
Does biology or chemistry determine the availability of toxic metals in soils and sediments?

Professor Bill Davison from Lancaster University, this year's ECG Distinguished Guest Lecturer, summarises the presentation he gave to the ECG at The Linnean Society of London in March 2003.

Environmental chemists and biologists have long known that they cannot study their subjects in isolation. The linkages between chemical and biological processes are key to a fundamental understanding of many environmental systems. This is particularly true in soils and sediments where chemical transformations are usually dependent on microbial activity and solute supply is easily limited.

Transport of solutes in soils and sediments is dominated by diffusion. When considering supply to plant roots or to microorganisms, the critical diffusional distance where gradients are steep is about 1 mm (Barber, 1995). Therefore to appreciate fully how the chemical supply operates measurements must be made on the same or smaller scale. The work of the groups at Aarhus and Bremen, led by Revsbech and Jørgensen, on the development and application of microelectrodes has led the way with respect to high-resolution measurements of oxygen and nutrients. During the 1990s we developed at Lancaster the technique of DGT (diffusive gradients in thin films) that can provide sub-mm scale information on trace metals (Davison and Zhang, 1994).

In DGT metals are trapped on a binding agent (Chelex resin) after they have diffused through a layer of gel of well-defined thickness. The simple, plastic devices are deployed for a known time (hours to days) and the accumulated metal is measured on retrieval. When they are deployed in sediments, or soils with high moisture content, the removal of metal by the Chelex causes a depletion of metal in the soil solution adjacent to the device. If the metal in soil solution is in dynamic equilibrium with the metal on the soil particles, it will be released

into solution, counteracting the depletion. The balance between removal by DGT and resupply from the solid phase determines the extent of depletion in solution and the concentration, C , at the interface between the soil and the device. The well-defined geometry and properties of the diffusion layer allows calculation of the mean concentration of metal at the surface of the device during its deployment, C_{DGT} , from the measured accumulated mass.

A dynamic, numerical model of the DGT-soil system, DIFS (DGT Induced Fluxes in Soils), has shown how the concentrations of metals in solution, and in associated solid phases, change with time (Harper et al., 1998). This depends on the kinetics of release from solid phase to solution and the size of the solid phase pool. For most situations, depletion of metal, and therefore the effect on the soil, does not extend beyond 1 mm, even for deployments in excess of a day. DGT has been used for different times, to provide the first measurements of the solid phase pool size and the kinetics of release in relatively undisturbed soil.

The major way that a plant perturbs the metal chemistry of the soil system is by removing metal. DGT does exactly the same thing. Therefore, it can be used as a surrogate for this plant process. C_{DGT} is determined by both the concentration in soil solution and its resupply from the solid phase. The effective solution concentration, that DGT or a plant experiences, is enhanced by this solid phase supply. This effective concentration, C_E , can be calculated directly from C_{DGT} as measured by DGT. A series of studies from around the world have shown that C_E correlates extremely well with concentrations of metals in plants for a wide range of metals and soil types (Davison et al., 2000; Zhang et al., 2001). As DGT responds only to the chemical and physical processes in the soil, it follows that these are the major processes controlling plant uptake. Therefore, in this case, the chemistry of the 1 mm layer of soil adjacent to the uptake surface (the roots of the plant) controls the acquisition of metals by plants.

DGT can be configured into thin, plastic probes that may be inserted into sediments. On retrieval the binding layer can be sliced into thin strips prior to analysis, or it can be dried and analysed by laser ablation ICP-MS at any spatial resolution down to 30 microns. The resulting vertical profiles of metals in sediments show classic changes in concentration associated with redox zones, but additionally there is often fine structure on a scale of about mm (Zhang et al., 1995). Highly localised remobilisation of Zn and Mn has been observed at the surface of a microbial mat (Davison et al., 1997). Measurements in two dimensions in sediments have shown that the spiky signals are due to release of metals from highly localised, approximately spherical microniches (Davison et al., 1997; Fones et al., 2003). A combined probe that measures sulphide and metals simultaneously showed that metals could be released concomitantly with sulphide from the organic matter that fuels sulphate reduction or from iron oxides that are simultaneously reduced (Motelica-Heino et al., 2003). This suggests that within the microniche there is a consortial microbial community that facilitates the different chemical transformations. Outside the microniche chemical control takes over as metals and sulphide are removed according to the solubility of fresh sulphide phases.

Whether or not microniches involve sulphate reduction, organic matter must fuel them. Translocation of parcels of reactive organic matter to depth within the sediment can only be brought about by macrobenthos. Decomposition of the parcel of organic matter is then microbially mediated. Clearly then, in this case, the biology is controlling the chemistry.

The precise nature of chemical and biological interactions can only be appreciated if measurements are made on the correct scale. DGT is a good surrogate for plant uptake because both plants and DGT perturb the soil system on the same scale (ca. 1 mm) and consequently consider similar rates of

supply. Information gleaned from DGT is then directly relevant to plant uptake. Metals released from microniches of presumably microbial colonies are only observed if measurements are able to detect their short range (ca. 1 mm diameter), near spherical distribution. To truly appreciate the details of chemical-biological interactions, it is necessary to study these highly localised environments. This new understanding can then be used to inform larger scale models and practical problems. For example the power of DGT as an assessment tool for potentially bioavailable metal is greatly enhanced by the firm base of underpinning scientific understanding.

References

Barber, S. A. *Soil Nutrient Bioavailability; a Mechanistic Approach*, Wiley, New York, 1995.

The EU's Water Framework Directive

In the first of two talks at the half-day symposium, which accompanied this year's ECG DGL, **Professor Brian Moss** from the School of Biological Sciences at University of Liverpool, spoke on the opportunities offered for improving the coastal and freshwater environments by the European Water Framework Directive.

Introduction

We are on the threshold of using some of the most revolutionary new legislation, the European Water Framework Directive, ever to improve our coastal and freshwater environments. Yet it may be undermined by government conservatism, commercial vested interests, civil service lack of flair, and the historic baggage of water management in the UK. It will involve much greater absolute involvement by both chemists and biologists, though the relative role of chemists will decrease a

little. Natural waters are enormously complicated because of the pre-eminence of living organisms in modifying the chemical template provided by the underlying geology. They are by no means simple chemical systems. The Water Framework Directive recognises this: it requires major changes in the way we monitor and manage natural waters. At present in the UK we do not even do half a job, and the maps produced by Departments of the Environment over the past twenty years showing apparently steady improvements in water quality are grossly misleading at best when it comes to a comprehensive view of the state of our habitats.

The Water Framework Directive

The Water Framework Directive is long and apparently complicated but in principle it is simple. We must start to manage whole catchments (River Basins in the phraseology of the Directive), not just the water-filled rivers and lakes (for whatever happens in the catchments determines to a large extent what happens in the lakes and rivers); we must reduce the concentrations of a specified list of

highly toxic substances to below the detection levels of the most sensitive methods available; and we must determine the ecological quality of all our aquatic habitats according to a scale from 'high' (virtually no human impact) through 'good' (slight deviation from 'high'), 'moderate', 'poor' and 'bad'. Then we must restore all our habitats (subject to some derogations) to good ecological status by 2015. In contrast, at present we have little legislation for regulating land use in catchments, we allow specified levels of toxic substances to persist on the basis of toxicological tests which, although repeatable in the laboratory, may have little relevance to what happens in complex ecosystems, and we monitor water quality, largely chemically, rather than ecological quality. Furthermore we monitor it essentially in respect of gross organic pollution, a problem of nineteenth century origin, now largely solved, and ignore several much larger modern problems.

The key to the Water Framework Directive is restoration T*t reC8ch larger5sn e

within the detailed provisions stated in Annexes to the Directive, even though these lag somewhat behind current ecological understanding. The Directive says we must first establish a typology, a geographical pigeonholing of different sorts of habitats, and then for each of the categories we must define the conditions for high quality sites. These parameters must include, for example in rivers, invertebrates, aquatic plants and fish, the physical structure of the habitat, and water chemistry and we must then prescribe what is meant by lesser degrees of status using the same system. This will mean using perhaps twenty or thirty variables, mostly biological, compared with the current five or so, largely chemical. A major problem is that tangible high quality sites are extremely scarce and probably absent in the more populated parts of Europe, including the UK. However, we are allowed to use a variety of approaches, including expert judgement and historical records, to establish what we mean by high quality conditions.

What is a river of high ecological status like?

For rivers, for example, we can do this from studies of north-temperate systems that have not been so severely damaged by engineering operations in the interests of hydroelectric generation, flood control, agriculture and waste disposal as those in the UK. I will take such a generalised river to make the points. This pristine river will have a catchment covered with natural vegetation, mostly forest, which will retain and recycle soil nutrients so that even in soft rock areas, the phosphorus and nitrogen concentrations in the water will be very low (a few micrograms for phosphorus, a couple of hundred micrograms of nitrogen at most). The upper reaches of the river will be overhung with forest and even as the river widens, there will be a great deal of tree debris in the channel. The debris and the rocks will accumulate leaves and small branches in many small, and some large, temporary debris dams.

This material is the main source of energy for the ecosystem of the upstream river. It is poor in nutritional quality, however, because the forest, before shedding them, will have translocated valuable nutrients from the leaves into trunks and roots for

re-use the following spring. However, the leaf debris in particular is colonised by a specialist group of fungi, the hyphomycetes, capable of absorbing nitrogen and phosphorus from low concentrations and converting the cellulose and lignin of the debris to fungal protein. The colonised leaves are then fed upon by invertebrates in a group called the shredders, which include freshwater shrimps and the larvae of crane flies ('daddy long-legs'). These tear the leaves apart as they seek out the fungal protein. They are messy feeders and create a stream of fine particles, many of them faecal material, which passes downstream.

Downstream, as the river widens and more light penetrates the forest canopy, diatoms and other algae will grow on the bed rocks, again drawing on the scarce dissolved nutrients in the water. Such algal films are fed upon by another group of invertebrates, the scrapers, such as freshwater limpets and mayfly nymphs, which also dislodge particles to enter the flow. The fine particles from shredders and scrapers as well as material washed in from the catchment become colonised by micro-organisms, which again convert refractory into much more palatable material. They are subsequently either filtered from the current by invertebrate collectors with nets or filtering limbs – blackfly larvae or caddis nymphs, for example, or collect in the quieter nooks of the channel, where burrowing invertebrates like midge larvae and oligochaete worms feed on them. In turn these invertebrates are eaten by small fish or larger invertebrate predators so that there is a major link between the catchment forest and the production of the river community.

Salmon, bears and nutrients

However, there is a much more exciting twist to this otherwise mundane story of food webs. North-temperate rivers in their pristine state support populations of big salmonid fish. These fish are migratory. They are born in the rivers but migrate to the sea after a year or so, spending several years as predators on other fish in the Atlantic or Pacific Oceans, accumulating nutrients in their bodies. Later they move back to the river system where they themselves were born,

recognising it from the subtly different water chemistry of every river, despite much dilution in the estuaries and coastal waters. They are unconsciously better chemists than we are. Once they enter the river systems, the salmon do not feed but use up a lot of stored energy on migration. Some die before reaching the spawning grounds and all from time to time congregate below waterfalls waiting for suitable conditions for the jump they must eventually make.

The carcasses and the vulnerable waiting fish are readily collected by brown bears, a major part of whose diet is made up of fresh (or slightly 'off') salmon. In turn, the bears, when they move through the forest in search of other components of their diet, such as berries or meat, excrete and defaecate and cycle nutrients ultimately derived from the sea to the forest. This we know from studies of the stable isotope signatures of nitrogen in the ocean, the fish, the bears' faeces –

Floodplain rivers

The river system changes as it reaches lower ground and has become big with the extension of its catchment. Its channel must widen to accommodate the water that comes down in winter and it makes a wide bed called the floodplain. Its summer channel also meanders to accommodate even the summer water flow. It is a grave mistake to think of such a river as unfortunately flooding what should be dry

that have been drained will, in many areas have to be reconnected to the summer channel. Even before contemplation of that will be considerable argument about how to define status categories. The Directive implies, and the current thinking of most water managers is, that there is a single set of conditions and a single collection of organisms that can be used to define ecological status in a given place. This is a reflection of previous chemically conditioned thinking. The reality is that ecosystems exist in multiple stable states and it is not possible to give a single set of conditions even for high status at a given site. Many species substitutions are likely and normal as a result of accidents of biogeography and natural random local extinction and re-colonisation. The statistical approaches that currently govern river classification on chemical bases will simply no longer work; ecological systems are much more complex than solution chemistry, though this nonetheless remains as a key component of the assessment.

These technical problems can be solved with the will to solve them. There is, alas, increasing evidence of a fifth column in Whitehall. The consultation documents issued by the Environment Agency and

the Scottish Environmental Protection Agency have already suggested the re-writing of the Directive to change the meaning of 'high' status so that standards for 'good' status can be reduced. This is undoubtedly illegal. There is strong resistance to the idea that floodplains are parts of rivers, ridiculous though this will seem to professional hydrologists and ecologists, and the most recent consultation paper from DEFRA reprints the water quality maps with the implication that these are a good basis for defining ecological status. This too is nonsense. There is opinion within the Environment Agency, reflected in the consultation documents, that what cannot be defined as precisely as a chemical concentration will simply be ignored. The upshot could therefore be merely derisory low standards, tightened point source pollution control, use of the derogation provisions to exclude many sites as too expensive to improve, concentration only on the sites designated under the European Habitats Directive as special areas of conservation and continued neglect of the wider countryside. In time there would then be prosecutions in the European Court of Justice, as there have been over the UK's failure to implement other Directives, that on Nitrates, for example, properly.

But all that takes time.

Better, if the spirit of the legislation is respected, we could have a far more interesting, stimulating and valuable countryside than the present desperately damaged one. It would be a tragedy if major changes do not come about as a result. The Water Framework Directive has much wider implications than ingdents,53asderogation The W25 Twlkn Gd

the EA pays £20 million for water sample collection each year but only £11 m for the analysis of the 3.8 million determinants associated with the 268 000 samples collected. Although the EA has a £750 m budget, only 1.3% of this is currently allocated to R&D. Hence the research necessary for the introduction

of changes in monitoring practice (particularly those related to the Water Framework Directive) will require some changes in funding priorities.

Web links for RAMP:

http://ioc.unesco.org/goos/RAMP_article.htm

<http://coexploration.org/ramp/index.htm>

Summary by **Dr LEO SALTER**,
Cornwall College,
Pool, Redruth, Cornwall

Arsenic hyperaccumulation in ferns: a review

The first report of a fern, which could accumulate arsenic, was published by Lena Ma *et al.* in *Nature* in 2001 (see *Environmental Chemistry Group Newsletter*

much academic and some commercial interest (Raskin *et al.*, 1994).

Plants growing on metalliferous soils can either take up large amounts of the metal into the above ground biomass (accumulators), or can block the transport of metals between root and shoot (excluders). Accumulator plants have the facility to concentrate metals from soils that contain low as well as high concentrations of metals. Plants that show exceptional uptake of metals are known as hyperaccumulators, the term first being used to describe plants that were found to contain over 0.1% nickel in the dried tissue (Brooks *et al.*, 1977). The threshold of 0.1% does not apply to all metal hyperaccumulation, 'hyper-accumulator' is an arbitrary term used to describe plants with the ability to accumulate at least an order of magnitude more of a particular metal than 'normal' plants. In the case of zinc, 1% of zinc in the dry plant tissue would suggest hyperaccumulation whereas for gold, 1 mg/kg of gold would indicate hyperaccumulation (Baker and Brooks, 1989).

Hyperaccumulator plants are often indigenous to particular metalliferous substrates and this feature is used as the basis for geobotanical exploration. Within the last quarter century, there have been many hyperaccumulator genotypes recorded, especially zinc and cadmium hyperaccumulators from the calamine soils of Europe, nickel and chromium hyperaccumulators from serpentine soils worldwide (and especially New Caledonia) and copper hyperaccumulators from the Copper Belt of Central Africa. However, although ferns have been noted to be growing on metalliferous substrate, no ferns have been reported in the literature as metal hyperaccumulator plants.

Hyperaccumulation of arsenic

Metalloid hyperaccumulator plants (plants that take up metalloids such as mercury, arsenic, uranium and selenium) are not as well documented as metal hyperaccumulators with the exception of selenium hyperaccumulators that were related to the occurrence of 'loco' disease in horses in the USA (Rosenfeld and Beath, 1964). Arsenic accumulation has been reported in grasses (Porter and Peterson, (1975); Meharg and Hartley-

Whitaker, (2002)). However, the first report of arsenic hyperaccumulation by a fern (*Pteris vittata*) (Ma *et al.*, 2001) created much interest among scientists
v56.ob062Iem7rc3 42e.oD(.aoed Crse1keiterest among sci7astratesu4814W)Tjbob0' dis

Arsenic in UK soils and the new intervention values

Guidance has recently been published by the UK government on the assessment of risks to human health from land contamination, including SGV's (soil guideline values) for a range of inorganic contaminants. The intervention value (SGV) for residential

References

- [1] DETR. *The Contaminated Land (England) Regulations 2000*. Department of the Environment, Transport and the Regions, London, 2000.
- [2] DETR. *The Contaminated Land (England) Regulations 2000: Annex 3, Chapter A - Statutory Guidance on the Definition of Contaminated Land*. Department of the Environment, Transport and the Regions, London, 2000.
- [3] DEFRA and Environment Agency (2002a) *Assessment of Risks to Human Health from Land Contamination: An Overview of the Development of Guideline Values and Related Research*, Report CLR7. Available from The R&D Dissemination Centre, WRC plc, Swindon, Wilts.
- [4] DEFRA and Environment Agency (2002b) Soil Guideline Values for Arsenic Contamination (SGV1). <http://www.defra.gov.uk/soil/guidelines/sgv1.htm> (http://www.defra.gov.uk/soil/guidelines/sgv1.htm).

The Loe Pool Management Forum

By Loe Pool

*THE pool glitters, the fishes leap in the sun
With joyous fins, and dive in the pool again;
I see the corn in sheaves, and the harvestmen,
And the cows coming down to the water one by one.
Dragonflies mailed in lapis and malachite
Flash through the bending reeds and blaze on the pool;
Seaward, where trees cluster, the shadow is cool;
I hear a singing, where the sea is, out of sight;
It is noontide, and the fishes leap in the pool.*

Arthur Symons
(1865-1945)

(Carvalho & Moss, 1995).

In June 1996 the Loe Pool Management Forum (LPMF) was established and four main objectives were identified (Wilson & Dinsdale, 1998):

1. To bring about a change from an algae-dominated turbid water state to a macrophyte-dominated clear water state characteristic of mesotrophy.
2. To establish more natural seasonal fluctuations in water levels and create conditions for a more diverse shoreline and submerged flora.
3. To maximise the nature conservation value of Loe Pool and its catchment.
4. To interest and involve the community in the management of Loe Pool and its catchment.

The management approaches used to achieve these objectives are discussed in this article.

Management

The Environment Agency via its system of LEAPs (Local Environment Agency Plans) is responsible for certain aspects (fisheries, flood defence, water quality, ()Tj0.7635o.ps]TJtw,18.3(i8y029 0.0Ed defence, 4,y

Pending the installation by SWW of phosphate stripping at the Helston STW the LPMF is now giving attention to the smaller RNAS Culdrose STW and to other, diffuse sources of phosphorus.

effectiveness of the carr as a pre-Pool

Water-level

Although Loe Pool was originally a mesotrophic lake with abundant underwater vegetation it is now an algae-dominated system with very limited plant growth. This has occurred principally because of nutrient enrichment but also because until recently, in order to improve dilution and inhibit algal growth, the water level in Loe Pool was manipulated in accordance with a water regime of high summer and low winter levels. Because this unnatural regime was singularly unsuccessful in inhibiting algal growth and was also detrimental to shoreline flora, it has been agreed to adjust the height of the adit weir under the bar to 3.5 m AOD in order to establish a mean water level in the Pool of 3.7-3.8 m AOD during autumn. Any threat of flooding to Helston would be dealt with by rapid lowering of the weir, (Haycock, 1999). A winter-high/summer-low regime is planned which would benefit the inundation/benthic plant communities partly because they are adapted to summer exposure and partly because they would not be submerged during periods of algal-induced stress in the Pool, (Stewart, 2000). A winter-high/summer-low regime would also benefit shoreline flora – though careful monitoring is planned to record the effect of this regime on communities on the seasonally exposed shore, (Wilson & Dinsdale, 1998).

Canalisation of the lower River Cober in 1988 (& 1946) compromised the ecology of Loe Pool and the surrounding area. First, it is thought to have initiated the drying out of one of Cornwall's largest remaining Willow (*Salix* spp.) carr areas (established during the early 20th century on the silts and clays from upriver mining activities). Secondly, continued dredging of the channel (1992, 1998) introduced Japanese Knotweed (*Fallopia japonica*) and Himalayan Balsam (*Impatiens glandulifera*) into the Willow and swamp area. Thirdly, dredging activity increased access to the Willow carr and this has damaged its conservation value. And fourthly, canalisation reduced the


Y g E i e al Che i Mee i g 2003

Wednesday 10th September 2003
At the British Geological Survey, Keyworth, Nottingham, UK
(<http://www.bgs.ac.uk/contacts/sites/keyworth/kwhome.html>)

The meeting is intended as a forum for young environmental chemists to present their research and discuss recent developments in the field. It will start at 9:30 am with coffee and registration and there will be talks, poster presentations and plenty of opportunities to mingle.

Professor Barry Smith of the British Geological Survey will be chairing the meeting and the day will include:

Forthcoming symposium

Ecotoxicology: Monitoring and Caring For Our Environment

A one day meeting on Tuesday 14 October 2003 at The Royal Society of Chemistry Headquarters, Thomas Graham House, Cambridge Science Park, Milton Road, Cambridge, UK

Organised by the RSC's East Anglia Region Analytical Division and the Environmental Chemistry Group

Every year, thousands of tons of chemicals are discharged into our environment as waste products of either industrial or household use. Not so long ago, few people cared about what effects these chemicals were having on the

environment, but that situation has changed as people have come to realise how fragile our ecosystems are and how this could affect all of us. Regulatory agencies, research institutions and responsible industrial companies are all working to develop and apply methodology to monitor, understand and prevent the decline of our environment. This meeting brings together these experts and covers many of the areas/classes of compounds of current concern.

Programme

09.45 onwards	Registration and coffee.
10.25 – 10.30	Chairman's Welcome and Introduction.
10.30 – 11.15	What is Ecotoxicology, and how are environmental standards set for things like endocrine disruptors? Dr G. Brighty, The Environment Agency, Wallingford.
11.15 – 12.00	The Fate and Effects of Veterinary Medicines in the Environment. Dr A. Boxall, Centre for Ecochemistry, University of Cranfield.
12.00 – 12.45	Pesticides in the Environment – Linking Fate & Effects, Methods and Data Interpretation. Dr K. Barrett, Consultant.
12.45 – 14.00	Lunch
14.00 – 14.45	The Biocidal Products Directive. Environmental Risk Assessment Strategies - where are we now and where are we going in the future? Dr J. Chadwick, Health & Safety Executive, Bootle.
14.45 – 15.30	Aquatic Ecotoxicology and the Marine Environment. Dr J. Thain, Centre for Environment, Fisheries & Aquaculture Science, Burnham on Crouch.
15.30 – 16.15	"Science in the box" – A Procter & Gamble Science Website to share Human & Environmental Risk Assessments & LCA to a wide range of the public. Dr E. Saouter, Procter & Gamble Public Relations Dept, Geneva, Switzerland.
16.15 – 16.30	Final Questions and Answers – All Speakers.
16.30 – 16.35	Chairman's Closing Remarks.

For further details contact Brian Woodget, Tel/Fax + 44 (0) 1438 811903, Email bwoodget@aol.com.

Registration Fees:- RSC Members £60, Non-Members £80, Students & Unwaged Members £30. To register, please complete the form below and send with a cheque made out to "East Anglia Region AD Trust" to Mr B. Woodget, 5, Meadow Close, Datchworth, Herts, SG3 6TD, UK.

Delegate Name: _____

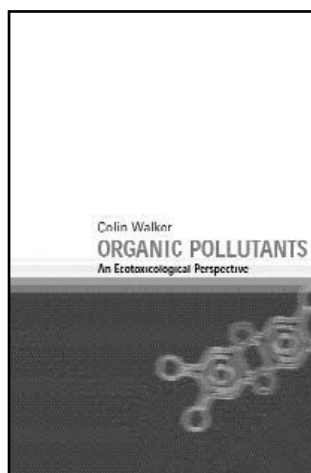
Meeting report: Coastal Futures 2003

Coastal Management for Sustainability organised its 10th Coastal Futures meeting on January 22nd and 23rd 2003 ('Coastal Futures 2003: Review and Future Trends') at the Brunei Gallery Lecture Theatre, School of Oriental and African Studies, University of London. **Leo Salter** reports on the meeting and its acronyms.

Attendance was by around 200 delegates comprised of a wide range of professionals working across many agencies and companies including statutory and non-statutory environment organisations, civil servants, industry (water, energy, resources) and local authorities with direct interests with coastal and marine issues.

The first day surveyed the developing

Recent books on the environment and on toxicology at the RSC



Organic Pollutants

An Ecotoxicological Perspective

Colin Walker, University of Reading, retired, UK

Taylor & Francis

246x174: 304pp:illus. 60 b+w line drawings