

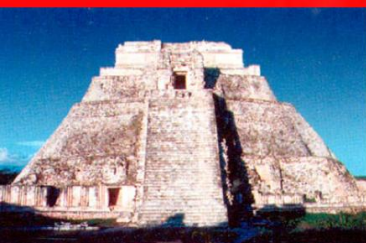
Birchall Centre for Inorganic Chemistry and Materials Science, Keele University  
and  
Centro de Investigación Científica de Yucatán



KEELE  
UNIVERSITY



CICY



THE SEVENTH KEELE MEETING ON  
**Aluminium**

# Life and Living in the Aluminium Age

**Saturday 24<sup>th</sup> to  
Wednesday 28<sup>th</sup> February 2007**

**Hotel Misión Uxmal  
Yucatán,  
México**

[www.keele.ac.uk/depts/ch/groups/aluminium/index.html](http://www.keele.ac.uk/depts/ch/groups/aluminium/index.html)

THE KEELE MEETINGS ON ALUMINIUM 1995, 1997, 1999, 2001, 2003, 2005

# SOCIAL AND SCIENTIFIC PROGRAMME

*Saturday 24<sup>th</sup> February 2007*

- 17.00 Registration and Poster Assembly
- 20.00 Welcome to Meeting / Welcome Buffet

*Sunday 25<sup>th</sup> February 2007*

The Conference is Open!

\*Graduate/Postgraduate Presentation

<sup>§</sup>Graduate/Postgraduate Bursary

## SESSION ONE

*In Silico Approaches to Understanding Aluminium*

**Chair: Christopher Exley** (*Keele University, UK*)

- 08.55 Introduction to the session by the Chair
- 09.00 [Platform 1](#) **Christopher Exley** (*Keele University, UK*)  
A systems biology approach to the biological availability of aluminium.
- 09.20 Discussion
- 09.30 [Platform 2](#) **James Beardmore\*** (*Keele University, UK*)  
Solving the blood-aluminium problem.
- 09.50 Discussion
- 10.00 [Platform 3](#) **Elixabete Rezabal\*<sup>§</sup>** (*University of The Basque Country, Spain*)

Protein side chains that facilitate  $Mg^{2+}/Al^{3+}$  metal exchange in model protein binding sites.

- 10.20 Discussion
- 10.30 [Platform 4](#) **Jerry Winter** (*Unilever, UK*)  
Towards improved understanding of the molecular genesis and acid-base properties of aluminium polyoxocations using various computational approaches.
- 10.50 Discussion
- 11.00 Concluding remarks from the Chair
- 11.5 COFFEE**

## SESSION TWO

### *Aluminium Chemistry*

**Chair: Thomas Kinraide** (*US Department of agriculture, USA*)

- 11.25 Introduction to the session by the Chair
- 11.30 [Platform 5](#) **Oleg Antzutkin** (*Luleå University of Technology, Sweden*)  
An  $^{27}Al$  and  $^{31}P$  MAS NMR surface study of adsorbed aluminium species at synthetic fluor- and hydroxy-apatite.
- 11.50 Discussion
- 12.00 [Platform 6](#) **Olivier Deschaume** (*Nottingham Trent University, UK*)  
Synthesis and characterisation of pure monodisperse aluminium polyoxocation and aluminium hydroxide solutions using a novel technique based on static

anion exchange.

- 12.20 Discussion
- 12.30 [Poster 1](#) **Xiao-Di Yang** (*Nanjing Normal University, China*)  
Aspects of the structural speciation of Al(III) complexes with bi-ligands in aqueous solutions.
- 12.35 Discussion
- 12.40 [Platform 7](#) **Agathe Fournier\***<sup>s</sup> (*Nottingham Trent University, UK*)  
Interactions of pure Al hydrolytic species – Keggin polyoxocations and hydroxide with biomolecules.
- 13.00 Discussion
- 13.10 Concluding remarks from the Chair
- 13.15 LUNCH**

## SESSION THREE

### *Environmental Bioinorganic Chemistry*

**Chair: Ondrej Drabek & Lubos Boruvka** (*Czech University of Agriculture in Prague, Czech Republic*)

- 14.30 Introduction to the session by the Chair
- 14.35 [Platform 8](#) **Michael Anderson** (*University of California, USA*)  
Alum treatment of lakes to control phosphorus recycling: Forms and transformations of Al.
- 14.55 Discussion
- 15.05 [Platform 9](#) **Jiri Kopáček** (*University of South Bohemia, Czech Republic*)  
Photochemical source of aluminium for lakes and its impact upon phosphorus cycling.
- 15.25 Discussion

- 15.35 [Poster 2](#) **Jaroslav Vrba** (*University of South Bohemia, Czech Republic*)  
A key role for aluminium in phosphorus availability, food web structure, and plankton dynamics in strongly acidified lakes.
- 15.40 Discussion
- 15.45 [Poster 3](#) **Arja Sarpola**\*<sup>\$</sup> (*University of Oulu, Finland*)  
Identification of hydrolysis products of aluminium and iron in water.
- 15.50 Discussion
- 15.55 COFFEE**
- 16.25 [Platform 10](#) **David Sigeo** (*University of Manchester, UK*)  
Energy and wavelength-dispersive X-ray microanalysis of Al and associated elements in freshwater phytoplankton.
- 16.45 Discussion
- 16.55 [Poster 4](#) **Lubos Boruvka** (*Czech University of Agriculture in Prague, Czech Republic*)  
Geostatistical analysis of forest floor characteristics in two areas with different anthropogenic inputs
- 17.00 Discussion
- 17.05 [Poster 5](#) **Antonin Nikodem**\*<sup>\$</sup> (*Czech University of Agriculture in Prague, Czech Republic*)  
Aluminium speciation in forest soils of a mountainous region with relatively low effects of acid deposition.
- 17.10 Discussion
- 17.15 [Poster 6](#) **Ondrej Drabek** (*Czech University of Agriculture in Prague, Czech Republic*)

Grass cover on forest clear-cut areas ameliorates soil chemical properties.

17.20

Discussion

17.25

[Platform 11](#) **Hans-Christian Teien** (*Norwegian University of Life Sciences, Norway*)

Mobilisation of river transported colloidal aluminium in estuaries and subsequent deposition on fish gills – sodium silicate as a countermeasure.

17.45

Discussion

17.55

Concluding remarks from the Chair

**18.00**

**END OF FIRST DAY**

**20.00**

**DINNER**

**Followed By**

**POSTER SESSION AND TEQUILA!**

*Monday 26<sup>th</sup> February 2007*

**SESSION FOUR**

*Plants*

**Chair: Teresa Hernández Sotomayor (CICY, Mexico)**

- 08.55 Introduction to the session by the Chair
- 09.00 [Platform 12](#) **Thomas Kinraide** (*US Department of Agriculture, USA*)  
Metal ion binding to some organic and inorganic ligands and to plant cell walls and membranes. A scale for binding strength closely related to charge and Pauling electronegativity.
- 09.20 Discussion
- 09.30 [Platform 13](#) **Jimmy Ramírez-Benítez\*** (*CICY, Mexico*)  
The role of organic acids in aluminium tolerance in cell suspensions of *Coffea arabica* L.
- 09.50 Discussion
- 10.00 [Poster 7](#) **Fausto Quintal-Tun\*** (*CICY, Mexico*)  
Aluminium-induced phospholipid signal transduction pathway in *Coffea arabica* suspension cells and its amelioration by silicic acid.
- 10.05 Discussion
- 10.10 [Poster 8](#) **Leticia Chee-González\*** (*CICY, Mexico*)  
Physiological response in suspensions of *Coffea arabica* L. cells exposed to different chemical forms of aluminium.
- 10.15 Discussion
- 10.20 [Poster 9](#) **Shuping Bi** (*Nanjing University, China*)  
Aluminium-induced effects on wheat's rhizosphere environment.
- 10.25 Discussion
- 10.30 Concluding remarks from the Chair
- 10.35 COFFEE**

## SESSION FIVE

## *Aluminium Biochemistry*

**Chair: Oleg Antzutkin** (*Luleå University of Technology, Sweden*)

- 11.05 Introduction to the session by the Chair
- 11.10 Platform 14 **Kelly Elkins** (*Armstrong Atlantic State University, USA*)  
Designing and testing peptides with aluminium specificity.
- 11.30 Discussion
- 11.40 Poster 10 **Rachel Bongini**\*<sup>S</sup> (*Armstrong Atlantic State University, USA*)  
Analysis of computational site-directed mutagenesis of ligands in the metal-ion binding site in an isolated EF-hand from troponin C.
- 11.45 Discussion
- 11.50 Platform 15 **Vasu Appanna** (*Laurentian University, Canada*)  
Aluminium-induced metabolic syndrome in hepatocytes mimics obesity-like conditions.
- 12.10 Discussion
- 12.20 Poster 11 **Ziqiang Meng** (*Shanxi University, China*)  
Effects of aluminium chloride on Na<sup>+</sup> current and transient outward K<sup>+</sup> current and delayed rectifier K<sup>+</sup> current in acutely isolated rat hippocampal CA1 neurons.
- 12.25 Discussion
- 12.30 Platform 16 **Walter Lukiw** (*Louisiana State University, USA*)  
Mechanism of inflammatory gene expression in aluminium- or iron-stressed aging human brain cells; rescue with desferrioxamine and Feralex-G.



12.50 Discussion  
13.00 Concluding remarks by the Chair

**13.05 LUNCH**

**FREE AFTERNOON**

**20.00 DINNER**

**LIGHT AND SOUND EXPERIENCE OF UXMAL!**

*Tuesday 27<sup>th</sup> February 2007*

**SESSION SIX**

*Animal Models of Aluminium Toxicity*

**Chair: Vasu Appanna** (*Laurentian University, Canada*)

08.55 Introduction to the session by the Chair

09.00 [Poster 12](#) **Goran Kovačević\*<sup>S</sup>** (*University of Zagreb, Croatia*)  
The effect of aluminium on green and brown hydras: preliminary observations.

09.05 [Poster 13](#) **Goran Kovačević\*<sup>S</sup>** (*University of*

*Zagreb, Croatia)*

The effect of aluminium on the planarian *Polycelis felina*.

- 09.10 Joint Discussion of Posters 12 & 13
- 09.20 [Platform 17](#) **Judie Walton** (*Australian Institute for Biomedical Research, Australia*)  
An aluminium-based rat model for Alzheimer-type dementia exhibits oxidative stress, inhibition of PP2A activity and hyperphosphorylated tau.
- 09.40 Discussion
- 09.50 [Platform 18](#) **Jose-Luis Esparza** (*Rovira I Virgili University, Spain*)  
Effects on locomotor, spatial learning and proliferation in a transgenic mouse model of Alzheimer's disease after exposure to low dose of oral aluminium.
- 10.10 Discussion
- 10.20 [Poster 14](#) **Daniel Orihuela** (*National University of the Litoral, Argentina*)  
Effect of aluminium on intestinal calcium absorption in pregnant and lactating rats.
- 10.25 Discussion
- 10.30 Concluding remarks by the Chair
- 10.35 COFFEE**

## SESSION SEVEN

*Human Exposure to Aluminium*

**Chair: Paolo Prolo** (*University of California Los Angeles, USA*)

- 11.05 Introduction to the session by the Chair
- 11.10 [Platform 19](#) **Christopher Exley** (*Keele University, UK*)

The body burden of aluminium: what is it?

- 11.30 Discussion
- 11.40 [Poster 15](#) **Usman Ahmed\*** (*Keele University, UK*)  
Elevated urinary aluminium in past and current users of illicit heroin.
- 11.45 Discussion
- 11.50 [Poster 16](#) **Simona Murko\*<sup>\$</sup>** (*Jožef Stefan Institute, Slovenia*)  
Speciation of high molecular mass Al in serum combining SEC and anion-exchange FPLC with UV, ETAAS and ICP-MS detection.
- 11.55 Discussion
- 12.00 [Platform 20](#) **Elisabet Bergfors** (*Göteborg University, Sweden*)  
What happens when children sensitised to aluminium receive aluminium adsorbed vaccines.
- 12.20 Discussion
- 12.30 [Poster 17](#) **Marcela Ávila-Díaz** (*Hospital de Especialidades, Centro Médico Nacional Siglo XXI, Mexico*)  
Aluminium levels in Mexican children with chronic kidney disease undergoing dialysis treatment.
- 12.35 Discussion
- 12.40 [Poster 18](#) **Judie Walton** (*Australian Institute for Biomedical Research, Australia*)  
Aluminium in osteoporotic vertebroplasty specimens.
- 12.45 Discussion
- 12.50 Concluding remarks by the Chair
- 12.55 LUNCH**

## SESSION EIGHT

### *Aluminium and Alzheimer's Disease*

**Chair: Christopher Exley** (*Keele University, UK*)

- 13.55 Introduction to the session by the Chair
- 14.00 [Platform 21](#) **Walter Lukiw** (*Louisiana State University, USA*)  
Alterations in micro RNA (miRNA) complexity in Alzheimer's disease (AD) and in metal-ion stressed human brain cells.
- 14.20 Discussion
- 14.30 [Platform 22](#) **Paula Gonçalves** (*Aveiro University, Portugal*)  
Neurotransmission impairment: an accomplice to aluminium neurotoxicity.
- 14.50 Discussion
- 15.00 [Poster 19](#) **Mauro Ferrara** (*University of Torino, Italy*)  
Dust exposure to iron and aluminium and impairment of lung function in apprentices living near a foundry.
- 15.05 Discussion
- 15.10 [Platform 23](#) **Erik Jansson** (*Department of the Planet Earth, USA*)  
A review: Aluminium – A causative co-factor of 'dementia' of Alzheimer's disease.
- 15.30 Discussion
- 15.40 [Platform 24](#) **Paolo Prolo** (*University of California Los Angeles, USA*)  
Aluminium vs. Alzheimer's disease: The evidence-based approach.
- 16.00 Discussion

- 16.10            [Platform 24](#) **Arthur Dalton** (*New York State Institute for Basic Research in Developmental Disabilities, USA*)  
Aluminium chelation therapy: Past, present and future.
- 16.30            Discussion
- 16.40            Concluding remarks by the Chair
- 16.45            COFFEE**

17.15            An Introduction to the JD Birchall Memorial Lecture

17.20

[JD BIRCHALL MEMORIAL LECTURE](#)

Professor Tom B Kinraide

*Personal experiences analyzing the interactive toxic and ameliorative effects of aluminum species and other ions.*

- 18.20            Discussion
- 18.30            General Discussion and Closing Remarks
- 20.00            CONFERENCE DINNER**

## **ADDITIONAL POSTERS**

**Peter Matúš** (*Comenius University in Bratislava, Slovakia*)

Analytical chemistry of aluminium – its total determination, fractionation and speciation analysis as different approaches for Al routine environmental pollution monitoring.

**Lisa Charles\*** (*Keele University, UK*)

Aluminium in breast tissue.

**Rita Chan-May\*** (*CICY, Mexico*)

Effect of  $\text{AlCl}_3$  on the growth of *Coffea arabica* L. plantlets and phosphoinositide signal transduction pathway

**Shuping Bi** (*Nanjing University, China*)

Differential pulse voltammetry studies of the influence of  $\text{Al}_2\text{O}_3$  nanoparticles on the activity of LDH.

**Shuping Bi** (*Nanjing University, China*)

A new presumption with regards to the precursor of the formation of keggin  $Al_{13}$  in aqueous solution.

**Daniel Orihuela** (*National University of the Litoral, Argentina*)

Effect of aluminium on calcium binding proteins and calcium handling in different target cells.

**Salvatore Polizzi** (*Servizio di Medicina del Lavoro – A.S.L. 8 Carignano Italy*)

Iron and aluminium pollution in the province of Turin.

Keele Meeting Abstract

**A systems biology approach to the biological availability of aluminium.**

Christopher Exley

*Birchall Centre for Inorganic Chemistry and Materials Science, Lennard-Jones  
Laboratories, Keele University, Staffordshire, ST5 5BG, UK.*  
[c.exley@chem.keele.ac.uk](mailto:c.exley@chem.keele.ac.uk)

In this talk I will look at the topical subject of systems biology and I will try to define it in such a way that it might be applied to our understanding of the inorganic chemistry of aluminium and its interface with Life on Earth. The idea is to identify that which is not yet accessible by benchtop experiments and elucidate potential in silico approaches to such problems. If successful the final outcome should be an improved capability to formulate new hypotheses on the biological availability of aluminium which could then be tested by the design and implementation of novel benchtop experimentation.



Keele Meeting Abstract

**Solving the blood-aluminium problem.**

James Beardmore and Christopher Exley

*Birchall Centre for Inorganic Chemistry and Materials Science, Lennard-Jones Laboratories, Keele University, Staffordshire, ST5 5BG, UK.*  
[c.exley@chem.keele.ac.uk](mailto:c.exley@chem.keele.ac.uk); [j.s.beardmore@epsam.keele.ac.uk](mailto:j.s.beardmore@epsam.keele.ac.uk)

How do you solve a problem like equilibrium? We know from laboratory studies that approximately 90% of blood-born aluminium is bound to the iron transport protein transferrin. At least this is the proportion of aluminium which is bound by the time that it is possible to enact the fractionation procedures and measure any subsequent distribution. The question that we are trying to resolve is if this is the proportion of total aluminium entering the blood which is actually transported by transferrin and if it is not how can we use an *in silico* approach to understand what happens to aluminium in the period of time between aluminium first entering the blood and when such an equilibrium condition is reached. To do this, we have adopted an *ab initio* approach based on the Monte Carlo method. Whilst we have considered and experimented with use of the Metropolis algorithm for experimentally-determined binding energies and literature-derived binding constants, a method is proposed whereby reaction probabilities are arbitrarily-assigned in order to produce a simulation that mimics a known system at thermodynamic-equilibrium. The system is then studied during the time interval between  $t=0$  and  $t=t_{eq}$ , the equilibrium-time, to determine the path taken during equilibration. A simulation of a blood-like system can then be gradually built up and studied on its path to equilibration at  $t=t_{eq}$ , which normally occurs significantly earlier than the earliest point at which current technology allows “conventional” measurements to be taken. This is one of several avenues of enquiry proposed in our recent paper *Exley, Beardmore & Rugg (2007): “Computational Approach to the Blood Aluminium Problem?”*, *International Journal of Quantum Chemistry*, Vol 107, pp.275–278.

Keele Meeting Abstract

**Protein side chains that facilitate Mg/Al metal exchange in model protein binding sites.**

Elixabete Rezabal, Jose M. Mercero, Xabier Lopez, Jesus M. Ugalde

*Kimika Fakultatea, Euskal Herriko Unibertsitatea and Donostia International Physics Center (DIPC), P. K. 1072, 20080 Donostia, Euskadi (Spain)*

Among the most frequent protein binding sites served by Mg(II) we have identified those which have higher affinity towards Al(III). Then, we have estimated the metal exchange free energies for all these binding sites taking into account the solvent effects explicitly. The obtained results reveal the possibility that thermodynamically favored Mg(II)/Al(III) exchange reactions can take place at a number these metal binding sites, which could eventually be related with some of the disfunctions of the Mg(II) dependent biological processes. Additionally, it sheds light on the molecular basis of the toxicity of Al(III) in living organisms.

Keele Meeting Abstract

**Towards improved understanding of the molecular genesis and acid-base properties of aluminium polyoxocations using various computational approaches**

Jerry Winter and K.L. Shafran

*Unilever Research and Development Centre, Port Sunlight, Wirral, United Kingdom*

In spite of great progress in identification and characterisation of new and existing aluminium polyoxocations made recently [1] the enigma surrounding molecular mechanism of formation of these hydrolytic clusters still persists [2]. Another major theoretical task is to build a comprehensive model correlating macroscopic acid-base properties of Al polyoxocations and their structure-determined microscopic properties. Aluminium Keggin ions (Al<sub>13</sub>-mers and Al<sub>30</sub>-mers) are of special interest in this regard as they are major components of various technologically and environmentally important materials and processes (*e.g.* pillared clay catalysts; flocculating agents; advanced ceramics, antiperspirants, *etc.*).

Main problem hindering elucidation of exact molecular mechanism of the formation of Al hydrolytic clusters is inability of most analytical techniques to detect minute quantities of extremely quickly forming/disappearing reactive intermediates. For instance, there are at least *three* different mechanisms explaining the formation of the most established Keggin cluster ( $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$  or Al<sub>13</sub>) based on different hypothetical intermediates proposed by J.W. Akitt [3], M. Henry [4] and L.J. Michot *et. al.* [5]. Only the last model (Michot *et. al.*) is based on the direct experimental observation of trimers and tetramers by EXAFS and NMR, but it was measured for Ga ions and then inferred for Al ions having similar hydrolytic behaviour.

A number of theoretical studies has been undertaken in order to explain acid-base properties of Al hydrolytic clusters on microscopic level [*e.g.*, 6-8]. However, many of them either failed or were unable to produce new information, often due to incorrect initial assumptions concerning structure or environment or some other intrinsic properties of the clusters in question.

In the present study the authors will describe their attempts to elucidate the molecular origin of the Keggin  $\epsilon$ -Al<sub>13</sub>-mer cluster using several computational approaches. The first approach included quantum-mechanical evaluation of the structure of small oligomeric Al species at the density-functional level of theory. Many of the chosen clusters with the total number of Al atoms not exceeding 13 have been identified or postulated previously for aqueous solutions and their structures were either computed in this study or taken from crystallographic data. The effect of aqueous medium on geometry of Al clusters was represented using COSMO model. Optimised geometries together with electron-density related parameters and energies were analysed as a function of various microscopic properties including ‘nuclearity’ (the number of Al atoms per cluster) and ‘intrinsic basicity’ of Al clusters (the ratio of (oxo)hydroxyligands to the number of Al atoms) and correlated to certain macroscopic parameters (*e.g.* available thermodynamic data).

Another computational approach implemented in the present investigation is based on structure-independent and structure-dependent versions of the Partial Charge Model (PCM) proposed by M. Henry [4, 9]. The model uses Sanderson’s principle of

electronegativity equalisation to calculate partial atomic charges, mean electronegativities and other parameters as a function of structure and surrounding medium (e.g. pH of aqueous solution). These parameters can also be correlated and used to predict various macroscopic properties of Al clusters (pH range of stability, reactive ability, and some thermodynamic data).

*References:*

1. W.H. Casey. *Chem. Rev.* (2005) **106** 1-16.
2. K.L. Shafran, C.C. Perry. Complete aluminium speciation in aqueous solutions – multi-phase, dynamic approach. The 6th Keele Meeting on Aluminium, 26th February-2nd March, 2005, Bussaco, Portugal.
3. J.W. Akitt, A. Farthing. *J. Chem. Soc. Dalton Trans.* (1981) 1617-1623.
4. M. Henry, J.P. Jolivet and J. Livage. *Struct. Bond.* (1992) **77** 153-206.
5. L.J. Michot, et al, *J. Am. Chem. Soc.* (2000) **122** 6048.
6. J. Sukkoriipi et. al. *PCCP* (2005) **7** 3785-3792.
7. J.R. Rustad. *Geochim. Cosmochim. Acta* (2005) **69** 4397-4410.
8. V. Pophiristic et al. *J. Phys. Chem. A* (2004) **108** 113-120; V. Pophiristic et al. *PCCP* (2004) **108** 919-923.
9. M. Henry. *ChemPhysChem* (2002) **3** 561 (and *ibid*, 607); *Coord. Chem. Rev.* (1998) **178-180** 1109.

Keele Meeting Abstract

**An  $^{27}\text{Al}$  and  $^{31}\text{P}$  MAS NMR Surface Study of Adsorbed Aluminum Species at Synthetic Fluor- and Hydroxyapatite"**

Dan E. Sandstrom, Mathias Jarlbring, Oleg. N. Antzutkin and Willis Forsling

*Division of Chemistry, Lulea University of Technology, S-97187, Luleå, Sweden*

Surface adsorbed aluminum species on synthetic fluorapatite in aqueous suspensions at different pH have been studied by means of  $^{27}\text{Al}$  single pulse and CP/MAS NMR and  $^{31}\text{P}$  CP/MAS NMR. At pH 4.6 the adsorbed aluminum-hydroxyl complexes were more adsorbed as inner sphere complexes at the fluorapatite compared to higher pH, where outer sphere complexes were formed at the mineral surface. At higher  $\text{Al}^{3+}$  concentrations more outer sphere aluminum-hydroxyl complexes were formed at the fluorapatite surface.  $^{31}\text{P}$  CP/MAS NMR spectra of fluor- and hydroxyapatite with adsorbed aluminum-hydroxyl complexes revealed an additional broad resonance line at -8.5 ppm, which indicates that the aluminum-hydroxyl species adsorb at the phosphorus surface sites forming aluminophosphate surface complexes. The reduced intensity of the resonance line at 0.8 ppm previously assigned to protonated phosphorus surface sites of fluorapatite, indicates that the aluminum species adsorb to these surface sites. Tentatively reaction constants of two main types of aluminum surface complexes, inner and outer sphere, have been estimated using the simulation program WinSGW. These novel results are compared with our previous studies on adsorption of phosphates at  $\gamma\text{-Al}_2\text{O}_3$  and gibbsite minerals.

Keele Meeting Abstract

**Synthesis and characterisation of pure, monodisperse aluminium polyoxocation and aluminium hydroxide solutions using a novel technique based on static anion exchange**

O. Deschaume<sup>1</sup>, K.L. Shafran<sup>2</sup>, C.C. Perry<sup>1</sup>

*1 – School of Biomedical and Natural Sciences, Nottingham Trent University, Nottingham, United Kingdom*

*2 – Unilever Research and Development Centre, Port Sunlight, Wirral, United Kingdom*

Recent publications by our group have described mechanistic studies on the formation and stability of various aluminium species in aqueous solutions [1-3]. As has been reported at the previous Al meeting [4] these studies have shown that the usual way of hydrolysing Al ions by the addition of strong alkali hinders high-precision thermodynamic and kinetic studies of the hydrolytic behaviour of these ions at Al concentrations above the ‘supersaturation limit’ (i.e. ca.  $5 \cdot 10^{-6}$  mol/L) due to the inevitable creation of a local pH gradient and the consequent formation of Al hydroxide which in most cases remains unaccounted by the majority of experimental techniques.

Two routes around this problem have been identified in the previous communication [4]. The first route is to take into account all the complexity surrounding the ‘premature’ formation of Al hydroxide, i.e. quantity, type, charge, size, morphology and other characteristics of this metastable colloidal phase [3]. However, the nature and the amount of metastable amorphous Al hydroxide was very difficult to identify due to the low stability, high disorder and complex morphology of the material. This problem, for instance, hindered progress with quantifying the kinetics of Al Keggin polyoxocation formation and breakdown [2, 3].

The second route is to completely avoid local pH perturbations caused by the addition of strong alkali to aluminium ion solutions by introducing totally different, ‘soft’ approaches to Al ion hydrolysis. Recently we have patented [5] and published in the open domain [6] a novel technique of hydrolysing Al ions using static anion exchange. The technique is based on the replacement of the chloride ions of  $AlCl_3$  solutions with hydroxyl-ions of an anion exchanger. The detailed studies have shown that it is possible to use a good control of kinetics and the quantitative character of anion exchange for the ‘soft’ synthesis of hydroxide-free solutions of various Al species (e.g. Keggin polyoxocations –  $Al_{13}$ -mers and  $Al_{30}$ -mers). Moreover, the same route can be utilised for the synthesis of highly monodisperse nano-sized Al hydroxide with tuneable particle size in the range 5-250 nm [5, 6].

The most obvious application of the single Al species solutions synthesised using the ‘soft’ anion exchange technique is in materials chemistry for the production of various Al-containing inorganic and hybrid materials allowing true molecular control over structure and morphology. However, another approach followed by our group is to use these solutions as ‘reference systems’ for systematic mechanistic studies of the formation of Al hydroxide and predetermined-speciation interactions of Al ions with organic and bioorganic polymers (e.g. proteins and carbohydrates). The latter work will be described in more detail in another contribution.

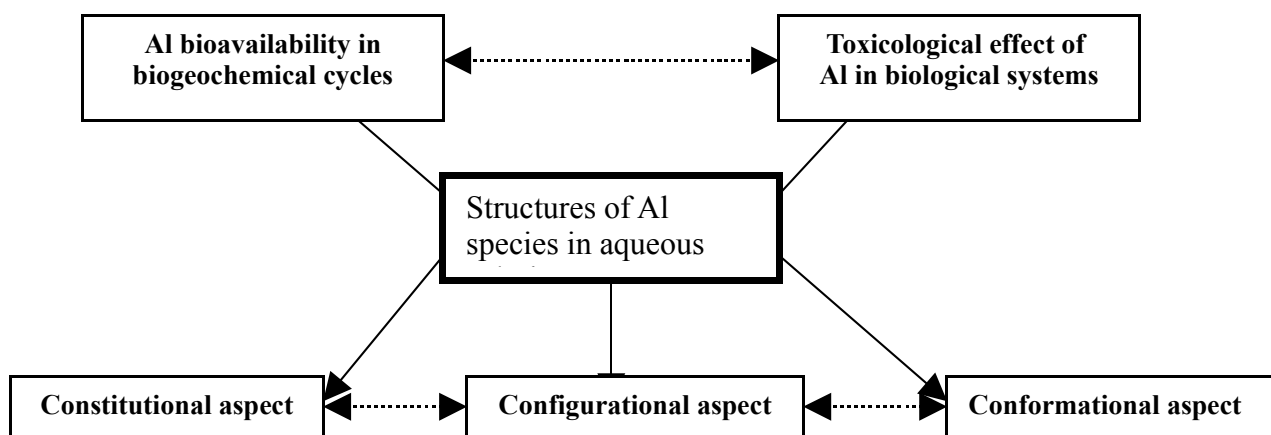
*References:*

1. C.C. Perry, K.L. Shafran. *Journal of Inorganic Biochemistry*, 2001, 87, 115-124.
2. K. Shafran, O. Deschaume, C.C. Perry. *Advanced Engineering Materials*, 2004, 6, 836-839.
3. K.L. Shafran, C.C. Perry. *Dalton Transactions*, 2005, 2098-2005.
4. K.L. Shafran, C.C. Perry. Complete aluminium speciation in aqueous solutions – multi-phase, dynamic approach. The 6th Keele Meeting on Aluminium (Lithosphere to Biosphere (and Back)), 26th February-2nd March, 2005, Bussaco, Portugal.
5. K.L. Shafran, O. Deschaume, C.C. Perry. Patent application WO 2006/103092 A1. Filed 31<sup>st</sup> of March 2005.
6. K.L. Shafran, O. Deschaume, C.C. Perry. *Journal of Materials Chemistry*, 2005, 15, 3415-3423.

## Structural speciation aspects of aluminum (III) complex with biligands in aqueous solutions

Xiao-Di Yang <sup>\*</sup>, Qian-Qian Zhang, Qi-Hong Zhao

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(X.D.Yang)



### Abstracts:

Aluminum complexes are essential for understanding the toxicity, bioavailability and transport mechanisms for elements in environmental and biological systems. Many methods have been developed during the last two decades. Since validation of what is really structure in these weak coordinated systems is very difficult, the analytical techniques for Al complexes structures in aqueous solutions are elucidated in the following three aspects: **(1) Constitutional studies:** The interactions of aluminum with  $\alpha$ -ketoglutarate were studied with pH-potentiometry (BEST&SPE program), UV-Vis, NMR, Raman spectra and MM calculation in acidic aqueous solution to measure the stoichiometries and its *keto-enol* tautomerism. Moreover, the individual isomers of Al-glutathione (GSH) complexes in aqueous solutions were confirmed by Gaussian calculation and ESI-MS technique. **(2) Configurational studies:** Glutamic acid (Glu) is an important acidic neurotransmitter in the central nervous system. Nature prefers L-amino acids rather than D-forms for the construction of proteins. However, many studies have shown mild accumulation of D-glutamate as an aging phenomenon and significantly higher levels in Alzheimer's disease affected brain regions and cerebrospinal fluid. Former studies have strongly suggested that, besides the negatively charged carboxylate donors ( $-\text{COO}^-$ ,  $-\text{COO}^-$ ), the amino group of Glu can participate in the tridentate binding ( $-\text{COO}^-$ ,  $-\text{NH}_2$ ,  $-\text{COO}^-$ ) of Al in the  $\text{AlL}^+$  and  $\text{AlLH}_1$  species in case of its deprotonation. Now, we proved that the complex abilities of  $\text{AlL}^+$  and  $\text{AlLH}_1$  in D-Glu-Al species were stronger than those of L-Glu-Al species, which were confirmed by pH-potentiometry and hyperchem calculations. These results can help to explain above biological and clinical phenomenon, which is also very important in the food chemistry. **(3) Conformational studies:** At biologically relevant pH and concentrations of Al and NADH, Al could increase the amount of folded forms of NADH, which will result in reducing the coenzyme NADH activity in hollow-dehydrogenases reaction systems. However, the conformations of  $\text{NAD}^+$  and  $\text{Al-NAD}^+$  depended upon the solvents and different species in the complexes, which



were confirmed with  $^1\text{H}$ ,  $^1\text{H}$ -NOESY-NMR spectroscopy. Since many analytical methodologies could provide more structural information, it could allow the identification of the bioligand and its complexes, not only in molecular binding sites, species, abilities and its effects, but also in molecular constitution, configuration and conformation. These structural aspects will yield in better understanding of the roles of aluminum (III) in biological and environmental systems. Also, in this case, we may need a new word “**STRUCTATION**” to represent the structural aspects after fractionation and speciation aspects.

**Keywords:**

Analytical methodology; Aluminum complexes, Structural speciation, Aqueous solution

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**Interactions of pure Al hydrolytic species - Keggin polyoxocations and hydroxide with biomolecules**

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Numerous studies of the interaction of aluminium species with various biomolecules have been conducted in the past. The Al species investigated previously are principally monomeric Al ions and their hydrolysis products as well as prevalingly mononuclear complexes of Al with geologically (e.g. silicates) and biologically relevant ligands (e.g. phosphate, oxalate, citrate, etc.). The concentration levels of Al and the biomolecules for these studies were usually chosen to represent the level of aluminium in the environment and the human body with the aim to explore various possible pathways enabling bioavailability and toxicity of this metal. Far fewer studies have been conducted at Al levels above the solubility limit of Al hydroxide (so called ‘supersaturated’ solutions of Al ions), although such conditions of ‘supersaturation’ with aluminium have been identified in several anthropogenically affected environmental media, e.g. soils and streams [1, 2].

The aim of the present study was to study interactions between pure aluminium species (Keggin Al polyoxocations – Al<sub>13</sub> and Al<sub>30</sub> and various Al hydroxide suspensions) and model proteins – bovine serum albumin (BSA) [3] and hen egg lysozyme. Pure Al species were prepared using the ‘soft hydrolysis’ technique of static anion exchange. The final aim of this study was to apply the obtained knowledge on Al-protein bio-interactions to create new bio-inspired Al-containing materials (e.g. toughened bio-ceramics) using a biomimetic approach. Although, the level of Al concentrations and biomolecules exceed those normally found in the human body and environmental media, we believe that a better understanding of Al species-biomolecule interactions would be of benefit also to those working in the biomedical and environmental sciences.

Interactions of Al species with the chosen biopolymers were studied at the molecular level using electrochemical techniques (pH-metry and conductivity measurements) and molecular spectroscopies (UV-Vis, FT-IR and <sup>27</sup>Al NMR). At the colloidal level the model systems of Al species and biopolymers were investigated using dynamic light scattering, vibro-viscometry and zeta-potential measurements. The morphology of freeze-dried colloidal materials produced by Al species-biopolymer interactions was studied using scanning electron microscopy (SEM).

The results have identified the predominantly electrostatic character of the interactions of Al species with biomolecules. Soluble Al species – Keggin polyoxocations (Al<sub>13</sub>-mers and Al<sub>30</sub>-mers) behave as large molecular ions interacting with the surface of biopolymers that are much larger in size than the polyoxocations. Practically none of the bio-ligands studied induced significant chemical breakdown of the Al species in question. Depending on the charge density and isoelectric point of a biopolymer polyoxocations surround it forming close ion pairs compensating the surface negative charge. Complete charge reversal can be observed for negatively charged biomolecules (e.g. BSA). Depending on the net charge and charge density of

the biopolymers, Al polyoxocations could form soluble complexes with biopolymers or precipitate them out. Al hydroxide on interaction with the biopolymers explored formed 'bio-colloids' of various types including flocculates and gels.

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Keele Meeting Abstract

**Alum Treatment of Lakes to Control Phosphorus Recycling: Forms and Transformations of Al**

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Alum has been used in water treatment for decades. More recently, alum additions to lakes have been used to bind phosphorus present within the water column and form a reactive barrier to slow the release of phosphate from sediment. In recent laboratory studies, we have quantified the forms, solubility and transformation of the Al floc formed in treated lake waters. Field and laboratory studies have also evaluated the efficacy of treatment for phosphorus control. Questions remain however, about the potential for formation of polynuclear Al species during alum treatment of lakes. I will summarize recent laboratory studies and field investigations and present new information about the importance and persistence of polymeric forms of Al in alum-treated waters.

Keele Meeting Abstract

**Photochemical source of aluminum for lakes and its impact on phosphorus cycling**

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Anoxic release of P is low from freshwater sediments with high concentration of  $\text{Al}(\text{OH})_3$ , resulting from elevated terrestrial export of ionic ( $\text{Al}_i$ ) or organically-bound ( $\text{Al}_o$ ) aluminium. A mass budget study of Al fluxes, palaeolimnological data on a ~14,000-yr sediment record, and photochemical experiments at Plešné Lake (Czech Republic) suggest that photochemical liberation from  $\text{Al}_o$  has been a significant natural source of  $\text{Al}_i$  for the lake, and  $\text{Al}(\text{OH})_3$  for its sediments throughout the Holocene. The Late Glacial sediment had most of P associated with  $\text{Fe}(\text{OH})_3$ , calcite, or apatite, and was able to release P during anoxia. The Holocene sediment had negligible P release during anoxia, because >90% of P was associated with  $\text{Al}(\text{OH})_3$ , immobilizing P. The P-sorption characteristics of sediment changed due to soil formation in the de-glaciated catchment. Soil organic acids carried  $\text{Al}_o$  to the lake, where it was liberated by solar radiation. Similar sediment composition of lakes in Maine (USA) suggests that this P-immobilizing process is general in lakes with high  $\text{Al}_o$  inputs.

**A key role of aluminium in phosphorus availability, food web structure, and plankton dynamics in strongly acidified lakes**

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Plankton biomass and composition, extracellular phosphatase activity (EPA) of planktonic microorganisms, aluminium (Al) speciation, and phosphorus (P) cycling were studied in acidified lakes of different trophic level in the Bohemian Forest. Enormous EPA and high planktonic C:P ratios suggested severe P limitation of the plankton. The terrestrial Al inputs, together with in-lake processes controlling the formation of particulate Al reduced P availability for planktonic microorganisms. At pH <5, moreover, ionic Al caused inhibition of extracellular phosphatases. Both particulate and ionic Al forms affected P availability, specifically shaped the plankton composition in the lakes, and delayed plankton recovery from acidification. The study demonstrated the key role of Al in overall P availability, food web structure, plankton dynamics, and recent recovery of chronically acidified lakes. The inter-lake comparison suggested that the Al-driven processes seriously affected stoichiometry of resources and consumers, as well as functional diversity of the acidified ecosystems.

Keele Meeting Abstract

## **Identification of Hydrolysis Products of Aluminium and Iron in Water**

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The aquatic chemistry of aluminium and iron is quite uncharted even they are the most abundant metals in the earth's crust and widely used coagulation agents in water treatment. Establishing the complete speciation of aluminium and iron in aqueous solution is difficult due the dynamic equilibrium between the complexes and versatility of polynuclear species. The conventional speciation methods are indirect and insensitive to various species. In our studies ESI-MS has been utilised to examine a wide range of aluminium and iron oxo hydroxides, chlorides and sulphates. Energetically most favourite structures for the aluminium anions and cations detected by the ESI MS were calculated by ab initio methods. The role of inorganic counter anions Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> was found to be remarkable on speciation. Our results have already shown the prevailing view of solution chemistry far too simple and sometimes even inconsistent.

Keele Meeting Abstract

**Energy and wavelength-dispersive X-ray microanalysis of Al and associated elements in freshwater phytoplankton.**

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Energy- and wavelength dispersive (WD) X-ray microanalysis of freeze-dried lake phytoplankton samples showed Al to be widely detectable in algal species, providing a major route of entry into the fresh water food chain. WDXRMA data on Al concentrations in micro-populations of diatoms, blue-green algae and green algae demonstrated significant correlations with a range of elements – including Si and transition metals (Cu, Zn and Fe). Principal component (PC) analysis showed Al to be part of a minor grouping (with Fe and other metals), consistent with its occurrence as an adsorbed cation at the cell surface. XRMA results from lake phytoplankton are compared to elemental correlations occurring in bulk analyses (ICPAES) of lake water, laboratory-cultured algae, bulk phytoplankton biomass and lake zooplankton.



Keele Meeting Abstract

**Geostatistical analysis of forest floor characteristics in two areas with different anthropogenic inputs**

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Soil acidification and aluminium behaviour in soils should be controlled by similar mechanisms and factors in different areas. This study aims in the description of spatial distribution of forest floor acidification and Al forms in two mountainous areas of the Czech Republic differing in the level of anthropogenic inputs. The Jizera Mts. is an area strongly impacted by acid deposition, the Novohradské Mts. is a region with rather low effect of deposition. The influence of stand factors (altitude, forest type, soil unit, geology, grass cover, liming) on forest floor characteristics was studied. Geostatistics, including cross-variograms and spatial correlation, was used as a tool. It was shown that in the Novohradské Mts., forest floor properties including Al distribution are controlled mainly by natural factors (soil unit, geology, vegetation). In the Jizera Mts., the effects of factors related to the deposition and human activities (altitude, grass expansion, liming, etc.) are more important.

Keele Meeting Abstract

**Aluminium speciation in forest soils of a mountainous region with relatively low effects of acid deposition**

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Soil acidification due to acid deposition, acid parent rocks, high precipitation, and specific vegetation is a problem especially in mountainous areas. It can result in a release of potentially toxic Al forms. This contribution presents an assessment of acidification and Al speciation in soils of the Novohradske Mountains region (Czech Republic), an area with relatively low effects of acid deposition. The soils are strongly acid, probably mainly due to spruce growing. Exchangeable Al content was controlled mainly by Ca content in the surface horizons (the effect of surface liming in the 1980s) and by pH in the deeper horizons. Speciation of Al forms by means of HPLC was determined in KCl and aqueous soil extracts. Water-extractable Al is bound mainly to non-toxic organic complexes. However, KCl-extractable Al is dominated by toxic Al<sup>3+</sup> forms which may present a significant danger in case of some potential changes of soil environment.

Keele Meeting Abstract

**Grass cover on forest clear-cut areas ameliorates soil chemical properties**

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Clear-cut areas formed after forest decline due to immissions or pest calamities in mountainous regions are often populated by grass (mainly *Calamagrostis villosa*). This study focused on the changes of soil chemical characteristics under the grass cover replacing the forest. Two areas were studied: bark-beetle calamity clear-cut area in the Bohemian Forest (Southern Bohemia) and immission clear-cut area in the Jizera Mountains (Northern Bohemia). The soils under grass cover exhibit higher pH values and lower exchangeable Al content compared to adjacent surviving forest in both areas. The proportion of mobile Al species is more favourable and the content of exchangeable base cations is slightly higher under the grass. The effect of grass, beside lower acidificant interception, is probably mediated mainly by organic matter changes. The temporary grass cover can therefore improve soil chemical quality for following reforestation. However, the differences are generally limited to the organic and surface mineral horizons.

Keele Meeting Abstract

**Mobilisation of river transported colloidal aluminium in estuaries and subsequent deposition on fish gills - sodium silicate as countermeasure**

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During flooding events, increased concentrations of toxic Al and negative effects on fish have been identified in Norwegian fjords, in experimental flow through tank systems receiving mixtures of seawater and river water (6 ‰) and in landbased fishfarms using mixtures of freshwater and seawater. Sea salt effects can mobilize Al from poorly buffered soils, and Al associated with river transported organic material can be mobilised in estuarine waters. Subsequently increased Al deposition on fish gills can occur in estuarine water causing fish mortality and/or reduced homing of wild Atlantic salmon. As a countermeasure sodium silicate has been continually added to Al-rich river water prior to mixing with seawater in short and long term experiments. Based on *in situ* Al fractionation of waters and sampling of gills from exposed fish, results showed that the concentration of mobilized Al<sub>i</sub> in water and the concentration of accumulated Al on fish gills decreased significantly in waters containing excess silicates.

Keele Meeting Abstract

**Metal ion binding to some organic and inorganic ligands and to plant cell walls and membranes. A scale for binding strength closely related to charge and Pauling electronegativity.**

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Equilibrium constants for binding to plasma membranes have been determined for seven metal ions, based upon adsorption studies and zeta-potential measurements. Log K values for the ions are these: Al<sup>3+</sup>, 4.30; La<sup>3+</sup>, 3.34; Cu<sup>2+</sup>, 2.60; Ca<sup>2+</sup> and Mg<sup>2+</sup>, 1.48; Na<sup>+</sup> and K<sup>+</sup>,  $\leq 0$  M<sup>-1</sup>. These values correlate well with Log K values for several organic and inorganic ligands. Log K values for metal ion binding to ten ligands were normalized and averaged to produce a scale for the binding of 48 ions. This binding scale correlates well with the values presented above ( $R^2 = 0.997$ ) and with those for each of the ten ligands from which it was derived ( $R^2$  ranged from 0.884 for F<sup>-</sup> to 0.992 for ATP). Furthermore, the scale appears to be related to charge ( $Z$ ) and Pauling electronegativity ( $PE$ ) of the 48 bound ions.  $R^2 = 0.937$  for  $Scale = -1.50 + Z(1.19 + 0.398PE)$ .

## **Keele Meeting Abstract**

### **THE ROLE OF ORGANIC ACIDS IN THE ALUMINUM TOLERANCE OF *Coffea arabica* L. CELL SUSPENSIONS.**

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The major mechanism of Al tolerance in plants involves the exudation and/or accumulation of specific organic acid species, which form non-phytotoxic complexes with  $Al^{3+}$  in physiological conditions. In our laboratory, a cell suspension line of coffee which exhibits Al tolerance (LAMt) has been isolated but the metabolic tolerance mechanism operating in this line remains unknown. The objective of this work is to determine the role of organic acids in the tolerance mechanism of the LAMt line. There are not significant differences in the malate dehydrogenase activity (a key enzyme of the organic acids metabolism) between protein extracts (7<sup>th</sup> day of culture cycle) of the L2 (Al sensitive) and LAMt (Al tolerant) cells, when the cell suspensions were treated or not with 100  $\mu$ M  $AlCl_3$ . Moreover, we found by HPLC analysis that the coffee suspension cells exudates malate and phytate when were incubated in a minimal solution (Trizma, 50 mM pH 8, sucrose, 30 g/L, KCl, 5 mM, EDTA, 0.1 mM), but that exudation was not enhanced by treatment with  $AlCl_3$  (100  $\mu$  M) in both cell lines. The accumulation of organic acids in the intracellular compartments in response of  $AlCl_3$  treatment remains to be determined.

This work was supported by the projects N° 45798-Z of CONACyT and by the fellowship N° 176793 of the same institution.

Keele Meeting Abstract

**Changes in wall polysaccharide components of suspension-cultured tobacco cells by aluminum**

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Al is one of the most abundant minerals in the soil, comprising approximately 7%. As the soil becomes more acid, aluminum is solubilized into a phytotoxic form. It has been assumed that aluminum is bound to the fixed negative charges of the wall, therefore the cation exchange capacity of the wall may play an important role in the expression of Al toxicity and Al resistance. In the present study the effect of aluminum on the cell wall components of suspension-cultured tobacco cells (*Nicotiana tabacum* L. cv. Burley 21) was investigated. According to the results treatment with 30 and 60  $\mu\text{M}$  of aluminum increased the amounts of pectin and hemicellulose A, but decreased the amount of hemicellulose B. The content of cellulose reduced with 30 $\mu\text{M}$  of aluminum, but not with 60  $\mu\text{mol}$  of aluminum. In both treatments, loss of cell viability led to decrease of the growth of cells.

Keele Meeting Abstract

**PHYSIOLOGICAL RESPONSE IN SUSPENSION CELLS OF *Coffea arabica* L. TO DIFFERENT CHEMICAL FORMS OF ALUMINIUM**

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In acid mineral soils aluminium (Al) is the main factor limiting the productivity of several crop species. *Coffea arabica* L. grows in acid soils where several toxic species of Al are present in different soluble forms. The most evident manifestation of toxicity by Al is the inhibition in the growth of the roots, this inhibition can be related to the effect of Al in the signal transduction pathways, which involve the phospholipids hydrolysis and the generation of second messengers like inositol 1,4,5-triphosphate (IP<sub>3</sub>) and diacylglycerol (DAG) by phospholipase C (PLC). There are reports about the inhibition of the PLC activity and growth in the suspension cells of coffee when are incubated with AlCl<sub>3</sub>. Besides AlCl<sub>3</sub> in acid soils, there are also other chemical forms of Al which little information about their toxicity and physiological effects is available. The goal of this work is to study the general physiological aspects of suspension cells line of coffee (L2) sensitive to Al, evaluating the growth of the cells in a culture cycle and PLC activity in response to different chemical forms of Al (AlCl<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub> and Al-citrate). Our results shown that the three salts of Al inhibited PLC activity in a similar form, in addition AlCl<sub>3</sub> and Al(NO<sub>3</sub>)<sub>3</sub> also inhibited the cellular growth.

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Keele Meeting Abstract

### **Aluminum-induced effects on wheat's rhizosphere environment**

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The wheat (*Triticum aestivum* L.) cultivar *Yangzhou 158* was cultivated to collect rhizosphere soil with a soil-culturing mode. Aluminum (Al)-triggered variations of the electrolytes, H<sup>+</sup>, sugar, organic acids, amino acids and secondary metabolites in rhizosphere soil were studied. Meanwhile, the endogenous hormones and Al content accumulated within wheat roots, as well as the distribution of Al in rhizosphere soil and non-rhizosphere soil were also examined. The research results show that rhizosphere Al alters wheat increment and constitutes of rhizosphere soil during wheat growth. Greater addition of Al might attribute to higher exudation of electrolytes, H<sup>+</sup>, and sugar. Initially, the amino acids secrete normally, but when Al<sup>3+</sup> concentration is over 10 mg kg<sup>-1</sup>, the constituents of amino acids change significantly. With the rhizosphere added Al<sup>3+</sup> increasing, the several original secondary metabolites disappear gradually, and some new secondary metabolites release simultaneously. Limited external Al stimulates the exudation of organic acids. The root growth of wheat and its rhizosphere pH are in response to Al. Moreover, the gibberellin and 3-indoleacetic acid in wheat roots increase, but abscisic acid decreases simultaneously with increasing added Al. The Al concentration in rhizosphere soil is slightly higher than that in non-rhizosphere soil. Al-stimulated changes in wheat increment and its rhizosphere environment apparently suggest a specific response of Al tolerance for wheat.

Keele Meeting Abstract

## **Designing and Testing Peptides with Aluminum Specificity**

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The EF-hand motif was discovered in calcium-binding proteins including calmodulin, parvalbumin, and troponin C, required for muscle contraction and calcium buffering in many organisms. Upon exposure to calcium and magnesium *in vivo*, the EF-hand binds the metal ions in a pH and concentration-dependent manner. We have compared the metal ion-binding sites of various EF-hands in order to relate metal ion charge, size, and electronegativity to ligand type. Recently, the X-ray crystal structure for a short EF-hand peptide bound to terbium was reported. The peptide was engineered from troponin C to bind lanthanide ions with high affinity and serve as a lanthanide binding tag. We are computationally redesigning and optimizing the peptide to bind aluminum *specifically* for potential use as a sensor or *in vivo* chelator. We are using fluorescence spectroscopy to study the aluminum ion binding affinity of the published peptide and plan to test our best computational redesign experimentally.

Keele Meeting Abstract

**Analysis of Computational Site-directed Mutagenesis of Ligands in the Metal Ion-binding Site in an Isolated EF-hand from Troponin C**

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We are re-engineering a short EF-hand peptide extracted from troponin C designed to bind terbium tightly to bind aluminum *specifically* and *tightly*. In previous studies, the residue at position 9 in the EF-hand has been shown to act as a “gateway” providing steric and electrostatic regulation to calcium binding and release. Data obtained from comparing the metal ion-binding sites of various EF-hand peptides is being used to guide our peptide design. We are using the published X-ray crystal structure of the EF-hand peptide to compare terbium and aluminum binding computationally. We have used two programs, DeepView and InsightII, to perform the computational site-directed mutagenesis of the metal ion-binding ligands and analyze our results. The results of the two computational methods are being compared directly and used to create an aluminum-specific peptide that can be tested experimentally for potential use as a sensor or *in vivo* chelator.

Keele Meeting Abstract

**Aluminum-induced metabolic syndrome in hepatocytes mimics obesity-like conditions.**

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Obesity is a global epidemic. It is a metabolic disorder that is characterized by increased lipid storage and decreased ATP production. Here, we show that aluminum (Al), a known environmental toxicant, triggers obesity-like conditions in human hepatocytes. This trivalent metal promotes mitochondrial dysfunction that results in the increased secretion of very low density lipoprotein (VLDL). Whereas numerous key glycolytic and lipogenic enzymes such as hexokinase (HK), pyruvate kinase (PK), acetyl CoA carboxylase (ACC), and isocitrate-dehydrogenase-NADP<sup>+</sup> (ICDH-NADP<sup>+</sup>) are upregulated, the mitochondrial enzymes such as aconitase (ACN), succinate dehydrogenase (SDH), and cytochrome C oxidase (Cyt OX), responsible for ATP synthesis are severely impeded. Fluorescence microscopic studies revealed lipid accumulation and ineffective mitochondria in the Al-challenged hepatocytes. Hence, these data point to the ability of Al to evoke a metabolic syndrome that mediates increased lipid synthesis and decreased ATP formation, conditions observed during obesity.

**Effects of aluminum chloride on Na<sup>+</sup> current and transient outward K<sup>+</sup> current and delayed rectifier K<sup>+</sup> Current in acutely isolated rat hippocampal CA1 neurons**

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The effects of aluminum chloride (AlCl<sub>3</sub>) on sodium current (I<sub>Na</sub>), the transient outward potassium (I<sub>A</sub>) and delayed rectifier potassium currents (I<sub>K</sub>) in hippocampal CA1 neurons of rats were studied using the whole-cell patch clamp technique. AlCl<sub>3</sub> reduced I<sub>Na</sub>, I<sub>A</sub>, I<sub>K</sub> in a dose-dependent and voltage-dependent manner. 1000 μ mol/L AlCl<sub>3</sub> decreased I<sub>Na</sub>, I<sub>A</sub> and I<sub>K</sub> approximately fifty percent. In addition, 1000 μ M AlCl<sub>3</sub> shifted the steady-state activation curves of I<sub>Na</sub>, I<sub>A</sub> and I<sub>K</sub> toward positive potential (I<sub>Na</sub> control V<sub>h</sub> = -51.32 ± 6.04 mV vs AlCl<sub>3</sub> V<sub>h</sub> = -47.53 ± 5.37 mV, n = 10, P < 0.05; I<sub>A</sub> control V<sub>h</sub> = 8.12 ± 1.27 mV vs AlCl<sub>3</sub> V<sub>h</sub> = 22.03 ± 2.68 mV, n = 10, P < 0.01; I<sub>K</sub> control V<sub>h</sub> = 16.55 ± 3.28, vs AlCl<sub>3</sub> V<sub>h</sub> = 29.76 ± 1.16, n = 10, P < 0.01, without changing the slope factor), and the steady-state inactivation curve of I<sub>Na</sub>, I<sub>A</sub> toward negative potential (I<sub>Na</sub> V<sub>h</sub> = -67.38 ± 5.49 mV, vs AlCl<sub>3</sub> V<sub>h</sub> = -71.35 ± 4.36, n = 10, P < 0.05; I<sub>A</sub> control V<sub>h</sub> = -52.87 ± 1.92 mV, vs AlCl<sub>3</sub> V<sub>h</sub> = -60.50 ± 1.36 mV, n = 10, P < 0.05, without changing the slope factor). These results imply that AlCl<sub>3</sub> may damage sodium and potassium channels of the hippocampal CA1 neurons from rats and this may be related to the mechanism of the damage to the central nervous system by aluminum.

Keele Meeting Abstract

**Mechanism of inflammatory gene expression in aluminum- or iron-stressed aging human brain cells; rescue with desferrioxamine and Feralex-G**

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Physiologically relevant concentrations of aluminum- and iron-salts induce pro-apoptotic, pro-inflammatory and pathogenic gene signaling in untransformed human neuronal and glial cells in primary culture. Neurotoxic metal-stressed brain cells model, in several aspects, gene expression profiles to those observed in Alzheimer's disease (AD) brain tissue. In these studies we examined desferrioxamine- (DF) and Feralex G- (FG) mediated reversibility of the genotoxic effects of nanomolar concentrations of magnesium-, iron- and aluminum-sulfate on gene regulatory and expression patterns in human primary brain cells exposed to 100 nanomolar magnesium-, iron-, or aluminum-sulfate for 7, 14 and 21 days. This represented trace metal exposure for up to two-thirds of brain cell lifespan *in vitro*. Unlike magnesium sulfate, aluminum- or iron-sulfates were found to be especially potent in their ability to induce stress-sensing, pro-inflammatory and pro-apoptotic gene signaling. The combination of iron- and aluminum-sulfate together exhibited synergism in up-regulating pathogenic gene expression. This effect was preceded by the evolution of reactive oxygen species (ROS) as measured by 2',7'-dichlorofluorescein diacetate assay. These results indicate that ROS, and related Fenton chemistry-triggered changes in specific transcription factor-DNA binding, such as NF-kB and HIF-1, promote mis-regulation of gene expression programs that trigger brain cell dysfunction. The iron and aluminum chelators DF and FG changed toxic metal-ion stressed brain cell gene expression patterns back towards more homeostatic levels. These results indicate the reversibility of metal-ion induced brain cell genetic dysfunction and therapeutic application with the appropriate use of chelators in the potential treatment of toxic metal-overload disease. These rescue effects are however dependent on the chelator application regimen, brain cell age, and the length and magnitude of neurotoxic metal exposure.

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Keele Meeting Abstract

**THE EFFECT OF ALUMINIUM ON GREEN AND BROWN HYDRAS-  
PRELIMINARY OBSERVATIONS**

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Since the effect of aluminium on living beings was little known until recently and it is possible to present a potential danger for freshwater organisms, the aim of this research was to explore its effect on green (*Hydra viridissima*) and brown (*Hydra oligactis*) hydra. Hydra is a simple metazoan organism that belongs to the Cnidaria phylum. It consists of ectoderm, mesoglea and gastroderm. Green hydra forms a symbiotic relationship with the endosymbiotic alga *Chlorella*, harboured inside the gastrodermal myoepithelial cells. Hydras were treated with four concentrations of aluminium sulphate (25, 250, 475, 500 mg/L) in laboratory conditions for three days and compared to the control. Only cellular layers of treated hydras contained the aluminium depositions: in green hydras depositions were found in gastroderm, including algae *Chlorella*, and in brown hydras they were found in ectoderm. We assume the appearance of these depositions to be the mechanism of cellular detoxication.

Keele Meeting Abstract

**THE EFFECT OF ALUMINUM ON THE PLANARIAN *POLYCELIS FELINA***

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The effect of aluminum on the planarian *Polycelis felina* Daly. in laboratory conditions was studied. Planarians are simple freshwater invertebrates which belong to the phylum Platyhelminthes, class Turbellaria, order Tricladida. Planarians were treated with four concentrations of aluminium sulphate (25, 200, 600 and 1100 mg/L; Kemika, Zagreb). Changes were observed on the fifth day after the treatment as well as on the fifth day of post-treatment recovery period. The results showed distinguished morphological changes on the planarian body as well as behavioral changes: various depigmentations, disordered locomotion, twisting of the body parts, hardly reacting to mechanical stimuli, also body contractions and mortality in the highest concentration. This work should also involve histomorphometrical analysis, showing if, how and where aluminum affected, and could be deposited in the planarian cells and tissue.



Keele Meeting Abstract

**An Aluminum-based Rat Model for Alzheimer-type Dementia Exhibits Oxidative Stress, Inhibition of PP2A Activity, and Hyperphosphorylated Tau**

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If rats are chronically fed aluminum over their lifespan at the high end of the human dietary aluminum range, they can develop an Alzheimer-like dementia in old age. This occurs despite their lack of amyloid plaques and neurofibrillary tangles which are species-specific. The present study examined cerebral tissue from rats with Alzheimer-like dementia to learn whether aluminum in their brains is associated with the early stages of plaque and tangle formation. In brains of humans with Alzheimer's disease, oxidative reactions precede and lead to the formation of amyloid plaques whereas inhibited protein phosphatase 2A (PP2A) activity results in hyperphosphorylated tau that polymerizes to form neurofibrillary tangles. Rat neocortical and hippocampal neurons were examined for co-localization of aluminum with markers for oxidative stress (anti-4-hydroxy-2-nonenal or HNE) and hyperphosphorylated tau (PHF-1). PP2A activity was compared in neocortical/limbic brain homogenates from rats with Alzheimer-like dementia and rats with normal cognition. PP2A activity was  $580.67 \pm 111.70$  pmol  $P_i/\mu\text{g}$  protein in cognitively-normal rat brains. PP2A activity was  $238.71 \pm 17.56$  pmol  $P_i/\mu\text{g}$  protein in brains of rats with Alzheimer-like dementia ( $p < 0.05$ ), amounting to 41% of the control value. HNE immunoreactivity increased in rat neurons during early stages of aluminum-loading. Hyperphosphorylated tau immunoreactivity increased during early to intermediate stages of aluminum-loading. Oxidative damage and disruption to phosphate metabolism are well-established forms of aluminum neurotoxicity. As neuronal aluminum can account for these early stages of plaque and tangle formation in rats with Alzheimer-like dementia, aluminum could also initiate plaque and tangle formation in Alzheimer's disease.

Keele Meeting Abstract

**EFFECTS ON LOCOMOTOR, SPATIAL LEARNING AND PROLIFERATION IN A TRANSGENIC MOUSE MODEL OF ALZHEIMER'S DISEASE AFTER EXPOSURE TO LOW DOSE OF ORAL ALUMINUM**

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Aluminum (Al), a non essential element, is used in a wide spectrum of compounds because of its inert properties and its low absorption after oral exposure. When Al is ingested, a little amount can access to the brain. By this way, Al is associated to various neurodegenerative disorders. Particularly with Alzheimer's disease (AD). Epidemiological studies indicated a possible link between water Al content and AD. Recent investigations have demonstrated that Al is linked to beta-amyloid deposition, increases beta amyloid deposits and induces oxidative stress. Some studies conducted with transgenic models of AD have already provided evidences to link Al and AD.

The aim of the present study was to assess the behavioral effects of Al in a transgenic animal model of AD (TG-2576) and evaluate if low doses of Al intake could accelerate behavioral, spatial learning deficits and alters cell proliferation in brain. Animals received normal chow (control wild and control TG-2576) or supplemented with Al (treated wild and treated TG-2576) in the form of aluminum lactate 1 mg/g of chow for 90 days. Behavioral assessment after 90 days, (at 9 months of age) was performed evaluating general state by a Functional Observation Battery, Open Field Activity and Water Maze Test. The results shown a diminished activity in Al exposed wild and transgenic mice. Differences in sensorimotor reactivity were also observed in the same groups. The open field activity did not show any significative differences. Acquisition of water maze task was impaired in transgenic mice and wild type mice exposed to Al. Retention of the task was not affected. An increased neural proliferation in transgenic mice was observed in the dentate gyrus of the hippocampus.

Keele Meeting Abstract

**Effect of aluminium on intestinal calcium absorption in pregnant and lactating rats.**

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During rat pregnancy occurs an early adaptive increase of intestinal calcium (Ca) absorption to allow maternal skeleton accumulates Ca to meet the peak of fetal demand by mid-pregnancy, and later in lactation. The aim of present work was to study the effect of oral aluminium (Al) overload on intestinal Ca transport (JCa) in these critical stages and the possible relationship with prolactin (PRL) levels. Adult female Wistar rats were orally treated from day 1 of pregnancy with 0 (control), 25 or 50 mg elemental Al (as chloride)/kg body weight per day. Half of animals in each group were injected i.p with 0.5 mg/kg body weight per day of bromocriptine (BrC), an inhibitor of PRL secretion, 24 h before JCa measurements were done. Ca transport was determined 48 h before delivery and at day 7 of nursing, by everted duodenal sacs technique using  $^{45}\text{Ca}$  as flux marker. Al produced a dose-dependent decreasing of JCa during both pregnancy and nursing. BrC treatment reduced the percentual inhibition of JCa by Al on a greater extension in lactation as compared to pregnancy. We can conclude Al reduces transcellular Ca absorption in the small intestine by interfering with physiological mechanisms of Ca transport partially mediated by serum level increment of PRL, observed in late pregnancy and mainly during lactation.

Keele Meeting Abstract

**The body burden of aluminium: what is it?**

Christopher Exley

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We are exposed to aluminium throughout our everyday lives and throughout our life through myriad different ways. In this talk we will explore where this aluminium goes in and about our bodies and present new evidence of sinks and sources of body aluminium. We will ask the question as to what constitutes the body burden of aluminium and how we might reduce such a burden as effectively and non-invasively as possible. Can we live in the '**Aluminium Age**' and not have a significant aluminium body burden?

Keele Meeting Abstract

**Elevated urinary aluminium in current and past users of illicit heroin.**

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The use of illicit heroin is associated with aberrant neurology of unknown aetiology and various psychiatric illnesses. Aluminium, which is a proven neurotoxin, is present in significant amounts in illicit heroin and may also be volatilised and inhaled following the vapourisation of heroin off aluminium foil ('Chasing the Dragon'). The purpose of this study was to establish if the use of illicit heroin was associated with an increase in the body burden of aluminium. We have used graphite furnace atomic absorption spectrometry (GFAAS) to measure the aluminium and iron contents of the urine of current and past users of illicit heroin and used these data to estimate body burdens of aluminium. Urinary excretion of aluminium is the most effective non-invasive indicator of the body burden of aluminium and was found to be significantly ( $P < 0.001$ ) higher in users of illicit heroin, range 14 to 3382 nmol/mmol creatinine (mean  $\pm$  SD;  $222 \pm 491$  nmol/mmol creatinine), than in a normal non-drug abusing control population, range 23 to 74 nmol/mmol creatinine (mean  $\pm$  SD;  $43 \pm 19$  nmol/mmol creatinine). Exposure to aluminium from the use of illicit heroin may be of particular significance since the urinary excretion of iron, another major contaminant of illicit heroin, in users (mean  $\pm$  SD;  $53 \pm 63$  nmol/mmol creatinine) was not significantly different ( $P > 0.05$ ) to the control population (mean  $\pm$  SD;  $38 \pm 18$  nmol/mmol creatinine). We have shown for the first time that the use of illicit heroin may be a significant contributor to the body burden of aluminium. Further research will be required to determine if adventitious aluminium has a role in heroin use-related neuropathology and neurology.

Keele Meeting Abstract

**SPECIATION OF HIGH MOLECULAR MASS Al IN SERUM COMBINING SEC AND ANION-EXCHANGE FPLC WITH UV, ETAAS AND ICP-MS DETECTION**

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Speciation of high molecular mass Al compounds (HMM-Al) in serum is usually performed by size-exclusion or ion-exchange chromatography. Size-exclusion chromatographic (SEC) columns are not able to completely separate transferrin from albumin. Anion-exchange fast protein liquid chromatography (FPLC) enables separation of these proteins. However, the possibility exists of coelution of LMM-Al species with HMM-Al species. It is therefore important to remove LMM-Al species before FPLC separation.

For this purpose a combination of SEC (Superdex 75 HR 10/30) and anion-exchange FPLC (Mono Q HR 5/5) with UV detection was applied. Serum was injected onto the SEC column. Protein peak was collected into a polyethylene cup and then a sample aliquot injected onto the FPLC column. Separated Al species were determined either »off line« by ETAAS or »on-line« by ICP-MS. For reliable determination of separated Al species by ICP-MS the applicability of dynamic reaction cell was critically evaluated.

Data indicated that  $90 \pm 5\%$  of Al in spiked serum of renal patient was eluted under the transferrin peak. The same analytical procedure may be applied for speciation of Fe.

Keele Meeting Abstract

**What happens when children sensitised to aluminium receive aluminium adsorbed vaccines?**

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Although considered extremely rare, hypersensitivity to aluminium (Al) has been demonstrated in about 500 children in Sweden after injection with vaccines adsorbed to Al hydroxide. Most of them also had intensely itching subcutaneous nodules at the injection site for many years. Sensitised children have reacted with localized itching eczema after skin contact with Al containing preparations.

For natural reasons, the children are recommended to avoid Al containing vaccines in the future. This causes a dilemma when they at the age of 10 shall receive a booster dose of diphtheria-tetanus-pertussis vaccine (DTP), as all vaccines available in Sweden today are adsorbed to Al hydroxide.

In the present study, Al sensitised children who received their booster dose of DT/P with vaccines either free from Al or adsorbed to Al phosphate or Al hydroxide were followed in order to evaluate how they reacted after the renewed vaccination and if any difference was seen between the three groups.

## ALUMINUM LEVELS IN MEXICAN CHILDREN WITH CHRONIC KIDNEY DISEASE UNDERGOING DIALYSIS TREATMENT.

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**Background:** The frequency of low-turnover bone disease (LTBD) in patients with chronic kidney disease (CKD) has increased in the last years. This change is important because LTBD is associated with bone pain, growth delay, and higher risk for bone fractures and extra-osseous calcifications as in the heart. Serum Aluminum level is a important risk factor.

**Objective:** To describe Al serum levels and others markers of low-turnover bone disease in pediatric patients with renal failure undergoing hemodialysis and peritoneal dialysis, using serum calcium and intact PTH levels as a diagnostic.

**Methods:** In this cross-sectional study 41 children with CKD undergoing dialysis treatment (31 on CAPD and 10 on HD) were included. There were not inclusion restrictions regarding gender, cause of CKD, or dialysis modality. The children were studied as outpatients. The demographic data, CKD course, time on dialysis, phosphate-binding agents and calcitriol prescription were registered, as well as weight, height, z-score for height, linear growth rate, and z-score for BMI. Serum Ca, P, Al, PTH, alkaline phosphatase, osteocalcin, glucose and creatinine were measured.

**Results:** There were 20 (48.8%) children with both PTH < 150 pg/ml and corrected total calcium > 10 mg/dl who were classified as having LTBD+; the remaining 21 (51.2%) children were classified as having no LTBD-. They had not differences regarding z-scores for height. The linear growth in six months was less than expected in both groups (-0.15±0.23 cm/mo), but the difference between expected and observed growth was higher in the LTBD+ group (-0.24 ± 0.14 vs -0.07 ± 0.28 cm/mo, **p<0.03**). Patients with LTBD+ also had lower serum creatinine: 8.69± 2.75 vs. 11.9 ± 3.17 (p<0.01), **higher serum Al levels [median (range)]: 38.4 (9-106) vs. 28.1 (9-62) µg/L, (p<0.05)**. A significant correlation was found between PTH and alkaline phosphatase (r=0.68, p<0.001), but not between PTH and Al.

**Conclusion:** LTBD+ biochemical profile was found in 48.8% of the children and it was associated with impaired linear growth. Aluminium contamination, evidenced by higher serum Al levels, may have had a pathogenic role in these disorders.



Keele Meeting Abstract

## ALUMINUM IN OSTEOPOROTIC VERTEBROPLASTY SPECIMENS

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Over their lifespan, many humans chronically consume a diet containing 50-95 mg aluminum/day in the form of additives. Up to 1% of ingested aluminum is absorbed and 4% of the blood-borne fraction is estimated to be retained in the skeleton. Aluminum weakens bone matrix by interfering with hydroxyapatite formation. Here, we examined whether aluminum, which accumulates in bone over time, could be a potential risk factor for osteoporosis, an age-related bone disease of unknown etiology. Trabecular bone specimens from vertebral bodies of patients with osteoporosis were obtained at vertebroplasty, methacrylate-embedded without decalcification, and sectioned. Control specimens were from cases without osteoporosis, either with blood disease or miscellaneous bone conditions. All samples were processed with the Walton histological stain for aluminum\*, modified for use in methacrylate sections, and examined by histomorphometry. We compared its efficacy for staining bone aluminum against the aluminon method. With the Walton stain, aluminum, where present, appears as a magenta outline of the trabecular surface or as magenta-colored cement lines within turquoise bone matrix. Most osteoporotic bone specimens exhibited some degree of aluminum staining. In some specimens, the aluminum was evident in poorly mineralized regions, appearing as pink to magenta-colored woven bone that exhibited birifringence when examined under polarized light. The aluminon method was less sensitive and stained less consistently than the Walton method.

\*Walton JR, A bright field/fluorescent stain for aluminum: its specificity, validation, and staining characteristics. *Biotech Histochem* 79 (2004) 169-176.

Keele Meeting Abstract

**Alterations in micro RNA (miRNA) complexity in Alzheimer's disease (AD) and in metal-ion-stressed human brain cells**

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MicroRNAs (miRNAs) constitute a family of recently discovered, non-coding ribonucleic acids that function in the regulation of messenger RNA (mRNA) complexity. miRNAs function by binding to the 3' untranslated region (3'UTR) of target mRNAs, and in doing so, silence the expression of that particular DNA transcript. While miRNAs are now known to be dynamically regulated during brain cell development, the expression patterns of these small 18-28 nucleotide miRNAs during brain cell aging, and their contribution to the molecular genetic mechanisms which induce neural degeneration are not well understood. This study examined miRNA abundance (1) in the hippocampal CA1 region of fetal, late adult and age-matched Alzheimer's disease (AD) brain *in vivo*, and (2) in aluminum- and iron-sulfate stressed human brain cells in primary culture. The data indicate that miRNAs encoding miR-9, miR-124a, miR-125b, miR-128 and miR-132 are abundantly represented in fetal human brain and are differentially regulated in late adult brain. Alterations in specific miRNA abundance were observed to occur in AD affected hippocampus when compared to age-matched controls. Aluminum- and iron-sulfate, but not magnesium sulfate, were found (1) to trigger extensive brain cell stress, (2) to up-regulate pro-inflammatory gene expression, and (3) to induce the mis-regulation of specific miRNA and mRNA populations *in vitro*. Up-regulation of several different miRNAs, which base pair to the 3'UTRs of important brain-specific cytoskeletal and synaptic mRNAs, were discovered. These findings may help explain the down-regulation of specific mRNAs encoding several key neuron-enriched synaptic elements, such as synaptotagmin, synaptophysin and synapsin, whose deficits are commonly observed in AD affected tissues. These data are consistent with the hypothesis that metal-ion induced, miRNA-mediated processing of neuron-specific mRNAs contribute to atypical mRNA complexity, driving synaptic neurotransmitter protein deficits and inter-neuronal signaling dysfunction in AD brain.

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Keele Meeting Abstract

**Neurotransmission impairment: an accomplice to aluminium neurotoxicity?**

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Neurobehavioral disorders, with the exception of their most overt form, tend to lie beyond the reach of clinicians. Presently, the use of molecular data in decision-making processes is limited. However, as the details of the mechanisms of neurotoxic action of aluminium become clarified, a more complete picture of sensitive molecular targets of aluminium can be anticipated, which promises to be particularly useful to better predict the neurotoxicological potential of aluminium associated with exposure. In practical terms, an appreciation of data on aluminium effects on neurotransmission can be of great benefit for expanding knowledge of the neurotoxicological potential of aluminium, especially because neurotransmission represents constant exchange of chemical messages between neurons. The review of these studies suggests that impairment of neurotransmission is a strong predictor of outcome in neurobehavioral disorders. Here, we integrate shaping findings from neurotransmission research across aluminium exposure to identify key questions and to set challenges for future research into aluminium neurotoxicity.

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Keele Meeting Abstract

**Neurocognitive effects in welders exposed to aluminium.**

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**Aims:** The various authors who in the last 30 years studied the effects of aluminium exposure on the NCS have reached different and often contradictory conclusions. The aim of this study is to help clarify the effects that the metal causes on cognitive ability in a group of naval welders exposed to aluminium.

**Materials and methods:** The study was performed on a sample of 86 male aluminium welders in a shipyard in Messina. The average value of environmental aluminium, recorded in the workplace, was 19.5 mg/m<sup>3</sup>. The blood levels of Al, Zn, Mn, Pb and Cr were monitored in all the subjects. The reagents used for the neuropsychic study were: the Wechsler Memory Scale (WMS), the Color-Word Test or Stroop Test and the Test of Attention Matrixes. The results were compared with those obtained in a similar control group, not exposed to aluminium and with an Al-b value of 6.93 µg/l.

**Results:** for all the mental and reagents used the reply is obtained in the sample of exposed subjects showed decreased cognitive response with regard to attention and memory performance. The comparison between the individual tests showed greater sensitivity of performance studied using the WMS and the Stroop Test compared to the Test of Attention Matrixes. The alterations encountered in the cognitive functions studied increased proportionally to time of exposure and quantity of metal absorbed.

**Conclusions:** the study confirmed that occupational exposure to aluminium causes alteration in cognitive responses which are more evident in complex functions.

Keele Meeting Abstract

**Dust exposure to Iron and Aluminium and impairment of lung function in apprentices living near a foundry.**

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*Objectives* - A cross sectional study was carried out among apprentices to assess their environmental exposure to ambient respiratory iron and aluminium in their residence area and its effects on their lung function tests.

*Participants* - Lung function was measured in 627 no smoking apprentices with no occupational exposure to lung toxicants or irritants. Ambient respiratory dusts concentration (iron and aluminium) was measured in their living area (105 samples collected) during a four months period including summer when industry activities were suspended. Information on respiratory and clinical history were collected from participants. Cumulative exposure to iron and aluminium was calculated according years of residency and metal concentration in environment.

*Results* - The mean value of iron pollution was  $1,39 \pm 0,93 \mu\text{g}/\text{m}^3$ , and for aluminium  $0,73 \pm 0,70 \mu\text{g}/\text{m}^3$ . Among the non exposed apprentices FVC and FEV1 were significantly lower in subjects living in areas with higher iron pollution. FVC coeff.  $\beta = - 0,151$   $p < 0,043$ ; FEV1 coeff.  $\beta = - 0,163$   $p < 0,003$  (data were controlled for anthropometric data and Body Mass Index). No correlation was found with aluminium air pollution and pulmonary function tests. Smoking habit did not significantly influence the effects of iron exposure on lung function.

*Conclusions* – Respiratory function in young apprentices was adversely affected by exposure to respirable iron dusts, but not aluminium, in subjects living near an industrial area with one the biggest aluminium and casting foundries. Further studies must evaluate if there is a cohort effect.

The present work was supported by grants obtained from Istituto Superiore Prevenzione E Sicurezza del Lavoro (ISPESL).

Keele Meeting Abstract

### **Aluminium vs. Alzheimer's Disease: The Evidence-Based Approach**

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The volume of the scientific literature is often practically prohibitive, for individuals to be able to review each published report systematically and critically. In contrast to medicine based on the evidence, evidence-based medicine rests on the long-established existing medical traditions, supplemented by a systematic evaluation of all of the pertinent, available and accessible individual pieces of research, which, even on an individual basis may, or may not, have undergone adequate or sufficient scientific scrutiny, even as they are sifted through the well-accepted, reliable and established peer-review system. According to these principles, and based on results from our laboratory, which point towards a correlation between aluminium (Al) content in drinking water and characteristics of dementia of the Alzheimer's type, at least at the cellular immune function level, we designed a best-case study to evaluate the current published literature on Al and Alzheimer's disease. Overall, an increased surveillance of people exposed to high content of Al in drinking water is certainly justified.

Keele Meeting Abstract

**A Review: Aluminum - A Causative Co-Factor Of “Dementia” of Alzheimer’s Disease.**

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Alzheimer’s Disease (AD) and the “dementia” of AD have been confused as having identical causation. Disagreement between the clinical identification of persons with dementia using cognitive testing, and brain autopsy findings based on plaque and tangle deposits reveals that AD, as presently defined, and its dementia lack identical causation. Study of 56 religious sisters (age of death 88 to 93) from the Nun Study found that fourteen died with AD measured by brain deposits, but with normal cognition. Another nineteen sisters had AD with dementia. The difference between the two AD groups was hippocampal volume, i.e. brain atrophy. Aluminum is an effective killer of brain cells in laboratory animals and humans. Dementia of AD is prevented by restriction of aluminum exposure. Brain atrophy is prevented by folic acid, also an aluminum chelator. Aluminum should be viewed as a causative co-factor in generation of brain atrophy and dementia.

Keele Meeting Abstract

**Aluminium Chelation Therapy: Past, Present, and Future.**

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The role of aluminium in Alzheimer's disease continues to be controversial pitting much of the scientific community against the aluminium industry and its supporters. Systemic chelation therapies that remove aluminum from brain tissues represent a reasonable and attractive strategy to alleviate the development and progression of neurological disorders which are linked to metal ion intoxication. In a single-blind, randomized, placebo-controlled, clinical trial involving 48 patients with a clinical diagnosis of Alzheimer disease, the use of the chelating agent, Desferrioxamine (DFO), was shown to slow down the progression of dementia in the treated group while the no-treatment/placebo group deteriorated twice as rapidly over a 24-month study period (Crapper-McLachlan, et al, 1991). This claim has been supported by the observation of a significant decrease in mean levels of aluminum content in neocortical AD-affected brain tissues, pia, and small cortical blood vessels of 3 patients who died while on DFO for an extended period of time compared to 3 other patients who died following only minimal DFO treatment (Crapper-McLachlan, et al., 1993). The claim has also been supported by other experiments showing the ability of DFO to reverse Al-evoked neurofibrillary degeneration in rabbits (Savory, et al., 1994) and its ability to remove aluminium from neurofibrillary tangles in Alzheimer disease brain sections (Murayama, et al., 1999). Nevertheless DFO is problematic for several reasons. DFO requires daily intra-muscular injection by someone well-trained in the injection procedures. These limitations make it difficult to administer DFO under most care-providing situations. It is now acknowledged that the design of aluminium chelators poses a difficult challenge due to the affinity of these compounds for iron, copper, magnesium, zinc, and other essential trace metals. Feralex-G, a relatively new aluminium chelator (Kruck and Burrow, 2002), holds much promise because it has low toxicity, it can be administered orally, and it is effective at physiological temperatures. The combination of Feralex-G with DFO and Ascorbate holds even more promise for the future in the treatment of Alzheimer disease (Kruck, et al., 2004). These studies need to be replicated because they have been largely dismissed along with the pioneering work of many other investigators world-wide which have linked Alzheimer's disease to aluminium neurotoxicity. Needless to say, the ever growing body of evidence will sooner or later shed considerable light on the science that describes the link between the two.



Keele Meeting Abstract

## **JD BIRCHALL MEMORIAL LECTURE**

### **Personal experiences analyzing the interactive toxic and ameliorative effects of aluminum species and other ions.**

Thomas B. Kinraide.

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For a century  $\text{Al}^{3+}$  has been assumed to be rhizotoxic, but its toxicity could not be differentiated from that of hydroxo-Al species, with which it coexists. Consequently, many authors appear to have assumed the toxicity of  $\text{AlOH}^{2+}$ ,  $\text{AlSO}_4^+$ , and additional species. The graduate student, David R. Parker, and I, independently, embarked upon programs to determine the relative toxicity of Al species and joined forces after learning of each others interests. Soon it became apparent that plasma membrane (PM) surface charge plays a critical role in  $\text{Al}^{3+}$  intoxication and its alleviation by cations. That led to a collaboration with Uri Yermiyahu to measure the required parameters of a Gouy-Chapman-Stern model to compute PM surface electrical potentials needed to compute PM surface ion activities. I shall describe how we determined the sequence of intoxicating effectiveness ( $\text{Al}_{13}^{7+} > \text{Al}^{3+} > \text{AlF}^{2+} > \text{AlF}_2^+$ ) and why an electrostatic approach is essential in toxicological studies.

**Analytical chemistry of aluminium – its total determination, fractionation and speciation analysis as different approaches for Al routine environmental pollution monitoring**

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The determination of total Al concentration and concentration of various Al fractions and species plays a crucial role in aluminium toxicity research [1]. The environmental chemistry of Al is complex and therefore the investigation of Al speciation is very difficult task. Numerous analytical methods have been developed for fractionation and speciation analysis of aluminium over last two decades, but many of them have limited selectivity and/or robustness. The most of such fractionation procedures is not standardized or harmonized and comparison of obtained results between different used methods is difficult and it is rarely reported. An current trend in Al speciation analysis is towards the development of more selective analytical techniques by the application of chromatographic methods coupled on-line or off-line with mostly used spectrometry detection techniques. In complex matrices like environmental samples, a combination of complementary fractionation and speciation analysis techniques is often necessary for reliable interpretation of obtained analytical data.

The validation of these methods is complicated by the fact that no relevant reference materials are available. The main reason for the lack of such materials is probably their low long term stability. The availability of such important quality control tool is hindered also by some problems connected with a clear definition of Al fractions or species and the formulation of unified sampling and sample storage protocol. Finally, quality assurance strategies and production of reference materials for various Al chemical forms in environmental samples would not only help to end a lot of the controversies still plaguing this type of analysis but would also facilitate the routine determination of various Al fractions or species in toxicological and clinical laboratories [2].

These and some other chemometric aspects (selectivity, robustness, precision, repeatability and accuracy) of aluminium fractionation (single and sequential extractions, ultrafiltration and ion exchange by solid phase extraction coupled with atomic absorption spectrometry techniques) will be reported and examined. Also the new analytical scheme for routine environmental pollution monitoring and risk assessment of labile and reactive Al in soil, sediment and water samples usable in a laboratory and moreover in a field will be proposed [3,4].

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Keele Meeting Abstract

**Aluminium in breast tissue**

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Recent research has suggested a link between the use of aluminium-based antiperspirants and the incidence of breast cancer. We have carried out the first examination of the presence and distribution of aluminium in breast tissue. The aluminium content of both breast tissue and breast tissue fat has been determined for each of four areas (quadrants) of the breast, axillary, lateral, mid and medial. We will report regional differences in the distribution of tissue and fat aluminium and speculate upon the possible source of aluminium in each region as well as any relationship with the known incidence of tumours.

Keele Meeting Abstract

**Aluminium-induced phospholipid signal transduction pathway in *Coffea arabica* suspension cells and its amelioration by silicic acid**

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Coffee breeding is an economically important activity on the world. In Mexico, which is one of the five principal coffee producers around the world, this crop is cultivated in acidic soils. These soils usually contains soluble phytotoxic aluminium ( $Al^{3+}$ ) forms. It has been shown that this Al forms affect the phosphoinositide signal transduction pathway on different plant species. The objective of this study was to evaluate the effect of soluble and a metastable form of Al species on the signal transduction pathway by phosphoinositide in cell suspension of *C. arabica* L. The effect of these Al forms was measured as the formation of Inositol 1,4,5-trisphosphate ( $IP_3$ ) and phosphatidic acid (PA) which are two components of the phosphoinositide-mediated signal transduction pathway. The results shows that the addition of  $AlCl_3$  decreases the formation of the second messengers PA and  $IP_3$  by 40% and 60% respectively, while hydroxyaluminosilicate (HAS) inhibits by 10% PA formation and by 40%  $IP_3$  formation. In conclusion, these results shown that Al can affect processes of cell signalling, even in the form of HAS in cell suspensions of coffee. This work was supported by the Projects No. 45798 and 55035 of the National Council for Science and Technology, and the fellowship No. 153781 to QTF.

## **Effect of AlCl<sub>3</sub> on the growth of *Coffea arabica* L. plantlets and phosphoinositide signal transduction pathway**

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Coffee (*Coffea arabica* L.) is one of the most important major economic crops in the world. Coffee plantations are mainly confined to acid soils, where several toxic forms of Al are present and Al toxicity has been a major factor limiting crop production throughout the world and it has been identified as the main symptom of aluminum toxicity for the inhibition of root growth. This inhibition could be related to signal transduction mechanisms, mainly involving to Phospholipase C (PLC). The objective of the present work is to evaluate the effect of aluminum on the growth of coffee plantlets. We modified the Murashige & Skoog media for *Coffea arabica* L. plantlets to produce aluminum toxicity in two conditions: 1) complete and half ionic strength and 2) pH 5.8 or 4.3. Additionally the plantlets were cultured with different concentrations of AlCl<sub>3</sub> (25, 50 and 100 μM). Then we evaluated the phenotypic parameters (size and number of the leaves) as well as biochemicals (amount of aluminum, chlorophyll and PLC activity). We observed that the leaves of the plantlets were very similar in appearance during the development in the presence of aluminum. On the other hand, the greater aluminum concentration in leaves was observed when the plantlets were cultivated with 100 μM AlCl<sub>3</sub>. The chlorophyll levels were similar for all plants regardless of treatment with AlCl<sub>3</sub> and finally, the PLC activity only decreased in leaves in presence of 25 μM of AlCl<sub>3</sub>.

This work is supported by CONACYT (45798-Z) and SNI (4422).

Keele Meeting Abstract

**The Differential Pulse Voltammetry Studies of the Influence of Al<sub>2</sub>O<sub>3</sub> nano particulates on the LDH Activity**

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In this paper, the differential-pulse voltammetry (DPV) was applied to study the influence of Al<sub>2</sub>O<sub>3</sub> nano particulates on the LDH activity. The characteristic parameters of  $K_m^{NADH}$ ,  $v_0$  and  $v_{max}$  in the catalytic reaction system of “ pyruvate + NADH + H<sup>+</sup> → lactate +NAD<sup>+</sup> ” were evaluated by monitoring DPV reduction current of NAD<sup>+</sup>. The influences of concentration and the diameter of Al<sub>2</sub>O<sub>3</sub> nano particulates, as well as the pH and temperature of the solution on the LDH reaction system were investigated. The results showed that all these factors had quite different effects on the LDH activities. The influences of solubility and disperse state of the Al<sub>2</sub>O<sub>3</sub> nano particulates in different environmental situations were also considered.

Keele Meeting Abstract

**A New Presumption with Regard to the Precursor of Keggin Al<sub>13</sub> Formation in aqueous solution**

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This paper presents a new theoretical hypothesis concerning the formation of Keggin Al<sub>13</sub> in aqueous solution. Under weak acidic or near-neutral conditions, [Al(OH)<sub>3</sub>]<sub>n</sub><sup>0</sup> may act as precursor for the formation of Keggin Al<sub>13</sub> through the surface hydroxylation to form [Al(OH)<sub>3</sub>]<sub>n-1</sub>·Al(OH)<sub>4</sub><sup>-</sup>. This new presumption can serve as a reasonable supplement and expansion for the traditional theory holding that Al(OH)<sub>4</sub><sup>-</sup> is the precursor in this process. Actually the above two theories are suitable to two different experimental conditions: Al(OH)<sub>4</sub><sup>-</sup> may act as the precursor in the rapid formation process of Keggin Al<sub>13</sub> under vigorous conditions including local perbasene and high pH while [Al(OH)<sub>3</sub>]<sub>n-1</sub>·Al(OH)<sub>4</sub><sup>-</sup> does so under mild conditions including aging, low pH (4~6), stirring vigorously and low rate of injecting base even without extra hydroxyl introduced, which is a set of more general conditions for the formation of Keggin Al<sub>13</sub> and excludes the possibility of Al(OH)<sub>4</sub><sup>-</sup> formation.



Keele Meeting Abstract

**Effect of aluminium on calcium binding proteins and calcium handling in different target cells.**

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The dysregulation of intracellular calcium (Ca) homeostasis has been proposed as cause of many neurodegenerative disorders including Alzheimer's disease. We have used both *in vivo* (chickens and rats) and *in vitro* (human neuroblastoma cultured cells) models to elucidate the likely role of aluminium (Al) on these events, in Al main target organs namely brain, small intestine and kidney, with emphasis in nervous cells. The expression of two major effectors of Ca signals: calmodulin and calbindin-D28k in different subcellular fractions, as well as radiocalcium fluxes across cell membranes under several experimental conditions, were analyzed. The results will be discussed in terms of the Al involvement on the "calcium hypothesis".

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## Iron and Aluminium pollution in the province of Turin.

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The present work reports the results of an environmental survey carried out in an industrial area in the Turin province: main aim is to assess the levels of iron and aluminium in the outside air.

The measurements were taken from four areas (as reported in Fig.1) with different distance from the industrial settlements on the territory and according to the prevailing winds directions, as deduced from the historical data in our possession;

The average values and the standard deviations (in brackets) of the iron and aluminium levels found in the outside air are reported in table 1.

The results of this survey show a no statically significant difference in iron and aluminium levels in the outside air in the four geographic areas. Values tended to be higher in the areas up to 3 Km far from the foundries location, probably for the prevalence of the winds direction and the fallout phenomena.

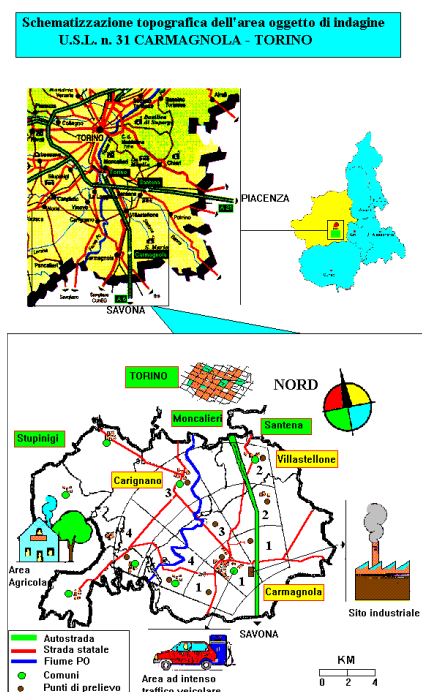


Fig.1 Map of the area