Chemistry IN NEW ZEALAND

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Articles and Features

Other Columns

Comment from the President

Welcome to the first issue of Chemistry in New Zealand for 2016. It is my genuine pleasure to be able to serve the NZIC as president for 2016. My thanks go to Ian Brown for his sterling work as immediate Past-President and also to the unsung heroes of the organisation - honorary general secretary Richard Rendle and treasurer Colin Freeman - who continue to serve the national body of the NZIC tirelessly.

This year will see the NZIC quite active on a national level. Look out for the NZIC salary survey in the first part of the year. The last one was published in 2006 (see: http://nzic.org.nz/CiNZ/articles/salary_70_3.pdf) so it will be rather interesting to see how the dynamics have changed in the intermittent ten years. In addition, the biennial (more or less) national conference is on again this year so please clear your calendars for 21 – 24 August. The Manawatu Branch is trying a few new things this time around, such as a mid-year conference in a winter wonderland. The location is at the Millennium Hotel in Queenstown. I invite you to check the website often for updates (www.nzic16.org). The plenary lectures are to be given by both international and national leaders in the chemical sciences and science communication fields.

It is clear from the biannual council meetings that membership of the NZIC is in slow decline. As part of my presidential tour of the Branches I intend to engage with local members to hear their thoughts on how the NZIC organisation can better help and represent the membership. There are clearly some things that could be improved upon such as communication between Branches and the NZIC website should serve as a platform for this. I encourage you to get involved with your local activities, as an active society is a strong society.

I find myself writing this after a recent meeting with the RSC NZ branch chair. There has been some heightened activity around a number of the international chemical societies in New Zealand in recent months, notably the RSC (and ACS). I see this as an opportunity for the NZIC to embrace and work alongside these organisations. The New Zealand chemical community is too small for a competitive environment amongst societies and I believe there is common ground which can strengthen all of the societies and ultimately the discipline of chemistry within New Zealand. It was pleasing to hear from the RSC representative that the intention is to work very closely with the NZIC.

I wish you all a productive and successful year and look forward to meeting you all during my Branch visits and at the conference.

Biographical Note

Paul Plieger is an associate professor specialising in inorganic and analytical teaching and research in the Institute of Fundamental Sciences at Massey University. He completed his undergraduate and postgraduate degrees at the University of Otago. His PhD, completed under the supervision of Professor Sally Brooker, involved the synthesis of both macrocyclic and acyclic dimetallic complexes, exploring the ability of these metals to communicate across a pyridazine bridge. Three postdoctoral positions followed, the first was located at Massey University in Palmerston North on a project lead by Professors Anthony Burrell and David Officer. The project involved the design and synthesis of large porphyrin arrays for light harvesting applications. This was followed by a position at the University of Edinburgh, Scotland, under the leadership of Professor Peter Tasker. In this project the design and synthesis of ditopic receptors were needed for use as reagents in the hydrometallurgic extraction of copper. The third and final postdoctoral position was undertaken at Los Alamos National Laboratory. This was under the joint leadership of Drs Kevin John and Anthony Burrell and required the design and synthesis of chelating ligands for the encapsulation of beryllium.

In 2004, Paul joined the chemistry staff at Massey University as a lecturer, moving to senior lecturer in 2006 and associate professor in 2014. His current research interests are concerned with the design and synthesis of new inorganic complexes for a variety of applications. He teaches into both the inorganic and analytical chemistry programmes. He is currently the chemistry major leader, which has the primary role of managing the chemistry degree undergraduate teaching at the Manawatu campus. As well as being a fellow of the New Zealand of Chemistry, he is also a member of the Royal Society of New Zealand, the Royal Society of Chemistry and the American Chemical Society.

Paul Plieger
NZIC President

From the Editor

Happy New Year!

As we welcome our new NZIC President for 2016, Paul Plieger, we extend congratulations to our immediate past President, Ian Brown, who was awarded both the Hector Medal by RSNZ and the Shorland Medal by NZAS in November. These awards recognise the significant contribution that Ian has made to materials chemistry research, more details of which can be found in this issue of *Chemistry in New Zealand*.

The NZIC salary survey will soon be made available, with all members encouraged to participate. It will take the form of an online survey which will be similar in format to the previous reader survey, although the questionnaire will be considerably more detailed. If you would prefer to complete a printed version of the survey, please contact me for a copy.

For contributors wishing to submit an article for publication, please check the submission deadlines and author guidelines by contacting either me or the appropriate Branch Editor. I am keen to see each issue being distributed to readers earlier in the month of publication which means there is less flexibility in accommodating late submissions. Please also support your Branch Editors when they ask for news items. The reader survey really highlighted the value that is placed on the Branch News section, so your input is vital to keeping this aspect of our publication relevant and interesting.

Best wishes for 2016.

Cath Nicholson

New Zealand Institute of Chemistry

supporting chemical sciences

January News

NZIC NEWS

In November Dr *Ian* ***Brown*** of Callaghan Innovation was awarded the Shorland Medal by the NZ Association of Scientists and the Hector Medal by the Royal Society of NZ. The Shorland Medal is awarded in recognition of major and continued contribution to basic or applied research that has added significantly to scientific understanding or resulted in significant benefits to society. The Hector Medal is awarded for work of great scientific and technical merit in chemical sciences (for further details see page 9).

AUCKLAND

The University of Auckland

Centre for Green Chemical Science

The successful launch of the Centre for Green Chemical Science and a one day symposium on green chemistry was held on 8 September at the University of Auckland. The day started with welcomes by the Head of School, Professor *Kevin* ***Smith*** and the acting Dean of Science, Professor *Jim* ***Metson***. The Centre was then formally launched by the Vice-Chancellor, Professor Stuart McCutcheon. Over 150 people from academia, government labs and industry attended the symposium. Two keynote addresses were given by Professor Milton Hearn, who is Director of the Green Chemistry Centre at Monash University. Invited speakers included Malcolm Rands – CEO of Ecostore, Chris Mulcare of Pure Advantage and Professor Paul Kilmartin from the School of Chemical Sciences. Another highlight of the day was the cluster of three-minute talks by University of Auckland researchers who spoke about their green chemistry research. Topics ranged from biomaterials derived from protein waste to smart catalytic surfaces for water purification. The day ended with a networking session that facilitated interaction between academics, industry participants and students.

Congratulations

We congratulate Professor *Penny* ***Brothers***, Professor *Jadranka* ***Travis-Sejdic*** and Professor *James* ***Wright*** who have been successful in the 2015 Marsden fund. This was remarkable success for the School of Chemical Sciences.

Dr *Marsilea* ***Harrison*** has received the 2015 Rutherford Foundation Trust Award. Marsil will work on a research project entitled *Promoting cartilage regeneration by the development of growth factor-loaded polymerosome carriers with analysis by electrochemistry* that she will undertake at Imperial College London, UK, in the laboratory of Professor Molly Stevens. Marsil obtained her PhD in 2013 under supervision of Professor Jadranka Travas-Sejdic.

Congratulations to Reece Oosterbeek (Photon Factory) who has been awarded a Woolf Fisher Scholarship to study for his doctorate at the University of Cambridge in the UK.

Congratulations to *Bowen* ***Liu*** who has commenced PhD studies at Stanford University. Bowen completed conjoint BSc and BCom degrees at the University of Auckland, and then in July completed a BSc (Hons) in the School of Chemical Sciences working with Penny Brothers and David Ware. Bowen's excellent academic record earned him the opportunity

Centre for Green Chemical Science: Prof James Wright (Director), Ms Anoma Ratnayake, Dr Viji Sarojini and Dr Jon Sperry

Prof Kevin Smith (Head of SCS) with the Vice-chancellor Prof Stuart McCutcheon at the inaugural one-day symposium of the Centre for Green Chemical Science

Centre for Green Chemical Science Steering Committee: Dr Jon Sperry, Prof James Wright (Director), Dr Viji Sarojini and Prof Penny Brothers with invited speakers Malcolm Rands (CEO Ecostore), Chris Mulcare (Pure Advantage), Prof Milton Hearn (Director of the Green Chemistry Centre at Monash University) and Prof Paul Kilmartin (SCS)

to study for a PhD at Stanford – he had to choose between offers from Cornell, Berkeley and Stanford! Well done Bowen!

Congratulations to Xindi (Andy) Wang who was one of six University-wide finalists in the PhD three-minute thesis competition. At the competition Andy talked about *Time resolved Raman spectroscopy of aryl diphosphenes* using just one slide and no other props.

Patricia Albani (supervised by Dr Douglas Elliot (Auckland University and ESR)and Dr Rachel Fleming (ESR)) won first prize for her poster on identifying blood using messenger RNA at the 2015 Faculty of Science poster competition. Andrew Chan (supervised by Dr Geoff Waterhouse) and Lakshika Perera (supervised by Professor Penny Brothers) were both awarded merit certificates. Congratulations to all three students, and their advisors!

Rakesh Arul (3rd-year BSc Chemistry & Engineering) has won a best poster prize at the 13th International Conference on Laser Ablation. He has been doing research in the Photon Factory since he was a first year student, and the project that won him a prize (and was submitted with him as lead author) is about direct writing graphene into graphene oxide using laser pulses.

The New Zealand Institute of Advanced Study (NZIAS), Massey University, Auckland

Our new organic chemist at Albany, Thomas Fallon, has received a Marsden fast-start working on *Molecular metamorphosis: new synthetic methods and design*. Peter Schwerdtfeger finished his (sold-out) Rutherford Medal Tour in New Zealand introducing super-heavy elements to a general audience.

CANTERBURY

Trivia and Truffles

On 16 September, the Branch (in conjunction with ChemSoc, the Chemistry Student's Society) held the annual Trivia and Truffles quiz night at the University of Canterbury Staff Club. The previous weekend various members of both committees (and some smaller, louder helpers) invaded *Jan* ***Wikaira*** and Don McNickle's house to make the truffles (and try not to eat them all). A fun time was had by all, although Jan is probably still picking coconut out of her carpet. Eleven teams entered the quiz, with a wonderful mix of undergraduate and postgraduate students, academic staff and chemistry professionals. There were lots of rounds, all with chemistry-related answers including a music round and a “Chemistry, the naughty bits” for which there was a spot prize of some sexy socks (won by *Sarah* ***Jamieson***). In that vein, the team from ChemSafety also won a spot prize for best team name, (not for printing here...).

To ease the strain on the marking team, at the end of each round peer-to-peer marking was invoked, leading to some rather interesting “motivational” comments, thanks Nic...

The Atoms Family who were *Nathaniel* ***Gunby**, Andrew* ***Wallace**, Andrew* ***Flanagan*** and *Chris* ***Burn*** took the overall honours. Jesse’s Taken (*Stewart* ***Alexander**, Vivek* ***Poonthiyil**, Jesse* ***Laurila*** and *Davey* ***Lim***) were second, with Stewart’s swotting for University Challenge obviously paying off! Entropy is not what is used to be (*Daniel* ***Smith**, Sylvia* ***Mongillo**, Alison* ***Faulls*** and *Sarah* ***Lilley***) were third, an excellent showing from them putting several staff teams in the shade!

Many thanks to *Michael* ***Edmonds*** (CPIT) for being our tireless quizmaster, *Jimmy* ***Whitmore*** (UC) and *Darren* ***Saunders*** (ESR) for checking the marking and adding up the scores, and to Charles and his Staff Club crew for help setting up the room and hauling pizza up the stairs!

NZIC Seminars

The NZIC President’s Lecture 2015 was given on 4 November by Ian Brown, Callaghan Innovation, entitled, *Modern ceramic chemistry – a journey from clay science to 3D Printing.* This well-attended talk described how the development of ceramic chemistry has transformed the bare bones ‘cups, saucers and bricks’ technology developed by the New Zealander J. W. Mellor and others in the early 1900s into the development of high performance, high functionality materials that we now recognise in contemporary ceramic tap washers, cutting tools, fuel cells, superconductors and space shuttle tiles. Modern ceramics research is very much shaped by application of research tools we now take for granted – electron microscopy, solid state NMR, thermal analysis and thermodynamic analysis software - tools that Mellor could never have imagined. The presentation showed how these and other tools have transformed ceramic and materials science in New Zealand and internationally through enabling understanding and use of the key relationships between ‘ceramic chemistry ↔ microstructure ↔ physical properties’. Many examples encompassing classical clay science, and Ian’s own research into non-oxide ceramics, membrane ceramics and state-of-art 3D printing were used to illustrate how this ever-advancing field continues to transform great chemical science into new technologies.

University of Canterbury

Awards and appointments

Congratulations to *Yifei* ***Fan***, supervised by *Emily* ***Parker***. Yifei was offered a place to visit Cherion 2015, the Synchrotron Science School in Japan, through the Australian Synchrotron Annual User Meeting, with only three places offered to New Zealand – a huge achievement!

Congratulations to Professors *Ian* ***Shaw*** and Antony ***Fairbanks***, who both received special awards as part of the 2015 UCSA Lecturer of the Year Awards. Ian received the *Gin and tonic award*, whilst Antony was the proud recipient of the *Most vigorous whiteboard marking award*. Rumour has it that Antony intends to increase the content of each of his undergraduate lectures by about 20% in 2016 in an effort to retain this prestigious award. Ian, who is also keen to retain his title, has been seen clutching a bottle of Bombay Sapphire.

Congratulations to the following academics who were successful in the Chemistry Department Contestable Funding recently: Antony Fairbanks received funding to support David Lim on a short synthetic project to exploit a discovery made by David during his PhD studies on the selective acetylation of the anomeric OH of sugars. This project will allow David to optimise the process and to test its applicability to other examples required to make a great publication. *Chris* ***Fitchett*** secured funding toward his project, *Propeller catalysts: a new approach to asymmetric chiral induction,* to help support Will Kerr to complete his PhD project through the purchase of a new chiral HPLC column. *Vladimir* ***Golovko*** also secured leverage towards a UC Summer Research Scholarship along with consumables funding. This will enable his group to establish a proof-of-concept system encompassing two flow-through reactors to demonstrate that scalable reactor architecture is feasible for high throughput testing of the performance of catalysts made in his laboratory. *Sarah* ***Masters*** also secured leverage towards two UC Summer Research Scholarships along with consumables funding. The aim of one project is to design a new robust very high temperature inlet nozzle for gas phase sample introduction to the Canterbury gas electron diffraction (GED) apparatus, whilst in the other a student will carry out simple quantum chemical calculations for a set of amine-boranes, and then work with Sarah on the GED data collection.

Congratulations to *Stewart* ***Alexander*** who has been awarded a Claude-McCarthy Fellowship to attend the 252nd National Meeting of the ACS in August 2016. The conference will take place in Philadelphia, and is titled *Chemistry of the people, by the people and for the people*.

Visitors

Erskine Fellow *Alistair* ***Boxall*** visited the Department until 4 October. Alistair is Professor in Environmental Science in the Environment Department at the University of York. Alistair’s research focuses on understanding emerging and future ecological and health risks posed by chemical contaminants in the natural environment. Alistair is a past member of the Defra Hazardous Substances Advisory Committee and the Veterinary Products Committee. He is currently coordinator of the 3.5 m Euro CAPACITIE project on pollution monitoring in cities and academic coordinator of the 9.8 m Euro iPiE project on intelligence-led assessment of pharmaceuticals in the environment. He regularly advises national and international organisations on issues relating to chemical impacts on the environment and has published extensively on the topic of chemical risks in the environment. While he was at Canterbury, Alistair contributed to teaching in environmental chemistry and environmental science. He also ran a workshop on environmental risk assessment for chemicals for postgraduate students.

OTAGO

The 2015 High School Chemistry Quiz was held at the Otago Museum's Hutton Theatre on 24 September. 41 teams from schools around Dunedin, Otago and Southland enjoyed pizza from Poppas Pizzeria, before tackling rounds of questions of both a chemical and a general trivia nature. A highlight, as always, was the chemical haiku round. When the dust settled *The Chemistry Club* (from John McGlashan College) were the winners, with *Newton's Flaming Laser Sword* (from James Hargest High School) second and *Total Borons* (from Southland Girls High School) third. The winning Haiku were:

I tried to light match

It burned for a bit then stopped

That's pre-phosphorus!!

by *Smart People and Jason* (Otago Boys' High School)

H_2SO_4

thought it was water, but no

lying dead on the floor

by *Pb Zeppelin* (Southland Girls' High School)

Finally Balanced

Equations are so easy

*!@, the oxygens!

by *Honk* (Logan Park High School)

Our thanks to Poppas, the University Bookshop, Otago University and the Otago Branch of the NZIC for their continuing support.

Ian ***Brown*** from Callaghan Innovation visited Dunedin in early November to present his NZIC President's Lecture, *Modern ceramic chemistry – a journey from clay science to 3D printing*, highlighting the contributions of Otago graduate Joseph Mellor to the discipline. The talk was followed by dinner with members of the committee at a local restaurant.

2015 High School Chemistry Quiz winners, *The Chemistry Club* (John McGlashan College)

Left to right: Professors Richard Blaikie, Harlene Hayne, Vernon Squire, Sally Brooker, Keith Hunter, Helen Nicholson and Lyall Hanton. Photo: Sharron Bennett

Left to right: Robin Brooker, Professors Sally Brooker and Harlene Hayne, Janis Brooker. Photo: Sharron Bennett

University of Otago, Department of Chemistry

On 12 November, *Sally* ***Brooker*** gave the 2015 University of Otago Distinguished Research Medal lecture (*Chemical connections: designer switches, "green" catalysts – it's a small world!*) and was then presented with the medal by the Vice-Chancellor, Harlene Hayne (see pictures of Sally with the academic party pre-lecture, and with the VC and her parents, to whom she dedicated this medal). The following week, *Dave* ***Larsen*** presented his inaugural Professorial Lecture (*Therapeutic molecules from sweet sugars and poisonous gases*).

Rob ***Middag*** spoke about *Limiting iron concentrations early in the season off the west Antarctic peninsula* at the 2015 Antarctic Science Conference, Christchurch, in late July. In August he attended the Goldschmidt conference in Prague, presenting work on *Aluminium in the west Atlantic Ocean and Mediterranean Sea*. As part of the 2014-2015 New Zealand - Germany Science & Technology Programme, *Trace metal-carbon dioxide interactions in the Southern Ocean (TM-CarDISO)*, Rob visited the Alfred Wegner Institute in Germany in November; a return visit by Mario Hoppema for five months will take place in February 2016.

The polymer group was awarded the inaugural Otago Division of Science award for best industrial links, largely due to the ongoing commercialisation of their medical gel, currently being manufactured by Glycosyn. Recent talks by the group include *Esmat* ***Jalalvandi*** and *Stephen* ***Moratti*** at the D4 conference here in Dunedin. We welcome *Louie* ***Harden-Bull*** and *Joanna* ***Houlihan*** who are working as summer students in the labs.

Daniel ***Lim*** from the University of New South Wales, Sydney visited the Department of Chemistry for three weeks in October 2015. Daniel worked with *Guy* ***Jameson*** to perform stop-flow studies on the immune regulatory protein indoleamine 2,3-dioxoygenase.

Plant & Food Research Unit, University of Otago

Congratulations to *Nigel* ***Perry*** and *Elaine* ***Burgess***, whose collaboration with University of Otago researchers has won the University of Otago Innovation's *Proof of concept* competition. This collaboration between Nigel and Elaine, Phil Heyward and Alex Tups from Otago's Department of Physiology, and Pat Silcock from Food Science, is developing a new nutraceutical to help regulate blood glucose levels to support treatment of type II diabetes. The *Proof of concept* competition awards a prize of $50,000 which the team will use to progress the product to clinical trial stage. The grant is offered by Otago Innovation, the University's commercialisation body, to support the transformation of ideas into marketable products. For more see http://www.otago.ac.nz/otagobulletin/news/otago120525.html

Aaria ***Dobson-Waitere*** has just started work with the Bioactives team and *Bruce* ***Smallfield*** (Breeding & Genomics) on a Plant & Food Research Summer Studentship. Aaria is at Victoria University, where she is doing a BSc in Ecology, Biodiversity and Māori Resource Management. She will be working with Bruce, *Catherine* ***Sansom*** and *John* ***van Klink***, and with Ngāi Tahu, on the traditional scent of taramea, from speargrasses. This is part of our continuing contribution to the development of taramea, alongside funding to Ngāi Tahu from the Sustainable Farming Fund.

Duong ***Nhu*** joins the *Bill* ***Hawkins*** group as a postdoc working with Bill, Nigel Perry, *Lesley* ***Larsen*** and Dave Larsen on the synthesis of tutin glycosides found in New Zealand toxic honeys. Duong joins the unit from the University of Melbourne/Walter and Eliza Hall Institute of Medical Research where she completed her PhD on *Studies towards the synthesis of rocaglamides*.

WAIKATO

2015 NZIC President, *Dr Ian* ***Brown*** visited recently and gave a very enlightening and well attended talk on *Modern ceramic chemistry – a journey from clay science to 3D printing*.

University of Waikato

In the annual ChemQuest competition, held recently by the Department of Chemistry, St Peter's School narrowly took out the keenly fought competition. A record number of students (nearly 250) from the greater Waikato region and Bay of Plenty participated. This was a fun-filled evening for students studying NCEA level 2 Chemistry with particularly enthusiastic participants this year.

Prizes were awarded as follows:

1st Place: St Peter's School: (Gaby Dumble, Rhys Duncan, Jeffrey Wise)

2nd Place: St Paul's Collegiate: (Jimmy Christy, James Krippner, Craig Stocker)

3rd Place: Hamilton Boys' High School: (Cameron Salisbury, Max Sharplin, Jeevan Vettivel)

4th Place: Hamilton Boys' High School: (Lauchlan Cate, Jacob Cheatley, Reuben Hattingh)

5th Place: St Peter's School: (Rebecca Goodman, Ben Hos, Simran Saini)

St Peter's School students Rhys Duncan, Gaby Dumble and Jeffrey Wise were the winners of ChemQuest 2015 shown here with Chairperson of the Waikato Branch, Dr Michael Mucalo (far left)

The quiz was generously sponsored by the Waikato Branch of NZIC (major sponsor), Hill Laboratories, James & Wells Intellectual Property and the Faculty of Science and Engineering, University of Waikato. Question master was *Michèle* ***Prinsep***, ably assisted by numerous other staff and students from the Department.

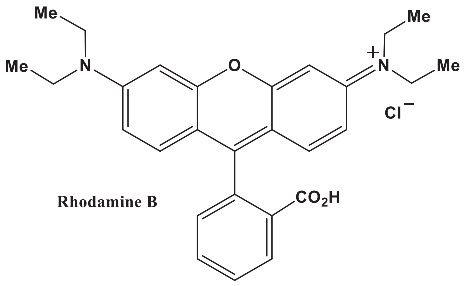
WELLINGTON

This is the last column from the Branch's long standing Branch Editor who is taking a well-earned rest. In order to facilitate the transition to his replacement, a Wellington member in each of the following organisations is needed to collect news snippets and forward them on a quarterly basis to his replacement. If you can help, please contact the Branch Secretary (details below):

AgResearch, Callaghan Innovation, Coal Assoc. NZ, Dulux Paints, ESR, Ferrier Institute, GNS, Mallaghan Institute, Ministry of Health, Ministry of External Affairs, NIWA, Opus Consulting, Resene Paints, and anywhere else that chemists are employed.

The Branch congratulates Dr *Justin* ***Hodgkiss*** (SCPS, Victoria University) on being awarded the Easterfield Medal and Dr *Paul* ***Benjes*** (GlycoSyn, Callaghan Innovation) and Dr *Phillip* ***Rendle*** (Ferrier Research Institute) for the *Shimadzu Applied and Industrial Chemistry Prize* as well as Drs. *Simon* ***Hinkley*** & *Timothy* ***Kemmitt*** (Callaghan Innovation), *Ralf* ***Schwoerer*** & *Olga* ***Zubkva***, (Ferrier Research Institute) and *Joanne* ***Harvey***, *Mattie* ***Timmer***, & *Bridget* ***Stocker*** (SPCS) on their election to NZIC Fellowship.

Victoria's first PhD graduate in chemistry (MSc: 1952; PhD: 1955), *William Hugh* ***Melhuish***, died in his sleep on 15 October 2015. Hugh was employed by the former Institute of Nuclear Sciences and represented NZ on the IUPAC Analytical Chemistry Division commissions on *spectrochemical and other optical procedures for analysis* for some 12 years over the late 1970s and through the 1980s. He was this country's most noted photochemist who authored three IUPAC reports on spectrochemical analysis. His citation count was legion as he developed the rhodamine B fluorescence counter in 1964 that was used extensively in that early era of fluorescence spectrometry.



Rhodamine B

September saw the inaugural *Curtis Lecture* given by Professor ***Sally Brooker*** (Otago University) entitled: *Research road trip: from a PhD in manganese macrocycles as models for PSII to designer iron complexes as switches and zinc macrocycles as catalysts.* In presenting her study she reminded us that New Zealand and Australia have played internationally significant roles in the development of macrocyclic chemistry and in particular Professor Neil Curtis's particularly notable contribution to this field in the early 1960s when he reported the first example of a metal-templated cyclisation (for a review see: N.F. Curtis in *Supramol. Cem.*, **2012**, *24*, 439). She then went on to describe the evolution of her own research interests, which began with her PhD in macrocyclic chemistry and now include both macrocyclic and designer acyclic ligands and complexes, along with their immobilisation on solid supports. Potential uses include switches, sensors, fluorescent labels and catalysts.

The Branch congratulates our 2015 President, Dr *Ian* ***Brown*** of Callaghan Innovation on the completion of his year of service that was topped off with the award of both the Hector Medal of the Royal Society of NZ and the Shorland Medal of the NZ Association of Scientists. His Presidential Lecture *Nano, micro, macro – using chemistry to design and control the properties of materials* was delivered to a sizeable audience on 14 October. Ian reminded us that more than ever before materials chemistry and the wider field of materials science provide us with the tools and knowledge both to design new and novel materials and to improve the properties and performance of many familiar materials. He then illustrated this by taking some of the themes introduced in his 2013 Mellor Lecture and drew on his research across many materials systems: ceramics, mineralogy, glass, cements, hydrogen materials and titanium metals. He examined the relationships between chemistry, microstructure and physical properties of solid materials and illustrated this with nanoscale ceramic membrane design and fabrication, the use of structural modelling to optimise pore structures and predict the engineering properties of titanium metal implants, and how heat treatment and additives can be used to control the microstructure and properties of high performance ceramics.

The November meeting followed both the National and Branch AGMs held at Victoria University. The lecture was delivered by Dr Monica Handler (School of Geography, Environment and Earth Sciences, VUW) on *A geochemistry taster: planetary formation* in which she the outlined the application of chemical tools and principles to investigate geological processes and the formation and evolution of Earth.

Dr *Shivali* ***Gulab***, a former student of Victoria Chemistry and a Branch Committee member, was named NZBIO Young Bioscientist of the Year by the New Zealand Biotechnology Industry Association in an awards ceremony at its conference in Wellington late last September. Shivali is now the CEO of Avalia Immunotherapies Ltd., a biotech company she helped establish to bring a novel vaccine therapy to the clinic. The vaccine technology is based on the work of the Ferrier Research Institute, in collaboration with the Malaghan Institute and the University of Otago. The aim is to harness the body's own immune system to treat a specific cancer or infectious disease. Shivali is based in New York, where she is developing Avalia's business to progress the therapy to the human clinical trial stage.

The 2016 Wellington Branch Officers are:

Chairperson: Dr *Joanne* ***Harvey***

(SCPS-VUW)

Secretary: Dr *Robin* ***Fulton*** (SCPS-VUW)

Treasurer: Dr *Ralf* ***Shwoerer*** (Ferrier Institute)

Victoria University – SCPS

September 4 saw Professor Dean Crick (Microbiology, Immunology & Pathology, Colorado State University) visit and speak on *Partial saturation of menaquinone in Mycobacterium tuberculosis: function and essentiality of a novel reductase, MenJ*.

Successful PhD completions since the last issue was published include (supervisor/s parenthesised) Galen Eakins, who completed in late September with a thesis entitled *Peptide-directed supramolecular self-assembly of N-substituted perylene imides* (*Justin* ***Hodgkiss*** & *Rob* ***Keyzers***) and Xuan Hao Chan in mid-October, *Synthesis and characterisation of shape-controlled metallic and bimetallic nanocrystals for catalysis and sensing* (*Richard* ***Tilley***). Mahroo Falah had a successful thesis with *Synthesis of new composites of inorganic polymers (geopolymers) with metal oxide nanoparticles and their photodegradation of organic pollutants* (*Ken* ***MacKenzie*** & *Ruth* ***Knibble***). Stefan Munneke (*Mattie* ***Timmer***, *Bridget* ***Stocker*** & *Gavin* ***Painter***) successfully completed his studies on *Novel methodologies for the synthesis of multivalent glycoconjugates* and his fiancée Marjorie Griffiths (*Kate* ***McGrath*** & *Bill* ***Williams***) with *A dual-trap optical tweezer approach to study emulsion droplet interactions*; the couple were married in San Francisco in December. *Davoud* ***Zare*** successfully completed his PhD on *Milk protein adsorption at oil/water interfaces: molecular to bulk behaviour* (*Kate* ***McGrath***) in late November.

Jingjing ***Wang*** (*Joanne* ***Harvey***) has submitted her PhD and joined NZ Pharmaceuticals in mid-November. Joanne and her student *Thomas* ***Bevan*** together with *Rob* ***Keysers*** and *Paul* ***Teesdale-Spittle*** of Biological Sciences attended the Pacifichem meeting in December.

The annual Bio-Discovery Centre symposium took place on 24 November. One of the keynote speakers was Dr *Selwyn* ***York*** (NZ Pharmaceuticals, Palmerston North) and he described NZP and its lead products - past, present and future to the sizeable audience; three of the SCPS graduate students gave short oral presentations on their work. The following day saw the SPCS chemists host the annual teachers day organised by Dr *Suzanne* ***Boniface***.

Dr *Peter* ***Tyler*** of the Ferrier Institute was awarded a Marsden grant of $790,000 for *Synthetic sulfated saccharides in cell signalling.*

NZIC Conference 2016 (NZIC-16)

21-24 August 2016, Millennium Hotel, Queenstown

Abstract submissions close 30 April 2016

NZIC-16 will host the 4th Supramolecular Chemistry in New Zealand and Australia meeting (**SCiNZA-4**). We therefore extend a special invitation to Australasian researchers in the field of supramolecular chemistry. Professor Peter Stang will present the supramolecular chemistry plenary talk, and one of the parallel sessions of the conference will be set aside for SCiNZA-4 talks. SCiNZA-4 delegates should register and submit abstracts via the main conference portal.

The conference will be held in the Queenstown, New Zealand at the Millennium Hotel from 21-24 August 2016. It is the latest in a series of biennial conferences celebrating chemistry in New Zealand and showcasing research from around the globe. The program includes plenary lectures from Donna Blackmond, Sam Kean, Peter Schwerdtfeger and Peter Stang and will include keynote lectures, invited presentations and poster sessions. The broad range of chemistry covered in the conference will be attractive to all chemists from academia, industry and will be particularly informative for student delegates.

www.nzic16.org

2015 Hector Medal: Making ceramics that don't shatter and other high value materials

Ian Brown receives the Hector Medal from Margaret Brimble at the 2015 Royal Society of New Zealand Research Honours dinner (Photo credit: Royal Society of New Zealand)

Dr Ian Brown FRSNZ has been awarded the Hector Medal for his research into materials chemistry, which has ranged from fundamental research through to industry applications.

Dr Ian Brown's materials chemistry research spans forty years, encompassing fundamental and applied research in glass, ceramics, minerals, metallurgy, nanomaterials and hydrogen materials.

"His multi-disciplinary approach and industrial experience has enabled both world class personal academic achievement and commercial success," the medal selection committee said.

Dr Brown, a Distinguished Scientist in the Advanced Materials Group at Callaghan Innovation, and his team have achieved world leading advances in the development of 'sialon' ceramic systems. Sialons are high performance or engineering ceramics that, unlike domestic ceramics like bricks or standard tableware, have outstanding properties such as extreme toughness, thermal shock resistance and durability. They are used in molten metal contact applications in aluminium smelting and foundries and may even be used to create bullet-proof body armour.

Dr Brown says that the way they are made allows them to be extremely dense, with few flaws or pores – leading to a very strong but lightweight three-dimensional structure.

Dr Brown's processing of reactive powder materials in controlled atmospheres has been applied to developing a new titanium powder metals processing industry sector in New Zealand. This young and rapidly growing sector is now being led by innovative export-focused companies in areas such as titanium metal powder synthesis, 3D printing and medical implant manufacture.

Dr Brown has gone on to innovate nano-scale ceramic membranes for purifying hydrogen gas for fuel cells and he also leads a programme to create high performance cements for the geothermal industry.

On receiving the Hector Medal, named for Sir James Hector, founder of the Royal Society of New Zealand, Te Papa and GNS Science, Dr Brown said: "When I was standing on the summit of Mt Hector in the Tararua range with my daughter in February this year I could not have imagined that I would be awarded this medal in honour of such an extraordinary scientist who was responsible for establishing so many of New Zealand's iconic science institutions. It's humbling, gratifying and exciting – all in the same breath. It's also a tribute to the many outstanding colleagues and students I've had the good fortune to work with throughout my career as well being a timely acknowledgement of the role that materials science is playing to deliver scientific and economic benefit to New Zealand."

Dr Brown was made a Fellow of the Royal Society of New Zealand in 1999 and he received Adjunct and Honorary Professorships at Victoria and Waikato Universities. He is the immediate Past-President of the New Zealand Institute of Chemistry.

Hector Medal: For work of great scientific and technical merit in chemical sciences.

Citation: To Ian William Murray Brown for his innovative transformation of fundamental materials science into major technology platforms of strategic and commercial significance in New Zealand.

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Salicylaldoxime iron cluster chemistry

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Keywords: *iron*, *salicylaldoxime*, *ligands*, *coordination chemistry*

Introduction

Super-paramagnetic behaviour in molecules allows molecules to store magnetic information. These molecules can retain the memory of an applied magnetic field even after its removal due to the need to overcome a high energy barrier (ΔE) to re-establish thermal equilibrium with associated randomised orientation of the magnetic moments within the complex. To achieve this state a complex requires a large total ground state spin (S) and a large zero field splitting parameter (D) which together favour a large energy barrier as defined by the following equations:

$\Delta E \propto S^2\,|D|$ (for integer spins) Eq. 1

$\Delta E \propto (S^2 - ¼)\,|D|$ (for half-integer spins) Eq. 2

The research field of molecular magnetism has been rejuvenated since the discovery of such behaviour as typified in the $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4].4H_2O.2MeCO_2H$ polynuclear complex by Lis *et. al.*[1] These new discrete molecules are called nano-magnets or single molecule magnets (SMMs).[2] Since this discovery, the manganese fragment $Mn_{12}Ac$ has been abundantly utilised to synthesise new Mn_{12}-carboxylato clusters by substitution with other carboxylates.[3] Some other transition metal complexes such as vanadium(III), cobalt(II), nickel(II) and mixed metal clusters also form SMMs.[4] In addition, slow magnetic relaxation has been observed in complexes containing only a single metal ion centre such as $[LnPc_2]^-$ (Ln=Tb, Dy, Ho; Pc=dianion of phthalocyanine).[5] The second properly identified SMM was $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ (tacn=1,4,7-triazacyclononane) and that discovery led to further studies of the magnetic properties of iron complexes synthesised using numerous ligands and co-ligands such as those with salicylaldoxime.

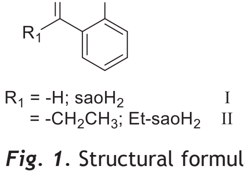


Fig. 1. Structural formulae of salicylaldoxime ligands discussed in the text

The first reported Fe(III)-salicylaldoxime complex $[Fe_4O(saoH)_4(sao)_4]$ was a tetranuclear species[6] which was further explored by Rapto-polou *et al.*[7] The complex has been synthesised using the simplest salicylaldoxime (see I in Fig. 1). There are many examples of Fe(III)-salicylaldoxime-derivatised complexes that have been reported over the past two decades. The nuclearity of those complexes varies from two to ten.[6-13]

In this article, we emphasise the structural and magnetic investigations of iron complexes synthesised with salicylaldoximes as ligands, specifically complexes containing one or more 'triangular' units consisting of three iron centres that are bridged by phenolate and oximato groups of ligands, some of which are additionally interconnected by an oxo/hydroxo group located in the metal triangle/triangles (Fig. 2). The iron complexes contain either 'non-linked' (single metal coordination site) or 'linked' (dual metal coordination sites) ligands which we have termed single-headed and double-headed salicylaldoxime ligands respectively.

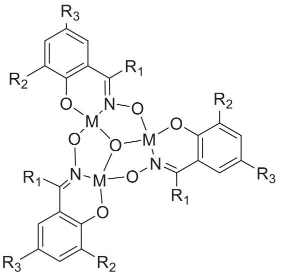


Fig. 2. The most common coordination arrangement for polynuclear complexes of salicylaldoximes, the $[M_3O(oximate)_3]^+$ moiety, where R_1 = H, R_2 = R_3 = alkyl groups

A number of trigonal prismatic assemblies including the hexanuclear Fe(III) complex $[HNEt_3]_2[Fe_6O_2(OH)_2(Et\text{-}sao)_4(O_2CPh(Me)_2)_6].2MeCN$ synthesised with a derivatised salicylaldoxime ligand (Fig. 1, II) have been reported by Mason *et al.*[9] An analogue of the trigonal prismatic core of the latter example has been observed by M. Hołyńska *et al.*[14] The presence of a central proton (H2) between the triangles, hypothesised by Mason *et al.*[9] based on a single crystal X-ray determination, was later proven in the analogous Fe(III) complex published by Hołyńska *et al.*[14] who provided additional experimental evidence such as X-ray diffraction to confirm the proton location. They also reported magnetic properties and Mössbauer spectroscopic studies (see Fig. 3).

In 2009, Plieger and his research group reported a hexacopper complex with a derivatised salicylaldoxime ligand,[15] 3,3'-[1,6-hexanediylbis[(methylimino)methylene]]bis[5-(1,1-dimethylethyl)-2-hydroxybenzaldehyde-1,1'-dioxime (see L in Fig. 4). This hexacopper complex was formed unexpectedly when the dinuclear helicate $[Cu_2(L\text{-}2H)_2]$[16-18] was treated with $NaPF_6$ in water.

The hexacopper complex consists of six copper ions strapped by three ligands in which each copper ion is bridged by phenolate and oximato groups of adjacent ligands. The complex is stabilised by the amine linkers between the salicylaldoxime units and the triangular units are brought close to each other by the hydrogen bond formed between the central oxygen atoms within the tricopper units. The complex is further stabilised by

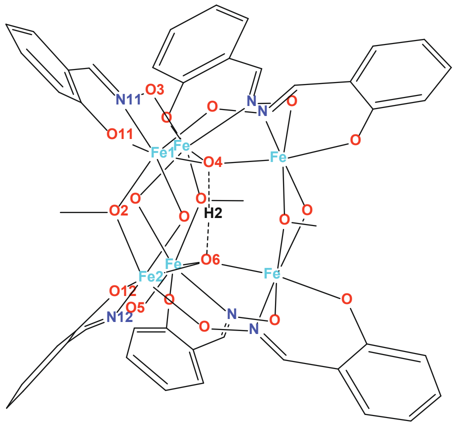


Fig. 3. Metallic core of the complex $[Fe_6O_2H(sao)_6(CH_3O)_3(OH)_3]^{3-}$ with the symmetry-independent part labelled. Note: all the H-atoms are omitted for clarity except the proton between the $[Fe_3O]$ triangles[14]

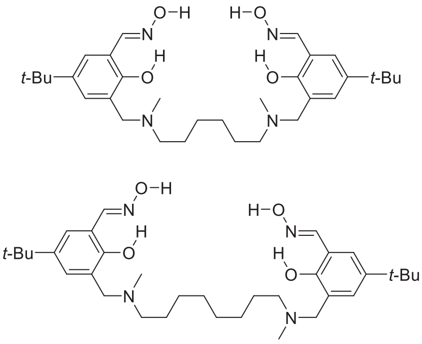


Fig. 4. Derivatised salicylaldoxime ligands: L (top) and L' (bottom)

the intramolecular hydrogen bonds between each alkylammonium NH group and its neighbouring phenolate oxygen atom. Therefore, the presence of amine nitrogen atoms and their protonation reinforce the stability of the complex (Fig. 5).

This hexacopper complex, $[Cu_6(L\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)](PF_6)_3$ has led a number of research groups to synthesise multinuclear clusters using linked salicylaldoxime derivatives and influenced our research direction towards exploring the chemistry of multi-iron complexes using the same class of ligands.

Since mid-2011, a series of both 'single-headed' and 'double-headed' salicylaldoxime ligands have been synthesised and the magnetic and solid state characterisation of these complexes have been undertaken to explore their potential as SMMs.

Structural properties of hexairon and heptairon complexes

In 2012, Brechin and co-workers reported the syntheses, structure, and magnetic investigation of two iron containing complexes.[19] They used pyridine in the synthesis which acted in a dual role – firstly, as a base and secondly (and possibly more importantly), to provide further donor groups to complete the octahedral coordination environment of each of the iron complexes. The first compound isolated was a heptairon-containing complex and was synthesised using the ligand L (Fig. 4), while the second complex utilised a slightly longer alkyl linker (8 carbons instead of 6, see Fig. 4, L') and resulted in the isolation of a hexairon complex with the formulation $[Fe_6O(OH)_7(H_2L')_3](BF_4)_3.4H_2O.9MeOH$.

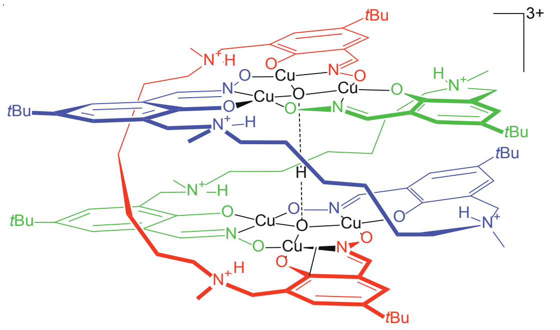


Fig. 5. Schematic representation of the hexacopper complex showing the three straps and the interplane $(\mu_3\text{-}O)\cdots H\cdots(\mu_3\text{-}O)$ hydrogen bond

This structure has similar features to that of the hexacopper complex of Plieger with one notable exception, the addition of the six bridging hydroxo groups connecting the upper trimer of iron atoms with that of the lower. In both cases it appears a central hydrogen bond is present between the μ_3-oxo groups (Fig. 6).

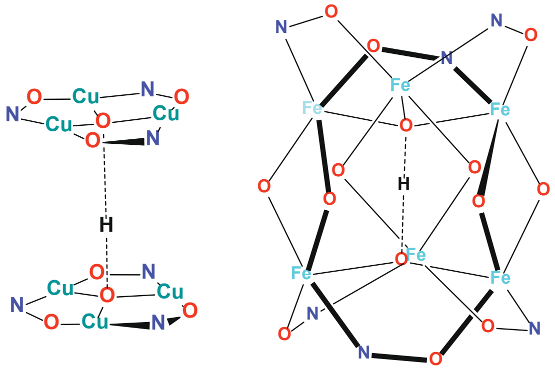


Fig. 6. Left: metallic skeleton of the hexacopper complex; right: metallic skeleton of the hexairon complex

These hydroxo bridges form an internal hexagon with the distance between the oxygen atoms ~ 2.4 – 2.7 Å (Fig. 7).

The clockwise atomic sequence of the oximato bridge between two adjacent Fe atoms is Fe-N-O-Fe on the upper triangle, while it is reversed on the lower triangle as Fe-O-N-Fe. It is reversed on both upper and lower triangles in the heptairon complex.

The two metal triangles of the heptairon complex, $[Fe_7O_2(OH)_6(H_2L)_3(py)_6](BF_4)_5.6H_2O\cdot14MeOH$ are linked by another Fe atom via six hydroxo bridges to the Fe atoms on the triangles in addition to the helical straps of the ligands (Fig. 7). In this complex, the central oxygen atoms on the triangles are displaced out of the triangular metal planes pointing away from the centre of the molecule. The remaining coordination site around each iron atom on the triangles is filled by an axial pyridine molecule. The charge of the molecule is balanced by five BF_4^- ions.

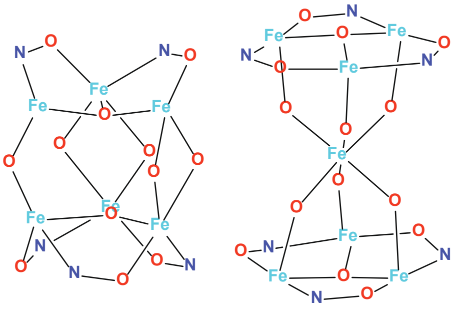


Fig. 7. Left: metallic core of the hexairon complex; right: metallic core of the heptairon complex (FeIII = olive green; O = red; N = blue)

Magnetic properties of hexairon and heptairon complexes

The temperature-dependant magnetic susceptibility (χ_T) of both iron complexes has exhibited consistent decrease of χ_T with decreasing temperature, suggesting overall strong antiferromagnetic interactions between the metal ions. The total ground state spin has been determined as zero for the hexairon complex and 3/2 for the heptairon complex.[19] Neither of these complexes exhibited SMM behaviour.

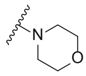
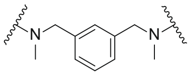
Single- and double-headed derivatised salicylaldoximes

An original series of single-headed and double-headed derivatised salicylaldoxime ligands was used to generate a number of iron clusters. Here, we briefly discuss structural and magnetic characteristics of analogous hexa- and hepta- iron complexes similar to those reported by Brechin *et al*.[19] Irrespective of whether the ligand is linked (double-headed) or non-linked (single-headed), the complexation reactions followed by crystallisation led to complexes of both high and low nuclearity.

Dinuclear and trinuclear iron complexes

Iron complexes of low nuclearity (Table 1) synthesised using both linked and non-linked ligands were found to contain boron (presumably by hydrolysis of the tetrafluoroborate counter anion) coordinated to the iron centres through oxo- and oximato- oxygen atoms (Figs. 8 and 9). It appears the inclusion of the boron atoms inhibits larger cluster formation. The remaining coordination site of each boron atom of the diiron compound is taken by a fluorine atom which was confirmed by a comparison with similar bond lengths in the literature[20,21] and by elemental compositional analysis. A similar core was reported by Rose *et al*. in 1992.[21]

Table 1. Low nuclearity iron complexes

Complex	Nuclearity	Number of links	Strap
C1	2	1	
C2	3	2	

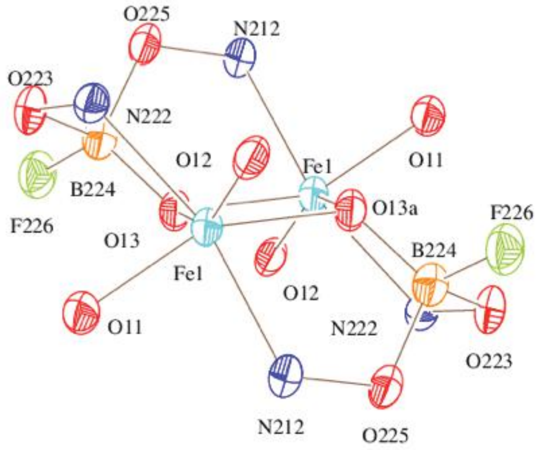


Fig. 8. Structural representation of the dimetallic core of the complex C1; ORTEP view at 50% probability level

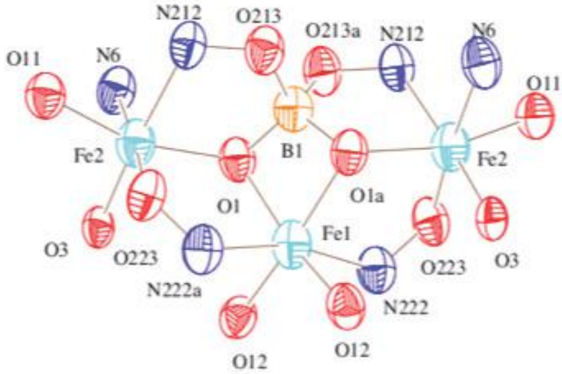
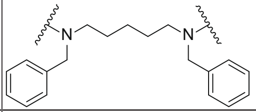
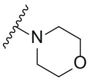
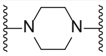
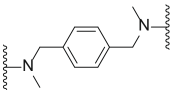
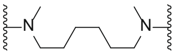
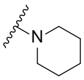


Fig. 9. Metallic core of the complex C2 (see the plane of Fe1- O5 - B1- O5a- Fe1); ORTEP view at 50% probability level

The molar magnetic susceptibility ($\chi_M T$) values of the non-interacting magnetic centres at room temperature for both complexes are higher than the experimental values at room temperature which is suggestive of the presence of sizeable antiferromagnetic interactions. The ground state spin of the C2 complex was found to be $S = 3/2$. The iron centres of both complexes are 3+ which was confirmed by Mössbauer analysis and charge balance considerations.

Table 2. High nuclearity iron complexes

Complex	Nuclearity	Number of links	Strap
C3	6	2	
C4	6	1	
C5	7	2	
C6	7	2	
C7	7	2	
C8	7	1	

The hexairon complexes

The two hexairon complexes (C3 and C4, Table 2) synthesised using both linked and non-linked salicylaldoxime ligands have prismatic metallic cores where the two metal planes are related by reflection. This is easily seen when viewing the molecules along the central O-O axis and observing whether the O-N direction is the same or opposite at each metal plane. The hexairon complex reported by Brechin *et al*. in 2012 has different directions of this bond at either metal plane and is therefore anti-prismatic.[19] Each complex contains a shared proton between the central O-atoms within the metal coordination core (Figs. 10 and 11). While this hydrogen atom was not able to be detected directly, its presence was confirmed by the short distance[22] between the central oxygen atoms: O10···O11 distance = 2.453(9) Å for C3 and O11···O11 = 2.730(11) and O55···O55 = 2.628(8) Å for the two independent molecules respectively in the structure determination of C4. The fact that the central O-atoms are also displaced towards each other is another indicator that there exists a hydrogen bond positioned between the metal planes (Fig. 10). This structural information was further corroborated by the infra-red spectroscopy analysis. The distances above bookend the value of the confirmed H-bond of the hexairon complex (2.526 Å) of Brechin *et al*.[19]

The magnetic measurement analyses suggest the total ground state spin for the complex C3 is equivalent to the results for the hexairon complex reported by Brechin *et al*.[19] The magnetic fitting was not performed on the complex C4 due to the two independent structures present.

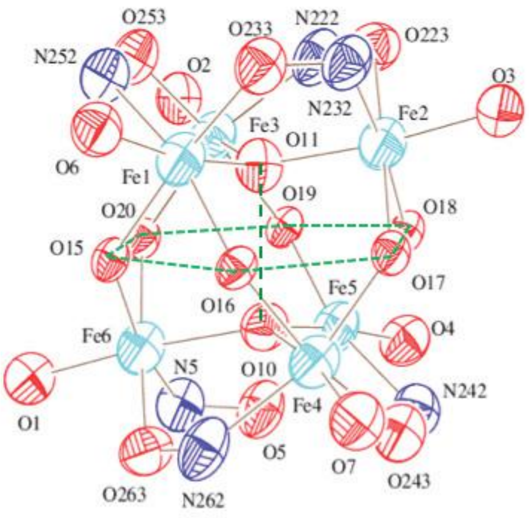


Fig. 10. The metallic core [$Fe_6O(OH)_7(L5\text{-}2H)_3]^{3+}$ of the complex C3 emphasising the hydrogen bond contact (dark green dotted line) between the central oxygen atoms (O10 and O11) of the lower and upper triangles and the internal hexagon (O15 through O20, shown in dotted light green line) (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level

The heptairon complexes

Both non-linked and linked salicylaldoxime ligands appear to be able to form heptairon clusters with the Mn(II) tetrafluoroborate metal salt. These largely prismatic structures are comprised of two oxo-bridged iron(III) triangles that are connected via a central iron(III) hexahydroxide moiety. All of the heptairon complexes, irrespective of the ligand used, form a very similar metallic core. The oximato bridging sequence on both triangles for complexes C6 – C8 (Table 1) are the same and are thus very similar to the heptairon complex reported by Brechin *et al*.[19] The exception to this is complex C5 (Table 2) which has an anti-prismatic arrangement of oximato bridges on the upper and lower metal triangles (Fig. 12).

In all cases, the Mössbauer spectra indicate the two distinctive iron environments with a consistent ratio of intensity (7:3) between them, a slightly reduced ratio than the expected 6:1. The magnetic results are suggestive of the presence of dominant antiferromagnetic interactions.

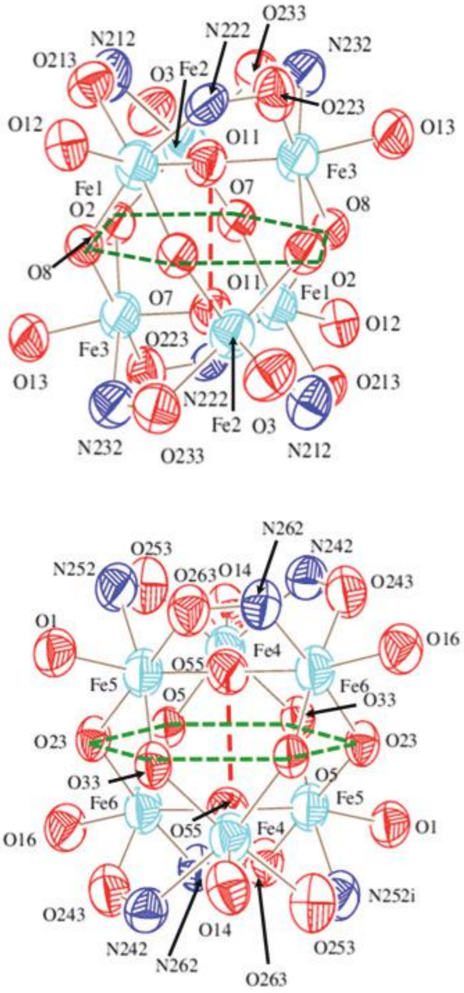


Fig. 11. The metallic cores of the two crystallographic independent molecules of [$Fe_6O(OH)_7(L1\text{-}H)_6]^{3+}$ C4 (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level

Conclusions

The salicylaldoxime ligands synthesised in this study centred around modifications to the amine connected strap between the salicylaldoxime units in the linked salicylaldoxime ligands for the double-headed oxime variants and amine appended derivatives for the single-headed oxime containing ligands. For the doubled-headed ox-

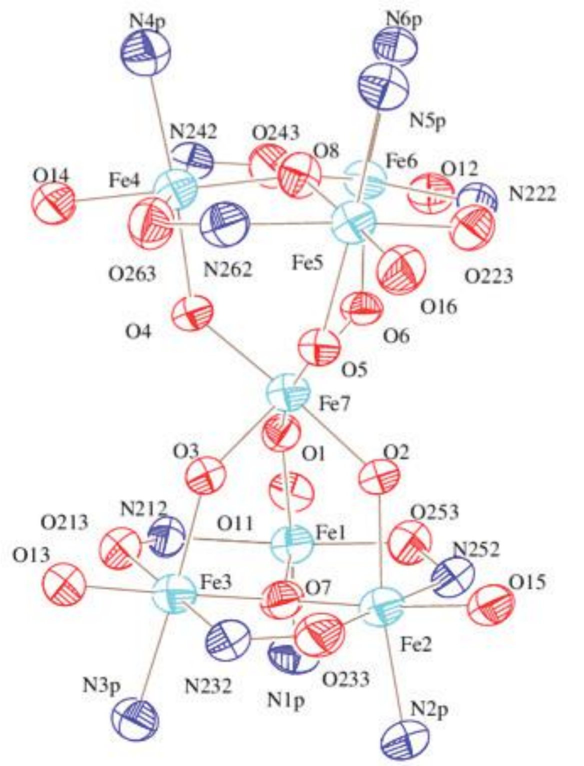


Fig. 12. The metallic core $[Fe_7O_2(OH)_6(L5\text{-}2H)_3]^{5+}$ of the complex C5 emphasising the anti-prismatic arrangement of the N-O bridging oximic bonds (Fe-cyan, N-blue, O-red); ORTEP view at 30% probability level

imes, structural features of the ligands such as helicity and flexibility were investigated for changes in the magnetic properties based upon variations in the structural parameters of the complexes such as iron nuclearity, bond lengths and angles, torsion angles, formation of H-bonds and proximity of the iron centres that could all lead to differences in magnetic properties. The high nuclearity of iron centres in the larger clusters lead to dominant antiferromagnetic interactions in all the complexes synthesised. A suitable future modification and one that has been employed with some success in the literature would be to modify the simple salicylaldoxime head by replacing the hydrogen on the oximic carbon with a more bulky substituent, i.e in Fig. 1 where R_1 = a bulky substituent. This has been shown to impart structural changes in the complexes, notably the torsion angle of the metal-N-O-metal units, which in turn drastically influence the magnetic properties of the resulting complex clusters.

Acknowledgements

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Innovations in chipseal road surfaces: the potential of epoxy-bitumen to create resilient, long life road surfaces

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Steve Bagshaw obtained his PhD from the University of Auckland in 1995, working with Ralph Cooney, where he developed his on-going fascination with nanoporous materials, clays, zeolites and materials chemistry. This was followed by successful and productive periods at Michigan State University with Tom Pinnavaia, and at ENSCM/CNRS Institut Charles Gerhardt Montpellier, France, with Francesco di Renzo leading research in novel templated mesoporous materials and zeolites, respectively. During and after almost 10 fantastic years at Industrial Research Ltd. in Wellington in the Advanced Materials team, Steve worked at the National Institute for Materials Chemistry, Tsukuba, Japan (Fujio Mizukami); the National University of Singapore (Chuah Gaik Khuan); the University of Kent at Canterbury Nanobiotechnology team (Ian Bruce); Landcare Research Ltd. Pest Control technologies team; for himself at Moto Academy NZ Ltd. and Innovative Moto Developments and is now helping lead research into new materials and chemical technologies for current and future roading applications at Opus Research.

Chipseals for NZ roads

Chipseals, rather than asphalt concrete (AC), are preferred and used in New Zealand as the primary surfacing on unbound granular pavements over 90% of the sealed road network.[1] While ACs are known to add strength to a pavement (road), chipseals are not known to add strength until perhaps they become several layers thick, after repeated resealing over time. In many countries chipseals are considered to be simple surface dressings used to extend the life of a road surface, but in New Zealand, Australia and South Africa they are more than just surface dressings and are used in many of the same ways that ACs are used in other countries. New Zealand is seen as a world leader in the science, technology and implementation of chipseal surfaces, in much part due to the very much lower costs of chipseal surfaces over AC surfaces. Without chipsealing, regardless of how it is perceived in the marketplace, it must be acknowledged that New Zealand would simply be unable to surface even a fraction of the roads that we currently do.

There are many different ways to design and construct chipseals to solve roading challenges[2] and likewise many ways in which they may fail to perform as desired or planned. Primary among the modes by which chipseals fail to meet the performance requirements are: chip loss (stripping, ravelling), texture loss (flushing and polishing) and cracking. The NZ Transport Agency will typically spend around 56% of their NZD$1.7b budget on pavement maintenance which includes resealing among many other actions.[3]

Opus Research Pavements Group has a strong focus on understanding the origins of roading problems and on developing innovations aimed at providing useful solutions and lifetime extensions for chipseal and asphalt surfaces alike. This paper focuses on one innovation we are exploring aimed at improving the resilience of chipseals towards chip loss, flushing and cracking. Chip polishing, the mechanical action which occurs over time as tyres and grinding particles polish off the sharp chip edges, is not specifically dealt with in this work.

First-coat chipseals, i.e. those placed on new roads, consist of a thin (approx. 1-2 mm) coating of bitumen applied over a road surface (typically an unbound granular surface), onto which aggregate chips are applied and then rolled in to form a cohesive stone mosaic attached to the pavement surface. Chipseals are not relied upon to add structural strength to the pavement, but rather to act as both a waterproofing membrane and as a ‘glue’ that holds the skid resistant friction course (chip). Chipseals are constructed from a wide range of bituminous materials and aggregates of different geologies and sizes. In NZ they are applied across the range from local and peri-urban streets to intercity national highways. Over time, reseals occur as seals wear or begin to fail. The demands placed on chipseals are therefore very high in terms of cost/benefit, lifecycle, supporting heavy traffic, waterproofing and skid resistance. The NZ context is one of the most complex and highly demanding in the world in terms of chipseal performance with demands that would not even be considered in many other jurisdictions. However, due to the rising costs of road construction and maintenance, the application of chipseals for uses beyond surface dressing is being increasingly considered in other jurisdictions such as the USA.

Chemical challenges for bitumen in roading

Bitumen is produced from the heavy fractions (resids) of petroleum refining and fractionation. As an aside, bitumen should not be confused with ‘tar’. The latter was typically produced from coal and is now considered to be quite toxic and indeed carcinogenic. The same is not believed to be true for bitumen, but it is probably not recommended to chew or otherwise coat oneself in it, as it was used back in the day! Bitumen is considered to be a viscoelastic material in that it possess a degree of elasticity in its cooled form, but also behaves viscously at elevated temperatures. The viscosity reduces as the temperature of the bitumen is increased so that at high temperatures (approximately >120 °C) it behaves as a viscous liquid, the viscosity of which can be controlled through blending and formulation. Bitumen is an extremely complex mixture of heavy petroleum fractions and on an individual basis can contain many hundreds of different compounds ranging from small solvent alkanes, through complex polycyclic aromatics and large heterocyclic molecules. Bitumens contain compounds that incorporate H, C, O, N, S and several metals all in various states and proportions. The general families of compounds are:[4]

- Saturates, saturated hydrocarbons, the % saturates correlate with the softening point of the material
- Naphthene aromatics, consisting of partially hydrogenated polycyclic aromatic compounds
- Polar aromatics, consisting of high molecular weight phenols and carboxylic acids
- Asphaltenes, consisting of high molecular weight phenols and heterocyclic compounds, some of which contain metals, such as V- and Mn-porphyrins.

As a result, bitumens are not specified at a molecular level as polymers might be, but are rather specified regarding their performance against a suite of long established test procedures, such as: penetration, ductility, oxidation behaviour and more recently, viscosity/rheology. The specification of bitumen in NZ/Australia is currently undergoing intense redevelopment, with researchers at Opus Research playing a leading role. The nature of the compounds in the bitumen mixture means that they have reasonably high reactivity, at least towards oxidation,[5] so much so that the properties of bitumen can be modified in the blending plant by using controlled high temperature air to oxidise various components of the bitumen and thereby modify the properties. At a basic level this will manifest as decreased elasticity and increased viscosity. The viscoelastic nature of bitumen means that its viscosity decreases with increased temperature, but unlike 'plastic' polymer materials, the softening temperature is not sharp, but rather occurs over an ill-defined range. Below the softening range some components of the bitumen will exist in crystalline or semi-crystalline form, some will be amorphous, some will still be liquid-like. The ease with which it can be heated and spread onto a surface, the high degree of 'tack' that it exhibits on dry surfaces, and its ready availability in our petroleum rich economies (which is an ever changing story) means that bitumen has become the 'go-to' material for road surfacing in all developed and developing countries. But as with all petroleum-based materials, the supply is limited and closely controlled and is also not consistent, hence the need for close specification and continuous testing. As an aside, it was once put, tongue-in-cheek, by a long-term bitumen researcher/practitioner that 'If we had a rank of 100 useful construction materials, bitumen might just be down there at number 98 or so!'

So, while the industry has figured out that it has its uses and how to use it, in terms of its chemical performance, bitumen faces several challenges for long-term durability and performance. The two that stand out are oxidative hardening and hydrophobicity. The former was discussed above, and like many fats and oils that harden as they are oxidised, bitumen behaves similarly. In service, bitumens become harder, less ductile (less elastic and more viscous) and more brittle/prone to cracking. Therefore, over time cracks can develop in bituminous road surfaces as the bitumen loses the ability to flow or rebound, even leading to pieces of the surfacing simply breaking away from the bulk. The problem that this creates for the pavement (road structure) is that the cracks/holes allow water to penetrate into the pavement. This leads to erosion and eventual failure of the road through potholing and loss of density which can lead to rutting. So, while during blending there is a degree of control that can be exercised to modify bitumen properties, in service there is no such control and oxidation occurs much more randomly, along with, of course, attrition of various components through physical stripping, washing out and volatilisation. Various studies have been done or are underway internationally in attempts to more fully understand and explain bitumen oxidation,[5] but to date there has been only limited success in attempts to mitigate its manifestation without compromising other properties of the bitumen.

The second major challenge is the formation of a hydrophobic interface (bitumen) with hydrophilic aggregate surfaces. The mineral aggregates (certainly those used in NZ) are predominately, but not exclusively, silicate-based, e.g. greywacke, basalt, and as a result possess hydroxylated, hydrophilic surfaces to one degree or another. Bitumen does contain certain hydrophilic compounds such as fatty carboxylic acids, but being a mainly organic material is predominantly hydrophobic. Hence aggregate and bitumen tend to be chemically incompatible and aggregate particles are retained within the bitumen matrix through complete physical encapsulation and/or weak van der Waals adhesivity (tack).[4] Bitumen possesses significant tack on dry surfaces, but unless an adhesion agent is added (typically long chain amino and amido-amino compounds),[6] in the presence of water this tack is reduced and can disappear altogether. Adhesion agents are sometimes used in AC construction, but are always used in chipseal construction at around 0.5 wt% loading. The surface free energy of the silicate aggregate-water interface is much more favourable than that of the aggregate-bitumen interface. Therefore, if water is allowed to penetrate into a chipseal or an AC matrix, the water can infiltrate the aggregate-bitumen interface to replace it with an aggregate-water interface. This then manifests as 'stripping' or aggregate loss from the asphalt matrix or chipseal or as flushing (the phenomenon that appears as an area of slick bitumen on the top of a road surface). We will all have seen these failures in various places on our roads, and chipseals in particular are highly vulnerable to both of these failures if a new chipseal is exposed to rain very soon after construction or water pools for long periods on the surface. Ultimately, chip stripping and flushing leads to reduced skid resistance and also to water penetrating into and eroding the underlying pavement, all culminating in the need to resurface or revise the pavement.

So among the challenges facing bitumen and road surfacing scientists and engineers are those of reducing the effects of oxidative hardening of bitumen, and of water induced stripping at the bitumen/aggregate interface and ultimately increasing the lifetime performance (reducing the cost) of road surfaces.

Epoxy-modified bitumen

An innovation that has been developed recently by the NZ Transport Agency and Opus Research has been the application of epoxy-modified bitumen (EMB) as a resilient and long-life binder in Open-Graded Porous Asphalt (OGPA) surfacings (OGPAs are used on high traffic zones, such as motorways, to reduce water spray and noise).[7] This work has progressed to the long-term road trial phase, is now specified by the NZ Transport Agency, and is also being investigated by other countries. EMB was first developed by Shell Bitumen in the 1950s as a means of adhering AC surfaces to the decks of steel bridges, predominantly in the USA, where it has been extremely successful.[8]

The potential of EMB as a chipsealing binder is now being explored,[9] so as to mitigate some of the failure modes associated with conventional chipseals. In particular, is it possible that EMB chipseals might:

- provide a treatment for flushed chipseal surfaces at reasonable life cycle cost or indeed stop flushing altogether through reduction/elimination of binder rise/chip embedment/binder stripping
- reduce cracking by lowering the rate of binder oxidation and retention of binder cohesion
- reduce water-induced chip stripping by providing enhanced binder to chip adhesion.

Polymer modified bitumens (PMB) using latex, styrene-butadiene-styrene and other polymers have been well known for many years and PMBs are used internationally. EMB is different to other PMBs in that the polymer component (epoxy) is a reaction-set polymer rather than a thermoset. It also creates direct chemical adhesion to aggregate surfaces, even in wet conditions, and provides permanent cohesion within the bitumen film that is retained with increased temperature. With these properties and the success of the EMB-OGPA work in mind, some of the possibilities for the construction of EMB chipseals are being investigated and developed.

Laboratory testing

A proprietary EMB tack coat product with an accelerated cure rate (kindly supplied by ChemCo Systems Ltd., CA, USA) was chosen for laboratory testing.[9] The base bitumen from which the EMB was made was approximately equivalent to an 80-100 penetration grade bitumen, which is a typical temperate climate chipsealing binder grade. The term binder is applied when bitumen is actually used to bind aggregates together. In the USA, the term asphalt can also be used in place of the term bitumen, whereas in NZ the term asphalt specifically applies to the mixture of bitumen and aggregates to create a bitumen concrete material, i.e. asphalt concrete, AC.

The very important ability of EMB to retain chip in wet conditions was tested with the Vialit Plate impact test, where standard chipsealing bitumen and EMB with dry, damp and also saturated chips were tested, along with the effect of freezing (-8 °C). Standard bitumen lost all damp or saturated chip and typically lost between 60-80% of dry chip. Uncured EMB (where the EMB was cured while in contact with the chip) retained all dry, damp and saturated chip. In dry, damp and wet chip conditions, strong chip retention was observed even when the chip was added to EMB that had several hours of curing. In some cases it was observed that the EMB fractured upon impact and when frozen this became more acute, especially with the rapid-cure EMB product. The rapid-cure epoxy seemed to produce a glassy material, explaining the fracture behaviour. This behaviour can be typical of epoxies that are cured quickly, but it can also be designed out of the epoxy through using different epoxy resin types, different mixing regimes, different curing temperatures and indeed with bitumen dilution. This latter, key aspect of the chemical design will form an important part of future investigations into the optimisation of EMB chipseals.

Long-term durability

Long-term durability of the EMB was tested by investigating the increase in cohesive energy of the material after long-term oxidation at an elevated temperature. A standard bitumen hardens over time due to oxidation of its components, which also tends to make the bitumen more brittle. In EMB hardening is also observed, but this is due also to epoxy curing (polymerisation) which helps to improve the strength of the EMB film rather than diminish it. The initial measured cohesive energy of the EMB was comparable to standard binders, but after curing, it climbed to almost 30 times that of the standards. This may or may not ultimately be desirable and may need tuning, but it may also imply that new ways of thinking are required about how bitumen and EMB materials are used.

Resistance to traffic loads

In order to understand the ability of EMB to resist chip embedment (pushing of chip into softer underlying layers) which contributes to bitumen flushing (the rise of bitumen to produce a slick, ‘flushed’ surface), a series of wheel tracker samples was prepared. The Opus Research wheel tracker (Fig. 1) consists of a 300 mm diameter domestic trailer tyre supporting a 100 kg weight on the end of a horizontally mounted pneumatic ram. The wheel is driven back and forth over a 750 x 300 mm steel sample plate with 25 mm deep borders, all inside an insulated, temperature-controlled box (5 to 50 °C). A 20 mm thick, 10% bitumen (180-200 penetration grade bitumen) sand mastic was laid, compacted and cooled on each plate. Chipseal made with either standard bitumen or EMB and Grade 3 (9.5 -13.2 mm diameter range) Wellington greywacke chip was then laid and rolled into each plate and left to rest or cure under a range of conditions including room temperature (approximately 15 °C) or elevated temperature inside the wheel tracker box (35 °C), for various lengths of time (12 h to 20 days) to allow different degrees of EMB curing to occur.

Each sample plate was wheel-tracked continuously for 12 h at 35 °C to replicate trafficking on a hot day, which leads to softening and mobilisation of the early-life chipseal bitumen. The experimental design suggested that if the chipseal lost cohesion during wheel tracking, the base mastic would also lose cohesion and not be strong enough to support the wheel load and chip embedment, rutting and bitumen tracking would occur. On the other hand, if the chipseal remained cohesive, the supporting mastic would offer sufficient strength to be able to support the wheel load without chip embedment, rutting or bitumen tracking.

The very dramatic difference between typical penetration grade chipseal bitumens (180-200, 80-100 and sometimes 40-50) and the EMB (20 days curing at 35 °C) after 12 h of wheel-tracking can be seen in Fig. 2 and followed in Fig. 3 for a 180-200 sample. The 180-200 grade bitumen chipseal sample shows a deep rut, embedment of chip and a mess of tracked bitumen. This behaviour is representative of a chipseal where the stone mosaic (the interlocked surface created by the aggregate chips themselves interlocking with each other) has been disrupted when the road gets hot soon after laying and/or is trafficked too soon. Both are real-world problems leading to chipseal damage. The EMB chipseal sample on the other hand, shows minimal damage to the sample (staining on the chip is from bitumen from previous experiments coming off the tyre). No chip roll-over or bitumen tracking, and only a very small amount of embedment were observed. Indeed, the rutting rate was reduced to between 10-25% of that of the standard bitumen chipseal sample. Similar results were observed with 5 and 10 day cured samples. This suggests that EMB chipseals develop a certain amount of load supporting strength and high degrees of internal cohesion over time and that it may be possible in the future to add a chipseal strength component into the design of pavements.

The next steps

The research to date has been focused on laboratory investigations of this novel sealing binder. Small field trials are underway in the Opus Research carpark/driveway and larger real-world field trials are planned.

In summary, laboratory investigations so far suggest that the use of epoxy-modified bitumen for construction of robust and long-life chipseals shows significant promise and that they may mitigate many of the chemical shortcomings of bitumen in roading applications.

Fig. 1. Opus Research wheel-tracker device with sample plate in place. At right, pneumatic driving ram; in centre, sample plate, tyre and 100 kg weight; centre left, worm drive to move plate perpendicular to wheel path.

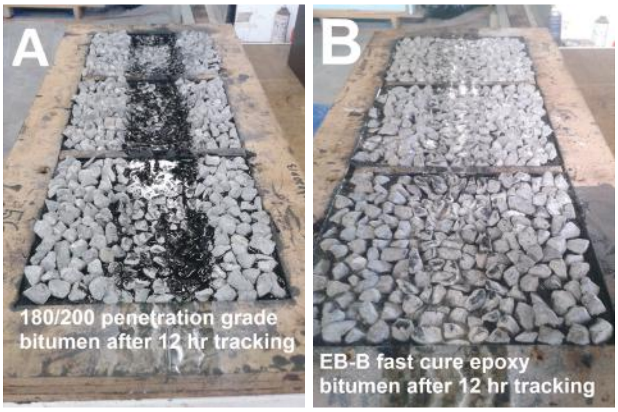

Fig. 2. Examples of wheel tracker chipseal plates after wheel tracking at 35 °C for 12 h. 180/200 penetration grade bitumen (A), fast cure EMB (B). The EMB sample was cured for 20 days at 35 °C prior to tracking. Samples cured for shorter periods showed similar results.

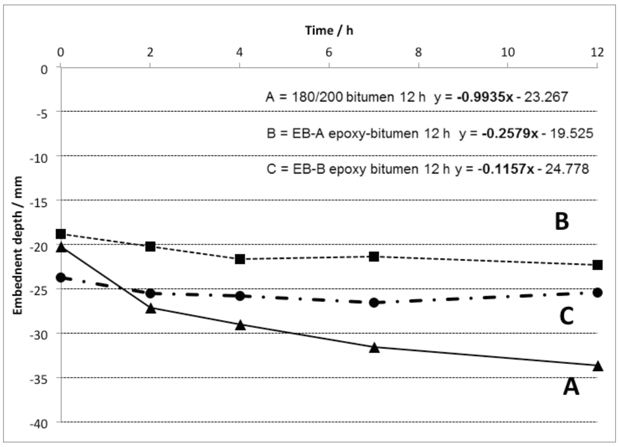

Fig. 3. Rate of chip rollover, embedment and rutting of chipseal samples. A: 180-200 penetration grade; B: slow cure rate EMB; C: fast cure rate EMB. Only the slope of the graphs is important, zero value is sample dependent.

About Opus Research

Opus Research (www.opus.co.nz/services/research) is based in Wellington, New Zealand, and is the principal centre of the global research activities for Opus International Consultants Ltd. Opus Research provides a range of research, consultancy and laboratory services to improve the design, performance of, and interactions with infrastructure for commercial and government clients. Our researchers include; chemists, materials scientists, physicists, environmental scientists, geographers, behavioural scientists and engineers working in multi-disciplinary teams. Our management and operating practices are accredited to the International Quality Management System, ISO 9001, and many of our laboratory services have ISO 17025 accreditation.

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The contribution of wet deposition and particulate matter to total copper, lead and zinc in stormwater runoff

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Biography

Louise Murphy successfully defended her PhD in April 2015 with the department of Civil and Natural Resources Engineering at the University of Canterbury. Louise is currently working with Tonkin & Taylor Ltd as an environmental scientist; her work interests include contaminated land, stormwater quality and atmospheric pollution.

Abstract

Wet deposition is an important process in the removal of heavy metal particulates from the atmosphere. However, the contribution of wet deposition to the total heavy metal deposition flux can vary widely between different airsheds. Understanding the contribution of wet deposition to the total metal deposition flux is important for accurate knowledge of local atmospheric deposition processes, which will subsequently help in the selection of appropriate stormwater treatment and management options. This research monitored Cu, Zn and Pb loads in wet deposition samples and in bulk deposition samples from modular concrete paving slab systems. In conjunction, ambient particulate matter (PM) concentrations were monitored to determine their contribution to the wet deposition flux. All research was conducted in an industrial land-use area in Christchurch, New Zealand. Results showed that wet deposition efficiently removed PM from the atmosphere, but after 1–2.5 antecedent dry days, PM concentrations recovered. Subsequent antecedent dry days, i.e > 1–2.5 d, did not influence PM concentrations. Pb loads in wet deposition were dependent on coarse PM (size range between 2.5 µm and 10 µm) concentrations. This suggested that there was a local source emitting coarse Pb particles into the atmosphere. Wet deposition was an important contributor of dissolved Zn to bulk deposition. However, dry deposition was the greatest source of total Cu, Zn, and Pb loads in bulk deposition. This is principally due to the low annual rainfall in Christchurch, which limits pollutant removal via wet deposition unlike dry deposition, which is continually occurring.

Introduction

Particulate matter (PM) is an atmospheric pollutant that is defined by its size rather than its chemical nature, structure, or origin.[1] PM is not a single pollutant, but rather a heterogeneous composite of particles varying in chemical composition, shape, size, solubility, residence time, toxicity, and origin.[1-2] PM is typically subdivided into two categories: $PM_{2.5}$ and PM_{10}. $PM_{2.5}$ comprises of particles with a diameter smaller than 2.5 µm and are referred to as "fine" particles. PM_{10} refers to particles with a diameter smaller than 10 µm, which also encompasses the $PM_{2.5}$ fraction. Particles with a size range between 2.5 µm and 10 µm are called "coarse" particles ($PM_{10-2.5}$). In most urban environments, both coarse and fine particles are present together, but the proportion of fine to coarse particles varies between different urban airsheds depending on the local geography, meteorology, and the emission source(s).[3] Fine particles, in comparison to coarse particles, have a longer atmospheric residence time and can be carried long distances, in some instances travelling 1,000-10,000 km from their source.[1]

The majority of regulation and research initiatives involving PM are driven by its effects on human health,[1] unsurprisingly, as the WHO considers PM as a major risk factor for human health.[3] In particular, fine particles are associated with the most adverse health effects from particulate air pollution because they can penetrate and lodge deeply in the lungs.[3] However, PM can also be a substantial source of organic and inorganic pollutants. For example, fine particles are typically composed of SO_4^{2-}, NO_3^-, NH_4^+, organic carbon, elemental carbon, and heavy metals; coarse particles are typically composed of bioaerosols, e.g. pollen, geological material, and sea salt spray.[4] PM containing heavy metals are important to research because they can exist in varying chemical forms, i.e. water soluble, loosely particulate bound, or insoluble forms,[5] and can be incorporated into stormwater pollution. In general, heavy metals are associated with fine particulates because fines have a greater surface area per unit mass and accumulate metals more efficiently.[6] As fine particulates have a longer residence time in the atmosphere, concentrations are typically more homogeneously distributed in an airshed as they get farther from the emission source.

The removal process of PM metals from the atmosphere is via atmospheric deposition. Atmospheric deposition occurs in two ways: dry or wet deposition. Dry deposition (DD) is the direct settling of PM onto land or water surfaces via impaction, gravitational settling, turbulence, or Brownian motion depending on the size of the PM.[7] Wet deposition (WD) occurs when PM leaches from the atmosphere with water droplets in the form of rain, snow, frost, fog, mist, and dew[8] and it is considered the cleanser of the atmosphere.[9] WD is one of the most important mechanisms through which airborne pollutants reach the land surface.[10] WD has been reported to remove up to 70-80% of the pollutants, principally fine PM, from the atmosphere.[11] However, this amount is dependent on the airshed studied, the chemical species, and the frequency of precipitation events.[12] Aside from being a major atmospheric pollutant removal pathway, WD is important because it leaches pollutants to a surface partly in solution, enhancing the possibility of biological interactions.[13] The solubility of the pollutant is affected by rainfall pH, pollutant concentration, and the type of particle the pollutant is affiliated with in the atmosphere.[14]

WD becomes stormwater runoff after contact with the land surface.[10] The runoff incorporates DD particles resulting in bulk deposition (BD) loads captured from an impermeable surface. Quantifying the relative contribution of WD and DD to BD loads is important for gaining knowledge on local atmospheric deposition processes, which will subsequently help in the selection of appropriate stormwater treatment and management options. In addition, ambient PM concentrations are also important to research as they can contain heavy metals, and thus, can contribute to WD and DD metal loads in stormwater. In particular, it is important to determine how ambient PM concentrations respond after a rain event as they will influence the amount of metal particulates available for deposition onto impermeable surfaces. Thus, this paper reports on research findings from monitoring the contribution of WD to the total Cu, Zn, and Pb deposition flux in an industrial area of Christchurch, New Zealand, a medium sized city with low intensity (95% events are < 10 mm/hr) and frequency (<81 wet annual days) of rainfall. PM concentrations were also assessed to elucidate relationships with WD metal loads and antecedent dry days.

Materials and methods

Study sites

Field investigations were conducted in a light industrial land-use area in Christchurch, New Zealand, from August 2013 to March 2014. The climate of Christchurch is associated with low rainfall and long antecedent dry periods, typically of a semi-arid environment. Christchurch is prone to smog events that commonly occur during cold calm nights when the atmosphere is stable and emissions from domestic heating are high.[15] Smog events are a principal result of the strong near-surface temperature inversions during anticyclonic synoptic conditions.[16] PM concentrations and WD were measured at an Environment Canterbury (ECan) air monitoring station that was within the vicinity of an old but operating gelatin factory, a shopping centre, and a shipping container terminal where air discharges were expected to be frequent. BD samples from concrete modular paving slab systems (here on referred to as boards) were collected 1.44 km away from the WD and PM samplers. The distance between the PM sampler and the board setup was due to the availability of secure and private land to host the experimental setup. BD was collected in the immediate vicinity of a shipping container terminal, liquid petroleum gas depot, retail premises, and warehouses.

Field sampling

The PM data were measured and analysed by ECan. PM_{10} and $PM_{2.5}$ were measured using a Tapered Element Oscillating Microbalance (TEOM) with a Filter Dynamics Measurement System (FDMS). PM data from August 2013 to the end of November 2013 were audited by ECan; however, data afterwards were not officially audited, but results are unlikely to have changed by more than 1 – 2 μg/m^3. WD samples were collected by a WD sampler (N-Con ADS Model 00-120-2). The WD sampler had an infrared transmitter and receiver that opened the sampler within 20 seconds of the onset of precipitation and closed it within a minute of the end of precipitation. BD samples were collected from four replicate impermeable concrete boards (as detailed in Murphy *et al.*[17,18]). The concrete boards were designed to capture atmospheric pollutant build-up (DD) and atmospheric pollutant wash-off (WD). The concrete boards (1,000 mm x 1,000 mm) were elevated 500 mm from the ground and inclined at a 4° slope. A collection area (718 mm x 400 mm) was incorporated into the concrete board design to account for pollutant loss via splash and spray. Runoff from the collection area was conveyed to a 20 l high density polyethylene collection chamber via a stormwater collection funnel. Rainfall data were obtained from Christchurch City Council's weather station located 0.87 km away from the PM and WD samplers.

Sample collection and analyses

Seventeen rain events were sampled from August 2013 (winter) to March 2014 (autumn) to analyse the relationship between WD loads and PM (Table 1). Eight WD samples were measured that could be directly compared to pollutant loads from BD (Table 1). WD and BD samples were collected and analysed for total and dissolved Cu, Pb, and Zn loads. All samples were stored below 4 °C after collection. Cu, Pb, and Zn concentrations were determined by ICP-MS (Agilent) following the APHA[19] method 3125-B. Total metals were HNO_3 digested following the method described by Wicke *et al.*[20] The detection limit for Zn was 10 μg/l; the detection limit for Cu and Pb was 1 μg/l. Any data below the detection limit (principally dissolved Pb) were removed from the dataset. QA/QC protocols including blanks, duplicates (at least 10% of samples), spikes, standards, and instrument calibration were conducted.

Statistical analyses

Statistical analyses were conducted using the R 3.0.2 package.[21] A multivariate analysis of variance (MANOVA) test was performed to ascertain whether statistical differences existed in the mean $PM_{10\text{-}2.5}$ and $PM_{2.5}$ concentrations with varying antecedent dry periods. Differences between antecedent dry periods were analysed by *post hoc* Gabriel analysis for its superior capabilities at handling unequal sample sizes.[22] All dependent variables were transformed (natural log) to comply with the normal distribution criterion. Homogeneity of variance was confirmed using Levene's test.[22] A Pearson's Correlation was used to determine statistical dependence between two variables.

Table 1. Summary of rain events captured during the sampling campaign [* = WD sampled; ** = WD and BD sampled]

Event no.	Date	Rain depth (mm)	Antecedent dry days (d)
*1***	03/08/13	5.8	10
*2***	25/09/13	2.0	2.7
*3***	08/10/13	33	8
*4***	13/10/13	8.4	2.5
*5***	25/10/13	5.6	7
*6***	31/10/13	2.0	5.5
*7**	22/11/13	5.6	19.6
*8***	25/11/13	13.0	3
*9***	08/12/13	3.8	11
*10**	17/12/13	5.2	6.8
*11**	20/01/14	10.6	13.5
*12**	26/01/14	3.6	5.4
*13**	12/02/14	15.6	11.2
*14**	23/02/14	9.6	9.4
*15**	28/02/14	11.8	4.8
*16**	03/03/14	138.4	2.1
*17**	05/03/14	1.8	0

Results and discussion

Particulate matter with varying antecedent dry periods

A MANOVA statistical analysis was conducted to ascertain if there was a significant difference in fine and coarse particulate concentrations with varying antecedent dry periods. The antecedent dry periods were categorised into six groups: <1 d, 1 - <2.5 d, 2.5 - <4 d, 4 - <5.5 d, 5.5 - 7 d, >7 d. The mean concentrations of ambient fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) particles varied significantly with changing antecedent dry periods (Pillai's trace [V = 0.166, F(10, 454) = 4.108, p-value < 0.001]). For coarse particles, there was a significant difference in their concentrations when the antecedent dry period was between 0-1 d. After one antecedent dry day, the concentrations of coarse particles did not alter significantly with increasing antecedent dry days (Table 2). Similarly, for fine particles, there was a significant difference in their concentrations when the antecedent dry period was between 0 - 2.5 d. After 2.5 antecedent dry days, the concentrations of fine particles did not alter significantly with increasing antecedent dry days (Table 2). Therefore, wash-off from a precipitation event had a significant effect on fine and coarse particle concentrations within the initial few days of the rain event occurring, but both fine and coarse particle concentrations were not influenced by longer antecedent dry periods (1 to 2.5 days). This differs to particulate build-up on urban impermeable surfaces, whereby, particulate build-up increases asymptotically with antecedent dry days, which ultimately plateaus after 6 days.[23] Therefore, particulate build-up on an impermeable surface is limited at the start of the antecedent dry period because wet deposition has removed the PM from the atmosphere.

The average concentrations of $PM_{10-2.5}$ and $PM_{2.5}$ (µg/m^3) within the light industrial land-use area with varying antecedent dry periods. Within each antecedent dry period, those sharing a common letter are not significantly different (p > 0.05) [n = number of cases analysed].

Particulate matter and wet deposition

A summary of WD pollutant loads and $PM_{2.5}$, PM_{10}, and $PM_{10-2.5}$ concentrations the hour preceding the rain event are shown in Table 3. The relationship between PM concentrations prior to rainfall and heavy metal loads in WD was determined using a Pearson's correlation. PM concentrations before rainfall did not show a significant relationship with heavy metal loads in WD, except for Pb, which had a significant relationship with $PM_{10-2.5}$ concentrations. This suggests that coarse particle concentrations in the atmosphere influenced Pb loads captured in WD. This finding was different to other research, which stated that Pb loads in WD were mainly associated with the submicron size range.[24] However, Lee and Park[25] also found that Cu did not correlate with PM, while Pb was highly correlated (p-value < 0.05) with PM in air emissions from an urban-residential and industrial land-use area in Ulsan, Korea. The reason that Cu and Zn were not statistically related to PM was probably due to the height of the PM monitoring station; PM concentrations were

Table 2. The average concentrations of $PM_{10-2.5}$ and $PM_{2.5}$ (µg/m^3) within the light industrial land-use area with varying antecedent dry periods. Within each antecedent dry period, those sharing a common letter are not significantly different (p > 0.05) [n = number of cases analysed]

	<1 d	**1 - <2.5 d**	**2.5 - <4 d**	**4 - <5.5 d**	**5.5 - <7 d**	**>7 d**
$PM_{10-2.5}$	9.03 ± 0.68^a	13.34 ± 0.84^b	16.11 ± 1.16^b	17.09 ± 1.61^b	15.44 ± 1.51^b	16.28 ± 1.23^b
$PM_{2.5}$	5.23 ± 0.31^a	6.78 ± 0.48^{a,b}	7.70 ± 0.54^b	7.72 ± 0.58^b	8.67 ± 0.91^b	7.81 ± 0.49^b
n	30	47	43	32	27	54

Table 3. The range (min – max) and mean values of PM measured at the light industrial land-use area one hour prior to the rain event (µg/m^3) and total metals (µg/m^2) in WD

	PM_{10}	**$PM_{2.5}$**	**$PM_{10-2.5}$**	**$tCu_{(WD)}$**	**$tZn_{(WD)}$**	**$tPb_{(WD)}$**
Range	6.2 – 93.2	0 – 13.0	2.7 – 78.1	1.5 – 509.2	17.4 – 888.6	n/d – 130.3
Mean ± SE	26.8 ± 5.6	6.2 ± 3.2	20.1 ± 5.0	56.5 ± 28.3	213.6 ± 56.7	20.2 ± 9.0

measured approximately 3 m above the ground, which only reflects PM concentrations at the lower tropospheric level. Cu and Zn particulate concentrations higher in the troposphere, e.g. where cloud formation occurs and rain-particle impaction occurs, were not wholly represented. It is likely that the correlation between PM and Pb was due to a local source of Pb contributing to WD loads, for example, from nearby old residential houses with Pb-based paint being demolished after the 2011 Canterbury earthquakes. A local source of particulate Pb would explain why there was PM Pb concentrations in the lower troposphere – particulate Pb did not have sufficient time to reach higher altitudes in the troposphere before being washed-out. On the other hand, if the source of Cu and Zn were farther away, the Cu and Zn particulates would have been able to reach higher altitudes.

Wet deposition

Determining the speciation phase of metals in WD is important because metals can occur in either the particulate or the dissolved phase. Metals in their dissolved forms are most concerning because of their increased mobility in the aquatic environment, and thus, availability for biological uptake.[26] The partitioning of trace metals to the dissolved or particulate phase depends on the quantity and solubility of trace metals in a rain event.[27] The percentage contribution of dissolved to total metals in WD (n=17) was 40.58% ± 7.38% and 83.07% ± 4.72% for Cu, and Zn, respectively. A ratio of dissolved to total Pb was not evaluated as dissolved Pb concentrations were frequently below the detection limit (1 µg/l). Particulate Pb dominated the total Pb flux because Pb had a low solubility in WD and was principally washed-out in particulate form. The ratio of dissolved to total Cu was relatively high, which suggested that Cu was easily soluble in WD. Zn was mainly associated with the dissolved phase (83.07%); therefore, Zn was highly soluble in WD. Similarly, Morselli *et al.*[28] found that Zn had the highest solubility in WD followed by Cu; Pb had a very low solubility in WD. Colin *et al.*[29] found that Zn concentrations in WD in France were mainly associated with the dissolved phase (approximately 96%). Freydier *et al.*[30] found that Zn had the highest dissolved to total distribution of all metals studied (which included Pb, but not Cu) in intertropical Africa. WD results from Otago, New Zealand, found Zn atmospheric loads were present in a dissolved or easily dissolved forms, and thus, stated that Zn originated from a non-crustal source because metals generated from anthropogenic sources tend to be loosely bound to airborne particles.[31] The results in this research differed to Conko *et al.*,[27] who found that Cu was more soluble than Zn in precipitate in Virginia, United States; however, this could be due to the lower rainfall pH in Virginia (3.7 – 4.7) than Christchurch (4.9 – 7.2)[27,32] or from different source emissions of metals in each airshed. Kaya and Tuncel[14] reported solubilities of 43% ± 29%, 49% ± 27%, 40% ± 35% for Zn, Cu, and Pb, respectively, in rainwater from Ankara, Turkey.

Contribution of WD to BD loads

Total Cu, Pb, and Zn loads from WD and BD from concrete boards (as previously discussed) are summarised in Table 4. The results show that WD contributed approximately 10 - 13% of the total Cu, dissolved Cu, and total Pb (dissolved Pb was negligible) loads in BD. Therefore, DD was the major pathway for Cu and Pb removal from the atmosphere (Figs 1 and 2 respectively). Conversely, WD was an important contributor of total Zn (34%) and dissolved Zn (133%) to BD (Fig. 3). The value of Zn above 100% was attributed to Zn being highly soluble in precipitate at the pH range (4.7 – 7.2) found in Christchurch rainfall. Moreover, concentrations of dissolved Zn from WD were higher than dissolved Zn concentrations in runoff from a concrete surface. The decrease in dissolved Zn concentration in the runoff was probably due to calcium carbonates and calcium hydroxides adsorbing dissolved Zn.[33] Although dissolved Zn loads were dominated by WD, DD was the biggest contributor to total Zn loads. Overall, the results demonstrate that DD was the important controller of atmospheric pollutant loads in BD due to limited precipitation in Christchurch. Although DD is a slow process, it is continually occurring unlike WD; therefore, it is of greater importance to net pollutant deposition. Mitigating atmospheric pollutant loads in DD should be the focus of stormwater management through improved source control legislation or by choosing the best pavement material for attenuating DD loads, i.e. concrete.

Conclusions

Knowledge of the pathways dominating atmospheric deposition is important because it increases our understanding of atmospheric pollutant removal processes. As the processes affecting pollutant deposition can vary for different airsheds due to different meteorology and land-use activities, it is important to quantify the contribution of wet and dry deposition for each airshed individually. The results presented here demonstrate the importance of WD in removing fine and coarse PM from the atmosphere. Following a rain event, atmospheric PM concentrations begin to increase; after one to two antecedent dry days, PM concentrations stabilise, i.e. PM concentrations are not influenced by longer antecedent dry periods.

DD was the dominant pathway for atmospheric metal removal due to the low rainfall frequency in Christchurch.

Table 4. The range (min – max) and mean values of total metals (µg/m^2) in BD from August 2013 to December 2013 and the percentage ratio of pollutant in WD to BD (mean ± SE) [n/d = not detected; n/a = not analysed due to insufficient data]

	dCu	**tCu**	**dZn**	**tZn**	**dPb**	**tPb**
Min	15.66	34.74	26.40	36.39	n/d	3.39
Max	202.87	254.26	223.08	693.71	0.91	78.50
Mean ± SE	62.80 ± 20.04	108.28 ± 22.43	118.09 ± 26.40	334.16 ± 77.57	n/a	35.79 ± 8.81
Ratio (%) to WD	12.44 ± 6.36	10.39 ± 2.52	132.71 ± 11.20	34.22 ± 5.31	n/a	11.64 ± 3.41

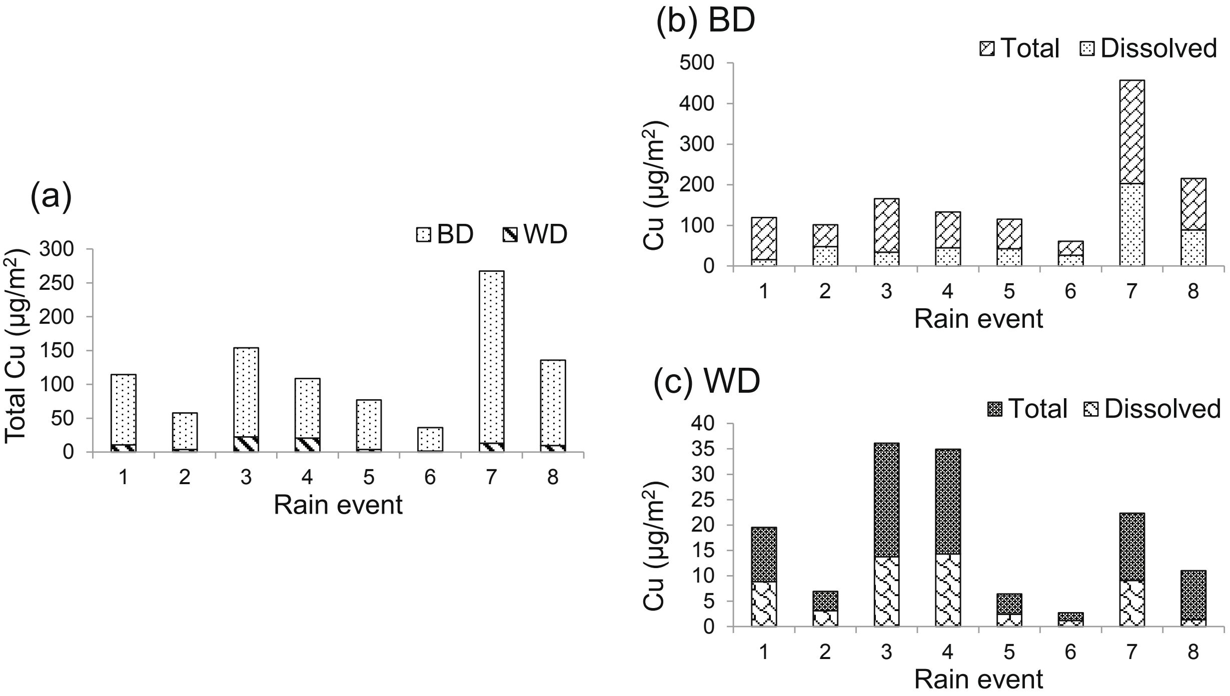

Fig. 1. (a) total Cu concentration in BD and WD; (b) the contribution of total and dissolved Cu in BD; and (c) the contribution of total and dissolved Cu in WD.

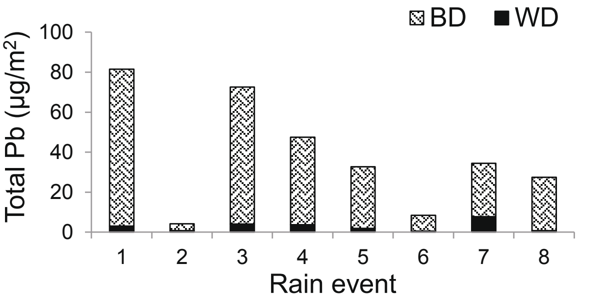

Fig. 2. Total Pb in BD and WD (dissolved Pb is not represented as it was frequently below detection limits)

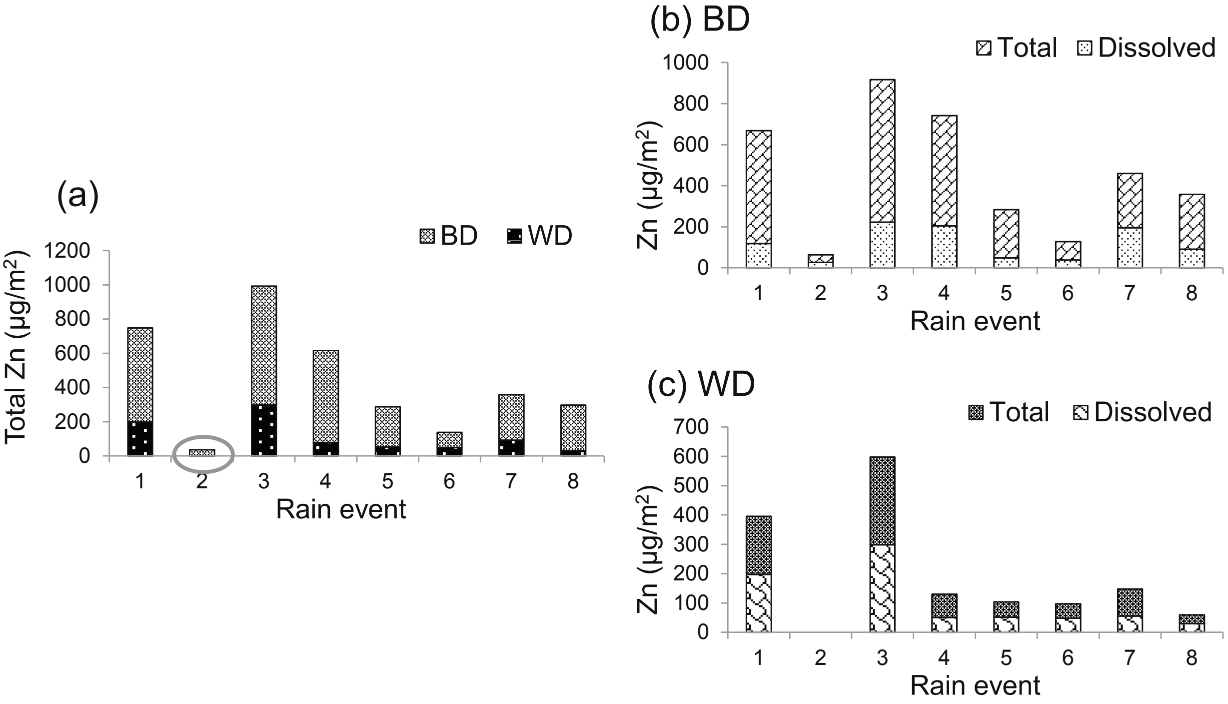

Fig. 3. (a) total Zn in BD and WD; (b) the contribution of total and dissolved Zn in BD; (c) the contribution of total and dissolved Zn in WD (Zn loads in WD from rain event 2 (circled) is not represented as it was below detection limit)

Therefore, from a stormwater manager's perspective, to manage atmospheric deposition as a source of stormwater pollution, emphasis should be placed on removing pollutant loads from DD. Frequent street vacuuming practices during dry days is an option; however, frequent street cleaning is costly and would not be suitable as a long-term pollution mitigation strategy. Implementing effective measures to mitigate atmospheric heavy metal deposition will be challenging unless effective legislation is enforced to mitigate heavy metal emissions to the atmosphere. Implementing controls on atmospheric heavy metal emissions in Christchurch, however, may not be effective (although, they should still occur) as pollutants can be transported from other regions beyond the legislative control, i.e. transboundary pollution (see Murphy *et al.*[17]). Therefore, current focus should be on treating the stormwater runoff as close to the source as possible. A high proportion of total Cu and total Zn are in the dissolved form; therefore, when treating stormwater pollution, emphasis should be placed more on treating the dissolved forms of Cu and Zn rather than the particulate forms.

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Salt and gold: mining the geothermal resource in New Zealand

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Colonial uses of geothermal waters in New Zealand made comparatively few demands on the resource. Tourists roamed the geothermal regions and revelled in the warm waters at the Pink and White Terraces, and apart from some graffiti on the silica terraces, did not alter them significantly. Even the diversion of water from near-surface hot springs to the pools and other facilities in bath houses at health resorts at Te Aroha, Hanmer Springs, and – particularly – Rotorua had relatively minor effects on the availability of the resource to others. Thus, recreational and medical use of the waters could co-exist without detriment to either use until the mid-twentieth century.

This situation changed rapidly with the development of large schemes through which the hot water resource was effectively mined to provide the feedstock for the thermal generation of electricity.

The development of nuclear power in post-war Europe had potential implications for New Zealand. Geothermal waters contain small amounts of deuterium oxide – heavy water, which has applications for slowing neutrons in nuclear reactors. The United Kingdom Atomic Energy Commission was interested in the use of geothermal water from Wairakei for this purpose, and the initial development of a geothermal power station there envisaged heavy water as a by-product.[1,2] Physico-chemical investigations (Fig. 1) and particularly drilling at Wairakei indicated sufficient geothermal fluid to operate the world's first binary phase geothermal power station, which began operations in 1958 and was completed in 1963.

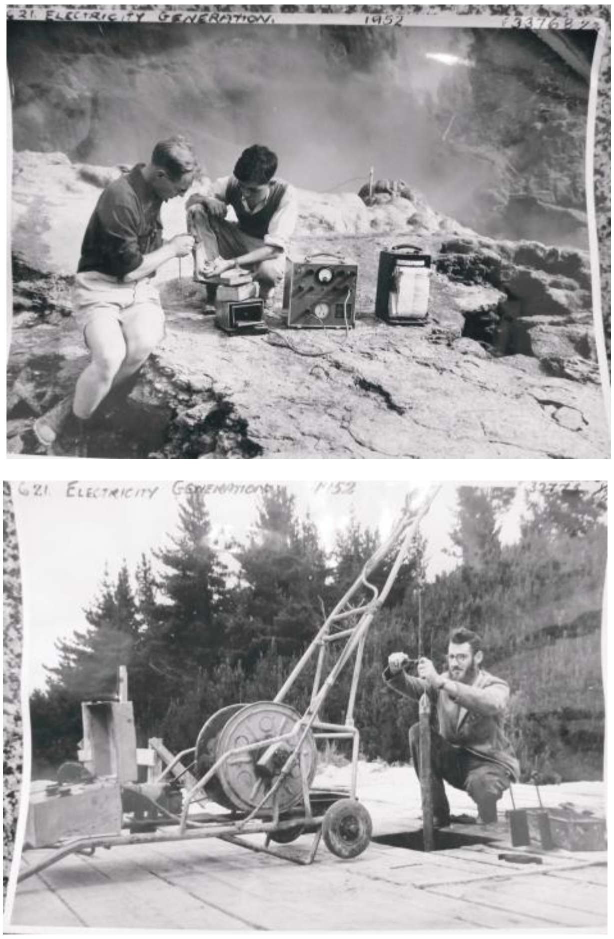

Fig. 1. Chemistry investigations at Wairakei in the 1950s. *Upper:* Radioactivity measurements at the Great Wairakei Geyser in 1952 (Image: Alexander Turnbull Library, F33768 ½). *Lower*: Lowering a temperature measuring device into a drill-hole (Image: Alexander Turnbull Library, F33775 ½).

However, Wairakei was not the first site in New Zealand to be considered for such a purpose.[3] As early as 1918, the Masterton Chamber of Commerce had suggested that the Public Works Department investigate the use of geothermal energy on the basis of the Italian success in generating electricity from natural steam at Lardarello since 1914. The presence of hydrocarbons at Waiotapu[4] attracted the attention of Auckland businessman G Hutchison in 1922, and although his scheme for recovery of these failed to gain Government approval, he next considered the prospect of electricity production. His discussions with the then Engineer in Chief of the Public Works Department allegedly produced the comment that the only likely result would be that "you or those working with you might be blown up".[5] The project did not proceed.[6]

The decline in geyser activity as a consequence of drilling wells to tap the deep geothermal fluid at Wairakei has been quantified,[7] and the demise of natural springs features recorded.[8] Even from a distance, the effect was obvious: the roaring steam from the Karapiti blowhole (Fig. 2), visible until the 1950s from Taupo township, was reduced to a whimper.

After all these years, there are still reminiscences of the recreational use of the natural hot pools in the area, as in the example below which describes the so-called Honeymoon Pool:

"If it's the one I visited many times as a wild teenager (and the location looks spot on) in 1964, called the Honeymoon back then, it was accessed through a track at the rear of a motor camp. Someone had dammed it at the top and about 20 feet below, with the really hot water cascading over each rim. It wasn't wide, about 15 feet and there was brush and trees all around. We usually went at night, when the frost and snow were all around and it was magic - probably the cans of beer we floated down from the top of the stream added to the 'magic'. I remember the

Fig. 2. Karapiti Blowhole, described in 1884 as "formed by a deep and apparently fathomless aperture, rounded like a funnel, and from which issued with a terrific force and unearthly screeching noise, a spiral column of transparent steam, which mounted high into the air as if forced upwards from below by a 100 horse-power engine. So great was the force of this column of steam as it blasted from the earth, that the branches of trees we threw into the funnel were at once ejected and hurled upwards with tremendous power... This curious steam-hole, which carries on its eruptions incessantly, may be distinctly seen all over the Taupo country."[9] (Image: Alexander Turnbull Library, 1/1-020260-G)

water was so hot the cans of beer (unopened) actually sank. Yes, we wore togs and I have amazing memories of those years until it was closed down - probably because of people like us! My boyfriend's parents had a holiday home at Taupo and he knew all the 'private' pools [Fig. 3] like this...."[10]

Fig. 3. Typical hot pool at Wairakei before the geothermal power developments in the 1950s (Image: Alexander Turnbull Library, 1/2-007633-G)

However, probably because tourist businesses in the 1950s were focused on Rotorua, the loss of natural geothermal features at Wairakei drew little criticism. It must also be remembered that the 1950s were times of electricity shortages in the North Island (Fig. 4),[11]and so the loss of some recreational swimming holes could readily be justified by the promise of reliable and adequate electricity supplies. Similarly, much of the geothermal area at Orakei Korako, which was visited by comparatively few people, was submerged under Lake Ohakuri as part of hydro-electric developments along the Waikato River.[12]

THE AUCKLAND ELECTRIC-POWER BOARD

POWER RESTRICTIONS

IN FORCE FROM MONDAY, MAY 12

1958

- NO DOMESTIC WATER HEATING FOR 12 HOURS PER DAY, BETWEEN THE HOURS 8 a.m. AND 10 p.m. MONDAY TO FRIDAY INCLUSIVE.
- NO WATER HEATING FOR ABLUTION PURPOSES IN COMMERCIAL OR INDUSTRIAL PREMISES.
- NO RADIATORS AT ANY TIME IN HOMES, COMMERCIAL OR INDUSTRIAL PREMISES.
- NO SIGNS, OF ANY CLASS, AT ANY TIME.
- NO FLOODLIGHTING OF BUILDINGS OR OPEN SPACES AT ANY TIME.
- NO ORNAMENTAL OR DECORATIVE LIGHTING (INTERIOR OR EXTERIOR) AT ANY TIME.
- NO SHOP WINDOW LIGHTING EXCEPT ON LATE SHOPPING NIGHT (from 5.30 p.m. to closing time).
- NO UNDER-VERANDAH LIGHTING AT ANY TIME.
- NO LIGHTING IN SHOPS OR BUSINESS PREMISES EXCEPTING WHEN OPEN FOR BUSINESS.
- ALL COMMERCIAL AND INDUSTRIAL CONSUMERS MUST SAVE 10% ON DAY-TO-DAY CONSUMPTION

FOR COMPLETE DETAILS SEE "PUBLIC NOTICE" IN THIS PAPER

Public notice about electricity restrictions in Auckland, New Zealand Herald, 10 May 1958.

Fig. 4. Public notice advising electricity restrictions in Auckland (Image: *New Zealand Herald*, 10 May 1958 [see reference 11])

Through the 1950s and 1960s the Public Works Department continued a programme of exploratory drilling in a number of geothermal fields,[13] complemented by the Department of Scientific and Industrial Research's (DSIR's) less intrusive geochemical investigations[14] and geophysical prospecting.

This is where 'salt' becomes important: the geothermal waters contain abundant dissolved salts – principally sodium chloride (but also others, to which curative properties were attributed in colonial times). While there is no suggestion of mining the salts in geothermal water, because the salts make the water conductive of electricity, the extent of saline underground geothermal water can be mapped by its resistivity,[15] a technique which can be demonstrated in a simple laboratory experiment (Fig. 5).[16]

The sodium, potassium, and calcium in the water are readily envisaged as derived by reaction with the silicate minerals in the rocks of the aquifer in which the water is confined. As an example,[17] an idealised reaction of water with potassium feldspar [$KAlSi_3O_8$; 'Kf'] to give the clay mineral kaolinite [$Al_2Si_2O_5(OH)_4$] releases potassium ions:

$$2\ KAlSi_3O_8 + 2H^+ + 9\ H_2O = Al_2Si_2O_5(OH)_4 + 2K^+ + 4\ H_4SiO_4$$

...from which an equilibrium constant can be written: $K_{Kf\text{-}Kaol} = (a_{K+}/a_{H+}).a_{H4SiO4}{}^2$, or equivalently:

$$\log K_{Kf\text{-}kaol} = \log (a_{K+}) + pH + 2 \log (a_{H4SiO4})$$

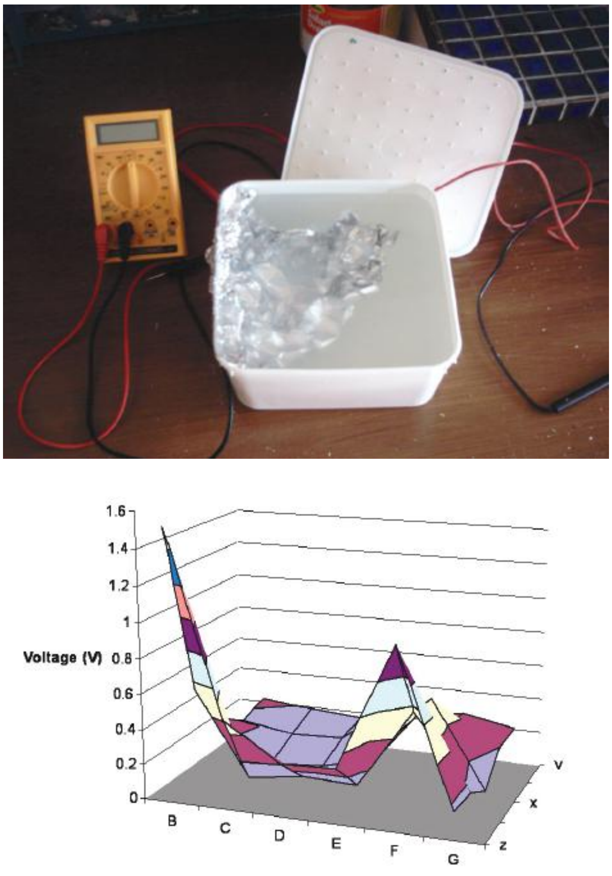

Fig. 5. Laboratory demonstration of resistivity mapping of a geothermal resource. *Upper:* Physical set-up, with crumpled tin-foil (representing the conductive fluid) in water (representing the poorly conductive country rock). *Lower:* The tin-foil as mapped measuring the voltage between an evenly spaced pair of electrodes (connected to a car battery) being moved systematically across the surface of the water (see reference 16)

Consideration of the reaction of water with the mineral albite (the sodium analogue to potassium feldspar [$NaAlSi_3O_8$, 'Ab']) enables the development of an expression wherein the ratio of sodium and potassium ions in solution is related to a ratio of equilibrium constants, *viz*.,

$$\log (a_{K+}/a_{Na+}) = (\log K_{Kf\text{-}Kaol} - \log K_{Ab\text{-}Kaol})$$

... and thence to temperature, since equilibrium constants are temperature-dependent. Thus the Na/K ratio constitutes a simple geothermometer. Expressions derived from reactions that yield other aluminosilicates, e.g. muscovite [$KAl_3Si_3O_{10}(OH)_2$], the clay mineral pyrophillite [$Al_2Si_4O_{10}(OH)_2$] or gibbsite [$Al(OH)_3$] are similarly functions of the Na/K ratio. Assuming these reactions are fairly slow, such ratios have found wide use in estimating the temperature of geothermal waters at depth.[18]

DSIR also experimented with the use of the hot water 'left over' from electricity generation to provide a heat source for experimental greenhouses, of which the prawn farm currently operating at Wairakei can be considered a legacy. Apart from an extension of the borefield at Wairakei to compensate for falling steam pressures, the Ohaaki power station – opened in 1989 was the last foray of central Government into large-scale 'mining' of the geothermal resource;[19] subsequent activities have been smaller stations,[20] some of which have been developed by tribal authorities that have tapped geothermal fluids underlying Māori land. Arrangements in respect of the Ohaaki power station on the Broadlands geothermal field represent the first significant negotiation between a tribal authority and the Government to obtain compensation for the effects that exploitation would have on the enjoyment and use of the resource by local Māori.[21,22]

This conflict between recreational/lifestyle use and more exploitative use emerged as a major issue in respect of Rotorua, where the decline in geyser and hot spring activity at the Whakarewarewa reserve was linked to depletion of the aquifers beneath the city as a consequence of decades of withdrawal for supplying hot water to houses, hotels and businesses. After much discussion,[23] draconian measures to curb use were implemented in the face of strong local opposition.[24] Although there has been some recovery of the natural activity at Whakarewarewa in more recent times,[25] the implementation of these measures was a clear demonstration that the geothermal resource is finite: it may be renewable on a natural time scale, but not at a rate to match 'industrial' exploitation. Although a comprehensive classification of New Zealand's geothermal fields in terms of their historic significance, recreational value, and development potential was developed,[26] there is a current belief that geothermal resources can be sustainably managed for power generation,[27] while still providing for tourism and recreation.

Although small-scale extraction of industrially useful minerals from geothermal areas has occurred in New Zealand for many years,[28] towards the end of the twentieth century New Zealand scientists recognised the chemical and geological similarity between active geothermal systems, e.g. Wairakei and Broadlands, and the gold deposits of the Coromandel Peninsula,[29] and precious metals and base-metal sulfides were recovered from the 'scale' of geothermal wells.[30] The concentration of precious and base metals in the scale was much higher than would be expected on the basis of the sulfides' solubility in water, prompting interest in the mechanism by which the metals could be transported and deposited. Initial suggestions favoured the precipitation of gold, silver and base metal sufides from aqueous metal complexes, typically involving sulphur species or chloride,[31] and many laboratory investigations have been undertaken that demonstrate this suggestion.[32] As an example, the solubility of gold in the system H_2O-H_2-HCl-NaCl-NaOH at temperatures of 300-600 °C and pressures of 500-1800 bar was "accurately described" by the reaction:[33]

$$Au_{(s)} + 2\,Cl^- + H^+ = AuCl_2^- + 0.5\,H_{2\,(gas)}$$

Experiments on one metal have enabled inferences to be drawn about another. An example is an investigation of the solubility of nickel in solutions of increasing temperature and/or chloride concentration which both identified and determined the formation constants of $NiCl^+$, $NiCl_{2(aq)}$ and $NiCl_3^-$ at temperatures up to 700 °C and pressures up to 2000 bar,[34] the report further noting:

"The solubility of millerite (NiS) and pentlandite

($Ni_{4.5}Fe_{4.5}S_8$) calculated using these constants shows that nickel dissolves in significantly higher concentrations in hydrothermal solutions than previously estimated. However, the solubility is considerably lower than for corresponding cobalt sulphide minerals. This may explain why hydrothermal nickel deposits are encountered so much less frequently than hydrothermal deposits of cobalt."

Comparisons between experimental data for metals and their natural occurrence have also been undertaken, e.g. for gold and silver,[35] and between lead and zinc.[36]

Laboratory experiments of course are but proxies for reality: a paper quaintly entitled "Heavy metals or punk rocks?" observing in its abstract:

"Most ore geologists now agree that fluids with metal contents sufficient to produce economic mineralisation are relatively common and that it is the lack of a suitable depositional mechanism that often limits ore formation. Temperature decrease alone cannot be the dominant mechanism, because the solubility of most metals in most hydrothermal fluids decreases by only a small amount over the temperature range determined for most deposits. Thus, other processes – such as boiling or immiscibility, fluid mixing, or fluid-rock interactions – must operate to promote the precipitation of all (or most) of the dissolved metals transported by hydrothermal fluids."[37]

In addition, the involvement of a high-temperature vapour phase as part of the mechanism for metal transport and deposition in the hydrothermal environment has been suggested:

"Magmatic fluids, both vapour and hypersaline fluid are a primary source of many components in hydrothermal ore deposits formed in volcanic arcs. These components, including metals and their ligands, become more concentrated in magma in various ways and from various sources, including subducted oceanic crust. Leaching of rocks also contributes to the hydrothermal fluid – a process enhanced where acid magmatic vapours are absorbed by deeply circulating meteoric waters."[38]

Experiments to test the idea's prospects have also been undertaken.[39] One specific example investigated the solubility of copper chloride in liquid under-saturated HCl-bearing water vapour at temperatures of 280-320°C and pressures up to 103 bar, for which a hydrated copper-chloride gas species was formed:[40]

$$3CuCl_{(s)} + nH_2O_{(gas)} = Cu_3Cl_3(H_2O)_{n\,(gas)}$$

However, the earlier developed notion of transport in solution still has its adherents, a 2005 paper noting, "Despite increasing evidence to the contrary, most economic geologists still assume that hydrothermal ore deposits form exclusively from aqueous liquid."[41]

There is nothing new in this debate between the mechanisms of metal transport involving liquid and gaseous phases; it recalls the difference between Agricola's contention in the mid-1500s that ores are derived from percolating groundwater, and Descartes' view of a century later that ores are derived from magma.[42] In the same way that isotopic composition of geothermal waters have long indicated that while most of the water is meteoric, i.e., derived from rain-water, a component has a magmatic source (Fig. 6),[43] it is likely that for precious and base metals either or both of solution transport, i.e, the Agricolan preference, and vapour transport, i.e, the Descartian preference operate.

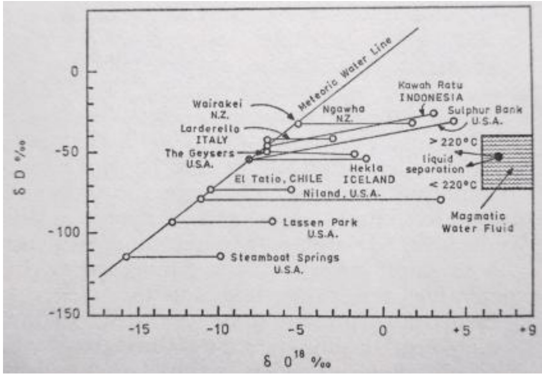

Fig. 6. Variation of isotopic composition of water in geothermal waters relative to the 'meteoric water' line and 'magmatic water' (see reference 43)

Whatever the mechanism, "active geothermal systems such as Ohaaki Broadlands and Rotokawa ... can transport and deposit significant quantities of gold... At Rotokawa, sulphide-rich surface muds contain up to 50 ppm gold and are still being deposited".[44]

Between 1862 and 1952 the Coromandel goldfields yielded 1,600 tonnes of gold-silver bullion, (much of it from Martha Hill in Waihi, Fig. 7) from about 16 million tonnes of ore, giving an overall yield of about 3 ounces per tonne, i.e. 84 ppm; with only about 20% of the bullion being gold, i.e. the yield of gold was about 17 ppm.[45] Comparison with the 50 ppm yield suggested in the previous paragraph, suggests that active geothermal fields could be mined for at least their gold (and possibly other metals), as well as or instead of their energy, adding a further complexity to prospects for exploitation of the geothermal resource.

Fig. 7. Waihi Gold Mining Company's no 5 shaft at Martha Hill, Waihi, in about 1910. The mined ore was taken by rail (foreground) to one of three stamper batteries where the gold-silver was freed from its confining quartz, before further processing. (Image: Alexander Turnbull Library, 1/2-057515-F)

The prospects of economic gold and silver deposits being recovered from active geothermal systems, particularly

Rotokawa, was the subject of renewed interest in mid-2015:

"Hundreds of kilograms of gold and silver could be harnessed from the thermal waters used to run Taupo's geothermal power stations. Researchers from the University of Auckland and the University of Utah found high-grade deposits of gold and silver in the hot springs of the Taupo Volcanic Zone. Gold also formed in sub-surface rocks but appeared to be low grade. New methods would need to be developed to extract the precious metals, or they could be left to build up inside the power stations' pipelines and harvested when the pipes were replaced."[46]

In principle, there is no reason why conflicting uses of the same finite resource cannot be managed effectively;[47] in other words, it might be possible to mine both precious metals and energy from geothermal waters. The suggestion of recovering gold and silver from the scale in pipelines would not provide a continuous source of revenue, but could offset some of the costs of decommissioning pipelines or indeed a geothermal power station itself. The recovery of gold from a siliceous sinter would probably be no more difficult than recovering gold from quartz, using the techniques currently in use. These are updated versions of the mechanical 'stamper batteries' of colonial gold-mining, which freed the gold-silver from the quartz in which it was deposited (Fig. 8); and chemical techniques, which purified the gold by formation and dissociation of a gold-cyanide complex followed by electrolytic refining (Fig. 9):

"In the basic process finely pulverised ore was percolated through a potassium or sodium cyanide solution for several days in large tanks. The pregnant cyanide solution (containing dissolved gold and silver) was then drawn off and passed through wooden boxes where the gold and silver precipitated on zinc shavings, while the cyanide was recovered and recirculated. Later it was found that the process worked more effectively if compressed air was used to agitate the solution. Finer crushing of the ore also proved beneficial.

"Recovery of the gold from the 'zinc slimes' precipitated from the cyanide solution was usually carried out at a refinery. Refining involved treating the slimes with acid to remove the zinc, and melting the residue into crude bullion bars. These were then made into anodes and the silver extracted by electrolysis in acid cells, while the gold was remelted and further refined electrolytically until it attained a purity of at least 99 percent."[48]

However, as a note of caution, a recent commentary on the economics of resource use observed that "... resource-rich developing countries seem unable to successfully convert their depleting exhaustible resources into other productive assets".[49] On this basis, the energy derived through thermo-electric generation from hot steam, with its opportunity for use in industries that serve local needs or produce goods for export, seems preferable to producing gold – essentially a non-productive commodity.

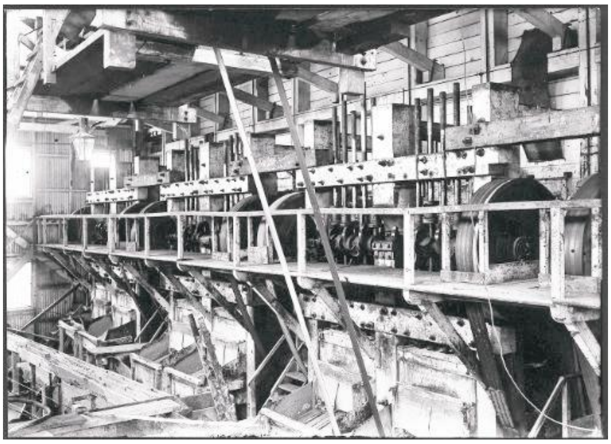

Fig. 8. The workings of the Waikino stamper battery, about 1900, one of three installations used for extracting gold-silver from the ore mined at Martha Hill. (Image: Alexander Turnbull Library, PAColl-7293-02)

Fig. 9. Electrolytic refining: separating silver from gold, Martha Gold Mining Company, Waihi, probably about 1900. (Image: Alexander Turnbull Library, 1/2-023684-G)

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Salt: hero to zero to villain

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Keywords: *salt, sodium chloride, brine, gabelle, solar evaporation, preserving*

Richard Rendle taught chemistry at secondary school level for 33 years before becoming self-employed. He continued his interest in chemistry education and subsequently taught part-time at the University of Canterbury Bridging Programmes. He has always been interested in the stories behind the chemistry and used these in teaching to give a human aspect to an already exciting subject. Through his work on NZIC chemistry exams, Richard became involved with NZIC administration and has held the role of Honorary General Secretary and Administrator since 2006.

While in Germany on an overseas trip, our host took us to a rather strange looking building in Bad Orb, a spa town about 60 km from Frankfurt. As the photos show, it is a long structure (perhaps up to 200 m as there were previously 10 of these buildings with a total length of 2000 m), 13 m high. The sides are packed with brushwood down which water from salt springs trickle and which form a tunnel through which you can walk.

These structures (gradierwerks) were originally part of the salt production industry centred on the salt springs in the area. The brine from the springs contained about 3% salt and was pumped up to the top of the gradierwerk and allowed to trickle down. In doing so, some water evaporated, concentrating the brine which saved on wood fuel needed to complete the evaporation process and as a result of the concentration process less soluble salts like $CaCO_3$, $MgCO_3$ and $CaSO_4$ crystallised out on the branches purifying the brine, over time forming thorn stone.

At its peak in the early 1800s, the Bad Orb saltworks produced about 2,000 tonnes of salt annually. Competition from other works and the discovery of underground salt deposits made production of salt at Bad Orb uneconomic in the mid 1800s. However, a pharmacist promoted the curing potential of brine and Bad Orb re-invented itself as a health resort. One of the gradierwerk structures was saved, is now restored and maintained by a “Friends of the Gradierwerk Association” and serves as an open-air inhaler. Patients suffering from respiratory illnesses (and inquisitive tourists) can walk through the tunnel in a climate considered to be as beneficial as the climate of the seaside.

These days salt is pretty much taken for granted and from a teaching point of view is the go to compound for discussing the formation of ions, simple crystal structures, conducting solutions, easily balanced equations, etc. Seeing this building in Germany and the fact that there used to be 10 of them reminded me that salt has a significant history, of which I knew little and it might be worth pursuing.

Over the Christmas holiday period I was browsing in a Christchurch second hand bookshop, for no particular reason, and came across a copy of *Salt and Civilisation* by S. A. M. Adshead[1] which my wife persuaded me to buy. Professor Adshead, was on the staff of the History Department at the University of Canterbury and had a special interest in the history of China. The history of the Chinese dynasties is inextricably linked with salt production through the salt taxes and salt administration. So it was inevitable that he had to become familiar with the history of salt. This book is a comprehensive academic treatise on the world history of salt from primitive human existence to modern times – very thoroughly researched, following different world civilisations through succeeding time periods with sound

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chemistry. From my point of view it is somewhat information overload and parts require intense concentration to keep track of the special technical terms used (often in the local language – particularly the Chinese sections).

For a more general approach I ordered a second hand copy of *Salt - A World History* by Mark Kurlansky.[2] This is a very readable history with some fascinating stories and concentrates more on the post-production history of salt and its use in foods, with lots of ancient recipes included.

Both books refer to *Neptune's Gift - A History of Common Salt* by Robert P. Multhauf[3] that I also bought second hand courtesy of Amazon. In his introduction Multhauf states: '*This book originated in a project for a history of industrial chemistry, in which the importance of common salt overwhelmed the original topic*'. This book focuses on the salt industry in Europe and Germany in particular, with references to other parts of the world for comparison. It also has an extensive section on the use of salt in industry. In the same way in which Adshead[1] uses Chinese terms, Multhauf[3] uses German terms which gets a little confusing.

The research carried out by all three authors is phenomenal. Adshead[1] and Multhauf[3] have a large number of references and an extensive bibliography. From his acknowledgements it is clear that Kurlansky[2] actually visited a lot of the places he writes about and had knowledgeable hosts. He also comments that an underground vault in the New York Public Library includes more than 1000 books on salt and he acknowledges a number of them in his bibliography.

The summary above may indicate that what seemed a good idea at the time was actually biting off more than I could chew. So it is hopefully understandable that it has taken me over 18 months working spasmodically to put this together. All three books[1-3] took a chronological approach to the topic so I have tried to be different and look at salt under different topics. What follows are some very brief, severely cropped snapshots. It is impossible to do justice to an enormous topic in just a few pages.

Physiological salt

All animals require salt for good health. It is generally accepted that the early nomadic hunter-gatherers got sufficient salt for their needs from the animals they killed for food. The change to a plant-based agricultural farming lifestyle is thought to have created the need for supplementary sources of salt, although there is evidence that this diet still contained enough salt for physiological requirements.

Why does the body need salt?

Sodium chloride is responsible for maintaining the electrolyte balance in cells and surrounding fluids. Sodium ions are the main cations in the extracellular fluids, including blood plasma, while potassium ions dominate inside cells. These ions create an electrical potential across the cell membrane that helps control nerve impulse transmission, muscle activity and a mechanism that enables molecules such as glucose to enter cells. There are a number of good animations showing how cells manage the sodium/potassium balance and glucose assimilation.[4]

Sodium ions are also responsible for maintaining blood pressure and liquid levels in the body. Chloride ions contribute to electrolyte activity and are an obvious component of stomach hydrochloric acid. Salt is lost through perspiration and sodium chloride levels are controlled by the kidneys releasing excess salt into urine. Liquids used by endurance athletes contain glucose for energy and salt to replace lost electrolyte. Taking in excess salt, such as shipwrecked people drinking sea water, creates a thirst craving for water as the electrolyte balance is upset with too much sodium chloride. It is not surprising that when I quizzed a doctor friend of mine about how the body uses salt I got a rather exasperated sigh and a statement along the lines of, "Where doesn't it use salt?" It has been said the human body is a miniature ocean encased in skin.

Saltiness is one of the four basic tastes that have receptors on the tongue, the others being sweet, sour and bitter. Some sources include a fifth taste 'umami' for the savoury sensation. It was introduced by the Japanese and is related to the taste of MSG.

The current estimate for an adequate intake of salt for an adult is about 3.8 g per day. This replaces that lost from the body in urine, through perspiration and other processes. 3.8 g is about twice what it is thought early humans acquired. About 1.3 g is considered the minimum to sustain existence.

It is clear that from early on humans had a predilection for salt over and above that needed for physiological purposes. Multhauf[3] states that, "*the circumstantial evidence that we want it – perhaps as the primordial narcotic! – is overwhelming*". It is estimated that humans deliberately add 3.5 kg of salt per year to food (the 3.8 g per day requirement equates to 1.4 kg per year).

Whether or not early farmers got sufficient salt from their crops it seems they had a hankering for more and also needed salt for their domesticated animals who could no longer get it for themselves. Wild animals, particularly herbivores, obtained salt from salt licks (surface outcrops of rock salt) or brine pools and it is likely early humans found these by following the animal trails. More recently explorers ventured into the interior of North America along the trails created by herds of buffalo seeking salt licks or brine springs. The trails ended at the salt source and the explorers settled there; hence, for example, the city of Buffalo, New York.

Extraction from rock salt was limited to sources at the surface. Mining of rock was restricted in Europe after 1000 BC as the dry climate of temperate zones changed to a wetter sub-atlantic climate and mines flooded. Plants and peat were burned and the ash mixed with sea water to extract the salt. This solution, brine spring water or sea water was heated in clay pots and evaporated to dryness. The salt was obtained by breaking the pots. The clay pieces were know as *briquetage* and their presence is good archaeological evidence for the presence of ancient salt works.

Preservation salt

A major problem facing early civilisations was maintaining a continuous food supply from the times of plenty in summer through the deprivation of winter. Most civilisations, at some point, became aware of the preserving property of salt; maybe observing that animals who died in salt marshes did not decompose at anything like the rate noted for those who died on dry land or maybe they extrapolated the healing nature of salt water on wounds. However it came to them, this revelation became a life saver when they developed processes for salting food to preserve it for winter months. It also allowed food to be transported long distances without spoilage. Salting became the main preservation method from early times until the development of "bottling" and canning in the 1820s and fast freezing in the 1920s – developed by Clarence Birdseye. Hands up those who thought the Birdseye brand was just a sales gimmick!! Supplies for the winter for a significant proportion of the world's population required a lot of food. Preserving it required a lot of salt. And so the salt industry flourished.

Procuring salt

The main early sources of salt were rock salt, sea salt, brine springs, and plants and peat from sea marshes that were impregnated with salt.

In Northern Europe and much of Britain the bulk of the salt was produced by evaporation of water from brine springs using wood as fuel. Some became larger operations to the extent that the towns and cities were named from salt. Examples are Salzburg (salt town or fortress), Halle, Hallstatt and Hallein in Europe (from the Greek word *Hal* for brine or brine springs). These towns were accessing salt from the same massive deposit. A variant of *hal* or *hel* is *gal* and this is thought to have given rise to names such as Gaul (for France) and Galatia. English place names ending with *wich* or *wych* meaning brine spring are sites of salt works (Northwich, Middlewich, Nantwich and Leftwich in Cheshire and Droitwich in Worcestershire).

The evaporation container changed from clay pots to lead pans and then iron pans. Pans were around 30 m^2 but later some were made with an area of 250 m^2. The base of each pan was covered with lime mixed with ferns and straw to protect against damage by salt water. The first sediment from boiling (referred to as "some kind of bastard salt") adhered to this layer and hardened. The whole mix had to be removed about four times a year. It was treated with water which was then boiled down to extract any absorbed salt.

Evaporation of brine in salt pans appears to have started in the 1100s. In addition to a brine source, the process required wood and that meant forests full of it. Over several hundred years vast tracts of land were deforested to provide fuel for salt making. Frequently when one area of forest was exhausted the boiling house was moved to another area and the brine piped from the spring to the new site. This was obviously some undertaking as in the 1500s there are records of brine being piped 16 km from its source to a new boiling house which required over 6,000 sections of wooden pipe. An existing piece shows the pipe had an internal diameter of about 12 cm. Major works in Austria and Germany produced millions of kilograms of salt each year, much of which was distributed to other parts of Europe. But there were many smaller operations serving local communities and communities were built up around the saltworks.

The management of works was often complex with ownership spread around different groups. Ownership of brine sources was frequently with the church, the forests owned by the local nobility, the works by local townsmen and the distribution managed by a further group.

Saltworks faced a number of threats such as flooding when the brine source would be contaminated with *wildwasser* "sweet (fresh) water" which diluted the brine, fire which destroyed the boiling houses (one having recorded three fires in the years 1630 – 1671), and war. Destroying the source of this essential commodity was a priority for invading forces and the invasion inevitably interrupted distribution lines. In the 21st century the equivalent is oil supplies.

The brine supplies varied from 1% to 25% brine and these sources were sometimes mixed to give a concentration of around 14%. Not all of this was sodium chloride which saturates at 36% solution. Less soluble salts like calcium sulfate (the "some kind of bastard salt") precipitated out first and became the pan scale. Sodium chloride was removed before evaporation was complete leaving the mother liquor. Part of the skill of the salt maker in the boiling house was deciding when to remove the salt. The mother liquor contained the more soluble magnesium salts which were eventually discarded.

The technology that was initially developed changed little over time. The production of salt was labour intensive with 100 – 300 people working at the larger sites. The power source was mostly human, e.g. human operated treadwheels or windlasses (sometimes operated by women) to lift brine. The woodsmen providing the wood was another labour force. Then there was the group engaged in the shipment and distribution of salt. Later animals replaced people on the windlasses, then came pumps and later still steam engines. Attempts were made to limit the amount of wood required. These included pre-heating the brine using surplus heat from the boilers and the graduation systems like that which introduced this article. These added another layer to the labour force.

Solar evaporation

In areas that were warm enough, salt was obtained by the solar evaporation of sea water after diversion into ponds or from salt-rich lagoons. Initially this was simply collecting "salt" that crystallised. If this included magnesium salts the product tasted bitter.

Improvements came with the development of a three stage evaporation process. The first concentration stage precipitated less soluble salts like calcium sulfate. Then there was a second concentration stage and finally the crystallisation stage where the salt was scraped from the surface leaving the mother liquor which was discarded.

In tropical regions salt crystallised in saline ponds and was scraped off using either human or animal "graders" pulling planks across the surface.

Salt quality

There was variability in the salt produced, most notably in colour due to impurities and crystal size due to rate of deposition. Salt makers learned to control crystal size in the evaporation pans by either fast or slow heating. Salt from solar evaporation was much harder to control due to weather variations. Small crystals were favoured for making butter and cheese, with larger crystals preferred for preserving meat and fish. The Chinese favoured fine grained salt and considered it to be of higher quality.

From 1905, vacuum evaporators developed by Henri Nestlé of chocolate fame were introduced which solved two problems; control of crystal size and the cost of fuel. Steam from one boiler was used to heat a second evaporator which was under partial vacuum so the water evaporated at a lower temperature. This process can be carried on through a series of evaporators giving huge savings in fuel costs. When crystals reached a certain size and weight they dropped through a grille at the bottom; too big and they were washed back up by incoming brine; too small and they didn't drop. The same process is used for making granulated sugar.

Traded salt

Salt, being a bulky commodity, was not easily transported. Trading of salt obtained from the major salt works in Europe was limited to neighbouring communities unless there was river access where barges made it possible to transport larger loads over greater distances.

Examples of land transport are the *via salaria* (the salt road) which transported salt from the west coast site of the evaporation ponds at Ostia to the city of Rome about 40 km away and the camel caravans of the Sahara. In places like Taghaza, salt was quarried from the ground in blocks. It is reported that the houses were made of blocks of salt. It was all that was available. Camels carried 90 kg blocks, one on each side, to the major trading and cultural centre of Timbuktu 600 km away. Buyers with a pile of gold and sellers with a pile of salt traded by silent auction, adding to or subtracting from their piles until agreement was reached. It was this process that led to an erroneous report in Europe that salt was sold for an equal weight of gold.

In the Mediterranean, Venice was originally a producer of salt but as sources became depleted the city transformed itself into a trader of salt, gaining a monopoly in the salt trade in that region using its large commercial fleet of ships which made long distance transport viable. Salt made up 30 – 50% of imported goods. From the 11th century the Venetian government regulated the trade and benefitted richly from its share of sales of high priced salt. This income was used to subsidise the importing of spices and grain and to finance the construction of impressive buildings and maintain the complex hydraulic systems that prevented flooding.

Preservation processes

Less desirable cuts of meat - the brisket (lower chest) and the tougher leg - were the cuts usually salted. This involved removing as much blood as possible (blood rapidly spoils the meat) and rubbing with salt (with some added saltpetre – KNO_3 – which keeps the meat red). This was packed in barrels, with added salt, as tightly as possible, sealed and stored turning the barrel regularly.

Salting fish – particularly cod and herring - was a huge business, with the demand for fish partly driven by the increasing number of medieval Catholic "lean" days when the eating of red meat was prohibited. Atlantic cod was particularly suitable for salting as it was fatless and could be air dried and salted. Fatty fish could not be exposed to air as the fat turned rancid and the fatty tissue resisted the uptake of salt. The Basque people were adept at boat building, fishing and salting their catch and fished for cod at huge distances from Europe taking salt with them and salting the fish while at sea. Herring, being a fatty fish, had to be preserved within 24 hours and the technique used was to pickle the herring which was then packed and sealed in barrels of brine.

Vegetables were preserved by pickling, but salted first to prevent decay before the pickling process started. Pickling is an anaerobic fermentation in which the sugars break down to form lactic acid which acts as a preservative. Without salt yeast forms and produces ethanol by fermentation. Cucumbers (pickles) and cabbage (sauerkraut) were commonly preserved vegetables. Butter and cheese were also salted to prolong their life.

Saucy salt

Salt sauces were produced to make an expensive product go further. In the Mediterranean, *garum* was made by filtering the juice off after a mixture of fish scraps and salt had been allowed to ferment. In China and Japan the mixture started out as fish, soya beans and salt. Later the fish was omitted giving the product we know as *soy sauce*. A later entry is Tabasco sauce which was first produced in 1868 by Edmund McIlhenny at Avery Island in Louisiana and is still the only place it is made. Avery Island is a salt dome 5 km long and 4 km wide. It is estimated to be about 12 km deep. Tabasco sauce is made by fermenting red peppers mixed with salt, a process that takes up to three years. Peppers are picked by hand and their ripeness is critical, verified by matching their colour to a red stick (*le petit bâton rouge*). Baton Rouge, the state capital of Louisiana, is named after a reddish cypress pole that marked a boundary of native hunting grounds.

Polluting salt

In the 1600s through to the1800s Britain became a major player in the world market. A significant source was the brine springs in Cheshire. Evaporating brine in the "-wichs" (Northwich, Middlewich, etc) was carried out by a large number of family operations. A network of canals enabled transport of both coal and salt and the port of Liverpool was the base for export of salt to Britain's colonies as outward ballast for the ships bringing in cotton and other materials for the growing industries. In the search for more local coal deposits rock salt was found and this added to production against the efforts of the brine operators. The environmental cost was significant with forests destroyed for fuel, vegetation killed off by dumped waste and mother liquor, an atmosphere laden with smoke and subsidence of land as vast volumes of brine were removed.

Political salt

Salt was one of the first consumer products subjected to a commodity tax. It was an attractive target. Everybody needed it. It was difficult to produce without production equipment being obvious. It was bulky to transport and therefore difficult to hide from tax inspectors.

Most salt producing countries had a salt tax. In China all salt was owned by the government. A salt tax was applied and varied in amount depending on administration requirements. It was a useful means of raising funds for a war effort. In most countries the salt tax was reasonable and accepted. In France, however, the tax was punitive, unevenly applied and rigidly policed. Those caught illegally making salt or smuggling faced time in the galley ships which was effectively a death penalty. Known as the *gabelle*, the tax was hated and was one of the factors that led to the French revolution in the 1790s.

Britain insisted that its colonies (notably India and America) used only salt imported from Britain. In India the British East India Company banned local production putting thousands of people out of work and in danger of starving. Even collecting crystals that formed at the edges of saline ponds was prohibited. Ghandi's protest march in 1930 was in part a protest against the harsh salt laws and ended at Dandi on the coast where thousands who had joined the march disobeyed British salt laws and scraped the crust of salt from the beach.

All races in the Americas used salt to a greater or lesser extent. Some North American tribes used no salt other than that in their diet. There were regular battles over salt sources. As Kurlanksy[2] put it, "*Whoever controlled the salt was in power*". The British arrived in North America while exploiting the abundant cod fishing grounds. They established themselves at Cape Cod among other places and built a solar salt works there in addition to accessing native salt resources. There was plenty of salt water but not much sun. Covers were built to protect the ponds when it rained. Exporting cod and animal skins required salt for preserving and curing. The British supplied the bulk of this either from Liverpool or from salt marshes they commandeered in the Caribbean.

American attempts to trade with nations other than Britain were not welcomed by Britain and the American Revolution started. A British tactic was to deprive the colonialists of salt either destroying the works or blockading them. After independence and the spread west, the vast resources of salt in America were slowly revealed from the salt flats of Utah to the salt domes in the south.

The 580 km long Erie canal (started in 1817 and completed in 1825) was built to transport goods, particularly salt, from traditional saltworks at Onondaga to New York by connecting Lake Erie to the Hudson River. It made the settlements of Buffalo, Syracuse and Salinas into cities and elevated New York to the biggest city and port on the eastern coast. There was even a town called Liverpool so they could trade on the name of British Liverpool salt. The cost of the Erie Canal was covered, in part, by a salt tax; one of the few worldwide that the local population did not object to. Salt supplies also featured in the American Civil War with the destruction of saltworks being a prime objective of advancing troops.

Picturesque salt

From the 10th to the 12th century salt was extracted from spring and shallow wells in Wieliczka, Poland. Around 1290, deep mining of rock salt started and by the 14th century the mine supplied one-third of the Royal revenue, extracting 8 million kg of salt each year. The mine had a significant downturn in fortunes in the 17th century with floods, a fire that lasted 8 months and invasion. Production was then revived and maintained at around 20 million kg per year with the use of horse driven machinery and employment of expert advisors. The mine was over 300 m deep and extended over 250 km. One visitor recounts descending 50 sets of ladders to reach the work chamber. Horses lowered into the mine to drive machinery never again saw daylight. Workers spent extended periods in the mine and in 1689 the Catholic Church held services underground for the workers. This was the start of the workers carving religious statues to augment their place of worship. The practice flourished and grew into the magnificent sculptures, chandeliers, cathedral, ballroom and dining hall that exist today. Initially only visited by aristocracy it now has 1.2 million tourist visitors per year. Salt mining was discontinued at Wieliczka in 1996 due to the downturn in salt prices and problems with flooding.

Petroleum and salt

From the beginning salt seekers have been frustrated by the presence of oil in some brine sources. It was nothing more than nuisance value to everyone except the entrepreneurs who bottled it as "Rock Oil" and sold it as the cure for all ailments.

As early as 70BC the Chinese had been aware of gases in their salt mines that adversely affected miners and created fire-wells. They eventually piped it and used it to fuel their salt evaporators.

In the 18th and 19th centuries, as the discipline of geology developed and the techniques of deep drilling improved, seeking resources deep in the earth became viable. Drilling technology was developed independently in different societies. The metal capped percussion chisel devised in America in 1797 had been used in China for several centuries. Drilling for coal in Cheshire hit salt deposits. Drilling for oil, now needed as a useful fuel, frequently hit salt and it became evident that huge deposits of salt, up to then considered a relatively rare resource, lay deep (and sometimes not so deep) beneath the surface of the earth.

Salt domes are thought to form as lower density salt in deep salt beds rises through denser sedimentary deposits during tectonic activity. The top often forms a mushroom-like dome. Salt is impervious to oil and if surrounding rock is also impervious, oil collects under the mushroom. Domes can be 1 – 10 km across and many kilometers deep. Geologists testing this idea drilled many dry wells

Chapel of St Kinga, underground at the Wielizcka mine, Poland. Copyright Nico Trinkhaus (www.sumfinity.com), used with permission.

until 1901 when drilling at a salt dome called Spindletop in Louisiana produced an oil gusher that resulted in the most productive oil well then known.

Petroleum and salt are also closely linked in the reactions of products from the petrochemical and chlor-alkali (electrolysis of sodium chloride) industries.

Mother liquor

It was known that most brine sources contained salts other than sodium chloride. Before sodium chloride crystallised, the less soluble calcium sulfate deposited. The salt maker also knew that sodium chloride needed to be removed before other components started crystallising, otherwise the salt tasted bitter and was deliquescent. For centuries the mother liquor was either discarded, added to the next batch of brine to extract more salt, or brine added to the mother liquor in a more or less continuous process.

Determining the components of the mother liquor was limited by the lack of understanding of the concept and behaviour of ions. The main interest of 17th century chemists was in compounds that had some medicinal application (iatrochemistry), no doubt with an eye on potential money earners. Two compounds related to salt or the mother liquor had been isolated from “curative natural springs” – Glauber’s salt - sodium sulfate - extracted by the German Johan Glauber in 1624 and later in the century Epsom salt - magnesium sulfate - crystallised from a spring in Epsom, England, by Nehemiah Grew.

Glauber kept the production of sodium sulfate secret but finally conceded it could be made from salt by the action of concentrated sulfuric acid:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl(g)$$

Interestingly, most textbooks quote this reaction as going to $NaHSO_4$. Possibly early chemists had a way of getting complete reaction or had a mixture of the two salts.

Epsom Salt was extracted from the mother liquor and finally magnesium chloride and calcium chloride were identified. If present in common salt these compounds imparted a bitter taste and made the product deliquescent.

When “alkali” – at that time sodium carbonate – was added to the mother liquor “magnesia alba”, a basic magnesium carbonate with valuable medicinal properties was obtained.

Industrial salt

With canning (bottling) and fast freezing the need for culinary salt for preserving decreased. As this happened the chemical industry with a need for salt was developing so there was still demand for salt. However, taxing salt for industry was not seen as economically beneficial and salt taxes started to be abolished with Britain the first to take the decision in 1825. The demand was for “alkali” seen as the base of the sodium part of sodium chloride. Initially this meant sodium carbonate but later also sodium hydroxide. It was used in the manufacture of glass and soap.

Leblanc process

This process was developed in the late 1700s and production lasted for a period into the 1800s. Salt was reacted with sulfuric acid:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl(g)$$

Glauber's salt was then heated with charcoal and lime:

$$Na_2SO_4 + 2C + CaCO_3 \rightarrow CaS + 2CO_2 + Na_2CO_3$$

Sodium carbonate was leached from the fused mass. The process was inefficient and the HCl and CaS were polluting waste products.

Electrolytic processes

A process for electrolysing brine was first patented in 1825 but proved non-viable as the chlorine produced stayed mixed with other components.

The Castner-Kellner cell used from 1895 solved the mixing problem by using a flowing mercury cathode. The sodium produced formed an amalgam with mercury and was run off to another cell where the sodium reacted with water to form sodium hydroxide. The other product is chlorine. At first sodium hydroxide was the more sought after product. Chlorine was combined with calcium hydroxide to form bleaching powder but was much less in demand. As the petrochemical industry developed, with the production of organic chlorine compounds, chlorine superseded sodium hydroxide as the product more in demand. The downside of the Castner-Kellner cell was the polluting effect of lost mercury. Two high profile cases were Minamata, Japan and Ontario, Canada where locals suffered illnesses from mercury poisoning after eating fish that had assimilated mercury from contaminated chemical plant waste water.

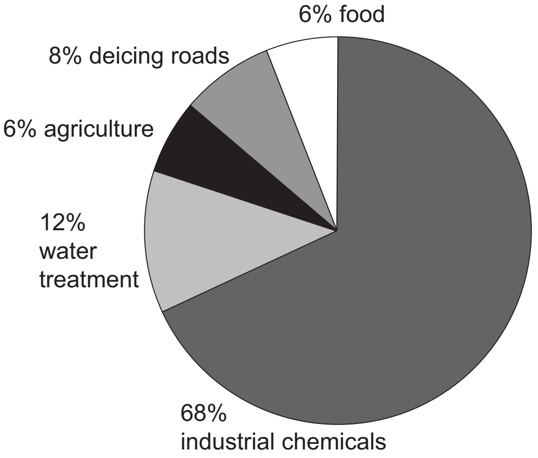
Later developments are the diaphragm and membrane cells which allow Na^+ ions to pass from the anode compartment to the cathode compartment through the semi-permeable diaphragm or membrane but prevent transfer of Cl^- and OH^-:

At the anode: $2Cl^- \rightarrow Cl_2 + 2e$

At the cathode: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

NaOH accumulates in the cathode compartment and the concentration of NaCl in the anode compartment decreases.

World production of salt in 2013 was 262 million metric tons. How it was used is shown in the graph.



Uses of salt 2013

The New Zealand salt industry

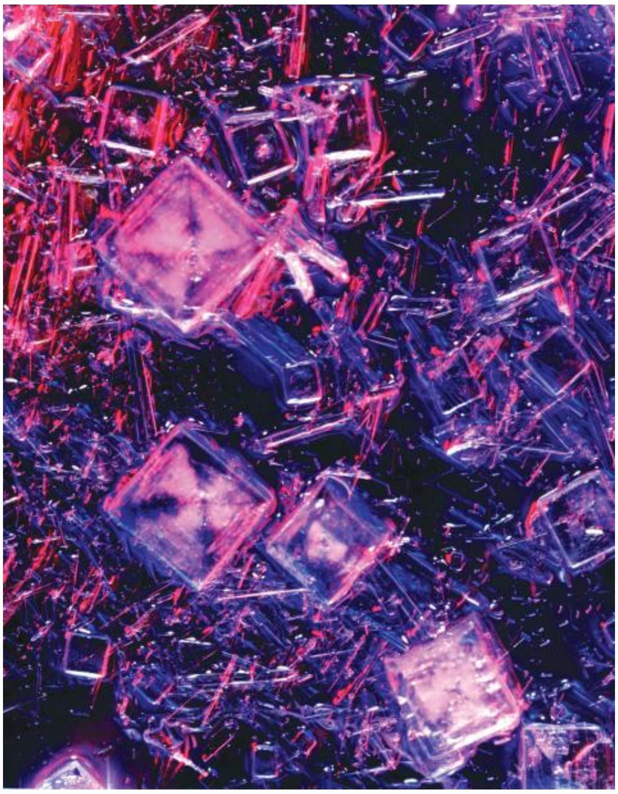
The information in this section is extracted from the brochure available for download from Dominion Salt.[5]

Production of salt in New Zealand dates back to 1943 when George Skellerup established the salt works at Lake Grassmere in Marlborough. The site chosen has a large area of flat land close to the sea with impervious soils not suitable for other uses. The region is also noted for its high sunshine hours, low rainfall and strong drying north-westerly winds. New Zealand's latitude is not ideal for solar evaporation but the combination of factors listed has made the venture successful.

The Grassmere works covers 1,416 hectares and produces salt by a multistage evaporation system. The main lake roughly doubles the 2.5% sea water salt concentration. A series of concentrating ponds bring about a step-by-step concentration during which calcium sulfate is deposited and finally brings the brine up to saturation level. Deep storage ponds hold the concentrated brines over the winter months after which it is transferred to crystallising ponds where, over the summer, a salt crust forms on the bottom, which varies in depth from 25 to 75 mm and is scraped off during the four to six weeks of harvesting starting in early March. A good day's harvest may exceed 6,000 tonnes. Rain-diluted brine is cycled back to ponds for re-concentration. Annual yields are very weather dependent and have ranged from nil to 130,000 tonnes. Harvested salt is subjected to washing, crushing, drying and screening. The largest user is the freezing industry that requires salt for treatment of hides and skins. Domestic grade salt preparation, packing and marketing is handled by a separate company using Grassmere salt.

Aerial view of Lake Grassmere salt works

Gypsum deposit at Grassmere salt works



Sea water crystallising. Needle-like crystals are calcium sulfate, cubes are sodium chloride (magnification x25, photographed using a Schott fibre optic light source and coloured filters). Copyright Sarah Bloom, used with permission.

The pink tinge seen in crystallising ponds is due to single-celled algae which are normally green but turn pink in concentrated brine. There are also pink brine shrimp present in their millions which become established naturally in most salt works.

The small size of the works makes it uneconomical for Dominion Salt to process the mother liquor and this is pumped back into the sea but plans are in place to harvest and market the calcium sulfate that has accumulated in the concentrating ponds over the 73 years of the plant's existence. Dominion Salt has a processing plant in Mount Maunganui. Dominion Salt companies also import salt to meet demand for domestic and export markets.

Iodised salt

New Zealand soils are deficient in iodine which means that food sourced from pastures, whether meat or plants, is low in iodine. In the past this resulted in a relatively high incidence of goitre where the thyroid gland in the neck enlarges due to an iodine deficiency. In the 1920s this was remedied by fortifying salt with potassium iodide. This was replaced in the late 1990s with potassium iodate, apparently because in wet conditions oxygen can oxidise iodide ions to iodine. Current regulations stipulate that iodised salt must contain 25-65 milligrams of iodine per kilogram of salt. Commercial processed food producers were not required to use iodised salt. This is thought to be behind recent decreases in iodine levels in the population and in 2009 the Ministry of Health regulated that commercial bread makers use iodised salt.

Salts by other names

Although the focus of this article has been on common salt - sodium chloride - deposits of other salts are well known and exploited around the world, for example:

Trona: $Na_2CO_3.NaHCO_3.2H_2O$ is now the main source of sodium carbonate as the Solvay process plants become old and uneconomical to repair or replace. Large deposits are present in USA, Kenya, Turkey and China.

Natron: $Na_2CO_3.10H_2O$ is found in Egypt, Chad, Tanzania, Hungary, Italy, England and the USA.

Chile saltpetre: $NaNO_3$ is mined from large deposits in the Atacama desert in Chile and Peru.

Saltpetre: KNO_3 was generally obtained by chemical means. It has been known since early times particularly for its use in gunpowder.

Magnesium salts: The Dead Sea has a higher concentration of Mg^{2+} than Na^+ which makes the taste very bitter. The concentration of salts in Dead Sea water is 340 g l^{-1}, while ocean water is about 34 g l^{-1}. Kurlansky[2] raises the rather disturbing image of bathers "marinating" in the Dead Sea.

Salt miscellany

If you tell anyone you are writing an article on salt the first piece of information you are given is that the word "salary" is derived from salt. This is certainly true but the reason – that Roman soldiers were paid in salt – is challenged by some historians and the derivation is shrouded in mystery. "Being worth his salt" is similar in that payment for slaves had some connection with salt and a good slave was worth the "money (salt?) paid.

Being "the salt of the earth" roughly translates to being a "good sort". It is derived from Matthew 5:13:

You are the salt of the earth. But if salt loses its saltiness, how can it be salty again? It is no longer good for anything, except to be thrown out and trampled by men. (New International Version).

Jesus is exhorting his followers to have qualities in the community similar to salt in its uses; seasoning, cleansing, preserving. I have sat through sermons cringing as preachers try and justify salt losing its saltiness, which at face value is an indefensible statement. Salt is sodium chloride is salt! My take on this is that the important word in the second sentence is "if" and Jesus is speaking hypothetically about salt. But he then turns it back on to his followers. If they cease to exhibit the qualities expected they will lose respect and it is very hard to get it back.

The other well-known Biblical reference is Lot's wife being turned into a pillar of salt. Above the Dead Sea there is a salt mountain – Mt Sodom. Erosion regularly creates pillars that the tourist guides point to as Lot's wife. Fortunately for the guides as one pillar erodes away another is formed.

Salt has many superstitions associated with it. Spilling salt

Stockpiled salt at Lake Grassmere

is said to bring bad luck and is featured in Da Vinci's painting of the last supper where Judas Iscariot has knocked over a salt container. The origin is possibly due to the value of salt and spilling it was a waste. The consequential "throwing salt over your shoulder" is to scare off the evil spirits that supposedly would bring the bad luck.

Salt is traditionally associated with prosperity and fertility and in some cultures salt is given to a bride, as a New Year gift, or when someone moves into a new home.

The full circle

Recently there has been an increase in the demand for coloured (impure) salt believing it to be free of nasty contaminants like authority-added iodine.

There have been proposals for a salt tax to combat the high intake from fast foods which have caused health issues.

It has even been used as a murder weapon. A woman force-fed a boy salt through a stomach tube because she craved the social media attention his illness brought her. The boy's sodium levels rose to a dangerous point with no medical explanation, leading to a swollen brain, seizures and death. She received a 20 year jail sentence.

The last word

This must go to Robert Multauf[3]: "*Salt is the one resource on the planet for which there is an unlimited demand and an inexhaustible supply*".

Acknowledgements

Thanks to Theresia Francissen, our host in Frankfurt, who took us to Bad Orb and started me off on my quest to know more about salt Also to Brett Hobson, Regional Sales Manager for Dominion Salt, who took the time to show me around the Grassmere Saltworks after the difficult period of the Seddon earthquakes and my sister Sarah for the photograph of sea water crystallising (also featured on the cover).

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The 2015 Nobel Prize in Chemistry

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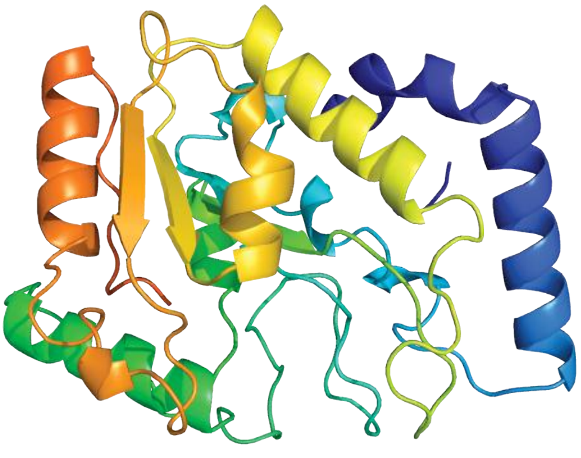
The Royal Swedish Academy of Sciences awarded the 2015 Nobel Prize in Chemistry on October 7 jointly to ***Tomas Lindahl*** (Emeritus Scientist, The Francis Crick Institute and Clare Hall Laboratory, Hertfordshire, UK), ***Paul L. Modrich*** (Professor of Biochemistry, Duke University, North Carolina and Howard Hughes Medical Institute, USA) and ***Aziz Sancar*** (Professor of Biochemistry and Biophysics, The University of North Carolina, Chapel Hill, USA) *for their mechanistic studies of DNA repair*.

Left: Prof. Tomas Lindahl (copyright: The Francis Crick Institute, with permission); centre: Prof. Paul Modrich (courtesy Duke University Photography); right Prof. Aziz Sancar (photo by Max Englund, courtesy University of North Carolina).

There are three reasons that humans are not constantly riddled with cancer, and the 2015 Chemistry Nobel Prize rewards the three biochemists who discovered those reasons — the ways that cells repair damaged DNA that can ruin bodies.[1] Swede Tomas Lindahl, American Paul Modrich and Turkish-American Aziz Sancar have been working independently for more than 40 years to describe and map the differing mechanisms that create errors in DNA and then the various ways that chemical and biological processes repair many of these problems and safeguard the genetic information.

The work started with ***Tomas Lindahl*** who was born in Stockholm in 1938. He gained his PhD in 1967 and an MD qualification from the Karolinska Institutet in Stockholm in 1970. Following postdoctorals at Princeton and Rockefeller Universities in the US, he joined what was the Imperial Cancer Research Fund in London as a researcher. From 1978–1982, he was Professor of Medical and Physiological Chemistry at the University of Gothenburg, Sweden, before joining the Francis Crick Institute in Hertfordshire, UK, where he is now Emeritus group leader and Emeritus Director of the Clare Hall Laboratory. His work was formerly recognised from the award of the Royal Society's *Royal Medal in 2007, the* Copley Medal *in 2010, and the French INSERM Prix Etranger in 2009.*

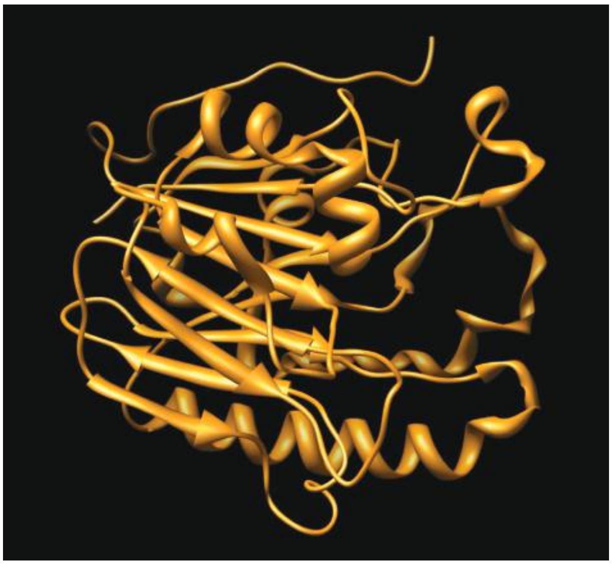
His postdoctoral work involved RNA study when he found this relative of DNA unstable to heat and to undergo rapid degradation. At that time it was felt that DNA had high stability but the fact that RNA was so heat sensitive drew Lindahl to seriously consider this matter. After returning to Sweden he began to study the stability of DNA and found that it underwent a slow but noticeable decay. He estimated that there were thousands of potential major injuries to the genome each day, a number that contradicted human existence on earth. The only possible explanation had to require a molecular means of repairing these DNA defects and, with this in mind, Thomas Lindahl opened a new field of study. Using bacterial DNA he began to search for enzymes that would repair the damage. By 1972 he had shown that cytosine undergoes significant hydrolytic DNA depurination under physiological conditions and stimulates DNA cleavage.[2] Most interesting was the demonstration of extensive and spontaneous cytosine deamination that generates uracil also under physiological conditions.[3] After such loss the uracil pairs not with guanine but with adenine in a highly mutagenic process that has long term implications (uracil is present in RNA but not DNA). Allowed to continue unabated this would lead to a mutation with high levels of cytosine deamination posing a risk of depleting the cytosine-guanine base pair stock and replacing it with the thymine-adenine pair.[3] That this does not happen most often could only come from some form of cell protection and, single-handedly, Lindahl identified the *E.coli* uracil-



The repair protein uracil-DNA glycosyase (UNG) (Wikimedia Commons)

DNA glycosyase (UNG) as the first known repair protein. Two years later he identified a second glycosyase specific for 3-methyladenine DNA.[4]

It is now known that there exists a large family of proteins that can bring about *base excision repair* of which UNG is the founding member. Lindahl showed that this enzyme was specific to DNA and that it acted on neither deoxymononucleotides nor any form of RNA. He also showed that the DNA backbone remained intact during the process and this implied involvement of another category of enzymes that proved to be the apurinic/apyrimidinic endonucleases. He outlined the basic concept of this base excision process in his 1974 paper.[3] Subsequently, he and others showed the proposed model to be correct and he went on to reconstitute the entire base excision repair from both *E.coli* and human cells.[5] The process starts when a DNA glycosylase recognises and hydrolytically cleaves the base–deoxyribose glycosyl bond of a damaged nucleotide. It is now known that many different lesions affect the bases without causing major structural perturbation in the DNA structure, yet they provide a significant challenge for the replication process; miscoding during either DNA replication or transcription is possible. By now some 100 different oxidative lesions have been identified with the majority corrected by base excision repair.



Apurinic/apyrimidinic endonuclease (Wikimedia Commons)

The DNA replication machinery is not error-free and the insertion of an incorrect nucleotide during the synthesis of a new DNA strand is always possible. This type of error is termed a mismatch and it, too, has the possibility to change the DNA sequence. To correct such an error the cell uses ***mismatch repair***. The early studies of this were carried out by geneticists in the early 1960s and by the mid-1970s it was thought to involve a strand-specific mechanism. The concept of methyl-directed mismatch repair was advanced in 1983 and represents the start of the Modrich contribution. ***Paul Modrich*** was born in 1946 in New Mexico, USA and gained his BS degree from MIT and a PhD from Stanford University in 1973. Currently, he is an Investigator at the Howard Hughes Medical Institute, and Professor of Biochemistry at Duke University School of Medicine both in Durham, NC. His involvement with DNA repair emanates from advice proffered by his father when he was in junior high school when he told him “You should learn about this DNA stuff”. The work has now involved more than 35 years of laboratory research.

During his PhD at Stanford, his postdoctoral at Harvard and then his assistant professorship at Duke University, Modrich examined a series of enzymes that affect DNA and then, towards the end of the 1970s, he became interested in the enzyme deoxyadenosine methylase (dam methylase) that adds methyl groups to DNA. He went on to show that the methyl groups could act as a signpost by helping a particular restriction enzyme to cut the DNA at the correct place. Direct evidence for methyl-directed mismatch repair had come from the work of the Meselson group[6] at Harvard in 1983 but they had proffered a different signalling function. Meselson suggested that it was perhaps the methyl groups on DNA that helped the bacteria identify which strand to use as the template during the correction. It is the faulty replica, the new DNA strand, that is unmethylated and it seemed possible that this allows for its identification and correction.

Modrich and Meselson collaborated and created a virus with a number of mismatches in its DNA. Modrich had, in 1983, developed an assay for analysis of the extent of DNA mismatch repair in cell-free *E. coli* extracts. By using this and dam methylase to add methyl groups to the strand deficient in them, the two workers concluded that DNA mismatch repair is a natural process. It corrects mismatches when a DNA strand is copied, recognising the defect strand from its unmethylated state.[7] This discovery led Paul Modrich into a 10-year programme of systematic work during which he and his group cloned and mapped one enzyme after another in the mismatch repair process. The work culminated in a ground-breaking paper[8] in 1989 which described a reconstituted DNA mismatch correction in a defined *in vitro* system. Later studies by Modrich (and others) have shown the conservation of mismatch repair in eukarotic cells and in 2004 the group was able to reconstitute human mismatch repair with purified factors only. Unlike the *E. coli* situation, DNA methylation does not direct strand specific repair in eukaryotic cells.

In contrast to these studies, it is the work of ***Aziz Sancar*** that led to the first type of DNA repair. This Turkish-American scientist was born into a lower-middle-class family in the Savur district of Mardin Province, southeastern Turkey in September 1946, the seventh of eight children. He gained an MD degree from Istanbul University in 1969 and a PhD from the University of Texas-Dallas in 1977. His longest running study has involved photolyase and the mechanisms of photoreactivation.

After practising as a medic for a few years, Sancar elected to study biochemistry in 1973, fascinated by the fact that after bacteria are exposed to deadly doses of UV radiation they have an ability to recover quite suddenly if irradiated with visible light, a phenomenon termed *photoreactivation*. That this photoreactivation was enzymatic and dependent on visible light had been demonstrated by Stanley Rupert during the late 1960s and caused by what is termed photolyase. It repairs UV-induced damage in plants but no longer works in humans and other placental mammals who instead rely on the less efficient nucleotide excision repair mechanism. Initially, Rupert's photolyase was simply an activity in an extract but in 1978 Aziz Sancar, then a PhD student in the group, cloned the *E. coli* photolyase gene and amplified it *in vivo*.[9] Studies in the 1960s had also shown that UV damage could be repaired by a second process termed *dark repair*. The ground-breaking contributions of the early workers showed that this repair was by way of excision and could correct UV-induced damage (lesions). This became known as *nucleotide excision repair* (NER), although the precise molecular mechanisms involved were not known. The group that Sancar joined at Harvard University had studied the dark repair using three UV-sensitive strains of bacteria that carried three different genetic mutations, namely the *uvrA*, *uvrB* and *uvrC* genes and he began to study the molecular way that dark repair takes place.

Within a few years Aziz Sancar had identified, isolated and characterised the enzymes coded by the *uvrA*, *uvrB* and *uvrC* genes.[10] He then went on to show in ground-breaking *in vitro* experiments that these enzymes are able to identify UV damage. Not only this but that the enzymes then go on to remove the damaged part of the DNA strand by cutting it on each side of the damaged part. In this way a fragment of 12-13 nucleotides that includes the damaged portion is removed. The gap is then filled and sealed by DNA polymerase and DNA ligase, respectively. This knowledge, published in 1983,[11] changed the way in which research in this field was approached. After moving to Chapel Hill in North Carolina, Aziz Sancar mapped the next stages of nucleotide excision repair and then he and his group went on to study it in humans. The excision of UV damage is more complex than its bacterial counterpart but it is chemically similar. Subsequent study has allowed Sancar to unravel the mechanism of photolyase revival in bacteria.

Thus, the three 2015 Nobel laureates in chemistry have deepened our fundamental biochemical knowledge of how the human functions. Because many known cancers have the repair mechanism(s) turned off, the laureates have also pointed a way for future drug development to move.

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Some Unremembered Chemists

A series of articles that explores the lives and work of selected chemists who have made a significant contribution to the advancement of the discipline, the profession and well-being of mankind, yet who are little remembered.

Carl Auer von Welsbach (1858-1929)

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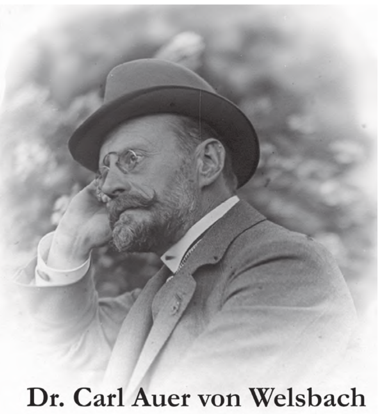


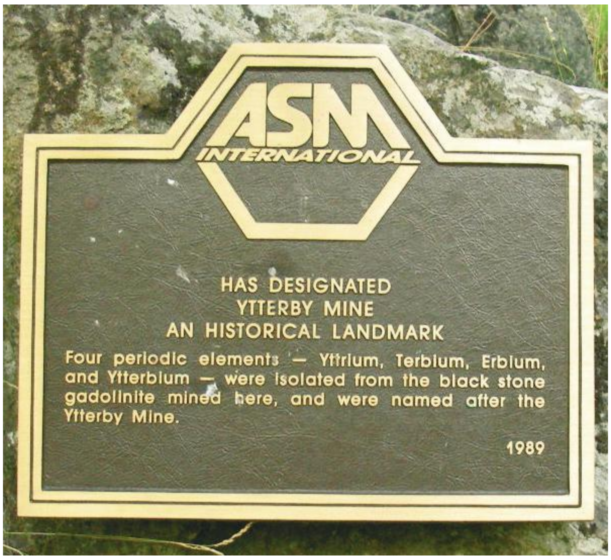
Courtesy of the Auer von Welsbach-Museum, Althofen, Austria

Carl Auer von Welsbach was born in Vienna on September 9, 1858, son of Alois and Therese (née Neuditschka).[1,2] Alois had trained as a compositor, became a printer, inventor and botanical illustrator most active during the 1840s and 1850s. He was appointed director of the Austrian Imperial printing office in 1841 and ennobled in 1860 to become 'von Welsbach' in the days of the Austrian Empire. His son Carl initially went to high school in the Viennese suburb of Mariahilf in 1869, but changed to Josefstad in 1873 where he completed his schooling in 1877. He then joined the Austro-Hungarian Army and was commissioned as a Second Lieutenant prior to entering the Technical University of Vienna in 1878. He studied maths, general inorganic and organic chemistry, technical physics, and thermodynamics with Professors Winkler, Bauer, Reitlinger, and Pierre, Bauer being the organic chemist and Pierre the physicist. In 1880, he moved to the University of Heidelberg (initially the Heidelberg University–Ruperto Carola when established in 1386) where he continued his studies in inorganic experimental chemistry with laboratory work under the direction of Robert Bunsen. It was here that he was introduced to spectral analysis and the history of chemistry, mineralogy and physics. He gained his PhD in 1882 from oral examination without thesis submission.[3] While still working with Bunsen, he noted the brilliant light emitted by rare-earth oxides when these are heated in the flame of a Bunsen burner and he returned to the University of Vienna with several samples and a strong interest in spectroscopy and lighting. There he worked as an unpaid assistant to Prof. Adolf Lieben, a former student of Bunsen, developing chemical separation methods for the rare earth elements.

The rare earths became known to the world in 1787 with the discovery of an unusually heavy greenish black rock in a small feldspar-bearing quarry near the village of Ytterby, on the island of Resaro about 45 minutes by road from Stockholm in Sweden. The quarry was originally mined for ironwork in the 1500s, and then in the 1700s feldspar was obtained for porcelain and the manufacture of glass. The unusual dark rock was found by amateur mineralogist and student of Berzelius, Lieutenant Carl Axel Arrhenius (1757–1824) who named it ytterbite, after the local village.[4,5] A few years later (1794) the black rock was analysed by Johan Gadolin, the professor of chemistry at the University of Abo in Finland. He showed the ore to contain about 38% of a new earth (*earth* was the early name for an oxide), 31% of silica, 19% of alumina and 12% of calcined iron (Fe_2O_3). Anders Ekeberg re-analysed the ore, finding it to be comprised of 23% silica, 55.5% yttria, 4.5% glucine (a monoclinic mineral containing beryllium, calcium, hydrogen, oxygen, and phosphorus), 16.5% of iron oxide and 0.5% volatile matter.[5] Although Ekeberg subsequently isolated beryllium from the ytterbite, he failed to recognise that the ore contained other elements. Thus it was that in 1885, at 27 years of age, Carl Auer resolved the rare earth substance then known as didymium into two elements by laborious fractional crystallisation of the ammonium nitrates. He performed some 100 fractional crystallisations each of which took up to 48 hours. That part which gave greenish salts he named praseodymium (from *Gk prasinos* - green and *didymos* - twin), while the part that gave pink salts he called neodymium (from *GK: neos* - new, and *didymos*) (see Table). Neodymium is about twice as abundant as praseodymium.

Rare earth oxides. Clockwise from top center: praseodymium, cerium, lanthanum, neodymium, samarium, and gadolinium (from www.ars.usda.gov/is/graphics/photos/jun05/d115-1.htm and wikipedia).

After more than 100 years of research by many prominent European chemists, it was eventually shown that the original black rock sample contained at least ten new rare earth elements that became known as dysprosium, erbium, gadolinium, holmium, lutetium, scandium, terbium, thulium, ytterbium, and yttrium. In recognition of Gadolin being the first person to isolate a rare earth element, the unusual Ytterby mineral was renamed gadolinite in 1800 by Martin Klaproth and allocated the composition $(Ce,La,Nd,Y)_2FeBe_2Si_2O_{10}$. The seventeen members of the rare earth group were discovered between 1794 and 1945, with fourteen of them found in the nineteenth century (see Table). Auer also discovered lutetium in 1907 but this was simultaneously with Georges Urbain in France and Charles James in the USA.[6] Since Urbain published first he was allowed to name the element. The rare earths cover the fifteen lanthanides as well as scandium (Sc; atomic no. 21) and yttrium (Y; atomic no. 39), which are considered rare earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties.[7]



Memorial plaque of the ASM International at Ytterby mine (Wikimedia Commons)

Apart from continuing his work on rare earth elements, Carl Auer von Welsbach made significant contributions to spectral analysis. He also knew how to use his knowledge of chemistry most effectively and is considered to be the founder of the industrial processing of the rare earth elements. One of his most significant achievements in this context is the gas mantle light, which illuminated towns all over the world and is still used in historical displays. With the knowledge that rare earth oxides became strongly luminescent in a Bunsen flame, Welsbach searched for a means to use this fact as the basis of a practical light source rather than trying to produce a gas that would burn with a luminous flame. Thus, whilst studying the separation of the lanthanides, Welsbach began developing incandescent gas mantles on the basis that the lanthanide elements increased the light emission of a flame. In 1885 he patented a mantle[8] that used a knitted guncotton gauze sleeve ('glustrumpt' or glow stocking) that had been impregnated with a solution containing lanthanum and zirconium oxides with, optionally, yttrium oxide. Hung above the gas light, the mantle provided a bright white illumination with a yellowish tinge but little infrared irradiation. However, it failed because of its lack of stability in humid conditions.

Table 1: The rare earths[a]

Year	Element	Origin of name	Discovery	Nationality
1794	Yttrium; Yb	Ytterby mine, Sweden	Gadolin	Finn
1803	Cerium; Ce	After asteroid Ceres	Berzielus	Swede
1839	Lanthanum; La	From *Gk*: lathano - didden	Mosander	Swede
1843	Erbium; Er	Ytterby mine	Mosander	Swede
1878	Terbium; Tm	Ytterby mine	Mosander	Swede
1878	Ytterbium; Y	from Ytterby mine	de Marignac	French
1879	Samarium; Sm	After samarskite	de Boisbaudran	Swede
1879	Scandium; Sc	After Scandinavia	Nilson	Swede
1879	Holmium; Ho	After *La*: Stockholm	Cleve	Swede
1879	Thulium; Tm	Ancient Scandinavia	Cleve	Swede
1880	Gadolinium; Gd	After Johan Gadolin	de Marignac	Swiss
1885	Praseodymium; Pm	From *Gk*: prasios(green) & didymos (twin)	Auer	Austrian
1885	Neodymium; Nd	From *Gk*: neo (new)	Auer	Austrian
1886	Dysprosium; Dy	From *Gk* dys (bad) prositos (approachable)	de Boisbaudran	French
1896	Europium; Eu	After Europe	Demarcay	French
1907	Lutetium; Lu	After Lutetia, *La:* place Paris founded	Urbain/Auer/ James	French/ Austrian/ American
1945	Promethium; Pr	After Prometheus, *Gk* Titan who brought fire to mankind	(radioactive)	

[a]Modified from Tasman Metals Ltd.; see ref. 7.

In 1886 he announced[9] his *Actinophor* mantle that also had thorium oxide (ThO_2) impregnated. This oxide is the highest known melting oxide and in the fierce heat of burning gas it does not melt but glows intensively with a bright white light. The new mantle went into commercial production in 1887 at a factory that Welsbach established in Atzgersdorf, some 15 km from central Vienna. His wealth grew and allowed him to have his own laboratory, initially in a small basement and then through progressively larger premises until he bought a pharmaceutical factory near Vienna in 1887.[10]

Unfortunately, the mantles were of inconsistent brightness and the factory closed in 1889. It took Welsbach much effort to show that the problem stemmed from the purity of the thorium oxide, and it was only by purifying a large sample provided by his former factory manager that the high quality needed for consistency was attained. The trials and tribulations that befell Welsbach over this period have been elegantly described by him in his essay on the history of incandescent gas lighting.[11] The thorium sample was obtained from the monazite sand then used as ship ballast carried from Brazil in the 1880s. This sand contains 6-10% thorium, was mined in Brazil, and was quickly adopted as the source of thorium and other lanthanides; it became the foundation of the rare earth industry. After extensive deposits were found in southern India, Brazilian and Indian monazite dominated the industry before World War II, after which major mining activity transferred to South Africa and Bolivia. There are also large deposits in Australia.

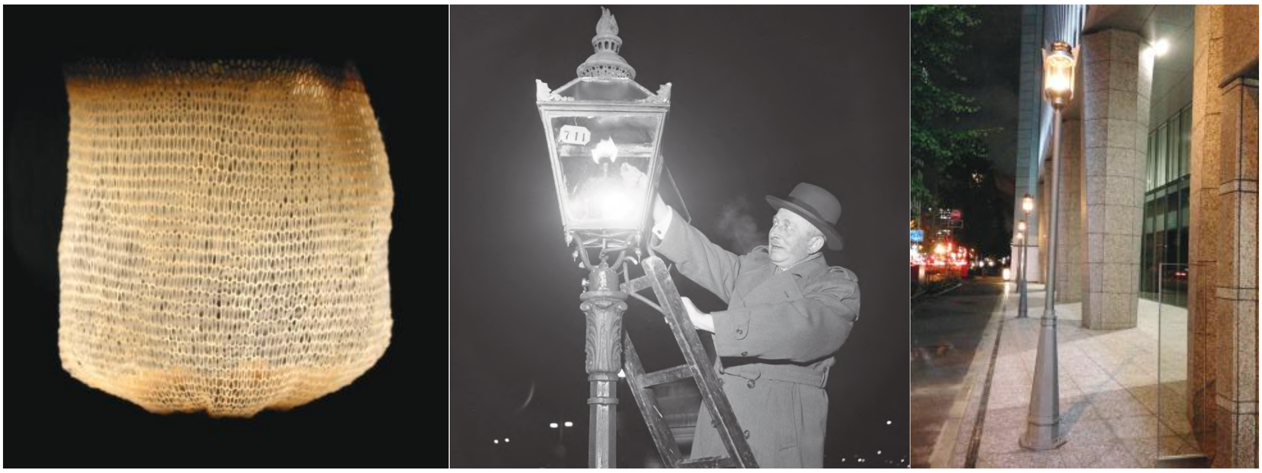
Monazite from Madagascar (Mineralogical Museum, Bonn, Germany).

Auer von Welsbach patented his new mantle impregnated with 99% pure thorium oxide and 1% cerium oxide but had also pressed ahead with production and it was commercially available late in 1891.[1,10] Its success in lighting the Vienna Café de l'Opèra gained Auer wide acclaim and made him independently wealthy. This mantle was used in street lighting to the extent that over the ten years from 1891 some 100,000 mantles were used to illuminate the streets of Berlin. During the period from 1892 until 2004, MSA Auer GmbH manufactured in excess of a billion incandescent mantles constantly improving the quality. They amount to about 2325 mantles per day! Furthermore, the *Auerlicht* Incandescent Mantles are still made by the Indo Auerlicht Manufacturing Company in India and they are used to light more than 90% of the existing street gas lamps around the world.

During his development of the gas mantle, Welsbach experimented with osmium dioxide and found that by pulverising it and then combining the powder with rubber and/or sugar he could form a paste that could be extruded through a nozzle into a linear thread. By firing the paste he was left with a fine metal wire which he hoped would provide a more durable gas mantle.

However, by then competition between electricity and gas was strong and he recognised that if the wire could provide a more durable mantle, it could also be used as a filament in an electric incandescent lamp. And so it was that Welsbach redirected his efforts towards the electric light. He took the unsatisfactory Edison carbon filament light bulb as his starting point as he felt that it could be improved by using a high melting metal filament fibre. He saw a possible solution in the osmium element and immediately bought the entire world's supply of this rare metal.[10] By 1898, he had developed a metal filament incandescent lamp that replaced Edison's carbon filament bulb. Welsbach presented the first osmium bulb at the word exhibition in Paris in 1900. This was some years ahead of the appearance of the Edison tungsten filament lamp in Europe that happened a year ahead of release in the US itself.

The shareholders in Welsbach's Austrian company, Auer-Gesellschaft, had the osmium lamp demonstrated to them at their meeting in January 1901 after which it went

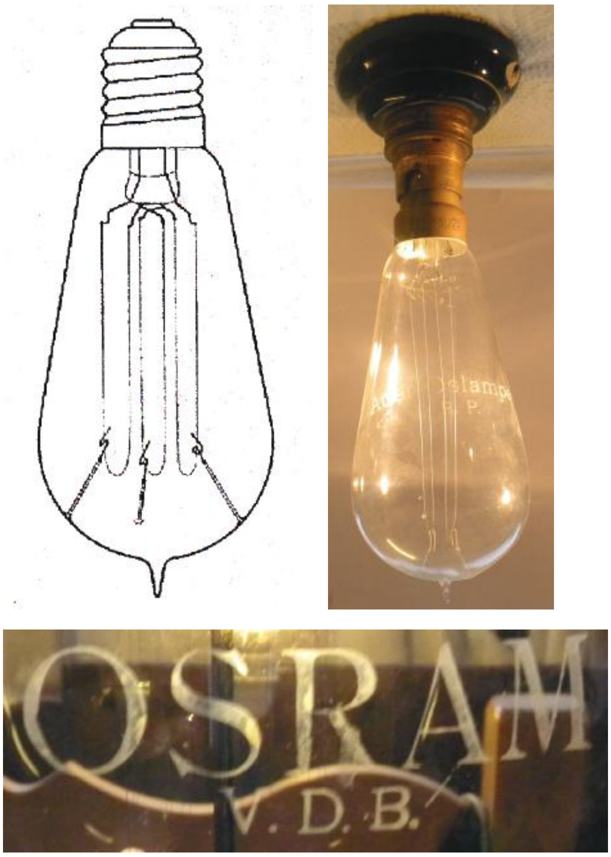


Left: Glowing gas mantle (by Fourpointsix at English Wikipedia). Centre: Gas lighting in Stockholm (1953) (by Gunnar Lanz). Right: Modern gas lighting along Japan Gas Association Building (Gasu-Kyokai_Building), Tokyo (by Yucjk). All from Wikimedia Commons.

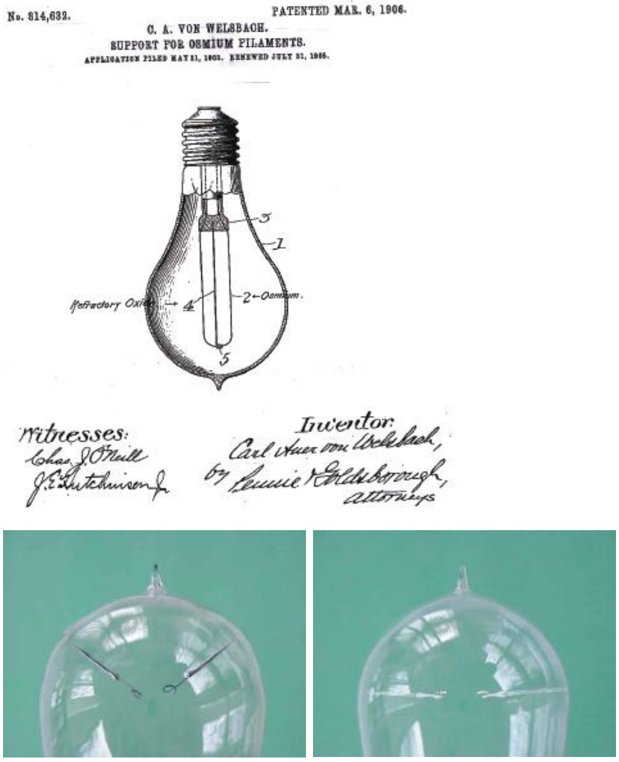
into production in Austria and Germany and was marketed locally and in Great Britain. Patenting the invention took Auer von Welsbach three attempts before success because of his earlier claims.[12] Yet the lamp was the first commercial metal-filament lamp produced and had a good a life at 1.5 watts/cp (cp is candle power and does not equate to a lumen; the former is unidirectional while the latter measures total illumination; a light source shining with 1 candle power *in all directions* would produce 12.57 lumens). Welsbach's osmium bulbs were used in considerable quantity in Vienna and Berlin where they were made.[13] Because the filaments were very fragile, the lamps were not shipped to distant points and, as the osmium metal was so valuable as much of it as possible was recovered by collecting the burnt-out bulbs. In 1902 this led to the lamps being rented rather than sold, so that the user would eventually return the lamps to the manufacturer. Then, in 1903, when a lamp cost $1.25, a purchaser could recoup $0.19 if the burned out, but unopened, lamp was returned to the manufacturer within 18 months. In that case the filament could be treated and reused. Unfortunately, the maximum operating temperature of the filament was not high and that restricted the light output. The trade name under which the lamp was sold in Austria was "Osmin", in Germany "Auer-Os", and in the UK it was "Osmi".[14] However, by 1905 the Vienna firm had stopped producing the lamp. In 1906, the brand name *Osram* was created from the materials needed at the time to produce filaments; initially **os**mium, and then wolf**ram** from Edison's tungsten bulb marketed in Europe that year. The name was registered by Auer-Gesellschaft (also known as Deutsche Gasglühlicht-Anstalt), then, in 1919 it became part of Osram Werke GmbH Kommanditgesellschaft when Auer-Gesellschaft, AEG, and Siemens & Halske AG combined their lamp production activities. Edison's tungsten lamps went on the US market only in 1907.

The design of the early electric lamp was hampered by the supports needed for the filament loops. In general, the lamps were burned in a vertical position with the bend facing down so as to prevent the filaments sagging, touching the bulb wall or each other. The supports were glass rods fused to the bulb with each carrying a metal loop at the end. The filaments passed through these loops but they tended to burn out at that position and improvements were necessary. In May 1901, Auer von Welsbach applied for but was granted only in 1906 US Patent 814,632 (see below) for the combination of an osmium filament and a support that was composed of sintered refractory oxide.

The 1901 patent sketch shows the bulb (1) and the osmium filament (2) sealed in the glass tube (3). The newly designed support (4) is also fused into the glass tube (3) at the top and has a spiral at the bottom that surrounds the filament (3) at the bend or the lowest point. The support was made from a material sufficiently rigid to sustain the heated filament, and was highly refractory so as not to fuse to the filament (to frit) in bright incandescence. It also had not to react chemically with the incandescent filament. The material consisted of a mixture of ten parts by weight of thorium oxide and one part



Osram lamps: Left: Auer bulb reproduced from archive internet (Electrical World and Engineer, 1905, Vol. XLVI, p. 360). Right and Lower: Osram lamps (from Lighting Gallery.net; www.lighting-gallery.net/gallery/displayimage.php?pos=-99116 and ….php?pos=-102827).



Top: Auer von Welsbach's 1901 Patent application diagram (adapted from the US Patent and Trademark Office – see ref. 11). Bottom: Left: the early supports and right: the improved white sintered supports (images kindly supplied by Ed Covington, see ref. 13).

by weight of magnesia although other oxides could also be used in place of the latter. The oxides were mixed as powders and put into a viscous binding solution of sugar, shaped appropriately, and one end fashioned into a small loop, hook or spiral subsequently to hold the filament. The paste was then dried, burned in air to remove all the organic material and heated to very high temperature to sinter the particles together. The oxide material was white and the lamps were best made for low voltage circuits.

Because tungsten and tantalum have even higher melting points than osmium, Werner von Bolton and Otto Feuerlien, employees of Siemens & Halske, soon had the tantalum bulb available for the market. These lamps became the first metal filament lamps offered for sale in the US[15] and then, in 1909, they became the first lamps to carry the Mazda trade-name. Both, however, were substituted by the tungsten (wolfram) bulb, to which Carl Auer's colleague and employee Anton Lederer made significant contributions in their development as demonstrated by his numerous patents.

Schloss Welsbach (Castle) (image by Grepakon, Wikimedia Commons)

By the mid-1890s Welsbach had amassed funds enough to establish his home with a large estate at Schloss Welsbach high in the Carinthian Alps, near Althofen (Treibach). Prior to his move there in 1898 where he continued his researches, he purchased the local ironworks and converted the mill into a chemical plant that became the Treibacher Chemische Werke (now Treibacher Industrie AG), the main employer in Althofen up to today.[16,17] Over the 1902-1903 period von Welsbach invented and gained a patent for what is today known as a flint. Not surprisingly this invention also came from his work on the rare earth elements, as the large residues left over after extraction of the thorium from the mozanite sand still contained large quantities of lanthanides. During his PhD studies with Bunsen, Welsbach came to know the work of William Francis on cerium and other rare earths in Heidelberg in 1875. This document provides the first record of cerium sparks from scratching or drawing the metal over a rough surface. Welsbach felt that this sparking action could be utilised for ignition purposes and with the quantities of lanthanides remaining in the significant residues of mozanite sand after extracting thorium he found the material for his flint. These residues contained some 60% of various rare earth oxides and he began exploring to find applications to which the rare earths might be put. Among his first discoveries to bear practical fruit was mischmetal (mixed metal) and the lighter flint, both of which continue to be used today. Cerium alone is too soft (and expensive) for use but by alloying the metal Welsbach found desirable pyrophoric materials. Iron reacts with the rare earths to form hard intermetallic compounds similar to those now used in neodymium magnets; they generate sparks quite easily when broken. The original Auer alloy consisted of 30% iron (ferrum) and 70% purified cerium – hence the name *ferrocerium* (or mischmetal –*mischmetall* or *Auermetall* in Europe) – which gives off sparks when scratched or struck. The alloy can now contain magnesium oxide. Three Auermetalls are known: Auermetall I is an alloy of (purified) cerium and iron, from which you can easily scrape sparks. Auermetall II is a lanthanum-enriched cerium-iron alloy that gives particularly

Left: Dr. C. Frhr. Auer von Welsbach (courtesy of the Auer von Welsbach-Museum, Althofen); Centre and Right: His obelisk outside the Chemistry Department, University of Vienna (from Wikimedia Commons) bright sparks. Auermetall III is produced by alloying iron with the impure "Cer" that accompanies the resource with still other rare earths. Originally called *earth metal*, it was renamed Auermetall III. Mischmetall is now an alloy of rare earth elements in various naturally occurring proportions. It is also called cerium mischmetal, rare earth mischmetal or misch metal. A typical composition includes approximately 50% cerium and 25% lanthanum, with small amounts of neodymium and praseodymium. Its most common use is in the ferrocerium flint ignition device of lighters and torches.

The Auer von Welsbach lighter became as famous as his incandescent mantle when it was produced on large scale in 1903. By 1930 production of ferroceium had reached 1,000,000 kg annually and served to prepare 500 million flints, which replaced six billion boxes of matches. This Welsbach invention remains in wide use in lighters today.

This same period led to the separation of the final rare earth element in 1907, namely lutetium. It was isolated almost simultaneously by Carl Auer, Frenchman Georges Urbain and American Charles James with Auer and Urbain in what seems to have been a bitter conflict.[18] Over the rest of his life Auer von Welsbach returned to pure chemistry and published a number of papers on chemical separation and spectroscopy. His primary interest was the search for missing elements, which he followed from early in the 20th century to the beginning of WWI and again after it. He was especially keen on finding element 61 (promethium; radioactive and discovered only in 1945) and he presented a major work on the separation of radioactive elements in 1922 to the Akademie der Wissenschaften in Vienna. He isolated a further three elements but was unable to separate them into pure entities.

In 1899 Auer von Welsbach married Marie Nimpfer in Helgoland, with whom he had four children: Carl, Herbert, Hermann and Hilde. He was given the title of baron (Freiherr) in 1901 by the Emperor Franz Joseph. Carl Auer von Welsbach died on August 4, 1929 a month before his 71st birthday in his castle in Carinthia, in southern Austria. He is buried in the family grave at the Hietzing Cemetery in Vienna with his parents, wife (who died in 1950), and children.

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Dates of Note

January

22 Sir ***Francis Bacon***, the English philosopher remembered for his influence promoting scientific method, was born this day in 1561.

23 ***Otto Diels***, the German organic chemist who with Kurt Alder was awarded the Nobel Prize for Chemistry in 1950 for their named synthesis, was born this day in 1876 as was ***Karl Karlovich Klaus*** (Claus) in 1796. He was the German-Russian chemist and biologist who was born and died in Russia, and discovered ruthenium (1844) - the last dense, inert, platinum-like metal to be found. This was also the day in 1911 that ***Marie Curie***'s nomination to the French Academy of Sciences was voted down by all-male membership. She was one of six candidates, of which only one was to be chosen. The result was 30 votes for M. Eduoard Branly, the inventor of the coherer for wireless telegraphy, and 28 for Mme. Curie. After the vote, an announcement was made to state that the vote did not reflect the attitude of the academy toward the admission of women in any sense, and the election was judged on merit for recognition. It was also the day in 1896 that ***Wilhelm Röntgen*** first made a public lecture-demonstration of his X-ray device (in Würzburg, Germany).

26 ***Alexander Macmillan***, the Scottish publisher who did much to promote science in the Victorian times by publishing the journal *Nature*, died in 1896.

28 ***Julian W. Hill***, the American chemist who discovered cold drawing (a method of strengthening polymer fibres by stretching) whilst working with Wallace Carothers on nylon, died this day in 1996. It is also the day in 1896 when the first speeding fine was handed out to a British motorist: Walter Arnold of East Peckham, Kent, was fined one shilling for doing 8 mph in a 2 mph built up zone.

30 In 1901, the world's tallest geyser was discovered by Dr Humphrey Haines on the North Island of New Zealand. He was following up reports of great clouds of steam, and found the Waimangu Geyser near Rotorua. It appeared after the Tarawera eruption of 1886. The Waimangu Geyser was the largest geyser in the world and erupted on a 36 hour cycle for four years, hurling black mud and rocks in the air.

31 ***Irving Langmuir***, the American physical chemist whose studies of molecular films on solid and liquid surfaces opened new fields in colloid research and biochemistry and gave him the 1932 Nobel Prize for Chemistry, was born this day in 1881.

February

1 This day in 1851 saw evaporated milk invented by Gail Borden and marks the death in 1976 of ***Werner Heisenberg*** of principle fame.

2 ***Ray McIntire***, the Dow chemical engineer who inadvertently created Styrofoam while working to develop a rubberlike polymer to be used as a flexible insulator, died in 1996.

3 ***Johann Beckmann***, the German chemist and economist who established the science of agriculture, died in 1811. It is also the day in 1891 that city-wide electrical lighting of London streets was marked by a ceremony where the Mayor laid the foundation stone of the principal junction box.

4 ***Friedrich Hund***, known for his rule involving molecular orbitals, was born this day in 1896. It is the day in 1941 that Roy Plunkett received his US patent for *Tetrafluoroethylene Polymers* (Teflon). It was assigned to his employer, Kinetic Chemicals Inc. of Wilmington, Delaware. It was also the day in 1936 that radon became the first radioactive substance to be produced synthetically in the US.

5 This day marks the discovery of germanium in 1886 by German chemist ***Clement Winkle***.

8 ***Moses Gomberg***, the Russian-born American chemist who initiated free radicals study following his 1900 preparation of the triphenylmethyl radical, was born 150 years ago today. ***Chester F. Carlson***, the American physicist who invented xerography, was born in 1906. ***Felix Hoffmann***, the German chemist who discovered aspirin while a researcher with Bayer & Co., died in 1946.

9 In 1996, a year after creating element 111, the team of German scientists led by ***Peter Armbruster*** at the Gesellschaft für schwerionenforschung (GSI) facility at Darmstadt, claimed one atom of element 112. Its nucleus has 112 protons and 166 neutrons, and mass number 277. As a new element it was named ununbium, symbol Uub.

10 ***Ira Remsen***, the inaugural professor of chemistry at Johns Hopkins University who co-discovered saccharin, was born in 1846.

11 ***Friedrich C. Hofmann***, the German chemist who polymerised isoprene to create synthetic rubber in 1909 and was granted the world's first patent for a *method for producing synthetic rubber*, was born 150 years ago.

12 The first injection of penicillin into a human test subject was conducted this day 75 years ago and, in 1851, gold was discovered at Lewis Ponds Creek, north of Guyong, NSW, Australia.

13 Element 103, lawrencium, was first produced in Berkeley, California in 1961.

16 ***John Rex Whinfield***, the English chemist who with James Tennant Dickson, invented polyethylene terephthalate from the condensation reaction of ethylene glycol with terephthalic acid in 1941, was born

in 1901. ***Julius Thomsen***, the Danish chemist who tabulated the amount of heat released or absorbed in 3,500 chemical reactions and originated the term *acidity* and prepared the first table of the relative strengths of acids, was born in 1826.

18 This day in 1876 saw the first direct telegraph link was established between Britain and New Zealand.

20 ***Henry Eyring***, the Mexican–American theoretical chemist whose primary contribution was in the study of reaction rates and intermediates, was born in 1901. ***Friedrich Sertürner***, the German chemist who discovered morphine in 1806 while trying to isolate the portion of opium that caused sleep, died 175 years ago in 1841.

21 This day in 1811 ***Humphry Davy*** introduced the name *chlorine* from the Greek for the bright yellow-green gas chemists then knew as oxymuriatic gas.

22 ***Carl Graebe***, the German chemist who, with Carl Liebermann, synthesised the orange-red dye alizarin in 1868 which supplanted the natural source of the dye from the madder plant root, was born 175 years ago.

23 In 1841, the Chemical Society (London) held its first organisational meeting.

25 ***Ida Noddack***, who with her future husband Walter co-discovered element 75, rhenium, in 1925 and named it after the Rhine River, was born this day in 1896. It is also the day 400 years ago in 1616 that the Minutes of the Inquisition recorded the judgment against Galileo on the heliocentric model when Pope Paul V summoned him in person to abandon his assertion that the earth moves around the sun.

26 ***Herbert Henry Dow***, pioneer in the American chemical industry and founder of the Dow Chemical Company who developed and patented electrolytic methods for extracting bromine from brine and in 1890 organised the Midland Chemical Company, was born this day in 1866. The Dow process was remarkable in that it did not result in a salt by-product, operated on comparatively little fuel, and it was the first commercially successful use of a direct-current generator in the US chemical industry. It is also the day that ***Otto Wallach***, the German chemist awarded the 1910 Nobel Prize for Chemistry for identifying terpene compounds, died in 1931.

27 ***Alfred Einhorn***, the German chemist who developed procaine (Novocain; 1905) whilst working with Adolf von Baeyer, was born in 1856.

28 ***Linus Pauling***, the US chemist who received the Nobel Prizes for Chemistry (1954) and Peace (1962) and charted the chemical underpinnings of life itself, was born this day in 1901.

29 In 1936, *Nature* carried ***Niels Bohr***'s *bowl of balls* explanation for the effect of bombarding particles on a nucleus (see: Vol. 137, p. 344).

March

1 ***Jacobus Henricus v'ant Hoff***, the Dutch physical chemist who was the first winner of the Nobel Prize for Chemistry (1901) *in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions*, died this day in 1911.

2 In 1896, ***Henri Becquerel*** reported his discovery of the penetrating rays of a uranium compound to the French Academy of Sciences. The photographic plate, fogged by these rays, showed the outline of a metal cross lying between the compound and the plate and is the first recognition of radioactivity.

8 ***Edward Calvin Kendall***, the American biochemist who shared (with Hench and Reichstein) the Nobel Prize for Physiology or Medicine in 1950 for studies involving the structure and biological effects of adrenal cortex hormones, was born in 1886.

9 ***Edward Goodrich Acheson***, the American inventor who discovered carborundum, the second hardest substance (after diamond), and later perfected a method for making graphite, was born in 1856. ***Hans Christian Oersted***, Danish physicist and chemist and accorded the title *father of electromagnetism*, died in 1851.

17 ***Irène Joliot-Curie***, the French physical chemist and wife of Frédéric jointly awarded the 1935 Nobel Prize for Chemistry for the discovery of new radioactive isotopes prepared artificially, died in 1956.

18 ***David Shemin***, the American biochemist who pioneered the use of radioactive and stable isotopes to trace chemical pathways in the body and discovered the metabolic pathway by which the cell synthesises heme, vitamin B12 and related compounds, was born in 1911.

20 It is 100 years ago today that ***Albert Einstein***'s Theory of General Relativity was published as an academic paper in *Annalen der Physik* (***49***, 769).

23 ***Hermann Staudinger***, the German chemist who received the 1953 Nobel Prize for Chemistry for his discovery of the structure of polymers as long-chain molecules, was born in 1881. ***Gilbert Newton Lewis***, the American chemist who with Langmuir developed a theory of valency, which introduced the covalent bond (c. 1916) whereby a chemical combination is made between two atoms by the sharing of a pair of electrons, one contributed from each atom and is best known for Lewis structures, died in 1946. This day in 1821 was when bauxite was discovered in Southern France.

26 ***Christian Boehmer Anfinsen***, the American biochemist who (with Moore and Stein) received the 1972 Nobel Prize for Chemistry for research on the shape and primary structure of ribonuclease, was born 100 years ago today. ***Harry Coover***, the inventor of super glue, died 5 years ago.

30 ***Antoine J. Balard***, the French chemist who in 1826 discovered the element bromine, determined its properties, and studied some of its compounds, died in 1876. This day in 1791 was when the French National Assembly finally chose the metre to be 1/10 000 000 of the distance between the North Pole and the Equator.

31 ***Robert Wilhelm Bunsen*** of burner fame was born in 1811. ***Archibald Scott Couper***, the Scottish chemist who, independently of Kekulé, proposed the tetravalency of carbon and the ability of carbon atoms to bond with one another to form long chains, was born in 1831.

April

1 Dame ***Kathleen Lonsdale***, the British crystallographer who developed several X-ray techniques for the study of crystal structure, and ***François-Marie Raoult***, the French chemist who formulated a law on solutions (Raoult's law) that made it possible to determine the molecular weights of dissolved substances, both died this day but in 1971 and 1901, respectively.

6 ***Feodor Lyne***, the German biochemist who shared (with Bloch) the 1964 Nobel Prize for Physiology or Medicine for his research on the mechanism and regulation of the cholesterol and fatty acid metabolism, was born in 1911.

7 ***Melvin Calvin*** was born this day in 1911.

14 ***William Nunn Lipscomb*** the American physical chemist who won the 1976 Nobel Prize for Chemistry for his research on the structure of boranes, died 5 years ago. It is the day in 1961 that the manmade element 103, lawrencium (Lr – formerly Lw), was produced in the US.

15 ***Nikolay Nikolayevich Semyonov***, the Russian physical chemist who shared the 1956 Nobel Chemistry Prize with Sir Cyril Hinshelwood for their research into the mechanism of chemical reactions, was born in 1896.

19 ***Pierre Curie***, French physical chemist and co-winner of the 1903 Nobel Prize for Physics with his wife Marie, died in 1906.

20 ***Franz Karl Achard***, the German chemist who invented a process for the large-scale extraction of table sugar (sucrose) from beets, died in 1921. The first national meeting of the American Chemical Society was held in New York City in 1876.

Patent Proze: Data exclusivity for pharmaceuticals and the TPPA

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The recently agreed Trans-Pacific Partnership Agreement (TPPA) contained several sections relating to protection of intellectual property (IP). Indeed much of the controversy surrounding the TPPA in New Zealand focused on the potential for broader IP rights, such as longer patent and copyright terms. One of the elements of the TPPA that was rarely discussed was the IP right of “data exclusivity” or “data protection”. Now that the Agreement has been finalised, data exclusivity has been highlighted as one of the key issues where New Zealand dug its heels in and held its ground.

What is data exclusivity?

For pharmaceuticals, data exclusivity refers to the protection of trial data generated by a drug originator to satisfy regulatory agencies. The trial data is generated for the purposes of demonstrating the drug’s safety, quality and efficacy. The data exclusivity period is the period that such data is kept confidential by the regulatory agencies, and therefore cannot be relied upon by other parties looking to obtain marketing approval.

Typically, the trial data includes pre-clinical and clinical trial data on animals and humans as well as toxicology and manufacturing feasibility studies. The data is included in a registration dossier and is submitted to the appropriate regulatory agency for that country to obtain marketing approval.

Once the data exclusivity period is over (and assuming there is no patent protection), competing drug suppliers can seek government approval for a generic version of the drug without having to conduct their own clinical trials. In order to be able to benefit from the data provided by the drug originator, the generic company must show that their product has the same qualitative and quantitative composition as the reference product and that it is bioequivalent. Data exclusivity therefore protects the originator's investment and risk in the trials and drug development.

Unlike patents, data exclusivity periods do not give a drug developer a true market monopoly. Other suppliers could conduct their own trials and make separate applications for approval for the same drug. In practice, however, the cost and time of doing so provides the drug originator with a temporary *de facto* monopoly, even in the absence of patent protection. Clearly then, data exclusivity periods become especially valuable where patent protection is found to be invalid or not enforceable against a generic provider, or where patent protection is simply not sought or is not available.

New Zealand and Australia currently provide a data exclusivity period of five years for all new drugs. The USA provides five years for new chemical entities or seven years for orphan drugs.[1] However, the USA also provides 12 years of exclusivity for new biological products ("biologics").[2] This 12 years is split with four years data exclusivity being provided with an additional eight years of "market exclusivity". Market exclusivity is the period of time during which a generic company may not *market* an equivalent generic version although their application for authorisation may be processed. Since marketing approval takes 1-2 years, market exclusivity means that the *de facto* monopoly period is actually limited to 12 years rather than being 13-14 years. For European states, eight years of data exclusivity is provided with an additional two years of market exclusivity.

What are biologics and why are they special?

Although there is some debate over their exact definition,[3] "biologics" or "biopharmaceuticals" are generally accepted to consist of therapeutic proteins created by either a microorganism or mammalian cell by using the metabolic processes of the organisms themselves. Biologics include insulin, monoclonal antibodies, vaccines, blood and blood products, protein hormones, cellular therapies, allergenic extracts, and gene therapy. Examples of biologics include Adalimumab (Humira), Trastuzumab (Herceptin), Etanercept (Enbrel), Bevacizumab (Avastin), and Rituximab (Rituxan).

As biologics tend to be derived from living cells, they differ from conventional "small molecule" drugs in important ways. Conventional small molecule drug compounds are produced according to exacting standards and have a structure which can be characterised by current analytical technology. This lends themselves to being precisely defined in patent specifications, and infringement being fairly clear cut. Biologics on the other hand are harder to define and usually require complex bioassays for characterisation and stability assessment, rather than chemical tests for identity and purity. A biologic's structure is particularly sensitive and can be affected by the cell system in which it is produced, the fermentation media, or operating conditions.

The variability of biologics and the sensitivity of production processes adds to the cost and difficulty of producing effective and commercially viable products. Production also typically yields small quantities. Although such quantities are suitable for preclinical analysis, during scale-up to commercial production issues are often encountered with product purity and batch-to-batch equivalence.

Fortunately, biologics do not require an exact composition in order to be effective at treating a disease; small modifications to the biologic (known as "biosimilars") may not make any difference to their efficacy. However, the potential for "biosimilars" to be introduced and compete with the original biologic makes biologics more difficult to protect with patents. Pharmaceutical companies that invest heavily in research and development are concerned that other manufacturers will be able to create biosimilars which are sufficiently different to the original to avoid patent infringement, but which are close enough to the original, i.e. sufficiently bioequivalent, that they can rely on the original clinical trial data. Innovators of new biologics wanted to plug this so-called 'patent protection gap' by extending data exclusivity to 12 years in New Zealand and Australia.

What would be the effect of extending data exclusivity?

The standard patent term is 20 years from the filing date of the patent application. However, a patent application is typically filed well before trials start to avoid compromising novelty of the drug. This means that for inventions (such as pharmaceuticals) that require extensive trials before sale, the effective patent term that can be used by the innovator to recoup their costs and make a profit is much reduced.

Marketing approval for new drugs generally occurs between 12 and 16 years after patent filing, thus giving an effective patent term of between 4 and 8 years. Therefore, an extension of data exclusivity provisions to 8 or 12 years would almost certainly work in favour of the drug originator by raising the barrier to entry for generics even after the patent has expired. This would also probably result in the originator maintaining higher prices and ultimately lead to increased government expenditure on medicines. On the other hand, the extra income for drug originators could make it more viable for pharmaceutical companies to develop biologics used to treat rare diseases where sales would be less.

New Zealand rejects the 12 year data exclusivity proposal

From leaked TPPA drafts, it is clear that the USA was pushing for a 12 year exclusivity period on biologics but Australia and New Zealand successfully argued for five years. Despite this, New Zealand has committed to provide 10 years of data exclusivity for new agricultural chemicals. Agrichemicals, however, have less of a delay in bringing a product to market due to the reduced regulatory requirements for trial data.

Data exclusivity of five years is already provided in New Zealand. NZ trade minister Tim Groser stated “Regarding data protection for biologic medicines, New Zealand's existing policy settings and practices will be adequate to meet the provisions we have finally agreed on”. The government’s press release relating to the TPPA[4] states “TPP countries have agreed to provide effective market protection for biologic medicines, through data exclusivity and other measures.” Although the TPPA still needs to be ratified by the Governments of each country in the agreement, it is expected to come into force within two years.

The existing five year data exclusivity period effectively acts as a balance to compensate drug originators where marketing approval is less than five years from patent expiry. However, it does not account for the “patent protection gap” that could lead to generic manufacturers relying on the originator’s marketing approval while avoiding infringement of any patent. Mechanisms to address this are already in place in the USA[5] whereby marketing approval is only granted to drugs not covered by patent protection. This concept is called “patent linkage”.

A TPP fact sheet[6] released by the Ministry of Foreign Affairs and Trade (MFAT) states that patent linkage will need to be provided by New Zealand. This means that the drug originator will be notified by the regulatory agency Medsafe when an application is made for marketing approval for a generic version of the patented product. The drug originator will then be free to take court action to prevent a patent-infringing generic/biosimilar from ever reaching the market. The MFAT fact sheet also stresses that Medsafe will not be required to directly prevent a generic from being put on the market, nor to rule on patent disputes that may arise.

It is a delicate balancing act to incentivise innovation by granting monopolies while at the same time pursuing free market policies to encourage competition and lower prices. Despite the patent linkage assurances providing some consolation for biologics originators, the TPP deal appears to weigh more in favour of the NZ taxpayer, at least in the short term. Long term, the lack of data exclusivity extensions may impact on the availability of biologics in New Zealand. The TPP data exclusivity provisions and patent linkage arrangements will be reviewed in ten years’ time. At that stage more data should be available on whether the existing provisions are sufficient, or whether data exclusivity should be extended.

If you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact:

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References and Notes

1. Orphan drugs in this context are defined as being those that are used to treat diseases or conditions that affect less than 200,000 individuals in the USA.

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5. Patent linkage is codified in the Hatch Waxman Act and applied though the publication of “Approved Drug Products with Therapeutic Equivalence Evaluations”, commonly known as the Orange Book.

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