# Introduction

This booklet contains abstracts for the 83 posters being presented by second year PhD students (and some third year students) in the Faculty of Science, on Wednesday April 2nd. A significant number second year students are away from Liverpool on field or laboratory work and will present next year.

This poster presentation day forms part of the first 'Postgraduate Research Week' to be held in this format for all Faculties of the University between March 31st and April 3rd, 2003.

Professor Stephen Flint
Director of Postgraduate Studies, Faculty of Science
April 2nd, 2003

# School of Biological Sciences

# TUBERCULOSIS IN WILD FIELD VOLES

**Sarah Burthe, M. Bennett, A. Kipar, X. Lambin, S. Telfer and M. Begon.**

*Population and Evolutionary Biology Research Group, School of Biological Sciences and the Centre for Comparative Infectious Diseases, Department of Veterinary Science.*

## Introduction

Field voles (*Microtus agrestis*) are the reservoir hosts for *Mycobacterium microti*, a member of the *Mycobacterium tuberculosis* complex that includes the causative agents of human and bovine TB. *M. microti* causes tuberculosis infection in voles, but human cases are also possible and increasingly reported. Infection of field voles was monitored bi-annually at 27 sites in Kielder forest, Northumberland, with the aim of relating infection status to vole density, and hence determining whether pathogens can affect host population dynamics.

## Methods

27 clear-cut sites were trapped bi-annually across three catchment areas (Kielder, Redesdale and Kershope) within the 600km$^2$ forest matrix. 12 traps were set on a 15m by 15m grid for three days. Field voles were killed and a necropsy performed. Tuberculosis was diagnosed by the presence of external characteristic dermal lesions or obvious lymphadentitis or by internal lesions. If TB was suspected then samples of all organs were taken for culture and histopathology, and if no TB was apparent the lungs and pooled lymph nodes were cultured.

## Results and conclusions

Three detection methods based on external signs, presence of internal lesions and culture of mycobacteria gave significantly different estimates for TB prevalence of 3.7%, 5.1% and 14.3% respectively. Therefore, culture reveals a subset of infected voles with no visible lesions and further work needs to be conducted into the role of these voles in disease transmission. TB infection was patchy across the forest but there was no significant difference in prevalence between catchments. Prevalence was not related to vole density, but past vole density needs to be compared. This study is the first detailed study of TB prevalence in voles over a wide spatial scale and will provide information on transmission, strain types, pathogenesis and prevalence patterns.

# DIVERSITY OF ARCHAEA ASSESSED BY 16S RRNA GENE PHYLOGENY

**Blencowe C[1]., Pickup R[2]. and Edwards C[1].**

*[1]Molecular and Environmental Microbiology Group, School of Biological Sciences, University of Liverpool. [2]Centre for Ecology and Hydrology, Windermere.*

In recent years advances in molecular biological techniques have had far reaching implications in the study of microbial ecology. Traditional microbiological techniques are now thought to ignore about 99% of the microorganisms present within any given environment. The use of techniques such as polymerase chain reaction (PCR) based 16S rRNA gene profiling have indicated that microbial diversity within a given environment is generally much higher than previously thought.

Archaea are a domain of prokaryotic organisms that are evolutionarily distinct from members of the domain bacteria. The Archaea can be divided into two kingdoms, Euryarchaeota and Crenarchaeota. Members of the domain Archaea have been traditionally associated with environments, of high temperature and salinity and extremes of pH and pressure. An increasing body of evidence suggests that these microorganisms are also abundant in more temperate, marine, freshwater and soil environments. Studies previously conducted at Liverpool have focused upon the presence of Crenarchaeotes within a hypereutrophic lake (Priest Pot) in the English Lake District. The principle aim of this research project is to extend this research to other eutrophic lake systems within the English Lake District.

# MODELLING CANOPY COMPOSITION AND GROUND VEGETATION IN BRITISH WOODLANDS; THE CONSERVATION IMPLICATIONS.

**Corney, P.M., Le Duc,M.G., Kirby, K., Smart, S. & Marrs, R.H.**

*Applied Vegetation Dynamics Laboratory, School of Biological Sciences, University of Liverpool.*

## Introduction

Repetition in 2002/3 of the Nature Conservancy's 1971 Woodland Survey offers unique opportunities for modelling national-scale woodland vegetation change as a function of environmental drivers. As a first step, floristic and environmental data from 1971 were analysed to quantify the role of bio-climatic factors in determining distribution of woodland vegetation.

## Multivariate analyses

In order to assess the factors likely to influence woodland composition at the site level, multivariate analyses were carried out with a two-fold aim. Detrended Correspondence Analysis (DCA) was used to determine the exact state of the woodland resource, while Canonical Correspondence Analyses (CCA) was used to examine those environmental variables *driving* woodland composition. Included in this analysis were variables falling into the following categories: Boundary type, Site Geometry, Geographic Position, and Surrounding Land Class.

## Results

Using a Forward Selection Model in CANOCO (significant using a Monte Carlo Permutation Test), those variables that explained most of the variation were drawn from each of the above variable categories ($F=4.059$; $P=0.001$; 999 Permutations).

## Conclusions

CCA analysis of this kind provides a powerful tool for exploring extant data sets such as the Nature Conservancy Woodland Survey of 1971. Moreover, it serves to demonstrate correlations between species composition & environmental variables and as such is as useful in hypothesis generation as in actual hypotheses testing.

This analysis showed that woodland shape has a role to play in determining woodland species composition and distribution and as such it should be given more emphasis in conservation management decisions. Land type was found to be strongly correlated with species distribution; yet this factor cannot be divorced from climatological and edaphic variables Thus, the work is currently being extended by analysis of recently acquired Weather, Pollution, Exposure and Edaphic data. Analysis also demonstrated that Boundary type has an effect on species composition. Therefore, further work examining the nature of disturbance effects will be conducted at the plot level.

Finally, site geographic position obviously determines species distribution, while survey timing will clearly effect species detection. However assessing the proportion of variance accounted for by *all* of these factors is an important first step towards understanding local, site-based change in a larger, cross-site context.

# HOST RANGE DETERMINANTS IN BACTERIOPHAGE THAT TRANSFER VEROCYTOTOXIN GENES BETWEEN BACTERIA

**Smith, D.L., Saunders J.R & McCarthy A.J**

*School of Biological Sciences, University of Liverpool*

Verocytotoxigenic bacteriophage (VT-phage) encode toxins that are major virulence factors in enterohaemorrhagic *Escherichia coli* (EHEC) strains. Serotype O157 is the most notorious having been responsible for a number of outbreaks associated with fatalities due to kidney failure, a site of action for these bacteriophage-encoded toxins.

The aim of this study is to characterise VT-bacteriophage infection of *E.coli*, with particular emphasis on the specificity of the tail fibre interaction with the associated bacterial outer membrane receptor. Previous and ongoing work in the department has identified an *E.coli* outer membrane protein Vpr and implicated its involvement in the VT-phage infection process. A range of molecular biological techniques is being used to elucidate the interaction between bacteriophage and host. Native VT-phage work is undertaken at Containment level 3, although we have the advantage of using two isogenic VT-phage with their toxin gene interrupted by different selectable markers, making it possible to work at level 2.

VT-phage exhibit modular horizontal transfer of genetic information and it is hypothesised that recombination between tail fibre regions can extend the bacteriophage host range and therefore lead to the evolution of new pathogenic strains. Minimal nucleotide sequence variation in this gene has been identified in VT-phage Φ24B and Φ3538 but these alterations may have an effect on host range. Equivocal data from studies with knockout mutants resistant to infection suggest that the role of Vpr in bacteriophage recognition is complex and that multiple factors may govern phage adsorption and infection. Loss of phage susceptibility can be complemented by the *vpr* gene, but Western analysis shows that Vpr is being expressed in the mutant. This could mean that the mutation affects location at the cell surface where the protein (host)-protein (tail fibre) interaction occurs. In addition to resolving these data, the work is being extended to other VT phages to determine whether this infection model is a general or specific phenomenon.

# CHARACTERISATION OF NEUTROPHIL DEGRANULATION AND ITS ROLE IN HOST CELL TOXICITY AND DEFENCE

**E. J. Naylor[1], M. Biffen[2], S. W. Edwards[1], B. Thong[2]**

*[1]School of Biological Sciences, University of Liverpool*
*[2] AstraZeneca. R&D Charnwood, Bakewell Rd, Loughborough,*

The neutrophil, or polymorphonuclear leukocyte (PMN) provides the first line of defence against bacterial and fungal infections, so must respond quickly and potently. The PMNs respond by phagocytosis of the microorganism responsible for inflammation. The efficiency of neutrophil activity depends on two simultaneous events occurring in the phagosome of stimulated neutrophils. These events are the generation of ROS by activation of NADPH oxidase, to produce superoxide ions ($O_2$-), and the release of neutrophil-derived microbicidal proteins from granules. One such microbicidal protein is myeloperoxidase (MPO). MPO converts hydrogen peroxide ($H_2O_2$) from the spontaneous dismutation of $O_2$- into hypochlorous acid (HOCl).

Chronic obstructive pulmonary disease (COPD) is a major health burden and is responsible for over 15,000 deaths each year in the UK. COPD is described as a progressive airflow obstruction resulting in an increasing shortness of breath and an inability to exercise. Neutrophils have been associated with lung injury, in particular with emphysema, and this led to the hypothesis that a substance that can inhibit MPO activity and decrease its inflammatory effect on host tissue could be a potential drug target for the treatment of COPD. PMN were isolated from heparinized venous blood of healthy volunteers by one-step centrifugation through Polymorphprep™ (AXIS-SHIELD) as described in the manufacturers instructions. In all cases the purity was > 95 % and neutrophil viability was > 97 %. PMN were treated with a range of protein kinase inhibitors (*see table 1*) and were stimulated with PMA (a soluble chemical stimuli) or unopsonised, human IgG opsonised or human serum opsonised latex beads (1 μm diameter), as a model phagocytic stimulus. Dose response experiments were carried out in order to find the $IC_{50}$ values of these inhibitors for inhibition of HOCl secretion.

| Inhibitor | Target |
|---|---|
| PD98059 | MAP kinase kinase (MEK) |
| SB202190 | p38 MAP kinase |
| Wortmannin | Phosphatidylinositol 3-Kinase (PI 3-kinase) |
| GFX | Protein Kinase C (PKC) |
| H-89 | Protein Kinase A (PKA) |

It has been observed that each stimulus required different protein kinases to remain active for the PMN to secrete HOCl.

PMN were also treated with heat-killed *Staphylococcus aureus*, a well-studied phagocytic stimulus, and live *Haemophilus influenzae*, a common occurring infection in COPD patients, in order to observe the effects on ROS production by PMN under different conditions. Both bacteria were opsonised with human IgG, human IgA and human serum. Opsonised *H. influenzae* caused an increased number of PMN to undergo apoptosis and lysis, compared to unstimulated PMN and PMN treated with *S. aureus*, latex and PMA. This could explain why *H. influenzae* infections are a problem for COPD patients. If PMN are apoptotic they would be unable to kill the bacteria, and lysed PMN would release the ROS causing more host cell inflammation.

# METAL POLLUTION IN A DAMMED VALLEY – THE SULBY RIVER, ISLE OF MAN

**Karen J Galtress**

*School of Biological Sciences (Port Erin Marine Laboratory)*

The impoundment of the headwaters of the Sulby River in the 1980s had a devastating impact on its biota, including extensive fish kills. A geochemical investigation concluded that aluminium-rich water issuing from the dam's foundation drain was the major source of the problem and limestone beds were installed through which some of the drainwater was diverted before discharge to the river.

The major aims of my project are to develop a detailed picture of the current chemical and biological quality of the Sulby River and to assess the effectiveness of the current treatment system and any potential additional or alternative mitigation systems.

Data so far suggest that the river is no longer severely impacted by aluminium, partly through a decrease in the concentrations found in the foundation drain. However, the drainwater, a substantial proportion of which still escapes to the river untreated, is also high in manganese. Compared with aluminium, research into the potential toxicity of manganese in acid waters is limited. This poster focuses on experiments aimed at exploring this issue in relation to salmonids.

# IDENTIFICATION AND CHARACTERISATION OF TOR SIGNALLING PATHWAY GENES IN *ASPERGILLUS NIDULANS*

**Gregory J. Fitzgibbon, Meriel G. Jones, Mark X. Caddick**

*School of Biological Sciences, Bioscience Building*

The TOR signalling pathway, first identified in *Saccharomyces cerevisiae,* is involved in the activation of a cell-growth programme in response to nutrients such as nitrogen and carbon. TOR1 and TOR2 kinases regulate nitrogen metabolism by controlling the nuclear localisation of the GATA transcription factor GLN3. Under good nitrogen conditions, TOR promotes complex formation between GLN3 and the cytoplasmic protein URE2, preventing expression of the genes activated under nitrogen limiting conditions. Nitrogen limitation or treatment with rapamycin, an immunosuppressive macrocyclic lactone, causes the inactivation of TOR resulting in nuclear accumulation of GLN3 by dissociation from URE2. TIP41 indirectly promotes nuclear localisation of GLN3 by binding and inhibiting TAP42. TAP42 is the inhibitor of SIT4, the phosphatase involved in the liberation of GLN3 from URE2. The TOR signalling pathways' sensitivity to rapamycin occurs by a direct interaction between the TOR proteins and rapamycin complexed with the rapamycin target protein FKBP12. Rapamycin is an antifungal agent causing G1 cell cycle arrest in *S. cerevisiae* cells resulting in reduced budding. Specific mutations within TOR, FKBP12, or TIP41 result in rapamycin resistant phenotypes. AREA is the GLN3 homologue in the filamentous fungus *Aspergillus nidulans*. It has been shown that in both good (e.g. ammonium) and poor (e.g. proline) nitrogen conditions, AREA is subjected to the same regulation as GLN3, although a TOR signalling pathway remains uncharacterised. Here we attempt to identify *A. nidulans* homologues of the genes involved in the *S. cerevisiae* TOR signalling pathway and characterise *A. nidulans* mutants with rapamycin resistant phenotypes. BLAST searches were performed for the TOR signalling pathway genes of *S. cerevisiae* against the incomplete *A. nidulans* genome. The most significant contigs were used as templates for the design of primers for PCR and rtPCR to complete the sequences of the homologues and characterise gene expression. Here we show the identification and cloning of *A. nidulans* homologues of *TOR1*, *FKBP12*, *TIP41* and *TAP42*. Sequence analysis of both the genomic and cDNA sequences of these genes have identified the intron/exon boundaries aiding the annotation of the *A. nidulans* genome. Initial computational analysis failed to identify an *A. nidulans* URE2 homologue. NMRA is however the nitrogen metabolite repressor protein believed to bind AREA and prevent its nuclear entry. Rapamycin resistant *A. nidulans* mutants were selected on minimal media containing rapamycin after exposure of the conidia to ultraviolet radiation. Growth of wild type *A. nidulans* strains on rapamycin containing media produces white colonies showing no conidiation. The rapamycin resistant mutants *rap5* and *rapc10* demonstrate conidiation in the presence of rapamycin but show poor growth on media containing nitrate and other nitrogen sources. Screening of these strains for mutations in either the *TOR1*, *FKBP12* or *TIP41* homologues revealed that an insertion in *TIP41* of the *rap5* mutant produced a truncated form of the protein. Loss of TIP41 function would explain rapamycin resistance and poor growth on alternate nitrogen sources through a reduction in the nuclear accumulation of AREA.

# CONFLICT MANAGEMENT AND CONFLICT RESOLUTION IN THE CHACMA BABOON (*PAPIO CYNOCEPHALUS*)

**Guillermina Echeverría-Lozano, Louise Barrett and Robin Dunbar**

*Evolutionary Psychology and Behavioural Ecology Research Group*

Conflict management and conflict resolution research has been an interesting and growing area of research since 1979, when de Waal and Roosmalen published a study on chimpanzees. In it they described the presence of post-conflict affiliatory behaviours between former opponents within a captive group. Since this first study, several studies have been conducted on a number of primate species (e.g. long tailed macaques: Aureli *et al*. 1989, vervet monkeys: Cheney and Seyfarth 1989, baboons Cheney and Seyfarth 1985, ring-tailed and red-fronted lemurs: Kappeler 1993, patas monkeys: York 1988, see a full list in Apendix A of Aureli and de Waal 2000).

However, the research on post-conflict interactions has been mainly focused in the study of reconciliation (post-conflict affiliative behaviour between former opponents), and only a few studies have considered other post-conflict interactions between the aggressor or the victim and other members of the group (e.g. Arnold and Barton 2001, Call *et al*. 2002, Das *et al.* 1997, 1998, Watts 1998). Of these latter studies, only one (Das *et al*. 1998), has evaluated the possible function that these interactions may have.

The present study both describes patterns of aggression in free-ranging chacma baboons, and evaluates patterns of conflict management within across age-class categories. Further, an attempt is made to evaluate certain dynamic aspects of long-term consequences of patterns of conflict management.

Data were collected from one of the two main study troops in the De Hoop Nature Reserve, Western Cape Province, South Africa between March 2001 and August 2002. The data gathered represent 1400 hours of observation. Behavioural data that were collected fall into 6 categories: 1) recording of conflicts and their characteristics, 2) Post-conflict observations, 3) Matched-Control observations of each PC and a Second Matched-Control observation performed 10 days later, 4) *Ad libitum* (Altmann 1974) recording of grooming bouts, 5) Scan samples every 30 min. and 6) *Ad libitum* recording of displacements.

# MOLECULAR ANALYSIS OF GENE FLOW BETWEEN RICE SPECIES IN VIETNAM

**Hayeit Tensaout, Prof. A. B Tomsett, Dr. M. Mortimer.**

*School of Biological Sciences, Biosciences Building.*

In Asia, cultivated rice (*Oryza sativa*) is the most important cereal crop. It is self-fertile, and almost exclusively inbreeding. Nevertheless it co-exists with wild rice species in some countries, and hence gene flow from wild to cultivated rice can occur at a low frequency. The wild rice species, *O. rufipogon* and *O. nivara*, are also self-fertile but outcross at a higher frequency, and thus the potential for pollen flow from crop to wild relative is significantly higher. Hybridisation between the crop and wild relatives is apparent because of the occurrence of "weedy" rices, which have an intermediate morphology and phenology. In the last decade, the persistence of weedy rice has threatened Asian farmers' livelihoods because weedy forms reduce both the yield of the commercial crop (by competition) and the quality of the harvestable crop (by grain contamination) Although it has not yet been possible to determine in which direction the pollen has been transferred, the weedy rice problem may be exacerbated by the widespread introduction of transgenic rice. Furthermore, if weedy rice acts as a 'genetic bridge' between crop and wild species, transgenes from GM crops may spread rapidly and affect natural biodiversity in feral populations. Wild rices have already been used to identify valuable agronomic traits for introduction into commercial *O. sativa*, and these natural sources of valuable germplasm could be lost through transgene introgression.

To investigate the possible evolutionary origin of weedy rice, the capacity of gene flow from cultivar to wild rices is being determined using two approaches. Firstly, by analysing the genetic relationship between cultivar and wild rices using available microsatellite markers. Secondly, by identifying markers specific to cultivars and absent in wild populations which will enable the detection of introgression of the cultivar genome into wild rice. These markers, based upon highly polymorphic MITE (Miniature Inverted-repeat Transposable Elements), are generated by a Transposon Display technique (TD). TD is a ligation-mediated Polymerase Chain Reaction (PCR), similar to Amplified Fragment Length Polymorphism (AFLP). Such markers present at a particular locus in the cultivars, but not in wild rices, represent novel MITE insertions in the cultivars since deviation from their ancestors.

The TD has been optimised to isolate cultivar-specific markers from rice from the Philippines, which will be applied to other rices from Vietnam. Those cultivar-specific markers will give us information about the frequency of gene flow to wild relatives and determine if weedy rice serves as a bridge for introgression of cultivar genomes into wild rices.

# SEX-BIASED INBREEDING DEPRESSION IN THE BUTTERFLY *BICYCLUS ANYNANA*

**Hywel ap D. Lloyd, Dr. I. J. Saccheri & Professor G. A. Parker**

*School of Biological Sciences, University of Liverpool, Biosciences Building, Crown Street, Liverpool. L69 7GS*

Many Lepidoptera show severe inbreeding depression. In *Bicyclus anynana* it has been found that this is largely due to male sterility, while female fertility is unaffected by inbreeding. This result questions simple models explaining variation in genetic load among traits by associations with fitness. It also has potentially far reaching consequences; from the maintenance of genetic load to the evolution of adaptive traits, and the broad aims of this project are to investigate these. In order to clarify the nature of the genetic load one objective is to identify the cause and any variation in the physiological mechanism of sterility in inbred males. Surprisingly, results obtained so far indicate that sterile males produce live and motile sperm.

One potential benefit of inbreeding is the opportunity allowed for the purging of deleterious recessive alleles. Sex-biased inbreeding depression may reduce the efficiency of such purging selection on the fertility load. Preliminary results support this prediction, with fertility appearing to recover slower in inbred lines than a measure of viability showing non-biased inbreeding depression. The efficiency of purging will be investigated further in an inbreeding and selection experiment and compared to the predictions of population genetic models. The translation of changes due to purging at the individual level into recovery at the population level will also be investigated for the first time. This is of obvious interest to the conservation of small or fragmented populations.

Through distorting the effective number of males sex-biased inbreeding depression has the potential to drive the evolution of alternative adaptive strategies in frequently inbred populations. Two candidate strategies are skews to the sex-ratio and an increased frequency of multiple mating by females. Changes in these traits will be monitored through the duration of the inbreeding and selection experiment and compared to the predictions of game theory models.

# AGRONOMICAL PARAMETERS FOR SCREENING BARLEY IN DROUGHT CONDITIONS

**Amir Hossein Keshtkar and Julian. C. Collins**

*School of Biological Sciences*

Water is the main factor limiting agricultural productivity and may result in considerable yield reductions around the world. Therefore, identification of genetic variation for drought tolerance is crucial for many crop plants such as barley. In this experiment thirty-five spring barley genotypes consisting of accessions, landraces and modern varieties originating from different parts of the world mainly arid, semi-arid and Mediterranean areas, were cultured in three solutions of PEG (6000) as an osmolyte in a controlled temperature growth room at 22±1°C (day/night), light (12 diurnal cycle at 27 $Wm^{-2}$ from fluorescent tubes) and relative humidity 40- 60%. Three stress levels at water potential -0.11, -0.45, -0.71 MPa (PEG) plus control were used, each made up in a tenth dilution of Long Ashton nutrient solution. All measurements were made at 7 days and 14 days after the onset of PEG treatments. Growth was measured as maximal root length, shoot height, coleoptile length, fresh and dry weights of root and shoot, seedling water content (WC%) and ratio of root to shoot dry matter. Absolute biomass production under drought stress (mg per plant) and relative reduction in biomass by water deficit were considered as two main criteria to evaluate the genotypic ability of genotypes.

The analysis of variance of some traits, for instance root length, root water content, shoot water content and shoot/root dry weight ratio, showed highly significant differences ($P<0.01$) among the genotypes and solutions. There were highly significant differences ($P<0.01$) between the two harvests for root length and water content of root, but the difference found for root/ shoot dry weight ratio at ($p<0.05$) was less significant, whereas there was no significant difference between two harvests for the shoot water content parameter. The interaction between treatment and genotype was also highly significant ($p<0.00$) for root length, root/ shoot dry weight, root and shoot water contents indicating that genotypes responded differently to PEG treatments. Also the same results were found for interactions between (treatment and harvest) and (harvest and genotype). Three-way interaction of genotype with harvest and treatment was highly significant ($p<0.01$) for all growth parameters.

Genotypes were ranked for different growth parameters, and also for the relative root length values of genotypes at –0.45 MPa and -0.71 MPa stress levels, from this the following were identified for future research landrace 25094 (tolerant); Iranian line (sensitive) and cultivar Rihane (intermediate).

# MENOPAUSE – ANOTHER MATERNAL STRATEGY?

**Marian Nelson**

*School of Biological Sciences*

INTRODUCTION

My starting premise is that the human menopause is an adaptation, since non-adaptive explanations of post-industrial artefact or general senescence are not supported by the evidence. Adaptive explanations, such as antagonistic pleiotropy, point to a life history fitness trade-off; human females invest in slow-maturing, bigger-brained offspring, an investment that would be jeopardised by continuing to reproduce to an advanced age.

The grandmother hypothesis, as proposed by Hawkes, O'Connell and Blurton Jones (1989), seeks to demonstrate that postmenopausal women of the Hadza in Tanzania spend more time in food acquisition than younger women, thus helping their daughters to provision offspring, and thereby increase their own fitness. If, however, grandmothering is a by-product of the menopause's principal function, which is, I suspect, to free up women for the task of nurturing, provisioning and educating offspring for a uniquely lengthy period of time, then as well as seeing benefits to mothers from grandmaternal care, one should also see an equivalent or greater maternal investment, prior to reaching grandmotherhood.

METHODS

A six-page questionnaire was circulated to women's organisations in the UK, covering a broad cross-section of adult women of all ages. 550 questionnaires were issued and 260 returned. Questions covered a range of attitudes, behaviour and situations in relation to both children and parents. Subjects were given a list of eight possible regular activities with children, ranging from giving advice, through spending time together to providing resources. From the responses given for each son and each daughter, total scores were computed and from those scores, an activity index was derived for investment in sons and daughters respectively.

The hypothesis is that, whereas mothers who have both sons and daughters will tend to invest in them in a similar pattern, in line with predictions that mothers will invest preferentially in daughters, there should be a difference in the level of investment between sons and daughters.

RESULTS

When investment in sons was compared to investment in daughters in a Pearson correlation, $r = 0.666$; $n = 137$; $p < 0.001$ (2-tailed). The same comparison in a paired samples t-test yielded $t(136) = -8.430$; $p < 0.001$ (2-tailed). When investment in adult sons was compared to investment in adult daughters, depending on whether the subject was or was not a grandmother and, if she was, whether her grandchildren were offspring of her son(s), daughter(s) or both, whereas there was no significant difference in the activity index between subjects who had no grandchildren and subjects who only had grandchildren through daughters, there was a significant negative difference between subjects with no grandchildren and subjects who had grandchildren only through sons; ($p < 0.05$ (2-tailed)).

CONCLUSIONS

Women significantly carry on more activities of a social, familial and instructional nature with their daughters than with their sons. When women who are grandmothers are compared with women who are not, they carry out fewer activities (though not significantly) with their adult daughters and significantly fewer with their adult sons.

# EFFECTS OF RESTORATION TREATMENTS ON THE DIASPORE BANK UNDER DENSE *PTERIDIUM* STANDS IN THE UK

**Ghorbani Pashakalaei, J., Marrs, R.H. & Le Duc, M.G.**

*Applied Vegetation Dynamics Laboratory, School of Biological Sciences, University of Liverpool, Liverpool L69 3GS, UK;*

The diaspore bank (seeds of higher plants and spores of ferns and bryophytes) was assessed in four experiments designed to control bracken (*Pteridium aquilinum*) and restore appropriate vegetation at two contrasting locations within the UK (Sourhope and Cannock Chase). At each, 6 bracken-control treatments – untreated, cutting once and twice per year, asulam application once, and two combination treatments (asulam plus a single cut; a single cut plus asulam) were applied as main-plot treatments, and site-specific vegetation restoration treatments applied at sub-plot levels. We tested the response of the diaspore bank with two approaches: first, using standard univariate analysis of variance, and second using multivariate analysis of variance, where significance of treatment effects were assessed using Monte Carlo permutation tests. Each method was used to analyse individual experiments and the paired experiments. The two approaches were complementary and together they improved the interpretation of these results. . There were considerable differences in the diaspore banks of the two sites and between the two experimental locations within sites. Within each experiment there were considerable differences in species composition, with species that were (a) common to both diaspore bank and vegetation, (b) those restricted to diaspore bank and (c) those restricted to the vegetation. There is clearly a possibility of increasing the biodiversity of the developing vegetation if some of the species present in the diaspore bank can be germinated. This was especially true for ferns where four species were found in the spore bank which were not present in the vegetation. There were few significant effects of management treatment on the diaspore bank, but a few species did have different densities in the different treatments (*Betula pubescens* at Cannock 1 and *Juncus effusus* at Sourhope 1 and bryophytes at both Cannock 2 and Sourhope 1). The relationship between the composition of the diaspore bank and vegetation was compared using a Mantel test at a range of spatial scales. Greatest significance was found at the top hierarchical level (entire dataset) and this progressively reduces with scale. We interpret this as a landscape\species pool effect: as the scale of the study reduces the correlation between diaspore bank and vegetation also reduces, at least over the time scale of our study (3-5 years).

# A GRAVIMETRIC ANALYSIS OF PROTEIN-OLIGOSACCHARIDE INTERACTIONS

**Tim Rudd[1, 2], David G. Fernig[1] and Richard J. Nichols[2]**

*[1]School of Biological Sciences and [2]Department of Chemistry, University of Liverpool, Liverpool, L69 7ZB.*

Interactions between an immobilized, heparin–derived, octasaccharide and growth factors have been observed using a quartz crystal microbalance-dissipation (QCM-D), a gravimetric technique, which can detect the amount of growth factor binding to the octasaccharide. The QCM-D differs from straight QCM in its ability to determine the dissipation of the system, i.e., how the adhered material 'damps' the surface vibrations. Dissipation can manifest itself in two different surface events, either the molecules adsorbed to the surface slip or they interact with the bulk solution. The octasaccharides were anchored through their reducing ends by the intermediary of an alkanethiol molecule, which covalently binds to the crystal surface through the thiol group. As expected, HS binding growth factors bound to the octasaccharide. Intriguingly, the change in mass of growth factor per unit change in dissipation is different for the different growth factors, suggesting that the complexes of growth factor-octasaccharide complexes have different structures. Thus, the changes in dissipation can give insights into the structure, orientation and packing of the oligosaccharide-growth factor complexes.

# ECDYSTEROID-REGULATED PROTEINS IN CRUSTACEAN OVARY: A PROTEOMIC-BASED APPROACH

**Sefton, E.M., Ruddell, C.J., Wainwright, G. and Rees, H.H.**

*Cellular Regulation and Signalling Group, School of Biological Sciences*

It has been demonstrated that ecdysteroids (steroid moulting hormones) are not only involved in moulting, but also in the regulation of ovarian development and yolk protein synthesis in *Crustacea*. Despite this, little is known of the molecular effects of ecdysteroids on the regulation of genes and proteins in crustacean ovaries. To characterise the effects of ecdysteroids we have undertaken a study of the hormonally induced changes in ovarian proteins in the edible crab, *Cancer pagurus*. A proteomic approach is taken, since it reflects post-translational modifications as well as changes in expression, and because proteins are the ultimate functional molecules.

Ovary tissue was incubated, *in vitro,* with or without physiological doses of ecdysteroids. The proteins were extracted and separated by 2-dimensional gel electrophoresis (2DE), which resolves the proteins by their charge and mass, to create a map of protein spots. PDQuest software (BioRad) was used to analyse the changes seen in the maps produced from tissues incubated with or without hormone. Spots that increase or decrease substantially indicate proteins that are affected by the ecdysteroid level and, therefore, may be part of the ovarian developmental process. To limit the number of false-positives (proteins that are differentially expressed when exposed to high levels of ecdysteroid, but play no role in ovarian development), gels were also produced from ovary tissue at different stages of development. The protein spots of interest from the incubations were located on these developmental gels to ascertain whether they also change in level throughout natural development.
Spots that change both *in vivo* and *in vitro* will be excised from the gel, trypsin-digested and analysed by tandem mass spectrometry to yield a partial amino acid sequence. Database searching will indicate the presence of similar proteins in other species and may produce a putative identification and function. This will provide a better understanding of the process of ovarian development in the edible crab.

# THE IDENTIFICATION AND FUNCTIONAL DOMAINS OF THE METASTASIS INDUCING, CALCIUM-BINDING PROTEIN, S100A4

**Shu Zhang, Roger Barraclough**

*School of Biological Sciences*

**Introduction:** S100A4 (p9Ka), a calcium-binding protein, is able to induce metastasis in rodent models of breast cancer. In a recent study, S100A4 was shown to be a valuable marker for the prognosis of patients with breast cancer. S100A4 has been immunofluorescently detected in association with the actin\myosin cytoskeleton, and the biochemical experiments *in vitro* have confirmed that it binds to components of the cytoskeleton. The protein contains two EF-hand regions in which the calcium ions are bound. The two EF-hand regions are the common feature of S100 proteins. The C-terminal flanking region (the tail) of S100A4 is longer than that of most of other S100 proteins. However, it is unclear which region of S100A4 is critical for the induction of tumour metastasis. The aim of this project is to identify the functional domains/regions of the S100A4 protein for its metastasis-inducing capabilities.

**Methods** The three domains of rat S100A4 gene were mutated using method of site-directed mutation, which include N-terminal EF-hand region, C-terminal EF-hand region and C-terminal tail. The three mutated S100A4 genes were cloned into the expression vector pJLA602 by *Xho* I and *BamH* I digestion and ligation. The mutant S100A4 proteins were expressed in *E.coli* strain R1180 transformed with the plasmids pJLA602 containing the three mutated S100A4 genes. The *E.coli* cell supernatants obtained by centrifugation were loaded on to a DEAE-Sepharose column. The S100A4 proteins eluted by a linear salt gradient (0-600 mM NaCl) were applied to a phenyl Sepharose column. The functions of the mutant S100A4 proteins were analyzed by determining and comparing the biochemical properties *in vitro*, which include assay by SDS-PAGE, Western blotting, and calcium-binding of S100A4.

**Results** The wild type and three mutant S100A4 proteins were expressed in *E.coli* R1180. The purified protein fraction with an apparent molecular weight of 9 kDa on SDS-PAGE gel yielded 95 % pure S100A4 proteins. Examination of the purified S100A4s by Western blotting showed that S100A4 exists as both SDS-resistant monomers and dimers. The molecule of the mutant S100A4-T protein is smaller than that of the wild type S100A4 as expected. Assay of calcium-binding by S100A4 mutants showed that mutation in the C-terminal EF-hand led to loss of the ability to bind calcium tested using $^{45}Ca^{++}$ gel overlay. The tail mutant showed a lower ability to bind calcium, but the N-terminal EF-hand mutant had similar calcium-binding to the wild type S100A4.

**Conclusions** The results of these experiments suggest that the C-terminal EF-hand region and C-terminal tail are important in calcium-binding of S100A4. This will further lead to the identification of the regions of S100A4, which are necessary for its metastasis-inducing capability.

# FIELD SCALE EXPERIMENTS IN RODENT-PATHOGEN INTERACTIONS: A PRELIMINARY REPORT

**Andrew Smith*, Malcolm Bennett‡, Kevin Bown‡, Sandra Telfer*, Sarah Burthe* and Mike Begon**

**School of Biological Sciences, Biosciences Building, and ‡Department of Veterinary Pathology, University of Liverpool*

**Introduction** Ectoparasites play an important role in the maintenance and transmission of a range of important zoonotic diseases, e.g. Lyme disease (ticks) and Plague (fleas). Less well understood is the role they and the pathogens they transmit play with regards to the fitness of their rodent hosts where non-zoonotic endemic infections are often maintained. To address this question we have initiated a large-scale field experiment targeted at reducing ectoparasite abundance within natural field vole (*Microtus agrestis*) populations while systematically monitoring hosts and their infection status (using the trypanosome *Trypanosoma microti* as a model), in both treated and naturally exposed control populations.

**Materials and Methods** The study site is located in Kielder Forest, a 600-km$^2$ pine plantation in Northern England. We established four 0.25ha grids (2 experimental, 2 controls), each containing 100 Ugglan Live Animal Traps set at 5m intervals. Grids were trapped each month 5 times (a.m. and p.m.) to allow a robust closed population estimate of vole abundance, following 3 days of pre-baiting. Treatment consisted of a single application of ~7.5 l of a non-systemic insecticide (Fipronil). All new animals were tagged on first capture with a subcutaneous electronic transponder chip. Each month, sex, age (based on coat colouration), weight, body condition, tick and flea count, reproductive status were recorded for each animal and a blood sample taken. Trypanosome infection was detected using a PCR based protocol aimed at the 18S ribosomal RNA gene.

**Results** Fipronil treatment is effective under field conditions: fewer than expected animals show flea infestation within each of the treatment grids relative to the appropriate control grid ($X^2_1 = 110.61, 49.61$, $P < 0.001$). The proportion of flea-infested animals was not significantly different between the two controls ($X^2_1 = 1.3$, $P \approx 0.25$). Logistic regression indicates that individuals are 2.7 times more likely to contract trypanosome infection within the non-treatment grids than within the Fipronil treated grids ($G_{df4} = 91.73$, $p < 0.001$). Recaptured adult males from treatment grids had significantly higher median body condition indices than those from their respective control grids (Kruskal-Wallace Tests: $H_1 = 8.38$, p 0.003 and $H_1 = 6.48$, p 0.011). However, adult recaptured females showed a significant increase in one grid ($H_1 = 5.4$, p 0.02) but a non-significant variation in the other ($H_1 = 1.0$, p 0.37).

## *Discussion*

This investigation has shown that it is possible to manipulate ectoparasites on a large spatial scale while simultaneously monitoring rodent hosts for changes in disease prevalence and body condition. Male voles on both treatment grids (fewer ectoparasites, less infection) were in better physical condition with regards to body fat levels than males on control grids. Results for females were more equivocal, despite the fact that they were in generally poorer condition than males. The nature of the study will allow, on completion of data collection, a survival analysis based on the capture-recapture histories of individually marked animals from habitats differing significantly with regards to the probability of exposure to disease. It will also include additional ectoparasite-transmitted pathogens, notably *Bartonella* sp.

# Department of Chemistry

# SELF-ASSEMBLED FULLERENE STRUCTURES ON AU SINGLE CRYSTAL ELECTRODE

**Akiyoshi Kuzume, Richard J. Nichols, David J. Schiffrin**

*Department of Chemistry, The Centre for Nanoscale Science*

Since its discovery in 1985, buckminsterfullerene ($C_{60}$) had been extensively investigated to understand its physical, chemical and electrochemical properties. It has a truncated icosahedron geometry with sixty hexagonal and twelve pentagonal faces. In electrochemical studies, fullerene has 8 different redox states. Because of these distorted structure and the variety of electrochemical states, fullerene is a good candidate as an electrocatalyst and an electrode material.

The main objective of the work is to understand the kinetics of the electrochemical oxygen reduction reaction on the fullerene. Previous work has used sublimation for the formation of fullerene overlayers on the electrode surface. In the present work, the fullerene overlayers was prepared by adsorption on single crystal Au from toluene solutions. The resulting fullerene overlayers were characterized by ellipsometry, STM, Cu UPD and X-ray photoelectron spectroscopy (XPS).

Fullerene overlayers were prepared by immersing a Au electrode in the toluene solution of fullerene purified by silica gel column chromatography. The comparison between voltammograms of Cu UPD with and without fullerene overlayers suggests that the Au(111) surfaces are completely covered by fullerene overlayers and that the interaction between Au and fullerene is stronger than that between Au and Cu. XPS results supported the presence of strong interactions between the Au surface and fullerene, probably due to partial charge transfer from Au to fullerene. STM measurements of fullerene overlayers on Au(111) single crystal surfaces show hexagonal close packed structures. Furthermore, STM images of fullerene overlayers on Au(332) and Au(554) show quasi-hexagonal structures. There is no evidence for the formation of multilayers, in agreement with ellipsometric results. The long-range order of the fullerene overlayers depends on the morphology of the substrate.

As a result of the present work, self-assembled monolayers of fullerene were formed on Au surfaces. It was found that overlayers have a close packed structure, full coverage over electrode surface, and adsorbed with strong interaction on Au surface. These well-characterised fullerene surfaces are being use as new carbon electrode materials.

# SELECTIVE HYDROGENATION OF CARBOXYLIC ACIDS TO ALDEHYDES

**Hacib Benaissa, Ivan Kozhevnikov**

*The Leverhulme Centre for Innovative Catalysis, Department of Chemistry*

Aldehydes are widely used for manufacturing fragrances and flavours as well as intermediates in the production of agrochemicals, dyes and other chemicals. Most aldehyde synthesis methods (vapor-phase oxidation of alkyl aromatics, halogenation of alkyl aromatics followed by hydrolysis, Rosenmund reduction of acid halides and oxidation or dehydrogenation of aromatic alcohols) have several disadvantages, such as low yield, undesirable by-products and large amounts of waste. Selective hydrogenation of carboxylic acids to aldehydes is seen as an alternative of significant interest.

$$RCOOH + H_2 \rightarrow RCHO + H_2O$$

The aim of this research is to study the selective hydrogenation of saturated and unsaturated carboxylic acids into the corresponding aldehydes using heteropoly compounds as catalysts.Heteropoly compounds comprise polyoxometalates that are nanosized metal-oxygen cluster anions of the general formula $(X_xM_mO_y)^{q-}$ ($x \leq m$) where M (M = W, Mo, etc.) is the addenda atom and X (X= P, As, Si, etc.) the heteroatom. The Keggin type heteropoly compounds, $(XM_{12}O_{40})^{q-}$, are the most important ones. They are widely used as acid and oxidation catalysts (1). Because of their redox properties, they may be considered as potential catalysts or catalyst precursors for the selective hydrogenation of carboxylic acids. Their acid and redox properties can be adjusted by varying the composition of the polyanion and by choosing apporpirate contercations. In this proje□ct, the hydrogenation of hexanoic acid is used as a model reaction. The reaction is carried out in a flow system under atmospheric pressure in the temperature range between 300 and 400 $^{o}$C. A hydrogen flow (40-80 ml/min) is saturated with the acid at 80-90$^{o}$C (2% acid concentration) and passed through a fixed-bed glass micro-reactor containing 0.2 g of catalyst. Analysis of the products is carried out online with a GC. Prior to the reaction, the catalysts are pre-treated in a nitrogen/hydrogen flow for 2 hours at the reaction temperature. The catalysts are characterised by elemental analysis (ICP), BET, FTIR, TG/DSC, and TPR.

(1) Ivan V.Kozhevnikov; *Catalysis for fine chemical synthesis, Vol. 2; Catalysis by polyoxometalates*. John Wiley & Sons, England, 2002.

# SUPRAMOLECULAR VARIATIONS ON A MOLECULAR THEME

**Jamie F. Bickley, Gavin T. Lawson, Philip I. Richards, Alexander Steiner**

*Department of Chemistry, University of Liverpool*

Herein, we introduce a molecular motif, which displays an unprecedented variety of supramolecular architectures in the solid state: Hexakis(organoamino) cyclotriphosphazene derivatives, $(RNH)_6P_3N_3$, contain a polar core comprising an equatorial belt of three ring nitrogen atoms and six NH functions sandwiched between hemispheres of lipophilic substituents R. A range of derivatives equipped with hydrocarbon side chains were synthesised and structurally characterised including R = *tert*-butyl, cyclohexyl, *iso*-propyl, benzyl, *n*-propyl, allyl, ethyl and methyl. The study shows that subtle alterations of the size and shape of R lead to considerable changes of solid-state aggregation pattern. With the exception of the *tert*-butyl derivative, all solid-state structures form intermolecular NH...N bonding featuring single, double, triple and quadruple H-bridges. Supramolecular architectures include monomer, dimer, cyclic hexamer, zigzag chain, linear chain, double chain, graphite-type sheet, rectangular grid and hexagonal close-packed sheet. The structural variety is due to easy rotation around exocyclic P-N bonds, which enables a delicate interplay between hydrogen bonding and side chain packing.

# MO- MODIFIED HZSM-5 ZEOLITE FOR THE DEHYDRO-OLIGOMERISATION AND AROMATISATION OF NATURAL GAS IN THE ABSENCE OF OXYGEN

**Chandra M Sinnathambi & Dr J. B. Claridge**

*Leverhulme Centre For Innovative Catalysis (Lcic),*
*Department Of Chemistry, University Of Liverpool*

Methane, the major component of natural gas, currently comparatively finds limited usage in energy industries, due to the remote nature of most reserves and high cost of transportation. Finding methods of converting methane to chemical feed stocks or transportation fuels economically represents a considerable challenge. Since Wang et al (1) reported a direct conversion of methane by a non-oxidative aromatisation over HZSM-5 zeolite catalyst modified with transition metal ions (TMI) considerable interest has been generated in this potential route. The products contain a mixture of light olefins (ethylene), aromatics (benzene, toluene and naphthalene) and potential amount of hydrogen. Molybdenum modified HZSM-5 prepared by impregnation with ammonium heptamolybdate at room temperature (Mo loading of 2-6 weight %) is the best catalyst precursor. The precursor is calcined in air between 500 to 700°C for one to several hours. The calcined precursor is then activated between 600 to 750°C under a stream of methane or a mixture of methane/hydrogen to produce the final reduced catalyst. It is generally accepted that the active components of the catalyst are the Mo carbide ( $\alpha$ or $\beta$ form) and HZSM-5, an example of a bifunctional catalysts. Methane can then be converted to the desired product at 700 to 850°C. The reaction is believed to proceed via initial formation of ethylene, which is further transformed to benzene, and on further condensation benzene is transformed to naphthalene and higher aromatics and carbonaceous deposit. It is this carbonaceous deposit that causes the rapid deactivation of the catalyst due to coking. Recent work in the LCIC (2) have shown that: Mo carbide is the main component for high stability at high temperature. HZSM-5 with a Si/Al ratio of 40 is the best choice for support. Catalytic activation is best carried out under a mixture of 10:1 $H_2/CH_4$ at 700°C. Co-feeding carbon monoxide increases catalytic stability at maximum conversion. Carrying on from this work the role of CO on catalyst stability, the effects of mixed feed to increase conversion of methane and the effect of molybdenum carbide structure on catalytic activity and stability are investigated.

1. Wang L, Tao L, Xie M, Xu G, Huang J, Xu Y. Catal. Lett. 21 (1993) 35.
2. Anderson J.R. PhD thesis Univ. of Liverpool (2001)

# SYNTHESIS OF OPIATE GLYCOSIDES: IODOSUGAR DONORS

**John R. Ferguson,[1] Jayne L. Law, [1] Feodor Scheinmann,[1] Andrew V. Stachulski[1]*§ and Jennifer A. Cottrell [2]**

*[1] Ultrafine UFC Ltd., Synergy House, Guildhall Close, Manchester Science Park, Manchester M 15 6 SY.*
*[2] Robert Robinson Laboratories, Department of Chemistry, University of Liverpool, Liverpool, L 69 7 ZD.*

Morphine-6-glucuronide **1**[1] shows significant advantages as an analgesic over morphine **2**, namely improved *in vivo* activity plus reduced respiratory depression, addiction and nausea. An effective synthesis of **1** is *via* the tri-isobutyryl imidate **3** which effects the glycosidation of 3-*O*-pivaloyl morphine **4** in 70% yield.[2]

Bromosugars **5** and **7** are effective glucuronyl donors with iodonium reagent activation.[3] We now report that the pivaloate iodosugar **6** is also a good glucuronyl donor *without* metal activation.[4] Methods of preparation of **6** will be summarised and some model reactions discussed. Finally the conditions for preparation of the morphine glucuronide ester **8** from **6** will be outlined.

**References:** **1**. Scheinmann, F. ; Lumbard, K. W.; Brown, R. T.; Mayalarp, S. P. International Patent, WO 93/3051,1993; **2**. Brown, R. T.; Carter, N. E.; Scheinmann, F.; Lumbard, K. W. *Tetrahedron Lett.,* 1995, **36**, 8661; **3**. Stachulski, A. V. *Tetrahedron Lett.,* 2001, **42**, 6611; **4**. Stachulski, A. V. British Patent Application No. 9914382.8, to Ultrafine UFC Ltd., July 1999.

# NUCLEOPEPTIDE FOLDAMERS; NOVEL PEPTIDE HELICES DERIVED FROM β-AMINO ACIDS

**A Davies*, R Cosstick**

*Department of Chemistry*

Proteins and RNA adopt very specific conformations and three-dimensional arrangements that make them distinct among polymers in nature. Due to their tertiary structure, they can perform the most sophisticated functions in nature.

It may be possible, therefore to design, develop and synthesise unnatural oligomers, which can adopt analogous well-defined conformations in solution. Excellent work published by Gellman and co-workers on b-peptides has provided an insight into the folding properties and function of numerous peptides. Gellman and Seebach have included examples that are analogous to DNA and the elucidation of peptide nucleic acid by Nielson in the early nineties provides new scope for the generation of nucleoside b-amino acids.

These novel nucleic acids utilize other isosteric backbones than the phosphodiester bond. The project focuses on the combination of the inherent helix folding properties of peptides derived from cyclic b-amino acids, with the associative characteristics of nucleosides to create novel functionalised foldamer units with predictable recognition properties. The initial monomers required to generate these nucleopeptide oligomers are modified nucleosides derived from thymidine. The research builds on previous work in the group on coupling these modified monomer units via an amide backbone to study the characteristics of the oligomer. Further studies have been done computationally using molecular mechanics programmes to model the helices and gain vital information about these systems.

# IONIC LIQUID/POLYMER MEMBRANE REACTOR DEVELOPMENT FOR CATALYTIC HYDROGENATION

**Cait M. Davies, Neil Winterton and Andrew I. Cooper**

*Department of Chemistry, University of Liverpool*

Every year the chemical industry uses a huge amount of organic solvents in the synthesis of commercial materials. These organic solvents are very damaging to the environment, and their high volatility means that they contribute heavily to atmospheric pollution. Ionic liquids represent a group of novel materials, which could potentially replace volatile organic solvents in catalytic reactions. They are non-volatile and can dissolve a wide range of organic, inorganic and polymeric materials.

This project focuses on the use of supported ionic liquids as a solvating medium for a homogeneous hydrogenation reaction. The catalyst $[Rh(nbd)(PPh_3)_2]PF_6$ will be dissolved in an ionic liquid, which will in turn be imbibed within the pores of a polymeric support to form a catalytic reactor system. Several different porous polymeric supports and ionic liquids will be investigated, as well as the synthesis of polymer/ionic liquid composite membranes.

The hydrogenation of the gas propene to propane will be used as a model reaction for the system. The resultant conversion of reactant to product will be monitored by gas chromatography using FID (Flame Ionisation Detection) with a fused silica column.

Initially the hydrogenation of propene to propane in ionic liquids and conventional solvents has been analysed in the bulk without the presence of a polymeric support. It was found that conversion was higher in conventional solvents than in the ionic liquids, and conversion in the ionic liquids was considerably lower than had been quoted in the literature. The reason for this is thought to be impurities in the ionic liquids of either chloride ion, which is well known to inhibit catalysis, or water, which can cause hydrolysis of the ionic liquids to produce hydrofluoric acid.

The amount of residual chloride remaining in the ionic liquids has been examined using potentiometric titration using a silver electrode. This shows that there is a small amount of residual chloride remaining. Another synthetic route to produce chloride free ionic liquids is currently being investigated.

When the problem of limited conversion has been resolved in the bulk hydrogenation reaction, work can start on using a porous membrane as a support for the ionic liquid/catalyst mixture. The addition of a membrane to the system will mean that an increased surface area of the ionic liquid/catalyst mixture will be seen by the reactant gas, so will theoretically be more efficient.

# SYNTHESIS AND CHARACTERISATION OF QUASI-ONE-DIMENSIONAL CHALCOGENIDES

**C.C. Auener, J.B. Claridge**

*Department of Chemistry*

Quasi-one-dimensional chalcogenides have the general formula $BaMX_3$, where M is V, Nb, Ta and X is S or Se.

The discovery of high-temperature superconductivity has rejuvenated ongoing research into compounds with desirable features such as metal-insulator transitions and antiferromagnetism. Recently, these desirable properties have led to renewed interest in the metallic ternary sulfide $BaVS_3$ which exhibits a quasi-one-dimensional crystal structure with linear chains of face sharing $VS_6$ octahedra, which run parallel to each other along the crystallographic c-axis.

Previous studies have shown this compound to undergo certain phase transitions with respect to temperature. A hexagonal-orthorhombic phase distortion occurs at ~ 240K, along with a metal-insulator transition at 70K where the material displays antiferromagnetism.

Our research has centred on looking at the effects of changing the electron populations of the transition metals along the c-axis by synthesising compounds with a substitution of vanadium for other first row transition metals such as Cr, Mn, Fe and Ni.

The compounds synthesised with the general formula $BaV_{1-x}M_xS_3$ have been characterised by powder x-ray diffraction and the crystals grown from these powders by single crystal x-ray diffraction. Their magnetic behaviour with respect to temperature has been studied using a SQUID magnetometer.

Initial single crystal x-ray diffraction results show that only slight changes of the electronic population along the vanadium chain inhibit the crystallographic distortion at ~ 240K, indeed the high temperature cell still remains unchanged at 100K.

The compounds also exhibit different magnetic properties at lower temperatures, with respect to the composition along the c-axis and also sulfur stoichiometry. Samples with slight sulfur deficiencies exhibit ferromagnetic behaviour, this may be due to the presence of a small amount of $V^{3+}/M^{3+}$ ions which also adds to a fluctuation in the electron populations of the 3d levels.

# SYNTHESIS OF HIGHLY FUNCTIONALISED NITROGEN HETEROCYCLES

**Neil Henry[a], Ian A. O'Neil[a], J. Mike Southern[a].**

*[a]Department of Organic Chemistry, University of Liverpool*

Tertiary amine oxides possessing a suitably positioned ß-hydrogen, are found to fragment on heating to give an olefin and a *N,N*-disubstituted hydroxylamine. This process is known as the Cope elimination.

Under certain conditions the reaction is reversible and the corresponding back reaction is refered to as the reverse Cope elimination, this describes the reaction of a hydroxylamine with an unactivated double bond giving rise to *N*-oxide products. It has been observed that by varying the solvents and reaction conditions such as temperature it is possible to control the outcome of the reaction. The reverse Cope elimination is stereospecific in that the *N*-oxide and the newly formed alkyl side chain are formed *syn* to each other.

Until recently this methodology has been heavily underutilized as a route into highly substituted morpholine amine *N*-oxides.

The use of *m*-CPBA as the oxidant in this type of reaction was found to provide a novel route into nitrones when a benzyl substituent was present on the nitrogen, and cyclisation to the corresponding highly functionalised bicyclic macromolecules was achieved.

These types of synthetic methodology are currently being applied to a wide variety of substrates.

# FRIES REARRANGEMENT OF ARYL ESTERS CATALYSED BY HETEROPOLY ACID

**E.F. Kozhevnikova, E.G.Derouane and I.V. Kozhevnikov**

*Department of Chemistry, University of Liverpool*

Heteropoly acids (HPA) are active catalysts for the Fries rearrangement of aryl esters (phenyl acetate, phenyl benzoate, and p-tolyl acetate) to yield the acylated phenols and esters together with phenols in homogeneous or heterogeneous liquid-phase systems at 100 – 170$^{o}$C. Amongst the HPA catalysts studied are bulk, silica-supported, and sol-gel silica-included $H_3PW_{12}O_{40}$ (PW), as well as bulk $Cs^{+}$ and $Ce^{3+}$ salts, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Ce_{0.87}H_{0.4}PW_{12}O_{40}$. The reaction with bulk and silica-supported PW occurs homogeneously in aryl esters (without solvent) or in polar solvents such as nitrobenzene and o-dichlorobenzene. In nonpolar solvents such as dodecane, the reaction is heterogeneous. The $Cs^{+}$ and $Ce^{3+}$ salts and sol-gel PW catalysts perform heterogeneously in all these media. From heterogeneous systems, the catalysts can be separated and reused, albeit with reduced activity. The homogeneous and silica-supported PW are much more active than $H_2SO_4$ and H-Beta zeolite, which is explained by the greater acid strength of HPA compared to the other acids. In contrast to silica-supported PW, the sol-gel PW catalysts show only a negligible activity in the Fries reaction of phenyl acetate, yielding mainly phenol with 92 – 100% selectivity. This may be explained by a weaker acid strength of the sol-gel catalysts and the presence of relatively high amount of water. $^{31}$P MAS NMR shows that the state of the PW anion in the sol-gel and silica-impregnated catalysts is similar, but different from that in the bulk PW.

[1] Kozhevnikova, E.F., Derouane, E.G., Kozhevnikov, I.V. Chem. Commun. 2002, 1178.

# TOWARDS A SUZUKI ROUTE TO POLYALKYLTHIOPHENES

**Iain Liversedge, Dr Simon Higgins**

*Department of Chemistry, University of Liverpool*

Since the realisation in the mid 1970's that the semiconducting conjugated polymer, polyacetylene, could be doped, to undergo a 12 order-of-magnitude increase in conductivity, the area of conducting organic polymers has become of great interest to the scientific community, recognised in 2000 with the award of the Nobel Prize for Chemistry to the pioneers. Synthetic chemists have explored numerous structural variations on the original polyacetylene, and can exert some control over the electrical and spectroscopic properties of these fascinating materials.

Polythiophenes are being intensively studied, as they have been found to combine considerable environmental stability with useful electrical properties. In particular, regioregular polyalkylthiophenes have been shown to have much higher field effect mobility and conductivity compared with non-regioregular materials.

The synthesis of highly functionalised regioregular conjugated polymers is still not trivial. The two current synthetic methods, by McCullough and Rieke respectively, both encounter problems when it comes to synthesising polymers with complicated functional groups attached.

This project is exploring the use of novel palladium based aryl-aryl coupling catalysts for the synthesis of functionalised polyaryls using Suzuki chemistry. We have successfully designed a monomer, which will couple with itself under strict reaction conditions. We are currently exploring various catalyst systems that will enable us to produce high molecular weight polymers with good regioregularity and good conductivity.

# ACCURATE $^{1}$H NMR PREDICTION OF HALOGENATED HYDROCARBONS; THROUGH SPACE CONTRIBUTIONS

**Mehdi Mobli[1], Raymond J. Abraham[1], Richard J. Smith[2]**

*[1] Chemistry Department*
*[2] GlaxoSmithKline, Medicinal Research Centre, Stevenage*

Our research group has developed a model, CHARGE, capable of accurately predicting proton chemical shifts in a wide range of organic compounds. The halogen substituent effect has previously been calculated by CHARGE using electric field and steric effects as the only through space contributions. We found this model to be inadequate once applied to haloaromatics, where the halogen can in cases be very close to the proton investigated. To overcome this problem two models were derived to explain the through space contribution of the halogens.

In model A we expand the current model of steric and electric field effects and introduce a new value for the steric term applied to halogens in aromatic systems. In model B we introduce the first model combining the electric field and steric effects with a magnetic anisotropy term. In this model we make no distinction between aromatic and aliphatic systems. The two models were tested on a range of compounds including 1-ax/eq-halocyclohexanes, 1-halobenzenes, 1-halonaphtalenes and 4-halophenanthrenes. The results showed little difference between the two models in all cases except for the 4-halophenanthrenes (see table of substituent chemical shifts below). The vicinity of the halogen to the proton proved model B to be the superior one.

We have found that the through space contribution of the substituent chemical shift of halogens can only be accounted for accurately if a combination of electric field, steric and magnetic anisotropy contributions are considered.

# DIRECTED EVOLUTION OF A *PSEUDOMONAS FLUORESCENS* LIPASE FOR RESOLUTION IN ORGANIC SOLVENTS

**Céline Parsy[a] Lesley Iwanejko[b], Andrew. J. Carnell[c]**

*[a,c]Department of Chemistry and [a,b]Department of Biological Sciences,*

*University of Liverpool and Pfizer Ltd, Sandwich*

A novel biotransformation has been developed in our laboratory for the preparation of homochiral enol acetates derived from prochiral ketones used for the synthesis of a tachykinin NK-2 antagonist used in the treatment of neuro-inflammatory conditions. 4-Cyano-4-aryl substituted cyclohex-1-enyl acetates such as 1 have been resolved with *Pseudomonas fluorescens* lipase (PFL) by transesterification with n-butanol in THF giving good to excellent enantiomeric purities (e.e.'s) for the chiral enol acetates. With an efficient recycling method (Scheme 1), even with a relatively low E value of 13, it is possible to isolate enantiomerically pure enol acetate (S)-1 in 82% yield after 4 cycles.

Scheme 1

i: PFL, nBuOH, THF; ii: Remove PFL; iii: add isopropenyl acetate and $^t$BuOK; iv: Add Dowex $H^+$ resin; v: Remove resin and add PFL and nBuOH

The aim of this project is to use this lipase resolution as a model system for developing a high throughput directed-evolution strategy for obtaining lipases with improved enantioselectivity for use in organic solvents. The *Pseudomonas fluorescens* lipase gene, *lipA*, has been cloned with a histidine tag and expressed in *E. coli*. This gene will be subjected to a radical mutagenesis protocol (ep-PCR) to generate a library of mutant enzymes. Due to the tag, the enzymes can be absorbed from the crude cell lysate using Ni-NTA coated microtitre plates, facilitating a high-throughput enzyme screening strategy in organic solvents. The e.e. screen is based on the use of pseudo-racemic $d^3$ - labelled enol ester 1 with electrospray ionisation mass spectrometry (ESI-MS) to detect M and M+3. Interesting mutants will then be sequenced to identify key mutations and may be subjected to further rounds of random mutagenesis or gene shuffling.

# SPECTROSCOPIC STUDIES ON CATALYTIC INTERMEDIATES INVOLVED IN THE Pd-CATALYSED METHOXYCARBONYLATION OF ETHYLENE

**Dr. Graham Eastham, Pr. Brian T. Heaton, Dr. Jonathan A. Iggo, Alexandre Pépin, Dr. Robin Whyman.**

*Department of Chemistry*

Methoxycarbonylation of ethylene is carbon monoxide and methanol addition to ethylene *via* a catalytic process giving methyl propionate, $CH_3CH_2COOCH_3$ (MeP).Pd complexes containing the bidentate ligand 1,2-$(CH_2P^tBu_2)_2C_6H_4$ ($d^tbpx$) have been shown to be extremely active and selective catalyst for MeP production. All the individual steps and reaction intermediates of a hydride based catalytic cycle have been unambiguously identified using spectroscopic measurements (Chem. Comm., 2000, 609). Details of the mechanism and the last step of the cycle, methanolysis of a Pd-acyl species, which is extremely rapid, are least well understood. Low temperature NMR spectroscopic work described here is providing useful information on which to support mechanistic proposals. In addition, in attempts to better understand the reaction mechanism, catalysts containing related diphosphine ligands with substituants and varying bulk are being examined via a coordination of test reactions, spectroscopic measurement and computer modelling.

# NOVEL BIOCATALYTIC APPROACHES FOR THE SYNTHESIS OF SECONDARY AND TERTIARY β-HYDROXY ESTERS

**M. J. Pursglove*, Dr. A. J. Carnell, Dr. L. Iwanejko**

*Department of Chemistry*

The synthesis of enantiomerically pure compounds has always been of great importance to organic chemists. However with the recent advent of FDA regulations on racemic drugs, approaches to the generation or separation of single enantiomers has drawn increasing attention. Employing mild reaction conditions, and avoiding the use of potentially polluting heavy metal catalysts, isolated enzymes and whole cell bacterial or fungal systems provide an attractive option for the generation of chiral synthons.

For this project the synthesis of one specific type of chiral synthon is focused upon. A tertiary β-hydroxy ester called 3-hydroxy-3-phenyl-hexanoic acid ethyl ester, forms part of an HIV protease inhibitor currently undergoing clinical trials for the treatment of AIDS. The aim of this project is the chemoenzymic synthesis of β-tertiary hydroxy esters, such as 3-hydroxy-3-phenyl-hexanoic acid ethyl ester, with high enantiomeric purity and yield. The route for the formation of the ester employs an epoxide hydrolase enzyme in an enantioconvergent synthesis. In this method both enantiomers in a racemic mixture are converted to a single enantiomer of the corresponding diol.

Initial work has had only very limited success with a range of gem-disubstituted substrates. A plate-screening assay is being used to find epoxide hydrolase enzymes with activity against the target substrate. Another approach uses a lipase enzyme resolution to separate a racemic mixture of the diol enantiomers. The incorrect enantiomer can then be converted back to the epoxide and then inverted to yield the opposite diol, therefore converting the initial mixture entirely to a single enantiomer. There is also the possibility to enhance the activity and specificity of the lipase or epoxide hydrolase using directed evolution and therefore improving the enantiomeric purity and yield.

# TOTAL SYNTHESIS OF NEOLIACINE

**Valerie Ross, Dr. Nick Greeves**

*Department of Chemistry*

The target compound, neoliacine (1), is a germanocrolide sesquiterpene belonging to the Neolitsea Acciculata Koidz plant family. Neoliacine exhibits antitumor properties in vitro in the form of its oxidized metabolite, neoliacinic acid; yet it is also an attractive target for total synthesis due to its structural complexity and high degree of oxygenation.

The synthetic strategy has been the generation of the methyl furoate (6) model via a palladium catalysed annelation reaction, which is to be oxidixed to the sulfoxide. Upon condensation with a ketone, the allylic sulfoxide will be generated which can readily undergo [2,3] allylic rearrangement to give an allylic alcohol. It is envisaged that following a sequence of steps, the spiroketal moiety of the neoliacine structure will be generated. Concurrently, a second model system has been examined to determine the superior route to the spiroketal. Following validation of the spiroketal step, methyl furoate (6) will be reacted with a ketene thioacetal thus generating the furan butenolide backbone of the structure. After the oxidation of the backbone to structure (4), a ring closing step is to be performed following the deprotonation of the sulfoxide alpha-carbon giving the allylic sulfoxide from which the allylic alcohol can be generated. Following TBDMS protection, this will give structure (3). At this step, the spiroketal ring closing step will be utilized to generate the neoliacine structure (1). Once generated, neoliacine would have synthetic application within the pharmaceutical industry as an antitumor drug.

# PALLADIUM CATALYSED CARBON MONOXIDE-ALKYNE REACTIONS

**Kelly Sheridan, Jon Iggo, Brian Heaton, Robin Whyman and Chacko Jacob**

*Department of Chemistry*

Both in terms of their high activity and selectivity attained under mild conditions, palladium complexes generated *in-situ* from mixtures of $Pd(OAc)_2$, pyridyl diphenylphosphine ($Ph_2Ppy$) and sulfonic acids are highly efficient catalysts for the methoxycarbonylation of propyne to methyl methacrylate (MMA). The alkoxycarbonylation and co-polymerisation reactions of CO with alkynes have been little studied in comparison with the analogous CO-alkene reaction and as such the mechanisms are poorly understood. Three possibilities have been proposed for the alkoxycarbonylation although the exact nature of the catalysts remains elusive although it has been proposed that the $Ph_2Ppy$ ligand coordinates to the metal centre in both a monodentate and bidentate orientation.

Synthetic studies have been undertaken to form potential reaction intermediates or related complexes, which will provide access to the catalytic cycle. [Pd($\eta^1$- $Ph_2Ppy$) ($\eta^2$- $Ph_2Ppy$)Cl][$BF_4$] has been unambiguously characterised using $^{31}P\{^1H\}$ NMR spectroscopy and x-ray crystallography. [Pd($\eta^1$- $Ph_2Ppy$) ($\eta^2$- $Ph_2Ppy$)($CH_3CN$)][$BF_4$]$_2$ has been characterised by $^{31}P\{^1H\}$ NMR spectroscopy. Detailed *in* and *ex-situ* studies of reactions of the palladium complexes with CO and alkynes will be performed to determine the factors governing the reaction pathway.

# FERROCENYL PHOSPHINES: CATALYSIS AND ORGANOMETALLICS

**Richard Peter Stead and Jianliang Xiao**

*Leverhulme Centre for Innovative Catalysis, Department of Chemistry*

Ferrocene has been exploited as the framework for a immense variety of chiral and non-chiral ligands since the first use of 1,1'-Bis(diphenylphosphino)ferrocene (dppf) in 1965. Dppf has found many uses in reactions such as Hayashi-Kumada C-C bond formation, the Buchwald-Hartwig C-N coupling reaction, and very recently hydroamination. In C-C bond formation its superior properties were linked to the bite angle made with Pd. The large P-Pd-P bite angle increases selectivity and activity due to faster rates of reductive elimination.

A range of novel ferrocene ligands have been synthesised that are based on a bis-arylated ferrocene-backbone. The key synthetic step is a Suzuki coupling of the diboronic acid of ferrocene with the desired aryl halide. We found this could be carried out with the appropriate phosphine oxides, constructing the ligand precursor in only one step. This approach allows for the synthesis of a variety of ligands, since the essential framework is created in this step, leaving only the reduction of phosphorus to afford a potential ligand. Diphenylphosphine groups have, initially, been used to functionalise the afforded framework at the *ortho, meta* and *para* positions of both aryl groups. The result is three bidentate diphosphine ligands. Crystal structures have been solved for the free-phosphines and their palladium complexes. A series of test reactions is under way which will compare the regioselectivity with dppf in the allylic alkylation, C-N coupling, Suzuki and Kumada-type C-C coupling reactions. The bite angle in the $PdCl_2$ complex of the *para* form is larger than dppf and this is hoped to give better selectivity than dppf in the various coupling reactions. This modular approach will be extended to other series of ligands by changing the substituents at the phosphorus from phenyl to a range of alkyl, and substituted phenyl groups. Hence the element of central chirality can be introduced at phosphorus, opening up possibilities for enantioselective reactions.

# NEW MODULAR PHOSPHINE LIGANDS FOR APPLICATIONS IN ASYMMETRIC CATALYSIS

**Daniele Vinci and Jianliang Xiao**

*Leverhulme Centre for Innovative Catalysis, Department of Chemistry*

Phosphines play a very important role in asymmetric catalysis. They are in general difficult to synthesize, however, the objective of this project is to discover, by using new synthetic methodologies, novel structures able to effectively transfer the required stereo information to substrates involved in a catalytic process. Towards this end, we have employed C-P coupling chemistry to join a chiral phosphine block, to an aryl backbone. This approach allows us to modulate steric and electronic properties of the ligands and thus makes it possible to:

-control the activity and stereoselectivity of the catalyst
-extend the scope of the reaction
-correlate structure and stereochemical properties of ligands with catalyst's performances

# THE IMPORTANCE OF SIZE TO THE ELECTRONIC STRUCTURE OF DODECANETHIOL DERIVATISED GOLD NANOPARTICLES

**C. A. Waters, K. A. Johnson, D. J. Schiffrin**

*Department of Chemistry, The Centre for Nanoscale Science*

Nanoscaled materials have distinctive properties that are between that of molecular and bulk materials. It is the desire for greater understanding of these materials and the anticipation for future applications in such areas as catalysis, chemical sensors, corrosion inhibition, lubrication, molecular recognition and quantum devices which have driven widespread studies in this area. Surface sensitive techniques such as X-ray photoelectron spectroscopy provide an excellent method of elemental analysis and electronic information about the atoms of a film.

Dodecanethiol derivatised gold nanoparticles were prepared by a two-phase method and were carefully purified. XPS measurements were carried out, focusing on the examination of the effect of nanoparticle size on the binding energies (BE) and FWHM values of the Au 4 f peaks and the S 2p peaks.

X-ray photoemission spectroscopy has been used to investigate 2 and 4 nm sized dodecanethiol derivatised gold nanoparticles. The results confirm the covalent nature of the sulphur-gold association and it is suggested that this is due to a combination of initial and final state effects. Quantitative analysis of the Au peaks revealed, as expected, an increase in the percentage of surface atoms. Purity of the nanoparticles was also demonstrated.

In conclusion, the XPS data obtained suggests that the thiolate molecules are bound covalently to the nanoparticles surface resulting in a chemical shift of the S 2p doublet to lower energies. The presence of a single doublet indicates that only one type of thiolate species is detectable. Two different types of gold atoms can be distinguished i.e. surface and bulk atoms. It is proposed that the Au 4f doublet undergoes a cluster shift to higher binding energies due to a combination of final state effects and initial state effects which are enhanced by decrease in cluster size. Therefore the gold atoms which have already been left electron deficient due to their association with the sulphur head group of the thiol molecule will have a further positive contribution due to the emission of a photoelectron resulting in core-holes which are left ineffectively screened. This work highlights the importance of size to the electronic structure of dodecanethiol derivatised gold nanoparticles.

# Department of Computer Sciences

# ALGORITHMS FOR K-SEPARATED MATCHINGS IN RANDOM REGULAR GRAPHS

**Mihalis Beis (Supervisor : Dr. M. Zito)**

*Department of Computer Science*

**Introduction.** A regular graph is a graph all vertices of which have the same degree, i.e. number of incident edges. A random r-regular graph is a regular graph generated by a stochastic process that, given r and n with $n > r > 0$, is equally likely to return any element of the class G(n,r) of all r-regular graphs on n vertices. A well-known construction that gives uniformly distributed r-regular graphs is the configuration model (a.k.a. the pairing model). Let n urns be given, each containing r balls. A set of $r \cdot n/2$ unordered pairs is chosen uniformly at random (u.a.r.), thus obtaining a pairing F. Each random pairing F corresponds to a r-regular multigraph with vertex set V=[n] and letting $\{i,j\} \in E$ if and only if there is at least one pair with one ball belonging to urn i and the other ball belonging to urn j. Of course, by definition a multigraph may contain loops (arising from pairs in F between two balls belonging to the same urn) and multiple edges (arising from two or more pairs in F whose balls belong to the same pair of urns). A pairing F not containing any edge joining balls from the same urn or two edges joining the same two urns corresponds to a simple r-regular graph G with vertex set V=[n], that is, a regular graph without loops or multiple edges. Since each simple graph corresponds to the same number of pairings, a regular graph can be chosen u.a.r. by selecting a pairing F u.a.r. and rejecting the result if it contains loops or multiple edges. This is a construction of the random graph G(n,r).
A matching is a set of non-incident edges; furthermore, if there is no edge in the graph joining any 2 edges in the matching, the matching is said to be induced. The distance between two vertices in a graph is the number of edges in any of the shortest paths between the two vertices. The distance between two edges $\{u_1,u_2\}$ and $\{v_1,v_2\}$ is the minimum of the distance between any two of vertices $u_i$ and $v_j$. For any positive integer k, a k-separated matching of a graph is a set of edges, M, with the additional constraint that the minimum distance between any two edges in M must be at least k. Let $\alpha_k(G)$ be the size of the largest k-matchings in G. The maximum k-separated matching (MkM) problem asks for a k-matching of size $\alpha_k(G)$.

Subject and Methods. In this project we investigate the performances of various strategies for finding large k-separated matchings in regular graphs. The analysis of these algorithms will be performed by approximating the algorithm dynamics through systems of differential equations following a method first introduced by Nick Wormald in the context of regular graphs. Alternative analysis strategies will be investigated too.

**Results.** A few algorithms for approximating the solution to the MkM problem, for each positive integer k, have been considered and their performance has been analysed on graphs generated according to the G(n,r) model using the differential equation method. In addition combinatorial upper bounds on $\alpha_k(G)$ which hold asymptotically almost surely (a.a.s.) if $G \in G(n,r)$ have been proved. The results of this work may be summarised in the following theorem:
*Theorem.* For each fixed positive integer k and fixed integer $r \geq 3$, there exist two positive real numbers $\alpha_k = \alpha_k(r)$ and $\beta_k = \beta_k(r)$, such that, if $G \in G(n,r)$, then $\alpha_k \cdot n \leq \alpha_k(G) \leq \beta_k \cdot n$ a.a.s.

# INFORMATION RETRIEVAL ON THE SEMANTIC WEB

**Ian Blacoe (Supervisors: M.J. Wooldridge, V. Tamma)**

*Department of Computer Science*

This research aims to facilitate the retrieval of information on the Semantic Web, by enabling the navigation and location of knowledge represented in semantically annotated web-pages. It intends to develop techniques and methods to query only those sources appropriate to the service required. In this way irrelevant information can be excluded from responses to queries, enabling more accurate and efficient retrieval of information.

The Semantic Web is intended as an extension of the current web, where information is accessed on the basis of the concepts represented by words, rather than just using the words themselves. In contrast to the current web, which is intended for human comprehension, the content of the Semantic Web is *machine understandable* and so available for reasoning. These semantics of concepts are described in *ontologies*, using specialised knowledge representation languages. Concepts are positioned within *taxonomies*, that show the parent/child relationships between them, and are described using *attributes* of the concepts.

The Semantic Web is an *open system*, where all types of resource providers and consumers can enter and leave at will and there are a multiplicity of ontologies defining concepts. However, the definition of a concept is dependent on the *purpose* for which the knowledge is represented, and so the same concept in different ontologies may be defined differently. Furthermore, different words can be used for the same concept (*synonyms*), and the same word can be used to refer to different concepts (*homonyms*). This heterogeneity between concept definitions can seriously hinder the sharing of information in an open system like the Semantic Web, as there will not usually be a pre-defined way of reconciling these differences. Therefore, we require *automatic* methods to determine correspondences between concepts, in particular the *semantic similarity* between them. By addressing the issue of semantic heterogeneity between concepts, the information available on the Semantic Web can be treated as a single coherent information resource, whilst retaining the differences between the different information sources.

In order to enable users to find information based upon the semantics of the terms used in queries and in the information resources, it is proposed to have a set of *indices* that will categorise information resources on the basis of the concepts found in them. Each index will represent a single concept (or a small group of related concepts) and will provide links to those information resources that contain *instances* of that concept. Semantically similar concepts from different ontologies can then be clustered together, either in the same index or in neighbouring indexes, and so slight differences between concept definitions are transparent to users. The indices are to be arranged in a hierarchy that reflects the concept hierarchies found in the ontologies, and are related to each other by semantic closeness and by the relations defined between the indexed concepts. Users can then navigate the index (and therefore the information resources), utilising the semantic relationships to find the information required. The indices are implemented as a *multi-agent system,* with each index being aware of the information it contains and able to direct queries that it cannot answer to another index that is more likely to be able to do so. The indices communicate with each other using a *peer-to-peer* approach, in which the communication between indices is characterised as that between equals. Each index has a subset of the indices as its *neighbours*, and this neighbourhood is defined by the relations between the indexed concepts.

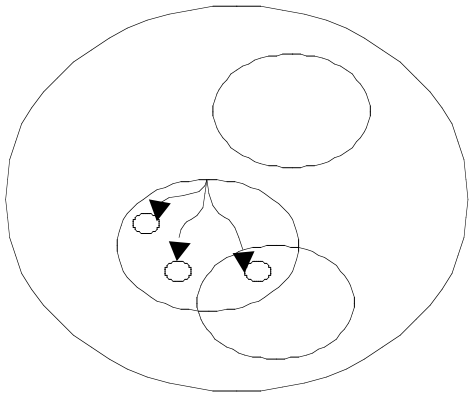
# PROGRAMMING RATIONAL AGENTS

**Benjamin Hirsch (Supervisors: M. Fisher, C. Ghidini)**

*Department of Computer Science*

Agent based systems have become a key topic in Computer Science over the last few years. However, as with many emerging technologies, there is no common definition of what is meant by the term "agents". Agents, as we understand them here, are pieces of software that are able to *act* (rather than *re*-act), *communicate* with other agents, and have a certain amount of *autonomy*, i.e. they can make decisions based on their own and the environment's state.
Agent-based systems promise to make the design, implementation, and scalability of complex software systems easier and more manageable. Due to the complexity of the agent systems, however, clear and formalized development techniques are paramount.
Using logic for the design and programming of agents not only gives us a formal language; it also allows us to test properties of specifications, and prove that those are not violated. Furthermore, logical descriptions are generally very concise and un-ambiguous.

We propose an agent programming language based on temporal logic - which allows us to reason about the agent's evolution over time - augmented with a powerful grouping structure. Groups are a natural way of structuring the potentially large agent space. As humans build groups to collectively solve problems, we can have groups of agents that work together.
This project is mainly concerned with developing a theory of groups within this framework. The implementation of a fully working agent platform supporting both groups and agents, and based on temporal logic, is the goal.
The main idea, on which the grouping theory is based, is to identify the notions of agents and groups. This means that agents not only can take part in groups, but they can *be* the group for other agents.
The advantages of using such an approach are numerous. Agents can use abilities of other agents, by inviting them into their group, and thus making them more easily accessible. They can also participate in several groups, and moving between groups as required.
In order to effectively use the group structure, we propose a powerful communication method, based on broadcasting. Our starting point is that each agent is able to broadcast messages to the agents it contains, as well as to the groups it participates in. We extend this by allowing agents to specify a communication schema that specifies where it wishes the message to go. For example, it is possible for an agent to specify that it wishes the message to be sent to all agents that share the same group. In addition, agents can exclude certain agents from the broadcast, to further streamline the efficiency of communication.



Agent Grouping and directed Communication - all ellypises represent agents.

The combination of temporal logic and flexible group and communication methods will provide an agent system that is powerful, extensible, scalable, and easy to use.

# COMPUTER AIDED AUCTION DESIGN

**Steve Phelps (Supervisor: M. J. Wooldridge)**

*Department of Computer Science*

**Introduction.** Economist Alvin Roth has suggested that designing auction mechanisms is an *engineering process*, in which economists design the rules of a market mechanism in order to meet particular objectives, either for certain participants, or for society as a whole. Examples of such objectives include: maximising allocative efficiency, achieving Pareto-optimal outcomes, maximising revenue, and ensuring the mechanism is fair. The difficulty for the mechanism designer is to ensure that these objectives are achieved even when the market is populated with autonomous agents acting for their own self-interest. The challenge is to design the rules of the game in such a way that agents will coordinate on the design objectives simply by following actions that maximise their own payoffs. As with any other design problem, each problem domain presents its own challenges for the auction designer, and each set of domain-specific requirements entails its own unique auction design; there is no ``one size fits all'' mechanism, and hence the design of novel auction mechanisms will be an ongoing engineering activity.

**Subject and Methods.** Traditionally, the design of auctions to meet particular requirements has been undertaken by economists, using analytic techniques drawn from game theory. However, use of these techniques may be problematic. For instance, in assessing a proposed auction mechanism, the designer must consider the trading strategies likely to be played by the agents trading under the mechanism. Deriving these for a particular market game - "solving" the game - is a non-trivial problem. This is because there is often no clear *dominant strategy*; rather, the optimal strategy depends on the strategies played by other agents. Nash defined a solution concept in which the strategy adopted by any given agent is a best-response to the best-response strategies adopted by all other agents, and proved that all n-player, non-zero-sum games admitted of such solutions. When evaluating an economic mechanism, the designer computes the Nash equilibria strategies for the given mechanism, and this forms the basis of a prediction about how participants will actually behave under this mechanism. The designer can then analyse market outcomes in equilibria and assess quantitively, for example, the likely impact on overall market-efficiency that a given tweak of the mechanism rules will yield. However, the Nash equilibrium solution concept suffers from several problems when applied in practice: (i) agents may be unable to compute their Nash equilibrium strategy due to resource bounds; (ii) even with unrealistically large amounts of computational and analytic power, many games defy solution; (iii) empirical evidence shows that human agents often fail to coordinate on Nash equilibria even for very simple games, whose solution is easily derivable under bounded-rationality assumptions; and (iv) some games yield many Nash solutions, and the theory gives practitioners little guidance on choosing plausible subsets of these as predicted outcomes. These difficulties have led to the development of cognitive game theory, in which models of learning play a central role in explaining and predicting strategic behaviour. Such multi-agent reinforcement learning models form the basis of our solution concept for optimisation of mechanism designs: rather than computing the theoretical equilibria for a given point in the mechanism search space, we run a number of multi-agent simulations using agents equipped with learning algorithms which determine their bidding strategies, and the outcomes of these simulations form the basis of our assessment of the fitness of each auction mechanism. Using such a computational solution concept, we are then able to attack the mechanism design problem as a straightforward computational optimisation problem; we can automatically search the mechanism design space using computational techniques. This research programme aims to develop tools and methods for the semi-automatic aquisition of auction mechanism designs.

# MERBIS, A MULTI-OBJECTIVE EVOLUTIONARY RULE BASE INFERENCE SYSTEM

**Christian Setzkorn (Supervisor R. C. Paton)**

*Department of Computer Science*

Knowledge Discovery from Databases (KDD) is a data driven approach to automatically infer accurate, comprehensible and potentially useful models from large data sets. KDD is a new research area and has been motivated by the steady growing gap between the generation of data collected from an environment and our understanding of it. This research focuses upon the inference of Classification Systems (CSs) from data.

Existing methods from disciplines such as statistics, machine learning and artificial neural networks require a great deal of expertise for appropriate deployment and for understanding of the CSs. This can be disadvantageous, especially when the constructed CSs are used to formulate general hypotheses with regard to the observed domain. To alleviate the problems associated with existing methods, we infer Fuzzy Classification Rule Bases (FCRBs) from data utilising a multi-objective evolutionary approach. FCRBs correspond to a linguistic knowledge representation form that can easily be understood. However, this is only true as long as the FCRBs are simple (e.g. the number of rules are moderate). The majority of extant evolutionary algorithms for FCRBs inference from data only focus upon the accuracy of the inferred CSs, possibly leading to incomprehensible and even over-fitted CSs. Our multi-objective approach allows the inference of CSs that exhibit trade-offs between accuracy and comprehensibility in a single run of the approach. Consequently, the domain expert is given a choice of CSs, ranging from comprehensible but less accurate CSs to less comprehensible but more accurate CSs. In practice, it is more likely the decision-maker will chose accuracy over comprehensibility. A disadvantage of evolutionary approaches is their extensive memory demands and computation time. To counter this, we use the JavaSpaces technology, which is known to simply the implementation of parallel applications. This technology is independent of hardware and software settings and allows the simple implementation of highly reusable applications. Hence, the computer power of an institution could be harvested by exploiting the computing power of idle computers. Moreover, our approach can cope with mixtures of categorical and continuous attributes and multiple class problems. We are currently applying our approach to real world data and investigating its performance in relation to benchmark data sets.

# EVALUATION OF DISCUSSIONS IN ONLINE CLASSROOMS

**Aiman Badri (Supervisors: F. Grasso, and P. Leng)**

*Department of Computer Science*

**Introduction**. In recent years computer supported cooperative learning (CSCL) has become one of the fastest growing research areas in education technology. Research has primarily focused on the modeling of students, in our research, conversely, we take the teacher's perspective.

**Subject and Methods.** We base our research on the analysis of a corpus of an online classroom interactions from an IT MSc degree program at the University of Liverpool using the SoftArc FirstClassTM system. The aim of our research is to explore the design of a system to support the instructor in her/his tasks, by providing a structured and objective analysis of the discourse.

**Results.** A Framework for Monitoring Classroom Discussion. We assume that the system operates on "contributions", i.e. textual messages posted by the various students to the virtual classroom. The system analyses and evaluates these contributions, the process involves various stages, each of which is represented by a separate component, described below.

*The Filter component.* The Filter selects the contributions which are relevant to the job at hand, by filtering out, for instance, repeated or out of topic contributions. There are several ways to approach the problem of relevance, a mechanism to decide whether a text is aligned with another, domain oriented dictionaries for a quasi-semantic analysis of a text for its relevance, and Latent Semantic Analysis. The Filter will apply techniques of these kinds to produce a list of relevant contributions that can proceed to the next stage of the process.

*The Tag Supplier Component.* It identifies and categorizes the single discussion elements in each contribution, tagging them with extra information based on their content. We are interested, however, not only in identifying what the contribution is about, but also in understanding how it relates to the rest of the discussion, and to create a dialogue meta-structure in which all the contributions are represented. We are especially interested in schemes that view a contribution as encoding one of a set of moves, expressing transitions in a dialogue. It must be decided what are the "basic units" of the contribution, and which types of rhetorical relation can exist among them. We plan to use shallow natural language processing techniques to retrieve the contribution content, and will focus on how the student's contribution relates to others in the discussion.

*The Discussion Manager component.* The Discussion Manager's role is to take the tagged discussion elements and use them to construct an image of the virtual classroom for the instructor. We envisage two main outputs: an Activity/Social Map and a Thread/Discussion Map. The Activity/Social Map is a visualization of the activities of the students in the virtual class, we plan to use a semantic approach. The Thread/Discussion Map will map the level of discussion of the class for a certain thread of discussion.

*The Reporter component.* It will be an alerting service for the benefit of the instructor, informing about events that happened and events that did not materialize.

**Conclusions.** The work described here is directed at providing intelligent support for teachers in online classes in which classroom discussion is a central feature of the pedagogy. We have identified relevant techniques, especially drawn from conversation analysis and dialogue game theory, which can be applied to the task. We now propose

# Department of Earth Sciences

# ULTRA HIGH RESOLUTION CORRELATION USING COAL SEAM MICRO-STRATIGRAPHY

**Roy C. Davies**

*Stratigraphy Group, Department of Earth Sciences*

Email: rdavies@liv.ac.uk Website: www.liv.ac.uk/~rdavies

Coal seams are highly sensitive indicators of changes in accommodation and organic productivity and enable extremely high-resolution correlation of parasequence-scale base level changes many kilometres landward of the coeval shoreline. The Sunnyside coal seam of the Cretaceous Blackhawk Formation in Eastern Utah contains two laterally extensive splits which open basinward into packages of shallow-marine sediments. Increases in the inorganic mineral and pyrite content of the coal combined with reduced vitrinite reflectance, provide clear signatures of the flooding surfaces related to these splits at least 15km back up depositional dip into the unsplit coal. The coal constrained by these flooding surfaces is therefore the coastal plain equivalent of the marine shoreface parasequence bounded by the same two surfaces further into the basin. Furthermore, changes in coal composition and vitrinite reflectance within this 2m thick package of coal enable us to identify a complete record of very high-resolution accommodation changes throughout the formation of this parasequence.

Vitrinite reflectance is especially useful as even small rises in base level which do not result in inundation of the mire can significantly suppress reflectance values. Similarly, falls in base level produce enhanced reflectance values due to slight oxidation of vitrinite precursors. In a single vertical section, mean reflectance values may reach 0.8% where high inertinite content indicates dry conditions, and then rapidly fall to around 0.5% at the points where base level rose. These sharp kicks in the reflectance profiles enable centimetre scale correlation of flooding surfaces between sections spaced over 15km of depositional dip.

# SEDIMENTS AS A SOURCE OF METALS AND COMPLEXING LIGANDS, A STUDY IN THE VENICE LAGOON, ITALY

**C. S. Chapman[1], C.M.G. van den Berg[1] and G. Capodaglio[2,3]**

*[1]Oceanography Laboratories, University of Liverpool, Liverpool, UK; [2]IDPA-CNR, Venice, Italy; [3]University Ca' Foscari di Venezia, Venice, Italy.*

Venice Lagoon is a shallow and in parts, contaminated, bay. Studies are underway to better estimate the extent and nature of the chemical contamination. It is hoped that this knowledge will aid in toxicological studies and possible future remediation of the lagoon. Chemical speciation is a key factor in assessing the bioavailability and hence toxicological impact of heavy metals to marine life. The aim of this work is to investigate the mobility of metals buried in the lagoon sediments.

The problem was tackled by using two approaches. Benthic chambers were designed to quantify the levels, fluxes and speciation of the metals and the corresponding ligands to and from the sediments. The chambers were placed within the lagoon in the Tresse Channel area, near the industrial plant of Porto Marghera over 56hrs, and samples were taken at 3-4hr intervals in addition to in-situ measurements of salinity, dissolved oxygen, and Eh. The samples were then analysed for a variety of dissolved metals and metal speciation. Dissolved thiols were also determined as a specific complexing ligand. With the exception of the benthic chambers these analyses were carried out using commercial apparatus. The second approach was the design of an in-situ system and a benthic flux plate for measuring metals, sulphide and oxygen concentrations as they were being released from the sediments.

A steady release of thiols was expected from the sediments, whilst the metal fluxes could be either positive or negative as a function of Eh or ligand concentration. Eh and $O_2$ data showed the gradual formation of a suboxic environment within the chambers as a result of biological oxygen removal in the sediments, indicating that the chambers were well isolated, and this work presents the metal and ligand data. Mn and Co showed a positive flux from the sediments, rising from 230 to 536 nM and from 7 to 25 nM respectively: this is in line with expectation as both Mn and Co tend to be released from sediments in reducing conditions. Copper on the other hand showed a negative flux decreasing in concentration from 39 to 20 nM and then stabilizing at an equilibrium concentration of 22nM after 12hrs. Pb and Cd data show no systematic trend. The thiol concentration showed a positive flux from the sediments rising from 50 to 200nM, and then tailed off towards the end of the experiment. To assess the effects of the thiol release, measurements were carried out to detect their complexing capacity on different metals, the results showed a different affinity for metals following the order Cu>Pb>Cd. Also presented is data collected in the lab from the in-situ analysis system.

Data collected from the chamber shows that they were successful in sealing of a section of the water column. The analysis of the samples continues with speciation and complexing capacity titrations. The second part of the project is the in-situ analysis system, which was used in the chambers. This had technical difficulties and work is continuing to resolve these issues.

# THE VERTICAL LOADING DEFORMATION DUE TO STORM SURGES AND ATMOSPHERIC PRESSURE

**Federica Fratepietro**
**Supervisors: Prof. Trevor Baker and Dr. Simon Williams**

*Proudman Oceanographic Laboratory*

A model of the vertical (radial) displacement of the UK due to loading by storm surges was developed and the magnitude of the radial deformation of the British Isles and northwest European coasts caused by sea mass variations in the North Sea was evaluated. The deformation was estimated at Sheerness and Lowestoft between January 1998 and April 2002. The attention was focused on the event of January 30$^{th}$, 2000, the biggest of the period investigated. A maximum surge of 1.8 m in Sheerness caused a vertical movement of – 18.1 mm. In Lowestoft a deformation of almost – 27.5 mm has been produced by a sea level increase of 1.55 m. It should be pointed out that the relationship between the local surge elevation and the vertical displacement induced is not linear. The reason is that the vertical displacement computed by the model is the result of an integral effect over all the grid of the model i.e. it is due to the sum of the contributions of all the cells of the grid and not just of that in which the site is situated. Maps of the spatial distribution of the loading deformation were computed and the seasonal and longer period deformation due to storm surge loading were evaluated as well.

The radial deformation due to atmospheric pressure variations was also computed considering first the contribution to the deformation due to loading of both land and ocean areas (the so called non-inverted barometer ocean, NIBO). In addition, the so called inverted barometer ocean (IBO) was used in which the atmospheric pressure loading over the oceans was set to zero. For the period of time investigated (1998–2000) the radial deformation was evaluated at Sheerness. The effects of the lateral extension of pressure distribution were studied in order to provide the air pressure correction values for high precision displacement measurements and to give an idea about the magnitude of the surface displacements induced by local and regional variations in atmospheric pressure. It was noted that the magnitude of the radial deformation increases when a broader area is considered to contribute to the displacement. In particular, the main contribution to the displacement comes from an area within 2000 km from the point of interest. A significant reduction in the value of the displacements was noticed when passing from the NIBO to IBO model. The crust under the nearby ocean no longer experiences the effect of pressure fluctuations and so no longer contributes to the deformations at the site.

The method used for computing the atmospheric and storm surge effects on vertical displacements was to perform a convolution between the local and the regional barometric pressure or sea level data and the mass loading Green functions. The convolution method achieves a great accuracy in the results.

The convolution atmospheric pressure results were then compared with those obtained with Rabbel and Zschau methodology (1985). Since the magnitude of the displacements is critically dependent on the spatial extension of the pressure anomaly, they proposed a two coefficient correction equation, one belonging to the long and the other to the short wavelength loading in order to achieve a precise air pressure correction. The discrepancies founded with the convolution results suggest that two coefficients are not sufficient for correctly evaluating the vertical displacement at the site considered.

Finally the admittance between radial displacement and local atmospheric pressure were computed. Air pressure correction values between -0.46 and -0.44 mm/mbar for an oceanless earth model, and between -0.26 and -0.24 mm/mbar for the inverted barometer ocean hypothesis were found for the site of Sheerness.

# SHIFTING CONTINENTS, RISING SEAS AND THE CAMBRIAN FOSSIL 'EXPLOSION'

**Michael Garton**

*Department of Earth Sciences*

When the Atlantic Ocean opened a piece of the North American continent was left behind. The foreign relic - sedimentary rocks of the far North West of Scotland - chart the rise of long vanished Cambrian seas lapping onto the American continent; the Scottish strata only make sense if they were once contiguous with a vast continent out to the north-west. Conversely, deep water was to the east, now Scottish mountains.

This research is attempting to understand the environmental conditions of that early Cambrian shelf sea by analysis of the sand that was left behind, seen today in cliffs of the 170 metre thick Eriboll Sandstone. How did sea level fluctuate? Why are fossils initially rare in the thick carpet of sand left behind? And then why do fossil burrows appear so abruptly? Why do the burrows continue through the upper half of the sandstone (the world famous Pipe Rock) in such high densities? Well in excess of a billion burrows – probably fossil worm holes – have not been studied before. Yet the testimony of the 'local inhabitants' can hardly be ignored when reconstructing the palaeo-environmental conditions.

At first sight the ancient sea gradually invaded the North American continent. Because the Cambrian shelf was wide (at least 70 km) and very shallow, sedimentation was very responsive to changes of sea level. Abrupt shallowing across such a width of shelf set up a jellyfish trap *par excellence*. Hence the newly discovered jellyfish impressions, the first Cambrian record in the UK. So far, seven abrupt changes have been noted in the sandstone and each appears to be continuous from Skye to the north coast. The uppermost records a deepening, expressed by a change from sand to mud. The deepening was so abrupt that mud preserved a snapshot of the sea floor complete with spiral casts atop the burrows. Across the globe the sea level rose throughout Cambrian times. Nonetheless, the Eriboll Sandstone testifies to surprisingly abrupt fluctuations in the overall trend, fluctations which data so far suggests might also be under global (eustatic) control rather than local movement of the land.

Burrow diameter in the Pipe Rock increases from two or three millimetres at the base to over 10 mm at the top, and crudely tracks grain size in the sandstone. In other words the worms? were sensitive to, somewhat controlled by their environment. An environmental control would also explain the Pipe Rock's greatest enigma – the sudden onset of burrowing. In 90 metres of sandstone below the Pipe Rock burrows are rare. Then densities abruptly exceed 4000 per sq metre. Burrows commence immediately above one of the outcrop-wide changes. As a working hypothesis, this change is interpreted as an abrupt deepening which moved the whole shelf into less energetic conditions which soft-bodied organism could exploit. Although broadly coeval with the 'Cambrian fossil explosion', fossil occurrence was strongly controlled by the palaeo-environment.

A thick (4 – 6m) bed in the Pipe Rock, presumably triggered by some event (large earthquake?) forms an outcrop continuous, chronostratigraphic marker horizon. In addition to precise correlation, the bed covers and preserves a large scale snapshot of the geometry and character of shelf as the sandstone was forming.

# MANTLE SEISMIC ANISOTROPY BENEATH THE 660KM PHASE TRANSITION GENERATED BY SUBDUCTION BODY FORCE STRESSES.

**S. Nippress [(1),] N. Kusznir [(1),] M. Kendall [(2)]**

*(1) Department of Earth Sciences, University of Liverpool,*
*(2) School of Earth Sciences, University of Leeds,*

Observations of seismic anisotropy can provide insights into the style of mantle dynamics near the 660km discontinuity. *Wookey et al.* (2002) report up to 7 seconds of shear wave splitting for rays generated by deep focus events from the Tonga subduction zone and recorded in Australia. The results suggest a transversely isotropic symmetry with the symmetry axis in the vertical plane, perpendicular to the ray direction. Thus, for horizontally travelling waves this would imply horizontally polarised shear waves (SH lead SV). They show that a topmost lower mantle model with anisotropy between 660-900km could produce theoretical shear wave splitting similar to that observed. Therefore, the seismic anisotropy observed by *Wookey et al.*, can be explained by an anisotropic region between 660-900km, with only a minimal contribution from above the 660km phase transition. The goal of this study is to try to explain the observed shear wave splitting using geodynamical modelling.

We use finite element (FE) modelling to calculate slab-induced models of fluid flow, total stress and deviatoric stress. A simple 2D subduction zone model with a prescribed viscosity structure and slab density is used. Large deviatoric stresses (maximum values ~ 40 MPa) are generated in the topmost lower mantle when the subducting slab encounters an increase in viscosity at the 660km phase transition. These stresses may induce mineral alignment in a broad region (lateral wavelength approximately  800km) in the topmost lower mantle below the slab. Perovskite may therefore be aligned with a rotated symmetry axis conformal to the shape of this region of high deviatoric stress. Aligned Perovskite rotated more than 30 degrees predicts *SH*-waves faster than *SV*-waves for horizontally travelling S-waves.

The formulation of *McKenzie* (1979) is used to calculate the finite strain accumulated by a mantle parcel as it propagates through the FE flow models. The computed strain ellipsoids align in a similar region (wavelength approximately 800km and depth 660-900km) as that of the deviatoric stresses. The strain fields are then mapped into seismic anisotropy. We initially assume that the anisotropy has hexagonal symmetry, with a symmetry axis aligned with the major axis of the finite-strain ellipse. The magnitude of the anisotropy is scaled by the degree of finite-strain ellipticity. We place a source at a depth of 660km and vertically ray trace through the seismic anisotropy model to a depth of 1200km. A model, which has an increase in viscosity at the 660km phase transition, produces a differential travel time of 2.5secs with *SH* faster than SV. Models with no viscosity increase at 660km show less than 1sec of differential travel time. Current work is directed at full ray tracing through similar travel paths as those observed by *Wookey et al.* (2002).

# AN INVESTIGATION OF BRITTLE FRACTURE USING CONTINUOUS ACOUSTIC EMISSION MONITORING

**B. Thompson [(1)], R. P. Young [1,2], K. Mair [1,2]**

*(1) Department of Earth Sciences, University of Liverpool*
*(2) Lassonde Inst., University of Toronto, Canada.*

Acoustic Emission (AE) investigations of brittle rock fracture in controlled laboratory experiments allow a detailed 3-D examination of the spatial and temporal evolution of micro-fracture growth. These observations provide valuable insights into the micro-mechanical processes involved in the development of macro-scale fault structures.

Processing techniques similar to those of Earthquake Seismology are employed to locate and resolve the focal mechanisms of AE events, however at this small scale, sampling rates of 10 MHz are required. At these high sampling frequencies, technological constraints necessitate the use of triggering logic in conventional AE recording hardware. After an event is triggered, a "downtime" period is experienced while the waveform data is downloaded. However, the AE rate increases to thousands per second, prior to dynamic fracture propagation, and so the inherent periods of downtime result in a very low proportion of events being recorded. Therefore the observational capacities of conventional AE systems are severely limited during the crucial period of fracture growth.

The importance of recording a complete AE data set during the critical moments of fracture prompted the development and manufacture of a novel ultrasonic monitoring system; The Giga Recorder. This system can record up to two minutes of waveform data onto a 40 GB Random Access Memory (RAM), sampled at 10 MHz, on 16 channels. The RAM continuously rewrites, meaning at any point in time, the preceding two minutes of waveform data are stored, and can be downloaded following the critical experimental period. In addition, triggered events are recorded throughout the entire period of AE activity.

Here we present results from the initial laboratory experiments using the Giga Recorder. A series of Chevron Notched Brazilian Disk granite samples were uniaxially loaded to failure, under a variety of loading rates. During each test, a tensile fracture propagated from the pre-cut notch, across the sample. The continuous acoustic records associated with macroscopic fracture have been processed, in both the time and frequency domain to yield a unique data set, demonstrating the microscopic evolution of a tensile fracture.

Future experiments will examine shear fracture and mixed mode fracture propagation on the laboratory scale, and will be compared to in-situ field scale tests at the Underground Research Laboratory (Atomic Energy of Canada, Ltd.).

# Department of Mathematical Sciences

# DISEASE-FREE DAIRY MODEL

**L. Tannerah, D. E. Hodgkinson**

*Department of Mathematical Sciences*

We discuss the stability of a disease - free model of a typical UK dairy farm. The cows are classified into four groups, called unweaned, weaned, dry and lactating. Assuming that the herd consists of a constant number of cows, the dynamics of the model predict a stable equilibrium point. We introduce a time delay into the model and investigate the stability of the new model.

We analyse the stability using algebraic and numerical methods and discuss the consequences for different values of the time delays. We intend to improve our use of the time delay differential equations to obtain a more realistic model of the dynamics of the herd.

# MATHEMATICAL MODELLING OF A COMPACT CATALYTIC REFORMER

**A. Selsil, A. B. Movchan, N. V. Movchan**

*Department of Mathematical Sciences*

The aim of this work is to develop a new design for an efficient and environmentally friendly compact catalytic reformer, used to produce hydrogen for fuel cells. The mathematical model of such a device involves a system of reaction-diffusion equations, coupled with algebraic equations, which describe chemical reactions that take place in thin channels of the reactor, as well as the effect of thermal interaction across the walls between the channels. In a conventional combustion chamber, heat is transferred via radiation at temperatures well in excess of  , when pollutants are formed. The challenge is to propose a workable design that combines catalytic combustion with catalytic reforming, where a large fire box is no longer needed. In this case the peak temperature reached is $1000^{o}C$ (when the pollutants are not produced), and the structures can easily be scaled up or down depending on the industrial requirements. The new design includes endothermic and exothermic reactions occurring in alternate channels with heat exchange between them, via thin walls. Our model incorporates an accurate asymptotic analysis exploiting the fact that the ratio of the width of the wall to the total length of the catalytic reformer is sufficiently small. We analyse the heat transfer across the thin-walled structure, resulting in `coupling' between the channels. Another aim is to maximize the overall heat transfer coefficient.

We first investigate the temperature distribution in a system of channels, separated by thin walls, with 2D inhomogeneous heat equations in the channels and 2D homogeneous heat equations in the walls. The asymptotic method reduces the dimensions for the leading order terms of the temperatures, and enables us to obtain solvability conditions, for the high-order terms, which leads to a `coupling' between the channels. A particular example is given to highlight industrial applications.

We then focus our attention on heterogeneous reactions occurring in a packed bed catalytic reformer. We use 2D heat equations in the wall, and modified 1D equations in the channels, which take into account energy and mass balances for the reactions. We analyse the `coupling' between the channels and run numerical simulations using industrial data.

Further work includes analysing the structure of the wall - having a wall with different layers of different thermal conductivities and modifying the mode of heat transfer to include radiation by introducing an air gap within the wall.

We also consider the effect of the pellets on the flow. We model this by replacing the real fluid by a homogenized fluid in an unobstructed channel, in order to obtain 2D equations describing the change in temperatures across as well as along the channels. Further work also includes the analysis of the case when the pellets are no longer present and the catalyst covers the wall, the introduction of transient terms in higher dimensions and generalisations to multi-channel interactions.

# A COMPARISON OF ASYMPTOTICS OF HEART AND NERVE EXCITABILITY

**Rebecca Suckley, Vadim Biktashev**

*Department of Mathematical Sciences*

## Introduction

We analyse the asymptotic structure of two mathematical models concerning the heart and nerve membranes in the body. These two models are the Hodgkin-Huxley (1952) model, which is used to describe the flow of electric current through a surface membrane of a giant nerve fibre, and Noble's (1962) model based on the Purkinje fibres of the heart. These two models are fourth order differential systems of equations.

We also want to verify the conjecture by Zeeman (1972) that there exists a cusp catastrophe in third order differential systems of equations, i.e. the resulting phase portrait contains a cusp and the trajectories of the system travels smoothly around the cusp point.

## Methods

We use Tikhonov's (1952) parametric embedding of fast-slow systems to introduce a small parameter $\varepsilon$ to these two models, so we are able to reduce the models to a third order system of equations. Although Noble's model is a modification of the Hodgkin-Huxley model, their structures with respect to the small parameter $\varepsilon$ are entirely different. This is because Hodgkin-Huxley's model has two slow and two fast variables, while Noble's model has one slow variable, two fast variables and one superfast variable.

## Results

From Tikhonov's embedding we found that the Hodgkin-Huxley model is reduced to three equations and Noble's model is reduced to two equations. This is because of how many slow variables the models contain. Therefore the phase portraits of the two models are different because for Hodgkin-Huxley's model we obtain a three-dimensional phase portrait, which describes the trajectories of this system travelling to a stable equilibrium point. We obtain a cusp in this system, but only after modifying one of the parameters, but even then the trajectories don't travel smoothly around the cusp point.

Noble's phase portrait describes a two-dimensional system where the trajectories are limit cycles because the equilibrium point is unstable; therefore we do not obtain a cusp.

## Conclusion

For these two models Zeeman's conjecture was not verified due to Tikhonov's embedding and a more adequate embedding may be to enter small parameters into the equations in a significantly different way.

# AN EFFECTIVE POTENTIAL CALCULATION IN QUANTUM CHROMODYNAMICS

**R. E. Browne, J. Gracey**

*Department of Mathematical Sciences*

Quantum Chromodynamics (QCD) is the theory we use in particle physics to describe the strong nuclear force; one of the four fundamental forces of nature. Although there has been much experimental verification of the theory in high energy particle accelerators (where QCD correctly predicts that we should see hundreds of weird and wonderful particles), there are still many areas of the theory which have proved extremely hard to test. This is not so much due to a lack of experimental apparatus suited to the job. The problem is that QCD is, mathematically, a very difficult theory to handle. Although we can write down the QCD equations, which we believe govern the strong nuclear force, there are only certain special cases for which we can find a good enough solution to the equations to test experimentally. In these special cases the theory passes the test, but for other cases we simply cannot find solutions to our equations. We therefore cannot fully test the theory. Further, QCD is a very non-intuitive theory and the governing equations themselves do not give very many clues as to how particles are going to behave in real life – for that you need the solutions to the equations, which we don't have. Hence many of the mechanisms at work on a fundamental particle level, for example inside a proton, remain a mystery.

The work we have been doing is concerned with trying to access solutions to QCD which have, so far, proved so difficult to find. Our approach is indirect in that we are calculating a quantity which, in itself, is not physically testable. However, it is hoped that it will be of use in future calculations which may then be testable against empirical results. As with a lot of other work in the field of particle physics, the calculation is performed using what are called Feynman diagrams. These are an extremely useful way of representing the maths required to solve a particular problem. For our calculation we have to evaluate over 150 of these diagrams. To do this by hand would take a very long time and so we have written computer programs to deal with the large amount of algebra involved. The quantity we are calculating is the effective potential of a particular operator in QCD and we are especially interested in ascertaining what happens when quark effects are included in the calculation. More details about this operator and its significance may be found on our poster. The poster is mainly aimed at providing an introduction to the concepts involved in this work; effective potentials; the quantum aspects of the theory; quarks and gluons; Feynman diagrams and some details about the method of calculation. The work is ongoing at the moment and so we shall present our latest results on the poster.

# EPIDEMIC MODELLING AND CONTROL

**Nathan Green**

*Department of Mathematical Sciences*

Using the general stochastic epidemic model, with homogeneous mixing in a closed population, we will investigate an intervention policy of isolating infectives, with costs assigned to infection and isolation of individuals. This set-up will facilitate the analysis of policy decisions when uncertainty about particular parameter values exists. Public health strategies may assume, for instance, the infection rate parameter to be known in order to implement some ideally optimal control action. By incorporating vague parameter knowledge into the model by way of a (prior) distribution on the parameter of interest, how will policy decisions alter? Under what conditions will we intervene unnecessarily?

In addition, information from past data can be utilised to determine a parameter estimate through the likelihood function. That is, we can combine prior experience of an infectious disease's behaviour with epidemic data. This is the Bayesian paradigm. Some interesting results are show with regard to when optimal intervention should be applied.

# ASYMPTOTIC ANALYSIS OF A CRACK IN A LAYER OF FINITE THICKNESS

**J. P. Bercial-Vélez, A. B. Movchan**

*Department of Mathematical Sciences*

There are several features that can be studied about a crack propagating through an isotropic material (a material whose properties are the same in any direction of the space). Amongst them, the propagation of waves along the crack front is our aim in this study. We can think of the waves that propagate during an earthquake, for instance, and our finite layer one of the strata comprising a certain configuration of materials.

In our mathematical model we analyse the solutions for the wave equation in a 3D layer of finite thickness containing a dynamic crack, following the work by Willis and Movchan (1995). In that paper, the dynamic weight functions were discussed for a semi-infinite crack extending at constant speed V in a 3D space.

The weight function (which gives an expression for the stress intensity factor as a convolution with the loads) appropriate to this case is constructed via Fourier transforms to develop and solve a scalar Wiener-Hopf problem. There are important qualitative differences, with the work mentioned above, as the homogeneity of the weight function does not exist, due to the Geometry. A relationship between the stress intensity factor and a small time-dependent perturbation on the edge of the crack will be found.

The analysis of the transfer function makes us conclude that in the case of a finite layer there are dissipative waves on the edge of the crack, in opposition to the infinite space problem.

# LATTICE QCD AND GLUEBALLS

**Steve Miller**

*Department of Mathematical Sciences*

Introduction.
Quantum Chromodynamics (QCD) is widely accepted as the theory describing the strong interactions in particle physics. This theory describes the interactions of quarks and their binding into mesons and hadrons. For example, QCD describes how three quarks bind to form protons and neutrons. These interactions are mediated by gluons, the so called gauge fields of the theory.

Subject/Method.
At low energies, we cannot use standard perturbative techniques to calculate quantities in QCD. As a result we discretise space-time into a 4-dimensional Euclidean lattice, where the quarks live on the sites of the lattice and the gluons on the links between the sites. We can then simulate QCD on the lattice and calculate low energy quantities, such as the meson mass spectrum. Lattice QCD also predicts the existence of bound states of gluons or glueballs, which have not yet been clearly observed in experiment. Lattice QCD can predict the masses of these glueballs and so give clues as to which observed resonances in experiments are candidates for glueballs.

Results.
Current measurements predict that the lightest glueball has a mass of around 1600MeV and the next lightest around 2300 MeV.

Conclusions.
Lattice QCD can confidently predict the mass of the lightest glueball states. However the problem is that the energy ranges where the glueballs are predicted to be found are particularly dense with states. These states could be glueballs or mesons or mixtures of the two. The goal is to disentangle these regions of the QCD mass spectrum.

# THE EVOLUTION OF SCALAR FIELDS IN D-TERM HYBRID INFLATION

**Matthew Broadhead, John McDonald**

*Department of Mathematical Sciences*

The inflationary paradigm as a model for the origins and evolution of the universe has been highly successful in giving a sound theoretical background to observed physical phenomena on large (cosmological) scales. We give a brief overview to inflation including how it predicts such phenomena as the CMB (Cosmic Microwave Background) and the origin of large scale galactic structure. We then present our model of inflation based on Supersymmetry breaking in the early universe and show how we arrive at the equations of motion that govern the evolution of the inflaton field and the other matter scalar field present in hybrid inflation. In this model of inflation, slow-roll in the de-Sitter phase is driven by the loop corrections to the inflation potential. We give the form of these loop correction and, as the full potential is not analytically solvable in the equations of motions, we show the numerical method we used to solve them.

The nature and growth of spatial perturbations in the matter and inflaton field is essential in making prediction about the shape and form of the CMB. We show how these are calculated in our model and present our results for the growth of these perturbations and, critically, show the regime for which these perturbations become non-linear. This regime is highly important as it will eliminate an area of parameter space (specifically the ratio of the couplings $\lambda/g$) for which objects called Q-balls or inflaton condensate fragments can occur.

Finally, we give a possible Q-ball solution for this hybrid model. Q-ball solutions have readily been found for single field inflation models. However, single field motivated models of inflation have become disfavoured in recent year and the discovery of a hybrid Q-ball would be highly valuable. This discovery could have important consequences for the re-heating of the universe and if these Q-balls are stable could form a good dark matter candidate.

# FILTERING AND POLARISATION OF ELASTIC WAVES BY 2D PHONONIC CRYSTALS

**S. B. Platts, N. V. Movchan**

*Department of Mathematical Sciences*

We study the scattering of elastic waves by a stack of gratings, infinite and periodic in the x-direction, of circular cylinders placed in an infinite elastic medium. The cylinders, which are infinitely long and aligned along the z-axis, can be voids, fluid filled or made of an elastic material with different properties to that of the surrounding medium. In the case of elastic inclusions the cylinders are either perfectly bonded to the surrounding medium or connected to it via a thin soft elastic layer.

The scattering properties of a single grating are calculated using a multipole method which was introduced by Lord Rayleigh in 1892. The method encapsulates the scattering properties of a single grating in the form of reflection and transmission matrices. To calculate the overall reflection and transmission properties for a finite stack of gratings we employ a recurrence procedure.

The objective of the study is to find band gaps, intervals of frequency for which the waves do not propagate through the structure. A range of practical applications for this study, including the design of earthquake shields and sound barriers, is described in the article by Ball[1]. Results of this study are presented in the form of transmission diagrams, plots of the amount of energy transmitted through the stack as a function of the wave frequency.

We present the governing equations with boundary conditions for each type of cylinder and give a brief outline of the method. Transmission diagrams are presented for the case of regular arrays of voids, fluid filled cylinders and elastic inclusions. We also demonstrate that it is possible to create band gaps for large frequency ranges by combining gratings of different cylinders.

[1] Philip Ball, ‘Sculpted sound’, New Scientist, 23rd March 2002.

# DESCRIBING THREE DIMENSIONAL SHAPES: CONSISTENCY CONDITIONS FOR THE MEDIAL AXIS

**Anthony Pollitt, Peter Giblin**

*Department of Mathematical Sciences*

How can we describe or represent the shape of an object? For example, organisms have simple shapes which are not usually equilateral triangles, squares or other basic mathematical shapes, so other ideas are required to obtain their simplicity. When organisms move or grow, what information about their shapes is preserved? A concept which can be used to answer such questions is the medial axis, or 'skeleton'. This mathematical object reduces the large amount of information of a shape, but retains the essential information necessary to differentiate between various shapes. For a shape in two dimensions, the method of obtaining this medial axis is to fit circles inside the shape so that they are tangent to the shape in at least two places. Then the medial axis is the centres of all such circles. For a shape in three dimensions the medial axis is analogous; we fit spheres inside the shape so they are tangent in at least two places, then obtain the centres of the spheres. An interesting question is that, given the medial axis of a shape, what extra information is necessary (if any) in order to reconstruct the original shape?

The medial axis in two dimensions is well understood; its various forms such as special points and smooth branches. Also, connections between the geometry and dynamics of a shape and of its medial axis are known, these are conditions which are necessary for a consistent reconstruction of the original shape. The three dimensional case is not so well understood; we understand its local forms, but consistency conditions analogous to those in two dimensions are not known. In three dimensions the original shape is called the boundary surface. The medial axis in three dimensions in a generic setting is locally one of the following: (i) a smooth sheet, (ii) three smooth sheets intersecting in a curve, (iii) edges of a smooth sheet, (iv) points where six smooth sheets meet, and (v) points where an edge of a smooth sheet meets another smooth sheet. The special points of the medial axis are cases (ii) to (v), and we give details of our discoveries so far of consistency conditions in these cases. These conditions impose limitations on the geometry and dynamics of the medial axis in these special cases. We also illustrate these conditions by using simple surfaces as medial axes.

Our work is completely theoretical, but there are applications in the fields of robotics and biology. For example, a robot needs to be programmed to recognize and differentiate between various shapes, so the medial axis provides the simplest mathematical tool to do this. In biology there is the question of what are the most likely shapes occurring naturally, and the consistency conditions are very useful for this.

# TWO–DIMENSIONAL NON-LOCAL MODELS IN A LATTICE

**S. Haq, A. B. Movchan and O. Selsil**

*Department of Mathematical Sciences*

A simple and efficient model, due to Ya. Frenkel and T. Kontorova, describes a chain of atoms harmonically coupled with their nearest neighbours. The chain is also subjected to a sinusoidal substrate potential. This non-linear model was first used by the authors to describe the structure and dynamics of a crystal lattice in the vicinity of a dislocation core.

In this work, we consider a two-dimensional lattice structure and assume that the upper-half of the xz-plane is covered by a set of Frenkel-Kontorova strings parallel to the z-axis. We use the ideas from [1], [2] and [3] to derive a discrete model and present numerical simulations for the equation at the boundary. We note that this equation is a discrete analogue of the well-known Peierls-Nabarro equation. We also discuss the regularisation procedure corresponding to a hexagonal lattice and analyse the motion of dislocation kinks on the plane.

## References

[1] Dudarev, S.L. (2003) Coherent motion of interstitial defects in the crystalline material, Phil. Mag. (to appear).

[2] Movchan, A.B., Bullough, R. & Willis, J. (1998) Stability of a dislocation: Discrete model, Euro. Jnl of Applied Mathematics} 9, 373-396.

[3] Movchan, A.B., Bullough, R. & Willis, J.R. (2003) Two-dimensional lattice models off the Peierls type, Phil. Mag. **83**, 569-587.

# Department of Physics

# AN INVESTIGATION INTO KNOWLEDGE AND ITS REPRESENTATIONS IN THE PHYSICAL AND BIOLOGICAL SCIENCES

**Brian Rea, Dr Dominic Dickson and Dr Ray Paton[1]**

*Department of Physics and [1]Department of Computer Science*

The main objectives of this research project have been to look at the similarities and differences between knowledge in the physical and biological sciences. This has primarily investigated the possibility of using these ideas to assist in communication between the two different disciplines. I have approached this research from a number of different yet complementary perspectives. These fall loosely under the categories of information theory, representations and interpretations, computational linguistics, scientific discourse and its analysis, as well as knowledge organisation and mobilization. Although these areas may seem unrelated they are all based upon or have particular ideas concerning knowledge at various levels of abstraction. I am currently looking at how knowledge and other formalised representations are used at each of these levels in both disciplines to discover any distinct rules of use or procedures particular to any of the fields. By analysing the use of these conventions by the practitioners I should be able to suggest previously unexamined areas that can cause problems with communication between the scientists of the different disciplines. As a related study this research will also consider communication between the specialist science expert and interested non-specialists by providing a common viewpoint.

One of the major outputs of this research is a software toolset that allows for information to be extracted from journal articles for both physical and biological sciences. This tool will use some of the major techniques developed for linguistic analysis in a combined form to not only allow for syntactic information to be collated but also enable semantic categorisation to be detailed through the use of biomedical ontologies. By combining these two views of the text I will be able to generate enough information to extract key concepts and their relationships from the texts. These relationships could then be mapped into a formal representation system that would act as a visual reference framework of related facts rather than the standard linear text based or more flexible hyper linked solutions. This innovative user-centred approach to representing the knowledge should offer new insights into multidisciplinary learning as well as provide a platform upon which further research into science communication, linguistics and knowledge processing can all be based.

The toolset as a whole uses novel techniques from a wide variety of disciplines ranging from natural language processing to educational psychology in an original manner to assist in extracting information from biological science resources. Future development based on the suggestions made during this project could also assist in the development of similar large-scale applications within the physical sciences. One example of this would be the creation and development of a new ontology to work with our system alongside the LHC: ATLAS project in particle physics. The efficiency of this tool for the analysis and management of all documents linked to the project would enable a much more holistic view of the whole system for all collaborators. This would provide the benefits of more integrated research and would reduce the amount of unnecessary repetition usually involved with such numbers of researchers.

# E-SCIENCE INFRASTRUCTURE FOR THE GRID

**David Jones and Prof. Themis Bowcock**

*Department of Physics*

Introduction

The Grid aims to make distributed computing resources available transparently, much like the World Wide Web (WWW) provides easy access to information distributed across the globe. Grid computing extends the WWW concept by allowing users to access and share distributed computing resources, such as: 'Farms' of computers for processing large problems (e.g. MAP, the Monte-Carlo Array Processor at Liverpool); Large information stores (data warehouses and databases); Scientific instruments, like remotely controlled telescopes, Particle Physics detectors, Medical Scanners.

The success of the WWW is based on communication protocols (TCP/IP, HTTP) and the document description language HTML, which allow information publishing and access across different computer platforms and operating systems. A similar set of tools are being developed for the successful realization of the Grid.

Subject and Methods

Achieving this world-wide sharing of computing resources poses significant challenges. A single operation on the Grid may involve several type of computing resources, often distributed across different organisations (universities, research centres) and geographical locations. Resources operation and access, as well as user authorisation and authentication methods, vary widely. The Grid aims to 'glue' all these resources together in a manor that makes them usable to end users in a seamless fashion.

To achieve this aim, Grid projects have introduced, and are implementing, the concepts of Virtual Organisation, Single Sign On, Definition of Elements on the Grid (Computational Elements, Storage Elements, User Interface Elements, etc), Resource Brokerage, etc.

My research is part of the EU-Datagrid, a European Union project aiming to produce a working Grid for scientific communities (Physics, Biology, Astronomy, Medicine).

My research contributes in the development of the Data Management Package (WP2), one of the 12 working packages that make up the EU-Datagrid project.

The main challenges for Data Management on the Grid are:

Data Replication: To make data available to the end user it is often necessary to make replica copies at different locations. There is of course a need to make sure each replica is consistent with the others; i.e. when one copy gets updated, the others must get updated as well.

Transparent access to data resources: Data can be stored in independent files or databases. Databases are often the preferred method for structured data because their reliability and scaling with use is well known, but methods of accessing different databases are different.

WP2 has produced a product known as Spitfire, which allows databases to be accessed in a transparent fashion. Spitfire uses SOAP (Simple Object Access Protocol) as a communication medium. This allows requests for information to be passed through the WWW and later on, over the Grid. This has been the main area of my research so far.

Results and Conclusions

In producing a Web based Administration package I am collaborating with the WP2 group and gaining experience which will be vital for my further work in turning MAP into a Grid resource.

# EVALUATING INNOVATIVE METHODS OF PRESENTING AND PROMOTING PHYSICS

**Laura Grant**

*Science Communication Unit, Department of Physics*

## Introduction

There are currently two (conflicting?) aims for Science education in the United Kingdom. Firstly; we want "Science for Citizenship": a Scientifically literate public who are able to make informed choices about the Science affecting their everyday lives. Secondly; we need to provide the Scientists and Engineers of the future with enough depth of Science knowledge to inspire and enable them to pursue fulfilling careers in academia or industry.

It is a well-known and often lamented fact that the numbers of entries into Physics at GCSE, A level and AS level have been declining for years. Females are being put off the subject at age 11-16 even more than their male counterparts.

## Subject and Methods

It is useful to understand public attitudes to Science and some of the reasons why Physics uptake is falling at schools and Universities. This information will form the basis for the research.

"Innovative Methods" will be defined as anything other than that which would take place in a physics lesson at school. It would be impossible, by the very nature of the term "innovative", to evaluate every possible method. However, a range of different case studies will be compared, and some of the issues involved in measuring their impact will be raised.

Evaluation methodology will include questionnaires and face-to face interviews used to gauge the impact of different interventions in the affective and cognitive domains.

## Conclusions

Innovative methods can be used to effectively target school or public audiences and produce a significant positive shift in attitudes towards Science and Physics in particular.

Development of an impact scoring system would be useful in continuing work of this nature

# Department of Psychology

# DOSE-DEPENDENT EFFECTS OF ALCOHOL ON APPETITE AND FOOD INTAKE

**S.J. Caton, M. Ball, A. Ahern, M.M. Hetherington,**

*Department of Psychology, University of Liverpool*
*samcaton@liverpool.ac.uk*

Evidence suggests that energy derived from alcohol is not only additive to the habitual diet, but may stimulate appetite leading to over consumption. To investigate a dose response effect of alcohol on appetite and food intake, 12 males attended the laboratory on three occasions. On each occasion they were given a standard breakfast and returned to the laboratory for an ad-*libitum* lunch and dinner. Ss received 330 ml of no-alcohol lager (62.62 Kcal: no-alcohol condition), the same amount of lager spiked with 1 unit (8g ethyl alcohol, 118.62Kcal) or 4 units of alcohol (32g ethyl alcohol, 286.62 Kcal) 30 minutes before lunch. Ss rated appetite and mood at intervals before and after the preload, lunch and dinner. *Ad libitum* intake at lunch (excluding energy from the pre-load) was significantly higher following 4 units of alcohol (1377.65 +/- 236 Kcal) compared to 1 unit (1173.31+/- 296 Kcal). Intake at dinner did not differ significantly in any of the conditions. Total energy intake at lunch and dinner (including energy from the pre-load) was significantly higher following 4 units of alcohol (2859.82 +/- 366 Kcal) in comparison to 1 unit (2523.86 +/- 513 Kcal). Hunger was rated higher following 4 units of alcohol across the day in comparison to no alcohol and one unit. The stimulatory effect of alcohol on food intake appears to occur only at doses above one unit, and this is not compensated later in the day.

# WHY DO INDIVIDUALS AT RISK OF CORONARY HEART DISEASE IGNORE THEIR GP'S ADVICE TO TAKE MORE PHYSICAL ACTIVITY?

**Helen Beers, Dr. Kate Bennett**

*Department of Psychology*

Inactivity has been identified as a risk factor for heart disease. However, in an environment that is becoming increasingly automated, adopting a physically active lifestyle is a difficult and complex challenge for individuals. Primary care based exercise referral models have been endorsed by the Government although as yet the most effective way of increasing physical activity in primary care has not been determined.

The research study focuses on how individuals respond to advice from their GP to become more active. It explores attitudes and beliefs about physical activity and the perceived and actual obstacles to change. Qualitative methods were used to collect data from individuals who had been advised by their GP's to increase their physical activity. Each participant in the study had risk factors for developing coronary heart disease yet decided not to make a change to their physical activity.

Findings indicate that whilst voicing concerns about their health problems, individuals have a tendency to accept them. They want a 'quick fix' solution, believe that physical activity is a difficult option and put up barriers to initiation. The implications of this are that individual's health will continue be at risk due to them remaining physically inactive, and also that primary care may need to rethink its approach to supporting lifestyle change.

# PSYCHOSOCIAL DIMENSIONS OF THE IRISH DIASPORA

**Eve Binks**
**Dr. Neil Ferguson**

*Department of Psychology*

Irish people currently constitute Britain's oldest and largest migrant ethnic group. Given the importance of Great Britain as a reception country and it's close proximity to both Northern and the Republic of Ireland, relatively little is known with regard to acculturation experiences and attitudes toward the on-going conflict in Northern Ireland for this subgroup of the Irish Diaspora. The aim of the current study was to examine specifically religiosity, social identity, political and historical knowledge and attitudes toward social and political solutions to the 'Troubles' in Northern Ireland. An opportunity sample of 75 respondents was selected. Within the sample, 54% were raised within the Catholic faith, 42% in the Protestant faith and 6% specified some other or no religious denomination. Significant differences were found between Catholic and Protestant social identity, religiosity and social and political solutions to the political violence. No significant difference was found between the political and historical knowledge of the respondents. The Irish in England do elicit strong social identifications, although Protestant respondents displayed a more complex identity. Catholic respondents exhibited a more orthodox and intrinsic attitude toward religion. Suggested solutions to the 'Troubles' in Northern Ireland differ greatly between the Catholic and Protestant Irish in England.

# TRUST AND SAFETY IN INDUSTRIAL ORGANIZATIONS

**Conchie, S.M., Donald, I.**

*Safety Research Unit, Department of Psychology*

Research has consistently shown the particular importance that organizational safety culture and individual attitudes play in establishing and maintaining high levels of safety performance. A factor of particular influence in shaping these organizational and individual factors is trust. The safety literature makes implicit reference to the role of trust in accidents and the effectiveness of safety initiatives, yet research aimed at understanding trust has not explicitly and directly examined its potentially crucial role in industrial safety. The research to be carried out will be one of the first to systematically study trust within a safety framework. The study will identify the antecedents and levels of trust in different areas of organizational functioning and their relationship with safety performance. Both qualitative and quantitative methods will be used to collect data. In this way an insight into the complexities of workers perceptions and understanding of trust will be gained, combined with a validation of the relative strength of these qualitative findings. Understanding the antecedents of trust and its relationship to safety will enable companies to incorporate a trust promoting element into safety initiatives, which will ultimately facilitate in the development of high levels of safety performance.

# MERSEYSIDE YOUTHS: A LOOK INTO A DEVIANT SUBGROUP

**Natalia Wentink**

**Professor David Canter (supervisor)**

*Department of Psychology*

Limited to a subgroup of Merseyside youths, this study explores the deviant values and beliefs held by some youths. Based upon youth interviews and questionnaires, the study examines these beliefs and possible relationships to the amount of contact youths spend with peers and adults and the types of deviant behaviour they have engaged in. The results are reported as well as a discussion on the directions for future research.

# SOMATOSENSORY STEADY-STATE IN THE HUMAN EEG

**Giabbiconi, C.-M, Zopf, R. & Müller, M.M.**

*Center for Cognitive Neuroscience, Department of Psychology*

Attention is one of the most crucial mechanisms in the brain that enables us to perceive accurately our rich and complex environment. Yet, little is known about selective attentional mechanisms in the somatosensory modality. The steady-state response (SSR) in the human EEG is often used in order to investigate such a mechanism as a way to circumvent inherent constraint of evoked potential (EP) recordings. Transient EPs imply a short presentation of the stimulus with long inter-stimulus intervals. In contrast, SSRs are elicited by a repetitive presentation at a fixed stimulation rate, which allows us to investigate a state of sustained attention. A further advantage of SSRs is the possibility to use synchronously multiple frequencies that can be analyzed separately in the EEG.
The greatest SSR amplitudes have been reported in the visual modality between 8 and 12 Hz and at approximately 40 Hz in the auditory modality. Despite the proposition that the greatest amplitude in the somatosensory modality could be found around 20 Hz, little is known about the physiological properties in this modality.

Therefore, the present study aims to investigate the physiological aspects of the somatosensory steady-state responses. The somatosensory steady-state evoked potentials were elicited by *mechanical* vibratory stimulation applied to the index's second metacarpal in 11 normal subjects. Two frequencies were used: 20 - 26 Hz with an intensity of 4.9 Newton. In the frequency domain we found peak amplitudes at the stimulation frequencies. The results will build the basis for future studies examining the attentional mechanisms in the somatosensory modality.

# THE EFFECTS OF THREE DIFFERENT STROOP TASKS ON PERCEIVED ANXIETY AND CHOCOLATE INTAKE.

**D.J. Wallis and M.M. Hetherington.**

*Department of Psychology, University of Liverpool*

**Introduction:** This study was designed to examine the effects of the modified Stroop colour-naming task on perceived stress and intake of chocolate. It has been proposed that a modified Stroop task (using stress-related words) could provide a standardised method to induce stress in eating behaviour research. In order to establish if any induced stress is due to experiencing the stress word condition or simply to the cognitive demands of the Stroop colour-naming task, three conditions were employed: stress words, matched neutral words and incongruent colour words.

**Methods:** Students and staff of the University of Liverpool volunteered to take part in a study on "The relationship between task performance, personal characteristics and taste perception". Participants completed the three tasks on separate days with at least three days between each session. Tasks were presented using SuperLab software to ensure accurate measurement of reaction time and errors and to control the response-stimulus interval (32ms has previously been found to provide sufficient time to produce anxiety). There were 288 words in each condition. Stress words incorporated three types of ego-threat (from others, self-directed and sociotropy threat) and neutral words were individually matched with these words. Mood and appetite variables were assessed before and after the tasks and after post-task ad Libitum intake of chocolate buttons.

**Results:** A preliminary analysis of 19 participants found a significant difference between stress ratings (using 100mm visual analogue scales) such that the greatest stress was produced by the stress-word condition (mean = 38.89) followed by the incongruent condition (mean = 35.89) and the lowest stress was reported in the neutral condition (mean = 22.06). Chocolate intake showed a similar, but non-significant trend in the same direction.

**Conclusions:** This preliminary analysis suggests that the incongruent colour-word and ego-threatening Stroop tasks induce similar amounts of stress and increase chocolate intake to the same extent

# DETECTIVE DECISION MAKING IN HOMICIDE INVESTIGATIONS

**Michelle Wright**

**Supervisor: Professor David Canter**

*Centre for Investigative Psychology, Department of Psychology*

There has been little academic research into understanding the routes through which Detectives develop systematic strategies in relation to homicide cases. The current research aims to make a first step in understanding the psychology of detective decision-making and gain an insight into how detectives make decisions and unpack the inferences that they make throughout the course of serious crime investigations such as homicide.

Descriptive data on all homicides from a large North West Police Force over a 15-year period (1987-2001) has been collected to examine the types of cases that have been investigated over this time span. This descriptive data will be drawn upon to select a sample of Detectives to interview that have investigated a range of different types of cases and have different experiences of investigating homicide in order to identify the types of decisions made by detectives in homicide investigations and identify factors that influence detective decision making.

# THE EXPERIENCE OF CRIME: EMOTIONS AND ROLES EXPERIENCED WHILE COMMITTING AN OFFENCE

**Maria Ioannou, Professor David Canter**

*Centre For Investigative Psychology, Department Of Psychology*

An area of criminality that has been overlooked is the actual experience of committing a crime. The study investigates the roles and emotions that are experienced by an offender while committing a variety of crimes. It is hypothesised that (a) the emotional experience of crime will reflect a circumplex for emotions for normal population, (b) there will be a number of different roles experienced by the offenders (e.g. Adventurer, Revenger etc) (c) a relationship will exist between the emotions and crimes experienced and (d) the experience of crime (positive or negative) will be related to particular types of offences committed. These hypotheses are derived from the Circumplex of Emotions (Russell, 1997), Narrative Theory (McAdams, 1988) and its link with Investigative Psychology (Canter, 1994).

Convicted for a variety of crimes, incarcerated criminals are interviewed and the results are subjected to Smallest Space Analysis (SSA), a non-metric multidimensional scaling procedure based upon the assumption that the underlying structure, or system of behaviour, will most readily be appreciated if the relationship between every variable and every other variable is examined.

The first results support all the hypotheses of the study as it was found that the emotions experienced by offenders while they were offending did reflect a circumplex, the roles that were experienced were those of the Adventurer, Criminal, Revenger and Victim, the emotions and roles were related as they could be differentiated on the basis of whether they were perceived to be either positive or negative experiences and different types of offences produced different types of experience, either positive or negative.

The implications for Investigative Psychology are discussed.

# YOUTHS WHO SEXUALLY ABUSE OTHERS-A PILOT STUDY

**Louise Almond**

*Centre For Investigative Psychology, Department Of Psychology*

From an extensive overview of the theoretical literature a number of key issues as to why young people sexually abuse have been highlighted. These issues will be discussed in relation to producing a model of youth sex offending behaviour. A pilot study containing 40 youths was carried out. The pilot study will be illustrated in terms of; sample, demographics and behaviour. Possible ways forward in producing a model of behaviour are proposed. The model aims to improve our understanding of the abusive incidents and behaviour of sexually abusive youths.