

Chemistry and Climate

New challenges for an old scientific discipline

Tromsø, Norway: 03-04.10.2011

FRAM – High North Research Centre for Climate and the Environment

A workshop on challenges and research priorities in modern international chemistry research in the context of the currently observed “global climate change”

Organisation committee:

Prof. Dr. Roland Kallenborn, Norwegian University of Life Sciences (UMB), Norway

Prof. Dr. Montserrat Filella (ACE President), University of Geneva, Switzerland

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Jointly organised by the Norwegian Chemistry Society (NKS), Group for Analytical Chemistry (FAK) and the European Association for Chemistry in the Environment (ACE)



Preface

The NKS-group for Analytical Chemistry, in co-operation with the European Association of Chemistry and the Environment (ACE), is glad to welcome you to our two-day seminar dealing with all aspects of “Chemistry and Climate”, held in Tromsø (Norway), from 3 to 4 October 2011 at the FRAM Centre for Climate and Environmental Research.

Chemistry research, in all its comprehensive aspects, has developed into a significant scientific tool to preserve, facilitate and monitor many facets of the living conditions and the standard of life of Western societies. As many other scientific disciplines contributing to the societal developments of our modern world, chemistry, in all its scientific aspects, also has to respond with scientific priorities and technology developments to the current challenges associated to global climate change. This includes the entire array of chemical developments, inter alia environmental chemistry, sustainable product development in chemical industries, pharmaceutical developments for the control of disease vectors, etc. We have the ambition to discuss in our workshop the progress needed in chemical research to cope with these complex challenges.

In addition to this, in the framework of the ongoing “International Year of Chemistry 2011”, we will offer an inspiring forum to discuss the current state of awareness, the scientific consequences and the appropriate research priorities of modern chemical sciences, as well as the expected requirements for future performing chemists.

Welcome to our meeting!



Montserrat Filella Dorte Herzke Roland Kallenborn

Workshop Programme

Location: FRAM – High North Research Centre for Climate and the Environment

Address: Hjalmar Johansens gata. 14, NO-9296 Tromsø, Norway

Monday, 03-10-2011

Time	Activity/ presentation	Author
0900 - 1000	Reception and Registration/ coffee break	Kallenborn/ Herzke/ Filella
1000 - 1010	Welcome: NKS and ACE	Kallenborn/ Herzke/ Filella
Lectures	Arctic issues	
1010 - 1050	Hexachlorocyclohexane (HCH) and mercury pathways within the Arctic cryosphere	Gary Stern
1050 - 1110	Health break	
1110 - 1130	Influence of climate and biomagnification in species of Arctic zooplankton	Ingeborg Hallanger
1130 - 1150	Factors of change: Using trophic magnification factors (TMFs) to assess changes in POP bioaccumulation in Arctic food webs	Nicholas Warner
1150 -1210	Influence of food web on spatial variation in mercury concentrations in Polar Bears (<i>Ursus maritimus</i>)	Heli Routi
1210 - 1300	Lunch break	
	Environmental processes	
1300 - 1340	Chiral chemicals as tracers of sources and fate processes in a world of changing climate	Terry Bidleman
1340 - 1400	Impacts of climate and feeding conditions on the annual accumulation (1986-2009) of persistent organic pollutants in a common terrestrial raptor	Jon Ove Bustnes
1400 - 1420	Temporal trend and spatial differences of perfluoroalkylated substances in harbour porpoise (<i>Phocoena phocoena</i>) livers from Northern Europe	Sandra Huber
1420 - 1440	Atmospheric transfer of important trace elements from Ocean to Land: how might it be affected by climate change?	Eiliv Steinnes
1440 - 1500	Health break	
1500 - 1600	Posters presentations and discussions (5+2 minutes (questions) / 5 slides)	Poster authors
1600 - 1700	Final remarks/ discussions	Kallenborn/ Herzke/ Filella

Tuesday, 04-10-2011

Time	Activity/ presentation	Responsible
0900 - 0910	Introduction and technical remarks	Kallenborn/ Herzke/ Filella
	General chemistry aspects	
0910 - 0950	Chemistry and Climate: A scientific discipline in change	Kenneth Ruud
0950 - 1010	Educational requirements and related aspects: An Environmental Chemistry perspective	Roland Kallenborn
1010 - 1030	Health break	
1030 - 1050	The photodissociation of ozone in the Chappuis band: a theoretical study	Clemens Woywod
1050 - 1110	Integrating climate research topics into the basic chemistry curriculum	Richard Engh
1110 - 1130	Contaminants in polar regions – COPOL	Anita Evenset
	Marine and freshwater processes	
1130 - 1210	Inland water transformations of terrestrial organic carbon during transport from soil to sea	Lars Tranvik
1210 - 1230	Temporal evolution of organic carbon concentrations in some prealpine lakes	J.C. Rodriguez-Murillo
1230 - 1330	Lunch break	All
1330 - 1500	Discussions, work distribution, white paper, publication plans	All
1500	Final comments and adjourn	Kallenborn/ Herzke/ Filella

Poster presentations

Presentation	Author(s)
On long term freshwater DOC studies	M. Filella, J.-C. Rodriguez-Murillo
A biomarker approach to monitor the influence of climatic change on contaminant input to receiving waters through effluent discharge	K.H. Langford, K.V. Thomas
Persistent organic Pollutants (POPs) in background Arctic surface snow and in vertical snow profiles. POP deposition and accumulation in snow samples from GEO Summit (Greenland) and Ny-Ålesund (Svalbard).	T. Weel Jensen, R. Kallenborn
Historical contamination from earlier IPY Research: The Kinnvika Story	R. Kallenborn, E. Harris, B. Luks
Atmospheric persistent organic pollutants (POPs) levels as chemical indicators for climate change in the Arctic. New data from the atmospheric POP monitoring at Zeppelin mountain (Ny-Alesund, Svalbard)	R. Kallenborn, S. Manø

Chiral chemicals as tracers of sources and fate processes in a world of changing climate

Terry Bidleman

Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

Phase-out of persistent chemicals under national and international protocols will shift emissions from “primary” to “secondary” sources. The latter involves remobilisation of chemicals from environmental reservoirs such as soil, oceans, lakes, glaciers and polar ice. Chiral compounds offer special advantage as tracers of environmental fate and transport processes, since enantiomers have identical physicochemical properties. Volatilisation, atmospheric deposition and achiral reactions (hydrolysis, photolysis) are not enantioselective and the proportion of enantiomers will not be changed by these processes if they are in the same chiral microenvironment. Enzymes are chiral molecules and frequently react with chiral substrates to degrade or transform them enantioselectively. For chemicals produced as racemates, the occurrence of nonracemic residues in the environment is an indicator of microbial degradation in soil and water or metabolism in higher organisms. Thus, determination of individual enantiomers using chiral-phase chromatographic methods affords the opportunity to identify chiral compounds which have been subjected to biological “weathering” in the environment. This presentation describes work by ourselves and others in using enantiomers of to trace sources and exchange processes. Throughout the talk, I will point out potentially fruitful areas of research in using chiral compounds to investigate climate-mediated processes, such as increased volatilisation due to ice cover loss in the Arctic, release from melting glaciers, and the enantiomer composition of chiral compounds in the atmosphere as an integrator of large-scale changes in metabolism in soils.

Impacts of climate and feeding conditions on the annual accumulation (1986-2009) of persistent organic pollutants in a common terrestrial raptor

Jan Ove Bustnes

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A recent analysis showed that the concentrations of various organochlorines and brominated flame retardants in tawny owl (*Strix aluco*) eggs declined (60-95%) between 1986 and 2004, in Central Norway. However, inter-annual variations in POP concentrations were great, and in this study the relationships between climate variability, feeding conditions and the annual accumulation of PCB, DDE and PBDE in eggs (n = 168) were assessed over a 24 year period (1986-2009). Winter climate

variables included the North Atlantic Oscillation (NAO) and snow conditions, whereas feeding conditions were assessed using vole abundance. The concentrations of all compounds declined between 79% (p,p'-DDE) and 86% (PBDE) over the time period. For PCB and p,p'-DDE the accumulation was positively associated with snow depth, and negatively associated with NAO (i.e. high accumulation in cold and dry winters) when vole abundance was low, suggesting trade-offs between winter severity and feeding conditions. That is, females mobilize more body fat reserves in cold winters when feeding conditions are poor, which results in increased circulating contaminant concentrations and maternal transfer to the eggs. Owls may also have been forced to feed on prey with higher contaminant loads due to restricted prey availability. For the recently banned PBDEs, the accumulation was high when NAO was low, while snow depth was positively associated with PBDE accumulation only when feeding conditions were good. This suggests somewhat different dynamics of PBDE in the environment or in the owls, compared to PCB and p,p'-DDE. However, climate and feeding conditions explained as much of the annual variation in concentrations of all POPs, as the overall decreasing trend over the 24 years. Hence, such factors should be considered in monitoring programs for POPs.

Integrating climate research topics into the basic chemistry curriculum

Richard A. Engh

Department of Chemistry, University of Tromsø, Norway

It is the physical chemistry of the atmosphere, oceans, geo- and biospheres that determine the extent and effects of anthropogenic global warming; it is the public perception of those determinants that steer public policy in democratic societies. Broad public training in basic chemistry, especially physical chemistry, should help promote clear thinking in the face of controversies like those now typical for global warming debates. By integrating climate research topics into lecture material, exercises, and examinations for physical (and general) chemistry, students are confronted with key climate data, experience the vital relevance of the chemistry disciplines, and can be trained in themes of uncertainty, causality and complexity. This knowledge is thus disseminated in the body politic. For example, the major greenhouse gasses of water, carbon dioxide, methane, and ozone provide ideal systems for teaching topics as diverse as combustion, phase transitions, supercritical properties, hydrogen bonding, pH, and infrared absorption, to name a few. When these are taught in the context of climate, students receive not only training in basic chemistry, but can be informed quantitatively about specific features of climate chemistry. It is also essential for basic chemistry training to consider simple topics in the context of systems and complexity--how uncertainty affects but does not eliminate predictivity; this most certainly applies to discussions of global warming as well. I present here a selection of basic physical chemistry topics illustrated by climate relevant examples. These include kinetics, ocean acidification, properties of gasses, energy, the global carbon budget, and so on. Consideration of examples such as these may contribute to enhancing climate awareness, first among chemistry students, and ideally in the general public as well.

Contaminants in polar regions – COPOL

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Global climate change has the potential to remobilize environmental contaminants and alter contaminant transport pathways, fate, and routes of exposure to Arctic organisms. The COPOL-project was initiated in 2007 under the International Polar Year (IPY). Its objective was to understand the dynamic range (including seasonal, annual and geographic variations) of contaminants in polar marine ecosystems, in order to better predict how possible future climatic change imposed alterations of the marine food webs will be reflected in levels and effects at higher trophic levels. To study this a “site for time” approach was selected. Different water masses will influence abiotic contaminant exposure, food web structure, food quality and energy pathways; altering the flux of contaminants through the food web. Therefore, two sites on Svalbard with different water masses were selected as study sites; Kongsfjorden (Atlantic water dominance) and Liefdefjorden (Arctic water dominance). Seawater, sediments, plankton, benthic invertebrates, fish, seabirds and seals were collected. All together about 2000 samples have been analysed for a suite of persistent organic pollutants.

Generally, low concentrations of contaminants (e.g. PCBs, pesticides, PBDEs, PFCs) were found in lower trophic level organisms from both fjord systems. However, analyses of samples collected in different seasons in Kongsfjorden shows that there are pronounced seasonal differences in contaminant levels, patterns and bioaccumulation factors in pelagic and benthic food chains. The seasonal variation may be due to changes in contaminant input from secondary sources (e.g. snow, glacial ice, terrestrial runoff), which gradually becomes more important as emissions from primary sources are reduced and climate changes facilitate remobilization of previously deposited contaminants.

Differences between the two study sites were also detected. These differences may be related to differences in physical environments, differences in phytoplankton bloom, food web structure or releases from secondary sources.

Based on data collected and published through the project concerning climate induced changes in food web structure, bioaccumulation models that can be used to predict changes in contaminant accumulation under different climatic scenarios are being developed. In a follow-up project, COPOL II, we plan to use different modeling tools, e.g. bioaccumulation models, air-transport models (FLEXPART), hydrological models (Teotil) and models combining abiotic and biotic compartments (SEDFLEX) to understand how changes in contaminant transport, revolatilization and food web structure affects POP bioaccumulation in Arctic marine food webs.

Influence of climate and biomagnification in species of Arctic zooplankton

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In a seasonal environment as the Arctic, it is important to have a good understanding of how bioaccumulation of contaminants varies with seasons to be able to differentiate between seasonal variation and possible climate change induced alterations. Zooplankton should be well suited for assessments on how climate change can alter bioaccumulation of contaminants in the Arctic ecosystem, since zooplankton reflect environmental changes in contaminant exposure faster than higher trophic level organisms. Most contaminants enter the marine food webs through the lower trophic level organisms, and zooplankton provides the link between primary production and upper trophic level organisms such as fish, seabirds, and mammals. Therefore, it is important to know the processes determining the contaminant burden in zooplankton to better understand and assess contaminant uptake and flux in marine food webs. The influence of seasons, climate and biomagnification on contaminant concentrations and patterns in zooplankton (7 species) was investigated using samples from Kongsfjorden and Liefdefjorden, Svalbard, sampled in 2007-8 in May, July and October. Seasonal variations in accumulation of contaminants were observed in the species of zooplankton, with a decrease in contamination concentrations from May to October. Differences in contaminant concentrations and patterns were observed between the two fjords. However, there may be confounding factors associated with fjords. There are a number of fjord specific characteristics that may explain the differences observed between the two fjords in contaminant concentrations such as duration of sea ice cover, domination of water masses, freshwater runoff, and primary production. These factors are all linked to seasonal changes within a year; therefore, the differences observed in species of zooplankton could be due to seasonal variation and not climate change. Within a season or fjord similar POP predatory species generally showed highest contaminant concentrations while herbivore species lowest concentrations, indicating that species of zooplankton do biomagnify contaminants.

Temporal trend and spatial differences of perfluoroalkylated substances in harbour porpoise (*Phocoena phocoena*) livers from Northern Europe

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Scientific concern about perfluoroalkylated substances (PFASs) has risen due to their global distribution, environmental persistence and bioaccumulation. In the recent years, PFASs have been detected in high-trophic biota like marine mammals, but little is known about temporal trends and long-term studies are rare. Within this study, harbour porpoise (*Phocoena phocoena*) liver samples were analyzed for ionic PFASs and perfluorooctane sulfonamide (PFOSA). The deceased or severely injured whales were caught incidentally in fishing nets or found ashore. Female juvenile (pre pubertal) animals were selected according to their weight and, if enough individuals were available, also according to their state of decomposition. A temporal trend was reconstructed for the populations in the German waters of the Baltic Sea and the North Sea from 1991 to 2008, where a total of 62 individuals were screened. In order to investigate spatial differences in exposure, distribution and levels of PFASs in liver samples from Icelandic ($n=5$) and Norwegian ($n=5$) female juvenile animals found in 2000 were compared with the populations in German waters of the Baltic Sea.

Ten analytes were detected in more than 50% of the samples, including C₆–C₈, C₁₀ perfluoroalkyl sulfonates (PFASs), PFOSA and C₉–C₁₃ perfluoroalkyl carboxylates (PFCAs). Saturated and unsaturated fluorotelomer carboxylates and short chain PFASs and PFCAs were not found. Perfluorooctane sulfonate (PFOS) was the predominant compound with a concentration range of 160 – 2425 ng/g wet weight (ww), followed by PFOSA (1 – 237 ng/g ww), perfluoroundecanoate (PFUnA, 3 – 124 ng/g ww) and perfluorodecanoate (PFDCa, 2 – 87 ng/g ww). Decreasing concentrations over time were found for PFASs and PFOSA, while, conversely, the C₉–C₁₃ PFCA concentrations increase. Contaminant concentrations were consistently higher in the Baltic Sea compared to the North Sea. Spatial differences were also found between the populations from Icelandic, Norwegian and German waters. This may be related to different PFAS levels and contamination sources within the ecosystems of the different populations. Local source contributions could originate from anthropogenic emissions, but also long range transport of PFASs via ocean currents and air has to be taken into account.

Educational requirements and related aspects related to global climate change: An Environmental Chemistry perspective

Roland Kallenborn

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The effects of global Climate Change (CC) are already affecting our daily life. Dramatic changes are expected in many regions of our world including the Arctic, where currently the lowest sea ice coverage of the past 5000 years is observed. For our western societies, the response to these challenges must be based upon scientifically sound judgments upon which again international balanced mitigation actions are put in action. Scientific experts reflecting to day on these complex scientific issues are required to respond with scientific knowledge crossing often the narrow frame of their original University educations. These educational needs,

however, are today not sufficiently implemented in the educational programs and study plans of our future scientists and researchers.

Environmental chemistry is today embedded as essential discipline in comprehensive environmental research. As environmental chemist, dealing with pollutant issues or other environment related scientific aspects, the researcher has to respond today to ecotoxicological, meteorological, geological, ecological, computer modeling and human health related topics within his research field. Thus, a broad scientific understanding of this multi-disciplinary working area is required in order to address this professional frame in a scientific balanced way. However, only few young scientists today are educated specifically for this purpose. Many early career environmental scientists (including environmental chemists) must, thus, gather this scientific strategies and experiences as postgraduate or post doctorate scientists in an additional educational efforts *ex-universitas* (based upon their personal motivation).

The presentation will outline requirements, educational priorities and future needs for the educational programs of environmental chemists specifically focusing on Climate change and consequences for human societies.

Temporal evolution of organic carbon concentrations in some perialpine lakes

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Long-term data sets of dissolved organic carbon (DOC) in rivers and lakes of Northern Europe and Northern America have revealed a clear tendency to the increase of DOC concentrations over the last 20-30 years. The concentration of DOC in waters is an important parameter linking terrestrial and marine carbon cycles. DOC is the result of various processes (carbon fixation, transport, mineralization, and sedimentation) that show a complex dependence on environmental factors as well as a strong variability at different spatial and temporal scales. Thus, it is not surprising if the main factors driving the observed variations in DOC concentration are often a matter of controversy.

However, in spite of the fact that the increase in freshwater DOC concentrations is increasingly being accepted as a widespread phenomenon, few studies have been published on the long-term evolution of DOC in temperate areas other than peatlands or forested zones affected by acid deposition. More studies in temperate areas of different characteristics may help to ascertain the generality of DOC increase.

In this study, we have analysed existing hydrology and water quality data recorded in several Swiss lakes: Geneva, Constance, Neuchâtel and Lucerne (two sampling points in Lake Geneva and Constance, one in the rest). A small, but significant, increase in DOC concentrations (TOC in the case of Lake Geneva) is observed in all, but one, of the lakes. Some possible causes will be discussed at the workshop, in particular the effect of temperature increase and the variation of DOC inputs into the lakes (both possibly related to climate change). However, the four lakes share a history of human caused eutrophication in the 1950-1980 period, followed until now by a re-oligotrophication process. These processes compete with the above-mentioned factors and may mask their effects.

Acknowledgments: The authors wish to thank the Service Cantonal de l'Écologie de l'Eau (SECOE), Geneva, Switzerland, the Commission Internationale pour la Protection des Eaux du Léman (CIPEL), and the Bundesamt für Umwelt (BAFU), Switzerland, for providing some temporal series of data for our study.

Chemistry and Climate: A scientific discipline in change

Kenneth Ruud

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Chemistry is intimately connected to climate change. The understanding of the chemistry of greenhouse gases, their fate in the atmosphere and the complicated chemical equilibria that govern the consequences of global warming, all require detailed chemical knowledge. Equally important is an understanding of the chemistry behind different means of curbing man-made emissions of greenhouse gases (CO₂ sequestration) and the consequences of the introduction of new technology. In the talk, I will highlight aspects of chemistry and climate that are currently being explored, and try to identify areas where more chemical knowledge is needed in order to address the challenges faced in climate research.

Influence of food web on spatial variation in mercury concentrations in polar bears (*Ursus maritimus*)

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Increasing emissions of mercury (Hg) in the Arctic environment and the effects of climate change on it raise a need to understand the fate of Hg in the arctic biota. Hg concentrations show wide geographical variation within circumpolarly distributed arctic species, for example polar bears. Several studies have documented the highest concentrations of total Hg in polar bears from the Beaufort Sea and lowest in southern and western Hudson Bay and the Chukchi/Bering Sea. The underlying reasons for these geographical differences are not completely understood. Trace element concentrations in arctic biota may be influenced by both physical factors including river output and geology as well as biological factors such as underlying food web structure that constitutes the diet. We hypothesized that polar bear subpopulation differences observed in Hg concentrations [1] are affected by variation in polar bear food web among subpopulations. In order to test the hypothesis, we investigated total Hg and dietary descriptors (nitrogen and carbon stable isotopes ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) and adipose fatty acid (FA) composition) in 121 specimens sampled from ten different

locations in Alaska (Chukchi-Bering Seas), Canada and East Greenland during 2005-2008. Concentrations of total Hg were positively related to $\delta^{15}\text{N}$ indicating that polar bears feeding at higher trophic level accumulated more total Hg compared to polar bears feeding at lower trophic level. Negative relationship between total Hg and $\delta^{13}\text{C}$ suggests polar bears feeding on areas with high input of terrestrial carbon by rivers accumulate more Hg than bears feeding on areas with low freshwater input. Hg concentrations were also positively related to FA20:1n-9, which is uniquely synthesized in *Calanus*-copepods. This result rises a hypothesis that *Calanus* may be an important link taking up Hg in the food web. The geographical trends for Hg corrected for the dietary tracers were significantly different compared to the non-corrected trends suggesting spatial variation in food web structure may affect observed geographical trends in Hg concentrations.

Atmospheric transfer of important trace elements from ocean to land: How might it be affected by climate change?

Eiliv Steinnes

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Iodine and selenium are essential to man, but their supply is often restricted by low contents in soils. It has been shown that soils in coastal regions are enriched in iodine as well as selenium relative to areas farther inland (1,2). The reason for this is apparently biological processes in the ocean: As a part of their metabolism algae strongly concentrate iodine and selenium from the seawater. The elements are released from the organisms as respectively methyl iodide (CH_3I) and dimethyl selenide ($(\text{CH}_3)_2\text{Se}$). These substances are volatile and insoluble in water and therefore released to the atmosphere (3,4), where they may be transported to land and deposited, possibly after photochemical transformation to other forms.

Insufficient supply of iodine and selenium has lead to severe health problems in many regions of the world in populations depending mainly from locally produced food. Most frequently these problems occur in areas far from the ocean. Corresponding problems are well known in domestic animals. The natural ocean-to-land transfer of these elements is therefore important to human and animal health globally.

Another possible example of transfer from ocean to land is indicated from atmospheric deposition surveys in Norway over the last 35 years based on moss samples. It appears that the mercury deposition is generally higher in coastal areas than in areas farther away, which indicates that the ocean might be a source of mercury as well to coastal regions. Further research is required to verify if this is generally the case and what processes might be responsible.

As the biological activity in the ocean varies with temperature, it may be hypothesized that climate change might influence the extent of these processes in the areas affected. This could in turn interfere with the living conditions of human and animal populations in these areas.

References

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Hexachlorocyclohexane (HCH) and mercury pathways within the Arctic cryosphere

Gary Stern

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As a dynamic interface between the atmosphere and the ocean, the sea-ice environment in the Arctic could potentially play a major role in affecting HCH and Hg bioaccumulation in Arctic marine ecosystems. As part of the International Polar Year (IPY) Circumpolar Flaw Lead (CFL) System Study, our group carried out an extensive study on the role of the sea ice environment on these chemicals in the southern Beaufort Sea of the Arctic Ocean from February–July 2008. Results will be discussed.

Inland water transformations of terrestrial organic carbon during transport from soil to sea

Lars J. Tranvik

Limnology, Uppsala University, Sweden

Inland waters receive substantial amounts of organic carbon (OC) from surrounding terrestrial ecosystems, mainly in the form of dissolved organic carbon (DOC). A large fraction of this OC is mineralized in lakes, resulting in methane and carbon dioxide emissions, and the rest is either stored in the sediments over geological timescales, or transported downstream towards the sea. Recently, it has been shown that these processes result in fluxes of importance in the global carbon cycle. It is therefore important to understand what regulates OC cycling in inland waters, and how the inland water carbon cycle may change with climate and anthropogenic influence. This presentation will give an overview of transformations of OC in inland waters, such as flocculation and sedimentation, and microbial and photochemical mineralization. I will also discuss the constraints on the metabolism of OC, and how they may shift in the future; e.g. temperature effects on the mineralization of OC. In addition, I will present an attempt to upscale from local processes to the global inland water carbon cycle, and discuss the importance of different processes and fluxes.

Factors of change: using trophic magnification factors (TMFs) to assess changes in POP bioaccumulation in Arctic food webs

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Greater influence of Atlantic water into Arctic regions can potentially increase persistent organic pollutant (POP) influx from more-contaminated equatorial regions. In addition, boreal species introduced as a result of water mass changes can cause alterations in food web structure, energy pathways, and POP uptake in Arctic food webs. Trophic magnification factors (TMFs) represent a useful tool in assessing the effects of climate change on POP biomagnification in Arctic food webs. Representing the average factorial change in lipid normalized chemical concentration per trophic level, TMFs account for changes in both trophic structure and POP concentration. However, seasonality in Arctic food webs can significantly affect TMF calculations leading to incorrect interpretations in POP accumulation. Sampling and TMF calculations for the Kongsfjorden (Svalbard, Norway) pelagic food web was carried out in May, July and October of 2007. Highest TMFs were found within July for most POPs, which was attributed to seasonal changes in trophic positions and POP concentrations within the food web. Higher TMFs in July were associated with higher degree of boreal species present within the food web, indicating that future warming and invasion of boreal species may result in increased food web biomagnification. TMFs utility to distinguish differences in POP biomagnification caused by changes in the physical environment was also assessed. In July 2008, pelagic food webs of Kongsfjorden and Liefdefjorden (Svalbard, Norway) were sampled, each being influenced by different ice cover and water mass conditions (Atlantic (Kongsfjorden) vs. Arctic (Liefdefjorden)). TMFs were significantly different for several POPs (PCB 118, -153, α -HCH and *cis*-chlordanes) between fjords. TMFs for PCB 118 and 153 were significantly higher in Kongsfjorden and may be influenced by changes in seabird feeding ecology caused by the dominance of Atlantic water in this fjord. Opposite trends were observed for α -HCH and *cis*-chlordanes with TMFs being significantly higher in Liefdefjorden compared to Kongsfjorden. This may be attributed to the presence of ice cover during the winter in Liefdefjorden, which will hinder volatilization and increase exposure of more volatile POPs (i.e., α -HCH and *cis*-chlordanes) compared to Kongsfjorden which remained ice-free throughout the winter of 2007-2008.

The photodissociation of ozone in the Chappuis band: a theoretical study

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The nonadiabatic photodissociation on the coupled potential energy surfaces of the 1^1A_2 and 1^1B_1 states of ozone has been investigated theoretically in the late 1990s [1,2,3]. Extended multiconfigurational electronic structure and quantum dynamical calculations have been performed to model the wave packet dynamics and to simulate the associated Chappuis absorption band as well as the observed product state distributions.

Taking this important reaction as an example, a brief overview of the methodology and of the results of this earlier study will be given and reference to recent developments in electronic structure and quantum dynamical methods that can be of relevance for the theoretical description of atmospheric photochemical processes will be made.

References

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On long-term freshwater DOC studies

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Inland waters have often been disregarded as relevant parts of the carbon cycle. However, the rate of burial of organic carbon (OC) in inland water sediments exceeds OC sequestration in the ocean floor and dissolved organic matter (DOC) is increasingly being recognized as a significant supplier of carbon to oceans. Over the past decades, an increase in DOC concentrations has often been reported in rivers of the Northern Hemisphere but driving mechanisms are poorly understood. Observations have been attributed to changes in: air temperature, solar radiation, precipitations, soil moisture, timing of ice break-up and snowmelt, length of seasons, land use, and atmospheric deposition chemistry (CO₂, N, S concentrations).

In this study, we have collated results from articles dealing with long-term changes in surface water DOC and attempted their critical evaluation from several points of view.

Regarding the type of systems studied, we have observed that: (i) data come from a limited number of countries; (ii) not all datasets are independent; (iii) all studies deal with water draining peat or forested areas; (iv) a few studies include data from climatic zones other than boreal systems; (v) many data come from networks devoted to the monitoring of acidic systems when DOC changes in such systems might be due to reasons linked to acidification recovery and not be generally applicable.

Concerning the methodological approach: (i) few studies detail the method used for DOC determination; (ii) no study attempts the quantification of the different types of natural organic matter (NOM). This is particularly unfortunate because the quantification of different types of NOM according to their lability might help to understand the OC response to environmental stressors (p.e., increases in refractory NOM may not be significant as a new source of CO₂ to the atmosphere as it will end up in the ocean or buried in the sediments).

Persistent organic pollutants (POPs) in background Arctic surface snow and in vertical snow profiles. POP deposition and accumulation in snow samples from GEO Summit (Greenland) and Ny-Ålesund (Svalbard)

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As a part of a collaborative project between NILU, UNIS, The University of Aarhus and the GEO-Summit research station, snow samples were collected during separate field campaigns near Summit Station, Greenland (June/July 2006 and 2007) and

Zeppelin atmospheric monitoring station, Svalbard (April 2008). Samples were prepared for analysis of 31 polychlorinated biphenyls congeners (PCB) and current and previously used pesticides (α -HCH, γ -HCH, cis-chlordane, trans-chlordane, aldrin, dieldrin and α -endosulfan). Chlordanes were measured at very high concentrations at Summit. HCH and mirex was measured at slightly lower concentrations but still high compared to studies at similar locations. The pesticide results are also highly affected by significant background levels in the field blanks, and it is, thus, likely that the samples were contaminated from contamination (local or transport). PCB levels ranged from 19 pg/L to 1,7 pg/L in surface snow (0- 10 cm) at Summit, and around 2 pg/L in surface snow (0- 40 cm) at Zeppelin. The concentrations were positively correlated with the surface snow temperature, and showed highest concentrations during periods of high air humidity, low solar radiation and in connection with precipitation (deposition events). During periods with high radiation, the concentrations decreased, indicating that increased sublimation of the surface snow enabled remobilisation of the compounds. Vertical snow profile samples collected from snow pits showed increasing concentrations at a level between 30 - 70 cm (Summit) and 40 - 80 cm (Zeppelin). Above and below these levels concentrations were significantly lower. These findings indicate that PCBs migrate and accumulate at certain layers within the snow pack. This hypothesis is supported by a significant increase of higher chlorinated congeners observed over the same depth range. In the Summit Snow pit the Σ 31PCB concentrations ranged from 11 pg/L to 1 pg/L, and in the Zeppelin snow pit from 88 pg/L to 2 pg/L. Seasonal variations of atmospheric contaminant levels (comparison with air monitoring data from the Zeppelin mountain monitoring site) and the here presented snow concentrations did not show any statistically significant correlation. This further supports the suggestion of chemical migration within the snow pack. Given the low temporal resolution of the snow pack samples and the lack of atmospheric data from Summit, it is difficult to prove anything conclusive based on the here presented data.

A biomarker approach to monitor the influence of climatic change on contaminant inputs to receiving waters through effluent discharges

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One of the major global environmental concerns is the effect of climate change on the environment. In many countries it has been predicted that with increased rainfall there will be an increase in storm water overflow events at wastewater treatment works, resulting in the more frequent discharge of untreated sewage to receiving waters. This has already been observed in the Oslofjord, Norway. In recent years there has been an increased focus on pharmaceutical compounds in wastewater effluent and receiving waters. The β -blockers atenolol, metoprolol and propranolol, and some of their metabolites, have been measured through the wastewater treatment system and been detected in the Oslofjord and some freshwater systems. To date they have been measured by liquid chromatography - tandem mass spectrometry (LC/MS/MS). However, β -blockers exist as 2 stereoisomers but using LC/MS/MS does not separate the isomers which is adequate for general screening and quantification. However,

using gas chromatography-mass spectrometry will separate the isomers which can be a useful tool for assessing the presence of untreated effluent. These 2 isomers are chemically stable but susceptible to biodegradation. The 2 chiral forms exist in specific ratios when they are excreted from the body and this ratio changes with degradation during wastewater treatment. Measuring the ratio of the chiral isomers of these compounds will enable us to determine the extent of storm water overflow. From the data collated it will be possible to map the extent of contamination and to predict the fate of other contaminants we know are discharged through wastewater streams into in the aquatic environment during high rainfall events

Historical contamination from earlier IPY research: The Kinnvika Story

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As a co-operation between the Polish Academy of Sciences and the University Centre in Svalbard (UNIS), this study investigated the distribution and sources of polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) contamination at Kinnvika station (N 79°58'46.1" E20°07'18.1"), established as research station under the international Geophysical Year (IGY 1957-58). The research program at the station was abundant shortly after IGY (1959). The Kinnvika station (Nord-Austlandet) was re-opened again for geophysical and biological research activities under IPY (2007-2009). Around 60 surface soil samples were collected in the vicinity of the station for contaminant analysis from scientists of the Polish Academy of sciences. All samples were prepared and analysed for PAH and PCB contamination at UNIS. As a direct result of this first survey, it was concluded that the PAH background of the area showed evidence of natural and anthropogenic input consistent with the local geology and regional pollution sources. Hot spots with high anthropogenic contamination for both PAH and PCBs were identified, around 50 years after the end of the official research activities. The results showed clearly that the Kinnvika area remained highly contaminated from past IGY activities. The spatial distribution of the contamination was also examined, and it was found that the contamination spread only a limited distance, and less sorbed compounds were more mobile than highly sorbed chemicals. Thus, the most lipophilic compounds remain in the highest levels in the Kinnvika soils.

Atmospheric persistent organic pollutants (POPs) levels as chemical indicators for climate change in the Arctic. New data from the atmospheric POP monitoring at Zeppelin mountain (Ny-Alesund, Svalbard)

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Persistent organic Pollutants (POPs) have been monitored at the Zeppelin station (Ny-Ålesund, Svalbard, Norway) for almost two decades. A core program including 4 cyclodiene pesticides, 2 hexachlorocyclohexane-isomers (HCH), hexachlorobenzene (HCB), 6 dichlorodiphenyltrichloroethane derivatives (DDT) as well as 33 polychlorinated biphenyls (PCB) has been performed during the entire monitoring period. As a part of the ongoing Arctic Monitoring and Assessment Programme (AMAP) a temporal trend evaluation has been performed for the entire monitoring period (1993 – 2007) using digital filtration (DF) as statistical tool developed by Environment Canada. A first evaluation revealed that during the past 8-10 years an increased frequency of atmospheric long-range transport episodes occurred for a series of monitored organic contaminants. Becker et al (2008) identified a clear correlation between the characteristic patterns of the Arctic Oscillation (AO) and the variability of the HCH concentrations found for Zeppelin air samples. Due to DF assessments for most of the POPs downward trends have been established. However, for the volatile hexachlorobenzene (HCB) as well as for selected PCBs levels are increasing during the past 4-5 years. These first results from the Zeppelin mountain POP monitoring program indicates direct changes in sources, and/or distribution processes and can be considered as first scientific proven early warning signs for the influence of ongoing climate change on the distribution and remobilization patterns for atmospheric pollutants.

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