Chemistry IN NEW ZEALAND

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Featuring

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On the Cover

The cover photograph was taken by Matt Walters, School of Biological Sciences, University of Canterbury.

New Zealand Institute of Chemistry

supporting chemical sciences

75th Anniversary - October News

Science on Stamps:

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The recent NZ Post stamp issue *Clever Kiwis* includes as its $1 issue ***Norris and Illingworth*** *Spreadable Butter*. Robert Norris is a Fellow of the Institute and David Illingworth was a member. It is nice to see chemists gaining recognition and especially such iconic status.

Chemistry Olympiad: A team of four high school students and two mentors represented NZ at the 39th Chemistry Olympiad held in Moscow. They gained four medals – two silver and two bronze, placing the NZ team 13th equal out of the 68 countries in the competition - and with the same result as Australia and UK! ***Jonathan Lin*** (Auckland Grammar) and ***Chuan-Zheng Lee*** (Mount Roskill Grammar) gained the silver medals while ***Michael Plunkett*** (Westlake Boys' High) and ***Thomas Wong*** (Auckland Grammar) were the bronze medallists.

The successful NZ Olympiad Team

The team was accompanied by Dr ***Suzanne Boniface*** (Victoria University) and Dr ***David Salter*** (Auckland University) as mentors. Congratulations to all involved; a truly great achievement that stems from the pioneering and continuing involvement of Dr ***Robert Maclagan*** (Canterbury) in ensuring a NZ presence at these events.

Council News

Conferences: Having congratulated the Auckland Conference Committee for organising the highly successful Rotorua meeting it invited the ***Otago Branch*** to organising the ***2008 NZIC Conference***. The Branch has accepted and it is be held ***7-11 December at the University of Otago.***

Chemistry in NZ: The possibility of archiving previous issues of Chemistry in NZ is being investigated.

ChemNZ: This is aimed primarily at the NZ secondary teacher and is distributed freely; it is also a part of the RSC worldwide Chemistry Education Package. ***Alan Happer*** (Editor) is concerned about future copy as some of the formerly reliable sources are no longer available. Any ideas or offers of contributions please contact: *alan.happer@canterbury.ac.nz*

Recruitment and membership: A working party is looking at recruitment and the role of corporate membership.

OVERSEAS NEWS:

New Zealander Prof ***Robin Clark*** CNZM FRS Hon FRSNZ (UC - London), has been awarded the Bakerian Lecture and Medal of The Royal Society for 2008.

The Bakerian Lecture is the Royal Society's premier annual lecture in the physical sciences (in practice, Physics, Chemistry, Mathematics, Meteorology, Metallurgy, Astronomy, Geology and related subjects) and dates from 1775. Previous awardees have included Humphrey Davy, Michael Faraday, James Clerk Maxwell, *etc.* and, since 1901 (when Nobel Prizes were inaugurated) 26 Nobel Laureates. The only other New Zealander to have been awarded the Bakerian Lecture and Medal was Ernest Rutherford in 1920.

IUPAC Appointments: At the recent Turin IUPAC General Assembly ***Richard Hartshorn*** was elected Vice-President of the Division of Chemical Nomenclature and Structure Representation and ***Greg Russell*** a Titular Member of the Polymer Division.

BRANCH NEWS

AUCKLAND

The Branch co-sponsored a presentation by Prof ***Penny Le Couteur*** entitled *Historical Connections – and Chemical Bonds* at the CHEMED 007 conference. Penny treated the audience to a very interesting talk. Prior to this, some members of the Branch (and their families) joined the conferencees at a Chemical Magic Show presented by ***Gordon Miskelly*** and three volunteers from the audience – concepts of reality TV have even made it to chemistry! CHEMED 007 ran over 1-4 July, and was a resounding success, with attendees from NZ, Australia, and even further afield.

University of Auckland

Margaret Brimble has been named as the Victoria Institute of Chemical Sciences distinguished visiting research fellow for 2008. This will entail visiting Bio21, Monash, RMIT, and other Victorian campuses for a month.

In the Centres of Research Excellence (CoRE) funding round, the Maurice Wilkins Centre, involving Margaret Brimble, ***Ted Baker*** and ***Bill Denny***, and the MacDiarmid Institute, involving ***Jadranka Travas-Sejdic,***

David Williams, and ***Jim Metson*** both received renewed approval. The new Massey-based Riddett Centre for Food research also has Auckland involvement, through ***Laurie Melton, Charmian O'Connor,*** and ***Paul Kilmartin***.

Keeping to the theme of Food Science, the University of Auckland 2007 Winter Lecture series was organized by Laurie Melton on the theme *Your Food Your Health*. Attendees to the six-week series were treated to lectures from food scientists and nutritionists through to ethicists on topics ranging from efficacy of vitamins to the ethics of genetic profiling.

In early July, the Chemistry Department took part in the Faculty of Science Incredible Science Day. Department contributions included Magic Shows from ***Douglas Russell*** and ***Gordon Miskelly***, glassblowing displays, talks on chemiluminescence (***Cather Simpson***), and colourful food (***Bronwen Smith***), and displays including slime-making, light metals, crystal gardens, food texture, and fingerprinting.

CANTERBURY

Department of Chemistry - University of Canterbury

New Academics

Several new academic appointments have been made. Dr ***Paul Kruger***, a senior lecturer in Inorganic Chemistry, arrived in late August. Dr ***Sally Gaw*** accepted a lectureship in Environmental Chemistry and Dr ***Vladimir Golovko*** one in Materials Chemistry; both arrived in mid-September.

Prof ***Eva Hey-Hawkins*** (Leipzig) is in the Department until mid-October as a ***Visiting Erskine Fellow.*** Her interests in transition-metal complexes will be extended by furthering collaborations with ***Owen Curnow***, and she has been teaching 300- and 400-level courses. ***Andrew Abell*** left the Department to take up his position at Adelaide following a farewell function on August 10th. Dr ***Akbar Mobini*** (Arak University, Iran) is visiting for six months sabbatical leave and working with ***Peter Steel***. He is accompanied by his wife and daughters (aged 10 and 11). ***Marc Cretin*** (European Membrane Institute, Montpellier), the latest of our French visitors, is working with ***Alison Downard*** (until November) during his sabbatical; his work is in the area of electrochemical grafting on carbon surfaces for biofuel cell applications. ***Michelle Hamilton***, who has been working with ***Richard Hartshorn*** and ***Susan Krumdieck***, has left for Oxford to take up a postdoctoral post with Prof. Hancock.

Duncan Ross, a former technician, passed away in July. Duncan had worked in the in the Store for about 14 years until his retirement in 1985. He always seemed in good humour, had an engaging personality, but was a heavy smoker (60 a day) for many years when it was permissible to smoke on the job (pre-PC *we'll-tell-you-how-to-live* days). He lived well into his 80s, latterly at Rannerdale.

MANAWATU

The Manawatu Branch held two events focused towards local high school students recently. ***Penny Le Couteur*** presented her *Napoleon's Buttons* talk to *ca.* 500 high school students from around the Manawatu region at Palmerston North Boys High School. The talk was very well received. The second event was the annual Manawatu Branch quiz night, held in August and this year. ***Adrian Jull, Ghislaine Cousins*** and ***Mark Waterland*** were the quiz masters and the event was generously sponsored by ***Merck*** (with thanks to ***Barry Scott*** and his team). There was another excellent turn out from the high schools, with teams coming from Levin and the Hawke Bay. ***The Alchemists*** (Palmerston North Girls High) took away the grand prize with ***The Zhu Keepers*** (Palmerston North Boys High) a close second. The open category was won by ***Atomic Piglet*** (***Trevor Kitson, Paul Plieger, Barry Scott*** and ***David Shillington***).

Massey University

Geoff Waterhouse has completed a FRST NZST Fellowship and has taken a position with ***Jim Metson*** (Auckland University). ***Ankur Sagar*** (Indian Institute of Technology, Bombay) has completed a three month summer internship with Mark Waterland fabricating silicon opals and inverse opals. ***Ross Davidson*** and ***Adam Swanson*** have gained their MSc degrees with 1st class honours. Ross, with a Massey Doctoral Scholarship, will undertake PhD work with ***Andrew Brodie, Eric Ainscough*** and ***Mark Waterland***. Adam has started as an actuary in Wellington.

Trevor Kitson entertaining pupils at the Massey Open Day

Landcare Research

Benny Theng has returned from Spain and Portugal where he spent three weeks in the Department of Mineralogy and Crystallography at the University of Seville. Apart from his research, he assisted graduates to write papers (in English) for publication. In Portugal he participated in Euroclay2007 (Aveiro University) in late July. The conference, attended by *ca.* 350 delegates representing 45 countries, was noted by the conspicuous absence of China. The physical and chemical properties of clays and clay minerals attracted the largest number of oral and poster presentations, followed by environmental interactions and paleoreconstruction. Interest in organoclays and pillared clays, however, appeared to be waning. ***Steve Bagshaw*** continues to search NZ for researchers interested in trying controlled pore inorganic materials in their work. Current targets are in confined space molecular orientation, controlled/sustained release concepts and nano-composite materials for opto-electronics, pest control and bio-degradable plastics. Any interest would be most welcome!

NZ Pharmaceuticals

The company has entered into an agreement with Massey University to sponsor Chemistry to the level of $10,000 p.a. for 5 years. It will provide increased funding for the annual chemistry competition for Year 13 school students by providing three bursaries ($1500 from NZP, $500 from Massey) plus $500 from NZP to each winner's school for chemical equipment providing the winner enrols in a Massey BSc programme the following year. Additionally, NZP are donating two $2000 bursaries, one to a second-year and one to a third-year Chemistry student. In this way, the company is demonstrating its dedication to Chemistry as a subject by support for local students at school and university. IFS is very grateful indeed for this generous commitment.

Chemist ***Mike Horner*** has joined the Product Development team. He is Durham graduate with a wealth of experience in synthetic chemistry and pilot plant operations.

OTAGO

Inaugural Professorial Lectures have been presented by ***Sally Brooker*** (Chemistry - *Colourful Chemistry*) and ***Kurt Krause*** (Biochemistry - *Meeting the Antibiotic Crisis: Can University Scientists Help Design New Drugs for our Future?* A subsequent Otago Staff Bulletin highlighted not only the excellent chemistry being undertaken in synthetic inorganic materials based on multi-nuclear Schiff-base complexes, but also the breadth of nations represented by her students and posdoctorals who hail from Ethiopia, Canada, England, Ireland, Germany, China, Mexico, Australia, and NZ! Kurt combines a PhD in chemistry with clinical training and he has a focus on using protein crystallography to design new tools to fight infectious diseases; he recently established the Otago Webster Centre for Infectious Diseases. Both lectures were excellent showcases for the application of chemistry to the solution of contemporary problems and both were inspiring presentations.

In other news of local NZIC members, ***Keith Gordon*** and ***Cushla McGoverin*** attended the 4th International Conference on Advanced Vibrational Spectroscopy in Corfu, Greece. Cushla presented her work on *Raman Spectroscopic Quantification of Vitamin Enriched Milk Powder* and Keith spoke on *Time-resolved resonance Raman Spectroscopy of Short-Lived Terthiophene Radical Cations*. Keith is a member of the organising committee for the 2009 meeting to be held in Melbourne. Keith also visited the Joseph Fourier University in Grenoble, the imaging and spectroscopy company *Teraview* in Cambridge, GSK in Harlow, the University of Keele, and the University of Helsinki. He gave a number of talks ranging from molecular electronics to chemometrics of pharmaceutical mixtures. Cushla also made good use of her time in Europe speaking at the University of Keele on chemometirc analyses of dairy products.

Dr ***Garth Irwin*** from the ***Gordon-Blackman*** group attended the 17th International Symposium on the Photochemistry and Photophysics of Coordination Compounds in Dublin, presenting his work on hexaazatrinaphthylene-based complexes. He has now moved to Canada to become a baccalaureate school instructor – we wish he and his wife well in this new endeavour. ***Penny Walsh***, who left the group earlier in the year, is now with IPONZ in Wellington; we wish her every success in this next step of her career. In July, Keith's group received a funding boost with the success of their collaborative research for industry through a grant entitled *PV Energy Solutions* [with ***Ashton Partridge*** and ***Simon Hall*** (Massey University) and ***David Officer*** (Wollongong). The aim of the project is to bring together, with considerable input form industry, renewable technologies in energy storage, generation and use. It should be an interesting few years of research.

Last but not least, early August saw Keith Gordon and Cushla McGoverin at ***Pablo Etchegoin***'s VUW laboratory carrying out a series of studies on protein lipid mixtures as part of Cushla's PhD study.

WAIKATO

At the August meeting, ***Robert Franich*** (Ensis – Rotorua) gave a well attended seminar entitled *Terrestrial Wood Chemistry under Venusian Conditions*.

The annual Analytical Chemistry Competition for Year 13 students was held in mid-June with 20 four-student teams attending the University for the day from all around the Waikato and Bay of Plenty regions; two teams came down from Auckland. The task was to analyse barium chloride using a gravimetric procedure (for Ba^{2+}) and a titrimetric method (for Cl^-), and hence deduce n in the formula $BaCl_2.nH_2O$. The task was demanding in the time available but some excellent results were achieved. 1st prize was shared between two near-perfect entries from ***Otumoetai College*** (Max Lynam, Adam Fenemore, Zac Taylor and Duncan Harding) and ***Tauranga Boys College*** (Tim Condor, James Bridgewater, Scott Lindsay and Michael Kim) with ***Rotorua Boys High*** (Alistair Collins, Jiacheng He, Kyle Smith and Matthew Collier) in 3rd place. Runners-up were ***Katikati College*** (Kevin Weller, Josh Scarrow, Reuben Meder and Claire Harris – 4th)) and ***Trident High*** (Max Brosnahan, Scot Mitchell, Nathan Highes and Simon Barr – 5th). Good results were also achieved by the ***Hillcrest High*** and ***Forest View High*** teams. Financial support from ***Hill Laboratories*** for generously sponsoring the prizes and for resources, the Branch for funding the lunches, and the University Chemistry Department for facilities and staff time is acknowledged with thanks.

Overall, the competition enabled keen Year 13 chemists to spend a day in University laboratories and mix with peers from other schools. It also provided an opportunity for the accompanying teachers to meet with each other and with University chemists.

Waikato, 1st place getters, with the Hills Laboratories representatives

University of Waikato

We have had a number of interesting talks from visiting speakers. Thus ***Chris Miles*** and ***Jared Loader*** (AgResearch) spokes on their recent work entitled *Structural and Chemi-*

cal Bases for Toxicity of Dinophysistoxins and Pectenotoxins from Dinophysis species and *Who did it? An Unusual Killer Microcystin in the Waikato*, respectively, while ***Kirk Torr*** (Scion) gave a seminar on *Genetic Manipulation of Wood Chemistry using Callus Cultures*. The RSC Australasian Lecturer ***Peter Schwerdtfeger*** gave a fascinating address entitled *Left or Right in Nature? The Origin of Biomolecular Homochirality.*

NIWA

Burns Macaskill has now officially retired from aquatic chemistry after many years service while ***Trevor Mathieson*** resigned from the end of August and has left.

Hill Laboratories

The organization continues to grow, now employing over 200 staff over four physical locations - the main laboratory in Hamilton East, a microbiology/air quality facility in the old building (Te Aroha St.) also in Hamilton East), a pesticides/food testing at Innovation Park on the Ruakura Campus, and a microbiology facility in Christchurch. Business is growing in all sectors with the current boom in dairying providing much confidence to the agricultural business, and the ongoing requirements for food safety and environmental responsibility driving steady demand for services in environmental and pesticide residue testing.

Steve Howse, from LIC (formerly Livestock Improvement) has been appointed as General Manager. Formerly he held a general management role in that part of LIC that provided animal recording and diagnostic testing services to dairy farmers across NZ. His experience working in a larger organisation, particularly with the business systems that can help an organisation the size of Hill Labs run efficiently, will enable the organization to grow while continuing to meet customers needs.

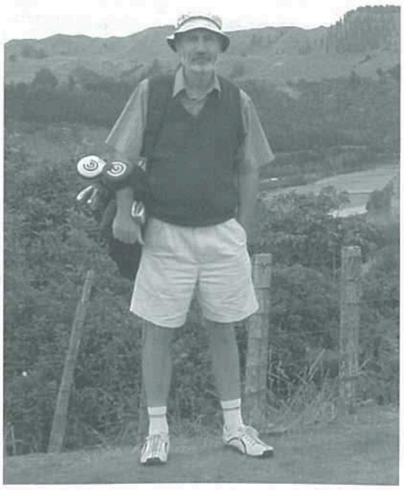
Steve Howse

Roger Hill continues as Managing Director and is still very much involved in testing for the agriculture sector, and investigating other opportunities for extending laboratory testing services both in NZ and overseas. With the appointment of a General Manager to look after the day to day operations of Hill Labs, Roger is turning his considerable experience to evaluate, and (where appropriate) pursue, new opportunities for business that requires such leadership and expertise.

HortResearch

On 31 July ***Denis Lauren*** retired after over 33 years at the Ruakura research campus. A well-attended function was held in the social club at which a number of speakers delivered a suitable mix of complements and anecdotes that covered most of Denis' professional career that began as an Honours student at Otago University in 1965 (PhD, 1971) (***Brian Nicholson***), to his early days at Ruakura (***Ron Henzell*** and ***Pat Holland***) to current times (***Janine Cooney, Wendy Smith***, and ***Dwayne Jensen***). HortResearch Science Operations General Manager, ***Bruce Campbell***, concluded with a brief presentation which included the nomination of Denis as an Honorary Research Fellow. Denis will continue to work with HortResearch on selected projects and in writing up research results, but he intends to devote most of his time to his sporting interests of golf and squash, and to his interest in breeding, racing, and helping in the training of Harness Racing horses.

After postdoctoral work in Canada, Denis returned to NZ in February 1974 to work with Ron Henzell and Pat Holland in what was MAF at Ruakura, initially on insect pheromones and in particular those of the native grass grub. In 1977 he purchased one of the first HPLCs to enter NZ for MAF, and since then has established a reputation as a skilled exponent of the art.After a year with Agriculture Canada in Ottawa he began what emerged as more than a decade of work with Dr ***Margaret di Menna*** (AgResearch; and others) establishing the mycotoxin risks in NZ grain. This was pivotal in establishing guidelines for the NZ maize industry to minimise mycotoxin contamination in the grain and in foods and animal feeds. He also had fruitful collaborations with Crop & Food Research (in particular Drs ***Jim Douglas*** and ***Nigel Perry***) in establishing and applying improved methods for analysis of the active principals of natural medicinals such as liquorice, ginkgo, and milk thistle. A long-term (mostly unfunded) interest shared with Dr ***Barry Smith*** (formally AgResearch) concerned the occurrence of the carcinogen, ptaquiloside, in bracken fern. This led to many international interactions with workers in Central and South America, the Azores, India, USA, Europe, and Australia. Since 2000, and as a result of funding shifts, Denis moved more into the area of beneficial bioactive components, in particular those found in fruit and other foods. From 2004 until shortly before retirement, Denis was one of four objective leaders of an innovative multi-institute programme looking to establish the capability of Nutrigenomics in food research for NZ, and was also involved in other programmes aimed at producing functional foods or food ingredients.



Denis Lauren

Gas Chromatography

The Waikato Institute of Technology is again providing courses on gas chromatography. The basic course runs 27-30 November and the more advanced course from 4 to 7 December. Further information is available from Bev Langmore: *Beverly.Langmore@wintec.ac.nz*

WELLINGTON

The Branch was saddened to learn of the death on June 25 of long-time Fellow and staunch supporter, ***Lester Stonyer***, at the age of 89 years. Lester had worked for Mobil (NZ) and in his retirement at Paraparaumu he was a regular contributor to the local U3A programme providing lecture courses and lectures on matters chemical.

June saw the annual Titration Competition and secondary schools Quiz Night and, once again numbers had to be limited to the space available in VUW's Union Hall. This year the events were formally recorded with a summary playing on National Radio's *Our Changing World*; it provided NZIC with much needed excellent publicity.

As part of her NZ tour ***Penny Le Couteur*** addressed some 44 members and guests at the monthly meeting on *Historical Connections – and Chemical Bonds* that summarised the approached and some of the stories told in her book *Napoleon's Buttons*. The July meeting comprised the annual mid-winter dinner, this time at the Ayutthaya Thai Restaurant, in Petone and a group of about 20 ventured out into a very cold night but thoroughly enjoyed themselves.

August has seen two meetings, the first the annual RSC Australasian lecture. Given by Prof ***Peter Schwerdtfeger*** on *The Chemistry and Physics of the Superheavy Elements* where the audience was treated to a engaging and captivating account of just how the next elements (above 114) are likely to be proven as standard spectroscopic studies (electronic, vibrational, rotational, NMR, *etc.*) on a single superheavy atom-containing molecule will be rather difficult if not impossible. The regular Branch meeting encompassed energy research and Dr ***Alister Gardiner*** of the Hydrogen and Distributed Energy Technology Platform at IRL posed the question to the 35 attendees: *Are We Doing Enough?* He discussed the IRL energy research emphasising the applied and pilot-scale demonstrations of microenergy systems and wave generation, and identified where new and improved materials and chemical processes are core to the commercial success of the technologies.

Victoria University

In June the essential CoRE funding for the MacDiarmid Institute for Advanced Materials and Nanotechnology based in the School of Chemical & Physical Sciences (see this *Journal*, April 2007) was reallocated for the six-year period 2008 – 2014.

Recent visitors to the School who have provided seminars have included Drs ***Richard Bowles***, a former student now an A/Prof at Canada's Saskatchewan University, and ***Vyacheslav Filichev*** (Massey University) who gave an outstanding lecture on intercalating nucleic acids and double stranded DNA targeting that covered strand invasion, the inhibition of transcription and triplex formation. Following the heterocyclic meeting in Sydney Prof Dr ***Ernst Schaumann*** (Clausthal Technical University) spent time in the Wellington area, visited the School and spoke on *Silicon migration in organic synthesis*. Prof Peter Schwerdtfeger visited and lectured on *The quest for absolute chirality* following his attendance at a Wellington RSNZ function and prior to delivering the Branch RSC Lecture. Most recently, in fact on copy date, Prof. ***Eva Hey-Hawkins*** (Leipzig) gave a fascinating account of her work *Bridging Organometallic and Coordination Chemistry* during an absence from her Erskine Fellowship at Canterbury.

John Ryan successfully defended his PhD submission in early July but remains in the School as its NMR administrator working also part-time for Varian. ***Peter Northcote*** attended the July Synthesis meeting at Cambridge and ***Joanne Harvey*** was at the14th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (Nara, Japan) where she presented *Palladium-Catalyzed Synthesis of C-Glycosides with Complete Stereochemical Control.*

Industrial Research

Dr ***Tim Kemmitt*** (Energy & Materials Team) was awarded a two-year ISAT travel grant to visit Prof Ping Chen at the National University of Singapore. The first visit, during April and May of this year initiated a new study on understanding hydrogen release mechanisms in some novel hydrogen storage compounds. The work is related to other objectives within a wider hydrogen storage programme funded by a FRST IIOF programme. IRL is a partner in a multinational hydrogen storage materials research team with members from Los Alamos National Lab (LANL), Pacific Northwest National Laboratory (US), and the Universities of Singapore and Oxford. This is an official project of the International Partnership for the Hydrogen Economy (IPHE) (see: *www.iphe.org*). NZ is a member country of this 17-nation international agency.

Dr ***Mark Bowden*** (Energy & Materials Team) is presently on six month leave at LANL (New Mexico) where he is researching new solid state storage systems for hydrogen. The materials being synthesised include derivatives of ammonia borane (NH_3BH_3), which contain chemically bound hydrogen at high mass percent, and provide opportunities to meet or exceed future US targets of hydrogen storage for fuel cell vehicle applications. Mark is undertaking studies on new synthetic pathways, structure analysis, the hydrogen release reaction path and kinetics, and potential for chemical reformation of spent materials. This work is a part an IRL FRST-funded IIOF programme.

A drug developed in-house for the treatment of the chronic and painful skin disease psoriasis has progressed to Phase II clinical studies in the US under the auspices of the pharmaceutical giant Roche (see: *http://www.roche-trials.com/patient/trials/trial110765.html*). The drug, BCX-4208, was developed in partnership with the Albert Einstein College of Medicine. Using revolutionary technology, the researchers designed a new range of potent enzyme inhibiting drugs that can be used to treat many problems, such as psoriasis, caused by an over-active immune system. The upcoming study will involve 60 patients with moderate to severe psoriasis in a double-blind, placebo-controlled randomized trial over six weeks. If successful, the next step will be to expand the trial to a larger number of patients. Instead of just treating the symptoms, BCX-4208 inhibits the production of T-cells in the blood. Psoriasis occurs when faulty signals in the immune system mistakenly activate T-cells into faster-than-normal regeneration of skin cells, which results in patches of thick red skin that can cause significant physical discomfort. BCX-4208, and related cancer-treatment drug Fodosine, have been developed from the IRL glycotherapeutic programme, recently endorsed with $25 million funding from FoRST over the next ten years. This ongoing programme has provided a number of other new drugs for treatment of malaria, bacterial infections, and cancers; they are currently in pre-clinical trials.

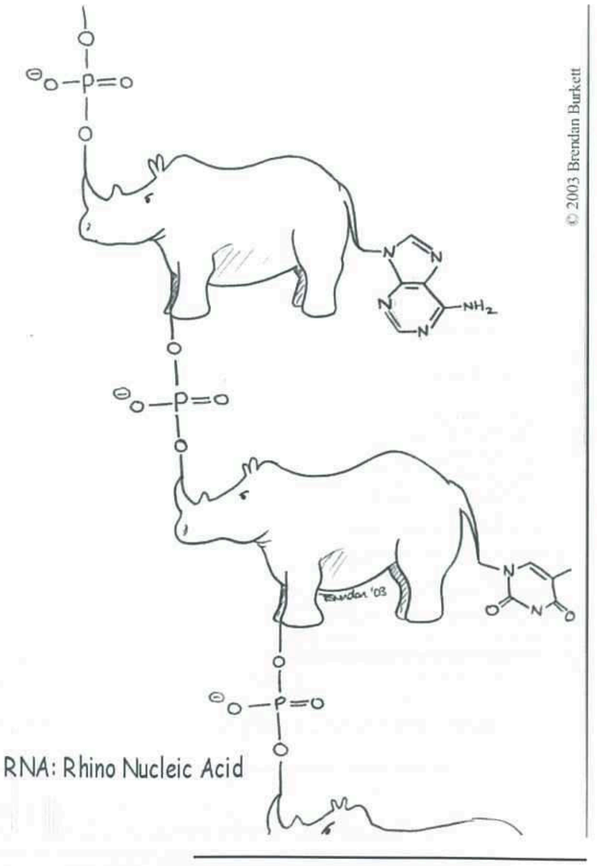
Editorial

This issue of *Chemistry in New Zealand* marks the last for 2007 and the 25th under the current editorship. The *Journal* has undergone changes in management and production since I took on the editorship and the format has been markedly improved by the Christchurch production team. The few criticisms we have received have been appreciated and helpful, while the accolades continue to provide a source of satisfaction and stimulation. Now might seem the appropriate time for me to pass the reins to another to reign. However, for reasons that I could not possibly imagine, no one has come forward. For me, at least, the contact and communication with a wide range of the NZIC membership, and the challenge to provide a high quality publication with appeal to the majority of the Institute membership is adequate recompense. I am persuaded, therefore, that I must away to the shops to buy a new pencil sharpener and pencils! On a serious note, though, it would be timely for someone to join me (a computer and internet access is all that is needed) by assisting with some of the editorial work and picking up the trade, so to speak. Somehow I do not see myself writing a comparable editorial in late 2013 for the next anniversary of note!

The change in timing of the December quarterly to a January issue is brought about with Council support. The change means that from 2008, *Chemistry in New Zealand* will be published quarterly from January. Despite this, the copy dates for the January issue remain unchanged (Articles: Oct. 1; News Oct. 30) so that production can proceed through November to mid-December to enable an early January mail-out. Back in the enlighten era, when we all able to take our annual holidays at the same time in the summer, it was impractical to issue the *Journal* during January. Indeed, many members liked to have their copy for reading over the vacation and the December issue was promulgated. In present times, many only take the statuary holidays over the summer and, when coupled with the preference of our advertisers, the change has become inevitable. Each October issue will (and this one does) contain the author and subject indices for its volume.

One of the difficulties that the editorial staffs have to face is the gain of appropriate and relevant copy. Whereas the release of new manufactured products and services are made clear to us, advancement and changes in the careers of our members is less easily gained. Each Branch has its own regional editor (AKL: Gordon Miskelly; WAI: Michèle Princep; WEL: Brian Halton; CAN; Darren Saunders: OTA: Julian Eaton-Rye) and they do their best to solicit local information. Unfortunately, and all too often, this comes only from the tertiary institutes. Can you help us to expand our news section? If so, let your Branch Editor know either by volunteering to gatherer news from your workplace or by providing your own. Even better would be a general interest item on the industry that you contribute to. Remember, the NZIC is no better than its members.

Brian Halton



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Climate Change Mythconceptions: Some Incorrect, Irrelevant and Misleading Arguments Made by Climate Change Denialists

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Introduction

Is Climate Change contentious? Is the science settled? How strong are the arguments against anthropogenic climate change?

Here we examine some of the common claims made by climate change denialists. We show that these arguments do not follow accepted standards of *good scientific practice* and in some cases show an ignorance of basic chemistry. A curious layperson can find any number of web pages on the topic of climate change. Some of the denialist sites (often hard to identify) make some seemingly compelling arguments and relate *facts* incompatible with the position held by the Intergovernmental Panel on Climate Change (IPCC). But do these arguments really stack up? Here we take a close look at some of the common arguments that are used by denialist groups and individuals.

Recently, one of the authors was chatting with a manager at Natural History NZ (NHNZ) about environmental chemistry. Naturally the topic of climate change came up. This manager said that, while obviously they were not expert, as far as they could see there were equal *amounts* of argument both for and against. They felt, therefore, that this meant that there was still doubt and uncertainty about the *concept* of climate change. Aghast, we decided to write this article. It is a rebuttal of some of the common claims made about climate change by prominent groups of denialists. We want this to be a resource that NZIC members can direct friends and family to so it is written for the layperson. There are some references but most are to websites that at the time of writing were well designed and easily understandable.

The NHNZ manager's confusion is perhaps warranted given the perceived wisdom journalists have about balance. The idea is a manifestation of cultural relativism and holds that if there are two view points both are equally valid and should receive equal airtime. One of us recently wrote to a local paper about a similar case and pointed out that '*If the paper received a letter about pixies at the bottom of the garden they would throw the letter out. If the paper received a letter claiming a previously overlooked loophole made it legal to drink and drive, the paper would probably run the letter past a lawyer for comment before publishing*'. But the paper had no qualms about publishing an *opinion-editorial* article that was misleading nonsense about climate change. Why did the paper not avail itself of the huge expertise just down the road at the local tertiary institution? Why does the paper not integrate basic science into all stories, the way it does with politics and economics. Why does science languish in a small column on the same page as the horoscopes and comic strips?

We have selected several of the most common arguments that can be found on numerous *climate change* denial web sites. Search Google for climate change with *doubt, hoax* or *fraud, etc*., to see the range available.

For the most part the purpose of this article is to show that some of the claims made by the denialists are simply *bad scientific practice* – regardless of the truth of the claim. By this we do not mean the interpretation of the data is bad - although we certainly show that much of the interpretation of data by denialists is grievously flawed. *Bad practice* refers to flaws in the scientific method. For example, the claim that '*Without the Greenhouse Effect there would be no life on Earth*' is true but it is irrelevant and not disputed by anybody. To call this *a fact that they do not want you to know* is misleading as it implies that those who say human induced climate change is occurring argue otherwise. We believe that this reflects the general approach of denialists and leave it up to the reader to decide what credence to give other denialist claims.

Common Argument 1

Britain is 1°C cooler now than it was at the time of the Domesday Book (1086)

This is not true (and would be irrelevant even if it were true). The temperature in Britain is currently the same as it was in the 11th Century. We assume the inference that readers are expected to draw is that if Britain is cooler now then no warming *anywhere* is occurring. Britain is ***not*** cooler. But would it matter to the case ***for*** climate change if it were? No! Firstly, the climate of Britain is ~5°C warmer than it should be because of the heat delivered to the North Atlantic by the Gulf Stream and the North Atlantic Drift. The Gulf Stream is largely powered by the temperature *difference* between surface seawater near Iceland and in the Gulf of Mexico. This means that temperatures in Britain are only secondarily related to global temperatures. Secondly, we hate to have to be the ones to point it out, but the island of Britain represents a grand total of 0.15% of the land surface of the world. In *most* places global air and sea temperatures are increasing, but these very changes lead to changes in the way heat circulates, meaning that is simply wrong to look at the climate in a single location.

Since there were no thermometers in Britain back in 1086, how do we know what the temperature was then? The answer is that we rely on proxies, or stand-ins. For example, tree rings provide a record of past climate. By comparing recent written records of weather conditions with the rings of trees recently cut down, it is possible to get a very good idea of the exact relationship between factors such as the thickness of tree rings and the climactic conditions while the tree was growing. By looking at different trees it is possible to overlap the sequence of rings and extend the record back a long time. For the very recent past, *i.e.* the last thousand years or so, written records of harvest yields also offer a good indication of climate. Since about 1850 there have been real thermometer readings and the number of stations making such measurements has increased with time. These direct temperature readings agree well with tree ring data and other proxies, so there is a high degree of confidence in the proxy estimates for the time before thermometer measurements.

One of the most comprehensive tree ring studies of recent times, the Moberg study, was published in the *Nature* in 2005.[1] *Nature* also published an introduction that highlighted the major findings and uncertainties of the Moberg study that is helpful for a lay reader.[2] The study presents tree ring data from around the world over the last 2000 years or so up to 1979. However, here we focus on the Northern Hemisphere as it is relevant to the claim about temperatures in Britain. The Moberg and other tree ring datasets do not go right up to today. In part this is due to a desire to use only mature trees and in part it results from the smoothing discussed below. The data from this study are plotted in Fig. 1. Here, the apparent y-axis distortion is deliberate so as to allow comparison with Fig. 2 (see below).

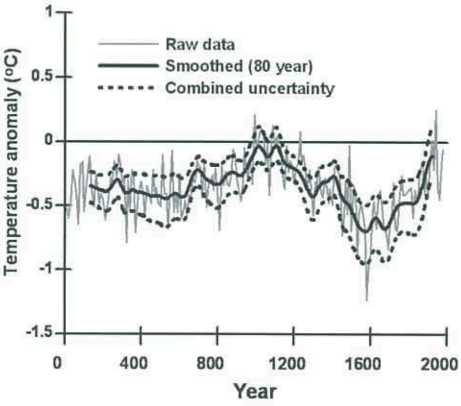

Fig. 1. Tree ring proxy-measured temperature anomaly (*ca.* 1960-1991) in the Northern Hemisphere from 133 – 1979 AD - data from Moberg ref. 1.

The data are plotted as temperature difference from the average during the 1961-1990 period. This is called the *temperature anomaly*. This period is used as a baseline and is a sort of *industry standard*. It was used by the IPCC in the development of the Kyoto Protocol and is commonly used to allow comparisons between different data sets. There are more than 2000 points for the raw, year to year data. To keep matters simple we have plotted every 10th year as the grey line (raw data). The study also used a smoothing technique (called *wavelets*) to take the wiggliness caused by the occasional very cold or very warm year out and this is given as the smoothed 80 year (thick black) line. Crudely put the smoothing uses proxies such as lake sediments that do not vary on a clearly defined yearly basis to dampen out the signal from occasional extreme year, *e.g.* the years following a big volcanic eruption, and is a sort of moving average. There are uncertainties in the proxy values and also in the smoothing procedure. These uncertainties are combined and shown by the dotted lines either side of the smoothed line.

A key point to keep in mind is that actual thermometer readings for the last 150 years show that while temperature in the whole Northern Hemisphere varies hugely from place to place, *cf.* Greenland *vs* Egypt, the *difference* (anomaly) at each place is consistent -with a few notable exceptions where temperature is affected by other factors. Thus, a temperature anomaly of +1°C means that for pretty much the whole Northern Hemisphere, temperatures in each location were 1°C higher than the *same* location during the baseline 1960-1991 period.

The Moberg dataset shows that it is entirely wrong to say that Britain is about 1ºC cooler than at the time of the Domesday Book (1086). Look across the graph in Fig. 1. We have drawn in a line to show the tree ring zero temperature anomaly, *i.e.* the average for 1960-1991. In 1979, where the graph ends, the temperature was pretty much the same as it was during the 11th Century. The difference is certainly nowhere near 1ºC. Does this show that there has been no warming since 1086? No! The Moberg data show that temperature varied over a century timescale even before the industrial revolution when the large scale emission of CO_2 began. This is not denied. What causes concern is that the *rate* of change seen in very recent times has never been seen before.

The Moberg dataset ends at 1979. As noted above, there are excellent world-wide thermometer measurements of temperature that go back about 150 years. These actual measurements agree well with the proxies. Fig. 2 shows the thermometer data for the Northern Hemisphere collated by the Hadley Climate Centre.[3] Here, the average temperature in each month for the years 1850 onwards is compared to the average temperature in the same month for the years 1960-1991.

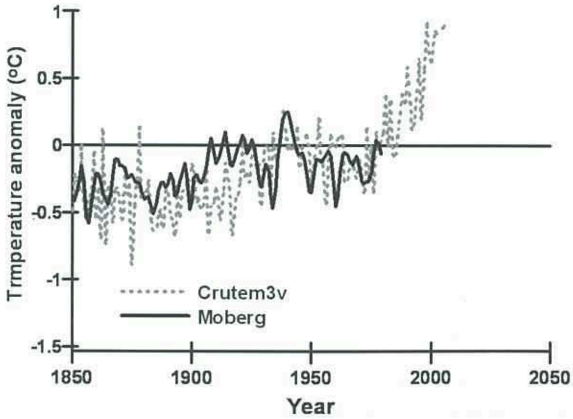

Fig. 2. Thermometer measured temperature anomaly (compared to 1960-1991) in the Northern Hemisphere from 1850 – 2007 AD overlaid with Moberg data. - source Hadley Centre.

For convenience we have not plotted all the data but instead have used yearly average differences, *i.e.* for each year the monthly differences were averaged to give a yearly value. For example, during 1905 the monthly differences (compared to the same months in 1960-1991) were

-0.65, -1.52, -0.57, -0.91, -0.39, -0.19, -0.16, -0.19, +0.01, -0.44 and +0.20ºC, thus giving an average difference for 1905 of –0.40ºC. Obviously, some months were warmer and some months were colder and using a yearly average has its pitfalls. However, the same trend is observed if you draw 12 separate monthly graphs for temperature anomaly compared to the same month in 1960-1991 so we can have confidence that the yearly approach works.

We see good agreement with the Moberg tree ring dataset during the period of overlap. We also see that over the last 15-20 years the temperature has, *in general*, shot up. Yes, some years have been colder but the temperature in the Northern Hemisphere has not been this warm in the last 2000 years. The discussion that follows below about Greenland shows the temperature has not been as warm as it is now at any time in the last 420,000 years.

Criticisms can certainly be made of the Moberg dataset but there are several other studies like the Moberg one. Some of the datasets are available free from the National Oceanic and Atmospheric Administration (NOAA), a scientific wing of the US Department of Commerce.[4] If you do not have the time to produce your own plots then a good compilation of 10 different studies has been plotted for Global Warming Art.[5] All the studies show the same three basic features: i) there was a temperature maximum between about AD 1000 and 1100 where the temperature was about the same as that during the baseline period of 1960-1991, ii) a minimum occurred at about AD 1600, and iii) over the last 15 years the temperature has increased rapidly and is currently warmer (by about 0.4ºC) than is has been at any time in the last 2000 years. Thus it is wrong to say that the temperature is now cooler than at the time of the Domesday Book but even if it were true it would be irrelevant.

Common Argument 2

Greenland got its name from the lush pastures that attracted the Norse in the 10th century. They carried on their normal way of life for 300 years until they were driven off by advancing ice and the Inuit took over. The ice and the Inuit are still there.

This is partly true but irrelevant. It is certainly possible that the Little Ice Age provided the *coup de grace* to the Norse but since the Inuit remained (and successfully inhabited lands further north) it was obviously survivable. Greenland got its name from spin doctoring to encourage Icelanders to go there. The best recent description for the general reader of the Norse settlements on Greenland is in *Collapse* by Jared Diamond.[6] There were only two small settlements in sheltered fjords with a total population of no more than 5,000. Diamond suggests that the Inuit are still there because they did indeed *carry on their normal way of life*. The problem is that their normal cattle farming way of life was well adapted to Norway but totally unsuited to Greenland and they quickly degraded the fragile artic soils. It even seems that the Norse refused to eat fish. The precise causes of the Little Ice Age are unclear, though the Gulf Stream was about 10% weaker than today. Speculation of a human cause as a contributing factor follows as: the Black Death killed a third to a half of Europe's farming peasants, because of which large areas of farmland reverted to forest. The forests soaked up CO_2 and prolonged (but probably did not cause) the Little Ice Age.[7]

As for the Greenland ice still being there, it now looks as if it will not survive for much longer. Ice loss increased from 90 km^3 during 1996 to 220 km^3 in 2005.[8] Two thirds of the loss was due to *ice dynamics, i.e.* the glaciers simply sliding off into the sea, and one third to melt run-off exceeding snow input. The sliding is most likely caused by warmer temperatures producing an increase in lubricating water under the glaciers. To be sure, Greenland's output of 220 km^3 adds only 0.6 mm per year to sea level and there is enough ice to last 11,000 years *if* the melting continues at the same rate without further acceleration.

Here is an experiment you can try at home: turn off your freezer and open the door. Estimate the volume of ice. Wait. After 20 min or so measure the amount of water dripping down. Using this value, show that it will take days for all the ice to melt. Wait a bit longer. Watch as large chunks of ice slide off the walls of the freezer and crash onto the floor where they quickly melt. Remember that if *all* the Greenland ice melts (either while in place or after sliding off and sinking a few cruise ships) the sea level will rise by 6.5 m. If the West Antarctic Ice Sheet is lost we will see another 7 m sea level rise. Both could happen *quickly* if large ice sheets slide off.

The unstated part of this common argument seems to be that ice ages come and go in natural cycles. And, yes they do, but the both the size and the rate of change seen in the last two decades are greater than any seen in the last 740,000 years. Lest we be accused in turn of setting up a straw man, the claim about natural climate variation is explicitly made in several documents, *e.g. Nine Facts About Climate Change* by Ray Evans of the Lavoisier Group,[9] an ironic name for a group that believes in the modern equivalent of phlogiston.

Many types of evidence show that ice ages come and go. Evidence includes glacial moraines (the rubble pile pushed in front of a glacier) and isotope measurements from ice cores. Heavy water has higher melting and boiling points and is denser than normal water. This means that the amount of heavy water that is evaporated from the sea and laid down later as snow and ice is related to the temperature. Therefore by looking at the amount of heavy water in deep ice-cores it is possible to calculate the temperature when the ice was formed. Other information can also be obtained from ice cores. For example, bubbles of air trapped in the ice contain CO_2, thus providing a record of CO_2 levels. There is, of course a caveat: until snow is compressed under more snow and forms hard ice, the bubbles are not locked in place and some exchange with the atmosphere occurs. This means the bubble record is smeared somewhat and lacks the fine time resolution of the isotope record. Dating of the core is also problematic and different methods give dates that vary by up to 5000 years for the bottom of the Antarctic Vostok core. Exact dating is not especially critical to the arguments used here as it has no effect on the *sequence* of events.

Several good ice core records have been obtained from Antarctica. Two of the best long ice core records are those of the European Project for Ice Coring in Antarctica (EPICA) and a core taken at Vostok Station. The EPICA core goes back about 740,000 years and covers 8 ice ages (or *glacial cycles*) and the Vostok core goes back about 420,000 years, covering 4 glacial cycles. The Vostok core was drilled in 1996 and the EPICA core in 2004, and not all EPICA analysis is complete yet. However, there is complete temperature (from isotopes) and CO_2 data (from bubbles) available for Vostok so the discussion here uses only the Vostok measurements.

We have plotted (Fig. 3) the temperature difference from the baseline period of 1960-1991 (data and references to the original are available at NOAA). Please note that the scales of the two plots have been adjusted to be similar to make comparison easier. Temperature is given by the vertical axis on the left and covers a 15°C range. CO_2 is given on the vertical axis on the right and covers a range of 160 ppm. Measurements of deuterium, the isotope used as a proxy for temperature, measurements (as proxy for temperature) were obtained continually throughout the core (over 3300 measurements), but for several technical reasons are discussed later, CO_2 measurements were only obtained at 365 points. The CO_2 datum points are separated by between 100-5000 years. In general, if it looked like the concentration was changing then samples were taken more closely by the researchers. It is possible that during the gap between samples the CO_2 fluctuated but the lack of fluctuations in deuterium argue strongly against this. To cut down on clutter in the graph, we have taken only every 10th deuterium point to give about the same number of points as the CO_2 dataset. All this is important for a point made below about synchronicity.

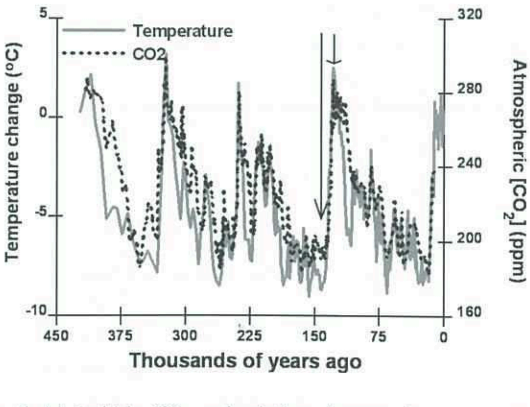

Fig. 3. Air bubble CO_2 and relative changes in proxy temperature (as given by deuterium) for the last 420,000 years from the Vostok ice core - data source NOAA.

The graph clearly shows that both temperature and CO_2 rise and fall naturally. Consider the time scale for the *start* of the glacier melting - when the temperature increases rapidly. The end of the last complete cycle (starting about 140,000 years ago) is indicated by arrows. The time taken for temperature to increase by 11.2°C (from -8.7°C below baseline average to +2.5°C above baseline average) and the time taken for CO_2 to increase by about 100 ppm (from 190 to 287 ppm) was 14,000 years. Despite what was depicted in the movie *The Day After Tomorrow*, actual glacial cycles occur over thousands of years. The start and finish of each cycle is characterized by wiggles up and down like the 1°C decrease seen between the 11th and 16th Centuries but with an overall trend in one direction. Table 1 gives the time for the increase phase of the other cycles.

Table 1. Periods of large temperature and CO_2 increase in last 420,000 years associated with the first phase of major deglaciations.

Start (y ago)	End (y ago)	Duration (y)	ΔT (°C)	Δ[CO2] ppm
18000	2000	15400	9.4	103
138000	128000	9900	12.0	84
251000	238000	12600	9.5	75
334000	324000	10100	11.2	98

Temperature and the concentration of CO_2 both change over cycles lasting several thousand years. Could it be that we are currently experiencing the high phase of one such cycle? We probably are **BUT** added to that is the effect of CO_2 released by humans from fossil fuel burning. It is hard to see from Fig. 3 but the Vostok ice core record stops about 2340 years ago. There is another Antarctic ice core dataset (the Law Dome - data at NOAA) that covers from about 1010 AD to 1975 and if we also add in the Mauna Loa data (from NOAA) we get Fig. 4, bringing us up to the present day.

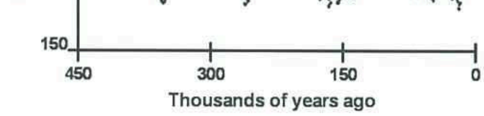

Fig. 4. Atmospheric CO_2 for the last 420,000 years. Data from the Vostok and Law Dome ice cores and Mauna Loa atmospheric station - data source NOAA.

Instantly we see that in the last few years the level of atmospheric CO_2 has broken out of the glacial-interglacial cycle it has been in for over 420,000 years. In fact, we see that the atmospheric CO_2 concentration first exceeded 280 ppm (the upper bound of all the previous cycles) about 250 years ago – just when the industrial revolution began. We have seen an increase in atmospheric CO_2 of 100 ppm in the 250 years since the start of the industrial revolution. This rate of change is 40-60 times faster than the fastest natural rate of change. It *is* natural for the climate to cycle. But the human caused changes are way outside the bounds of the natural cycle.

Common Argument 3

Water vapour is the dominant greenhouse gas and contributes more to global warming than CO_2

In part this is true but it is irrelevant. The concentration of CO_2 is approaching 400 parts per million by volume (ppmv). The water concentration is enormously variable but a rough global average of 2000 ppmv will do here. These figures translate to there being roughly 5 water molecules for each CO_2 molecule. However, different molecules absorb energy (heat) differently and water is not as good at absorbing infrared as CO_2. Also, water vapour is indeed a potent greenhouse gas and it amplifies the effect of CO_2 *but* the water content of the atmosphere is a result of a *positive feedback* process and it is not a *forcing* agent while CO_2 is.

Normally ecosystems are in a *steady state* where input and output balance each other. Consider a large earthen dam holding back a sizeable lake. While the dam is intact all is well and the lake level can be stable for long periods. If something makes a small hole at the base of the dam (a forcing agent) then water begins to escape. The water then carries away some earth and enlarges the hole. This allows more water to pass through and widen the hole still further, allowing more water to pass through and so on (positive feedback process).

The resolution of Fig. 3 is insufficient to show that at the end of glaciations the temperature began to increase a few centuries before CO_2 begins to rise quickly. The end of the last pre-human glaciation is shown in Fig. 5. This *lag* is frequently said by denialists to show, therefore, that CO_2 does not cause warming.

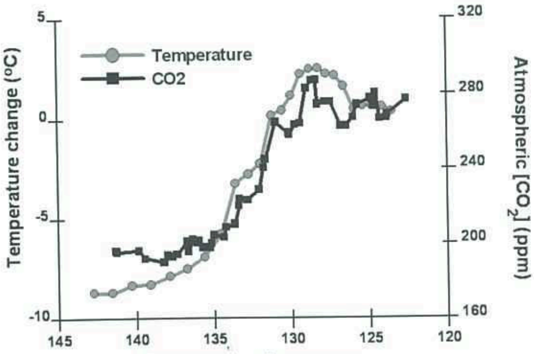

Fig. 5. Atmospheric CO_2 and proxy temperature for the end of the last pre-human glaciation showing that CO_2 lags the initial rise in temperature - data source NOAA.

Though real, the lag time is difficult to quantify. CO_2 is a well mixed gas. There are no significant variations in CO_2 from one part of the world to another. Conversely, if CO_2 has changed by 100 ppm in one part of the world (Antarctica) then it has changed by 100 ppm everywhere. However, temperature (heat) is not well mixed and a change of 10°C in one part of the world does not mean that it changed by that amount everywhere (but it probably did change by some unknown amount everywhere). Also the smearing effect described already for CO_2 in bubbles further muddies the picture. But regardless, the lag is probably on the order of 600-800 years.

Some initial event causes a small rise in temperature and changes in CO_2 levels will follow (one of the blog sites charmingly calls the event *magic* for purposes of discussion). Milankovitch Cycles, a series of wobbles in the Earth's orbit with periods of many thousands of years, are as good a suspect as any. Regardless of the initial event, *afterwards* CO_2 feedbacks [and perhaps albedo changes (extent of reflection), *etc.*] cause the rest of the warming. Nobody denies that the initial small temperature rise at the end of a glaciation occurs before the concentration of CO_2 begins to occur. But in no way does it then follow that CO_2 does not cause the rest of the warming.

The removal of CO_2 from the atmosphere is difficult and occurs via photosynthesis and by dissolution in the ocean (and increasing ocean acidity). The slack in these CO_2 removal processes has largely been taken up. There is simply nowhere to put the 27,000 million tonnes of CO_2 annually generated by fossil fuel burning other than the atmosphere. So, even if we stopped producing CO_2 tomorrow, it would still take many centuries for the atmosphere to return to pre-industrial levels. Remember that the fossil fuels that are now being burnt were laid down over many millions of years, but humans are releasing all that CO_2 over a few centuries. There are perfectly good removal systems but they simply cannot cope with the deluge and that is why atmospheric CO_2 is increasing.

In contrast, there is no easy way for excess water to stay in the atmosphere. As it gets warmer there is more evaporation and more water enters the atmosphere. The extra water has a strong greenhouse effect and causes more warming and more evaporation. If the humidity gets too great then water droplets start to form and soon fall as rain thus removing the water from the atmosphere. What all this means then is that CO_2 *causes* an increase in temperature while water vapour *is caused by* an increase in temperature.

Common Argument 4

Without the Greenhouse Effect there would be no life on Earth

This is true and is not disputed, but it is utterly irrelevant. Essentially this means that without an atmosphere the Earth would be colder – no real surprise there then. Yes, the Earth is about 25-35°C warmer on average than it would be without greenhouse warming. Equally, however, life is impossible on Venus, where the average surface temperature 460°C. It is not just warmer because it is closer to the Sun; Venus receives about 1.7 times as much solar energy per square kilometre as does the Earth. Venus is hot because of a runaway Greenhouse Effect – the atmosphere is very dense (surface pressure about 90 times that on earth) and almost entirely (96.5%) made of CO_2.

A related objection, made by some denialists, is that Mars is also warming and, therefore, this shows human released CO_2 is not responsible for any change on Earth.[10] The *evidence* is that the Martian polar caps of solid CO_2 and water ice have been shrinking for 3 Martian years in a row (each about twice as long as an Earth year). Somehow, as several blogs have noted, it is ironic that 3 local years of change at the Martian pole are taken as proof of global change on Mars but similar measurements for Earth going back several decades are dismissed as being part of a minor natural cycle. Mars has been closely studied (by orbiting craft) for only 15 Martian years so it is probably premature to say what constitutes normal on Mars. The atmosphere of Mars is very much thinner than that of Earth; the surface pressure is about 0.6% that on Earth. As such, the atmosphere takes very little to heat or cool and globally temperatures are strongly influenced by huge dust storms that occasionally sweep Mars. In 1971 the Soviet probes Mars 2 and 3 and the US probe Mariner 9 arrived at Mars to find the entire planet engulfed in a dust storm and it was several months before the atmosphere cleared sufficiently for photographs to be taken. The climate of Mars is so different to that of Earth that no comparisons can be made.

Common Argument 5

Temperature measurements by satellite and radiosonde balloons show no significant warming

It is true that there are difficulties in obtaining good quality temperature measurements and, for this reason, weather stations follow strict procedures. It is also true that the number of stations making measurements has increased from a handful in the 1850s to over 3000 during the baseline period 1960-1991. However, the upward trend in temperatures taken at the same stations under the same conditions is still clear.

The US government Climate Change Science Program (CCSP) said in the abstract of their executive summary report of February 2007 that previously reported discrepancies between the amount *of warming near the surface and higher in the atmosphere have been used to challenge the reliability of climate models and the reality of human induced global warming. Specifically, surface data showed substantial global-average warming, while early versions of satellite and radiosonde data showed little or no warming above the surface. This significant discrepancy no longer exists because errors in the satellite and radiosonde data have been identified and corrected. New data sets have also been developed that do not show such* discrepancies.[11] One hopes that this report will see an end to this particular common argument.

Common Argument 6

Computer models of the climate are worthless

In no way does this show climate change is not happening. Yes, models make assumptions based on limited data. Good models (and there are many) include uncertainties to take account of the assumptions so that the answer includes a range of probable results. Models are tested by inputting past conditions and seeing if they come up with something like the modern conditions. Many models have performed well in *predicting* the climate conditions of today based on past data. This surely is proof that the models work. Additionally, most of these models are beginning to converge and give similar answers for future conditions based on the data of today.

There is much confusion about what measures of accuracy should apply to climate models. Consider this: *The University of Otago is at 46°52' S, 170°31' E. The 24th of July 2007 was warm and many students wore t-shirts and other light clothing.* No climate model could have predicted this a month previously. Yet none of the students thus attired would be surprised if a climate model made in February predicted that: *Based on measurements of sun angle and day length, a period of coldness is on the way. Probably this will result in average temperatures in July being cooler than in February.* Similarly, larger scale climate models can not and do not pretend to predict the weather tomorrow. The models have a longer coarser focus and instead show good agreement for long term general regional trends in climate.

Common Argument 7

There is no **consensus.** *Thousands of scientists, including 72 Nobel Laureates, signed the Heidelberg Appeal (1992), calling for a rational scientific approach to environmental problems and 19,000 scientists signed the Oregon Petition*

These petitions and several others like the Leipzig Declaration have been seriously compromised. Do a quick search yourself. Other people have written at great length about this. Home for all these petitions is the Environmental Science and Policy project (SEPP).[12]

The Heidelberg Appeal (issued at the Rio Earth Summit in 1992) does not even mention climate. It is entirely made up of Barnum statements like 'We intend to assert science's responsibility and duties toward society as a whole. We do, however, forewarn the authorities in charge of our planet's destiny against decisions which are supported by pseudoscientific arguments or false and nonrelevant data'. The *Statement by Atmospheric Scientists on Greenhouse Warming* was also launched at the Rio summit. In the 15 years since then it has gather a massive 47 signatures including several TV weather presenters.

Here is a quote from an editorial sidebar in the October 2001 issue of *Scientific American* about the Oregon Petition: '*Scientific American* took a sample of 30 of the 1,400 signatories claiming to hold a PhD in a climate-related science. Of the 26 we were able to identify in various databases, 11 said they still agreed with the petition — one was an active climate researcher, two others had relevant expertise, and eight signed based on an informal evaluation. Six said they would not sign the petition today, three did not remember any such petition, one had died, and five did not answer repeated messages. Crudely extrapolating, the petition supporters include a core of about 200 climate researchers – a respectable number, though rather a small fraction of the *climatological community*'.[13]

Conclusion

Do not take our word for it that these are representative of the arguments used by many denialists – conduct your own research. We have shown that *these* common arguments used by denialists are false. Worse, they use *bad science*. Interested readers may wish to examine *other* denialist arguments and seek similar flaws. While it is valid to question, it is not valid to create misleading arguments of the type shown here to be false. The CO_2 already in the atmosphere will continue to cause change for many decades, even if no more is added. We can expect to see significant climate change in our own lifetimes.

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The 3-His Motif: A New Subset of Non-Heme Mono-Iron Enzymes

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The chemistry of iron has undergone something of a renaissance in the last ten years. This increase in activity has been heavily influenced by biochemical investigations into non-heme iron enzymes and it stands out as a good example of healthy interaction between the fields of chemistry and biochemistry. On the chemical side, higher oxidation states[1-3] (up to VI) have been accessed through macrocyclic ligands other than heme groups and new reactivity has been unearthed. Iron tends to like to hold on to at least five of its d-electrons and, therefore, any states higher than Fe(III) usually have been treated as novelties. Recently, however, principally through work by Que and Wieghardt, the landscape of iron chemistry has shifted considerably. Karl Wieghardt[1] has reported the formation of an Fe(VI) complex other than the well known FeO_4^{2-}. Meanwhile, Lawrence Que[2] has produced a series of Fe(IV) complexes with different macrocyclic ligands that allowed their spectroscopic characterization and their chemistry to be probed. This should enable the formation of such species in biochemical systems to be examined more closely.

In particular, the Fe(II)-dependent non-heme mono-iron enzymes have provided fertile ground in the search for interesting chemistry. Taurine/α-ketoglutarate dioxygenase (TauD) has provided the first example[4] of a non-heme iron-oxo species in biology and other members of the family have been extensively studied. Nearly all of these enzymes display characteristic coordination of the Fe(II) centre: two histidines and a carboxylate. Recently, however, two enzymes have been discovered which use three histidines[5,6] – a coordination configuration favoured by zinc (in for example the carbonic anhydrases).[7] These may well be only the first of a new subclass of non-heme mono-iron enzymes and one in particular, cysteine dioxygenase, is the subject of this article.

Cysteine dioxygenase (CDO) is an enzyme from the cupin superfamily (Fig. 1A), which catalyses the addition of both atoms of molecular O_2 onto the thiol sulfur of cysteine side chains, generating cysteine sulfinic acid (see Scheme 1). It achieves this using a single Fe(II) cofactor which is four-coordinate in its resting state. Three of the ligands for this metal site are from protein histidine side chains, with water occupying the final position.[8] Further modifying this unique metal environment is an equally rare post-translationally modified pair of side chains, a cysteine Sγ cross-linked to the aromatic Cϵ of tyrosine. This is in contrast to the active sites of other members of the same family, which carry out an array of reactions such as oxygenative bond cleavage, bond formations and hydroxylations using an octahedral Fe(II) with a two histidine and one carboxylate facial triad of ligands. It might be significant that most previously described dioxygenases catalyse the cleavage of aromatic rather than aliphatic substrates.

There appear to be, in fact, very few enzymes with Fe(II) that do *not* use a two histidine carboxylate motif. Examples include acetylacetone dioxygenase (Dke1) (which coordinates Fe(II) through three histidines),[6] SyrB2 halogenase (which coordinates through two histidines),[9] and a chloride, and apocarotenoid-15,15'-oxygenase (which coordinates through four histidines).[10] Importantly, however, Dke1 is the only other known enzyme to use three histidines. It catalyses the cleavage of acetylacetone and adds one oxygen to each product from molecular O_2 generating acetate and methyl-glyoxal.

The CDO resting state has been shown to be tetrahedral in an X-ray crystal structure analysis, coordinated by three histidine ligands with a well-refined solvent water molecule filling a fourth site as shown in Fig. 1B. This water is hydrogen bonded to a further solvent water molecule and the post-translationally modified tyrosine. It is important to note that such a tetrahedral coordination of Fe(II) is unique in this protein superfamily. From the structure of human CDO co-crystallised with cysteine, the substrate can be seen to coordinate to the metal through the thiol sulfur and amino terminus nitrogen,[11] thus expanding the coordination sphere to distorted octahedral. However, this appears to be in disagreement with the results of extended X-ray absorption fine structure (EXAFS) analyses, which showed all coordination likely to be through O or N atoms. Furthermore, sulfur ligands were specifically *excluded* because they gave a poorer fit to the observed data.[12] These EXAFS studies were carried out on *oxidised* protein with the iron centre in the Fe(III) state and this could readily account for the different coordination environments reported. Coordination of the substrate oxygen may occur in an end-on fashion following the coordination of the cysteine. Affinity of the metal for oxygen increases dramatically after this first substrate binding step, likely serving to protect the enzyme from oxidative damage when no substrate is present.

The post-translational modification 4.2 Å from the metal cofactor, linking a cysteine side-chain to a tyrosine side-chain Cϵ shows co-planarity of Cβ and Sγ of cysteine with the aromatic ring of the tyrosine, suggesting that this has some partial double bond character.[8] This type of modification has been observed only in the enzyme galactose oxidase[13] until now. This enzyme catalyses the reduction of a range of primary alcohols to aldehydes using a mono-copper centre, for which the cross-linked tyrosine is a ligand through the phenolic oxygen. The extended aromaticity of this ligand is thought to stabilize a free radical likely formed in the galactose oxidase mecha-

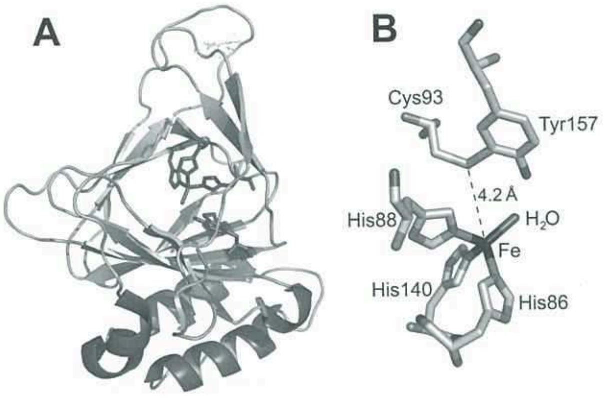
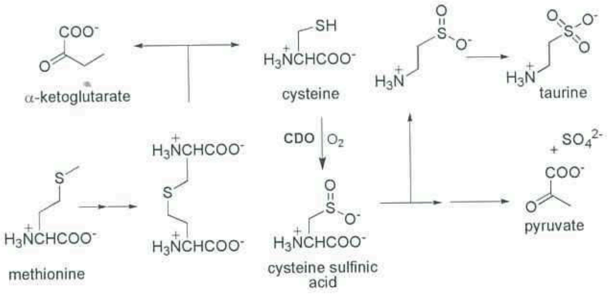


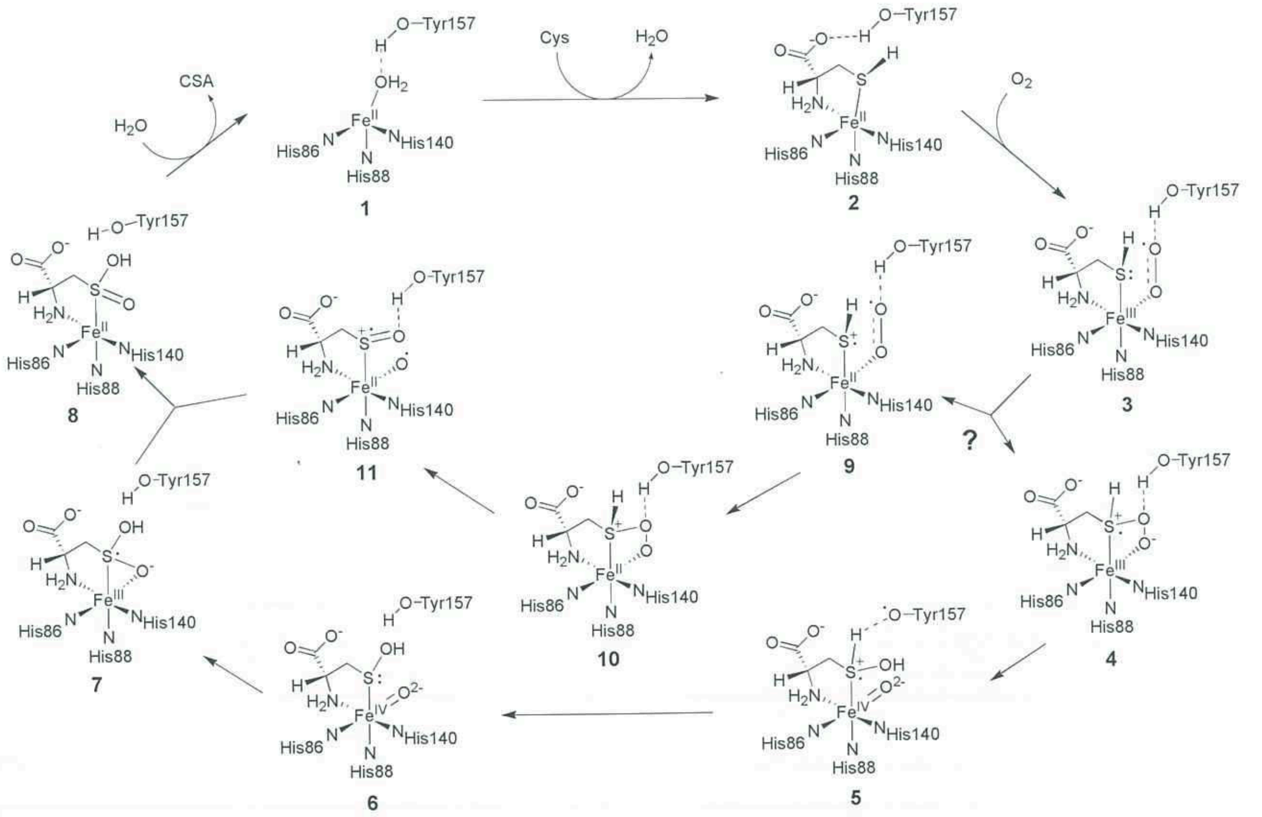
Fig. 1. (A) *Rattus norvegicus* cysteine dioxygenase structure (CDO, PDB 2B5H) clearly showing the active site present within the *β*-barrel of the cupin fold, and (B) the active site showing the unique geometry of the Fe(II) in the resting state and the proximal post-translationally modified thioether. Diagrams produced with PyMOL, see: http://pymol.sourceforge.net.

nism. Electron donation by this cross link also serves to reduce the bond dissociation energy of the tyrosine -OH, giving it unique electronic properties. In CDO this post-translational modification is thought to have two roles.[11] Structurally, this modification may aid in placement of the tyrosine to participate in the enzyme catalytic activity. Electronically, it has been suggested that it prevents formation of HO• by the enzyme. The modification is not universally conserved as it is not present in some prokaryotic forms, and so it cannot have a crucial role in preventing free radical formation *in vivo*. The electronic properties would, however, help to stabilise the tyrosine radical proposed in the mechanism based upon the human CDO structure.[11] It has been suggested that this modification takes place by a single turnover of the enzyme using intramolecular substrates. Thus, electron transfer to the metal centre generates a phenyl radical on the tyrosine that is attacked by the protein cysteine thiol. Following electron transfer and proton loss this generates the mature cross-link.[8]

The CDO-catalysed reaction is the first step in the catabolic pathway of cysteine which yields pyruvate and sulfate as eventual end products (Scheme 1). The product of the CDO catalysed-reaction is also converted into taurine through two further reactions. Sulfur from methionine ultimately also passes through this same pathway after conversion into cystathionine, which is cleaved to yield cysteine and α-ketobutyrate.[14] A block in cysteine metabolism at CDO is thought to be involved in several disease states, including rheumatoid arthritis, liver disease, Parkinson disease, Alzheimer disease, motor neuron disease, and systemic lupus erythematosus. In these cases, blood levels of cysteine are elevated while taurine and inorganic sulfate are depleted.[8] This has several adverse



Scheme 1. Metabolic pathway for decomposition of sulfur-containing amino acids to pyruvate, and sulfate and production of taurine. Central is the CDO-catalysed conversion: cysteine to cysteine sulfinic acid using molecular oxygen.



Scheme 2. The mechanisms proposed for CDO. It is not yet clear which pathway is followed after intermediate 3; the point of bifurcation is denoted by the question mark - see text for discussion.

effects. High levels of cysteine are toxic in rats,[15] and it is thought to be neuroexcitotoxic and can form toxic species also with other compounds.[16] Low levels of sulfate prevent sulfation out of proteins, and this is important in the modulation of many protein-protein interactions.[17] Finally, low levels of taurine have been associated with many abnormalities, mostly involving neuron and photoreceptor function.[18] CDO thus catalyses a reaction that is biologically very important.

X-ray crystallographic data from native forms of CDO from mouse and rat, and human CDO in complex with its substrate L-cysteine, have become available in the last few years. Based upon these, several mechanisms for the CDO catalysed reaction have been proposed. These differ in the order of S=O and S–O bond formation, the oxidation states of the iron, and the coordination/binding of the substrate. Scheme 2 summarises some of the more pertinent features of these mechanisms. The tetrahedral resting state **1** binds cysteine followed by oxygen to give the iron(III) superoxide **3**, which has an increased coordination number and is possibly octahedral. Ye *et al.*[11] have suggested that this is followed by attack of the distal oxygen on the thiol sulfur to produce the peroxo intermediate **4** that homolytically cleaves to form an Fe(IV)-oxo species **5**. This Fe(IV) species can then further oxidise the sulfur in two one-electron steps, *via* **6** and **7**, to produce the iron bound cysteine sulfinic acid **8** that can then be released. In contrast, Stipanuk[8] and Phillips[5] and their groups suggest that the thiol radical cation **9** is first produced through reduction of the iron. Radical recombination then produces the cyclic peroxo species **10**. Cleavage of the peroxide O-O bond in **10** results in the metal-bound sulfoxy-cation **11**, which can react with the activated iron oxygen atom, again to produce the metal bound **8**.

Unfortunately, these mechanisms at present lack spectroscopic or kinetic support, and are formulated purely from a study of the active site environment of the native and substrate-bound enzyme structures. Hence experimental testing of this proposal will be extremely valuable to understanding this exciting and unique enzyme system. The biological significance of understanding this system has already been made clear and due to the author's interests in neurodegenerative diseases[19] kinetic and spectroscopic investigations into the mechanism are being carried out in Dunedin.

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News Bits

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Australian Dust: From Uplift to Uptake

Doug S. Mackie and Keith A. Hunter

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Simply put the Southern Ocean is anaemic! That is to say that primary production is often limited by the availability of iron. As phytoplankton grow they take up carbon from surface waters allowing more CO_2 from the atmosphere to dissolve and thus lowering its concentration in the atmosphere. Aeolian dust delivers iron to oceans and in the late 1980's John Martin's *iron hypothesis* mused about how more dusty conditions during the last glacial maximum might have increased the *drawdown* of CO_2 from the atmosphere by phytoplankton. He famously joked that *give me a tanker of iron and I'll give you an ice age.*[1] The NZ-led Southern Ocean Iron Enrichment Experiment (SOIREE) tried just that. The results (nicely summarised at the RSNZ website *www.rsnz.org*), that conclusively show the dramatic effect of iron additions, also raised some questions about the *real world* delivery of iron, as opposed to simply mixing an iron solution into the prop wash of a ship.

More than 80% of global dust deposition to the oceans is to those in the Northern Hemisphere from large sources like the Sahara and Gobi deserts. But the impact of dust on biota in a particular region is not necessarily a function of mass flux. Quite the contrary - the scarcity of dust in the Southern Hemisphere means that dust processes there are of especial importance but observational data is sparse. The cartoon (Fig. 1) shows the overall process from uplift of Australian soil and production of dust to uptake of iron by phytoplankton.

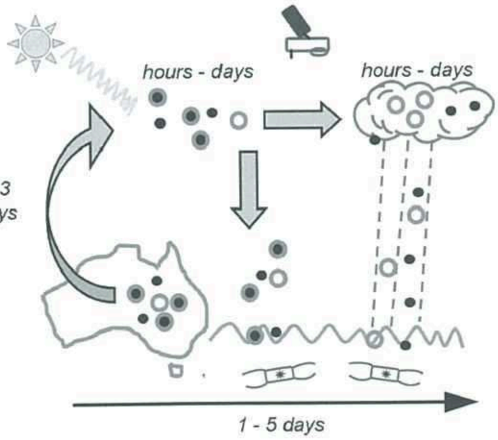

Fig. 1. Schematic sequence of events from uplift of Australian dust to uptake of iron by biota.

In general iron is taken up from seawater by phytoplankton from the dissolved phase via a ligand-mediated process. Therefore, factors that influence the dissolution of iron from dust also govern the uptake of iron by phytoplankton. During uplift and transport by dust storms, abrasion of soil produces fine particles. Abrasion processes can also redistribute more soluble forms of iron onto smaller grains.[2] Other dust interactions during transport with light[3] and cloud water[4] also influence the dissolution of iron from dust.

Some models for the dissolution of iron from dust, based on Northern Hemisphere data,[5] explicitly include the solubility enhancing effect of pollutants like SO_X and NO_X. But an important consideration for the Australian case is that the atmosphere of the Southern Hemisphere is pristine in comparison. For this reason, our laboratory-based solubility experiments are carried out in pure water acidified with sulfuric acid and use both soils collected from dust source regions and dust collected during dust storms. The Southern Hemisphere case may be a good model for the influence of the atmosphere on the iron cycle during the dustier, last glacial maximum and will, in any event, inform predictions of iron supply as Australian dust emissions increase due to human-induced land-surface degradation.

The major dust storm of 23 October 2002 (Fig. 2) was the largest event in more than 40 years and it entrained dust from large areas of Eastern Australia. The storm front was some 2400 km long, 400 km wide, and 1.5-2 km high and the image also shows smoke plumes from large bushfires. The total suspended load was estimated at 3.4-4.9 million tonnes.[6] After the event passed off the Queensland coast, satellite pictures and wind back trajectories showed that the plume bifurcated, with dust being deposited into both the high-nitrate, low-chlorophyll (HNLC) low iron waters south of NZ, and into the low-nitrate, low-chlorophyll (LNLC) low iron waters NE of NZ and into the Gulf of Carpentaria to the north of Australia.

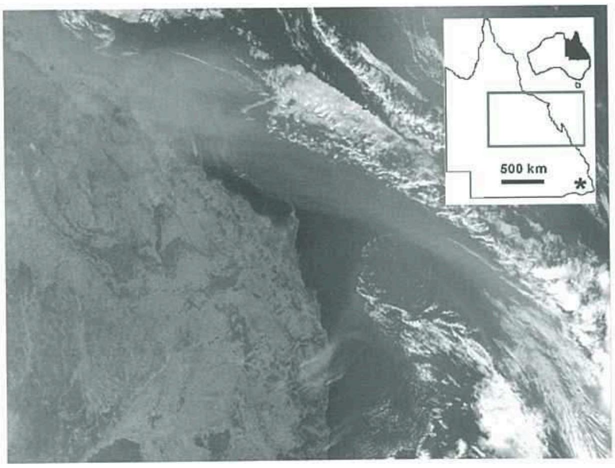

Fig. 2. The 23 October, 2002major dust storm. This SeaWIFS image (courtesy of NASA) shows the storm ca. 2400 km long x 400 km wide x 1.5-2 km high; inset map * = Brisbane.

Dust supply to the southern HNLC region might be expected to stimulate iron-limited diatoms in these waters, and in the northern LNLC region, dust supply might have stimulated nitrogen-fixers such as *Trichodesmium*, which is known to be Fe and/or Fe + P limited. However, examination of composite satellite ocean color images after the event revealed no significant increase in chlorophyll concentrations across this region. Why not? We believe the answer lies in the way in which iron dissolved from dust.

We began with simple experiments to assess the limits of iron solubility in the atmosphere in the absence of high energy UV radiation and ligands (like oxalate, SO_X and NO_X). The results (Fig. 3) agree with the general trend of Norther Hemisphere studies and show that the iron component of soils and dusts can be partitioned into three classes, namely *readily-released* at <1% total iron, *acid-leachable* at up to 15-30% of total iron, and the remainder *refractory*.

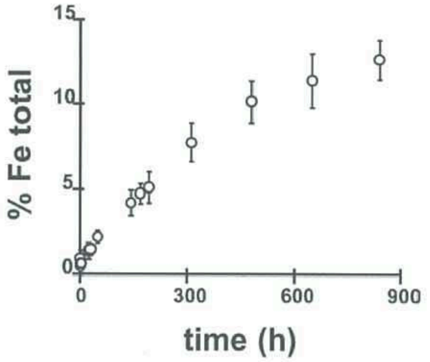

Fig. 3. Dissolution of iron from untreated Thargomindah soil over time at pH 2.1; data from the middle of the Malee dust producing region - 2/3 to the west along the Queensland/NSW border and averaged for grain size fractions 5-11, 11-20, 20-30, 30-44, 44-53, and 63-75 μm.

Readily-released iron is that which is found in the dissolved phase after not much more than the mixing time of our system – just a few minutes, *viz.* the y-intercept of a dissolution plot. Readily-released iron seems comparable with the *instantaneously soluble fraction* of Fe and Al in natural aerosols reported by other workers,[7] and may represent ferrihydrite (frequently and incorrectly described as *amorphous iron oxide*). The acid-leachable portion comes out more slowly, a period that ranges from hours to many days. The portion of this that is bioavailable can be approximated by a tangent to the dissolution curve.

Based on these arguments, we would not expect to see a response by biota in the weeks immediately following a dust delivery event. Rather, such events would serve to top up a supply of slow release iron where iron supply is limited by processes that retain dust, or at least the iron rich coatings from dust grains, in surface waters. This buffering of iron supply may explain the lack of rapid response by biota to dust events. Our current work is following this line of enquiry.

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Letter to the Editor

Re: *Back to the Basics* (*This Journal,* **2007**, *71*, 50-53)

I read Peter Schwerdtfeger's article *Back to the Basics* in the last issue of the journal with considerable interest and sympathy. I also reflected on the numerous articles with similar messages that I have read over the last twenty or so years.

As far as Government funded Research, Science and Technology is concerned, why, if it is so obvious, do the powers that be not get the message that investment in R&D is a good thing? The public servants who put the message forward and the politicians who read it are some of the brighter people around. They are used to making long-term decisions around complex subjects. Deciding on an appropriate level of research funding for New Zealand should be straightforward. So is it possible that they have the view that the current amount allocated is about right? In fact, given that the level of Government spending on R&D as a percentage of GDP is drifting down year by year, they may well think that it is too high as it is?

In which case, if we are to persuade the decision makers to allocate more funding to research, basic or applied, then the first step is surely to try and understand where they are coming from? If we can do that, then possibly we can then formulate an argument that will persuade decision brokers and makers that spending more on R&D is a better option than more spending on health, education, welfare, *etc*.

So let me give you a challenge: think like a Treasury official or a Cabinet Minister or a politician with all the multitude of different demands being made on you in allocating the tax-take. Rather than think of reasons why funding should be increased, do the reverse and submit in 100 words or less your reason(s) why research funding should **not** be increased.

I am hoping that collectively we may already know the answer, and if it can be clearly expressed we may then be able to formulate an appropriate *plan of attack* that would see R&D expenditure in New Zealand raised to that found in other OECD countries. If nothing else, I might expect some humorous responses from my more imaginative colleagues.

Yours sincerely
David M. Bibby, FNZIC.

Please send your responses to the Editor: *brian.halton@vuw.ac.nz*

Ocean Acidification and the Changing Carbonate Speciation in Seawater - Should We be Worried?

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Ocean acidification is one of the effects of global climate change.[1] The ocean takes up some of the CO_2 produced as a by-product of human activities and this results in a change in the carbonate speciation of the seawater. In particular, both the pH of the seawater and the carbonate concentration ares decreasing. Organisms which are dependent on carbonate to form part of their structure are vulnerable to these changes.

Prior to the Industrial Revolution, the carbon cycle was in a steady state. The burning of fossil fuels has accelerated the flux of carbon between the geological reservoir and the atmosphere; deforestation and biomass burning has perturbed the biosphere-atmosphere flux. These perturbations have had a flow on effect to the other reservoirs, in particular the terrestrial biosphere and the ocean.

Direct measurements of atmospheric CO_2 concentration first began in Hawaii[2] in 1958, and subsequently measurement programmes have been set up at many other locations, including Baring Head near Wellington, NZ. Earlier values of atmospheric CO_2 concentration have been obtained by looking at air bubbles trapped in ice and, from the ice-core record, it is estimated that the present-day atmospheric concentration of CO_2 is greater than for 420 000 years. In 1958, when direct measurements began, the atmospheric concentration was 316 parts per million by volume (ppmv), while in 2005 the concentration in clean background air was 381 ppmv. A comparison of the atmospheric CO_2 concentration with what would be expected from fossil fuel and other anthropogenic emissions indicates that about 60% of the excess or *anthropogenic* CO_2 has been transferred to other reservoirs. The ocean has taken up a substantial amount of this anthropogenic carbon.

The flux of CO_2 across the air-sea boundary depends on the concentration gradient (normally expressed as a gradient in CO_2 partial pressure, pCO_2, or fugacity, fCO_2) and the sea surface conditions, such as the extent and size of waves and bubble injection by breaking waves. The invading CO_2 reacts with carbonate ions in the seawater to form bicarbonate ions (Eq. 1).

$$CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^- \text{ (Eq. 1)}$$

The resulting bicarbonate/carbonate equilibria (Eq. 2) involve hydrogen ions and the distribution of the carbonate species is pH dependent. At typical surface seawater conditions, the dissolved inorganic carbon is present as 91% HCO_3^-, 8% CO_3^{2-}, 1% $CO_{2(aq)}/H_2CO_3$, and the pH ranges from 7.9 to 8.3.

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \text{ (Eq. 2)}$$

The net result of an influx of atmospheric CO_2 to the ocean is:

- an increase in $CO_2(aq)/H_2CO_3$ concentration
- a decrease in CO_3^{2-} concentration
- an increase in HCO_3^- concentration
- an increase in H^+ concentration
- an increase in C_T (total dissolved inorganic carbon concentration)
- no change in total alkalinity (A_T)
- an increase in pCO_2
- a decrease in pH

Since the Industrial Revolution the pH of surface seawater has decreased by about 0.1 pH units.[3] This equates to a change in $[H^+]$ from about 6.3×10^{-9} mol L^{-1} to 7.9×10^{-9} mol L^{-1}, an increase of about 25%. When the oceanic uptake of CO_2 occurs over long time periods (>100 000 years) the changes in carbonate chemistry are buffered by interactions with carbonate minerals. However, on shorter time scales the ocean is more sensitive to pH changes.[3]

It is predicted that if the rate of anthropogenic emissions of CO_2 to the atmosphere remain at the current level (so called *business-as-usual* scenario), then the average pH of the surface ocean will decrease by about 0.4 pH units by the end of this century.[4] This equates to increasing the $[H^+]$ to approximately three times the present value.

Solid carbonate is present in the ocean predominantly as calcium carbonate. It forms carbonate structures of many marine plants and animals, and it is also a substantial component of the sea-bed material. The equilibrium constant of dissolution to Ca^{2+} and CO_3^{2-} depends on pressure (depth in the water column), temperature, and ionic strength (salinity of the seawater). The ocean $[Ca^{2+}]$ is approximately constant and the extent of $CaCO_3$ dissolution is dependent primarily on $[CO_3^{2-}]$. This decreases through the water column as shown in the profiles for the Atlantic and Pacific oceans (Fig. 1); the equilibrium concentrations of the two most common forms of $CaCO_3$ – aragonite and calcite – are also shown. The depth at which the actual carbonate ion concentration and the equilibrium carbonate ion concentration are the same is termed the *carbonate compensation depth* (CCD). From Fig. 1, it can be seen that the CCD for aragonite occurs at about 1000 m in the Pacific Ocean, and at 2500 m in the Atlantic Ocean (calcite is at 3500 and 4500 m, respectively). The CCD in the Southern Ocean is shallower due to the colder water temperatures.

When the $[CO_3^{2-}]$ in the water is greater than the equilibrium concentration, precipitation will occur and the formation of solid $CaCO_3$ is possible, but when it is less dissolution will occur. Thus, above the CCD solid $CaCO_3$ is present, both in the water column (as parts of floating or swimming plants and animals), and on the sea floor (as parts of bottom dwelling organisms or as sediment). Below the CCD solid

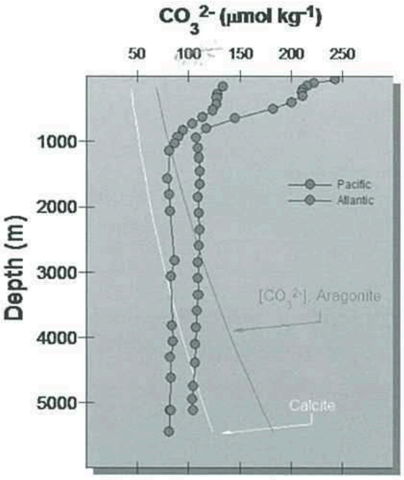

Fig. 1. Typical depth profiles of carbonate ion concentration in the Atlantic (right) and Pacific (left) Oceans. The equilibrium carbonate concentrations for aragonite and calcite are also shown.

$CaCO_3$ is not present. In fact, the depth at which dissolution occurs is not a sharp line but a zone known as the saturation horizon, the upper bound of which is termed *the lysocline* and the lower bound the CCD.

As CO_2 enters the ocean it decreases [CO_3^{2-}] as described above, and the depth at which [CO_3^{2-}] = CCD becomes less, *i.e.* the depth above which solid $CaCO_3$ can exist moves closer to the surface. It has been calculated that the CCD has shoaled by between 50 m and 200 m since the Industrial Revolution. Modelling studies predict that even if the atmospheric [CO_2] is stabilised at 450 ppmv, aragonite and calcite will be undersaturated in most of the deep ocean.[4]

Why is this important one may ask? It is well known that many marine organisms use $CaCO_3$ to make hard parts of their structure and in order to do this the water has to be supersaturated with CO_3^{2-} ions. Some organisms actively raise the pH of the surrounding water in order to increase [CO_3^{2-}] which is then used for calcification. Some species use aragonite, the more soluble, orthorhombic crystal form of $CaCO_3$ (Table 1) while some use the less soluble calcite; some use a mixture of the two, or a variant that incorporates other cations into the structure. The carbonate structure forms a protective framework for some marine species: molluscs form shells, coccolithophores (single-celled algae) form intricate plates, echinoderms form endoskeletons and spines, and corals and corraline algae construct complex exoskeleton structures which form coral reefs.

A decrease in pH and the accompanying decrease in carbonate ion structure reduce the ability of these organisms to calcify and thus compromise their structural and metabolic functions. Experiments in which the pH of the seawater is manipulated have shown a deterioration of existing carbonate structures and defects in the organism's new growth.[5] Fig. 2 shows scanning electron micrographs (SEMs) of a coccolithophore grown in seawaters whose pH values equate to overlying atmospheres of 300 and of 780-850 ppm.[5] The damage to the carbonate structure of the organisms grown at the lower pH is clearly visible and similar experiments demonstrate that damage also occurs to other calcifying species.

Table 1. Characteristics of the two forms of $CaCO_3$, aragonite and calcite.

	Aragonite	**Calcite**
Structure	orthorhombic	trigonal
Solubility	high	low
Calcifying species	corals, pterods, macroalgae, molluscs	foraminifera, macroalgae, coccolithophores, crustacean, echinoderms, molluscs

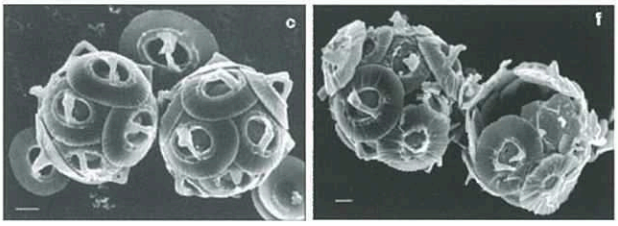

Fig 2. SEMs of the coccolithophore G. oceanica grown under pH conditions of 8.15 (left) and about 7.75 (right); note the malformed carbonate coccolith structure in the latter. Adapted by permission from Macmillan Publishers Ltd: *Nature* **2000**, *407*, 364-367; see ref. 5.

Calcifying species often occupy keystone niches in the ecosystem as they are major predators or grazers. They also form the basis of the marine food chain, particularly in the Southern Ocean, so that any change in the make-up of the population or species will have a consequence in higher trophic levels. They are also an important part of the biological pump for carbon cycling within the ocean as they removing carbon material from the surface ocean when they die and then sink to depth. Calcifying organisms such as mussels, paua and other shellfish are of economic and cultural importance. The natural variation in pH that these coastal dwelling organisms experience is relatively large, but their susceptibility to damage with long-term pH change is not known.

It is not fully known how organisms, species, communities and ecosystems will adapt to changing pH and changing concentrations of the dissolved inorganic carbon species, but the rate of change is slow. Species that actively use $CO_{2(aq)}$ for photosynthesis, such as sea grasses and some algae, may benefit from the increasing concentration.[6] Indirect effects of ocean acidification that could also impact on marine organisms include the changing composition of nutrients, *e.g.* phosphate, silicate and borate, changing speciation and solubility of trace metals, and the effects on physiological gas exchange and reproductive physiology in higher marine animals.[7] A recent report by the Royal Society[7] states: *We conclude on the basis of current evidence that ocean acidification is an inevitable consequence of continued emissions of CO_2 into the atmosphere, and the magnitude of this acidification can be predicted with a high level of confidence. However, its impacts, particularly on marine organisms, are much less certain and require a substantial research effort. Ocean acidification is a powerful reason, in addition to climate change, for reducing global CO_2 emissions.*

Direct determinations of pH and other analytical parameters for CO_3^{2-} have been made in the equatorial Atlantic Ocean near Bermuda[8] since 1984. The decrease of 0.0012 pH units per year reported there equate to that expected if ocean pCO_2 was increasing at the same rate as that in the atmosphere. Long term changes consistent with invading atmospheric CO_2 have also been detected in the equatorial Pacific Ocean near Hawaii,[9,10] and in the North Atlantic Ocean near the Canary Islands.[11] A joint NIWA–Otago University programme running since 1998, involves measuring[12] pCO_2 and pH in the waters off the Otago coast (Fig. 3) every 2 months (Fig. 4). This Munida Time Series transect includes neritic waters (ones modified by coastal influence), modified subtropical waters, and sub-antarctic surface waters. Seasonal cycles and interannual variability in pCO_2 and pH arise from fluctuations in sea surface temperature, biological uptake and release of carbon (photosynthesis, respiration, and decay), and mixing with deeper water. The region is a sink for atmospheric CO_2. Gleaning a long-term trend from data with high variability is nontrivial; it is necessary to separate the effects of temperature, biology, and mixing before attributing any observed changes to the uptake of anthropogenic CO_2. At this time it is not possible to say that changes consistent with the invasion of anthropogenic CO_2 are observable in the waters studied on the Munida Time Series. This highlights the need for long-term, high quality monitoring, and this is difficult to implement both analytically and logistically. The continuation of the time series remains a priority research area.

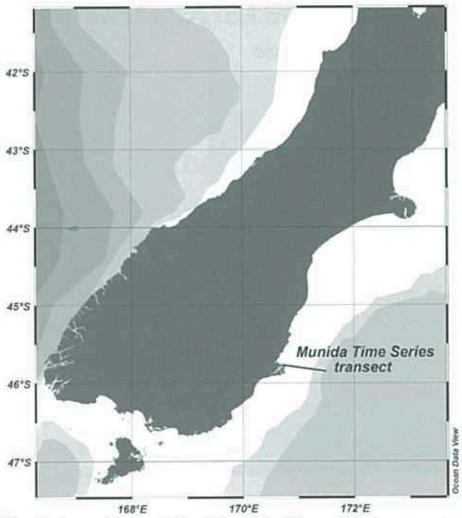

Fig 3. Location of the Munida Time Series transect

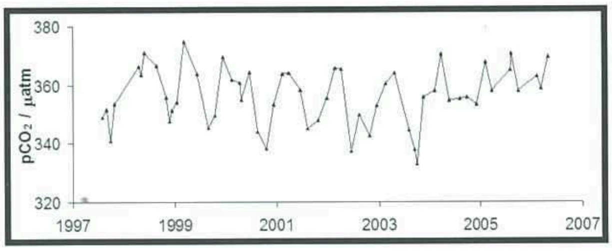

Fig 4. pCO_2 in subantarctic surface water from the Munida Time Series transect

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Dates of Note

A new regular feature from the Editor of *Chemistry in New Zealand.*

September 18 2007 marked the 100th anniversary of the birth of ***E. M. McMillan*** who discovered neptunium and plutonium and received the 1951 Nobel Prize in Chemistry.

October 2 2007 was the 100th anniversary of the birth of ***Alexander Robertus Todd, Baron Todd***, PC, OM, FRS (2 Oct. 1907 – 10 Jan. 1997) He was a Scottish biochemist whose research on the structure and synthesis of nucleotides, nucleosides, and nucleotide coenzymes gained him the 1957 Nobel Prize for Chemistry. In 1955 he elucidated the structure of vitamin B12. Later he worked on the structure and synthesis of vitamin B1 and vitamin E, the anthocyanins (pigments of flowers and fruits) from insects (aphids, beetles) and studied alkaloids found in hashish and marijuana. He served as chairman of the British government's advisory committee on scientific policy from 1952 to 1964, was knighted in 1954 and made ***Baron Todd***, of Trumpington in the County of Cambridgeshire, in 1962. He was Master of Christ's College, Cambridge (1963-1978) and became Chancellor of the University of Strathclyde in 1975, and a member of the Royal Order of Merit in 1977.

October 6 2007 marked the 200th anniversary of ***Humphry Davy***'s first preparation of potassium metal from the electrolysis of molten potassium hydroxide.

October 31 2007 marks the 175th anniversary of ***Walter Weldon***'s birth. He invented the process named after him for the preparation of chlorine from hydrochloric acid.

So Who Was Nobel Anyway?*

Brian Halton

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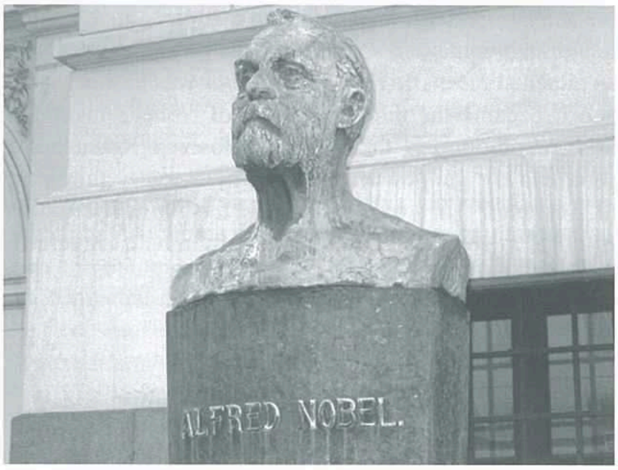
(e-mail: brian.halton@vuw.ac.nz).

*Dedicated to Drs. Ron Easthope, Phil Matsis and Mark Simmonds with appreciation for their care, consideration, and intervention for almost a quarter of a century.



Alfred Nobel statue, Oslo © 2005, 2006, 2007 by Bjørn Erik Pedersen (public domain image from *http://commons.wikimedia.org/wiki/Image:Alfred_nobel_statue_oslo.jpg*).

Ask anyone who ***Nobel*** was and you will get a reply that gives either *someone involved with explosives* or *the man behind the Prizes*, or both. Correct of course, but there is much more to Alfred Nobel than any such simple statement could imply. With the 2007 Prizes about to be announced, a brief synopsis of this most amazing of men seemed appropriate.

Alfred Bernhard Nobel was born in Stockholm on October 21st 1833, the third of four sons to Immanuel and Andrietta (Ahlsell). His father (1801-72) was a man of genius – an inventor, building constructor and contractor – who built bridges and houses in Stockholm. Financial misfortune, including a disastrous fire and the loss of three barges carrying building supplies for a bridge he was building, led to bankruptcy in the year Alfred was born. In order to escape Swedish jurisdiction (apparently imprisonment) he moved to the then Russian controlled Finland in 1837 leaving his wife and sons behind.[1,2] It was five years before they were able to join him, now in St. Petersburg, where he had established a mechanical workshop providing equipment for the Russian army; he was a pioneer in arms manufacture and steam engine design but with interests in explosives. He persuaded Tsar Nicholas I and his Generals to a belief in the naval mines that he had developed. These comprised wooden casks filled with gunpowder and they were deployed below the surface of the Gulf of Finland in the Crimean War (1853-56); they are credited with saving St. Petersburg from attack by the British Navy. Immanuel was awarded the Imperial Gold medal by the Tsar in 1863 despite being a foreigner.

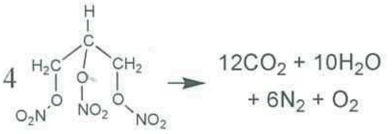
Alfred received but cursory formal education in Sweden prior to his moving to Russia when he was eight years old; it comprised a mere three terms of primary education at the parish school. However, during his Russian sojourn, his father had his sons under the tutelage of private teachers with training in languages, literature and the natural sciences. By 17 Alfred was fluent in Swedish, Russian, German, French, and English, and held interests in chemistry, physics, English literature and poetry. But his father thought him something of an introvert and sent him overseas in 1850 (Sweden, Germany, France, USA). In 1852 he was asked to return to Russia as the family business was in strong heart from its military patronage. However, the subsequent end of the Crimean war led to cancelled orders and Nobel and his father had to seek new products.[1,2]

Clockwise from top: Robert, Ludwig, Alfred and baby Emil Nobel in St. Petersburg, *ca.* 1843 (public domain image from: http://commons.wikimedia.org/wiki/Image:Nobel_3.jpg)

While in Paris, Alfred worked in the laboratory of Jules Pelouze (Zinin, his Russian chemistry tutor was a former Pelouze pupil), gaining an interest in nitrated organics. Pelouze was the first to isolate nitrocellulose (1837) and another of his pupils, Italian Ascanio Sobrero, was the 1847 discoverer of *piroglycerin* (nitroglycerine - NG, **1**) from slow addition of glycerine to nitric and sulfuric acids. In one experiment, he and his laboratory colleagues were injured in the ensuing explosion. Because of this he refused to exploit his discovery further. Indeed, NG could explode (Scheme 1) at any time if handled carelessly or when impure from nitric and nitrous acid contaminants, thus making it more than difficult to work with. It was not until he was encouraged by Zinin that Alfred Nobel began experiments with NG as an explosive in construction work, and in these he was ably assisted by his father. Nonetheless, the death of Tsar Nicholas I in1855, the end of the war, and a change in government resulted in promises of trade being ignored and the workshop became bankrupted. Immanuel returned to Stockholm with his wife and youngest son Emil in 1859, broken and almost as poor as when he had left.

$$2KNO_3 + 3C + S \longrightarrow 3CO_2 + K_2S + N_2$$

gunpowder



$$4\,C_3H_5N_3O_9 \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

1, nitroglycerine
$C_3H_5N_3O_9$

Scheme 1. Gunpowder and nitroglycerine decompositions

Alfred remained in St. Petersburg staying in an apartment with his brothers [who subsequently established the *Branobel* (Brothers Nobel) oil company in Baku (Azerbaijan) in 1876 and started distilling oil on a 24-hour basis on an idea proposed by Dmitry Mendeleyev (during the late 19th century it became one of the largest oil companies in the world)]. He turned the kitchen into a laboratory and began the search for a ***safe*** way to manufacture NG on a large scale. He tamed the chemical to detonate at will, while simultaneously exploiting its power. Thus, a firmly stoppered glass tube placed inside a metal tube packed with black powder (the original gunpowder and almost the only known propellant and explosive until the mid-1800s) when ignited with a fuse and tossed into a waterway caused a notable underwater explosion.

Branobel wells, Baku (public domain image from the archive of Hazar Nesimi: http://en.wikipedia.org/wiki/Image:Oil_Nobel.jpg)

Rejoining his family in Sweden in 1863, Alfred continued work with NG and repeated the St. Petersburg experiments. He and his father had obtained a loan that allowed pursuit of their NG interests and they began manufacture at Heleneborg on the southern outskirts of Stockholm. Here, Alfred reversed the packing order by placing a small tube of gunpowder with its fuse attached into a tube of liquid NG. The results were excellent as explosion of the primary charge triggered the NG detonation and released the full power of the *blasting oil*. The initial device was simple and comprised a small wooden cylinder about 5 cm in length that contained a sealed charge of gunpowder with an attached fuse. The *Patent Detonator* was thus invented and it became the most important of Nobel's invention as it revolutionized the use of explosives. Refinements soon had the gunpowder replaced by mercury fulminate (**2**, Scheme 2)[3] in a copper tube and this *blasting cap* was patented in 1865.[4] Detonation of the fulminate triggered a shock-wave that, in-turn, detonated the NG.

$$Hg(CNO)_2 \longrightarrow 2CO + N_2 + Hg$$

2, mercury fulminate

Scheme 2. Mercury fulminate decomposition

On September 3rd in 1864 the Heleneborg plant suffered a major explosion that was heard throughout Stockholm. It demolished the workshop and six people died, including Alfred's 20-year old younger brother, Emil.[5] The accident has been attributed to Emil himself and had a dramatic impact on his father who never really recovered. The subsequent enquiry led to the first regulations on NG and these prohibited manufacture in residential areas of the city. Despite this, and the impact that it had on him, Alfred continued his work, at first on a barge moored in the middle of Lake Mälaren, a lake that flows to the Baltic Sea and past Stockholm at its outlet. Business prospered and an NG manufacturing plant was built at Vinterviken (Winter Bay), just outside Stockholm. Within a short time other plants were built in Germany, Norway and the USA as the use for the (NG) blasting oil in mining and construction work grew significantly. A further explosion in 1866 destroyed the Krümmel plant in Germany.

United States Patent Office.

ALFRED NOBEL, OF HAMBURG, GERMANY, ASSIGNOR TO JULIUS BANDMANN, OF SAN FRANCISCO, CALIFORNIA.

Letters Patent No. 78,317, dated May 26, 1868.

IMPROVED EXPLOSIVE COMPOUND.

The Schedule referred to in these Letters Patent and making part of the same.

Frontispiece of Nobel's 1868 US Patent 78317 taken from ref. 6.

Nobel was more than aware that the problems with NG lay in its transport and he had been conducting experiments to find a method of stabilizing the liquid. While working on a raft on the river Elbe outside Hamburg,[2] he found that the diatomaceous earth, kieselguhr, could absorb up to four times its own weight of NG giving a red powder that was safe to handle. Not only this, but it could be detonated with the mercury fulminate blasting cap and give the same force of explosion as liquid NG. Dynamite was born. It was patented in Sweden in 1867 and in the USA in 1868 as *Improved Explosive Compound*.[6] This invention is second only to his blasting cap.

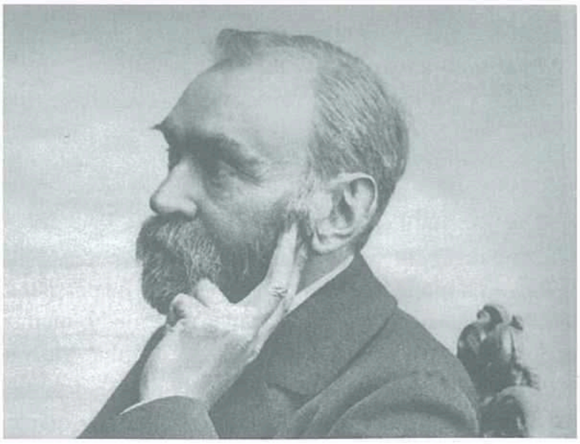
Replacement of the diatomaceous earth by nitrocellulose (guncotton or collodion and known from 1846) led to blasting gelatin or gelignite whose properties can be varied according to need; it was a favourite of the IRA in the not too distant past. By increasing the amount of NG to *equal* that of the nitrocellulose, Nobel obtained a material that was capable of being heated between rollers and pressed to a brick-like substance that could be pulverised. This was patented by Nobel in 1887 (while he was living in Paris) as *ballistite* [Nobel gunpowder; the composition was 10% camphor, 45% nitroglycerin and 45% collodion (nitrocellulose)] and, contrary to gelignite, it exploded less violently on detonation. Ballistite lent itself as a propellant ballistic force that resulted in subsequent improvements in the manufacture of ammunition. Nobel's ballistite competed quite successfully in many countries with the first smokeless powder, the French *Poudre B* (1886; *Poudre Blanche* or *Vieille powder* after inventor chemist Paul Vieille[7]), and also with the British *cordite*, a minor variation of ballistite.[8]

Despite success in many parts of the world, Nobel had problems in Britain. Parliament enacted a law in 1869 that prohibited the manufacture, import, sale, or transport not simply of NG but of any substance containing it. It was two years before Nobel was able to gain the support of Glaswegian businessmen and build a manufacturing plant at Ardeer on the Clyde estuary in North Ayrshire; NG production from *The British Dynamite Company* began in January 1873. After his death the name was changed to *Nobels' Explosives Company* and, in 1926 at the behest of its then chairman, it amalgamated with British Alkali, British Dyestuffs, and Brunner Mond to form *Imperial Chemical Industries*.[9] ICI accepted a take-over bid from Akzo Nobel in mid-August of this year. The delays in gaining access to Britain and its Empire, and in not patenting dynamite in Australia until 1872 (Patent No. 315, 30.5.1872) led to one Friedrich Krebs importing a dynamite variant *Lithofracteur* there. Despite violation of the patents, manufacture began at Deer Park, Victoria in 1874 with the *Australian Explosives and Chemicals Company* named in 1888. This aside, importation from Nobel's Explosives Company grew dramatically and the Nobel shareholding in the small Australian enterprise was increased such that, in 1898 it was acquired, became *Nobel (Australasia)* in 1925;, three years later incorporated into *ICIANZ*, which transformed into *ICI Australia*.[10]

From the mid-1860s until his death on December 10, 1896, Nobel built up an empire of about 90 different factories and laboratories in some 20 countries, normally retaining control himself. Despite the ever exhausting round of travel, he continued his studies not only into high explosives but also on many diverse chemical topics such as artificial silk, synthetic rubber and leather, anesthesia and blood transfusion (prior to the recognition of blood groups) such that, at the time of his death he held some 355 patents.[2] With his very competent, even brilliant investigators, he had tamed NG and provided a whole range of explosives for specific tasks. Thus, modest explosives were designed for mining coal and decorative stone while high brisant explosives (ones in which the maximum pressure is attained so rapidly that a shock wave is formed) were used for blasting hard rock.

The intensity of his work and travel did not leave much time for a private life and at age 43 apparently he felt like an old man. At this time he advertised for a *lady of mature age, versed in languages, as secretary and supervisor of household* and accepted Austrian Countess Bertha Kinsky who, after a very short time, returned to Austria and married Count Arthur von Suttner. Despite this the two remained friends and kept in contact. Over the years Bertha became increasingly critical of the arms race, wrote *Lay Down Your Arms* (1889) and was prominent in the peace movement seeking (and receiving) financial support from Nobel for a peace conference in Bern in 1892.

Following Nobel's death in San Remo (Italy), it came as a surprise to most that his amassed fortune of 33 M Swedish Crowns was to be devoted to prizes in chemistry, physics, physiology or medicine, literature, and peace. It seems that Nobel was a pacifist believing that his explosives ultimately would deter war, and he was sensitive to the criticism that rather than being a pacifist he was a promoter of war. Inclusion of the peace prize in the will was likely also influenced by Berta von Suttner. Importantly, his estate was not left to family members (his brothers were already dead) who had expectations. His executors were two employees Ragnar Sohlman, his personal assistant over his last three years, and Rudolf Lilljequist. The fact that the will was carried out with little opposition has to be credited to Nobel's nephew, Ludwig's son Emanuel, declaring to the King that he would do his best to ensure his uncle's wishes were respected. In mid-1898 a proposal was made that the children of his brothers receive one and a half years income conditional upon recognition of the will and agreement to make no further claims on the estate. This was accepted and the Articles for the Nobel Foundation were approved by King Oscar II on 29 June 1900.



Alfred Nobel from a photograph by Gösta Florman (1831–1900) (public domain image from *http://commons.wikimedia.org/wiki/Image:Mininobel.jpg*)

The first Nobel Prizes were awarded in 1901: van't Hoff (Leiden University, Netherlands) the chemistry recipient for *his discovery of the laws of chemical dynamics and osmotic pressure in solutions*; Roentgen (University of Würzburg, Germany) the physics winner *in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays (or x-rays)*; von Behring (University of Marburg, Germany), physiology or medicine *for his serum therapy to treat diphtheria*; René-François-Armand (Sully) Prudhomme (France) was the literature laureate *in special recognition of his poetic composition, which gives evidence of lofty idealism, artistic perfection and a rare combination of the qualities of both heart and intellect*; the Peace Prize was shared between Swiss businessman Henry Dunant *founder of the Red Cross and initiator of the Geneva Convention* and French economist Frédéric Passy *founder and President of the Société d'arbitrage entre les Nations*. The Norwegian Parliament awarded the 1905 Nobel Peace Prize to Bertha von Suttner.

The chemistry and physics prizes are decided by the Swedish Academy of Sciences, the physiology or medicine prize by the Medical Nobel Assembly at Karolinska Institute in Stockholm (one of the leading medical universities in Europe), literature by the Swedish Academy, and the peace prize by the Norwegian Nobel Committee. The awarding ceremonies take place in Stockholm and Oslo (Peace) on December 10 each year, the anniversary of Nobel's death. The Economics prize was added in 1968 by the Bank of Sweden at their tercentenary and first awarded jointly in 1969 to Norwegian Ragnar Frisch and Dutchman Jan Tinbergen *for having developed and applied dynamic models for the analysis of economic processes*.

The scientific brilliance of Alfred Nobel as chemist and chemical engineer, coupled with outstanding business and entrepreneurial acumen, are embedded in the gift to humanity of the Prizes that are named after him.

Postscript - Trinitrin and Alfred Nobel

To a chemist ***trinitrin*** (GTN)[11] is the same as nitroglycerine (NG) and, like the anticoagulant Warfarin that is a rat poison, it is named pharmacologically so as not to dispel public acceptance. It appears to have been reasonably common among chemists in the mid-nineteenth century to smell and/or taste the chemicals they made. Sobrero reported placing a small quantity of NG on his tongue finding it to be sweet, pungent and aromatic, but with the decided disadvantage of causing a severe headache. Two years later, in 1849, Constantine Hering tested NG on healthy volunteers finding that headache was caused with *precision*. As a pioneer homeopath in the US, he persisted with testing and used NG as a headache remedy, manufacturing it with the help of Philadelphia chemist Morris Davis who also assisted in the experimentation.[11]

In Britain, physician Alfred Field used NG in an old lady with severe chest pain and, following this 1858 success, others began to experiment with its use. However, Frederick Guthrie's 1859 studies on isoamyl nitrate (first synthesised in 1844 by Ballard who is more noted for his discovery of bromine from sea-water in July 1826) noted[12] that one of its most prominent properties was from the inhaled vapour to the extent that two drops of the liquid on an absorbent paper and held to the nostrils gave a throbbing of the arteries in the neck after about 50 sec. This was followed immediately by flushing of the neck, temples and forehead, and acceleration in heart rate. Guthrie suggested its use in resuscitation but its use as a vasodilator was recognized and it was in use for the next 20 years.[11] It was William Murrell who, in 1878, began to use NG for the relief of angina because of its immediate effect as opposed to the delay that occurs with isoamyl nitrate. Within the next four years NG was recognized as *the* remedy for angina.[11] Trinitrin in tablet form, or now more commonly as Nitrolinguol® spray, remains the most efficacious remedy for angina pectoris.

What must not be overlooked is that the workers in the NG factories unknowingly *tested* its effects simply by being there. Severe headaches and dizziness were common during the first few working days in the factory but the effects wore off after as tolerance grew. However, the tolerance is short-lived and the phenomenon of *Monday disease* (a recurrence of the symptoms) was seen among those not exposed over the weekend such that it became quite common for men to take a piece of the solid NG-containing product home to rub on their skin or else for them to wear work clothes contaminated by the NG during the rest periods so as to avoid the problems. Worse still was nitrate dependence that some of those chronically exposed gained. This manifested itself over the weekend when there was no exposure and gave rise to a significant over-compensation resulting in severe heart pain; in the worst cases death resulted from the *Sunday heart attack* and it claimed a few workers each year.[11]

But what has this to do with Alfred Nobel one may ask? Well, we know that Nobel suffered from poor health for most of his life. He complained of indigestion, headaches, and sometimes depression, and had a stay at a Bohemian spa as early as 1854.[13] Towards the end of his life he had spasms of intense pain (angina) and in 1890 his physicians recommended use of NG – he declined. In letters to Ragnar Sohlman he repeatedly commented on his state of health and the heart problems he was suffering. Some seven weeks before his death, he said (translated) *'My heart trouble will keep me in Paris for another few days at least until my doctors are in complete agreement about my immediate treatment. Is it not the irony of fate that I have been prescribed N/G 1 to be taken internally! They call it **Trinitrin** so as not to scare the chemist and the public'*.[13] He died some seven weeks later following a stroke that left him with partial paralysis.

One cannot but wonder how Nobel was affected by his constant exposure to NG. He was still working in the laboratory and performing experiments himself some eight weeks before his death. Thus, it seems more than reasonable to suggest that much of his ill health was caused by constant NG exposure over some 40 years and that, in essence, he suffered at his own hands and developed NG poisoning.[14] It is now known that tolerance to NG increases as the thiol (-SH) groups on vessel walls are oxidized and prevent stimulation of the guanylyl cyclase, the critical step in vasodilation; this tolerance is short-lived.

Continuous exposure to it (and other organic nitrates) can lead to malfunctioning of the cardiovascular system and can lead to ischemic heart disease, even in the absence of any narrowing of the arteries. The symptoms shown by Alfred match well to these, now recognised, features of long term exposure.

The essential discoveries concerning physiology of NG decomposition to nitric oxide and it behaviour as a signalling molecule in the cardiovascular system led to the 1998 award of the Nobel Prize in physiology or medicine to Robert Furchgott, Louis Ignarro and Ferid Murad.

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8. Cordite comprised 58% nitroglycerin, 37% guncotton and 5% vaseline by weight and, in acetone, it could be extruded as spaghetti-like rods initially called *cord powder* but subsequently termed cordite. It was patented in 1889 by Abel and Dewar, both members of the British government *Explosives Committee* that monitored foreign developments in explosives. Neither Poudre B nor Ballistite met with British satisfaction but cordite was accepted. The patent led to a major dispute with Nobel as the composition was, in his view, but a minor variation of his ballastite; Nobel lost the case but the decision was considered by one of the judges as unjust. Subsequently Nobel, who manufactured cordite for the British government at Ardeer in Scotland was paid a royalty not just on the NG but also on the cordite – see ref. 1, p. 331.
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Nanotechnology - Lessons From Mother Nature*

Alan Smith

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*In an earlier article (*This Journal, **2006**, *70,* 48-49*), the author asked* Does Nanotechnology Have a Sporting Chance? *and reviewed briefly the hype surrounding the field. In this article, Alan Smith illustrates how lessons from Mother Nature are resulting in the design of new nanotechnology applications. These applications, which relate to our everyday life, provide excellent examples that children and adults can relate to, and should be used to promote good science.*

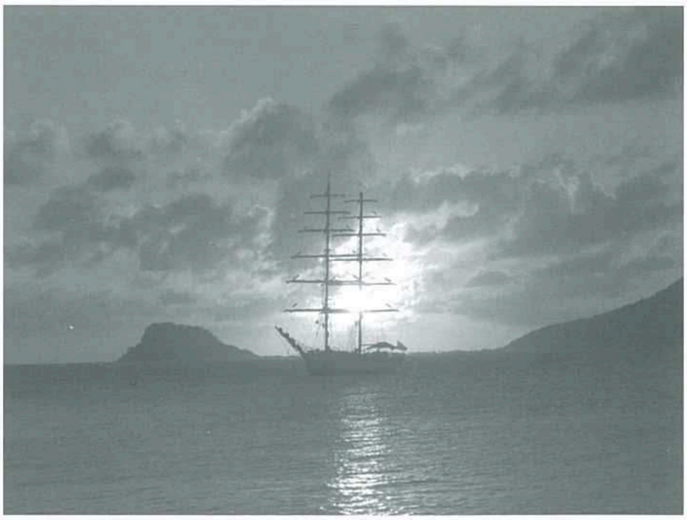


Photo credit: Alan Smith - Sunset over the Grenadines (Caribbean)—Palm Island.

Over the last hundred years Nobel Prizes have been awarded in medicine, chemistry, and physics for work that would nowadays be described as nanotechnology. Nanotechnology is certainly not new; Mother Nature has been the best exponent since creation!

For those not familiar with the nanoscale, it is about as small as you can get, and down at that molecular or atomic level it has been found that properties of things can change. To help understand how small the nanoscale is, it would take 80,000 nanoparticles in a row to be just the diameter of a human hair, and if a sea gull landed on the deck of an aircraft carrier the ship would sink in the water by only one nanometre (a millionth of a millimetre).

Although scientists are developing exciting new products that make use of the new properties offered by nanotechnology, nature has been the leader in this science. Geckos hang upside down on the ceiling because of nanoscale *hairs* on each toe. Each hair grips with a miniscule force, but when there are millions of these hairs on each toe it is able to support its own weight when it is upside down. In fact, if it was 200 times its own weight it would still be able to hang there. Industry is looking at copying this ability by developing more-effective adhesives.

There is a beetle that lives in the scorching heat of the Namibian Desert that gets its water through nanotechnology. Its back has a surface which repels water, but some bumps on its shell do not have this special surface. In the early mornings the water in the atmosphere condenses on those bumps and when the drop gets large enough it runs down the water repellent surface straight into the beetle's mouth. Such *hydrophobic* surfaces are now being used in textile applications; Hugo Boss sells suits that have self-clean surfaces based on nanotechnology coatings. Similar effects are being used by Gortex for wind and waterproofing. It is known as the lotus effect, since water just runs off lotus leaves.

Moths' eyes are antiglare and antireflective; if they were not then their predators would be able to pick them off much more easily. Scientists have copied the nanotechnology structure of those eyes and are able to produce antiglare and antireflective films, which could lead to digital camera screens that consumers can see on sunny days.

Many colour effects in nature are the result of nanotechnology. The colours in butterfly wings or the pearl effects of shells are due to light being bounced off nanoscale layers in the structure of the wing or shell. Christian Dior has copied this effect with their *Pure Poison* perfume bottle, which looks like a pearl due to nano-layers on the inside of the bottle. Dior was not the first to produce nanotechnology colour effects, the Romans left behind a glass cup known as Lycurgus' cup. Estimated to be 1600 years old, this piece in the British Museum looks jade green in natural light but when a bright light shines through it, it becomes a spectacular red color. This is because of a minute amount of nanoparticles of gold and silver in the glass that reflect light in a novel way. The effect is similar to the reds and yellows one sees at sunsets, where the light bounces off nanoparticles in the atmosphere. After Krakatoa exploded in 1883, there where incredible sunsets for decades, all due to nanoparticles.

Many sunscreen products use nanoparticles to bounce off the bad ultraviolet light and let through the good, tanning UV light. Each year, 1300 people in Australia die from skin cancer, so there should be some benefit from this nanotechnology.

Our own skeletons are self-assembling nanostructures. Again, scientists are copying such structures to make new materials that are stronger and lighter in weight. These new nanocomposite materials are finding applications in many cars now, where replacement of heavy metal parts with these strong and lighter-weight materials, enables more miles per gallon. Ford, General Motors, BMW, and others are all reducing the weight of their car models.[†] In addition, Mercedes has developed an anti-scratch surface for its cars that is based on nanotechnology. Sporting goods manufacturers are also making use of nanotechnology structures to obtain different properties. Roger Federer's tennis racquet, Easton baseball bats, and Padraig Harrington's golf clubs are made from nanocomposite materials.

It is estimated that there are already over 700 nano-based products on the market. So, it is no wonder that governments worldwide are investing heavily in this technology. It has been said that if developed countries are not involved in nanotechnology, they will become third-world nations very quickly. The timescales for taking ideas through research to production are shorter now than they have ever been. Nanotechnology is particularly multidisciplinary and the speed at which products are being introduced exceeds most previous developments.

We still have a lot to learn about nanotechnology from Mother Nature!

In addition to the energy saved by reducing the weight of cars (and aircraft), there are other applications that are beneficial to mankind. The UK company Oxonica has developed an additive based on cerium oxide nanoparticles that is added to diesel fuel at less than 5 ppm. The ingredient helps catalyze the *burn* better; improving mileage by up to 15 percent and reducing polluting exhaust fumes.

At the nanoscale, it is possible to detect things faster and more sensitively; a sniffer dog can find a human after an earthquake or a trace of a drug in someone's luggage because it is working down at the molecular level. A great deal of research is being conducted to detect diseases using nanotechnology before they get a hold in the body. In this regard, the US government is investing heavily in its *Cancer Nanotechnology Plan*. In terms of healthcare we are only seeing the tip of the iceberg.

Following the SARS outbreaks in the Far East, silver nanoparticles, which are commonly incorporated into wound dressings because of their antimicrobial properties, are now being used in other applications. Washing machines and refrigerators have been developed that use this technology to prevent mold. There are baby milk cartons, socks, and even underpants that use silver nanoparticles to reduce the possibility of infection.

The University of Leeds has a group of researchers using nanotechnology to develop nanofluids. By suspending nanoparticles in water or other liquids, these nanofluids can transfer heat up to 400 percent faster than other liquids. In a central heating system, nanofluids could increase efficiency without the need for a more powerful pump, thereby saving energy and providing major environmental benefits. Some researchers have theorized that nanofluids could be used during critical surgery to cool the brain so it requires less oxygen, thereby enhancing the patient's chance of survival and reducing the risk of brain damage. The technology could also be used to produce a higher temperature around tumors to kill cancerous cells without affecting nearby healthy cells.

I'll bet there is a creature somewhere that developed this technology long before the University of Leeds team applied it. We still have a lot to learn about nanotechnology from Mother Nature!

Dr Alan Smith is an associate director of the UK government's Micro Nano Technology Network, which is coordinating activities in nanotechnology throughout the UK. He is a member of the IUPAC Bureau and a member of the Committee on Chemistry and Industry.

[†] Note added by the editor: Most recently this has been noted in the Boeing 787 Dreamliner aircraft.

Chemistry Behind the News

Formaldehyde - the facts

Alarming headlines including phrases like *poisons in clothing* and *toxic clothing scare* have appeared recently. They were referring to the formaldehyde testing carried out by consumer watchdog programme, Target.

A rash of articles across the world reported similar facts including results from testing on the show that were *up to 900 times above the safe level.*

On the show formaldehyde testing was carried out on some items of clothing. The presenter said the tests measured the total formaldehyde in the garments both bound and free. The highest result of 18,000ppm was found for a pair of stain resistant pants. The safe level the programme quoted was 20ppm hence the reporting of a level 900 times above the safe level.

A Chemical Assessment Document on formaldehyde sponsored by several international bodies including the World Health Organisation, states for the general population 1-2% (10,000-20,000mg/l) formaldehyde, in solution, is likely to cause skin irritation. For hypersensitive people 0.003% (30mg/l) can cause dermatitis. The US Department of Labour states inhalation of formaldehyde above 5ppm can cause coughing and lower airway irritation.

A 1986 review paper by Hatch and Maibach said formaldehyde combines with protein in the skin by nucleophilic addition at the carbon atom. Formaldehyde also reacts readily with free amino groups so a glycine derivative is formed by contact between free formaldehyde and the skin. The paper also mentioned that between 0.1% to 10% was absorbed when radiolabeled formaldehyde treated fabric was applied to the skin.

Formaldehyde began being used in about the 1920s to produce durable press and wrinkle resistant textiles. Cotton is mainly made up of cellulose chains with only hydrogen bonds between them. There are no covalent crosslinks to keep the cellulose chains in the same position when wrinkled or washed. The process to produce wrinkle resistance uses formaldehyde in a reaction bath. Formaldehyde is reacted with a variety of other chemicals, one of the more common being dimethoxymethyl dihydroxyethylene urea. The reaction leads to crosslinks between adjacent cellulose molecules in the fabric that makes it wrinkle resistant by keeping the cellulose chains in position. Excess formaldehyde is generally not washed out by the manufacturers because it adds to the cost of production.

After the initial excess formaldehyde is washed out at home, ongoing release of formaldehyde from that bound in the clothing is dependent on a number of different factors. Generally its release decreases each time the clothing is washed. Chlorine bleach can stop the decrease of the release of formaldehyde if the chlorine affects the formaldehyde resin by breaking down the bonds. Also if a melamine based formaldehyde resin is used, chlorine can make the garment turn yellow. Sometimes increased pH can affect the resin finish leading to an increase in formaldehyde release after several washings since home washing is usually in alkaline conditions. Increase in temperature and humidity can also increase formaldehyde release.

Over the years better preparations with lower formaldehyde release have been developed. Patented formaldehyde free agents are now also available but at a higher cost. One example uses a polycarboxylic acid to react with the cellulose in the fabric while in the presence of a cyanamide catalytic agent.

There are no consistent limits worldwide on formaldehyde in clothing or textiles.

Japan has the tightest requirements. In 1973 to try and control exposure to hazardous substances, the Japanese introduced *The Control of Household Products Containing Harmful Substances Act*. Formaldehyde was one of the substances listed in this act. Japan based their formaldehyde limits on toxicity tests with a significant margin of safety. Clothes for babies aged zero to twenty-four months cannot contain any formaldehyde and other textile products must have a formaldehyde content below 75ppm. Clothing with a level below 75ppm only occasionally causes dermatitis in sensitive individuals.

Some of the articles about the recent New Zealand testing quoted European Union formaldehyde limits as being 30ppm for clothing in contact with the skin and 300ppm for other garments and fabrics. These levels however, are part of the requirements for the European Union eco-label. The formaldehyde limits are for the amount of free and partly hydrolysable formaldehyde in the final fabric. This label is a voluntary European Union scheme to encourage minimising the environmental impact of products.

This is no consistent mandatory limit for formaldehyde in textiles within Europe. Germany's Dangerous Substance Act states products with formaldehyde content of more than 1500ppm must bear labels stating; "This product contains formaldehyde and users are advised to wash the product before wearing so that the skin can adjust to it." Finland's standards are; a maximum allowable content of formaldehyde in products for babies under two, 30ppm, textiles with direct skin contact, 100ppm and textiles with no direct contact, 300ppm.

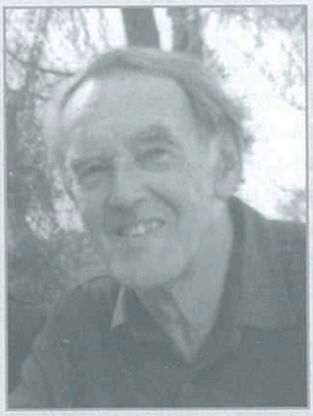
According to the New Zealand Ministry of Consumer Affairs and the Australian Competition and Consumer Commission, there are no standards for formaldehyde levels in textiles in either New Zealand or Australia.

Interestingly a report for the Organisation for Economic Cooperation and Development in 2006 found that despite mandatory requirements in various countries and Japan's law being quite strictly enforced for the last thirty years, textile and clothing exporters in the Philippines were often unaware of formaldehyde standards. It was also found there were limited certified product testing facilities to carry out the testing.

The New Zealand Ministry of Consumer Affairs has begun its own investigation into formaldehyde levels in clothing.

Formaldehyde is also used in many products including medium density fibreboard, some cosmetics and some soaps.

R.M. (Mac) SINCLAIR, MSc.(Hons), FNZIC (1920-2007)



In retirement

Robert Malcolm Sinclair was born in Christchurch on 15 June 1920, and died there on 2 May 2007. He was a Scientist, Science Manager and Innovator in the professional development of colleagues and young people.

Mac, as he was known to many, was educated at Christchurch Boys High School (1933-37) and, following matriculation, attended Canterbury College of the then University of New Zealand. He graduated MSc Chem (Hons.) in 1942 and subsequently was admitted as MNZIC and later honoured with Fellowship.

Following graduation, and at a time of urgency due to the war effort, he was initially drafted into the Army Medical Corps in February 1942. In May of that year he was assigned to the Melbourne Munition Supply Laboratories (part of Australian Defence at Maribyrnong) where he worked with Larry Hill and other colleagues under the formidable John Rischbeth for 5 years. These were his formative years in learning skills associated with coatings technology. Over this period he made some lasting friendships with personalities within the Australian coatings industry.

Mac returned to New Zealand in 1947 and took up a position as Chief Chemist with International Paints Ltd., in Miramar, Wellington. In December of that year he married Betty, at St Mary's Merivale, a church that touched his life at its beginning, zenith, and ending.

Undoubtedly, from a career perspective, the transition from government-structured wartime service to commercial reality must have proved challenging, and reflected the norms of that period. In a letter to this writer in 2003 he was moved to comment: *"When I joined International Paints in 1947 as Chief Chemist, I wasn't given a copy of the Code used for identifying raw materials – I was only a technical person. I of course quickly picked it up from the containers when sampling for quality control"*.

Mac was then offered a position at the DSIR Dominion Laboratory at Gracefield and in 1948 became Section Leader of the Paint and Oil Section of Chemistry Division. This position he held until his retirement in 1980 during which time he ably took an additional management responsibility as a Group Leader – with some three Sections (in various scientific disciplines) under his immediate care.

Research into paints had been carried out at Chemistry Division since the early 1930s with studies of paint durability on timber initiated by L.W. (Les) Wilkinson and carried on by G. Chamberlain. These were paralleled by tests on radiata pine by Forest Products initiated by A. W. (Alan) Mackney and I. J. (Van) Hodder. Under Mac Sinclair, the paint group was responsible for extending these studies to cover the effect of preservative treatments and the degradation of wood surfaces under clear coatings by light. In fulfilling its role of evaluating paint performance for government use it studied metal protective paints, underwater paints, road marking paints, and many others. When the writer joined the section in 1972 there was already a long established but small group of dedicated people attending to this work (including Len Bruce, John Kos and Sam Lister) and we all supported Mac in contributing advice to government agencies and the public at large. The Section's work also included oils under the guidance of Barry Jackson, Gavin Dougherty and Charles Harkin. Many within DSIR and the industry envied the reputation established by the Paint and Oils Section under Mac's guidance.

When the writer joined the Paint and Oil Section he was immediately taken under the wings of Mac Sinclair and Len Bruce. This was a very formative period for the writer and the essential disciplines of integrity, professionalism, and precision of expression in verbal and written English were instilled then; Mac's prowess as a teacher and mentor will never be forgotten. His mentoring also extended to another young scientist of that time, Mr Gavin Dougherty, who also remained his close friend in retirement.

Mac's professional interests in coatings extended well beyond the confines of the Laboratory. He was one of several dedicated personalities who established the fledgling Oil & Colour Chemists' Association in 1951 as the NZ Section of the parent UK body, being the founding Secretary. Later, in 1959, Mac was honoured by his election as Vice-President. He supported the Association in a quiet and unassuming manner, and with diplomatic skill, continuously until his retirement in 1980. The Association in 2001 further honoured him (along with Phil Hunt and Tom Slinn) with Life Membership on the recommendation of this writer.

In retirement Mac and Betty moved, first to Devonport and then subsequently to his beloved hometown of Christchurch. At this time his talents were turned to the enjoyment of literary groups and writing.

In conclusion, it can be said that Mac brought to his chosen profession, and in all his dealings with people, an unequalled integrity and sensitivity. He was an inspirational life model to all who had the privilege of his company. *"He lived respected and died regretted by all who knew him."*

His delightful wife Betty, children John and James and his four grandchildren survive him.

K.W. Dalzell, FNZIC

Conference Calendar

Biocide Basics, Internet, 16-17 October 2007,

A web tutorial designed to teach the basic materials and concepts involved in modern biocide systems.

www.coatings.de/webevents/tutorials_ec/biocides.cfm

8th International Seminar on Polymer Science and Technology, Tehran, Iran, 23-25 October 2007

Covering all aspects of polymer science, engineering and technology.

www.ispst2007.com

10th Conference on Pharmacy and Applied Chemistry, Ascona, Switzerland, 21-24 October 2007

www.eurostar-science.org

11th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-11), Internet, 1-30 November 2007

Further details available at the website: *www.usc.es/congresos/ecsoc/11/ECSOC11.htm*

2007 Symposium on Chemical Physics, Waterloo, Ontario, Canada, 9-11 November 2007

http://scp.uwaterloo.ca/

21st Conference of Residue Chemists, Melbourne, Australia, 12-15 November 2007

3rd Conference for the International Congress of Chemistry and the Environment, Kuwait City, Kuwait, 18-20 November 2007

Oil - the environmental impact

http://www.icce-kwt07.kuniv.edu/

What's in Our Water: The significance of trace organic compounds, Canberra, Australia, 21-22 November 2007

2nd Australian symposium on ecological risk assessment and management of endocrine disrupting chemicals, pharmaceuticals and personal care products in the Australasian environment.

www.clw.csiro.au/conferences/ourwater/

Molecular Modeling 2007, Melbourne Australia, 27-30 November 2007

www.wehi.edu.au/news/events/MM2007/index.html

CHEMRAWN XII, The Role of Chemistry in Sustainable Agriculture and Human Wellbeing in Africa, Western Cape Province, South Africa, 2-5 December 2007

http://www.chemrawn.co.za/

The 10th Pacific Polymer Conference, Kobe, Japan, 4-7 December 2007

www.spsj.or.jp/ppc10/

Singapore International Chemistry Conference 5 & APCE Asia-Pacific International Symposium on microscale separation and analysis, Singapore, 16- 19 December 2007

http://sicc2007.org/

International Symposium on Catalysis and Fine Chemicals 2007, Singapore, 17-21 December 2007

www.cfc2007.org/

Trends in Surface Chemistry, Bolans Village, Antigua and Barbuda, 7-10 January 2008

The 10th Eurasia Conference on Chemical Sciences, Beyond Borders, Manila, Philippines 7-11 January 2008

http://eurasiachem10.philippinechem.org/

2008 Winter Conference on Plasma Spectrochemistry, Temecula, California, USA, 7-12 January 2008

http://icpinformation.org/uploads/2008_Winter_Conference_Registration.pdf

Drug Discovery Conference 2008, Small Molecule Drug Discovery: from early-stage to the clinic, Bolans Village, Antigua and Barbuda 17-20 January 2008

Isranalytica 2008, 11th Annual meeting of the Israel Analytical Chemistry Society, Tel-Aviv, Israel 22-23 January 2008

www.isranalytica.org.il/

Tenth International Symposium on Advances in Extraction Techniques 2008, Bruges Belgium, 28-29 January 2008

www.ordibo.be/htc/index.html

New Zealand Trace Elements Group Conference 2008, University of Waikato, 13-15 February 2008

www.tracenz.org

International Symposium on Biothermodynamics, Frankfurt, Germany 21-22 February 2008

http://events.dechema.de/Biothermodynamics_2008

Chem. 05, Green and Sustainable Chemistry for Developing Countries, Cairo, Egypt, 3-6 March 2008

http://chem05.cu.edu.eg/

Pittcon 2008 conference and expo; 59th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, USA 1-7 March 2008

www.pittcon.org/

Organic Process Research and development, the original process chemistry conference Dublin, Ireland, 11-14 March 2008

10th Young Scientists conference on Chemistry, Rostock, Germany, 27-29 March 2008

www.jcf-fruehjahrssymposium.de/2008/

Post codes

The NZIC office would like members to email their new postcodes to so we can update our records.

Please email your new postcode to: *nzic.office@nzic.org.nz*

European Patent Law Update

By Blair Hesp

As New Zealand is a relatively small country, a large proportion of any returns on intellectual property investment are likely to be derived from large markets such as Europe and the US. Many of the 32 member states of the European Patent Convention (EPC) are likely to rank highly on the list of countries in which a New Zealand patent applicant will want to obtain protection. Therefore, it is worth keeping up to date with European patent law to appropriately tailor your IP strategy for that market, especially with the EPC 2000 coming into force in December 2007.

Post-grant Amendment Of European Applications

For many reasons a patent owner may decide that it is necessary to amend a patent specification after the patent has been granted. For example, patent examination and grant may occur at different times in different jurisdictions. If any issues affecting the validity of a patent arise during the examination of an application in one jurisdiction, it may be desirable to amend any corresponding patents which have already been granted.

Previously the owner was required to request an amendment to a granted European patent in each state where the patent is in force. Under EPC 2000 this process has been streamlined. Now it will be possible to file amendments to a granted European patent centrally at the European Patent Office, rather than in each individual state. This should reduce the costs and inconvenience associated with requesting amendments after grant in up to 32 countries.

European Incentives For Drug Development

There are also two provisions for extending pharmaceutical patent terms in Europe which may not be well known. It is well known that a number of years may pass between the grant of a patent for a pharmaceutical compound, and approval for sale. Because of this delay many jurisdictions, including Europe, offer drug development incentives, such as extensions beyond the standard 20 year patent term. However, it is also possible to gain additional extensions for particular classes of pharmaceuticals.

Firstly, an additional extension of up to two years may be granted for "orphan drugs". Orphan drugs are developed to combat relatively rare diseases. Given the low prevalence of some diseases, and therefore the limited potential return on any investment in drug development, an extended patent term is offered as an incentive to develop orphan drugs.

Secondly, European Regulation No. 1902/2006 has introduced an alternative additional extension of up to six months for pharmaceuticals, provided that data supplied in conjunction with the request for European drug marketing approval includes data gathered using an approved paediatric investigation plan. This provides an incentive to perform paediatric investigations during clinical trials, and to develop drugs for childhood diseases. However, this extension may not be granted in addition to an orphan drug extension.

Second Medical Use Claims

The original EPC was drafted over 30 years ago, and did not contemplate the introduction of "Swiss style" claims as an alternative to claims directed to methods of medical treatment of humans.

In Europe, claims for a new non-medical industrial use of a known compound can be drafted as follows:

A compound X for use in process Y.

While a similar claim format could also be used for a first medical use of a compound, the introduction of EPC 2000 has resulted in this claim format being considered to be acceptable for subsequent novel medical uses, as well as novel non-medical uses of known compounds. With this claim format being considered to be allowable for claims directed to medical uses of known compounds, "Swiss style" claims may effectively become redundant in Europe.

New Addition To The Epc Countries

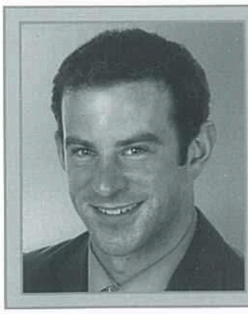
As of 1 January 2008 Norway will become the 33rd country to be included within the bounds of the EPC. Norway has been a party to the EPC since its inception in 1973, but has only recently decided to fully accede to the convention. For patent applicants wanting to file in Norway this is likely to result in significant cost savings because of the streamlined regional examination and grant procedures associated with the EPC.

When planning an intellectual property protection strategy it is important to keep up to date with the changes in potential markets. An intellectual property strategy should be tailored to each jurisdiction in which you want to gain protection, as well. This also demonstrates that professional intellectual property advice should be sought early in order to realise all options for the commercialisation of intellectual property.

A reminder: if you have any queries regarding patents, or indeed any form of intellectual property, please direct them to:

Patent Proze
Baldwins
PO Box 852, Wellington

Email: *email@baldwins.com*



Blair Hesp of Baldwins specialises in chemistry and biotechnology patents. Blair joined Baldwins in 2006. He has a PhD in pharmacology from the University of Otago as well as a NZDipBus with a management focus. Blair is currently studying towards a law degree and registration as a patent attorney.

Target Compound Analysis: A Step Ahead with Multi-Targeting LC-ESI-TOF MS

Matthias Pelzing, Bruker Biosciences Pty Ltd, Bio21 Institute, University of Melbourne,
Petra Decker, Christian Neusüß, Bruker Daltonik GmbH

The usefulness of LC–MS-MS methods for the unambiguous identification and quantification of pesticides in complex matrix samples is well known. Especially triple quadrupole systems have proven to be useful for this task due to their high specificity in MS-MS mode and their low detection limits.

However, working in MS-MS mode makes any MS system blind for all other compounds than the current MS-MS transition is designed for. Therefore, it is difficult to develop methods for simultaneous analysis of high numbers of pesticides. Thus, other ways of achieving specificity are of interest, such as the high mass accuracy and mass resolution of an ESI-TOF system. It can generate high specificity without limiting the number of simultaneously observed target compounds: Multi-targeting (2,3).

Molecular Formula Generation: The Isotopic Pattern filter

With high mass accuracy alone, confident molecular formulae mostly cannot be generated. An isotopic abundance pattern filter needs to be applied to reduce the number of molecular formula candidates (1) if for example the presence of a putative compound has to be confirmed.

Using an actual ESI-TOF MS and a sophisticated software solution, ESI-TOF MS is a key to both, simultaneous screening for multiple targets and sum formula confirmation:

1. Due to mass accuracy apparently independent of peak intensity, it is possible to generate extracted ion traces with a window down to a few mDa, allowing for extreme selectivity and simple and fast identification.

2. Due to the conserved correct isotopic pattern, it is possible to reduce the number of possible hits within a given mass interval by at least an order of magnitude. The derived SigmaFit™ strongly helps to find the correct elemental composition (*Figure 1*). For a similar confidence with mass accuracy alone, 50 ppb (parts per billion; 10–9) would be required - based on the unambiguous formula generation from reserpine; a 609 Da molecule.

Experimental

Different matrix samples, spiked at various levels with a commercial pesticide standard (Ehrenstorfer, Pesticide Mix 34) were analysed using an Agilent 1100 LC system (Agilent Technologies) interfaced with a micrOTOF ESI-TOF MS (Bruker Daltonics). An RP-HPLC column (3 µm particles, 2.1 x 125 mm Hypersil ODS. C18 material, 0.2 mL/min flow-rate) with an acetonitrile/water (1 mM NH4OAc)- gradient (5–55% ACN in 45 min) was applied for separation. The micrOTOF was equipped with an orthogonal ESI source and operated in positive mode. Calibration was performed externally prior to a sample series with a sodium formate solution, and additionally internally for each chromatogram by injecting the calibrant at the beginning and at the end of each run via a six port divert valve equipped with a 100-µL loop.

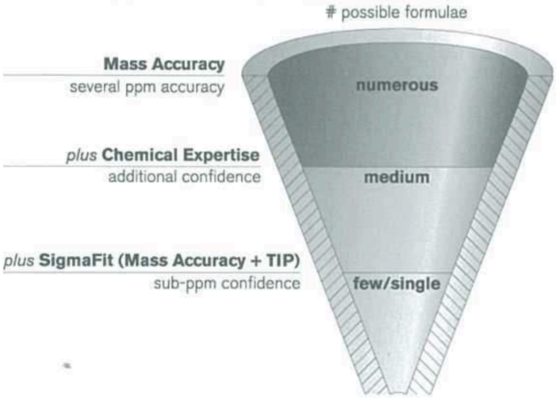


Figure 1 Reduce the number of molecular formula candidates: Mass accuracy, chemical knowledge and SigmaFit, the combination of accurate mass and True Isotopic Pattern analysis (TIP) clearly limit the number of possible formulae - for confident determination of the elemental composition of a given peak in LC–MS.

Experiment 1: Selective Recovery of Three Pesticide Isoforms from a Plant Extract

The selectivity of the method based on accurate mass traces is demonstrated for three azine isoforms spiked in chamomile (*Figure 2*). A window of 10 mDa does give a dozen of peaks, whereas a selectivity of a mass trace defined to a window of 3 mDa is sufficient for unequivocal identification. Retention time is required for the attribution of the individual isomers. Detection limits well below 2ppb have been determined, both for standards (*Figure 3*) and for spiking this amount in various matrices (*Figure 4* for lettuce extract).

A basic requirement for reliable detection of compounds with such narrow mass traces is the mass stability for a wide dynamic range over the entire peak. As figure 3 shows, this mass stability is given for at least 4 orders of magnitude.

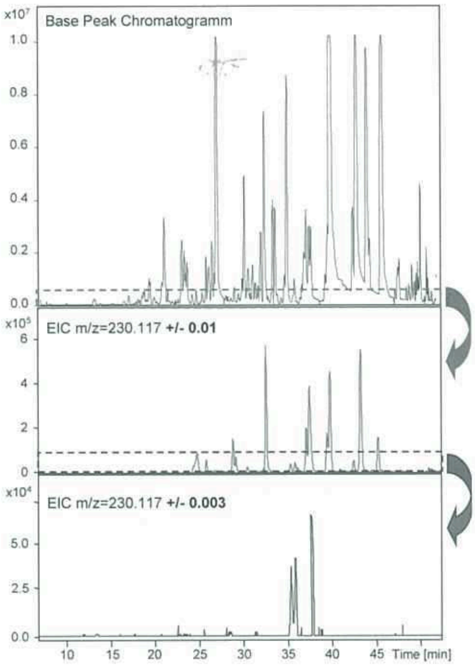


Figure 2 Base Peak chromatogram (top) of a chamomille extract spiked with pesticides on the level of 10 ppb. Mass traces of m/z = 320.117 (corresponding to [M+H]+ of the spiked Sebutylazine / Propazine / Terbutylazine ($C_9H_{16}ClN$)) are shown with an accuracy of 10 mDa (middle) and 3mDa (bottom).

Experiment 2: Multi Target Compound Analysis: Automated Detection of Multiple Pesticides with Database Search

Automated target detection for the pesticide standard mix spiked to a lettuce extract can be achieved by automated peak detection on the EICs expected for the [M+H]+ ions of each compound in a database. This database contains the names, sum formulas, exact masses and retention times for about 230 pesticides.

As shown above, a mass window of 3 mDa allows for selective detection of the compounds - if present. Based on accurate mass and known retention times the compounds present in the sample are identified. For each identification candidate additionally the theoretical isotope abundance pattern is compared to the experimental one. The derived SigmaFit™ values serve either for confirmation of the putative compounds or prevent from false positive identifications. *Figure 4* shows the EICs and database search results for the spiked lettuce extract.

Conclusion: Exponentiate the Confidence of ESITOF MS Measurements

Screening of several hundreds of possible pesticides is easily feasible with one single ESI-TOF MS run. Based on accurate mass, a high selectivity is achieved. Even over a dynamic range of 4 orders of magnitude, the mass traces could be defined within 0.003 Da. With sensitivity in the sub-ppm-range, pesticides can be readily characterized on the level of policy requirements in a variety of matrices.

Efficient multi-target screening using this system was also reported elsewhere: Toxicological drug screening in urine was based on accurate mass, SigmaFit isotopic pattern analysis and automated database search. In automatic runs, correct SigmaFit values and accurate masses were achieved over a wide dynamic range, while a mean mass error was only 2.51 ppm (4). Compared to classical approaches by triple quadrupole instruments, an ESI-TOF MS solution allows to screen a high number of targets within one LC-run and without the loss of sensitivity; it allows identification of unknown peaks based on accurate mass and isotopic pattern information (SigmaFit) while data can be archived and reprocessed later for additional compounds as well as data can be profiled for further statistical evaluation.

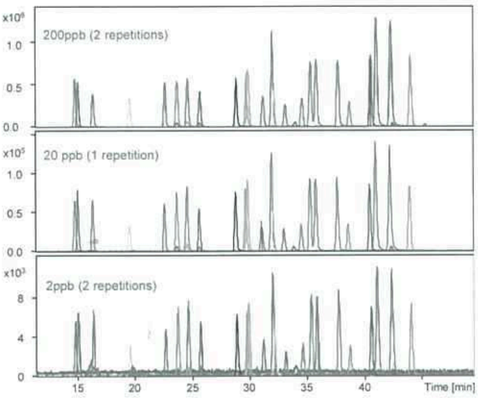


Figure 3 Five repetitions at three concentrations of a pesticide standard, containing 28 pesticides.

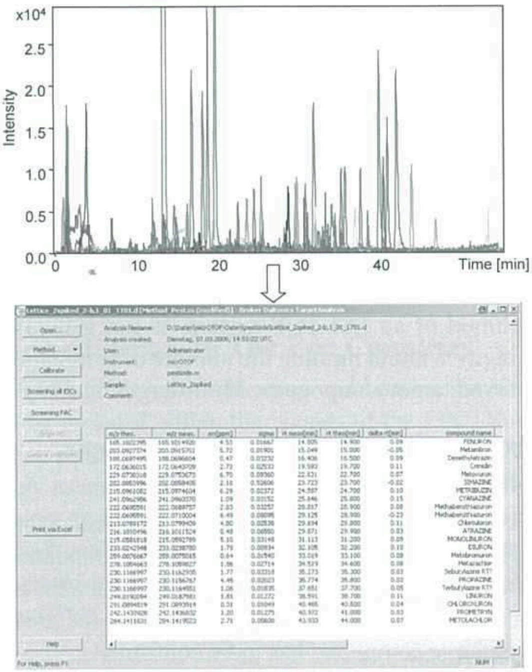


Figure 4 Mass traces of 28 pesticides spiked to an extract of lettuce on the level of 2 ppb (top) and resulting search in a database, based on accurate mass, sigma fit and retention time.

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Help Wanted

Dr ***Joan Mattingly*** is writing a biography of the late ***Brian Shorland*** and would like to identify as many as possible of those in the photograph. ***Dick Grimmett*** is seated (in suit) and ***Peter de la Mare*** and ***Brian Shorland*** are the 2nd and 3rd from the left. The other members are could be former co-authors with Brian and are thought to comprise: ***L. W Bruce, S. Brooker, F. Collins, Doris Johanneson, K, Seelye, C. Barnicoat, Winifred Tuck, Miss. J. Russell, D. M .P. Sorrell, L. Bruce, K. Heyes***.

If you think you can identify anyone please let the Editor know (*brian.halton@vuw.ac.nz*).

New Zealand Science Mathematics and Technology Teacher Fellowship Scheme - *Chemistry Projects Needed*

NZ Sciences, Mathematics and Technology Teacher Fellowships, funded by the NZ Government and administered by the Royal Society of New Zealand (RSNZ) allows teachers paid release from school for up to twelve months to work on research or technological projects. Teachers work with a host organisation in the development of the project. Applications are due mid-July each year. In the thirteen years that the Teacher Fellowship Scheme has been in existence few teachers have applied for chemistry related projects.

During 2007/2008 RSNZ is also trialling Short Term Teacher Fellowships where teachers are placed within a host organisation for up to two terms to carry out an assigned project. RSNZ has recruited hosts and has identified projects suitable for these Teacher Fellowships.

Currently projects have been identified for primary or secondary teachers in many geographic areas of the country. Contexts include: social sciences, mathematics, statistics, environmental education, conservation, physics, astronomy, robotics, science, biology etc. Projects are frequently being developed and are advertised on the RSNZ website as they come available. Closing dates for these Fellowships vary throughout the year.

Currently we have no chemistry related projects. John is actively seeking hosts with potential projects.

For more information about the trial and projects go to:

Website:	www.rsnz.org/awards/teacher_fellowships
Contact:	john.auty@rsnz.org

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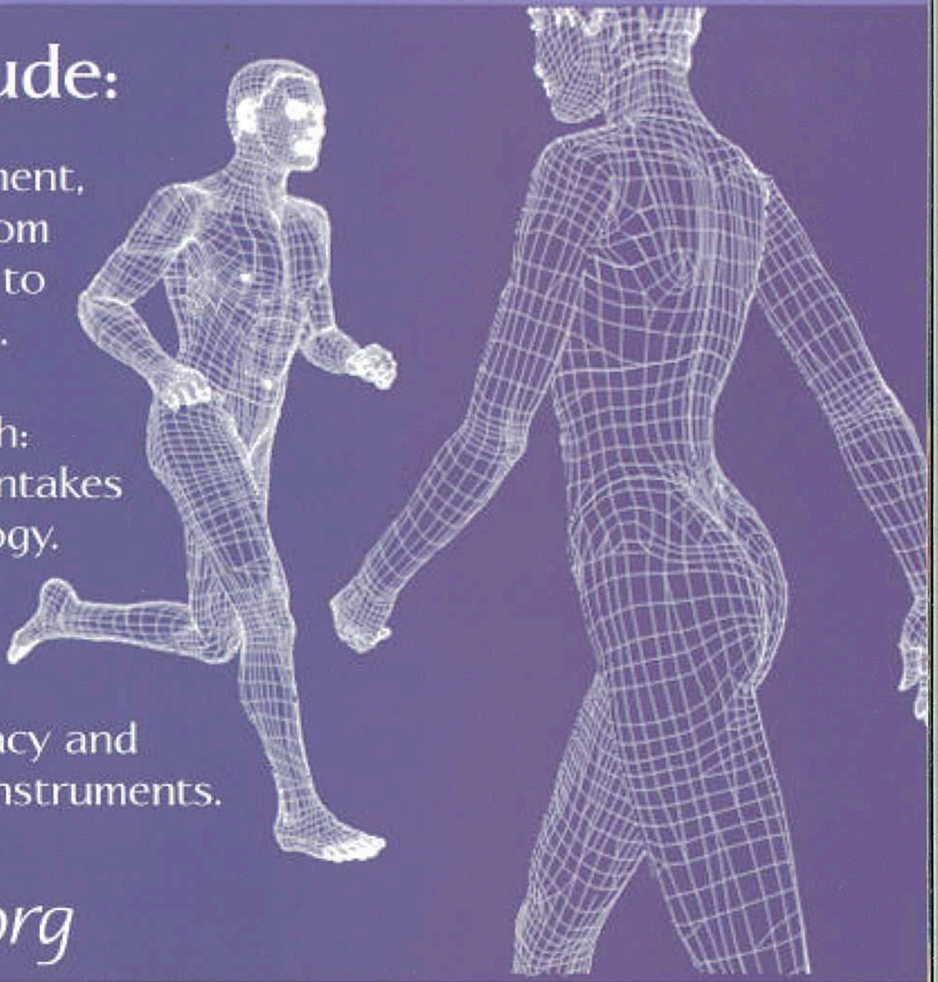

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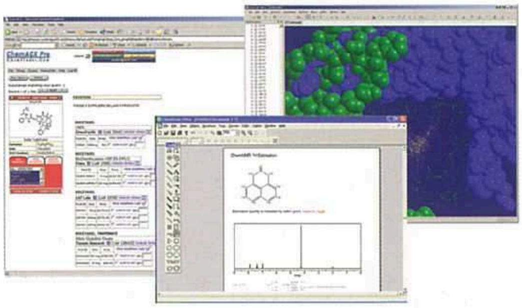

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