon is also noteworthy onto the surface.

It is thus clear that the adsorption of humic substances onto oxides involves an extensive modification of the chemical composition of these extracts, and of the formed entities (aggregates). This can be probed in an indirect manner by TRLS (cf. § 4.4, page 63), through the evolution of the chemical environment of europium(III) in contact with the supernatant from adsorption experiments. In the case of Suwannee River fulvic acid and purified Aldrich humic acid shown in Figure 5-11 [15], the  ${}^7F_2/{}^7F_1$  ratios are decreasing with the  $R_{HS}$  ratio between the mass of HS over the mass of  $\alpha\text{-Al}_2\text{O}_3$ . The decreasing proportion of aromatic molecules that can provide an energy transfer to the  ${}^5D_1$  manifold *via* their triplet state induces the decrease of the  ${}^7F_2/{}^7F_1$  ratio. The ratios of the most fractionated sample are comparable to those obtained on simple organic acids such as acetic acid or glycolate (PLANCQUE *et al.*, 2005; KUKU *et al.*, 2010) under comparable conditions. STUMPF *et al.* (2002a) reported different  ${}^7F_2/{}^7F_1$  ratios for the  $Eu(III)$  glycolate system, but for different conditions.<sup>†</sup> One can think that the complexes are not the same.

As we have seen in the previous chapter on structural studies (cf. § 3.2, page 20), humic substances are showing fractal structures in aqueous suspension. The studies on mineral colloids are also showing such aggregation processes (AMAL *et al.*, 1990). In mineral/HS systems, the presence of humic substances imposes a surface fractal organisation. AMAL *et al.* (1992) evidenced a fractal organisation, the structure of which evolves with time; at low surface coverage, a surface fractal dimension is evidenced, the slope of which is decreasing with the HS/surface ratio, to finally end up with a fractal

<sup>\*</sup> Collaboration with the Institut für Nukleare Entsorgung from Karlsruhe Institut of Technology, Forschungszentrum Karlsruhe, Germany; <http://www.fzk.de/fzk/idcplg?IdcService=FZK&node=0048&lang=en>

<sup>†</sup>  $[Eu] = 3 \cdot 10^{-6} \text{ mol.L}^{-1}$ ,  $c(\text{glycolate}) = 1 \text{ mol/L}$ ,  $I = 2 \text{ mol.L}^{-1}$  ( $\text{NaClO}_4$ )

dimension of less compact object. It seems then that the structure of humic substances, and most likely NOM, is in constant evolution as a function of the coverage ratio and physico-chemical conditions.

### 5.3. TERNARY SYSTEMS METAL/HUMIC SUBSTANCES/OXIDES

In the light of the results on the HA/surface system, one can understand that the linear additivity of binary systems is generally not respected, or at least strongly deviates either on oxides (ROBERTSON & LECKIE, 1994; VERMEER *et al.*, 1999; CHRISTL & KRETZSCHMAR, 2001; LUMSDON, 2004; HEIDMANN *et al.*, 2005), or even on clays (SAMADFAM *et al.*, 1998b). Almost thirty years ago, Tipping *et al.* (1983) perceived that the reactivity of adsorbed HA was modified during adsorption and that “extra uptake sites” with higher reactivity were *created* on the surface, or more likely revealed during adsorption. The modifications of structure and functionality allow apprehending these differences, at least from a qualitative point of view. It is noteworthy that the fruitful attempts were met in the case of fulvic acids (HEIDMANN *et al.*, 2005; WENG *et al.*, 2008), which are farther less sensitive to aggregation processes compared to humic substances. Commonly, the linear additivity under-predicts the metal adsorption in the ternary systems above the adsorption pH-edge (VERMEER *et al.*, 1999; CHRISTL & KRETZSCHMAR, 2001; KAR *et al.*, 2011).

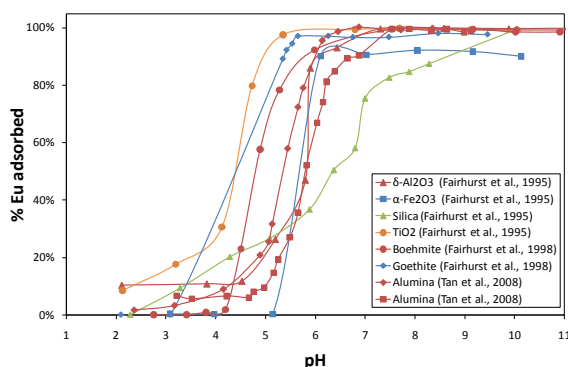


Figure 5-12. Influence of pH on the Eu(III) adsorption on oxides (FAIRHURST *et al.*, 1995a, 1995b; FAIRHURST & WARWICK, 1998; TAN *et al.*, 2008). Lines are guides to the eye – from [81].

In soils the compartment of lanthanides and actinides(III, IV) is strongly linked to the fate of natural organic matter (PÉDROT *et al.*, 2009). The adsorption of these metals is often comparable as a function of pH in the case of oxides for different humic extracts. Referring to the metal/surface pH isotherm (Figure 5-12), humic substances induces an increase of adsorption for the pH before the pH-edge and a decrease of adsorption after the pH-edge. As shown otherwise the position of the adsorption edge is strongly correlated to the first hydrolysis of the metal (DEGUELDRE, 1997; BRADBURY & BAEYENS, 2005, 2009). BRADBURY & BAEYENS (2005, 2009) proposed a linear free energy relationship between  $\log_{10}^* \beta$  and  $\log_{10}^S K$ .



We have mainly focused our work on ternary systems with actinides, or analogues: europium(III) for actinides(III), and thorium for actinides(IV). Mineral surface were metallic oxides:  $\alpha$ -alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>).

### 5.3.1. Europium(III)/aluminium oxide system

#### 5.3.1.1. Macroscopic studies

##### a. Influence on the adsorption of the humic extract

Even if the linear additivity of binary systems is not respected, it is essential to have quantitative information on the binary systems to either model or make predictive calculations on the ternary systems. It is also important to compare the different information. As an example the quantification of humic acid adsorption in the HA/surface system is scarcely verified for the ternary systems metal/HA/surface. KŘEPELOVÁ *et al.* (2006) have proposed this information in the HA/kaolinite and U(VI)/HA/kaolinite systems, but only reported an important difference for a 0.01 mol L<sup>-1</sup> ionic strength and not at 0.1 mol L<sup>-1</sup> (NaClO<sub>4</sub>). For the Eu/HA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system we evidenced an increase of the adsorbed humic acid proportion in the presence of Eu(III) – Figure 5-13, from [8]. The commonly proposed interpretation is the formation of metallic bridge between the surface sites and the humic complex. This proposition is particularly difficult to verify. The modification of the HS structure in bigger aggregates after complexation could also be envisaged (CACECI & BILLON, 1990; CACECI & MOULIN, 1991; PLASCHKE *et al.*, 2002). This would also satisfy the observations from KŘEPELOVÁ *et al.* (2006). The increase in size of the aggregates when ionic strength is decreasing, also observed in ultrafiltration [40], or in viscosity (REY *et al.*, 1996; AVENA *et al.*, 1999; RICE *et al.*, 1999), would allow understanding the lack of U(VI) effect on the adsorption of the synthetic humic acid from KŘEPELOVÁ *et al.* (2006) at 0.1 mol L<sup>-1</sup> (NaClO<sub>4</sub>), but at a lower ionic strength.

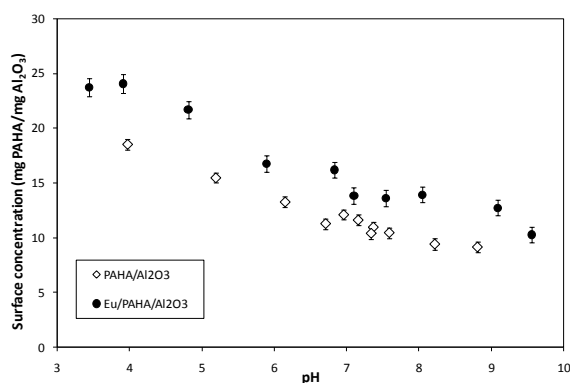
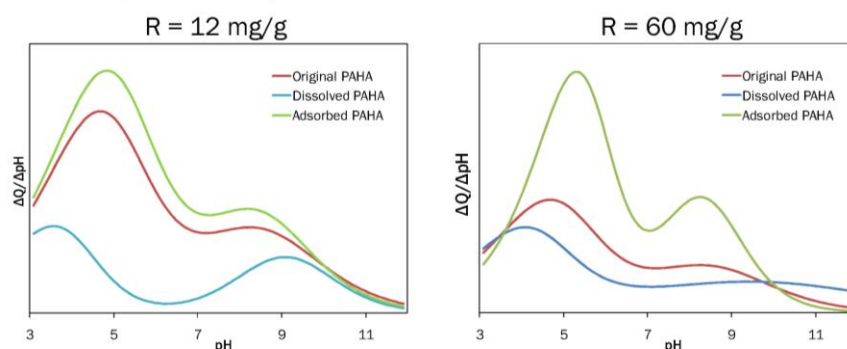


Figure 5-13. Adsorption of Aldrich HA onto  $\alpha$ -alumina as a function of pH in the Eu(III)/HA system and in the Eu(III)/HA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system – from [8] © 2011 American Chemical Society, [81].

##### b. Quantification of the modification of functionality of adsorbed and non-adsorbed humic substances

From the different experiments that we have done so far, the fractionation of NOM is strikingly similar [15,20,81]. The spectrophotometric titration protocol in § 5.1 (page 73), from differential

absorption spectra [10], was applied to the supernatant of PAHA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> experiments at pH 6.8. Here also, the different “humps” which were identified in JANOT *et al.* [10], were also observed for the supernatant, but with significantly different ratios [7,81]. The titration of the supernatant were treated with operational conversion factor [10] between absorbance and charge variation which ends up in a significant decrease of both  $Q_1$  and  $\log_{10}\tilde{K}_{H^+,1}$  as fractionation increases, *i.e.* as the coverage ratio  $R$  decreases; no significant variation of the heterogeneity parameter  $m_{H^+,1}$  can be evidenced. Also, no variation of the high affinity sites could be evidenced as only a non-significant proportion of these sites are ionized at pH 6.8. These variations in  $Q_1$  and  $\log_{10}\tilde{K}_{H^+,1}$  mean that the fractionated humic acid samples are showing a lower functionality with higher acidity. The latter parameter can be reconciled with the comportment of low molecular weight organic acids, the maximum adsorption of which are directly correlated with their  $pK_a$  value; at a certain pH, the lower the  $pK_a$ , the lower the adsorption – see Figure 5-1 from [52]. One can also remind that the first  $pK_a$  of aromatic phthalic and salicylic acids are *approx.* 3 and are showing a very low adsorption (GU *et al.*, 1995; KRAEMER *et al.*, 1998). By analogy, under the neutral pH conditions of our experiments, those kinds of ortho substituted benzoic acids would be comparatively less adsorbed than para substituted benzoic acids, *e.g.* protocatechuic acid\* (DAVIS & LECKIE, 1978a; EVANKO & DZOMBAK, 1998).



**Figure 5-14. Differences in the distribution of functionality at two different surface coverage ratios expressed in  $\text{mg}_{\text{PAHA}} \cdot \text{g}^{-1}_{\alpha\text{-Al}_2\text{O}_3}$  – adapted from [7 © 2010 Elsevier Ltd, 81].**

Knowing the functionality of the original PAHA and of the supernatants of the fractionated samples, the functionality of the adsorbed sample is obtained through mass balance. If the  $\log_{10}\tilde{K}_{H^+,1}$  values are comparable to the original sample, the  $Q_1$  value is increasing for the adsorbed PAHA. As there is no modification in the high affinity-type sites in the supernatant the parameters of the adsorbed sample are also identical for the second distribution. A visual evolution of the affinity distribution is given in Figure 5-14.

### c. Influence on the adsorption of metals

From our results on the chemical environment of Eu(III) in the supernatant of adsorption experiment [15], there is a modification of the chemical composition of humic substances during the adsorption onto mineral surface. This fractionation includes a modification of composition, as well as

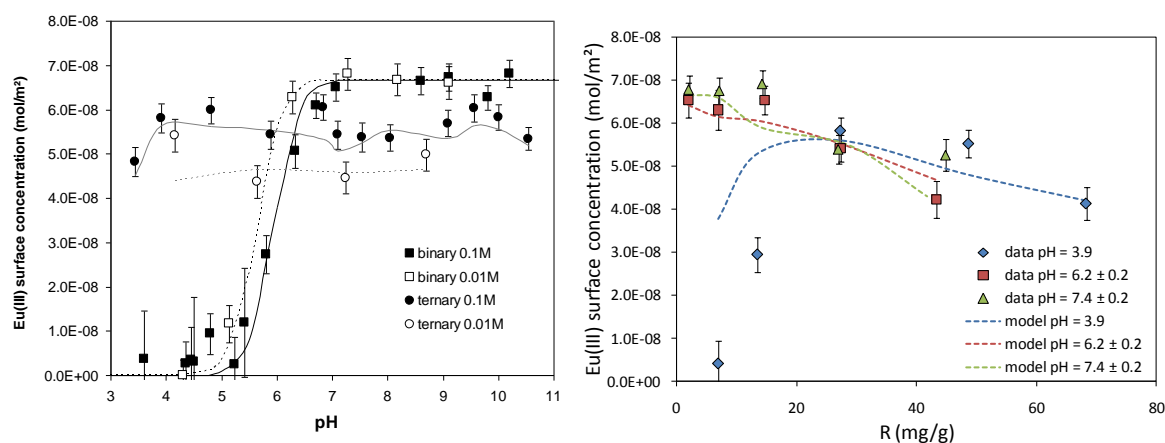
\* 3,4-dihydroxybenzoic acid

functionality (Figure 5-14), the quantification of which were done in an operational manner by spectrophotometric titration (see § 5.1, page 73) [10]. This operational strategy was applied to the prediction of adsorption experiments in the Eu(III)/PAHA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system (Figure 5-15).

One can remind the proposition of TIPPING *et al.* (1983) of the *creation* of extra uptake HA sites of high affinity upon adsorption, which are more likely revealed by the adsorption and fractionation process.

The modelling of the adsorption of the Eu(III)/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system – square symbols in Figure 5-15a adapted from [3,81] – was done using CD-MUSIC model (HIEMSTRA *et al.*, 1989a; HIEMSTRA *et al.*, 1989b; HIEMSTRA & VAN RIEMSDIJK, 1996). The pH-edge is comparable to other system (see Figure 5-12, page 81) and is weakly dependant on ionic strength suggesting inner-sphere surface complexation (RABUNG *et al.*, 1998; RABUNG *et al.*, 2000; CHRISTL & KRETZSCHMAR, 2001; WANG *et al.*, 2006; TAN *et al.*, 2009). The obtained constants were satisfactorily tested on independent data from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (RABUNG *et al.*, 2000) and hydrous alumina (TAN *et al.*, 2008).

Another factor is the influence of metal-HS complexation on HS adsorption onto mineral. This has been evidenced on different systems – Pb(II)-FA in HEIDMANN *et al.* (2005), and Eu(III)-HA in the Janot's PhD thesis [81] – but this is not common to all systems – Cu-FA in HEIDMANN *et al.* (2005). HEIDMANN *et al.* (2005) noted that the difference between Cu(II)- and Pb(II)-FA systems were linked to the H<sup>+</sup>/M<sup>2+</sup> molar exchange ratios, *i.e.*, *ca.* 1 for Pb<sup>2+</sup>, and *ca.* 1.5 for Cu<sup>2+</sup>, respectively (CHRISTL *et al.*, 2001). The authors linked the differences in adsorption compartment to the possible metal-induced aggregation of FA after the decrease in negative charge. The molar H<sup>+</sup>/M<sup>n+</sup> ratios means that 1 mole of complexed M<sup>2+</sup> leads to the release of 1 mole of H<sup>+</sup> for Pb<sup>2+</sup>, and 0.67 mole for Cu<sup>2+</sup>, respectively for (CHRISTL *et al.*, 2001; HEIDMANN *et al.*, 2005). Hence, the reduction in negative charge due to complexation is more important for Pb<sup>2+</sup>. In the case of Eu<sup>3+</sup>, we obtained a H<sup>+</sup>/Eu<sup>3+</sup> molar exchange ratios of *ca.* 1.3 and 1.6 [2,3,10,17,19,81], which are comparable to the H<sup>+</sup>/Cu<sup>2+</sup> system, but with a higher metal charge; the reduction in negative charge is thus more important for Eu<sup>3+</sup> than for Cu<sup>2+</sup>, and is coherent with the proposition of HEIDMANN *et al.* (2005). It is worth noting that HEIDMANN *et al.* (2005) studied a clay (kaolinite) whereas we used  $\alpha$ -alumina [2,3,10,81].



**Figure 5-15. Evolutions as a function of pH and ionic strength ( $\text{NaClO}_4$ ) of the adsorption of Eu(III) in  $\text{Eu}/\alpha\text{-Al}_2\text{O}_3$  (squares) and  $\text{Eu}/\text{HA}/\alpha\text{-Al}_2\text{O}_3$  (circles) systems – from [3] © 2013 Elsevier Ltd., [81].**

The difficulty to describe the ternary system is due to HA fractionation and modification of reactivity after adsorption onto the mineral surface. After the spectrophotometric quantification of the non-sorbed PAHA, two PAHA pools are defined: one staying in solution after centrifugation of the suspension, noted  $\text{PAHA}_{\text{sob}}$ , and one adsorbed onto the mineral, noted  $\text{PAHA}_{\text{ads}}$ ; each one having different NICA-Donnan parameters. The parameters determined by spectrophotometric titrations of supernatant from adsorption experiments of binary PAHA/ $\alpha\text{-Al}_2\text{O}_3$  systems [Z,81] to modify original PAHA europium(III) binding parameters. Hence,  $\log_{10}^{\text{ads}} \tilde{K}_{\text{Eu}^{3+},i}$  were modified according to  $\log_{10}^{\text{ads}} \tilde{K}_{\text{H}^+,i}$ , *i.e.*  $\log_{10}^{\text{ads}} \tilde{K}_{\text{Eu}^{3+},1} = 0.9$  and  $\log_{10}^{\text{ads}} \tilde{K}_{\text{Eu}^{3+},2} = 4.05$ . The  $p_j$ ,  $n_{i,j}$  values were not modified according to the non-modified  $m_{i,j}$  for  $\text{H}^+$ . The prediction in Figure 5-15a is satisfying without any further fitting. The increasing adsorption of Eu(III) with ionic strength is also well represented as also noted by CHRISTL & KRETZSCHMAR (2001). It is noteworthy that this increase of  $\log_{10}^{\text{ads}} \tilde{K}_{\text{Eu}^{3+},i}$  is reminiscent to the proposition of TIPPING *et al.* (1983) on the modification of reactivity on the surface, without *creating* more sites.

The data at varying coverage ratios in Figure 5-15b show the limitations of the approach. The adsorption data of PAHA/ $\alpha\text{-Al}_2\text{O}_3$  system was obtained at pH 6.8; hence the data at pH 6.2 are well described as well as those at pH 7.4. Even if the general trend is present, the behaviour of Eu(III) at pH 4 is clearly overestimated. Under these conditions the fractionation is more extensive, with a high adsorption of PAHA and a greater modification of reactivity. The disagreement between experimental and calculated concentrations under these conditions may be due to the values chosen for adapted protonation parameters of both PAHA fractions, which correspond to a median fractionation (around 70 %). This may be the reason for the difference at pH 4 and  $0.01 \text{ mol}_{\text{NaClO}_4} \text{ L}^{-1}$ . Moreover, the protonation parameters used for the modelling were calculated from titrations made on supernatant from binary PAHA/ $\alpha\text{-Al}_2\text{O}_3$  system. Now, presence of Eu(III) may have an influence on the fractionation of humic moieties, as complexation supposedly involves mainly the carboxylic groups at low pH values (NABER *et al.*, 2006).

It seems that the affinity of Eu(III) for an adsorbed humic acid is effectively greater than for the original sample. The implication is that the non-linear additivity of binary systems seems to be the

cause of a stronger metal adsorption on the humic covered surface than anticipated from the individual binary systems additivity – see also Figure 4 of CHRISTL & KRETZSCHMAR (2001), for Cu/FA/hematite.

### 5.3.1.2. Spectroscopic studies

#### a. Structural aspects of the binary metal/surface systems

The europium(III) chemical environment at the surface of sapphire (aluminium oxide,  $1\bar{1}02$ ) mono crystal probed in scanning near-field optical microscopy using TRLS [16], revealed the presence of different surface complexes. But these observations are not easily transferable to natural conditions as the  $(1\bar{1}02)$  face is not major on the natural oxide, and that the acid-base properties of massive surfaces are not the same as the ones of the individual faces (FRANKS & MEAGHER, 2003; FLÖRSHEIMER *et al.*, 2008). In the Eu(III)/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system, the evolution of the Eu(III) chemical environment is strongly modified during adsorption (Figure 5-16): the forbidden  $^5D_0 \rightarrow ^7F_0$  transition is increasing with the on-going adsorption, as well as the asymmetry ratio  $^7F_2/^7F_1$  (see also RABUNG *et al.*, 2000 for  $\gamma$ -alumina). The  $^5D_0 \rightarrow ^7F_1$  transition, which is not very sensitive to complexation, undergoes a broadening [2,8,46,80,81] (see also STUMPF *et al.*, 2002b, for the Eu(III)/smectite system). On the other hand, ionic strength does not seem to have a great influence on the chemical environment of the adsorbed Eu(III) species as it was awaited from the macroscopic data.

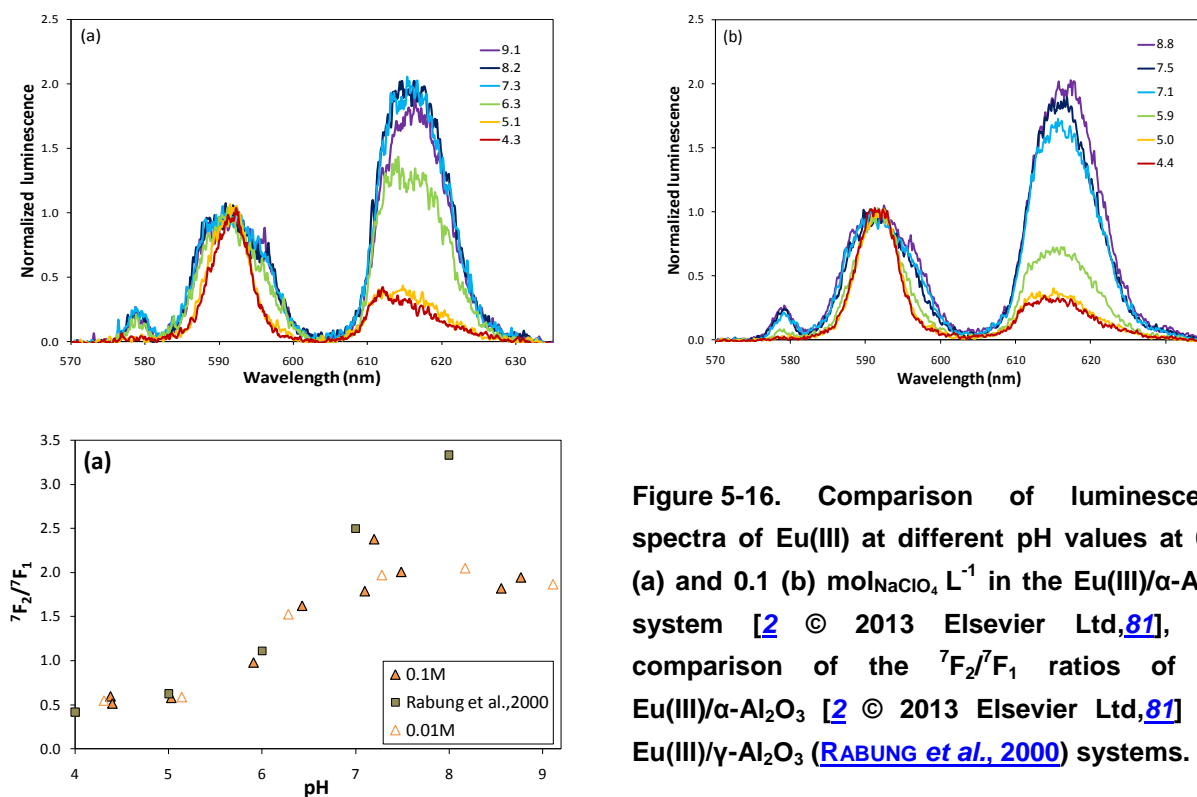
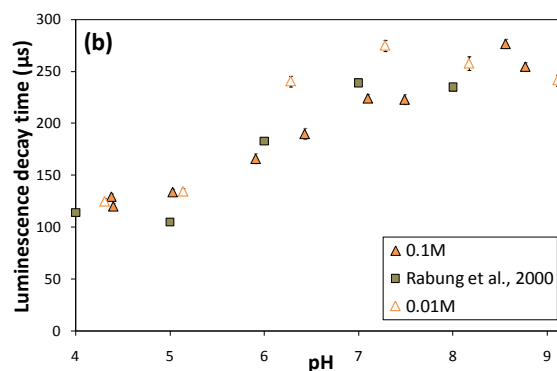


Figure 5-16. Comparison of luminescence spectra of Eu(III) at different pH values at 0.01 (a) and 0.1 (b) mol NaClO<sub>4</sub> L<sup>-1</sup> in the Eu(III)/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system [2 © 2013 Elsevier Ltd,81], and comparison of the  $^7F_2/^7F_1$  ratios of the Eu(III)/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [2 © 2013 Elsevier Ltd,81] and Eu(III)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (RABUNG *et al.*, 2000) systems.

### b. Temporal aspects of the luminescence in the Eu(III)/surface systems

The luminescence decay time after the pH-edge is systematically higher than  $\tau(\text{Eu}^{3+})$ , evidencing a higher de-excitation probability of the excited complex (Figure 5-17). Conversely, before the pH-edge, there are two groups for the Eu(III)/surface systems: (i) a group where  $\tau < \tau(\text{Eu}^{3+})$  (TAKAHASHI *et al.*, 2000; KOWAL-FOUCHARD *et al.*, 2004; TERTRE *et al.*, 2006) [16]; and (ii) a group where  $\tau \geq \tau(\text{Eu}^{3+})$  (RABUNG *et al.*, 2000; STUMPF *et al.*, 2002b; RABUNG *et al.*, 2005) [2,81] and  $\tau \geq \tau(\text{Cm}^{3+})$  (WANG *et al.*, 2004). The comparison of the experimental protocols of these two groups also allows evidencing that in the former the solid phases were centrifuged and more or less dried before the TRLS analyses, whilst in the latter group, the TRLS observations were done directly in suspension. The presence of iron(III) in the phases of the former group is also an important luminescence quenching parameter (HARTMANN *et al.*, 2008). In the latter group the authors observed the progressive adsorption of Eu(III) onto the surface and a mix of free  $\text{Eu}^{3+}$  and weakly adsorbed species. On the other hand, in the former group the authors extracted the weakly adsorbed complexes leaving free  $\text{Eu}^{3+}$  in the supernatant; in the particular case of reference [16], the mono crystalline surfaces were soaked into a Eu(III) solution and dried before SNOM/TRLS analyses. HARTMAN *et al.* (2008) in the case of Cm(III) propose the luminescence quenching by Fe(III) in the case of montmorillonite and of synthetic clays, which is less likely in the case of kaolinite (TERTRE *et al.*, 2006) or of sapphire mono-crystals [16].

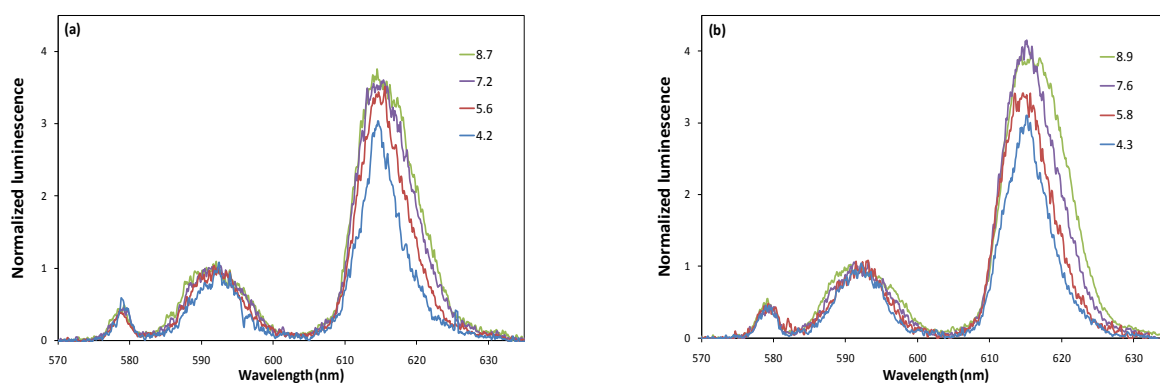


**Figure 5-17. Evolutions of the luminescence decay times as a function of pH and ionic strength.  $\text{C}(\alpha\text{-Al}_2\text{O}_3) = 1 \text{ g L}^{-1}$ ,  $[\text{Eu(III)}] = 10^{-6} \text{ mol L}^{-1}$ . Eu(III)/ $\gamma\text{-Al}_2\text{O}_3$  system, (RABUNG *et al.*, 2000) compared to Eu(III)/ $\alpha\text{-Al}_2\text{O}_3$  system [2 © 2013 Elsevier Ltd,81].**

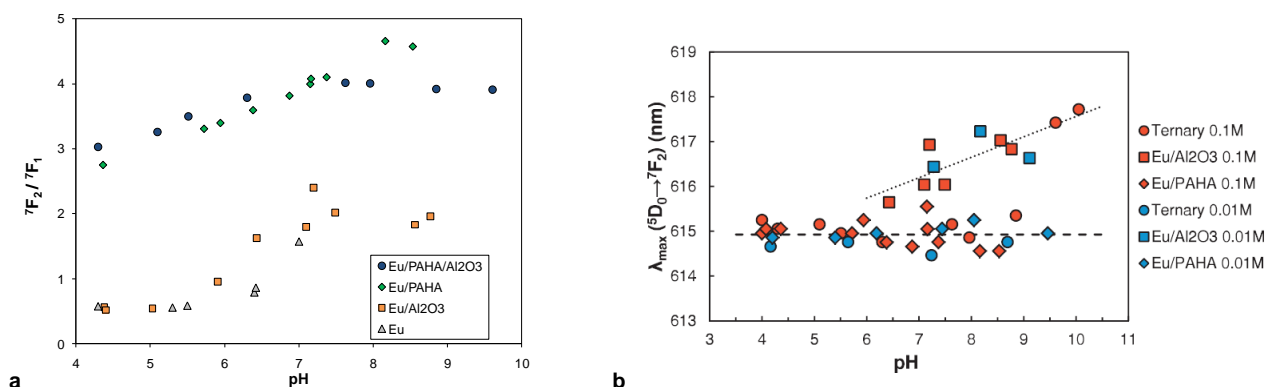
### c. Spectral aspects of ternary systems

The comparison of the different ternary system is not straightforward as: (i) the Eu/HA/surface systems were obtained with different gratings (TAN *et al.*, 2008) [2,81], which implies different signal convolutions with the spectrometer parameters; and (ii) one must compare Eu(III) and Cm(III) that are showing different de-excitation patterns – de-excitation of  $\text{Eu}^{3+}$  ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ) and of  $\text{Cm}^{3+}$  ( ${}^6\text{D}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ ) are different, and the information retrieved by the spectra are not totally comparable (CARNALL *et al.*, 1968; CARNALL & RAJNAK, 1975). For europium(III), a non-degenerated level is transferring energy to a degenerated level, more peaks are observed which intensities are varying with

very weak peak shift\*; for Cm(III), both implied levels are showing the same degenerescence, a broad massif undergoes shift and change in shape as a function of complexation strength.† From our observations, it seems that the chemical environment of Eu(III) in the ternary systems is always under the influence of HA. As a function of pH, the asymmetry ratios, as well as the shapes of the transitions, are not directly comparable between Eu(III)/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Figure 5-16) and Eu(III)/HA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Figure 5-18) systems. On the other hand, the  ${}^7F_2/{}^7F_1$  ratio of the Eu(III)/HA system is very much alike the one of the ternary Eu(III)/HA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system, as long as the pH value is not greater than the pH-edge – Figure 5-19a from [8]. For higher pH values, a broadening the  ${}^5D_0 \rightarrow {}^7F_2$  transition is observed with the increase in  $\lambda_{\max}$  – Figure 5-19b from [2,81] –, the compartment of which is similar the binary Eu(III)/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system. Nevertheless, as the asymmetry ratios are not totally comparable between the binary and the ternary systems, it is evident that the chemical environment of Eu(III) is strongly influenced by the presence of the adsorbed HA fractions.



**Figure 5-18.** Luminescence spectra of Eu(III) in the ternary systems at different pH at  $I = 0.01 \text{ mol L}^{-1}$  (a) and  $0.1 \text{ mol L}^{-1}$  (b) NaClO<sub>4</sub> ( $R = 27.4 \pm 0.5 \text{ mg}_{\text{PAHA}} \cdot \text{g}^{-1}_{\alpha\text{-Al}_2\text{O}_3}$ ) – from [2 © 2013 Elsevier Ltd,81].



**Figure 5-19.** Evolution (a) of the asymmetry ratios  ${}^7F_2/{}^7F_1$  and (b) of the  $\lambda_{\max}$  of the  ${}^5D_0 \rightarrow {}^7F_2$  transition of the different systems – from [2 © 2013 Elsevier Ltd,8 © 2011 American Chemical Society,81].

\* Shift of some nm for Eu(III)

† Shift of some 10 nm for Cm(III).



#### d. Temporal aspects of the ternary system

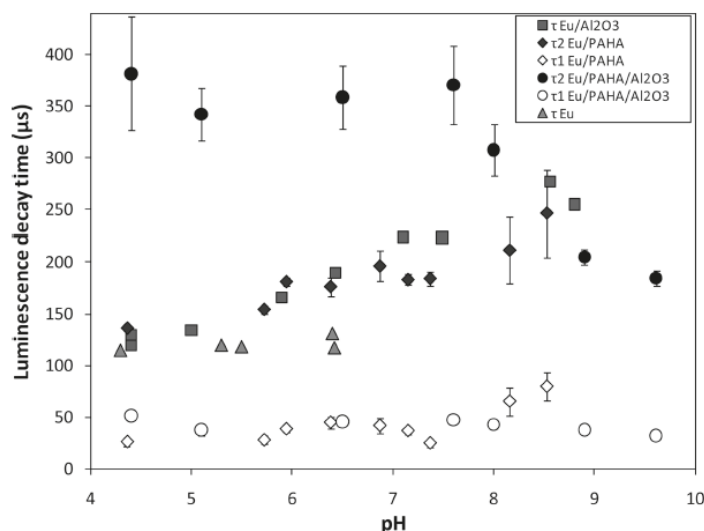
The temporal aspects of the ternary metal/HA/surface systems were not extensively observed in TRLS. TAN *et al.* (2008) proposed values of decay times  $\tau$ , but the step between each delay seem to prevent them from evidencing the bi-exponential decays, which we evidenced [8,81]. The most striking evolutions are seen on Figure 5-20. First, one can clearly see that at whatever pH value the luminescence decay is always bi-exponential in presence of HA. No systematic variations can be evidenced for the fast decay  $\tau_1$ . But one can see the differences of decay times between the binary Eu/HA and the ternary Eu/HA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, when pH  $\leq$  8. Even more interesting is the difference before the Eu adsorption edge, *e.g.* when pH  $\leq$  5. Under these conditions no or only weak adsorption can be awaited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and the increase in Eu adsorption occurs through the bonding of Eu-HA complex. Nevertheless, there is a large increase in  $\tau_2$ , which can be interpreted either as a loss of a water molecule in the first hydration shell (KIMURA & CHOPPIN, 1994), or as a decrease in the probability to lose energy through other mechanisms than radiative de-excitation. The first hypothesis implies a modification in the geometry of the complex at the surface, which would also imply a modification of its symmetry and a change in the spectrum; this was not observed here. According to the relationship from KIMURA & CHOPPIN (1994)\*, this would mean that *ca.* 7.5 water molecules would be present in the binary complex and *ca.* 2.5 would remain at the surface with no change in the complex's structure. This seems rather unlikely. The second hypothesis is more likely in the light of the recent works from EITA (2011a, 2011b) who showed that a Gorleben humic acid is more rigid on the surface of alumina. This increased rigidity would offer greater constrains in the adsorbed HA and would then increase the radiative de-excitation of Eu(III). Moreover, EITA (2011b) showed that Gd(III) was not in contact with the surface at low pH values in the presence of HA.

WANG *et al.* (2004) showed a decrease in  $\tau_2$  for the Cm(III)/HA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system, but as already stressed, the luminescence processes of Cm(III) and Eu(III) are different, the direct comparison may not be straightforward.

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\*  $n(\text{H}_2\text{O}) = \frac{1.07}{\tau} - 0.62$





**Figure 5-20. Luminescence decay times of Eu(III) in ternary system at  $I = 0.01$  and  $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$  as a function of pH ( $R = 27.4 \pm 0.5 \text{ mg}_{\text{PAHA}} \cdot \text{g}^{-1}_{\alpha\text{-Al}_2\text{O}_3}$ ) – from [8] © 2011 American Chemical Society, [81].**

### 5.3.2. Importance of the addition order: the particular case of tetravalent cations?

From a thermodynamic point of view, if the systems are comparable the addition order of the constituents must not be important. Nevertheless, the effect of addition order has been observed in some cases in ternary systems: Cu/HA/Al<sub>2</sub>O<sub>3</sub> (DAVIS, 1984), Cd/HA/α-Fe<sub>2</sub>O<sub>3</sub> (DAVIS & BHATNAGAR, 1995; VERMEER, 1996), Zr-Hf/HA/SiO<sub>2</sub> (TAKAHASHI *et al.*, 1999), Th/HA/α-Fe<sub>2</sub>O<sub>3</sub> [23], Cm/HA/γ-Al<sub>2</sub>O<sub>3</sub> (WANG *et al.*, 2004), Pu(III)/HA/kaolinite (BUDA *et al.*, 2008), or Cm/HA/SiO<sub>2</sub> (KAR *et al.*, 2011). In the case of Cm<sup>3+</sup> cations, it seems that this effect is only apparent at short contact time and not at long contact times (WANG *et al.*, 2004). But it also seems that this effect is linked with the total concentration of metal for Cd<sup>2+</sup>/HA/α-Fe<sub>2</sub>O<sub>3</sub> (DAVIS & BHATNAGAR, 1995). Hence, it is quite plausible that this effect is due to incorporation into the structure of the mineral.

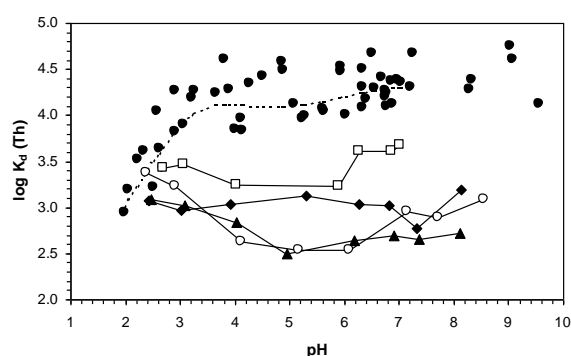
BUDA *et al.* (2008) also observed this effect on the initially Pu(III)/HA/kaolinite system. No difference was observed below the pH-edge of the binary Pu(III)/kaolinite when clear differences appeared above the pH-edge. One must recall that MARQUARDT *et al.* (2004) noted an oxidation of Pu(III) to Pu(IV) for pH ≥ 6. Moreover, BUDA *et al.* (2008) report that adsorbed Pu on kaolinite is at the +IV oxidation state. The oxidation of Pu(III) during the experiment cannot be rejected *a priori*.

As noted earlier, the pH-edge of a metal is strongly linked to its first hydrolysis constant. An<sup>4+</sup> cations undergo a pH-edge onto oxides *ca.* pH 2 (ÖSTHOLS, 1995) [23-25].\* Since the operational definition of humic acids implies precipitation at acidic pH it is often not straightforward to observe the awaited increase of the adsorption of a metal before the pH-edge (Figure 5-21 and Figure 5-22). The ternary systems with a tetravalent element are implying a particular difficulty, which is the addition order of the different compounds. In a more classical system, the humic extract is

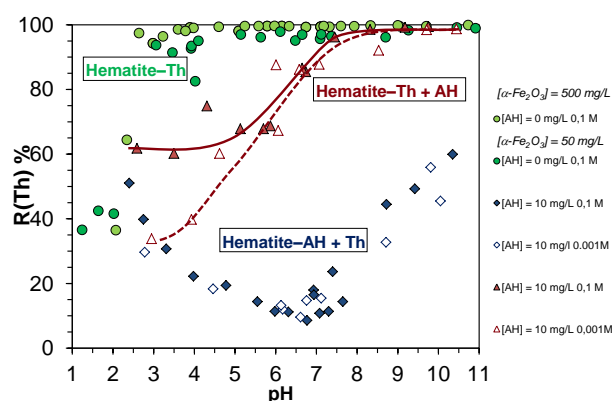
\* Projet européen HUMICS [26,27]

equilibrated with the surface beforehand, and the metal is added afterwards. When this protocol is followed, the evolution of the system is directly comparable to other elements. The interpretation of the data beyond the pH-edge is the same as for Eu(III)/HA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system; the increase of humic acid concentration prevents the metal adsorption on the mineral surface. The evolution as a function of pH is also comparable to the other metals; the adsorption of the metal is decreasing as long as the surface concentration of humic acid is important and increase when the humic acid is mainly in aqueous solution. In the case of silica, beyond pH 6.5 the system is purely competitive as the adsorption of humic acid can be neglected [24]. Conversely, the case of hematite is directly comparable to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> since the humic acid adsorption is important up to pH 9-10 [25].

The influence of ionic strength is also apparent in Figure 5-22 when Th(IV) is added first.



**Figure 5-21. Evolution of the adsorption of thorium(IV) as a function of pH onto colloidal silica,  $I = 0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ ,  $C_{\text{SiO}_2} = 0.25 \text{ g L}^{-1}$ ,  $[\text{Th(IV)}] = 1.5 \cdot 10^{-12} \text{ mol L}^{-1}$ ,  $\bullet C_{\text{HA}} = 0$ ,  $\square 1 \text{ mg L}^{-1}$ ,  $\blacklozenge 10 \text{ mg L}^{-1}$ ,  $\blacktriangle 50 \text{ mg L}^{-1}$ ,  $\circ 100 \text{ mg L}^{-1}$  – from [24 © 2003 de Gruyter].**

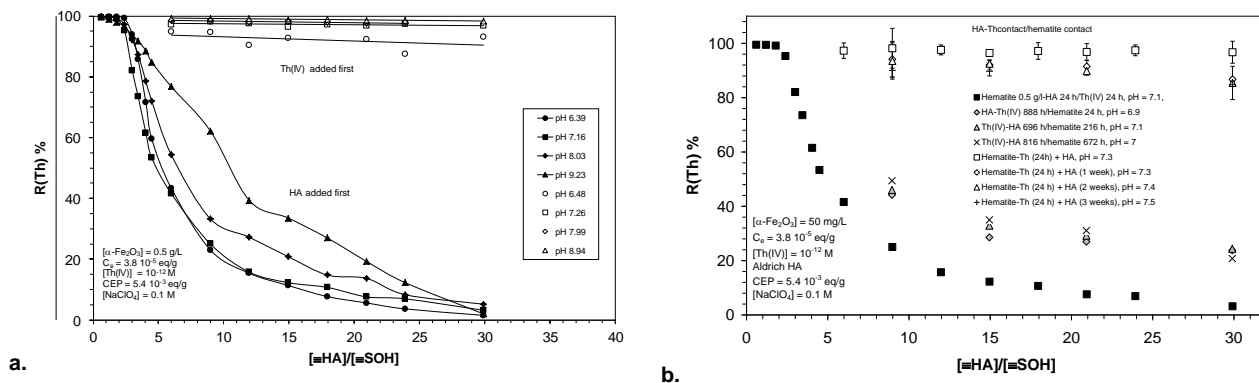


**Figure 5-22. Influence of the addition order for the Th(IV)/HA/hematite system: circles,  $C_{\text{HA}} = 0$ ; diamonds, HA added first; triangles, Th(IV) added first – from [23 © 2005 American Chemical Society].**

The influence of the addition order on the adsorption in ternary systems  $M^{4+}/\text{HA}/\text{surface}$  was evidenced by TAKAHASHI *et al.* (1999) on the Zr-Hf<sup>4+</sup>/HA/kaolinite system. This process also occurs in the Th(IV)/HA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> system [23], comparing to a preceding study [25] where the HA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> system was equilibrated beforehand. The evolution of the pH-isotherm is also reflected in the different concentration isotherms (Figure 5-23a), but the decrease in adsorption is farther less important when the Th(IV)/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> binary system is equilibrated beforehand and the humic acid is added afterwards.

Several hypotheses can be proposed: (i) the adsorptive fractionation of humic acid favours the adsorption of the most hydrophobic fraction, and leaves the more hydrophilic fractions in solution (VAN DE WEERD *et al.*, 1999), the reactivity of which should be more important towards Th(IV) by analogy to marine organic matter (GUO *et al.*, 2002; QUIGLEY *et al.*, 2002); and (ii) during the 24 hours equilibration thorium(IV) can be incorporated in the hematite structure and is not longer available for complexation by humic acid. To test the latter hypothesis, kinetic experiments were done

(Figure 5-23b). It appears that a longer contact time of the previously equilibrated systems would induce a convergence of the different system, but did not allow proposing a definitive conclusion. Spectroscopic information would be interesting but would require rather high concentration of Th(IV), for instance in X-ray spectroscopy.



**Figure 5-23.** Influence of a humic acid on the adsorption of thorium(IV) onto hematite and of the addition order after 24 hours of equilibration. Closed symbols – from [25 © 2002 Elsevier Ltd.] –: HA added beforehand; open symbols: Th(IV) added beforehand; (a)  $[\text{Th}] = 10^{-12} \text{ mol L}^{-1}$ ;  $C(\alpha\text{-Fe}_2\text{O}_3) = 500 \text{ mg L}^{-1}$ ;  $I = 0.1 \text{ mol}_{\text{NaClO}_4} \text{ L}^{-1}$  – from [23 © 2005 American Chemical Society] –, and (b) kinetic test at  $\text{pH} \approx 7$  – adapted from [23 © 2005 American Chemical Society].

## 6. PERSPECTIVES

Even if important advances have been done on the relationship between structure and reactivity of humic substances in the past fifteen years, there still lies several “shadowed areas”. The structure of the humic substances constituents is still a matter of controversy. Every complexation models are still in essence operational models using extra-thermodynamic function and/or correlation with high uncertainties. The variations of parameters as a function of pH, ionic strength, or total concentration of metal are clear illustrations.

As the results and implications were rather detailed in the presentation of research, I only will here give personal point of views on perspectives, and stress on some points that I hopefully will be exploring.

### 6.1. STRUCTURE AND COMPOSITION OF HUMIC SUBSTANCES

In the light of the most recent developments, it seems that humic substances are composed of small entities that are forming larger aggregates [6]. These aggregates can fractionate under various conditions, and the forces that are at stake to “hold these aggregates together” are necessary weak. The vision of *micellization* of the smaller entities is tempting (GUETZLOFF & RICE, 1994; PICCOLO *et al.*, 1996; VON WANDRUSZKA *et al.*, 1997; VON WANDRUSZKA, 1998; TERASHIMA *et al.*, 2004), and maybe misleading. Nevertheless, the theoretical background that permits to mathematically describe the aggregation phenomenon is still missing in such heterogeneous mixtures.

It seems clear now that the organization of humic substances aggregates in solution is showing a strong fractal character (WERSHAW *et al.*, 1967; ÖSTERBERG & MORTENSEN, 1992; RICE & LIN, 1993; ÖSTERBERG *et al.*, 1995; REN *et al.*, 1996; RICE *et al.*, 1999; REDWOOD *et al.*, 2005) [47], that seems to slightly depend on the origin and composition of the extract. As it was done for the titration and complexation data (TIPPING, 1998; MILNE *et al.*, 2001; MILNE *et al.*, 2003; TIPPING *et al.*, 2011), there is a need to gather information on the diversity and commonalities in the structure of humic substances extracts. As an example, we have seen that extracts from different origins are showing similar properties – *i.e.* size determined in surface tension [47,53], TDA [6] –, but are showing slightly different aggregate structure [47], and composition (PLANCQUE *et al.*, 2001) [26]. But even then, the physical description of the aggregation mode(s) will still remain to be built.

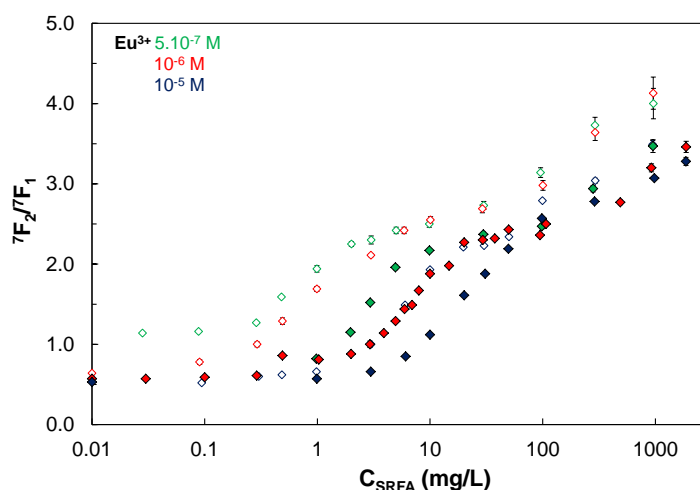
### 6.2. INFLUENCE OF IONIC STRENGTH AND HS CONCENTRATION

The influence of ionic strength and HS concentration on the complexation of metals is either not easily represented by Debye-Hückel related models, or under the form of a potential of various kinds. The interrogations of SAITO *et al.* (2005) on the very nature of this potential of the humic entities leaves open questions.

Very recently, in the framework of Yasmine Kouhail’s on-going PhD works [45], we evidenced two different regimes of Eu-FA interactions (Figure 6-1). The first occurs at lower FA concentration,

whereas a second regime occurs at higher FA concentration. These two different regimes are not described by existing complexation models. The typical behaviour obtained at varying concentration of metal, here Eu(III), is observed for the two environments. But the influence of ionic strength is not straightforward to interpret. If the typical complexation behaviour – decrease of interaction with ionic strength in agreement with the Debye-Hückel Theory (LYKLEMA, 1995a) – occurs for the first regimes, *i.e.*, at the lower FA concentration, the opposite effect if occurring at higher FA concentration – an increase of interaction with ionic strength.

One plausible interpretation of the second regime can be the interaction of Eu(III) with different FA entities or aggregates. These entities are showing surface potential that are influenced by their Debye length. With increasing ionic strength, different entities can see their distance of approach varying with ionic strength, and fixed Eu(III) could then act as a bridge between two different entities. This proposition is difficult to integrate within the NICA-Donnan model. As described in SAITO *et al.* (2005), within the NICA-Donnan model the description of the surface potential is not needed; only a Donnan potential within the particles is considered. Nevertheless, SAITO *et al.* (2005; 2009) proposed that a combined Donnan electric double layer model could also be considered. Further works are on-going on this point.



**Figure 6-1.** Evolution of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  ratio depending on  $C(\text{SRFA})$  at  $I = 0.1 \text{ M}$ , pH 4 (open symbols) and pH 6 (filled symbols).

### 6.3. COMPETITION BETWEEN CATIONS

From the point of view of the competition between cations, as satisfactory as they may appear, the confrontation between our spectroscopic and potentiometric results should not obfuscate the semi-empiric nature of these models. On the other hand, if the simplest (discrete) models allow presenting an efficient representation of laboratory cases on actinides, there is a too much level of uncertainty on the treatment of competition. As such, the uncertainties on the NICA-Donnan parameters for the actinides(III), and the incoherence on the estimated parameters for actinides(IV), prevent from reliable speciation calculation of real systems where the competition between cations of similar charges should occur. It seems that a compilation effort – comparable to the works from MILNE *et al.*

(2003) – should be done particularly for the actinides(IV), especially for Np and Pu that are particularly sensitive to the redox properties of humic substances.

A certainly interesting point would be competition between lanthanides. Only few data were reported. The works from POURRET *et al.* (2007a, 2007c) were actually performed in competitive conditions – 50 ppb of each elements, *i.e.*  $0.36 \mu\text{mol L}^{-1}$  for La and  $0.29 \mu\text{mol L}^{-1}$  for Lu – but no information on eventual competition between complexation modes in HS could be obtained. The use of time-resolved luminescence would certainly allow attaining such information. Competition between luminescent lanthanides (Sm, Eu, Tb, Dy), in conditions near to those of POURRET *et al.* (2007a, 2007c) could be done following Eu(III) or Tb(III) luminescence following the works from MARANG *et al.* [14] on Eu(III)-Cu(II) and Eu(III)-Ca(II).

#### 6.4. FORMATION OF MIXED COMPLEXES

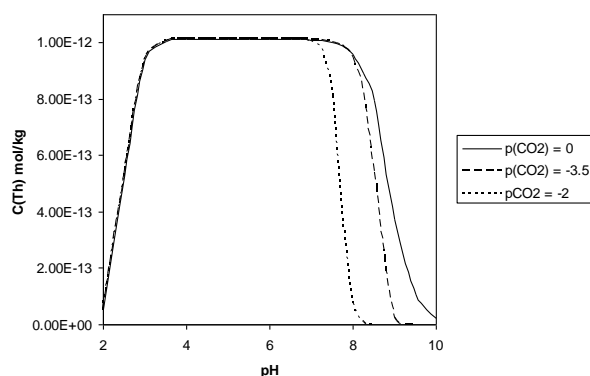
The formation of mixed complexes, *i.e.* M-OH-HA or M-CO<sub>3</sub>-HA complexes, should also draw attention as they are still a matter of debate (PANAK *et al.*, 1996; POURRET *et al.*, 2007c). The determination of mixed hydroxo and carbonato complexes of uranium(VI) is certainly a great advance, but the interaction constants rely on inherent hypotheses that makes then not easy to adapt to other models. Reinterpretation of raw data and dedicated experiments should be undertaken, including the variety of humic samples.

Particularly we have seen that POURRET *et al.* (2007c) seemed to reject the formation of mixed carbonato complexes, whereas it seems that a close inspection of their data reveals the formation of a mixed complex. Furthermore, the spectroscopic data from PANAK *et al.* (1996) are rather demonstrative of the presence of a mixed complex, even if too few data point were presented. DIERCKX *et al.* (1994) proposed the formation of carbonate mixed complexed that are questioned by POURRET *et al.* (2007c). GLAUS *et al.* (1995) evidenced weaker than expected mixed complexes, but significant nonetheless. MOULIN *et al.* (1999) also proposed the formation of a mixed carbonato humic complex.

Within the Yasmine Kouhail's PhD thesis work we are focusing on both the evidence of a complexation humic mode in carbonate media in luminescence spectroscopy, which is particularly adapted both to Eu(III)-HS [11,13] and carbonate studies (BERTHOUD *et al.*, 1989; VERCOUTER *et al.*, 2005).

Also the case of actinides(IV) could be of interest. As stressed earlier (cf. Figure 4-6, page 48), the example of carbonate competition or mixed complex formation is an illustration. The major environmental inorganic ligand of cationic radionuclides is CO<sub>3</sub><sup>2-</sup>. In the case of actinides(IV) high concentration are necessary to out-compete hydrolysis. Using the operational expression (Equation 4-8) to calculate the  $\log_{10} {}^{\text{HA}}\beta$  for ThHA at each pH value, and imposing an equilibrium with atmospheric CO<sub>2</sub>(g), carbonates would only have an influence for pH higher than 8.5 (Figure 6-2). As

the prevalence of An(IV)-NOM complexes covers a wide pH range (STOCKDALE *et al.*, 2013) [18,22], it would be important to check the limitation of this range by the carbonate competition.



**Figure 6-2. Influence  $\text{CO}_2(\text{g})$  partial pressure on the concentration of ThHA complex,  $[\text{Th}] = 10^{-12} \text{ mol L}^{-1}$ ,  $C_{\text{HA}} = 100 \text{ mg L}^{-1}$ , and  $5.4 \text{ mmol}_{\text{site}} \text{ L}^{-1}$ , from Equation 4-8.**

### 6.5. MICRO-SOLUBILITY EFFECT

As seen earlier, the total concentration of metal, particularly An(IV), shows a marked influence of the interaction with humic substances: interaction decreases with the ratio between metal and HS, and the formation of micro-phases within the structure of HS seems to occur (PLASCHKE *et al.*, 2004; WEBER *et al.*, 2006b; ANTONIOU *et al.*, 2011; MARSAC *et al.*, 2014; PRODROMOU *et al.*, 2014), the presence of which could be at the origin of the lack of, or at least limited influence, on the solubility. It can be envisaged that this effect is linked to the existence of the Donnan potential within the structure of HS. In § 4.3.2.1 (page 53) it has been proposed that the apparent solubility of uranium(VI) in a Donnan membrane is lowered due to the Donnan potential (Equation 4-17). If in the case of  $\text{UO}_2^{2+}$  a factor of *ca.* 20 is computed at  $0.1 \text{ mol L}^{-1}$ , a factor of *ca.* 75 is awaited for Fe(III), lanthanides, and actinides(III), and *ca.* 300 for actinides(IV) – see Table 4-1 page 53.

It could be interesting to address this problem through (i) coupled studies of complexation, including spectroscopic data on the metal; (ii) solubility studies of mineral phases including structural characterisations of mineral phases with the evaluation of crystallites size; and (iii) apparent sizes of HS aggregates using different determination techniques.

### 6.6. SPECTROSCOPIC AND LUMINESCENCE DECAY DATA ON LANTHANIDES/ACTINIDES-HUMIC COMPLEXES

The analysis of spectroscopic data on luminescent lanthanides(III) and actinides(III) complexed by – and adsorbed on mineral surfaces with – humic substances are not numerous (WANG *et al.*, 2004; KUMKE & EIDNER, 2005; RABUNG *et al.*, 2005; RABUNG *et al.*, 2006; TAN *et al.*, 2008; HUITTINEN *et al.*, 2009; MARMODÉE *et al.*, 2009a; RABUNG & GECKEIS, 2009; ANTONIOU *et al.*, 2011) [2,7,8,11,13]. The univocal determination of the Ln(III)-HS complexes' symmetry could be attained either using high dispersing gratings directly in solution, or by using low temperature measurements (MARMODÉE *et al.*, 2009a; KUKE *et al.*, 2010).



The origin of the bi-exponential decay of lanthanides and Cm(III) complexes is also a matter of concern. There is a lack of compilation of data which would help in levelling the importance of the complexation environment *vs.* the physical phenomena hidden behind the bi-exponential decay. Necessarily, there are two different deexcitation mechanisms if a bi-exponential decay occurs, the nature of which is still up to now totally concealed by the heterogeneity of these substances and the impossibility to propose a structure. The fact that the faster decays of Eu(III) and Cm(III) are not comparable, *i.e.* faster than free aquo-ion  $\text{Eu}^{3+}$  (and also  $\text{Tb}^{3+}$ ) and mostly equal to  $\text{Cm}^{3+}$ , does not help for comparison. The interesting advance proposed on Cm(III)-HS complexation ([FREYER \*et al.\*, 2009](#)) has to be checked at least on Eu(III) and Tb(III), which are showing the longest decay times. The systematic study of relevant *simple* complexants, *e.g.* based on EXAFS decomposition as in MANCEAU & MATYNIA ([2010](#)), could be of a great help. Link to the evolution of aromatic acids is also to consider (cf. Figure 4-23, page 69).

### 6.7. ADSORPTIVE FRACTIONATION

The fractionation of natural organic matter and adsorption onto surface is not always easily linked to the modification of NOM. The operational relationships that we have proposed cannot be straightforwardly applied without verification to other systems, but the methodology could be applied to other samples without any major difficulties. We also have seen the difficulties in the extrapolation of these relationships outside their calibration domains. However, we have shown that it is necessary to account for the chemical modifications of humic substances during adsorption. From my point of view, adapting the electrostatic properties of the adsorbed humic substances without modifying the interaction properties with protons and eventually with metal is only a partial approach. The account of the chemical modification will certainly be time consuming because it would have to cover a wide parametric domain. This is directly linked to the difficulty to propose a clear definition of the HS' structure and composition.

### 6.8. APPLICATION TO IN-FIELD DATA

The history of nuclear events has shown that a better knowledge of the interaction between NOM and metallic pollutants is of particular concern ([OLLUI MBOULOU \*et al.\*, 1998](#); [FUJIKAWA \*et al.\*, 1999](#); [BRUDECKI \*et al.\*, 2009](#); [XU \*et al.\*, 2014](#)). In the case of reactor accident, Pu isotopes, Am,  $^{137}\text{Cs}$ ,  $^{131}\text{I}$ , and  $^{90}\text{Sr}$  are released to the environment ([KAWASE & YOKOYAMA, 1973](#); [LEE & LEE, 2000](#); [QUANG \*et al.\*, 2004](#)). The interaction of the short lived  $^{131}\text{I}$  with NOM is well known [[26,35,36,40](#)] and observed in-field ([BULMAN, 1986](#); [ASHWORTH & SHAW, 2006b](#); [SCHWEHR \*et al.\*, 2009](#); [KAPLAN \*et al.\*, 2011](#); [TANAKA \*et al.\*, 2012](#); [KAPLAN \*et al.\*, 2014](#)). The case of  $^{137}\text{Cs}$  is less clear as the interaction with NOM is rather low ([SHABAN & MACÁŠEK, 1998](#)) [[6](#)], but the indirect influence of NOM is clear ([VIDAL & RAURET, 1993](#); [DUMAT & STAUNTON, 1999](#); [RAJEC \*et al.\*, 1999](#); [RIGOL \*et al.\*, 2002](#)). Strontium also show a moderate interaction with NOM ([JUO & BARBER, 1969](#); [IBARRA \*et al.\*, 1979b](#); [SAMADFAM \*et al.\*, 1996](#); [HELAL \*et al.\*, 1998](#); [SAMADFAM \*et al.\*, 1998a](#); [PAULENOVA \*et al.\*, 2000](#)) and its adsorption on



minerals is affected ([BUNZL \*et al.\*, 1998](#); [SHABAN & MACÁŠEK, 1998](#); [MACÁŠEK \*et al.\*, 1999](#); [BELLENGER & STAUNTON, 2008](#)). The knowledge and quantification of the Cs- and Sr-HS interactions are of great importance when it comes to discuss about remediation strategies.

Very recently, a French national project “DEMETERRES”<sup>†</sup>, financed through the Program “Investissement d’Avenir”<sup>†</sup>, proposes to address the problems of remediation and rehabilitation of contaminated soils, using phytoremediation, decontamination either by ligands in supercritical CO<sub>2</sub>, or by flotation techniques. Our role will be to provide quantification of Cs and Sr interaction with soils components, including mainly clays and NOM. A PhD thesis has begun in October 2014 for three years.

## 6.9. RATIONALE

As a rationale, I would certainly stress that the main missing *brick* in the knowledge of humic substances’ reactivity is the difficulty to propose a theoretical background for their structure. At least we cannot, up to now, compute every observable data. As a matter of fact, even if the amount of individual component of the mixtures can theoretically be known, then the question of the physical and chemical forces that hold the humic substances aggregates together is still not at hand, yet. Maybe following [FEYNMAN \(1965 page 164\)](#), we would have to find some *moos* or *goos* to provide a description of the experimental data. To my opinion, no single analytical technique could help in unravelling the *mystery* of humic substances structure. The eluding structure of these fractal objects (mixtures) must be taken into account.

A lot of advances have been achieved since our works on the application of ESI-MS to the characterisation of humic substances. The use of the exact mass determination, *via* Fourier transform ESI-MS, allows now determining more precise repartition of molecules from the very complex humic substances mixtures ([CHO \*et al.\*, 2012](#); [WITT, 2013](#); [GALINDO & DEL NERO, 2014](#)). Nevertheless, as powerful as these analyses may be, they do not give information on the particular aggregation compartment of humic substances, the extent of which largely controls the complexation and adsorption behaviours

Only the confrontation of the different point of views of different advanced techniques can help. The proposition of a *humeomic science* ([PICCOLO \*et al.\*, 2006](#); [NEBBIOSO & PICCOLO, 2011, 2012](#); [NEBBIOSO \*et al.\*, 2014](#)) is certainly an interesting input and would require a much broader community that would have a common interest.

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\* Développement de Méthodes bio- et Eco- Technologiques pour la Remédiation Raisonnée des Effluents et des Sols en appui à une stratégie de réhabilitation agricole post-accidentelle. <http://portail.cea.fr/dsv/ibeb/Pages/recherches/projets-ibeb.aspx?Type=Chapitre&numero=1>

† Recherche en matière de Sécurité Nucléaire et Radioprotection

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