ABSTRACTS:

Chemical Ecology in the Anthropocene:

Oral Presentations

In programme order

Session 19 (Part I), Session 22 (Part II)

Chemical ecology as inspiration for global change

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Humans are currently altering this planet more than any single species in the history of Earth. In fact, this phenomenon has lead to the dawn of a new geological age, known as the Anthropocene. Humans not only impact the environment itself, but the ecological interactions between organisms, including chemical communication. The ubiquitous nature of chemical ecology across all life on Earth offers a unique opportunity to understand the impact humans are having on our natural world. Our field also allows us to potentially develop ways we can adapt to the impacts of humans on the very means by which organisms interact with each other. Here I will briefly outline our research on chemical communication in the current Indian context, particularly concerning pollination and environmental pollution, and discuss how the tenets of chemical ecology have inspired a new global network to increase the communication between science and society. We hope our journey inspires chemical ecologists to use their unique multidisciplinary knowledge to engage with their communities.

Keywords: *Urbanization; Pollution*; *Global change; Chemical communication; Outreach*

Field-scale effects of air pollution on invertebrate community composition in wheat

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Air pollution has the potential to affect invertebrates both directly (e.g. physiologically) and indirectly (e.g. via changing plant chemistry of host plants or by disrupting volatile organic compounds used in communication). This study determined the effects of two common air pollutants, diesel exhaust emissions (including nitrogen oxides – NO_x) and ozone (O_3), both individually and interactively, on the community composition of predominantly ground-active invertebrates within a field of winter wheat over two years. Pitfall traps within 8-meter diameter fumigation rings were used to collect invertebrates, which were then taxonomically identified and characterized by functional group (i.e. predator, parasitoid, herbivore, fungivore, detritivore or pollinator), diet specialization (i.e. generalist or specialist-feeding) and the presence of wings. Taxonomic richness and Shannon's diversity were calculated from the most precise taxonomic resolution identified. Moderate increases in the levels of NO_x (diesel treatment) and O_3 had adverse impacts on invertebrate community composition, with greater declines in invertebrate abundance and taxonomic richness observed under diesel exhaust-pollution compared with O_3-pollution. For both pollutants in combination, the effect on invertebrate abundance and taxonomic richness was reduced compared with diesel pollution alone, likely due to the reaction between atmospheric NO_x and O_3. Moreover, specialist-feeding and winged invertebrate species responded more negatively to air pollution treatments than generalist feeders and wingless species, respectively. Understanding how invertebrate groups respond to multiple interacting air pollutants such as diesel exhaust and O_3 facilitates predictions into how terrestrial environments will respond to future changes in anthropogenic emissions, especially as we shift away from fossil fuel dependence.

Keywords: Free-Air Diesel and Ozone Enrichment (FADOE); functional group; ground-active invertebrates; insect ecology

Effect of ozone pollution on the chemical signal emitted by a Mediterranean tree to attract its specific pollinator

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Since the industrial time, the drastic increase in atmospheric pollution contributes widely to the present global change and causes real pressures on species interactions, especially between plants and pollinators. Among these pollutants, tropospheric ozone (O_3) is a strong oxidizing agent that has the potential to affect the quality of the chemical signals emitted by plants. We tested if O_3 affects the attraction of pollinators towards their host plants via (i) an effect on the blend of Volatile Organic Compounds (VOCs) emitted by flowers and/or (ii) an alteration of the chemical signal during its lifetime in the atmosphere. Our working model is the interaction between the Mediterranean fig tree, *Ficus carica*, and its unique pollinator, *Blastophaga psenes*. To evaluate these effects we simulated O_3 pollution peaks under controlled conditions. Thanks to Gas Chromatography-Mass Spectrometry and Proton Transfer Reaction-Time of flight-Mass Spectrometry analyses we (i) quantified VOCs emitted by fig trees exposed to a high O_3 concentration during 5h and (ii) we determined VOCs reactivity with O_3 as well as the secondary organic compounds formed by ozonolysis. Our results show (i) a decrease in the abundance of some VOCs emitted by the fig trees, and particularly some of the compounds attractive for the pollinator, and (ii) the degradation of some of these compounds and the formation of new VOCs. Thus the proportions of VOCs that constitute the attractive chemical signal for the pollinator are drastically modified. We are currently evaluating if these changes can alter pollinator attraction towards figs.

Keywords: VOCs emission; ozonolysis; atmospheric pollution; specific interaction; chemical communication

Impact of elevation and global warming on plant–pollinator relationships in the Eastern Himalayas

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Climate and environmental change can significantly impact biotic interactions such as plant–pollinator relationships. The Himalayas have been identified as one of the most vulnerable areas in the world regarding climate change impacts. In our study, we examined how elevation and warming impact floral odor profiles and pollinator response in the Eastern Himalayas across three elevations (3000, 3500 and 4000 m above sea level). We selected four alpine meadow flower species, and also conducted an *in situ* warming experiment on a fifth species, using open top chambers that simulate future global warming. We also compared pollinator-visitation rates across elevations for three of the species. Our results show that both elevation as well as warming significantly affected the quantity and quality of floral odor profiles. However, in a cross-species comparison, the floral odor profiles of a particular species were more similar to each other across elevations than to other species at the same elevation. Further, pollinator-visitation rates on each of the flower species did not vary significantly with elevation. We therefore conclude that while elevation-related environmental factors significantly alter floral odors, they do not affect total pollinator-visitation rates in these environments. This indicates the potential for constancy in perception of floral odors by pollinators in a diverse floral community in the face of environmental change. Our study has implications in understanding how floral odor profiles change in response to environment, and contributes to our understanding of plant–pollinator interactions in a changing climate.

Keywords: climate change; climate warming; floral VOCs; perceptual constancy; tropical alpine meadows

Land-use stress and pesticides alter the chemical communication of wild bees

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In the last years, insect pollinators are significantly declining in agricultural areas by evidence. These declines are due to many factors e.g. habitat and food loss, emergent diseases, pesticides and climate change. In intensified agricultural areas pollinators are chronically exposed to various pesticides that were found to negatively affect foraging bees by altering orientation and learning behaviour. Effects of pesticides or other stressors on chemical communication, however, have rarely been investigated. We studied the effects of stressors, which affect pollinators in intensified agricultural areas, on chemical communication of wild bees. *Bombus lapidarius* workers were caught in grasslands with different land-use intensities in Germany. In chemical analyses of cuticle surface odours with a function in chemical communication, we found a significant effect of land-use intensity on scent bouquets. In a further study, we tested the effect of single stressors such as neonicotinoids, on communication and antennal sensitivity for semiochemicals. Bumblebees and mason bees were treated with field realistic doses of neonicotinoids. Workers of *B. terrestris* differed significantly in their chemical profile after treatment with thiamethoxam or clothianidin. In the mason bee *Osmia bicornis*, clothianidin decreased antennal sensitivity to common floral volatiles. In our study, we found an effect of neonicotinoids on the production and perception of semiochemicals in bumblebees and mason bees. For *B. lapidarius*, it is not finally clarified, which stressor led to the changes in the scent bouquet. However, our results indicate that agricultural management and practice may have a negative effect on chemical communication and pollination.

Keywords: agricultural management, *Bombus*, cuticular hydrocarbons, electrophysiology, *Osmia*

Impact of ozone on the perception of olfactory signal by generalist pollinators

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Concentration of tropospheric ozone (O_3) has dramatically increased since pre-industrial times and could threaten the functioning of ecosystems. Negative effects on both emission and transport of plant-emitted volatile organic compounds (VOCs) have been already highlighted, which does not augur well for the attraction of insects that relies on these chemical signals, particularly pollinators. Surprisingly direct effects of O_3 on the attraction of insect itself have not been considered so far. To investigate the effects of O_3 on the VOC detection and the behavioral response of *Bombus terrestris* foragers, electrophysiological experiments and behavioral assays were carried out under controlled conditions. In order to simulate a peak of O_3, naïve foragers were exposed to ozone at a given concentration (i.e. 0, 80, 120 or 200 ppb) for 60 min or 180 min. Following the exposition, the responses of bumblebee antennae were measured for different concentrations (i.e. 0.1, 1, 10 and 100 µg/µL) of three synthetic VOCs mimicking compounds generally found in floral scents (i.e. (–)-linalool, benzaldehyde and nonanal). Our results show that ozone exposition affects volatiles perception by bumblebees but that this effect depends on the O_3 exposure (i.e., concentration and duration) as well as on the VOC and its concentration. Besides behavioral assays using glass Y-tube olfactometer showed a modification of their behavioral response to a VOC stimulus (i.e. benzaldehyde) after ozone exposition, depending on both concentration and duration of O_3. These results indicate that ozone-rich environment can affect plant-bumblebee interactions, interfering with both host detection and attraction.

Keywords: Air pollution; Antennal detection; Behavioral response; Bumblebees; Plant-pollinator interactions

Highly diverging effects of increased temperatures on floral scents of crop species

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Global temperatures are expected to increase in this century by up to 5°C. However, little is known about the effect of increased temperatures on floral scent emissions and chemical communication between plants and their pollinators. Here we analyzed flower scents of three insect pollinated crop plants (buckwheat, *Fagopyrum esculentum*; oilseed rape, *Brassica napus*; strawberry, *Fragaria x ananassa*) at two different temperature scenarios: physiological optimal and 5°C warmer than optimal temperatures. Floral scents were sampled by dynamic headspace and analyzed using gas chromatography coupled to mass spectrometry. The floral scents of buckwheat and oilseed rape were dominated by 2- as well as 3-methylbutanoic acid and p-anisaldehyde as well as linalool, respectively, no differences of total amount and scent composition between the two scenarios. In strawberry, however, both the amount and composition of scent was strongly affected by increased temperatures. In the warmer scenario the emission decreased eightfold and *p*-anisaldehyde was replaced by 1,4-dimethoxybenzene as the strongly dominating compound. Our results highlight that responses of floral scent emissions to increased temperatures are crop species-specific. As next step we will test in strawberry how the detected changes in scent emission influence attractiveness of flowers to pollinators.

Keywords: climate changes; chemical communication; crop pollination; floral volatiles

Natural products from Antarctic marine benthic invertebrates

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Recent research in our lab is focusing at new approaches to study the natural products from Antarctic marine benthic invertebrates and their chemical ecology. A part of the description of the new compounds found and their bioactivities, we are looking at the production of these metabolites under situations of stress, trying to see changes in gene expression related to natural compounds synthesis. Global change is one of the key factors that may affect benthic communities, inducing stress (for example, water temperature increase), and understanding how this may interact with production and use of natural products in the relationships among organisms is of crucial relevance. We are using temperature increase and predation pressure to determine changes in naturals products presence and diversity in several benthic invertebrates. On the other hand, we are using CADD (Computer-Aided Drug Design) techniques to help us in the search for bioactivities for these compounds, and experimentally validating these results. For all these, we are studying selected tunicate and gastropod molluscs compounds, but also sponges, bryozoans, and others. In this talk, a summary of these recent developments will be provided.

Keywords: Marine chemical ecology, marine benthos, CADD, temperature stress, bioactivity.

Sponge Watch Program- An intitative towards 'one ocean-one health' approach in the age of Covid-19

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In the Anthropocene epoch (also known as 'Age of Plastics'), plastic pollution has become a global problem, contributing to 80% of marine litter. India produces an estimated 25,940 tonnes of plastic waste every day, 40% of which remains uncollected and ends up in our oceans. These plastics are further broken down into tiny pieces (= Microplastics, MPs) that enter the marine food web affecting >70% of marine species and humans as well. At present, we do not sufficient techniques to efficiently detect or remove MPs from our oceans. But what if the answer lies in our world's oldest animal – the marine sponge. Marine sponges are the most efficient filter-feeders with the capacity to filter more than six times their volume per minute and the ability to thrive in polluted waters. We used a self-designed combinatorial approach to isolate and characterise MPs from common species of sponges found in coastal regions of the Gulf of Mannar, India. It was found that marine sponges can accumulate significantly higher MPs ($p<0.05$) as compared to ambient seawater and sediment. Moreover, different species of sponges showed varied bioaccumulation of MPs inside their body, suggesting species-specific responses to MP. We aim to understand the mechanisms behind MP bioaccumulation and explore the potential bioindicator and/or bioremediation capabilities of sponges. This will offer unique insights for marine conservation, sanitation, and waste management, and has the potential to find new bioinspired ways to remove microplastics from our water and understand how it is affecting our living world, especially in the age of COVID-19. We aim to establish these marine sponges as a suitable system to monitor environmental health such as microplastics pollution. It is important to identify monitoring parameters and to determine the most appropriate biological indicators for long-term microplastics monitoring. These parameters can be listed out and designed in the form of user-friendly kits to allow the common public to take part in such environmental monitoring programs. Our intregrated approach will help in developing a science-citizen program to take care of our ocean and our health.

Keywords: marine pollution; biofiltration; bioindication; bioremediation; marine chemical ecology and health, one ocean-one health concept

Anthropogenic influences on marine food webs: the case of plastic ingestion.

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A hallmark of the Anthropocene is the ubiquitous presence of plastic waste in the world's oceans. Plastic marine debris is of growing concern to ecologists, due, in part, to the deleterious impact it has on wildlife that consume it. Although it has commonly been assumed that ingestion occurs because organisms mistake plastic marine debris for food, this behavior has only recently been examined in relation to the chemical signals that are thought to drive foraging interactions. My laboratory has been investigating plastic ingestion in this context, focusing on the procellariform seabirds as a model system. This is a diverse order of highly pelagic species, many of which have been shown to track prey using dimethyl sulfide (DMS) as a foraging cue. DMS is produced from phytoplankton and other marine algae, and is a critical info-chemical across a wide range or organisms and marine habitats. We and others are beginning to explore how attraction to this compound is associated with plastic ingestion. My presentation will provide a brief overview of these findings to illustrate how this keystone foraging cue contributes to this ecological trap.

Keywords: dimethyl sulfide; ocean; marine debris; pollution; seabird

ABSTRACTS:

Chemical Ecology in the Anthropocene:

Poster Presentations

In programme order

Poster Session 3

Climate change and chemical ecology: Determination of natural products in an Antarctic and a Mediterranean bryozoan species

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The marine environment is exposed to global change and one of its effects is the increase of the water temperature, affecting all marine living species, even changing their metabolism. Many benthic organisms produce secondary metabolites (natural compounds) which are used as a defensive system against predation, competitors, microorganisms, pathogens, fouling, etc. In our study, our goal is to determine if there are variations in the natural product composition of two species of bryozoans when temperature is higher than usual. Therefore, two species of bryozoans were selected, representative of two different environments, *Himantozoum (Himantozoum) antarcticum* (Calvet, 1909) from Antarctica, and *Chartella tenella* (Hincks, 1887), from the Mediterranean Sea. The experiments consisted in keeping the animals at three different temperatures, 15ºC, 20ºC, and 25ºC for the species *C. tenella*, and 0ºC, 5ºC, and 10ºC for the species *H. antarcticum*. The experiments were done in filtered seawater aquaria, with a total of 40 organisms, 20 of each species for a total of two weeks for the Mediterranean samples and four weeks for the Antarctic samples. After organic extraction and clean-up of the samples, the determination of the different compounds was done using chromatography techniques coupled to ultraviolet-visible and a mass spectrometry detector (HPLC-MS). Chromatogram profiles show different composition between bryozoan extracts coming from the two environments, and samples kept at different temperatures present different chemical pattern, and therefore an effect of temperature on bryozoan natural products is observed.

Keywords: *Chartella tenella, Himantozoum antarcticum,* HPLC-MS, Marine benthos, Temperature.

Natural products in Antarctic sponges: the case of *Mycale acerata*

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Many benthic invertebrates, including sponges, are known to develop defensive strategies against potential predators and fouling. The constant and accelerated global change of our planet could have an effect on these functions, altering the normal relationships within communities. The aim of this study is to evaluate the potential effect of rising temperatures due to climate change on the Antarctic demosponge *Mycale acerata*. Furthermore, the influence of predation in the natural products of this species is tested too. Samples were collected in Livingston Island, an Antarctic island in the Southern Ocean (South Shetlands Archipelago). Sponges were kept alive at different temperatures (0ºC, 5 ºC, 10ºC) and with two predation situations (macropredation with starfish, micropredation with amphipods), against some controls, in Antarctica. After 4 weeks samples were frozen and transferred to the University of Barcelona. Organic solvents were used for extracting the natural products and HPLC for further analysis and quantification. Variations related to temperature and/or predation may produce significant changes in the chemical defense compounds of *M. acerata*, and thus affect their ability to survive in the field. Since Porifera are significant components of Antarctic biodiversity, the entire ecosystem could be compromised.

Keywords: Marine chemical ecology, marine benthos, climate change, temperature stress, predation, bioactivity.

Production of defensive metabolites by *Pinus patula* x *Pinus tecunumanii* hybrids in response to *Fusarium circinatum* infection

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Pine trees defend themselves from attack by insect pests and microbial pathogens through a complex system of physical and chemical defenses. These defenses can be constitutive, present in the tree before an attack, or inducible, produced in response to an attack. Defensive chemicals induced upon fungal infection include terpenes and phenolics, large groups of structurally diverse compounds with known antifungal and fungistatic properties. However, the specific chemical defense response in pines to *Fusarium circinatum* infection is unknown. In this study, the defensive secondary metabolites produced by *Pinus patula* x *Pinus tecunumanii* hybrids in response to infection by *F. circinatum* were tested under different experimental parameters. Infection by a more virulent strain of *F. circinatum* correlated with longer lesion lengths on the stems of infected seedlings. However, LCMS analysis revealed that stronger virulence did not lead to a significant increase in production of defensive phenolic compounds. Furthermore, a general increase in production of defensive phenolics occurred as the time post-inoculation increased. GCMS analysis will determine whether similar trends can be observed in the production of defensive terpene compounds. Ongoing research will reveal whether low elevation and high elevation *Pinus* hybrids differ in their chemical defense response, as well as the effect of greenhouse temperature on secondary metabolite production in *Pinus* hybrids. This study also aims to reveal whether chemical markers for *F. circinatum* resistance or susceptibility can be identified and utilized in pines.

Keywords: defense; terpenes; phenolics; pine trees; disease resistance

Structural and Functional Comparison of 2-Phenylethylamine and Dopamine as Infochemicals for Hermit Crabs under Climate Change

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2-phenylethylamine (PEA) is a known predator cue in terrestrial environments. Our previous results, however, show an attraction of hermit crabs (*Pagurus bernhardus*) to this biogenic amine. This raises the question of the ecological role of PEA for current and future marine environments. Considering the close structural similarities between PEA and dopamine, this study relates functional to structural common features between the two neurotransmitters as infochemicals. Similarly to PEA, the role of dopamine for external signalling is largely unknown, but internal dopamine levels are known to be high during courtship and agonistic behaviour in crustaceans. We study their potential signalling function for hermit crabs in paired dose-dependent choice experiments, whereby different motion parameters are compared. Our experimental design also accounts for the influence of the hermit crab's sex and size on its response to the tested compounds. These are important factors in the context of courtship behaviour and also known to play a role in establishing dominance hierarchies in crustaceans. As the continuing uptake of atmospheric carbon dioxide reduces oceanic pH conditions, marine chemical environments are changing. We therefore additionally explore the pH-dependency of the hermit crab's behavioural responses. Using quantum chemical calculations, we compare structural features of PEA and dopamine in different protonation states and relate these to the animal's responses. This study provides an insight into the potential roles of neurotransmitters and structurally related compounds as external chemical signals for crustaceans in current and end-of-the-century oceanic pH conditions.

Keywords: Chemoattractant; Computational Chemistry; Neurotransmitters; Ocean Acidification; *Pagurus bernhardus*

The effect of temperature in the chemical defense of the nudibranch *Doris kerguelenensis* (Mollusca: Heterobranchia)

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Doris kerguelenensis is an Antarctic marine mollusc possessing a wide range of natural products, including many terpene glycerides, used for defense against potential predators. The ability to produce those chemicals is paramount for its survival and it could be compromised by climate change or enhanced by predators. Therefore, we studied here the impact of rising temperatures and predator's presence on the chemical defense of this slug. Nudibranchs were collected at Deception Island (South Shetland Islands, Antarctica). The experiments were carried out in water tanks with three different controlled temperatures: 0ºC, 5ºC and 10ºC, as well as a control, and 5 replicates each. For predation pressure experiments, the omnivorous macropredator, the sea star *Odontaster validus* was placed with the nudibranchs in the tanks. After 4 weeks samples were frozen and transported to the University of Barcelona for further analysis. Chemical extractions with organic solvents and HPLC were used to assess the chemical variations between the different treatment groups. Any variations respect to the controls may affect the survival of the species and thus, affect the interactions in their habitat and by extension, the ecosystems where these animals live in.

Keywords: Marine chemical ecology, marine benthos, climate change, temperature stress, predation, bioactivity.