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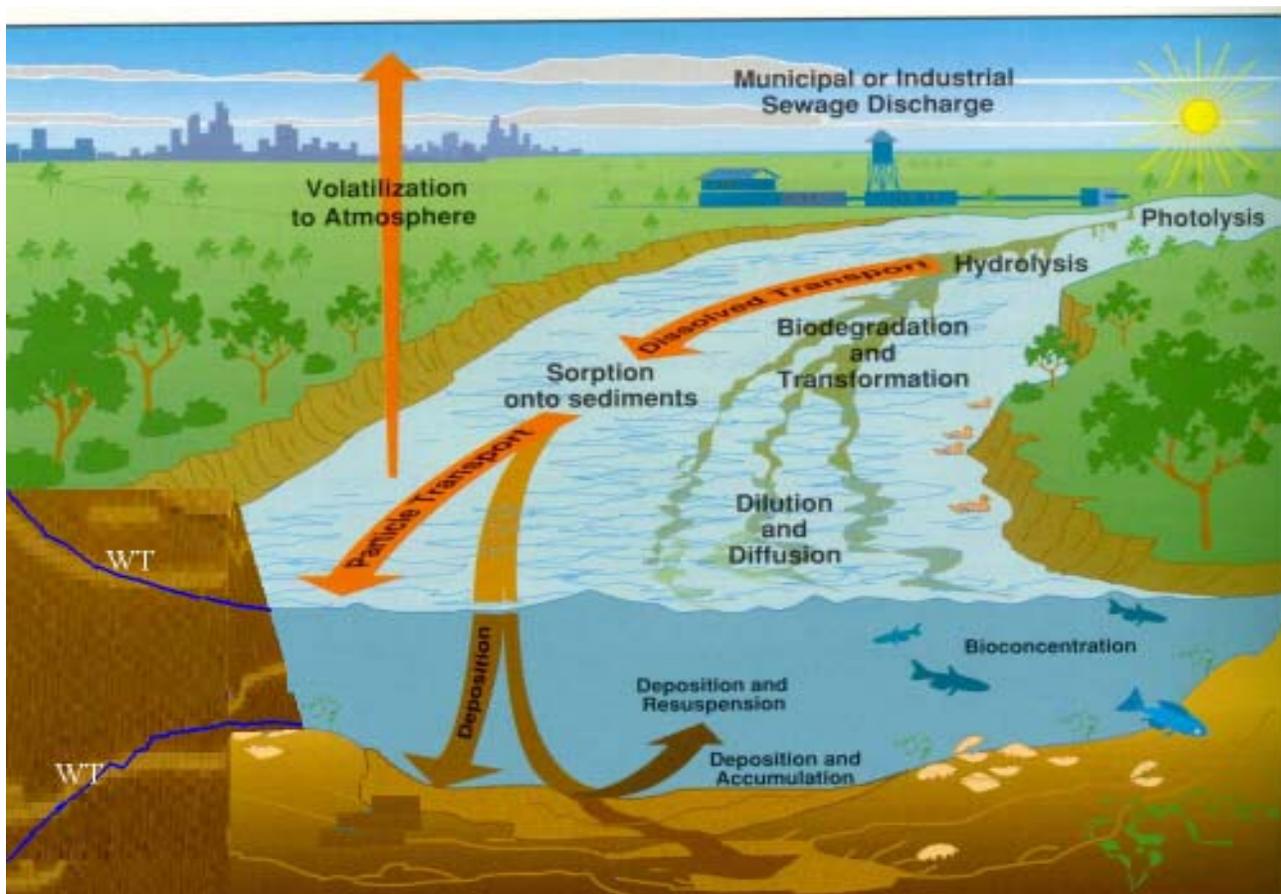
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LATEST ABSTRACTS ON BIOGEOCHEMISTRY

EDITORIAL

This volume represents the compilation of relevant abstracts published in India and also in international journals on topics related to Biogeochemistry. The front cover shows the cycling behavior of the Arsenic that is the focus of study by many investigators from many countries since it is very topical and relevant to the Indian sub-continent. After circulation of our last issue, we got good input from the readers and their comments have been taken note of while compiling this volume. This issue is for the period November 2004 to March 2005. As usual, email address of authors, wherever available, are also mentioned so that interested readers can directly get in touch with them for farther communication.

Needless to say, we have just got over the major natural water based disaster- Tsunami and a lot has appeared in press both scientific and journalistic. The key impact of this episodic phenomenon on water quality, nutrient fluxes and soil biogeochemical behavior remain to be seen over the next few years. One of the important research needs is to understand the long term implication of salt water intrusion on biological production, supply and removal of nutrients, dispersal of contaminants etc.

As more and more publications come out related to Tsunami, we will try to sort out only the scientific ones and bring out a special issue to address these research needs.

Readers comments are welcome. Happy reading!

V. Subramanian
Editor

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BIOGEOCHEMISTRY

Amelioration of Indian urban air pollution phytotoxicity in *Beta vulgaris* L. by modifying NPK nutrients

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Air pollution levels are increasing at an alarming rate in many developing countries, including India and causing a potential threat to crop production. Field experiments were conducted to examine the impact of urban air pollutants on biomass (yield) and some physiological and biochemical parameters of palak (*Beta vulgaris* L. var. All Green) that grew from germination to maturity at seven periurban sites of Allahabad city having different concentrations of air pollutants under different levels of nutrients. The 6 h daily mean NO₂, SO₂ and O₃ concentrations varied from 2.5 to 42.5, 10.6 to 65 and 3.5 to 30.8 $\mu\text{g m}^{-3}$, respectively at different locations. Levels of air pollution showed significant negative correlations with photosynthetic pigments, protein, ascorbic acid and starch contents and catalase activity of palak leaves. A significant negative correlation was found for total biomass with SO₂ ($r = -0.92$), NO₂ ($r = -0.85$) and O₃ ($r = -0.91$) concentrations. The increased fertilizer application (N, P and K) over the recommended dose resulted in a positive response by reducing losses in photosynthetic pigments and total biomass. This study proved that ambient air pollution of Allahabad city is influencing negatively to the growth and yield of palak plants. Air pollution caused adverse impact on growth and biomass accumulation of *Beta vulgaris* L. plants while higher fertility levels showed reduced yield losses.

Weathering of the Ganga alluvial plain, northern India: implications from fluvial geochemistry of the Gomati River

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In the northern part of the Indian sub-continent, the Ganga alluvial plain (GAP) feeds its weathering products to the Ganga–Brahmaputra River system, one of the world's largest fluvial systems. The authors present a geochemical study of the GAP weathering products transported by the Gomati River (the Ganga River tributary) to understand weathering processes of an alluvial plain in a humid sub-tropical climate. A total of 28 sediment samples were collected during the monsoon season and were analysed by X-ray fluorescence spectrometry for 25 major and trace elements. Bulk chemistry

of the channel, flood and suspended sediments mostly consists (>90%, >80% and >75%, respectively) of three elements; Al, Si and Fe. Major element concentrations normalised with respect to upper continental crust (UCC) show strong depletion of highly mobile elements (Na, Ca) and enrichment of immobile elements (Ti, Si). Silica enrichment in the sand fraction is probably caused by chemical weathering of feldspar. Mineral sorting during fluvial transportation acts as the single important factor that controls the geochemistry of these weathering products and also strongly influences major and trace element distribution in the individual sediment samples. Trace element (Ba, Cr, Cu, Nb, Ni, Pb, V and Zn) concentrations were strongly correlated with major element (Si, Al, Fe, Mn and K) concentrations indicating that the abundance of trace elements is controlled by the same processes that control the major element distribution in these sediments.

The GAP weathering products were geochemically distinguished as arkose to litharenite in rock classification. Chemical mobility, normalised with respect to TiO_2 in UCC, indicates that Si, Na, Zr, Ba and Sr, mainly derived from feldspar, muscovite and biotite, are lost during weathering. Iron and Zn remained immobile during weathering and were strongly adsorbed by phyllosilicates and concentrated in fine-grained sediment fractions. The chemical index of alteration indicates that the GAP has experienced chemical weathering of incipient to moderate intensity. The GAP weathering products also demonstrated a progressive incomplete alteration in the alluvial sequence made-up of the Himalayan-derived sediments. A model has been proposed to better understand weathering processes and products of the GAP in temporary storage of 50 ka in a humid sub-tropical climate.

Geochemical and isotopic anomalies preceding K/T boundary in the Cauvery basin, South India: Implications for end Cretaceous events

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CURRENT SCIENCE, VOL. 87, NO. 12, Pages 1738-1747. 2004

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The Upper Cretaceous–Lower Tertiary deposits of the Cauvery basin show prominent geochemical and isotopic anomalies preceding the K/T boundary. Analyses of stratigraphic variations of whole-rock elemental concentrations and stable isotopic compositions in the light of sedimentation history, petrography and mineralogy of the rocks reveal that these anomalies may be due to increased detrital influx caused by sea-level and climatic changes, Deccan volcanism and release of volatile gases from buried hydrocarbons, presumably gas hydrates. Comparison of these interpretations with that of K/T sites located in Guatemala, New Mexico and Israel re-vealed that these interpretations are in conformity with records on gradually increasing environmental stress during Upper Cretaceous that culminated with two major catastrophic events such as bolide impact and Deccan Trap volcanism. Thus this communication provides additional support to the growing acknowledgement of the theory that higher faunal turnover across the K/T boundary the world over might have been the result of gradual environmental deterioration rather than a sudden impact in the global scale.

Nitrogen-fixing azotobacters from mangrove habitat and their utility as marine biofertilizers

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Journal of Experimental Marine Biology and Ecology, Volume 312, Issue 1, Pages 5-17, 2004.

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A dearth of information is available for nitrogen-fixing bacteria in coastal mangroves, and hence, the present study has been undertaken to analyse 44 root and associated soil samples, derived from a mangrove habitat of southeast coast of India. The root samples exhibit high counts of total heterotrophic bacteria and azotobacters along with high rates of nitrogen fixation, as compared to the rhizosphere soil samples. Among the plant species, *Bruguiera cylindrica* records high microbial counts and nitrogen fixation. From the samples analysed, three species of *Azotobacter*, viz., *A. chroococcum*, *A. virelandii* and *A. beijerinckii* were isolated, purified and identified. These species exhibit high growth, nitrogen fixation and in vitro production of phytohormone (Indole Acetic Acid, IAA) at NaCl salinity of 30 g l⁻¹. The azotobacters, which were inoculated with *Rhizophora* seedlings, increased significantly the average root biomass up to by 98.2%, the root length by 48.45%, the leaf area by 277.86%, the shoot biomass by 29.49% as compared to controls and they also increased the levels of total chlorophylls and carotenoids up to by 151.0% and 158.73%, respectively. Thus, azotobacterisation is beneficial in raising vigorous seedlings of mangroves in coastal wetlands.

Biostratigraphic Studies and Correlation of the Middle Cambrian Successions of Northwestern Kashmir Himalaya

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The Middle Cambrian successions of Himalaya are well exposed in the Pohru Valley of northwestern Kashmir Himalaya. The fossiliferous successions are exposed in the Kandi, Nutunus, Takiwadopura, Zachaldor, Khanpura, Neilipora and in the Magam areas of the Kupwara district of northwestern Kashmir. This is one of the highly fossiliferous parts of the Cambrian successions of northwestern Kashmir. The fauna is characteristic of the early Middle Cambrian Maochuangian stage to the late Middle Cambrian representing Maochuangian, Hsuehuangian stages of the Middle Cambrian. The lower part of the Middle Cambrian Maochuangian is poorly fossiliferous, but the Middle Hsuehuangian and upper parts of Changhian of the successions are profusely fossiliferous. Several faunal assemblages have been recorded which includes some revised as well as new faunal elements. The fauna mainly includes polymerid and agnostid trilobites and few inarticulate brachiopods. In the light of the

present biostratigraphic studies attempts have been made to correlate these Middle Cambrian faunal assemblages of Kashmir with the known analogous Middle Cambrian successions of the Tethys Himalaya and preliminarily with other corresponding successions of the Middle Cambrian, on the basis of polymerid and agnostid trilobite fauna.

Organic-walled microfossils from the Neoproterozoic black phosphatic stringers in the Gangolihat Dolomite, Lesser Himalaya, India

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A well-preserved microbiotic assemblage is recorded from the Jhiroli magnesite, eastern Kumaun Lesser Himalaya. The assemblage contains cyanobacterial filaments, coccoids and acritarchs identified mainly as Siphonophycus robustum, S. typicum, S. capitaneum, Gunflintia minuta, Oscillatoriopsis obtusa, Chloroglo-eaopsis contexta, Sphaerophycus parvum, Leiosphaeridiacrasa, Trachyhystrichosphaera vidalii, Trachyhystrichosphaera sp., Micrhystridium pallidum and Cymatio-sphaera minuta. Presence of acanthomorphic acritarchs such as Trachyhystrichosphaera, Cymatio-sphaera and Micrhystridium is important in assigning the age of the Gangolihat Dolomite. On the whole the microbiotic assemblage suggests Vendian or younger age for the Gangolihat Dolomite.

Controls on the genesis of some high-fluoride groundwaters in India

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India has an increasing incidence of fluorosis, dental and skeletal, with some 62 million people at risk. High fluoride groundwaters are present especially in the hard rock areas south of the Ganges valley and in the arid north-western part of the country. The phenomenon is related to groundwater with residual alkalinity ($\text{Ca}^{2+} < \text{HCO}_3^-$). Fluoride concentrations are governed by adsorption equilibria and by fluorite solubility. Evapotranspiration leads to a precipitation of calcite, a lowering of Ca activity and increase in Na/Ca ratios, and this allows an increase in F^- levels. In southern India, Mg seems to be controlled by dolomite, while sepiolite and palygorskite are Mg sinks in Rajasthan but may then release F^- under alkaline conditions. The latter two minerals are probably also important sources and sinks for F^- in the hydroxy-positions. The increase in the extent of sodic soils as a result of irrigation is a contributing factor to the increasing incidence of fluorosis. Remedial measures including addition of gypsum and rainwater harvesting are needed even in areas where the sodicity does not cause structural problems in the soil.

Rhizolithic Calcrete in Teris, Southern Tamil Nadu: Origin and Paleoenvironmental Implications

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The early-modern red coastal/or inland sands (“Teris”) in the coastal tract of southern Tamil Nadu show the infrequent occurrence of rhizolithic calcretes in the vadose zone. These are reddish brown coloured, cemented and cylindrical in form. No other types of rhizolith and/or calcrete have been recorded from here. Textural and mineralogical studies show that these rhizoliths contain notable amounts of acid insoluble detrital sands (essentially quartz and opaques) and mud, and are presumed to be derived from the host, i.e. teris. Petrographic studies reveal that these detritals are embedded in a micritic matrix and the carbonate cement shows rim, vein and blocky structures. Further, floating, alveolar and clotting textures are also noticed. Clay minerals in the rhizoliths include kaolinite as the singular component.

Rhizoliths are presumed to be formed by surface weathering and pedogenic processes in the vadose zone. The pedogenesis of host teri sands might have released Ca²⁺ ions and were later deposited in the root cavities formed by the decay and complete removal of the tissues of roots. Another source of Ca²⁺ would be the calcareous sediments which underlies part of the teris. The absence of root anatomy is a characteristic feature of these rhizoliths.

A sample of rhizolith collected at Sattankulam at a depth of 2.5 m gave a ¹⁴C age of 3680±110 years B.P. Hence, semi-arid conditions of the present day in the Teri tract of southern Tamil Nadu, should have set in at least as way back as 3680±110 yr. B.P.

Major turbidity flows in the Western Indus Fan between 290 and 360 kyr

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Calcium carbonate (CaCO₃), aluminium (Al), titanium (Ti), and terrigenous matter analyses were carried on the Ocean Drilling Programme Site 720A from the Indus Fan in the Arabian Sea. CaCO₃, Al, Ti and terrigenous matter values range from 4.5 to 74.4%, 1.4 to 7.8%, 0.03 to 0.4% and 5.5 to 66.7%, respectively. High CaCO₃ (40–60%) in association with low values of Al, Ti and terrigenous matter from 0 to 290 kyr (0 to 18 mbsf) and low CaCO₃ (< 10%) with high values of Al, Ti and terrigenous matter suggest that CaCO₃ fluctuations at this site were controlled by terrigenous dilution. Low Al, Ti and terrigenous matter percentages from 0 to 290 kyr and strikingly high values from 290 to 360 kyr reveal that the supply of terrigenous matter to the Indus Fan was significantly higher during 290 to 360 kyr (18 to 28 mbsf depth) due to massive turbidity flows triggered by slumping.

Biogeochemistry of organotin compounds and tin in a forested catchment in Germany

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Organotin compounds (OTC) are highly toxic pollutants that have been shown to affect many aquatic ecosystems. Little is known about the input and fate of OTC in terrestrial ecosystems. Here, soil pools, concentrations and fluxes in bulk precipitation, throughfall, fog, litterfall and runoff of OTC and Sn_{total} were investigated in a forested ecosystem (*Picea abies*, Karst.) in NE Bavaria, Germany. The concentrations of OTC and Sn_{total} were generally in the order fog>throughfall>bulk precipitation. Average concentrations of OTC_{total} ranged from 57 ng Sn l⁻¹ in fog to 5.8 ng Sn l⁻¹ in bulk precipitation. Concentrations of Sn_{total} were in the same order but between 490 ng Sn l⁻¹ in fog and 140 ng Sn l⁻¹ in bulk precipitation, on average.

Average OTC_{total} concentrations in litterfall were 12.9 ng Sn g⁻¹ and those of Sn_{total} in litterfall 38 ng Sn g⁻¹. All OTC concentrations in runoff were lower than in bulk precipitation, while those of Sn_{total} were similar to the concentrations in bulk precipitation. Monobutyltin was the dominating OTC in bulk precipitation, throughfall, fog and litterfall, but was seldom detected in the runoff. The annual total deposition of OTC_{total} (calculated as throughfall+litterfall) was 172 mg Sn ha⁻¹ year⁻¹, with 45 mg Sn ha⁻¹ year⁻¹ represented by litterfall. The annual runoff from the catchment of OTC_{total} amounted to 25 mg Sn ha⁻¹ year⁻¹. The total deposition of Sn_{total} was 4.9 g Sn ha⁻¹ year⁻¹, of which 0.2 g Sn ha⁻¹ year⁻¹ was litterfall. The annual runoff of Sn_{total} was 2.4 g Sn ha⁻¹ year⁻¹. The mass balance showed a high retention of OTC and Sn_{total} in the catchment. The forest soils act as a strong sink for OTC and Sn_{total}. Only small amounts of deposited OTC are released to runoff. The ratio of soil pools to annual accumulation for total OTC (46 years) indicates that OTC inputs have been occurring already for many decades or have been substantially higher in the past than today.

Additional Terminal Proterozoic Organic-walled Microfossils from the Infra-Krol Formation, Nainital Syncline, Lesser Himalaya, Uttaranchal

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Black carbonaceous shale associated with black chert nodules of Infra Krol Formation, Baliana Group yielded diversified assemblage comprising 20 taxa of organic-walled microfossils (OWM) represented by acritarchs and cyanobacterial remains. Out of these, 16 taxa are reported for the first time from this area which include five genera of acritarchs (sphaeromorphida subgroup) viz. Margominuscula simplex, Granomarginata primitiva, Satka colonialica, Paracrassosphaera dedalea, Microconcentrica incrustata, and six genera (sphaerohystrichomorphida subgroup) viz. Baltisphaeridium perrarum, Trachyhystrichosphaera vidalii, Gorgonisphaeridium maximum, Micrhystridium echinatum, M. regulare, M. eatonensis, Archaeohystrichosphaeridium cellulare, A. semireticulatum, Germinosphaera unispinosa; four taxa of the cyanobacterial remains viz. Globophycus rugosum,

Bavlinella faveolata, Eomicrocystis malgica, Tetranychus hebeiensis, Eophormidium orculiformis belong to Synaplomorphitae subgroup and single genus of VSM viz., Melanocyrrillium hexodiadema. The recovered microbiotic assemblage compares well with the assemblages known from the Terminal Proterozoic sediments. The large sized acanthomorph Trachyhystrichosphaera vidalii, recorded here for the first time, is known globally after Varanger glaciation and before diversification of Ediacaran biota. An analysis of the recovered microbiotic assemblage in the Infra Krol Formation suggests its autochthonous nature. It was deposited in stable, shallow water, restricted pond or lake which had occasional contact with the open sea.

Decentralised composting of urban waste – an overview of community and private initiatives in Indian cities

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The national waste legislation, introduced in India in 2000, endorses the principle of “Recycle Before Disposal” and clearly stipulates composting as an option for organic waste treatment. It also recommends waste separation as prerequisite for treatment. Although various composting schemes of different scale, type and organisational structure currently exist in the country, a general overview is lacking and very little independent site-specific information is available. This paper presents the results of a study assessing 17 decentralised systems from the cities of Bangalore, Chennai, Pune, and Mumbai. The schemes were classified according to their organisational setup into: (1) citizens’ and community initiatives; (2) business and institution initiatives operating on their premises; and (3) small and medium-size private sector initiatives. These categories also coincide with different operational scales. Community initiatives have developed from unreliable collection services, and composting emerged mainly as a spin-off activity from the collection system to reduce waste delivery to the communal containers emptied by the municipal services. The potential to launch and sustain decentralised composting schemes is dependent on the municipal provision of adequate space. This paper summarises further key issues pertaining to the assessed schemes and reveals overall deficiencies in the field of accounting and transparency, composting technique and marketing, as well as municipal authority involvement.

Ca and Sr dynamics in the Indo-Gangetic plains: Different sources and mobilization processes in northwestern India

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The leachable fraction of the sediments from the Thar Desert fringe and the adjacent Ganges alluvial plains, has been studied to determine the sources and the processes responsible for the mobilization of Ca and Sr using Sr isotopes and Ca/Sr ratios. In the desert the leachable fraction of the soil/sediments is probably derived from mixing of old marine carbonates, microfossils with the sea-spray of the Arabian Sea and rainwater. Aeolian reworking of soil carbonates of this mixed origin could have provided the carbonate found at the desert fringe. The sub-humid zone of the Gangetic plains, just outside the desert fringe, has relatively higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with lower Ca/Sr ratios, indicating silicate weathering as the major contributor of leachable fraction. The spatial geochemical differences could also be related to the ineffectiveness of dust transport and accumulation processes in the humid Ganga plain. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the present-day dust leachate from the polluted city of Delhi indicates that its Sr source is petroleum burnt residues.

**Techniques for Landslide Hazard Zonation – Application to
Srinagar-Rudraprayag Area of Garhwal Himalaya**

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The present work deals with the development and evaluation of landslide hazard zonation techniques which have been applied to parts of Garhwal Himalaya. The binary relationships between the factors and landslides have been determined. These relationships revealed the degree of susceptibility to landslide occurrence. The two techniques developed for landslide hazard zonation are the Subjective Rating Technique (SRT) and Objective Rating Technique (ORT). Although the SRT employs the inferred relationships between the landslide occurrence and the terrain factors to assign ratings to the factor categories, yet the rating assignment to the individual factors is subjective. The ORT reduces the impact of subjectivity in rating assignment, by deriving these from the frequency distribution of landslides. In this technique an attempt has also been made to judiciously classify the different hazard classes. Finally, the maps prepared from two different techniques have been validated and compared. The work presents a systematic approach to a comprehensive landslide hazard assessment of a large region.

Used lubricating oil recycling using hydrocarbon solvents

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A solvent extraction process using new hydrocarbon solvents was employed to treat used lubricant oil. The solvents used were liquefied petroleum gas (LPG) condensate and stabilized condensate. A demulsifier was used to enhance the treatment process. The extraction process using stabilized condensate demonstrated characteristics that make it competitive with existing used oil treatment technologies. The process is able to reduce the asphaltene content of the treated lubricating oil to 0.106% (w/w), the ash content to 0.108%, and the carbon residue to 0.315% with very low levels of contaminant metals. The overall yield of oil is 79%. The treated used oil can be recycled as base lubricating oil. The major disadvantage of this work is the high temperature of solvent recovery. Experimental work and results are presented in detail.

Site-specific ground response analysis

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CURRENT SCIENCE, VOL. 87, NO. 10, Pages 1354-1363. 2004

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The local soil conditions have a profound influence on ground response during earthquakes. The recent des-structive earthquakes have again demonstrated that the topography, nature of the bedrock and nature and geometry of the depositional soils are the primary factors that influence local modifications to the underlying motion. We highlight the engineering importance of site-specific ground response analysis and difficulties

faced in conducting a complete ground response analysis. Steps to be followed in conducting a meaningful site amplification study are explained. Difficulties/uncertainties in choosing an input ground motion are discussed and the various methods currently available for site amplification study are summarized. A case study on ground response analysis of a site in Ahmedabad City during the Bhuj earthquake is presented. The study shows that the varying degree of damage to multistorey buildings in the close proximity of Sabarmati river area in Ahmedabad was essentially due to amplification of the ground. Amplification was attributed to the fact that the natural frequencies of the building and frequency content of the ground motion recorded on the ground floor of the Regional Passport Staff Quarters building are in close proximity.

Influence of the carbon source on the anaerobic biomass adhesion on polyurethane foam matrices

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This work focuses on the influence of the source of organic matter on the process of biomass adhesion on polyurethane foam matrices in fixed-bed anaerobic immobilized-sludge reactors. Five experiments were performed in differential 'gradientless' reactors fed with meat extract (protein),

glucose, starch, lipids and complex substrate. The polyurethane foam colonization process was monitored temporally in each experiment to identify the amount of biomass buildup, extracellular polymer production and the morphological characteristics of the cells adhering to the support. Different immobilization patterns were observed for the different substrates used. The morphological variety was found to be dependent on the substrate constituents. Polymer excretion was apparently crucial in the colonization process of the polyurethane matrices and was likely related to cell fixation on the support. The production of extracellular polymeric substances speeded up the initial fixation of microorganisms on the polyurethane surface.

DEM-based modelling of surface runoff using diffusion wave equation

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A digital elevation model (DEM)-based overland flow routing model was developed for computation of surface runoff for isolated storm events. The model operates on a grid or cell basis and routes the rainfall excess generated over the cells, following the DEM-derived drainage paths, to the catchment outlet. The rainfall excess for each cell of the catchment was computed using the Philip two-term infiltration model utilizing the physical properties of the cell. The overland flow was described by a finite volume-based numerical solution of the diffusion wave approximation of the St Venant equations. The cell physical properties, such as topographic characteristics, land use, soil, etc., were extracted from published maps for discretized cells of the catchment using a Geographic Information System. The results of model application indicate that the model satisfactorily predicted the runoff hydrograph. The cell-based structure of the model allowed for generation of spatially distributed catchment information in terms of the model-computed variables, such as the depth of flow and discharge.

Modelling of earthquake damage using geotechnical centrifuges

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Earthquakes can cause tremendous loss of human life and can result in severe damage to a wide variety of civil engineering structures. The behaviour of foundation systems and soil strata subjected to earthquake loading is complex. Dynamic centrifuge modelling is a powerful tool that offers a possibility of understanding the true behaviour of foundation systems under earthquake loading. In this paper the principles of dynamic centrifuge modelling are elucidated. Implementing dynamic centrifuge modelling needs specialized equipment and instrumentation and the details of such equipment are presented. The application of dynamic centrifuge modelling to investigate the seismic behaviour

of embankments on liquefiable foundation and pile foundation subjected to liquefaction-induced lateral spreading are presented. Results from these two applications reveal the usefulness of dynamic centrifuge modelling in understanding the true failure mechanisms. It will be shown that such an understanding can have direct bearing on both advancement of knowledge as well as on geotechnical practice used in the design of future structures or in retrofit attempts on existing structures.

The Great Rann of Kachchh: Perceptions of a Field Geologist*

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The Great Rann of Kachchh comprises a unique geomorphic entity of the Indian sub-continent. It is a mysterious and fascinating tectonic landscape generated during last 10,000 years, in an area marked by sea-level changes. Tectonically, the region of Kachchh is located quite close to the junction of the Western Continental Margin and the geosynclinal belt of Sindh-Baluchistan. Its proximity to the triple junction formed by the Indian, Arabian and African plates has further complicated its tectonics. The region is frequently visited by earthquakes, whose focal mechanisms indicate reverse faulting generated in a compressional stress field. Geomorphically, the Great Rann can be divided into four units, based mainly on the topographic characteristics and annual inundation pattern. Kachchh in general and the Great Rann in particular have been visited by earthquakes all throughout their geological history. Two major seismic events of the near historical past are the 1819 Allah Bund Earthquake along the northern margin of the Great Rann, and the 2001 Bhuj Earthquake that was located on the southern margin. Apart from its geomorphic and seismic uniqueness, the Great Rann has considerable geoarchaeological significance. A few thousand years back, perhaps even prior to the times of Rig Veda, several Himalayan rivers viz., Sindhu (Indus), Shatadru (Proto-Sutluj) and Sarasvati, flowing across the northwestern plains of India, emptied their waters into a shallow sea that now marks the site of the Great Rann. Navigating along these rivers, mainly Sarasvati, the Indus Valley people came to Gujarat and established several important Harappan towns.

This paper provides an insight into the close relationship that existed between the geomorphology, seismicity and archaeology of the Great Rann.

Effects of inorganic nutrients on the regrowth of heterotrophic bacteria in drinking water distribution systems

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Three laboratory-scale water pipe systems were set up to study the effects of adding three inorganic nutrients (ammonium, nitrate or phosphate) on biofilm formation in water pipes. The results showed that the effects of adding ammonium or nitrate on the biofilm formation were insignificant when levels below 0.1 mg N/l were added. Analogous results were observed when phosphate was added at

levels below 0.005 mg P/l. However, as the addition of ammonium increased to 0.5 mg N/l, significant effects on biofilm formation were observed. Similar results were obtained phosphate was added at levels above 0.01 mg P/l. Batch tests were also conducted using water samples collected from a Taiwanese drinking water distribution system. The results indicated that the addition of ammonium, nitrate or phosphate to treatment plant effluent stimulates bacterial growth. In the distributed water of an urban area, the addition of nitrate or phosphate stimulated bacterial growth. The bacterial growth in the distributed water of a suburban area was not stimulated by adding any of these three inorganic nutrients.

Fauna and palaeoenvironment of a Late Quaternary fluvio-lacustrine basin in Central Kumaun Himalaya

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In recent years, vertebrate faunas recovered from the Late Quaternary lake deposits have become increasingly important, especially for phylogenetic relationship, evolutionary pattern, comparison with the Recent counterparts, palaeoecology and palaeoenvironment. We describe the Late Quaternary fauna from a tectonically formed palaeolake basin at Dulam, Kumaun Central Himalaya. The age of the fossil horizon is estimated as ca. 30 ka BP. Murids and other faunal elements have been recovered from the Kumaun Himalaya. The large mammals are represented only by Bovidae, whereas the small ones are dominated by murid rodents. The bones have greater frequency compared to the teeth. Based on the faunal components, four palaeocommunities are proposed. The savanna grassland community is represented by the large mammals, the lacustrine community by Cyprinidae fishes, ostracods and freshwater gastro-pods, the upland community by *Soriculus* and *Mus*, and semi-arid bushland community by *Golunda* and lizards.

A new methodology to calculate the environmental protection index (E_p). A case study applied to a company producing composite materials

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Environmental indicators can be used as a first stage in progress towards comprehensive environmental impact measures [J. Environ. Manage 65/3 (2002) 285]. In this article, we develop a 'pollutant interaction matrix method' that allows calculation of a global environmental protection index (E_p) in order to verify the eco-compatibility of an industrial activity. Two methods are proposed for the E_p index evaluation (which represents the numerical measure of the environmental sustainability): the Direct Method (E_{pd}) and the Weighted Method (E_{pw}).

Both methods need to define, in the whole industrial process, homogeneous sectors (defined as construction sites where activities of the same type are carried out). Furthermore, for each activity

a set of parameters (t , duration of pollution effect, P , quantity of pollutant produced, G , hazard of the pollutant) are required to evaluate the relative pollution index Y . All indices calculations were carried out using a set of matrices. The correct use of E_p evaluation provides an improvement in the total environmental performance of companies because it points out possible critical operations in each homogeneous sector which require solutions.

The methodology is applied to evaluate the environmental pollution risk of a company that produces polymer materials and to improve their environmental performance. The results obtained show that the whole productive process has a low environmental impact factor. Nevertheless the applied methodology puts in evidence some processes that generate local pollution in specific areas of the factory and which could be dangerous for the workers' health.

Palaeoenvironmental Deductions of Microfossil Flora and Fauna of the Shiala and Yong Formations, Tethyan Garhwal Himalaya

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The present study is an interdisciplinary approach to put forward a precise picture of Ordovician-Silurian acritarcha and other associated microfossil distribution in the Lower Palaeozoic Tethyan sequence of the Garhwal Himalaya, India. For this purpose, sedimentological data, macrofauna and microflora from the Shiala and Yong Formations have been considered to constrain the environmental distribution of the microfossils. It has been found that chitinozoa and melanosclerites as well as acritarcha of Garhwal Tethys Himalaya have a wide range of adaptation. The acritarcha bloomed during cool marine condition whereas chitinozoa and melanosclerites preferred mainly in warm-water condition of blooming. The Shiala Formation was deposited under cool-water conditions in a shallow pulsating basin with a rapid variations in the depositional environment and frequent sea-level changes. This formation has been affected by the fluvial influx intermittently and possibly there was a sea-level drawdown at Ordovician-Silurian boundary. An attempt has been made to correlate this phenomenon with a possible Late Ordovician glacioeustatic event and it is found that the Hirnantian glaciation was probably not situated in the Himalayan region. The Yong Formation was deposited mainly in a shallow subtidal setting in a tranquil and low energy ancient warm-water mass.

Removal of Fe(II) from the wastewater of a galvanized pipe manufacturing industry by adsorption onto bentonite clay

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Bentonite clay has been used for the adsorption of Fe(II) from aqueous solutions over a concentration range of 80–200 mg/l, shaking time of 1–60 min, adsorbent dosage from 0.02 to 2 g and pH of 3. The process of uptake follows both the Langmuir and Freundlich isotherm models and also the first-order kinetics. The maximum removal (>98%) was observed at pH of 3 with initial concentration of 100 mg/l and 0.5 g of bentonite. The efficiency of Fe(II) removal was also tested using wastewater from a galvanized pipe manufacturing industry. More than 90% of Fe(II) can be effectively removed from the wastewater by using 2.0 g of the bentonite. The effect of cations (i.e. zinc, manganese, lead, cadmium, nickel, cobalt, chromium and copper) on the removal of Fe(II) was studied in the concentration range of 10–500 mg/l. All the added cations reduced the adsorption of Fe(II) at high concentrations except Zn. Column studies have also been carried out using a certain concentration of wastewater. More than 99% recovery has been achieved by using 5 g of the bentonite with 3 M nitric acid solution.

Cleaner production in the ammonia–soda industry: an ecological and economic study

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Five methods to reduce the negative influence of soda ash factories on the natural environment are presented:

1. obtaining calcium–magnesium phosphates by treating the suspension from raw brine purification with orthophosphoric acid (H_3PO_4),
2. production of precipitated chalk from soda processing waste,
3. production of gypsum and semi-brine,
4. desulphurisation of fume gases from the factory power plant,
5. utilization of distiller waste.

The tests, accomplished on a laboratory scale, showed the high efficiency of these methods. Economic analysis has proved that only four out of the five presented processes can have a positive financial effect on soda ash factories, as well as being well justified economically. The value of two of the innovations presented is confirmed by their implementation in factories.

Palynofacies Analysis and Depositional Environment of Bihpuria Well–A, North Bank of Brahmaputra River, Upper Assam Basin
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Dispersed organic matter of Cenozoic sediments are analyzed for palaeoenvironmental purposes of Bihpuria well – A, situated in the North Bank of River Brahmaputra, Upper Assam Basin. Distribution pattern of the organic matter types with respect to various strata has been assessed to observe changes in depositional environment. Despite using well cutting samples, quantitative and qualitative

palynofacies analyses in various sequences viz.,

Late Palaeocene – Upper Eocene and Late Miocene to Plio-Pleistocene have been defined by core lithotypes, log data and characteristics of organic matter content. The results show a significant difference between anoxic and oxic facies with relative distribution of structured and non-structured debris. Depositional set-up of anoxic/oxic facies is directly related to the supply of detritus from various sources, lithotypes and organic particles embedded therein, which also affect their preservation and biodegradation. Palaeocene-Eocene sediments deposited under shallow marine conditions exhibit highly degraded phytoclasts (amorphous, grey and highly pyritized amorphous and biodegraded terrestrial/aquatic organic matter types) supplied from both terrestrial and marine sources. These accumulated at basal horizons of the basin leading to anoxic conditions. Carbonaceous shale of Kopili Formation (Late Eocene) is represented here by thin bed than in other sections in the Assam-Arakan Basin, deposited under restricted marine conditions. Upper part of the sections represented by the Tipam Group and Namsang Formation, which are examples of fluvio-lacustrine deposits, characterized by land derived, less biodegraded and moderate to richly oxidized phytoclasts. The nature, occurrence and frequency of organic matter in these sedimentary sequences is discussed in detail.

Effect of sequentially combining methanol and acetic acid on the performance of biological nitrogen and phosphorus removal

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A sequentially combined carbon (SCC) source using methanol and acetic acid was investigated for biological nitrogen and phosphorus removal in a wastewater treatment process consisting of an anoxic zone, an oxic zone and a final settling tank. The anoxic zone was divided into two separate anoxic zones to feed methanol in the first anoxic zone and acetic acid in the second anoxic zone. Methanol and acetic acid, each as the sole carbon source, were also tested for comparison.

The use of SCC was superior in nitrogen removal with all combined COD ratios of methanol/acetic acid tested, yielding 95.8–97% efficiency (less than 1 mg N/l in the final effluent). The highest phosphorus removal of above 92% (final effluent concentration of 0.12 mg P/l) was achieved when only acetic acid was used at a quantity equivalent to 50 mg COD/l. However, when SCC was used, the acetic acid dosage of 50 mg COD/l could be reduced down to 20 mg COD/l when 30 mg COD/l was replaced by methanol; this resulted in a final effluent phosphorus concentration of 0.6 mg P/l. Additional benefits of SCC included the excellent sludge settling properties compared to the use of methanol or acetic acid alone.

Optimal Desilting for Improving the Efficiency of Tanks in Semi Arid Regions

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A research study has been carried out to evaluate the economically viable depth of desiltation in old tanks to achieve a substantial increase in percolation and storage. Two tanks — an old minor irrigation tank and a newly constructed percolation tank were selected in a granite terrain and infiltration studies were carried out with different thickness of silt removal. Tritium tracer studies were coupled with the infiltration studies to follow the infiltrated water and evaluate the effectiveness of silt removal in percolation. The study indicated that in the case of irrigation tank, a steady state infiltration rate of 67 mm/h has increased to 350 mm/h with the removal of 65 cm silt showing a six-fold increase in infiltration rate. Infiltration rate was found to be reducing by removal of 25 cm and 50 cm silt and the analysis of soil fraction indicated presence of clay at these depths. The study at percolation tank indicated that the infiltration rate of 10-20 mm/h has increased to a maximum of 310 mm/h with removal of 40 cm silt. The tritium tracer migration study supported a faster movement of percolated water at desilted sites by showing a greater dilution of tracer concentration and deeper penetration. The research study strongly supports a necessity of carrying out infiltration studies at different places within the tank bed area with removal of varying thickness of silt to decide the optimal level of desiltation especially in old tanks before commencing the revival of tank system.

A fuzzy knowledge-based decision support system for groundwater pollution risk evaluation

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In this paper we propose a decision support system that can provide information on the environmental impact of anthropic activities by examining their effects on groundwater quality. We use the combined value of both intrinsic vulnerability of a specific local aquifer, obtained by implementing a parametric managerial model (SINTACS), and a degree of hazard value, which takes into account specific human activities. Incomplete information is notoriously common in environmental planning. To overcome this deficiency we apply an algorithmic and a qualitative approach, based on expert judgment incorporated into the system's knowledge base. The decision support system takes into account the uncertainty of the environmental domain by using fuzzy logic and evaluates the reliability of the results according to information availability.

Hybrid moving block bootstrap for stochastic simulation of multi-site multi-season streamflows

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The Hybrid approach introduced by the authors for at-site modeling of annual and periodic streamflows in earlier works is extended to simulate multi-site multi-season streamflows. It bears significance in integrated river basin planning studies. This hybrid model involves: (i) partial pre-whitening of standardized multi-season streamflows at each site using a parsimonious linear periodic model; (ii) contemporaneous resampling of the resulting residuals with an appropriate block size, using moving block bootstrap (non-parametric, NP) technique; and (iii) post-blackening the bootstrapped innovation series at each site, by adding the corresponding parametric model component for the site, to obtain generated streamflows at each of the sites. It gains significantly by effectively utilizing the merits of both parametric and NP models. It is able to reproduce various statistics, including the dependence relationships at both spatial and temporal levels without using any normalizing transformations and/or adjustment procedures. The potential of the hybrid model in reproducing a wide variety of statistics including the run characteristics, is demonstrated through an application for multi-site streamflow generation in the Upper Cauvery river basin, Southern India.

Regional inventory of soil surface nitrogen balances in Indian agriculture (2000–2001)

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Nitrogen regulates several ecological and biogeochemical processes and excess reactive nitrogen in the environment can lead to pollution problems, including the deterioration of air quality, disruption of forest processes, acidification of lakes and streams, and degradation of coastal waters. Much of the excess nitrogen inputs are related to food and energy production. An important step to understanding the sources of nitrogen and ultimately defining solutions to excess nitrogen is to describe the geographic distribution of agricultural nitrogen contributions from different regions. In this study, soil surface nitrogen loads were quantified for different states of India for the period 2000–2001. Nearly 35.4 Tg of nitrogen has been estimated as inputs from different sources, with output nitrogen from harvested crops of about 21.20 Tg. The soil surface nitrogen balance, estimated as inputs minus outputs, is found to be about 14.4 Tg surplus from the agricultural land of India. Livestock manure constituted a major percentage of total inputs (44.06%), followed by inorganic fertilizer (32.48%), atmospheric deposition (11.86%) and nitrogen fixation (11.58%). Nitrogen balance varied from deficit to surplus for different states. The highest nitrogen surplus was found in Uttar Pradesh (2.50 Tg) followed by Madhya Pradesh (1.83 Tg), Andhra Pradesh (1.79 Tg), etc. A negative nitrogen balance was found in Orissa (-0.01 Tg), Andaman Nicobar Islands (-0.32 Tg) and for some of the northeastern states. Major fertilizer consumption states were found to be Tamilnadu (204 kg/ha), Haryana (132 kg/ha), Punjab (148 kg/ha), followed by others. Similarly, nitrogen inputs from total livestock excretions were found to be high for Kerala (616 kg/ha), Jammu and Kashmir (389 kg/ha), Tamil Nadu (338 kg/ha), etc. The average nitrogen surplus of about 54 kg/ha observed for the agricultural land of the entire country of India is comparatively higher than the average surplus of about 31 kg/ha reported for European countries. These results, obtained from nutrient mass balance calculations, will be useful to formulate nutrient management plans relating to fertilizer usage, livestock management and for adopting some best management strategies at a state level in India.

Geological and Geochemical Appraisal of Uranium Bearing Gulcheru Formation of Cuddapah Supergroup, Gandhi Area, Cuddapah District, Andhra Pradesh

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Gulcheru Formation constitutes 200 m-250 m thick siliciclastic sediments. Based on grain size texture and colour of the sediments, four distinct facies are demarcated. They are pink massive quartzite, cross bedded grey quartzite, purple siltstone and pitted quartzite. The ratios of Si/Al is higher (62.9 to 292.18) in pitted quartzite and lowest (2.122 – 18.247) in siltstone, where as grey quartzite has wide range of 3.78 – 8637.67. This difference is essentially due to higher quartz content in pitted quartzite and dominance of clays/shaly component in siltstone. The wide range of Si/Al ratio in grey quartzite is due to interlayering of siltstone/shale laminations/bands. Distribution of uranium indicates grey quartzite (av. $U_3O_8 = 9.9$ ppm) and siltstone (av. 15.42 ppm) have higher intrinsic uranium than that of pitted quartzite (average 5.6 ppm) and pink massive quartzite (average 7ppm) which is considered very high in comparison to normal sandstone (av = 0.5ppm, Taylor, 1965). Trace elements like Mo, V, Ni, Cu and Pb are enriched in mineralised grey quartzite. Pitchblende is the main uranium mineral in grey and pitted quartzite units. It occurs as fracture fillings and also as interstitial material, associated intimately with chlorite. Close association between pitchblende and sulphides like pyrite, chalcopyrite and galena is seen when pitchblende occurs as fracture fills. Uranium in siltstone, is generally in adsorbed form with ferruginous material, where as associated trace elements like Mo ($r = 0.515$), V ($r = 0.806$), Ni ($r = 0.4$) and even TiO_2 ($r = 0.87$) are well correlated with Al_2O_3 , suggesting their association with clays/phyllsilicates. U/Pb dating of uraniumiferous grey quartzite indicated ages of 1336 ± 14 Ma and 446 ± 29 Ma suggesting remobilisation and concentration of intrinsic uranium.

Development of performance indicators for small Quebec drinking water utilities

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This study presents a comparative performance analysis of small drinking water utilities in Quebec (Canada). The investigation bears on 10 utilities that use surface water or groundwater under the direct influence of runoff and apply chlorination as the only treatment before distribution. The utilities under study were divided into two groups: four utilities that had never or rarely provided water violating provincial drinking water microbiological standards (relating to fecal and/or total coliform bacteria), called nonproblematic utilities, and six utilities that quite often violated the standards, designated as problematic utilities. The objective of the study is to develop utility performance indicators capable of explaining current and historical distributed water quality. Indicators are based

on operational, infrastructure, and maintenance characteristics of utilities that are integrated using a multivariable weight-based index. Results show that utility performance indicators are systematically better for the nonproblematic group of utilities as compared to the problematic group. Disinfection-related, infrastructure, and maintenance variables are those that most contributed to indicator values. Sensitivity analyses served to assess the impact on indicator results of excluding variables and changing their weights.

The Main Frontal Thrust (MFT), Northwestern Himalayas: Thrust Trajectory and Hangingwall Fold Geometry from Balanced Cross Sections

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The Himalayan foreland fold-thrust belt supposedly overrides the alluvium of the Indo-Gangetic plain along the Main Frontal thrust (MFT) at the mountain front. Although the MFT is taken to extend for more than 2500 km all along the Himalayan mountain front, its surface trace is not observed in the field in many areas. In order to constrain the trajectory of the MFT, we have modelled the geometries of the folds occurring in the Siwalik rocks immediately north of the mountain front at five localities in the northwestern Himalayas using the techniques of cross-section balancing. In four of these areas, the MFT has flat-ramp-flat trajectories with the ramp anticlines being fault-bend folds. The upper flat of the MFT is buried below the forelimb of the ramp anticlines and/or alluvium derived from the same anticline. Only at one locality the ramp anticline is a fault-propagation fold and the MFT breaks through to the surface. We suggest that the usual lack of surface exposure of the MFT in major parts the Himalayan mountain front may be a consequence of flat-ramp-flat trajectory of the MFT with the upper flat buried. We also suggest that the intermontane valleys (locally called *Duns*) in the Himalayan foothills formed on the trailing synclines of the MFT-related fault-bend folds.

Modelling hydroenvironmental and health risk assessment parameters along the South Wales Coast

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This paper highlights the increasing concerns relating to hydroenvironmental issues and cites recent examples of the challenges now being regularly faced by hydroenvironmental scientists and engineers. The limitations and restrictions of both physical (or laboratory) and numerical (or computer based) hydraulic models used in the planning and management of aquatic basins are discussed. General details are given of numerical models used for flow and water quality concentration predictions in estuarine waters, with particular application to the challenges occurring along the South Wales coast. A highly accurate and non-diffusive finite difference scheme that solves the transport equation for

predicting water quality indicators and suspended sediment concentration distributions is also discussed. In particular, details are outlined of the extension of the water quality indicators of faecal coliforms, as required to comply with the EU Bathing Water Directive, to predict health risk assessment, in the form of predicting the risk of gastroenteritis.

Three example research projects along the South Wales coast are described; the projects involve the application of two-dimensional and three-dimensional hydroenvironmental models to predict flow patterns and water quality indicator organism distributions in the coastal receiving waters. These studies include: (i) a curvilinear finite difference approach to modelling flows in the Bristol Channel, (ii) coastal health risk predictions in Swansea Bay using combined water quality and epidemiological models, and (iii) combined sewer overflow discharges into Cardiff Bay.

Pesticide persistence and bound residues in soil—regulatory significance

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The paper discusses key aspects of the European Union (EU) regulatory policy related to the persistence and bound residues of agricultural pesticide active substances in soil. This is examined in the context of the EU Authorisations Directive (91/414/EEC) which will gradually replace existing national systems of agricultural pesticide regulation within EU Member States. Discussion is concentrated on this directive, looking in particular at the Uniform Principles therein and the possible ways that these decision-making guidelines could be developed into a regulatory framework. The aim in this process of negotiated development is to identify any questions or data requirements that will be needed for persistent pesticides or soil bound residues, over and above those generally required for all compounds. The present EU regulatory position on soil non-extractable or bound residues is examined and possible future improvements to the system are described and discussed.

Characterizing Bounded and Weathered/Jointed Rock Aquifers: A Case Study from Alathur Village, Near Chennai City

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Presence of a hydrogeological barrier boundary was identified from the interpretation of time-drawdown data obtained by conducting pumping test in an area underlain by hard rocks. Interpretation of electrical resistivity data also confirmed that a geological boundary exists in the zone identified as barrier boundary, indicating a role for resistivity surveys in the characterization of hard rock aquifers.

Geology and Fracture-Related Hypogene Hydrothermal Alteration and Mineralization of Porphyry Copper Deposit at Sungun, Iran

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The porphyry copper deposit at Sungun is located in East Azarbaijan, NW of Iran. The magmatic suite in the Sungun area is a part of NW-SE trending Cenozoic magmatic belt of Iran. The Sungun porphyries (Oligo-Miocene) occur as stocks and dykes, and intrude a series of Oligocene dacitic breccias and tuffs and trachy-andesitic lavas, Eocene arenaceous-argillaceous rocks, and Upper Cretaceous carbonate rocks. The porphyry stocks are divided into two groups: (1) the porphyry stock I (quartz monzo-diorite) and (2) the porphyry stock II (quartz monzonite, granodiorite, and granite). The porphyry stock II hosts the copper ores. Four series of cross-cutting dykes (DK₁, DK₂, DK₃ and DK₄), ranging in composition from quartz monzo-diorite to granodiorite intruded the Sungun porphyry stocks and surrounding enclosing rocks. The whole-rock chemical analyses of the samples for major and trace elements showed that the parental magma of the Sungun porphyries formed in continental margin tectonic setting, and was mainly calc-alkaline in character.

Four types of hypogene alterations are present at Sungun: (1) potassic, (2) potassic-phyllic, (3) phyllic and (4) propylitic. The potassic, potassic-phyllic, and phyllic alteration zones were principally developed in the porphyry stock II, whereas the propylitic alteration zone is chiefly restricted to the peripheral porphyry stocks I and dyke series DK₂ and DK₃. The phyllic and potassic-phyllic occurred in zones where the rocks underwent severe hydro-fracturing manifested by numerous and various cross-cutting veinlets and micro-veinlets of quartz, sulphides, silicate, carbonates, and sulphates. The hypogene mineralization is characterized by the introduction of hypogene sulphides such as pyrite, chalcopyrite, molybdenite, tetrahedrite, bornite, and chalcocite. Three stages of hypogene mineralization, though continuous, were recognized: (1) early, (2) middle and (3) late. The early stage was contemporaneous with the development of the early-type quartz veinlets and potassic alteration. The middle stage that is the main stage of copper mineralization, was contemporaneous with the phyllic alteration. Pyrite, chalcopyrite, and molybdenite along with trace amounts of tetrahedrite, bornite, and chalcocite are also associated with this stage. The sulphides are mainly concentrated in the phyllic and potassic-phyllic zones, and their abundance gradually decreases downward toward the potassic zone. The abundance of copper-bearing hypogene sulphides gradually decreases upward towards the upper parts of the phyllic zone where pyrite is relatively abundant. Only locally small amounts of sulphides (<2 wt%) are associated with rocks that underwent propylitic alteration. The XRF and electron-probe micro-analyses data combined with microscopic evidence suggest that the alteration of ferromagnesian liberated considerable Fe which in turn acted as a major factor for the fixation of the magmatically-derived sulphur in the ore-bearing solutions. Copper and molybdenum were introduced by the hydrothermal ore-bearing fluids.

Formation and release of non-extractable ¹⁴C-Dicamba residues in soil under sterile and non-sterile regimes

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The role of native soil microorganisms in the formation and release of non-extractable ^{14}C -residues, previously treated with ^{14}C -Dicamba, was investigated to examine their significance to the longer-term environmental effects on non-extractable pesticide residues. A 90 d study compared the fate of Dicamba under sterile and non-sterile regimes. In addition, soils were aged for 30 d and repeatedly extracted with a 0.01 M CaCl_2 solution, to an extraction end point, to produce non-extractable residues. The extracted soil containing non-extractable residues was mixed with clean soil that had been freshly spiked with non-labeled Dicamba at 0.2 mg kg^{-1} to increase the bulk volume of the soil and stimulate microbial activity. Sub-samples were then introduced into microcosms to compare the extent of microbially facilitated release and mineralisation with release rates in sterile microcosms. The results show that microorganisms play a significant role in the formation and release of non-extractable Dicamba residues. The release of ^{14}C -activity in sterile microcosms was linked to physical mixing of the extracted soil with field soil prior to the beginning of the incubations. The released ^{14}C -activity may be further mineralized, reincorporated into humus, or taken up by plants or other soil inhabiting biota.

Kachchh Earthquake of 2001: Seismically Triggered Deformed Structures in the Intertidal Sediments of Mandvi Coast in the Gulf of Kachchh, Gujarat

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On 26 January 2001, a major earthquake of magnitude of 7.7 caused extensive damage in Kachchh and other parts of Gujarat. Mandvi coast in the Gulf of Kachchh, which is 150 km far from the epicentral zone, is also highly affected by the high magnitude seismic waves causing deformed structures in soft sediments. These induced deformed soft sediment structures are recorded in the small lagoon adjoining the beach area. The structures include sand blows, cracks, micro faulting, deformed cross-laminae, flume and pillar structures and large injection structures, which are attributed to intrusion spout phenomena. Abnormal behaviour of suspension feeding *squillidean* stomatopod, *Oratosquilla striata* species, was also observed. These structures are interpreted to originated by the process of fluidisation and liquefaction of cohesionless peaty subsurface layer underneath the clastic sediments. The shear stress related to earthquake acted as trigger agent.

Influence of plants on the chemical extractability and biodegradability of 2,4-dichlorophenol in soil

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This study investigated the fate and behaviour of [UL-¹⁴C] 2,4-dichlorophenol (DCP) in planted (*Lolium perenne* L.) and unplanted soils over 57 days. Extractability of [UL-¹⁴C] 2,4-DCP associated activity was measured using calcium chloride (CaCl₂), acetonitrile–water and dichloromethane (DCM) extractions. Biodegradability of [UL-¹⁴C] 2,4-DCP associated activity was assessed through measurement of ¹⁴CO₂ production by a degrader inoculum (*Burkholderia* sp.). Although extractability and mineralisation of [UL-¹⁴C] 2,4-DCP associated activity decreased significantly in both planted and unplanted soils, plants appeared to enhance the sequestration process. After 57 days, in unplanted soil, 27% of the remaining [UL-¹⁴C] 2,4-DCP associated activity was mineralised by *Burkholderia* sp., and 13%, 48%, and 38% of ¹⁴C-activity were extracted by CaCl₂, acetonitrile–water and DCM, respectively. However, after 57 days, in planted soils, only 10% of the [UL-¹⁴C] 2,4-DCP associated activity was available for mineralisation, whilst extractability was reduced to 2% by CaCl₂, 17% by acetonitrile–water and 11% by DCM. This may be due to the effect of plants on soil moisture conditions, which leads to modification of the soil structure and trapping of the compound. However, the influence of plants on soil biological and chemical properties may also play a role in the ageing process.

Mineralogy and Geochemistry of Siwaqa Travertine, South Amman, Jordan

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Siwaqa Travertine occurs about 70 km south of Amman, in the vicinity of Siwaqa strike-slip fault. Representative surface and subsurface samples of travertine have been analyzed by X-ray diffraction, ICP and wet chemistry to study the mineralogy and geochemistry of travertine. Data of Siwaqa travertine is compared with travertines from other localities in Jordan. Calcite is the most dominant constituent. Dolomite, quartz, kaolinite, gypsum/bassanite, and hematite are present in minor amounts. Presence of clay minerals and iron oxides have resulted in the departure of travertine from its creamy white colour. CaO with an average of 50.9% is mainly attributed to carbonate minerals, particularly calcite. Relatively rich trace element content in Siwaqa travertine compared to Mujeb travertine is attributed to leaching of underlying oil shale and/or marble. Higher concentrations of some of the elements probably resulted due to diagenetic processes and syngenetic mineralization.

Recycling EDTA solutions used to remediate metal-polluted soils

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The objective of this research was to investigate the recycling of ethylenediamine-tetraacetic acid (EDTA) used for the removal of trace metals from contaminated soils. We successfully used Na₂S combined with Ca(OH)₂ to precipitate the trace metals allowing us to recycle the EDTA. The results of batch and column leaching experiments show that both Ca-EDTA and Na-EDTA are powerful chelating agents with a similar soil remediation potential. The major advantage of Ca-EDTA is the preservation of soil organic matter. We found that Na₂S was capable of separating the metals Cd, Cu and Pb from EDTA; however, the precipitation of Zn required the addition of Ca(OH)₂. After reusing the reclaimed EDTA seven times, over a 14-day period, EDTA reagent losses ranged from 19.5% to 23.5%. Successive washing cycles enhanced the removal of trace metals from contaminated soils. The metal sulfide precipitates contain high concentrations of metals and could potentially be recycled.

Zn, Cd and Pb accumulation and arbuscular mycorrhizal colonisation of pennycress *Thlaspi praecox* Wulf. (Brassicaceae) from the vicinity of a lead mine and smelter in Slovenia

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Significant hyperaccumulation of Zn, Cd and Pb in field samples of *Thlaspi praecox* Wulf. collected from a heavy metal polluted area in Slovenia was found, with maximal shoot concentrations of 14 590 mg kg⁻¹ Zn, 5960 mg kg⁻¹ Cd and 3500 mg kg⁻¹ Pb. Shoot/root ratios of 9.6 for Zn and 5.6 for Cd show that the metals were preferentially transported to the shoots. Shoot bioaccumulation factors exceeded total soil Cd levels 75-fold and total soil Zn levels 20-fold, further supporting the hyperaccumulation of Cd and Zn. Eighty percent of Pb was retained in roots, thus indicating exclusion as a tolerance strategy for Pb. Low level colonisation with arbuscular mycorrhizal fungi (AMF) of a Paris type was observed at the polluted site, whereas at the non-polluted site Arum type colonisation was more common. To our knowledge this is the first report of Cd hyperaccumulation and AMF colonisation in metal hyperaccumulating *T. praecox*.

Thlaspi praecox Wulf. (Brassicaceae) is a newly discovered Cd, Zn and Pb hyperaccumulator able to form symbiosis with arbuscular mycorrhizal fungi.

Comparison of root water uptake modules using either the surface energy balance or potential transpiration

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Numerical models simulating changes in soil water content with time rely on accurate estimation of root water uptake. This paper considers two root water uptake modules that have a compensation mechanism allowing for increased root uptake under conditions of water stress. These modules, proposed by Lai and Katul and Li et al. [Adv. Water Resour. 23 (2000) 427 and J. Hydrol. 252 (2001) 189] use potential transpiration weighted, for each soil layer, by a water stress and a compensation function in order to estimate actual transpiration. The first objective of the paper was to assess the accuracy of the proposed root extraction modules against two existing data sets, acquired under dry conditions for a winter wheat and a soybean crop. In order to perform a fair comparison, both modules were included as possible root water extraction modules within the Simple Soil Plant Atmosphere Transfer (SiSPAT) model. In this first set of simulations, actual transpiration was calculated using the solution of the surface energy budget as implemented in the SiSPAT model. Under such conditions, both root extraction modules were able to reproduce accurately the time evolution of soil moisture at various depths, soil water storage and daily evaporation. Results were generally improved when we activated the compensation mechanisms. However, we showed that Lai and Katul [Adv. Water Resour. 23 (2000) 427] module was sensitive to soil hydraulic properties through its water stress function, whereas the Li et al. [J. Hydrol. 252 (2001) 189] module was not very sensitive to the specification of its parameter. The latter module is therefore recommended for inclusion into a larger scale hydrological model, due to its robustness.

When water balance models are run at larger scales or on areas with scarce data, actual transpiration is often calculated using models based on potential transpiration without solving the surface energy balance. The second objective of the paper was to assess the loss of accuracy in such conditions for the Lai and Katul and Li et al. [Adv. Water Resour. 23 (2000) 427 and J. Hydrol. 252 (2001) 189] modules. For this purpose we compared results from the SiSPAT model solving the surface energy balance with those of a degraded version where only potential evapotranspiration was imposed as input data. We found that actual transpiration and evapotranspiration were in general underestimated, especially for the Lai and Katul [Adv. Water Resour. 23 (2000) 427] module, when we used the potential evapotranspiration as calculated from FAO standards. The use of crop coefficients improved the simulation although standard values proposed by the FAO were too small. The definition of the potential evapotranspiration was the major source of error in simulating soil moisture and daily evaporation rather than the choice of the root extraction modules or the inclusion of a compensation mechanism. When used for water management studies, a sensitivity to the definition of potential evapotranspiration used to run the models is therefore advisable.

Absorption of decabromodiphenyl ether and other organohalogen chemicals by grey seals (*Halichoerus grypus*)

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An input–output balance study was performed for polybrominated diphenyl ethers, polychlorinated biphenyls and some organochlorine pesticides on three captive, juvenile grey seals (*Halichoerus grypus*). The animals were fed a diet of herring for six months, during the last three months of which this study was performed. A supplement of decabromodiphenyl ether was included in the diet during the second month of the study. Consistently high absorption (>89%) was observed for all of the chemicals studied, whereas work on other animals has generally shown high (>80%) net absorption at $\log K_{ow} < 6$, dropping towards higher $\log K_{ow}$, and very low absorption of decabromodiphenyl ether. The half-life of decabromodiphenyl ether in blood was estimated to be between 8.5 and 13 days. Measurable concentrations of decabromodiphenyl ether were detected in seal blubber at the end of the study, indicating that this chemical can be stored in adipose and may bioaccumulate. Current understanding of the mechanism of absorption of organohalogen chemicals and the potential for accumulation of decabromodiphenyl ether will need reassessing in the light of these results. Decabromodiphenyl ether is absorbed effectively from the diet by grey seals, and can be stored in the blubber even after exposure ceases.

Isotopic approach of rainfall and groundwater circulation in the volcanic structure of Tahiti-Nui (French Polynesia)

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A chemical and isotopic study was conducted on rainfall, river and spring waters from the northern half of Tahiti-Nui tropical oceanic island, in order to constrain a conceptual model of groundwater circulation within a discontinuous volcanic structure. Tahiti-Nui comprises a main shield cut by a huge landslide to the north. This major flank collapse yielded the formation of a northern depression, in which rapidly grew a second shield. Additional volcanic activity occurred along the rims of the depression, as revealed by local concentrations of dykes. The island is now volcanically inactive and is strongly dissected by erosion. Rainfall collected during a complete hydrological year at different altitudes are characterized by seasonal and altitude gradients in $\delta^{18}\text{O}$. Some of them have a deuterium excess upto +20‰, likely due to inland vapour recycling. Over the hydrological year, non-evaporated precipitation defines a mean annual δ -altitude gradient of -0.7‰/km. The mineralization and isotopic contents in river waters vary according to the geology. Rivers incising the main shield have low total mineral charges and are relatively enriched in stable isotopes ($\delta^{18}\text{O}$ around -3‰ vs.

VSMOW), whereas rivers in the northern post-collapse in-fill exhibit greater electrical conductivity and lower $\delta^{18}\text{O}$ due to the contribution of more mineralized spring water. Springs sampled at different elevations along the NW rim of the N landslide depression have homogeneous stable isotopic compositions corresponding to signature of elevated rainfall. Recharge of these springs thus occurs on a localized area, upto 1500 m above their altitude of emergence. Dominant infiltration occurs at or above the geological discontinuity between the thick impermeable base of the second shield and the late overlying fractured volcanic flows. Dykes from the peripheral part of the system are poorly active in terms of infiltration and water storage, but likely connect the underground circulations. The huge geological discontinuity between the main shield and the post-collapse edifice may also concentrate the groundwater circulation. This main resurgence likely occurs at a deep level of the northern submarine slope of Tahiti-Nui.

The maximum reservoir capacity of soils for persistent organic pollutants: implications for global cycling

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The concept of maximum reservoir capacity (MRC), the ratio of the capacities of the surface soil and of the atmospheric mixed layer (AML) to hold chemical under equilibrium conditions, is applied to selected persistent organic pollutants (POPs) in the surface 'skin' (1 mm) of soils. MRC is calculated as a function of soil organic matter (SOM) content and temperature-dependent K_{OA} and mapped globally for selected PCB congeners (PCB-28; -153; -180) and HCB, to identify regions with a higher tendency to retain POPs. It is shown to vary over many orders of magnitude, between compounds, locations and time (seasonally/diurnally). The MRC approach emphasises the very large capacity of soils as a storage compartment for POPs. The theoretical MRC concept is compared to reality and its implications for the global cycling of POPs are discussed. Sharp gradients in soil MRC can exist in mountainous areas and between the land and ocean. Exchanges between oceans and land masses via the atmosphere is likely to be an important driver to the global cycling of these compounds, and net ocean-land transfers could occur in some areas.

Major global terrestrial sinks/stores for POPs are identified and the significance of gradients between them discussed.

Biosensor-based diagnostics of contaminated groundwater: assessment and remediation strategy

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Shallow groundwater beneath a former airfield site in southern England has been heavily contaminated with a wide range of chlorinated solvents. The feasibility of using bacterial biosensors to complement chemical analysis and enable cost-effective, and focussed sampling has been assessed as part of a site evaluation programme. Five different biosensors, three metabolic (*Vibrio fischeri*, *Pseudomonas fluorescens* 10568 and *Escherichia coli* HB101) and two catabolic (*Pseudomonas putida* TVA8 and *E. coli* DH5 α), were employed to identify areas where the availability and toxicity of pollutants is of most immediate environmental concern. The biosensors used showed different sensitivities to each other and to the groundwater samples tested. There was generally a good agreement with chemical analyses. The potential efficacy of remediation strategies was explored by coupling sample manipulation to biosensor tests. Manipulation involved sparging and charcoal treatment procedures to simulate remediation engineering solutions. Sparging was sufficient at most locations. Luminescent bacteria complement chemical analysis and support remediation technology.

Glacier hydrochemistry, solute provenance, and chemical denudation at a surge-type glacier in Kuannersuit Kuussuat, Disko Island, West Greenland

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In 1995–1998, an 11 km terrestrial surge of Kuannersuit Glacier, an outlet glacier of the largest ice cap on Disko Island, West Greenland, affected the catchment dramatically. In order to estimate solute fluxes and provenances, bulk meltwaters were sampled at the main subglacial outlet during the initial part of the quiescent phase. The hydrochemistry is significantly influenced by a subglacial basaltic weathering regime with absence of carbonate minerals. The results show that marine and aerosol derived solutes have minimal contribution to the total ion content, whereas sequestration of atmospheric CO₂ associated with carbonation of Ca-rich feldspar and reactive volcanic glass is more dominant than previously reported from glacierized catchments. Application of a sampling strategy dividing water samples into four groups to determine the content of dissolved HCO₃⁻ and CO₃²⁻ shows that the cationic equivalent weathering rate range is 683–860 meq⁺ m⁻² a⁻¹ and solute flux ranges between 76 and 98 t km⁻² a⁻¹. The crustal denudation rate is estimated to 26 t km⁻² a⁻¹, and the transient CO₂ drawdown amounts to 8500–13700 kg C km⁻² a⁻¹.

Effects of increased deposition of atmospheric nitrogen on an upland moor: leaching of N species and soil solution chemistry

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This study was designed to investigate the leaching response of an upland moorland to long-term (10 yr) ammonium nitrate additions of 40, 80 and 120 kg N ha⁻¹ yr⁻¹ and to relate this response to other indications of potential system damage, such as acidification and cation displacement. Results showed increases in nitrate leaching only in response to high rates of N input, in excess of 96 and 136 kg total N input ha⁻¹ yr⁻¹ for the organic Oh horizon and mineral Eag horizon, respectively. Individual N additions did not alter ammonium leaching from either horizon and ammonium was completely retained by the mineral horizon. Leaching of dissolved organic nitrogen (DON) from the Oh horizon was increased by the addition of 40 kg N ha⁻¹ yr⁻¹, but in spite of increases, retention of total dissolved nitrogen reached a maximum of 92% and 95% of 80 kg added N ha⁻¹ yr⁻¹ in the Oh and Eag horizons, respectively. Calcium concentrations and calcium/aluminium ratios were decreased in the Eag horizon solution with significant acidification mainly in the Oh horizon leachate. Nitrate leaching is currently regarded as an early indication of N saturation in forest systems. Litter C:N ratios were significantly lowered but values remained above a threshold predicted to increase leaching of N in forests.

Nitrate leaching from an upland moor podsol was significantly increased only in response to rates of N deposition in excess of 96 kg N ha⁻¹ yr⁻¹.

Atmospheric versus biological sources of polycyclic aromatic hydrocarbons (PAHs) in a tropical rain forest environment

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To distinguish between pyrogenic and biological sources of PAHs in a tropical rain forest near Manaus, Brazil, we determined the concentrations of 21 PAHs in leaves, bark, twigs, and stem wood of forest trees, dead wood, mineral topsoil, litter layer, air, and *Nasutitermes* termite nest compartments. Naphthalene (NAPH) was the most abundant PAH with concentrations of 35 ng m⁻³ in air (>85% of the 21PAHs concentration), up to 1000 µg kg⁻¹ in plants (>90%), 477 µg kg⁻¹ in litter (>90%), 32 µg kg⁻¹ in topsoil (>90%), and 160 µg kg⁻¹ (>55%) in termite nests. In plants, the concentrations of PAHs in general decreased in the order leaves > bark > twigs > stem wood.

The concentrations of most low-molecular weight PAHs in leaves and bark were near equilibrium with air, but those of NAPH were up to 50 times higher. Thus, the atmosphere seemed to be the major source of all PAHs in plants except for NAPH. Additionally, phenanthrene (PHEN) had elevated concentrations in bark and twigs of *Vismia cayennensis* trees (12–60 µg kg⁻¹), which might have produced PHEN. In the mineral soil, perylene (PERY) was more abundant than in the litter layer, probably because of in situ biological production. *Nasutitermes* nests had the highest concentrations of most PAHs in exterior compartments (on average 8 and 15 µg kg⁻¹ compared to <3 µg kg⁻¹ in interior parts) and high PERY concentrations in all compartments (12–86 µg kg⁻¹), indicating an in situ production of PERY in the nests. Our results demonstrate that the deposition of pyrolytic PAHs from the atmosphere controls the concentrations of most PAHs. However, the occurrence of NAPH, PHEN, and PERY in plants, termite nests, and soils at elevated concentrations supports the assumption of their biological origin.

Evidence of non-pyrolytic, biogenic production of PAHs is provided.

Selenium in pregnancy: is selenium an active defective ion against environmental chemical stress?

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Transportation of selenium from mother to fetus and its possible effects on mother's zinc, copper, cadmium, and mercury levels were studied together during the first trimester and at term in 216 mothers. Mothers came from three geographical places with different selenium intakes. The role of selenium as a biomarker for the vital function was estimated by studying the associations between tissue or blood selenium content and placental cytochrome P450 enzyme activities and the newborn's birth weight. Regardless of the selenium intake of the mothers, higher concentrations were found in the cord blood than in mother's blood reflecting active transportation of selenium to the fetus. Active smoking was associated with higher placental selenium concentrations like it is associated with higher placental zinc concentrations. When the cadmium concentrations were high in placenta, as in smokers, the transfer of selenium from blood to placenta was increased, decreasing the selenium levels in blood. On the other hand, the high selenium concentrations in blood were connected to lower cadmium concentrations in placenta also in nonsmokers. Selenium had correlations with copper and zinc. ECOD activity in placental tissue, mercury in mothers' hair, mothers' age, and selenium concentrations in cord blood and placental selenium all seem to have connections with xenobiotic-metabolizing enzymes linked effects among mothers. These data suggest that selenium

has an active role in the mother's defense systems against the toxicity of environmental pollutants and the constituents of cigarette smoke.

Environmental exposure to cadmium at a level insufficient to induce renal tubular dysfunction does not affect bone density among female Japanese farmers*¹
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Some recent research suggests that environmental exposure to cadmium, even at low levels, may increase the risk of osteoporosis, and that the bone demineralization is not just a secondary effect of renal dysfunction induced by high doses of cadmium as previously reported. To investigate the effect of exposure to cadmium at a level insufficient to induce kidney damage on bone mineral density (BMD) and bone metabolism, we conducted health examinations on 1380 female farmers from five districts in Japan who consumed rice contaminated by low-to-moderate levels of cadmium. We collected peripheral blood and urine samples and medical and nutritional information, and measured forearm BMD. Analysis of the data for subjects grouped by urinary cadmium level and age-related menstrual status suggested that cadmium accelerates both the increase of urinary calcium excretion around the time of menopause and the subsequent decrease in bone density after menopause. However, multivariate analyses showed no significant contribution of cadmium to bone density or urinary calcium excretion, indicating that the results mentioned above were confounded by other factors. These results indicate that environmental exposure to cadmium at levels insufficient to induce renal dysfunction does not increase the risk of osteoporosis, strongly supporting the established explanation for bone injury induced by cadmium as a secondary effect.

Real time control of urban wastewater systems—where do we stand today?
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This paper presents a review of the current state of the art of real time control (RTC) of urban wastewater systems. Control options not only of the sewer system, but also of the wastewater treatment plant and of receiving water bodies are considered. One section of the paper provides concise definitions of terms frequently used in the literature. Recent developments in the field of RTC include the consideration of the urban wastewater system in its entirety. This allows information from all parts of the wastewater system to be used for control decisions and can lead to a significant improvement of the performance of the wastewater system. Some fundamental concepts of this approach are outlined. Particular emphasis in this paper is laid on methodologies of how to derive a control procedure for a given system. As an example of an RTC system operational in practice, the Québec Urban Community global predictive RTC system is presented. The paper concludes with an outlook into current and future developments in the area of real time control. The authors are members of the Working Group on Real Time Control of the Joint Committee of the International Association of Hydraulic Research (IAHR) and the International Water Association (IWA).

Chromosomal aberration analysis in workers exposed to chemical and biological hazards in research laboratories

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Cytogenetic monitoring of individuals occupationally exposed to chemical and biological hazards has found increased frequencies of cells with chromosomal aberrations. During the present study we analyzed the frequency of chromosomal aberrations in cells from individuals working in various chemistry and biology research laboratories of the University of Brasilia, Brazil. When evaluated jointly and compared to a control group there was no significant increase in the frequency of chromosomal aberrations in the laboratory personnel. However, a group constituted of individuals of the Genetics Laboratory showed a statistically significant increase in the frequency of structural chromosomal aberrations of the chromatid gap type.

Mapping vulnerability to multiple stressors: climate change and globalization in India

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There is growing recognition in the human dimensions research community that climate change impact studies must take into account the effects of other ongoing global changes. Yet there has been no systematic methodology to study climate change vulnerability in the context of multiple stressors. Using the example of Indian agriculture, this paper presents a methodology for investigating regional vulnerability to climate change in combination with other global stressors. This method, which relies on both vulnerability mapping and local-level case studies, may be used to assess differential vulnerability for any particular sector within a nation or region, and it can serve as a basis for targeting policy interventions.

Regime interplay: the case of biodiversity and climate change

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In this paper, the interplay between the biodiversity and climate change regimes is examined in the context of a case study. An understanding of how the regimes interact is crucial to their successful operation, since it provides insight into how policy options might be drawn up to create synergy rather than conflict among the respective regimes' objectives. Despite the increasing importance of the study of regime interplay, due to its potential influence on regime effectiveness, there is limited understanding of why regimes interact and how their interplay may affect their successful operation, since few empirical studies have been conducted in this area. By analysing the causes of the regime interplay and the potential effects thereof, this paper draws policy implications regarding how the interacting regimes might be better co-ordinated to create synergy.

Are climate change impacts already affecting tropical forest biomass?

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Tropical forests contain large stocks of carbon and any change in the balance of inflows and outflows of carbon to the biomass of standing forest has potentially important consequences for the global carbon cycle and related greenhouse warming, as well as for tropical biodiversity. Despite unresolved controversies over observed changes in biomass and gas fluxes, current observations indicate the likelihood that additional climate change would have substantial impacts on tropical forests and would reinforce their contributions to global climate change. Climate change impacts are already affecting tropical forest biomass.

Drinking and Na⁺/K⁺ ATPase activity during early development of European sea bass, *Dicentrarchus labrax*

Ontogeny and short-term regulation following acute salinity changes

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The short-term osmoregulatory capacity of sea bass (*Dicentrarchus labrax*) larvae and juveniles at consecutive developmental stages was evaluated by an analysis of drinking rates and whole-body and branchial Na⁺/K⁺ ATPase activity. The effect of acute salinity stress on those parameters was assessed from hatching to the juvenile stage. Drinking rate normalised to body weight (DR_{bw}) decreased throughout postembryonic development. DR_{bw} was not affected by salinity in yolk sac larvae. However, significant differences were observed in older larvae and in juveniles submitted to hypo- and hyperosmotic challenges. Post yolk sac larvae and juveniles always drink, but at a lower rate in hypoosmotic media compared to hyperosmotic media. A correlation was established between DR_{bw} and blood osmolality during the postembryonic development of the sea bass. Na⁺/K⁺ ATPase specific and total activity in whole larval homogenates decreased from hatching to the 5-mm yolk sac larva stage and increased in 10-mm stage larvae. The enzyme specific activity in the gills, from post yolk sac larvae to juveniles, decreased whereas the total activity increased during the same period. Developing sea bass have a better capacity to cope with hypoosmotic than hyperosmotic media.

The effects of temperature and nutrient concentrations on nitrate and phosphate uptake in different species of *Porphyra* from Long Island Sound (USA)

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Uptake rates of nitrate and phosphate were measured for four species and one variety of *Porphyra* from Long Island Sound (USA) at two temperatures and two nutrient medium concentrations at increasing intervals over a 24- or 48-h period. Maximum uptake rates found were: $V_{30\text{ iM}}^{0-1\text{ h}}=73.8\text{ }\mu\text{mol NO}_3\text{ g}^{-1}\text{ DW h}^{-1}$ and $V_{3\text{ iM}}^{0-1\text{ h}}=16.7\text{ }\mu\text{mol PO}_4\text{ g}^{-1}\text{ DW h}^{-1}$, in the two thinnest *Porphyra*. We found that the nitrate uptake rates were significantly greater at 30 iM than 3 iM NO₃ concentration, and that the uptake rates decreased with time of exposure. Temperature (5, 15, and 25 °C) did not have as strong an effect on nitrate uptake rates as did nutrient concentration. Q_{10} values and uptake rates at four different nitrate concentrations indicated that nutrient uptake at 5 °C was initially

an active process. After 24 h, the processes involved appeared passive as Q_{10} values were between 1.0 and 1.3 and nitrate uptake curves were linear. Nitrate uptake rates correlated positively with the surface area/volume (SA/V) ratio. No coherent trends were found for uptake of phosphate, except that the uptake rates were significantly higher in 30 μ M NO_3^- medium as opposed to 3 μ M NO_3^- . We did not find any significant difference in uptake rate and pattern between the summer species *Porphyra purpurea* (Roth.) C. Agardh, the eurythermic *Porphyra suborbiculata* Kjellm., the winter species *Porphyra rosengurttii* J. Coll and J. Cox, and the two varieties of *Porphyra leucosticta* Thur. Le Jol. (both winter species).

Biodiversity of benthic invertebrates and organic matter processing in shallow marine sediments: an experimental study

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The main objective of this study was to measure the impact of benthic invertebrate diversity on processes occurring at the water–sediment interface. We analyzed the effects of interactions between three shallow water species (*Cerastoderma edule*, *Corophium volutator*, and *Nereis diversicolor*). The impacts of different species richness treatments were measured on sediment reworking, bacterial characteristics, and biogeochemical processes (bromide fluxes, O_2 uptake, nutrient fluxes, and porewater chemistry) in sediment cores. The results showed that the three species exhibited different bioturbation activities in the experimental system: *C. edule* acted as a biodiffusor, mixing particles in the top 2 cm of the sediments; *C. volutator* produced and irrigated U-shaped tubes in the top 2 cm of the sediments; and *N. diversicolor* produced and irrigated burrow galleries in the whole sediment cores. *C. edule* had minor effects on biogeochemical processes, whereas the other species, through their irrigation of the burrows, increased the solute exchange between the water column and the sediment two-fold. These impacts on sediment structure and solute transport increased the O_2 consumption and the release of nutrients from sediments. As *N. diversicolor* burrowed deeper in the sediment than *C. volutator*, it irrigated a greater volume of sediments, with great impact on the sediment cores.

Most treatments with a mixture of species indicated that observed values were often lower than predicted values from the addition of the individual effects of each species, demonstrating a negative interaction among species. This type of negative interaction measured between species on ecosystem processes certainly resulted from an overlap of bioturbation activities among the three species which lived and foraged in the same habitat (water–sediment interface). All treatments with *N. diversicolor* (in isolation and in mixture) produced similar effect on sediment reworking, water fluxes, nutrient releases, porewater chemistry, and bacterial characteristics. Whichever species associated with *N.*

diversicolor, the bioturbation activities of the worm hid the effect of the other species. The results suggest that, in the presence of several species that use and modify the same sediment space, impact of invertebrates on ecosystem processes was essentially due to the most efficient bioturbator of the community (*N. diversicolor*). In consequence, the functional traits (mode of bioturbation, depth of burrowing, feeding behaviour) of an individual species in a community could be more important than species richness for some ecosystem processes.

Carbon stocks, soil respiration and microbial biomass in fire-prone tropical grassland, woodland and forest ecosystems

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A thorough understanding of the role of microbes in C cycling in relation to fire is important for estimation of C emissions and for development of guidelines for sustainable management of dry ecosystems. We investigated the seasonal changes and spatial distribution of soil total, dissolved organic C (DOC) and microbial biomass C during 18 months, quantified the soil CO₂ emission in the beginning of the rainy season, and related these variables to the fire frequency in important dry vegetation types grassland, woodland and dry forest in Ethiopia. The soil C isotope ratios (¹³C) reflected the 15-fold decrease in the grass biomass along the vegetation gradient and the 12-fold increase in woody biomass in the opposite direction. Changes in ¹³C down the soil profiles also suggested that in two of the grass-dominated sites woody plants were more frequent in the past. The soil C stock ranged from being 2.5 (dry forest) to 48 times (grassland) higher than the C stock in the aboveground plant biomass. The influence of fire in frequently burnt wooded grassland was evident as an unchanged or increasing total C content down the soil profile. DOC and microbial biomass measured with the fumigation–extraction method (C_{mic}) reflected the vertical distribution of soil organic matter (SOM). However, although SOM was stable throughout the year, seasonal fluctuations in C_{mic} and substrate-induced respiration (SIR) were large. In woodland and woodland–wooded grassland C_{mic} and SIR increased in the dry season, and gradually decreased during the following rainy season, confirming previous suggestions that microbes may play an important role in nutrient retention in the dry season. However, in dry forest and two wooded grasslands C_{mic} and SIR was stable throughout the rainy season, or even increased in this period, which could lead to enhanced competition with plants for nutrients. Both the range and the seasonal changes in soil microbial biomass C in dry tropical ecosystems may be wider than previously assumed. Neither SIR nor C_{mic} were good predictors of in situ soil respiration. The soil respiration was relatively high in infrequently burnt forest and woodland, while frequently burnt grasslands had lower rates, presumably because most C is released through dry season burning and not through decomposition in fire-prone systems. Shifts in the relative importance of the two pathways for C release from organic matter may have strong implications for C and nutrient cycling in seasonally dry tropical ecosystems.

Effects of modified Pb-, Zn-, and Cd- availability on the microbial communities and on the degradation of isoproturon in a heavy metal contaminated soil

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The effects of modified heavy metal (HM) availability on the microbial community structure and on the microbe-mediated degradation of herbicide isoproturon (IPU) were evaluated in soil with a long-term HM contamination. The fate of ¹⁴C-ring labelled IPU was investigated for over 60 days under controlled microcosm conditions. Phosphate mineral apatite and a water solution of Pb, Zn, and Cd salts were previously homogeneously mixed into the soil material to reduce and to increase the proportion of bioavailable HM, respectively. The availability of Pb, Zn, and Cd was determined by HM fractionation and plant uptake 110 days after the addition of amendments, shortly before IPU addition. Apatite treatment reduced the availability of HM, but did not affect the microbial biomass and the microbial community structure on the genotype level (total soil DNA-RAPD). However, it changed the microbial community structure on the phenotype level, based on the composition of phospholipid fatty acids (PLFA) at the end of the degradation experiment. The degradation of IPU did not change. In contrast to apatite treatment, HM supplementation increased the bioavailability of Pb, Zn and Cd, which resulted in biomass reduction and changes of microbial community structure on the genotypic (total soil DNA-RAPD) and phenotypic (PLFA) level. Increased bioavailability of HM also significantly reduced the rate of IPU degradation and mineralisation. The total mineralisation over a period of 60 days decreased from 12 to 5% of initial ¹⁴C. Increased HM bioavailability did not influence the degradation pathways and kinetics of IPU.

Decomposition dynamics of plant materials in relation to nitrogen availability and biochemistry determined by NMR and wet-chemical analysis

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Improved understanding of the interactive relationships of plant material decomposition kinetics to biochemical characteristics and nitrogen availability is required for terrestrial C accounting and sustainable land management. In this study, 15 typical and/or native Australian plant materials were finely ground and incubated with a sandy soil at 25 °C and 55% water holding capacity without nitrogen (-N) or with nitrogen (+N) addition (77 mg N kg⁻¹ soil as KNO₃). The C mineralisation dynamics were monitored for 356 days and the initial biochemical characteristics of the plant materials were determined by NMR and wet-chemical analyses.

Under the -N treatment, C mineralisation rates of the plant materials were positively correlated with their initial N contents during the first several weeks, and then negatively correlated with lignin and

polyphenols contents during the late stages of incubation. Thus the ratios of lignin/N, polyphenols/N and (lignin+polyphenols)/N had more consistent correlation with the cumulative amounts of C mineralised throughout the incubation than did any single component. In terms of the C types determined by NMR analysis, the C mineralisation rates were initially related positively to carbonyl C contents, and then negatively to aryl and *O*-aryl C contents from day 3 onwards.

Addition of NO_3^- -N accelerated C mineralisation during the early stages, but resulted in lower cumulative C mineralisation at the end of the incubation for most plant materials. Under the +N treatment, the decomposition rates were correlated with the contents of lignin and the sum of cellulose+acid detergent-extractable non-phenolic compounds, or with aryl, *O*-aryl and *N*-alkyl+methoxyl C contents. Regardless of the N treatment, the ratios of aryl/carbonyl, *O*-aryl/carbonyl and (aryl+*O*-aryl)/carbonyl C had the closest and most consistent correlations with the cumulative C mineralisation among all biochemical indices examined.

A double exponential model with defined mineralisation rate constants for the active and slow pools was used to describe the C mineralisation dynamics. The biological meanings of the kinetically estimated active and slow pool sizes are interpreted and their relationships to the initial chemical/biochemical composition of the plant materials are explored.

Quantifying the contribution of dissolved organic matter to soil nitrogen cycling using ^{15}N isotopic pool dilution

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Dissolved organic matter (DOM) has been recognised as a key carbon and nitrogen (N) pool involved with soil–plant–microbe interactions. Yet few studies have quantified this contribution in agricultural soils. In this study we leached DOM from a sandy loam and sandy clay loam soil under either grassland or arable cropping. Two weeks after DOM removal microbial respiration from soils was not altered. However, a significant ($P<0.05$) decline in microbial biomass-N, potentially mineralizable-N, gross N mineralization and gross nitrification occurred after leaching. This data illustrate that whilst DOM is a small component of the soil OM it contributed up to 25% of microbial N supply within these agricultural soils.

Can ^{31}P NMR spectroscopy be used to indicate the origins of soil organic phosphates?

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The relationship between organic P status of 4 soils, 20 microorganisms isolated from these soils (2 bacteria and 3 fungi for each soil) and 13 dominant plant species of typical natural ecosystems of these soils was evaluated. The soils used were represented by two pairs with different ratios of monoester and diester P, and of DNA and other diester P. A Dystric Podzoluvisol and an alpine Umbric Leptosol were characterized by a relatively high proportion of diester P including much DNA P, while a Calcic Chernozem and subalpine Umbric Leptosol had lower proportion of diesters containing relatively less DNA P. The proportions of P compounds in bacteria and plants were very similar on average, based on the monoester to diester P ratio and on the proportions of different diesters in alkaline extract, whereas fungi contained considerably higher proportions of monoesters and polyphosphates, and a higher proportion of phospholipids in the diester fraction. The results showed that the P_{org} composition of NaOH extracts from different soils was more similar to the composition of extracts from different groups of microorganisms. There was no clear correspondence between soil and microbial diester P proportion and composition. A high proportion of polyphosphate P including pyrophosphate P in soil extracts indicates a significant contribution of fungal P compounds in the soil while the monoester to diester P ratio, and DNA to non-DNA P ratio should be used with caution to interpret the origins of soil P_{org} . The relative contributions of microorganisms and plants to monoester and diester P in soils is only partially understood.

Sources of spatial and temporal variability of inorganic nitrogen in pure and mixed deciduous temperate forests

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We investigated the influence of tree canopy composition and structure on the spatial and temporal variability of (i) concentrations of inorganic N (NH_4^+ and NO_3^-) and (ii) net N-mineralization and net nitrification, within the temperate forest floor. We compared a pure European beech stand (PS) with a mixed beech–hornbeam one (MS). Three sampling areas were chosen in each stand. Within the PS, the tree locations represented a decreasing gradient of light intensity reaching the forest floor. Within the MS they represented a gradient in the amount of hornbeam leaves present in the litter. In the field NH_4^+ and NO_3^- concentrations were measured in the upper mineral soil (UMS) and the overlying organic layers (OL and OF+OH). Field exposures using buried bags were carried out on UMS over 1 year to measure in situ net N-mineralization and net nitrification. Potential net N-mineralization and net nitrification were investigated in summer with UMS, OL and OF+OH incubated at 28 °C for 28 days in the laboratory. We hypothesize that with the presence of a mull-forming species (hornbeam) within a stand dominated by a moder-forming one (European beech), (i) the spatial and (ii) temporal patterns of soil inorganic N concentrations, net N-mineralization and net nitrification would be different in the two stands. Our main results show that tree species composition has an influence on both spatial and temporal patterns of nitrification. The PS exhibited its highest peaks of UMS NO_3^- concentration and net nitrification in spring and early summer while they were highest in the MS in winter. Furthermore, PS exhibited a higher rate of net nitrification than MS. We discuss this unexpected result and suggest that dissolved organic C may be the controlling factor for net nitrification in the MS.

Cadmium-tolerant plant growth-promoting bacteria associated with the roots of Indian mustard (*Brassica juncea* L. Czern.)

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Eleven cadmium-tolerant bacterial strains were isolated from the root zone of Indian mustard (*Brassica juncea* L. Czern.) seedlings grown in Cd-supplemented soils as well as sewage sludge and mining waste highly contaminated with Cd. The bacteria also showed increased tolerance to other metals including Zn, Cu, Ni and Co. The isolated strains included *Variovorax paradoxus*, *Rhodococcus* sp. and *Flavobacterium* sp., and were capable of stimulating root elongation of *B. juncea* seedlings either in the presence or absence of toxic Cd concentrations. Some of the strains produced indoles or siderophores, but none possessed C₂H₂-reduction activity. All the strains, except *Flavobacterium* sp. strain 5P-3, contained the enzyme 1-aminocyclopropane-1-carboxylate (ACC) deaminase, which hydrolyses ACC (the immediate precursor of plant hormone ethylene) to NH₃ and α -ketobutyrate. *V. paradoxus* utilized ACC as a sole source of N or energy. A positive correlation between the in vitro ACC deaminase activity of the bacteria and their stimulating effect on root elongation suggested that utilization of ACC is an important bacterial trait determining root growth promotion. The isolated bacteria offer promise as inoculants to improve growth of the metal accumulating plant *B. juncea* in the presence of toxic Cd concentrations and for the development of plant-inoculant systems useful for phytoremediation of polluted soils.

Modelling nitrogen mineralization from manures: representing quality aspects by varying C:N ratio of sub-pools

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The mineralization/immobilization of nitrogen when organic sources are added to soil is represented in many simulation models as the outcome of decomposition of the added material and synthesis of soil organic matter. These models are able to capture the pattern of N release that is attributable to the N concentration of plant materials, or more generally the C:N ratio of the organic input. However, the models are unable to simulate the more complex pattern of N release that has been

observed for some animal manures, notably materials that exhibit initial immobilization of N even when the C:N of the material suggests it should mineralize N. The APSIM SoilN module was modified so that the three pools that constitute added organic matter could be specified in terms of both the fraction of carbon in each pool and also their C:N ratios (previously it has been assumed that all pools have the same C:N ratio). It is shown that the revised model is better able to simulate the general patterns on N mineralized that has been reported for various organic sources. By associating the model parameters with measured properties (the pool that decomposes most rapidly equates with water-soluble C and N; the pool that decomposes slowest equates with lignin-C) the model performed better than the unmodified model in simulating the N mineralization from a range of feeds and faecal materials measured in an incubation experiment.

Dissolved organic nitrogen uptake by plants—an important N uptake pathway?
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The direct uptake of dissolved organic nitrogen (DON) by plants has the potential to be a primary Factor in ecosystem functioning and vegetation succession particularly in N-limiting environments. Clear experimental evidence to support this view, however, is still lacking. Further, many of the experimental approaches used to assess whether DON is important may be compromised due to the use of inappropriate methods for comparing and quantifying plant available inorganic and organic soil N pools. In addition, experiments aimed at quantifying plant DON capture using dual-labelled (¹⁵N, ¹³C) organic N tracers often do not consider important aspects such as isotope pool dilution, differences in organic and inorganic N pool turnover times, bi-directional DON flows at the soil–root interface, and the differential fate of the ¹⁵N and ¹³C in the tracer compounds. Based upon experimental evidence, we hypothesize that DON uptake from the soil may not contribute largely to N acquisition by plants but may instead be primarily involved in the recapture of DON previously lost during root exudation. We conclude that while root uptake of amino acids in intact form has been shown, evidence demonstrating this as a major plant N acquisition pathway is still lacking.

Short-term controls over inorganic phosphorus during soil and ecosystem development
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Geochemical sorption and biological demand control phosphorus (P) retention and availability in soils. Sorption and the biota predominantly utilize the same inorganic form of P, from the same soil pool, on the same time scale, and thus are likely to compete for P as it flows through the available

pool. In tropical soils, P availability is typically quite low and soil geochemical reactivity can be quite high. We tested whether greater P sorption strength in tropical soils resulted in lower biological uptake of available P. Since the strength of soil sorption and biological demand for P change as ecosystems develop and soils age, we used soils from the two upper horizons from three sites along a 4.1 million-year-old tropical forest chronosequence in the Hawaiian archipelago. We evaluated the strength of geochemical sorption, microbial demand, and the partitioning of added available P into biological versus geochemical soil pools over 48 h using a $^{32}\text{PO}_4$ tracer. Soil sorption strength was high and correlated with soil mineral content. The amount of added phosphate geochemically sorbed versus immobilized by microbes varied more between the organic and mineral soil horizons than among soil ages. Microbial activity was a good predictor of how much available P was partitioned into biological versus geochemical pools across all soils, while sorption capacity was not. This suggests that microbial demand was the predominant control over partitioning of available P despite changes in soil sorption strength.

Elevated CO_2 concentration and nitrogen fertilisation effects on N_2O and CH_4 fluxes and biomass production of *Phleum pratense* on farmed peat soil

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The effects of elevated CO_2 supply on N_2O and CH_4 fluxes and biomass production of *Phleum pratense* were studied in a greenhouse experiment. Three sets of 12 farmed peat soil mesocosms (10 cm dia, 47 cm long) sown with *P. pratense* and equally distributed in four thermo-controlled greenhouses were fertilised with a commercial fertiliser in order to add 2, 6 or 10 g N m^{-2} . In two of the greenhouses, CO_2 concentration was kept at atmospheric concentration (360 $\mu\text{mol mol}^{-1}$) and in the other two at doubled concentration (720 $\mu\text{mol mol}^{-1}$). Soil temperature was kept at 15 °C and air temperature at 20 °C. Natural lighting was supported by artificial light and deionized water was used to regulate soil moisture. Forage was harvested and the plants fertilised three times during the basic experiment, followed by an extra fertilisations and harvests. At the end of the experiment CH_4 production and CH_4 oxidation potentials were determined; roots were collected and the biomass was determined. From the three first harvests the amount of total N in the aboveground biomass was determined. N_2O and CH_4 exchange was monitored using a closed chamber technique and a gas chromatograph. The highest N_2O fluxes (on average, 255 $\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ during period IV) occurred just after fertilisation at high water contents, and especially at the beginning of the growing season (on average, 490 $\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ during period I) when the competition of vegetation for N was low. CH_4 fluxes were negligible throughout the experiment, and for all treatments the production and oxidation potentials of CH_4 were inconsequential. Especially at the highest rates of fertilisation, the elevated supply of CO_2 increased above- and below-ground biomass production, but both at the highest and lowest rates of fertilisation, decreased the total amount of N in the aboveground dry biomass. N_2O fluxes tended to be higher under doubled CO_2 concentrations, indicating that increasing atmospheric CO_2 concentration may affect N and C dynamics in farmed peat soil.

Hydroxylated and methyl sulfone PCB metabolites in adipose and whole blood of polar bear (*Ursus maritimus*) from East Greenland

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Persistent methyl sulfone (MeSO₂-) and hydroxylated (HO-) polychlorinated biphenyl (PCB) metabolites have emerged as important classes of environmental contaminants in vertebrate, aquatic biota and humans. In the present study, PCB, MeSO₂-PCB and HO-PCB concentrations and congener patterns were determined in the whole blood and adipose tissue of male ($n=7$) and female ($n=12$) polar bears (*Ursus maritimus*) of random age (3–25 years of age), and collected in 1999–2001 from the Ittoqqortoormiit/Scoresby Sound area in central East Greenland. There was no significant difference ($P<0.05$) between males and females with respect to PCB or PCB metabolite concentrations in either tissue. The mean sum (∑) PCB concentrations were 7020±3366 ng/g lipid weight (lw) (range 2708–18148 ng/g lw) and 46.1±44.6 ng/g wet weight (ww) (range 12.6–204.2 ng/g ww) in adipose and blood, respectively. The mean -HO-PCB concentration in whole blood was 182.3±72.1 ng/g ww (range 93.8–382.1 ng/g ww). The mean -HO-PCB to -PCB concentration ratios in whole blood were 4.59±3.58 (range 1.03–11.88) and 8.30±5.56 (range 2.16–19.47) in females and males, respectively, which are the highest ratios reported so far for polar bears from any population, or for any free-ranging animal. -HO-PCB concentrations were greater than all other major classes of organochlorines (i.e. -PCBs, -MeSO₂-PCBs, -chlordanes (CHLs), -hexachlorocyclohexanes (HCHs) and -chlorobenzenes (CBzs)). The mean -MeSO₂-PCB concentrations were 699±836 ng/g lw (range 127–3920 ng/g lw) and 10.9±9.6 ng/g ww (range 4.3–52.1 ng/g ww) in the adipose and blood, respectively. Regardless of age and sex, in both adipose and whole blood the MeSO₂-PCB congener pattern was dominated by 3'- and 4'-MeSO₂-CB101 and -CB87, and 4'-MeSO₂-CB149 (approx. 70% of the -MeSO₂-PCBs). Minor differences in the MeSO₂-PCB congener pattern were observed between blood and adipose, which suggests the possible influence of metabolite structure on mobilization and/or deposition to the adipose tissue. Sixteen HO-PCB congeners and one di-HO-PCB congener were identified, and five HO-PCB isomers and one di-HO-PCB isomer were detected. However, congener patterns were dominated by 4'-OH-CB120, 4'-HO-CB146/3'-HO-CB153, 4'-OH-CB187, 4'-HO-CB172, 4'-HO-CB193 and 4,4'-di-HO-CB202 (>10 ng/g ww). HO-PCB congener patterns in whole blood were not significantly different ($P<0.05$) between males and females. Other chlorinated phenolic contaminants, pentachlorophenol (0.3±0.3 ng/g ww) and 4'-HO-heptachlorostyrene (7.5±2.9 ng/g ww) were also detected in blood. To our knowledge, this is the first report comparing PCBs, MeSO₂-PCBs and HO-PCBs in whole blood and adipose tissue in a free-ranging wildlife species. HO-PCBs and MeSO₂-PCBs are both important circulating contaminants in polar bears from this

eastern Greenland population. Given the known toxicities of PCB metabolites, this population of polar bear may be experiencing health risks due to exposure to a complex loading of organohalogen contaminants that include HO-PCB and MeSO₂-PCB metabolites.

Comparative studies of atmospheric trace elements: improvements in air quality near a copper smelter

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Measurements of trace element concentrations, including heavy metals in the atmosphere near a copper smelter in Port Kembla, New South Wales, have shown improvements in air quality, attributed mainly to modernisation of the plant, with more than 85% decrease (for each element) in airborne Cr, Zn, Se, Ag, Cd, Sb, Au and Pb, associated with 74% reduction in Cu concentration. This data was obtained by analysis of air particulate sampled in 2001–2002 for comparison with measurements at the same location in 1978. As expected, measurements of Na and Cl derived from the marine aerosol at this coastal location showed no corresponding change.

The recent analysis of air particulate shows significant correlations between the monthly concentrations of Cu, Zn, Se, Ag and Pb, associated with industry, hence giving a high enrichment in airborne particulate by reference to the element/Sc ratios in 'average' soil. These enrichments, shown by heavy metals in particular, were two orders of magnitude greater than the values recorded in the atmosphere of rural areas; however, it is clear that air quality at Port Kembla is much improved and predominantly related to the modernisation of the smelter.

Potential biogeochemical and ecological development of a flooded tailings impoundment at the Kristineberg Zn–Cu mine, northern Sweden

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The potential short-term (=10² years) and long-term (>10² years) biogeochemical and ecological effects of diverting stream water (pH 4.9–6.7) into a limed, flooded tailings impoundment (pH 8–12) were studied by combining geochemical and biological data. In the long-term perspective, the successional development of lakes was used as a natural analogue. Based on the vertical distribution of temperature and total dissolved solids (TDS<0.22 m), the impoundment can be characterised as a continuous/discontinuous cold polymictic lake, with holomictic summer circulation. A re-inoculation study indicated that the growth of autotrophic, aerobic bacteria (presumably *Acidithiobacillus ferrooxidans*) presently is inhibited by the high pH in the impoundment.

In a short-term perspective, termination of liming and diversion of stream water into the impoundment will result in a complex interplay between physical, biogeochemical and ecological effects. A reduced vertical mixing of the ~2-m-deep water column, dissolution of calcite and gypsum (compounds of a sludge formed in the impoundment) and an enhanced microbiological activity are major expected effects. The dissolution of calcite may act as a pH buffer and result in metal remobilisation from the sludge. Excluding autochthonous organic matter produced in the impoundment, streamwater input of suspended matter and formation of settling flocculants are expected to result in a sediment accumulation rate of ~1.5 mg cm⁻² year⁻¹ (1.6–3.3 cm/10² years). Settling allochthonous organic C (0.15–0.30 mg C cm⁻² year⁻¹) may serve as an oxygen barrier and as a reservoir of organic compounds capable of driving redox reactions.

In a long-term perspective, a hydrosereal development into a wetland/peatland can be expected, with a bog lake, poor fen or flat bog as final stage. This development presupposes a decreasing pH when liming is terminated and stream water is diverted into the impoundment. It also assumes that the impoundment will be similar to an acidified lake, and that the succession is driven by *Sphagnum* colonizing the impoundment. If the hydrological conditions/water level is affected (e.g., by climatic changes or a dam failure), a terrestrialization culminating in coniferous forest on peat soil may occur.

Bioavailability of heavy metals from polluted soils to plants

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The aim of this work was to estimate, on the basis of soil extraction procedures, whether a given soil is suitable for cultivation of plants used as food or feed. The paper discusses the transfer of metal ions (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn) from contaminated soils to plants in terms of transfer factors (TF). The knowledge of transfer factors for a given element should enable prediction, before plants are sowed, whether a given soil is suitable for the cultivation of plants for consumption purposes. TF can only be evaluated when a linear relationship is observed between soil and plant composition for a given element. Such a relationship is rarely observed between the total soil content of a given metal and that of the plant. For this reason, it was necessary to develop an extraction procedure that would represent the content of metal available to plants during growing season. Several extracting agents were tested. The extracting agent that fulfilled these criteria was 2% (w/v) ammonium citrate. Statistically significant correlation coefficients were determined between the citrate-soluble fraction of soil and content in plant in the case of all the elements studied, except Ni. If a statistically significant correlation exists, it is then possible to evaluate the soil–plant transfer factor for a given metal in plants.

Microbiology of a wetland ecosystem constructed to remediate mine drainage from a heavy metal mine

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A pilot passive treatment plant (PPTP) was constructed to evaluate the potential of a composite wetland system to remediate acidic, metal-rich water draining the former Wheal Jane tin, in Cornwall, England. The treatment plant consists of three separate and controllable composite systems, each of which comprises a series of aerobic wetlands for iron oxidation and precipitation, a compost bioreactor for removing chalcophilic metals and to generate alkalinity, and rock filter ponds for removing soluble manganese and organic carbon. To understand the roles of microorganisms in remediating acid mine drainage (AMD) in constructed wetland ecosystems, populations of different groups of cultivatable acidophilic microbes in the various components of the Wheal Jane PPTP were enumerated over a 30-month period. Initially, moderately acidophilic iron-oxidising bacteria (related to *Halothiobacillus neapolitanus*) were found to be the major cultivatable microorganisms present in the untreated AMD, though later heterotrophic acidophiles emerged as the dominant group, on a numerical basis. Culturable microbes in the surface waters and sediments of the aerobic wetlands were similarly dominated by heterotrophic acidophiles, though both moderately and extremely acidophilic iron-oxidising bacteria were also present in significant numbers. The dominant microbial isolate in waters draining the anaerobic compost bioreactors was an iron- and sulfur-oxidising moderate acidophile that was closely related to *Thiomonas intermedia*. The acidophiles enumerated at the Wheal Jane PPTP accounted for 1% to 25% of the total microbial population. Phylogenetic analysis of 14 isolates from various components of the Wheal Jane PPTP showed that, whilst many of these bacteria were commonly encountered acidophiles, some of these had not been previously encountered in AMD and AMD-impacted environments.

Biogeochemistry of the compost bioreactor components of a composite acid mine drainage passive remediation system

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The compost bioreactor (“anaerobic cell”) components of three composite passive remediation systems constructed to treat acid mine drainage (AMD) at the former Wheal Jane tin mine, Cornwall, UK were studied over a period of 16 months. While there was some amelioration of the preprocessed AMD in each of the three compost bioreactors, as evidenced by pH increase and decrease in metal concentrations, only one of the cells showed effective removal of the two dominant heavy metals (iron and zinc) present. With two of the compost bioreactors, concentrations of soluble (ferrous) iron draining the cells were significantly greater than those entering the reactors, indicating that there was net mobilisation (by reductive dissolution) of colloidal and/or solid-phase ferric iron compounds within the cells. Soluble sulfide was also detected in waters draining all three compost bioreactors which was rapidly oxidised, in contrast to ferrous iron. Oxidation and hydrolysis of iron, together

with sulfide oxidation, resulted in reacidification of processed AMD downstream of the compost bioreactors in two of the passive treatment systems. The dominant cultivatable microorganism in waters draining the compost bioreactors was identified, via analysis of its 16S rRNA gene, as a *Thiomonas* sp. and was capable of accelerating the dissimilatory oxidation of both ferrous iron and reduced sulfur compounds. Sulfate-reducing bacteria (SRB) were also detected, although only in the bioreactor that was performing well were these present in significant numbers. This particular compost bioreactor had been shut down for 10 months prior to the monitoring period due to operational problems. This unforeseen event appears to have allowed more successful development of AMD-tolerant and other microbial populations with critical roles in AMD bioremediation, including neutrophilic SRB (nSRB), in this compost bioreactor than in the other two, where the throughput of AMD was not interrupted. This study has revealed new insights into the operation of compost bioreactors used to remediate mine waters and has shown that, when operated under appropriate conditions, they can be highly efficient at generating alkalinity and removing metals from extremely acidic, metal-rich AMD.

The Wheal Jane wetlands model for bioremediation of acid mine drainage

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Acid mine drainage (AMD) is a widespread environmental problem associated with both working and abandoned mining operations. As part of an overall strategy to determine a long-term treatment option for AMD, a pilot passive treatment plant was constructed in 1994 at Wheal Jane Mine in Cornwall, UK. The plant consists of three separate systems, each containing aerobic reed beds, anaerobic cell and rock filters, and represents the largest European experimental facility of its kind. The systems only differ by the type of pretreatment utilised to increase the pH of the influent minewater (pH <4): lime dosed (LD), anoxic limestone drain (ALD) and lime free (LF), which receives no form of pretreatment. Historical data (1994–1997) indicate median Fe reduction between 55% and 92%, sulphate removal in the range of 3–38% and removal of target metals (cadmium, copper and zinc) below detection limits, depending on pretreatment and flow rates through the system. A new model to simulate the processes and dynamics of the wetlands systems is described, as well as the application of the model to experimental data collected at the pilot plant. The model is process based, and utilises reaction kinetic approaches based on experimental microbial techniques rather than an equilibrium approach to metal precipitation. The model is dynamic and utilises numerical integration routines to solve a set of differential equations that describe the behaviour of 20 variables over the 17 pilot plant cells on a daily basis. The model outputs at each cell boundary are evaluated and compared with the measured data, and the model is demonstrated to provide a good representation of the complex behaviour of the wetland system for a wide range of variables.

Heavy metal content in soil reclaimed from a municipal solid waste landfill

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Residues reclaimed from a municipal solid waste (MSW) landfill were characterized for the concentrations of a number of heavy metals. The residue fractions analyzed included a fine fraction (<0.425 mm), an intermediate fraction (>0.425 and <6.3 mm) and a fraction consisting of paper products that could ultimately degrade to a smaller size. The intermediate fraction appeared to be organic in nature, while the fine fraction was more soil-like. In general, the metal concentrations were greatest in the intermediate fraction and lowest in the fine fraction. The effect of sample age on the elemental content was also investigated. The concentrations of several elements were greater in older samples (sample ~8 years in age) when compared to newer samples (sample ~3 years in age). Limitations associated with the land application of residual soil (composed of the fine and intermediate fractions) were assessed by comparing measured concentrations to regulatory threshold values. In general, most metal concentrations were below regulatory thresholds for use in unrestricted settings. At the concentrations measured, however, several elements might limit reuse options, depending on which regulatory threshold serves as a benchmark. Elevated concentrations of arsenic presented the greatest limitation with respect to common US thresholds while elevated cadmium concentrations presented the greatest limitation when compared to UK thresholds. The source of the arsenic was determined to be the waste, not the cover soil.

Assessing the impact of land-applied biosolids from a thermomechanical (TMP) pulp mill to a suite of terrestrial and aquatic bioassay organisms under laboratory conditions

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The potential impact on a variety of bioassay organisms when pulp-mill biosolids from a thermomechanical pulp mill (western Canada) were applied to a reference soil has been investigated in a laboratory setup. The current research assessed acute, chronic, and reproductive impacts using a battery of terrestrial and aquatic organisms. Terrestrial organisms were exposed to soil amended with different concentrations of biosolids, while aquatic organisms were used to assess the impact of biosolids' runoff into receiving waters. The former bioassays showed that an application rate of 20 tonnes hectare⁻¹ (t ha⁻¹) "bone-dry" biosolids applied to reference soil produced no observable adverse impact on the terrestrial organisms. In the latter assays, undiluted (100%) and 50% diluted biosolids' runoff into receiving water had a detrimental impact on the aquatic organisms. However, concentrations not exceeding 25% (environmentally relevant concentrations) had neither an acute nor chronic impact compared to reference populations. The organisms' abilities to reproduce were also unaltered. While this study only examined the biosolids from one mill, there is the potential that land-application of characteristically well-defined pulp mill biosolids *may* constitute an acceptable way of disposing of pulp and paper mill biosolid residues. However, the biosolids coming from different mills, with differing processes, must be dealt with on a case-by-case situation. Each series of biosolids must be rigorously tested for toxicological impact in the laboratory under tightly controlled conditions. Subsequently, field experimentation must be conducted before definitive conclusions can be made.

Mitigating nutrient leaching with a sub-surface drainage layer of granulated tires

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Markets for scrap tires have expanded since the early 1990s with the development of value-added applications such as tire-derived fuel and crumb-rubber-amended asphalt. Granulated tires have also displayed the ability to adsorb volatile organic compounds, indicating that the rubber material can be a useful filter media. Sand-based root zones, typically used for golf course putting green and athletic field construction, lack sufficient cation exchange capacity to restrict nitrogen and phosphorus migration through the root zone and into sub-surface drainage systems. Therefore, the adsorptive properties of tire rubber for retaining nitrogen and phosphorus were studied when applied as a distinct sub-surface drainage or intermediate layer in golf course putting greens. A statistically significant reduction in the concentration of nitrate in leachate was achieved by replacing traditional pea gravel with equally sized granulated tires for the drainage layer media, although the mechanism of nitrate mitigation remains unclear. The results indicate that using granulated tires as a drainage layer or fill material beneath sand-based root zones does not compromise the function of the profile or quality of the vegetation while creating an environmentally beneficial and value-added option for scrap tire reuse.

Urban nitrogen biogeochemistry: status and processes in green retention basins

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Nitrogen (N) cycling has been poorly characterized in urban ecosystems. Processes involving N are of specific concern due to increasing anthropogenic inputs from fertilizer uses and fossil fuel combustion in cities. Here we report on a study of N biogeochemistry in city green retention basins and city parks in the Phoenix metropolitan area, Arizona, USA. City retention basins receive N inputs from street runoff, and along with city parks, fertilizer input from management, making these urban patches potential hot spots for biogeochemical cycling. We sampled soils from six retention basins and two non-retention city parks and measured soil organic matter (SOM) content, net N mineralization, net nitrification, denitrification potential, and intact core denitrification flux and nitrate retention. Our results showed significantly higher SOM, extractable nitrate, nitrification rates and potential denitrification rates in surface soils (0–7.5cm; soil that is directly affected by fertilizer N input, irrigation, and storm runoff) than in deeper soils. We also observed a distinct horizontal trend of decreasing SOM and denitrification potentials from inlet to outlet (dry well) in the retention basins. Denitrification rates, measured both as potential rates with substrate amendment (390–

1151ngN₂O–Ng⁻¹soilh⁻¹), and as intact core fluxes (3.3–57.6mgNm⁻²d⁻¹), were comparable to the highest rates reported in literature for other ecosystems. Management practices that affect biogeochemical processes in urban retention basins thus could affect the whole-city N cycling.

The imprint of coarse woody debris on soil chemistry in the western Oregon Cascades

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Coarse woody debris (CWD) may create a spatially discrete soil imprint through the release of carbon rich, acidic dissolved organic matter (DOM). DOM has been implicated in many soil processes such as humus formation, nutrient immobilization, podzolization, and the dissolution of soil minerals. We investigated a potential CWD imprint on soil chemistry by sampling leachates and soil solutions under CWD at different stages of decay and under the forest floor as controls. Solutions were analyzed for total dissolved organic carbon (DOC) and polyphenol concentrations. DOC was further separated by chemical fractionation. We also sampled soil from underneath CWD and from control areas without CWD. Samples were analyzed for pH, base saturation, exchangeable acidity, and several aluminum and iron fractions. The pH of CWD leachates was lower ($p < 0.001$) and contained more polyphenols ($p < 0.0001$) and DOC than control leachates, although chemical DOC fractions from CWD and the forest floor were similar. Surface mineral soils under CWD were lower in pH ($p < 0.005$), had more exchangeable acidity ($p < 0.002$) and more exchangeable aluminum ($p < 0.04$) and iron ($p < 0.06$) than forest floor soils. At depths greater than 5cm, there were no differences between forest floor soils and soils under CWD. Our results suggest that CWD in the middle stages of decay acidifies the surface soil as it decomposes by decreasing exchangeable bases and increasing exchangeable acidity and aluminum. Soils under the most highly decayed CWD, or deeper soils were not affected by CWD. Although we hypothesized that well-decayed CWD would show a spatially explicit imprint on soils, the effect of CWD on soil chemistry was small and limited to surface mineral soils.

Nitrate removal in a first-order stream: reconciling laboratory and field measurements

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A combination of laboratory and field experiments were carried out to evaluate nitrate(NO₃) removal during stream transport in a first-order agricultural drainage stream. Intact stream sediment cores overlain with stream and NO₃-amended stream water indicated NO₃ losses averaging 93 – 353mgm⁻²day⁻¹, with NO₃ concentration exerting a primary control on loss rate. Isotopic data indicated enrichment of NO₃ - ¹⁵N over time as NO₃ concentrations decreased, indicating a denitrification loss. Field experiments were designed to evaluate dilution of streamwater with low-

NO₃⁻ groundwater in addition to other NO₃⁻ removal processes during transport. A series of bromide tracer and NO₃⁻ - addition experiments were carried out in the field; groundwater dilution dominated the downstream NO₃⁻ concentration trends, accounting for all observed decreases in NO₃⁻ concentration. Isotopic data did not point to denitrification downstream as a major NO₃⁻ removal process. This apparent disparity between simulated laboratory and *in-situ* stream removal rates appears to be a function of the hydrological processes controlling exchanges between stream bottom sediments and the overlying water. These results suggest that caution must be exercised in extrapolating potentials for NO₃⁻ removal measured in laboratory experiments to the field, as these rates could be overestimated in some watersheds.

Biogeochemistry of trimethyllead and lead in a forested ecosystem in Germany

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Lead compounds, especially ionic organolead compounds (OLC), are highly toxic and mobile pollutants strongly affecting many ecosystems. Soil pools and fluxes with precipitation, litterfall and runoff of trimethyllead (TML), one of the dominant ionic OLC in the environment, and Pb_{total} were investigated in a forested ecosystem in NE-Bavaria, Germany. In addition, ad/desorption of TML to soils was studied in batch experiments and its degradation in soils was investigated using long term incubations. Total soil storage in the catchment was 11.56mg Pbha⁻¹ for TML and 222kg Pbha⁻¹ for Pb_{total}. More than 90% of the soil storage of TML was found in the wetland soils of the catchment representing only 30% of the area. Most Pb_{total} (>90%) was found in the upland soils. In upland soils, TML was only detectable in the forest floor. The annual total deposition from the atmosphere, estimated as throughfall+litterfall fluxes, amounted to 3.7mg Pbha⁻¹ year⁻¹ for TML and 52g Pbha⁻¹ year⁻¹ for Pb_{total}. The contribution of litterfall was 1.5 and 32%, respectively. The concentrations of TML and Pb_{total} in wet precipitation were: fog>throughfall>bulk precipitation. The annual fluxes with runoff from the catchment was 0.5mg Pbha⁻¹ year⁻¹ for TML and 2.8g Pbha⁻¹ year⁻¹ for Pb_{total}. TML degraded rapidly in the forest floor (Oa horizon) with a half-life (*t*) of 33.5 days. The degradation of TML in Fen (*t*=421 days) and in the mineral soil (Bw-C horizon, *t*=612 days) was much slower. Emission of tetramethyllead from wetland soils was not observed during the 1 year incubation. The adsorption affinity of TML to different soils was Fen>Oa>ABw-C. The ratio of total soil storages to the present annual input were 3.6 years for TML. TML and Pb_{total} are still deposited in remote areas even after the use of tetraalkyllead as additives has been terminated for years. The rates of deposition are, however, much lower than in the past. Forest soils act as a sink for deposited TML and Pb_{total}. TML is accumulated mostly in wetland soils and seems to be stable under anoxic conditions for a long time. In upland soils, TML decomposes rapidly. Only small amounts of TML are transferred from soils into runoff.

Contribution of plant photosynthates to dissolved organic carbon in a flooded rice soil

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Dissolved organic C (DOC) plays important roles in nutrient cycling and methane production in flooded rice ecosystem. The microcosm experiment was carried out to measure directly the contribution of photosynthates to DOC by using a ¹³C pulse-chase labeling technique. DOC was operationally divided into water-extractable organic C (WEOC) and salt-extractable organic C (SEOC) by successive extraction firstly with deionized water and then with 0.25M K₂SO₄. Total WEOC increased with plant growth, whereas SEOC concentration did not change significantly over the growing season. About 0.037–0.36% (mean 0.16%) of the assimilated ¹³C was incorporated into WEOC immediately after ¹³CO₂ assimilation (Day 0), but only 0–0.025% (mean 0.01%) was incorporated into SEOC. At the end of the growing season, the ¹³C amounts of WEOC substantially decreased, while those of SEOC slightly increased. The estimated net plant C contribution was 21mgCplant⁻¹ to WEOC and 6mgCplant⁻¹ to SEOC, corresponding to 33.8% of total WEOC and 20.2% of total SEOC at the end of the growing season, respectively. The results suggest that the incorporation and decomposition of the photosynthesized C occurred rapidly in rice soil which significantly affected the WEOC dynamics, but SEOC appeared to be in equilibrium with the native soil organic matter, receiving less effect from the plant growth.

The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed

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Abstract Long-term, weekly measurements of streamwater nitrogen and phosphorus concentrations in the West Fork of Walker Branch, a 1st order forested stream in eastern Tennessee, were used to assess the importance of in-stream processes for controlling stream concentrations and watershed exports. Over the period from 1991 to 2002, there was a slight declining trend in watershed export of dissolved inorganic N via streamflow, despite relatively high and constant wet N deposition rates (5 kg/ha/y). The watershed retains >90% of N deposition inputs. Concentrations of NO₃⁻ and soluble reactive phosphorus (SRP) showed distinct seasonal patterns with autumn and early spring minima and summer maxima. An end-member mixing analysis indicated that these seasonal concentration patterns were largely a result of seasonal variations in in-stream uptake processes, with net uptake of NO₃⁻ and SRP having the greatest impact on streamwater concentrations in November (reductions of 29 g N/l and 2.5 g P/l, respectively). This was likely a result of high rates of uptake by microbes colonizing new inputs of leaf detritus. For NO₃⁻ there was a secondary peak in net uptake in March and April (about 9 g N/l) resulting from increased uptake by stream algae and bryophytes. Summer was a period of net release of NO₃⁻ to streamwater (peaking at 9 g N/l in July) and minimal net effects on SRP concentrations. On average, in-stream processes resulted in removal of about 20% of the NO₃⁻ and 30% of the SRP entering the stream from the catchment

annually. This study, as well as other recent work, suggests that in-stream processes are important buffers on stream nutrient concentrations and exports reducing the effects of changes in inputs and retention in terrestrial portions of watersheds.

Long-term effects of elevated nitrogen on forest soil organic matter stability
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Nitrogen addition may alter the decomposition rate for different organic-matter pools in contrasting ways. Using a paired-plot design, we sought to determine the effects of long-term elevated N on the stability of five organic-matter pools: organic horizons (Oe+a), whole mineral soil (WS), mineral soil fractions including the light fraction (LF), heavy fraction (HF), and a physically recombined fraction (RF). These substrates were incubated for 300 days, and respiration, mineralized N, and active microbial biomass were measured. Samples with elevated N gave 15% lower cumulative respiration for all five substrates. Over the 300-day incubation, the Oe+a gave twice the cumulative respiration (gCkg^{-1} initial C) as the LF, which gave slightly higher respiration than the HF. Respiration was 35% higher for the WS than for the RF. Mineralized N was similar between N treatments and between the LF and HF. Net N mineralized by the LF over the course of the 300-day incubation decreased with higher C:N ratio, due presumably to N immobilization to meet metabolic demands. The pattern was opposite for HF, however, which could be explained by a release of N in excess of metabolic demands due to recalcitrance of the HF organic matter. Mineralized N increased with respiration for the HF but showed no pattern, or perhaps even decreased, for the LF. WS and RF showed decreasing active microbial biomass near the end of the incubation, which corresponded with decreasing respiration and increasing nitrate. Our results show that long-term elevated N stabilized organic matter in whole soil and soil fractions.

Dissolved organic carbon dynamics in the peat–streamwater interface

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A series of experiments were conducted to address the fate of dissolved organic carbon (DOC) in the peat–stream interface zone linking a minerotrophic poor fen and an ombrotrophic mire with surrounding stream water in the drainage area of Lake Öträsket in northern Sweden. Transport and

mineralisation of DOC were quantified in peat–stream interface cores in response to variations in pore water velocity, DOC concentration and the molecular size and source of DOC. Mineralisation and CH₄ production were positively correlated with pore water velocity at rates between 0.08 and 0.20cmh⁻¹ and negatively correlated at rates between 0.20 and 0.40cmh⁻¹. The DOC concentration of the effluent from the peat cores was independent of the pore water velocity but proportional to the DOC concentration of the source water. Higher concentrations of DOC were exported from than imported to the peat cores, and the cores exported DOC molecules of smaller average molecular size than received. Carbon mineralisation in the peat, assessed in a static system, was independent of the concentration of DOC. DOC with a nominal cutoff at 100Da was mineralised faster by streamwater bacteria than DOC dialysed with a cutoff at 3500Da, and their mineralisation rate was positively correlated with the DOC concentration. Streamwater bacteria mineralised streamwater DOC at a lower rate than the peat–stream interface zone pore water DOC. The pattern of velocity dependence of mineralisation was the same for both sources of peat DOC but the mineralisation rates, average molecular size, and bioavailability of DOC were different, emphasising the importance of the compositional heterogeneity of the peat–stream interface zone for the DOC budget of streamwater.

Occurrence and distribution of long-chain acyclic ketones in immature coals

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Seven coal and carbonaceous mudstone samples were collected from outcropping Jurassic coal beds, on the margin of the Dingxi Basin, Northwestern China. The *n*-alkane distributions in all of the samples are characterised by high concentrations of the C₁₉–C₂₉ homologues, and very much lower amounts outside of this range. C₂₃ or C₂₄ are usually the most abundant *n*-alkanes. Straight chain *n*-alkanes from C₂₃ to C₂₉ show moderate odd-to-even C number predominances (CPI range: 1.26–2.70). Long-chain acyclic *n*-alkan-2-ones, *n*-alkan-3-ones and *n*-alkan-4-ones ranging from C₁₅ to C₃₃ with moderate odd-to-even C number predominances, were detected together with one isoprenoid methyl ketone (6,10,14-trimethylpentadecan-2-one) in all of the samples. The C number distributions of the three series of alkanones show a similar distribution to that of the *n*-alkanes, but the correspondence is not sufficient to substantiate a product–precursor relationship. It can be concluded that the *n*-alkan-2-ones are a mixture of the products of microbially-mediated α -oxidation of corresponding *n*-alkanes in the sediments and from the microbial oxidation of higher plant-derived *n*-alkanes prior to incorporation in the sediments. The *n*-alkan-3-ones and *n*-alkan-4-ones were formed from microbially mediated oxidation of the corresponding *n*-alkanes in the β and α positions, respectively. Generation of the ketones from higher plant *n*-fatty alcohols and *n*-alkanoic acids could be a possible way to form some of the ketones observed, but it can only play a minor role in the samples analysed.

Iron monosulfide formation and oxidation in drain-bottom sediments of an acid sulfate soil environment

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Iron monosulfide formation and oxidation processes were studied in the extensively drained acid sulfate soil environment of the Tweed River floodplain in eastern Australia. Porewater profiles of pH, Eh, SO_4^{2-} , Fe^{2+} , Fe^{3+} , Cl⁻, HCO_3^- , and metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) were obtained using in situ dialysis membrane samplers ('peepers'). Concentrations of acid volatile S (AVS), pyrite, total S, reactive Fe, total and organic C, simultaneously extracted metals (SEMs) and total elemental composition by X-ray fluorescence, were determined on sediment samples. The oxidation of pyrite in the surrounding landscape provides a source of acidity, Fe, Al, SO_4 and metals, which are exported into the drainage system where they accumulate in the sediments and porewaters. Negative porewater concentration gradients of SO_4^{2-} and Fe^{2+} , and large AVS concentrations in the sediments, indicate Fe monosulfides form rapidly under reducing conditions and consume acidity and metals. Oxidation of the sediments during previous drought episodes has resulted in the conversion of monosulfides and pyrite to oxidised Fe minerals and the release of acidity, SO_4^{2-} , Fe^{3+} , and metals to the surface waters. These formation and oxidation cycles show that Fe monosulfides play an important role in controlling water quality in the drainage system.

Biogeochemistry and natural attenuation of nitrate in groundwater at an explosives test facility

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An interdisciplinary study was conducted to characterize the distribution and fate of NO_3^- in groundwater at Lawrence Livermore National Laboratory (LLNL) Site 300, a high-explosives test facility in the semi-arid Altamont Hills of California. Site 300 groundwater contains NO_3^- concentrations ranging from <0.5 to >200 mg NO_3^-/L . Several lines of evidence strongly suggest that denitrification is naturally attenuating NO_3^- in the confined, O_2 -depleted region of the bedrock aquifer under study (Tnbs₂): (a) both NO_3^- and dissolved O_2 (DO) concentrations in groundwater decrease dramatically as groundwater flows from unconfined to confined aquifer conditions, (b) stable isotope signatures (i.e., ¹⁵N and ¹⁸O) of groundwater NO_3^- indicate a trend of isotopic enrichment that is characteristic of denitrification, and (c) dissolved N_2 gas, the product of denitrification, was highly elevated in NO_3^- -depleted groundwater in the confined region of the Tnbs₂ aquifer. Long-term NO_3^- concentrations were relatively high and constant in recharge-area monitoring wells (typically 70–100 mg NO_3^-/L) and relatively low and constant in the downgradient confined region (typically <0.1–3 mg NO_3^-/L), suggesting a balance between rates of NO_3^- loading and removal by denitrification. Chemolithoautotrophic denitrification with pyrite as the electron donor is plausible in the Tnbs₂

aquifer, based on the low dissolved organic C concentrations (<1.5 mg/L) that could not support heterotrophic denitrification, the common occurrence of disseminated pyrite in the aquifer, and the trend of increasing SO_4^{2-} as groundwater flows from aerobic, unconfined to anoxic, confined aquifer conditions. Nitrate sources were investigated by experimentally determining the ^{15}N and ^{18}O signatures of NO_3^- from three potential anthropogenic sources of NO_3^- at Site 300: $\text{Ba}(\text{NO}_3)_2$ (mock explosive), HNO_3 , and photolysis of the explosive RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). The isotopic signatures of these potential NO_3^- sources were markedly different than those of NO_3^- in Tnbs₂ groundwater samples, suggesting that other sources must contribute significantly to the NO_3^- loading at Site 300. In particular, NO_3^- and NO_2^- resulting from RDX photolysis reflected dramatically depleted ^{15}N (ca. -7.4‰) and ^{18}O (ca. -25.7‰) values.

Determination of bromide and potassium in saline groundwaters by capillary electrophoresis without prior dilution

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Two capillary electrophoretic analysis methods are presented; one optimized for the analysis of Br^- and the other for determination of K^+ in groundwaters of high conductivity. The water sampling was performed from the planned final disposal facility area for spent nuclear fuel at Olkiluoto in the municipality of Eurajoki, Finland. Bromide was analysed in an acidic electrolyte solution containing 5 mM formic acid and 42 mM NaCl (pH 3.5) and using direct UV detection (200 nm). Sample stacking was needed for the preconcentration. Potassium was analysed at pH 4.5 using imidazole-18-crown-6 ether solution. The accuracies of the Br^- and K^+ methods were tested using laboratory-made reference sample mixtures with high salt concentration. In the Br^- analyses, the limits of detection and determination were 0.1 and 1 mg L^{-1} , respectively. The developed CE analysis for K^+ in saline water was repeatable (RSD% 14.5–18.0) and the detection and the determination limits were 0.5 and 2.0 mg L^{-1} , respectively. The interlaboratory results showed that CE measurements of Br^- and K^+ were compatible with those made with traditional solvent chemistry techniques.

Transport of juvenile clams: effects of species and sediment grain size

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Erosion and transport of juvenile benthic invertebrates, including bivalves, have the potential to alter patterns of distribution and abundance during the early post-settlement period. However, the factors influencing rates of postlarval dispersal are not well understood. Both hydrodynamics and behaviour (e.g. burrowing) are likely to play a role in determining patterns of transport of juvenile bivalves.

To determine the relationship between sediment transport and bivalve dispersal, experiments were conducted in a racetrack flume to examine the effect of grain size, flow, and clam size on rates of erosion of two species of juvenile clams (*Mya arenaria* and *Mercenaria mercenaria*). Results of the experiments were compared to predictions of erosion thresholds based on the physical characteristics of the sediment and clams. Erosion of *Mercenaria* was greater than *Mya*, the opposite of predictions based on *Mercenaria*'s greater density, indicating the importance of burrowing behaviour. In most cases, erosion also was greater in the finer sand, in contrast to the predicted similarity of erosion thresholds of the two sediments. However, clam erosion did increase with increasing shear velocity and decrease with clam size, as expected. The results of this study indicate that both hydrodynamics and behaviour play roles in the transport of these two species of juvenile bivalves and that their vulnerability to passive erosion cannot be predicted solely from knowledge of sediment transport.

Effects of marine organisms extracts on microtubule integrity and cell cycle progression in cultured cells

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Marine organisms have been reported to be a rich source of biologically active compounds, but when compared with plants, their use is much more restrict in popular medicine. Among marine animals, sponges and ascidians are two of the most prominent sources of new compounds with cytotoxic potential. In this study, we tested 40 extracts of marine sponges and ascidians from southeastern Brazilian coast aiming to evaluate their anti-proliferative effects on cultured cells. The extracts of *Amorphinopsis* sp., *Arenosclera brasiliensis*, *Cystodytes dellechiajei*, *Cliona* aff. *celata*, *Didemnum* sp., *Hadromerida* and *Scopalina ruetzleri* showed an IC₅₀ ?30 µg/mL and produce strong effects on microtubules organization and on the cell cycle progression.

Fish otolith chemistry influenced by exposure to multiple environmental variables
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There is an increasing desire for researchers to use the elemental concentrations in fish otoliths to reconstruct environmental histories of fish. These reconstructions may be plausible due to the unique incorporation of elements into discrete layers of otolith material that correspond to daily growth, and because environmental variables of temperature, salinity, and water chemistry can influence otolith chemistry. However, it is essential to establish exactly how temperature, salinity, and the ambient concentration of elements influence otolith chemistry in order to interpret environmental histories of fish. Using a controlled laboratory experiment we tested the relative and interactive effects of temperature, salinity, and ambient concentration of strontium (Sr) and barium (Ba) on the resulting concentration of Sr and Ba in otoliths of black bream *Acanthopagrus butcheri* (Munro 1949). Salinity and concentration, and temperature and concentration interacted to affect the elemental concentration of Sr:Ca and Ba:Ca in otoliths. Regression analysis revealed that temperature and ambient concentration contributed most to the trend in otolith chemistry for both elements. Importantly, this is the first experiment to combine three environmental variables and assess their effect on otolith chemistry. Based on these results, it should be possible to use changes in the elemental concentration in otoliths to better reconstruct previous environments of temperature, salinity, and ambient water chemistry, which is especially useful when determining occupancy in habitats such as estuaries that display variable environmental characteristics.

Environmental management of construction and demolition waste in Kuwait
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There is an increasing pressure on the construction industry to reduce costs and improve the quality of our environment. The fact is that both of these goals can be achieved at the same time. Although construction and demolition (C&D) constitutes a major source of waste in terms of volume and weight, its management and recycling efforts have not yet seen the light in Kuwait. This study focuses on recycling efforts leading to the minimization of the total C&D waste that is currently landfilled in Kuwait. This paper presents the current status of C&D waste disposal system in Kuwait and identifies the potential problems to the environment, people and economy. Then, it investigates alternative solutions to manage and control this major type of waste in an economically efficient and environmentally safe manner. Next, the paper describes the feasibility of establishing a C&D waste recycling facility in Kuwait. It concludes by highlighting the major benefits and bottleneck problems with such a recycling facility.

Energy conservation and CO₂ emission reductions due to recycling in Brazil
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The present paper aims to make the energy saving potential provided by waste recycling in Brazil evident by pointing out more specifically the benefits regarding climate change mitigation. In this case, based on the energy saved due to the recycling process of an exogenous amount of waste, we have built two scenarios in order to show the potential for indirectly avoiding CO₂ emissions in the country as a result of the recycling process. According to the scenario, 1 Mt and 3.5 Mt of CO₂, respectively, would be avoided per year due to solid waste recycling. The international context for greenhouse gas emissions reduction, such as the United Nations Framework Convention on Climate Change and its Kyoto Protocol has been taken into account.

Sorption studies of chloroanilines on kaolinite and montmorillonite

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Batch experiments have been performed in order to evaluate the ability of the two reference clays kaolinite (KGa-1) and Na-montmorillonite (SWy-1) to retain three representative chloroanilines: 3-chloroaniline, 3,4-dichloroaniline and 2,4,6-trichloroaniline. Systems containing the clay mineral and the pollutant solution (at concentration levels ranging between 1.0 and 10.0 mg/L) were considered and RP-HPLC methods were employed to follow the sorption processes as a function of time. The results indicate that montmorillonite shows a general higher sorption capacity with respect to kaolinite and that for both the reference clays, in the concentration range investigated, the amount of pollutant sorbed increases with concentration. The sorption coefficient K_d ranges between 0.0030 L/g for the system 3-chloroaniline–kaolinite and 0.0488 L/g for the system 2,4,6-trichloroaniline–montmorillonite. The most lipophilic trichloroaniline shows the greater sorption. X-ray analyses suggest for kaolinite a preferential sorption onto the mineral surface, while for montmorillonite a progressive swelling of the structure is observed, likely due to sorption processes that also take place in the interlayer. Chloroanilines are sorbed by clay standard kaolinite and Na-montmorillonite at different extents and likely by different mechanisms.

A systems analysis tool for construction and demolition wastes management

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Managing construction and demolition (C&D) wastes has challenged many municipalities with diminishing waste disposal capacity. Facing such challenges, the Massachusetts Department of Environmental Protection proposed a policy restricting the landfill disposal of certain C&D waste materials, if unprocessed. This research is to study the potential economic impact of such restriction on construction contractors and C&D waste processors. A spreadsheet-based systems analysis model has been developed to assist the cost-benefit evaluation for various C&D waste management scenarios. The model, developed based on the mass balance principle, is designed to track a C&D waste stream through the various stages of a waste management system, i.e. generation, source separation, processing, recycling, and final disposal. This model, by incorporating the material flow data with the cost/revenue data associated with each management activity, can then provide an economic analysis for a proposed C&D waste management scenario. A case study illustrating the application of this model for Massachusetts is also presented.

Corrosion behavior of glass and glass-ceramics made of municipal solid waste incinerator fly ash

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Glasses and glass-ceramics were prepared by melting municipal solid waste (MSW) incinerator fly ash and their corrosion properties were evaluated. Corrosion of both materials proceeded in two different steps. At the initial stage, the corrosion process is a diffusion-controlled process. After ~10 h at the initial stage, weight losses increased linearly with time due to the total dissolution of glasses or glass-ceramics. Leaching of heavy metals from glasses and glass-ceramics were well within international environmental regulations. Corrosion proceeded uniformly in fly ash glass while Na₂CaSiO₄ crystalline phase was preferentially dissolved in the glass-ceramics.

Heavy metals in urban soils of central Jordan: Should we worry about their environmental risks?

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Forty soil samples collected from central Jordan were analyzed by atomic absorption spectrophotometry for Pb, Cd, Zn, Cr, and Hg. The samples were also investigated for mineralogy using X-ray, electron, and optical microscopes. Sequential extraction procedures were used to predict the percentages of the Pb, Zn, Cd, and Cr present in each of the soil geochemical phases. The clay mineral assemblage encountered in the analyzed samples is composed of kaolinite, smectite,

illite, and illite/smectite mixed-layer. The nonclay minerals of the sand-sized fraction are composed mainly of quartz and calcite as major minerals with pyroxene, biotite, and feldspars as minor minerals. The enrichment factors of the measured heavy metals Pb, Cd, Zn, Cr, and Hg in the clay fraction (<2 µm) of the collected samples are 3.1, 16.6, 1.5, 0.9, and 4.5, respectively. According to the index of geoaccumulation, the soils of the study area are considered to be moderately contaminated with respect to Cd, uncontaminated to moderately contaminated with respect to Pb, Hg, and Zn, and uncontaminated with respect to Cr. The measured metals correlated positively with the determined physicochemical factors such as pH, clay content, organic matter content, and carbonate content. The relatively high concentrations of Cd, Pb, and Hg in the soils of the study area are related to anthropogenic sources such as cement industry, fertilizers, and vehicle exhausts. It was found that Pb, Zn, and Cr are associated mainly with the residual phases and are relatively immobile. On the other hand Cd is enriched in the carbonate phase of the analyzed soil samples. It is possible to suggest the sequence of mobility for Pb, Zn, Cd, and Cr in the analyzed soil samples as the following: Cd>Pb>Cr>Zn.

Microbial and biochemical soil quality indicators and their potential for differentiating areas under contrasting agricultural management regimes

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The aim of this study was to examine interrelationships between functional biochemical and microbial indicators of soil quality, and their suitability to differentiate areas under contrasting agricultural management regimes. The study included five 0.8 ha areas on a sandy-loam soil which had received contrasting fertility and cropping regimes over a 5 year period. These were organically managed vegetable, vegetable–cereal and arable rotations, an organically managed grass clover ley, and a conventional cereal rotation. The organic areas had been converted from conventional cereal production 5 years prior to the start of the study. All of the biochemical analyses, including light fraction organic matter (LFOM) C and N, labile organic N (LON), dissolved organic N and water-soluble carbohydrates showed significant differences between the areas, although the nature of the relationships between the areas varied between the different parameters, and were not related to differences in total soil organic matter content. The clearest differences were seen in LFOM C and N and LON, which were higher in the organic arable area relative to the other areas. In the case of the biological parameters, there were differences between the areas for biomass-N, ATP, chitin content, and the ratios of ATP: biomass and basal respiration: biomass. For these parameters, the precise relationships between the areas varied. However, relative to the conventionally managed area, areas under organic management generally had lower biomass-N and higher ATP contents. Arbuscular mycorrhizal fungus colonization potential was extremely low in the conventional area relative to the organic areas. Further, metabolic diversity and microbial community level physiological profiles, determined by analysis of microbial community metabolism using Biolog GN plates and the activities of eight key nutrient cycling enzymes, grouped the organic areas together, but separated

them from the conventional area. We conclude that microbial parameters are more effective and consistent indicators of management induced changes to soil quality than biochemical parameters, and that a variety of biochemical and microbial analyses should be used when considering the impact of management on soil quality.

Carbon dioxide, nitrous oxide and methane dynamics in boreal organic agricultural soils with different soil characteristics

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The annual carbon dioxide (CO₂), nitrous oxide (N₂O) and methane (CH₄) dynamics were measured with static chambers on two organic agricultural soils with different soil characteristics. Site 1 had a peat layer of 30 cm, with an organic matter (OM) content of 74% in the top 20 cm. Site 2 had a peat layer of 70 cm but an OM content of only 40% in the top 20 cm. On both sites there were plots under barley and grass and also plots where the vegetation was removed. All soils were net sources of CO₂ and N₂O, but they consumed atmospheric CH₄. Soils under barley had higher net CO₂ emissions (830 g CO₂-C m⁻² yr⁻¹) and N₂O emissions (848 mg N₂O-N m⁻² yr⁻¹) than those under grass (395 g CO₂-C m⁻² yr⁻¹ and 275 mg N₂O-N m⁻² yr⁻¹). Bare soils had the highest N₂O emissions, mean 2350 mg N₂O-N m⁻² yr⁻¹. The mean CH₄ uptake rate from vegetated soils was 100 mg CH₄-C m⁻² yr⁻¹ and from bare soils 55 mg CH₄-C m⁻² yr⁻¹. The net CO₂ emissions were higher from Site 2, which had a high peat bulk density and a low OM content derived from the addition of mineral soil to the peat during the cultivation history of that site. Despite the differences in soil characteristics, the mean N₂O emissions were similar from vegetated peat soils from both sites. However, bare soils from Site 2 with mineral soil addition had N₂O emissions of 2–9 times greater than those from Site 1. Site 1 consumed atmospheric CH₄ at a higher rate than Site 2 with additional mineral soil. N₂O emissions during winter were an important component of the N₂O budget even though they varied greatly, ranging from 2 to 99% (mean 26%) of the annual emission.

Influence of warming and enchytraeid activities on soil CO₂ and CH₄ fluxes

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To determine the sum of 'direct' and 'indirect' effects of climatic change on enchytraeid activity and C fluxes from an organic soil we assessed the influence of temperature (4, 10 and 15 °C incubations) on enchytraeid populations and soil CO₂ and CH₄ fluxes over 116 days. Moisture was maintained at 60% of soil dry weight during the experimental period and measurements of enchytraeid biomass and numbers, and CO₂ and CH₄ fluxes were made after 3, 16, 33, 44, 65, 86 and 116 days. Enchytraeid population numbers and biomass increased in all temperature treatments with the greatest increase produced at 15 °C (to over threefold initial values by day 86). Results also showed that enchytraeid activity increased CO₂ fluxes by 10.7±4.5, 3.4±4.0 and 26.8±2.6% in 4, 10 and 15 °C treatments, respectively, with the greatest CO₂ production observed at 15 °C for the entire 116 day incubation period ($P<0.05$). The soil respiratory quotient analyses at lower temperatures (i.e. 4–10 °C) gave a Q₁₀ of 1.7 and 1.9 with and without enchytraeids, respectively. At temperatures above 10 °C (i.e. 10–15 °C) Q₁₀ significantly increased ($P<0.01$) and was 25% greater in the presence of enchytraeids (Q₁₀=3.4) than without (Q₁₀=2.6). In contrast to CO₂ production, no significant relationships were observed between net CH₄ fluxes and temperature and only time showed a significant effect on CH₄ production ($P<0.01$).

Total soil CO₂ production was positively linked with enchytraeid biomass and mean soil CO₂-C production was 77.01±6.05 CO₂-C ig mg enchytraeid tissue⁻¹ day⁻¹ irrespective of temperature treatment. This positive relationship was used to build a two step regression model to estimate the effects of temperature on enchytraeid biomass and soil CO₂ respiration in the field. Predictions of potential CO₂ production were made using enchytraeid biomass data obtained in the field from two upland grassland sites (Sourhope and Great Dun Fell at the Moor House Nature Reserve, both in the UK). The findings of this work suggest that a 5 °C increase in atmospheric temperature above mean ambient temperature could have the potential to produce a significant increase in enchytraeid biomass resulting in a near twofold increase in soil CO₂ release from both soil types. The interaction between temperature and soil biology will clearly be an important determinant of soil respiration responses to global warming.

Environmental routes for platinum group elements to biological materials—a review

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The increased use of platinum group elements (PGE) in automobile catalysts has led to concern over potential environmental and biological accumulation. Platinum (Pt), palladium (Pd) and rhodium (Rh) concentrations have increased in the environment since the introduction of automobile catalysts. This review summarises current knowledge concerning the environmental mobility, speciation and bioavailability of Pt, Pd and Rh. The greater proportion of PGE emissions is from automobile catalysts, in the form of nanometer-sized catalyst particles, which deposit on roadside surfaces, as evidenced in samples of road dust, grass and soil. In soil, PGE can be transformed into more mobile species through complexation with organic matter and can be solubilised in low pH rainwater. There are indications that environmentally formed Pd species are more soluble and hence more mobile in

the environment than Rh and Pt. PGE can reach waterbodies through stormwater transport and deposition in sediments. Besides external contamination of grass close to roads, internal PGE uptake has been observed for plants growing on soil contaminated with automobile catalyst PGE. Fine particles of PGE were also detected on the surface of feathers sampled from passerines and raptors in their natural habitat, and internal organs of these birds also contained PGE. Uptake has been observed in sediment-dwelling invertebrates, and laboratory studies have shown an uptake of PGE in eel and fish exposed to water containing road dust.

The available evidence indicates that the PGE, especially Pd, are transported to biological materials through deposition in roots by binding to sulphur-rich low molecular weight species in plants. PGE uptake to exposed animals have uptake rates in the following order: Pd>Pt>Rh. The liver and kidney accumulate the highest levels of PGE, especially Pd. Urinary Pd and Rh, but not Pt, levels are correlated with traffic intensity. Dental alloys may lead to elevated urinary Pt levels. Platinum is a well-known allergen and Pd also shows a strong sensitisation potential.

Temporal trends of total and potentially available element concentrations in sewage biosolids: a comparison of biosolid surveys conducted 18 years apart

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The application of biosolids to agricultural land is becoming increasingly popular because of the many benefits they can offer in terms of improved soil fertility and productivity, and also because land application offers an economically viable disposal option. However, the heavy metal and nutrient content of biosolids are potential causes for concern due to the possibility of their accumulation in soils to levels that may adversely affect the environment. Therefore, total concentrations of elements in biosolids and the fraction potentially available to organisms must be known in order to accurately gauge the risks and to classify the biosolids. In 1983, deVries (deVries, MPC. Investigations on twenty Australian sewage sludges-their evaluation by means of chemical analysis. Fert Res 1983;4:75-87.) conducted a survey to determine the total and available contents of elements in biosolids collected from various treatment plants around Australia. We conducted a similar survey on biosolids collected in 2001, and thus were able to identify temporal trends in biosolid characteristics. The 2001 survey included biosolids from several treatment plants sampled in 1983, thus some direct comparisons were possible, and in four cases, it was possible to examine temporal trends in biosolid characteristics within individual treatment plants. Total element concentrations were determined by aqua regia digestion, and available element concentrations were determined by 0.01 M CaCl₂ extraction. Results showed total concentrations of Cu, Mn, Ni, Na, and Ca changed little over the period examined, however the 2001 median values of Cd, Mg, Pb, and Zn were all reduced by 60% or greater. Median total concentration of K was more than 50% higher, and P 120% higher, in the 2001 survey. Changes in the availability of elements surveyed in 1983 and 2001 were varied for different elements and for different biosolids. Extractable element concentrations

(viewed as percentages of total concentrations) of Cu, Cd, and Ni all fell by 50–72% between 1983 and 2001, while K extractability fell by 35%.

Decomposition of ^{14}C -labeled roots in a pasture soil exposed to 10 years of elevated CO_2

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The net flux of soil C is determined by the balance between soil C input and microbial decomposition, both of which might be altered under prolonged elevated atmospheric CO_2 . In this study, we determined the effect of elevated CO_2 on decomposition of grass root material (*Lolium perenne* L.). ^{14}C -labeled root material, produced under ambient (35 Pa p CO_2) or elevated CO_2 (70 Pa p CO_2) was incubated in soil for 64 days. The soils were taken from a pasture ecosystem which had been exposed to ambient (35 Pa p CO_2) or elevated CO_2 (60 Pa p CO_2) under FACE-conditions for 10 years and two fertilizer N rates: 140 and 560 kg N ha⁻¹ year⁻¹. In soil exposed to elevated CO_2 , decomposition rates of root material grown at either ambient or elevated CO_2 were always lower than in the control soil exposed to ambient CO_2 , demonstrating a change in microbial activity. In the soil that received the high rate of N fertilizer, decomposition of root material grown at elevated CO_2 decreased by approximately 17% after incubation for 64 days compared to root material grown at ambient CO_2 . The amount of $^{14}\text{CO}_2$ respired per amount of ^{14}C incorporated in the microbial biomass ($q^{14}\text{CO}_2$) was significantly lower when roots were grown under high CO_2 compared to roots grown under low CO_2 . We hypothesize that this decrease is the result of a shift in the microbial community, causing an increase in metabolic efficiency. Soils exposed to elevated CO_2 tended to respire more native SOC, both with and without the addition of the root material, probably resulting from a higher C supply to the soil during the 10 years of treatment with elevated CO_2 . The results show the importance of using soils adapted to elevated CO_2 in studies of decomposition of roots grown under elevated CO_2 . Our results further suggest that negative priming effects may obscure CO_2 data in incubation experiments with unlabeled substrates. From the results obtained, we conclude that a slower turnover of root material grown in an ‘elevated- CO_2 world’ may result in a limited net increase in C storage in ryegrass swards.

Contribution of plant photosynthates to dissolved organic carbon in a flooded rice soil

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Dissolved organic C (DOC) plays important roles in nutrient cycling and methane production in flooded rice ecosystem. The microcosm experiment was carried out to measure directly the contribution of photosynthates to DOC by using a ^{13}C pulse-chase labeling technique. DOC was operationally divided into water-extractable organic C (WEOC) and salt-extractable organic C (SEOC) by successive extraction firstly with deionized water and then with 0.25M K_2SO_4 . Total WEOC increased with plant growth, whereas SEOC concentration did not change significantly over the growing season. About 0.037–0.36% (mean 0.16%) of the assimilated ^{13}C was incorporated into WEOC immediately after $^{13}\text{CO}_2$ assimilation (Day 0), but only 0–0.025% (mean 0.01%) was incorporated into SEOC. At the end of the growing season, the ^{13}C amounts of WEOC substantially decreased, while those of SEOC slightly increased. The estimated net plant C contribution was 21mgCplant⁻¹ to WEOC and 6mgCplant⁻¹ to SEOC, corresponding to 33.8% of total WEOC and 20.2% of total SEOC at the end of the growing season, respectively. The results suggest that the incorporation and decomposition of the photosynthesized C occurred rapidly in rice soil which significantly affected the WEOC dynamics, but SEOC appeared to be in equilibrium with the native soil organic matter, receiving less effect from the plant growth.

Losses and biogeochemical cycling of soil organic nitrogen with prolonged arable cropping in the South African Highveld – evidence from - and -amino acids

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We know little about the mechanisms that cause rapid losses in the soil organic N pool during cropping. As the analysis of amino acid enantiomers can provide insight into both the fate of microbial N and the ageing of cells in the environment, we used this technique as a tool to examine how the pool of protein-bound N in subtropical Plinthosols responds to increasing duration of arable cropping. The samples comprised bulk soils (0–20cm) and clay fractions from each of three agro-ecosystems in semiarid South Africa; the sites have been cropped for periods varying from 0 to 98 years. The amino acid enantiomers contributed 34% to the total N content. With increasing number of years a piece of land has been cropped, the amino acid concentrations declined bi-exponentially to about 30% of their initial level in the native grasslands. Changes of the remaining soil protein-N pool were indicated by alterations in the -content of individual amino acids. As the years of arable cropping increased, the proportions of -alanine and -glutamic acid increased relative to the respective -enantiomers. This was attributed to an accumulation of N in residues of bacterial cell walls. In contrast, the /-ratios of leucine and aspartic acid declined in the long-term cultivated plots, probably reflecting losses of old amino acid-N reserves at the most degraded arable land.

Spatial and temporal patterns of water-extractable organic carbon (WEOC) of surface mineral soil in a cool temperate forest ecosystem

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Water-extractable organic carbon (WEOC) drives the C and N cycles in forest ecosystems via microbial activity. However, few studies have considered both the spatial and temporal patterns of WEOC in forest soils. We investigated the spatial and temporal variation in WEOC along a topographic sequence in a cool temperate deciduous forest. The concentrations of WEOC, carbohydrates, total phenols, and other organics were 126±51, 40±15, 1.5±0.5 and 85±43 mg C kg dry soil⁻¹, respectively. Carbohydrates and phenols accounted for 33±11 and 1.5±1.0% of WEOC, respectively. The effect of season on the WEOC concentration was stronger than that of slope position the growing season, although most of the soil properties varied markedly with slope position. The concentration of carbohydrates in WEOC showed similar seasonal patterns across slope positions. The carbohydrate concentration peaked in May and August. The results suggest that carbohydrates are controlled by the recent production of C, rather than by organic C that has accumulated in soil.

Long-term soil organic carbon dynamics in a subhumid tropical climate: ¹³C data in mixed C₃/C₄ cropping and modeling with RothC

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Scanty information on long-term soil organic carbon (SOC) dynamics hampers validation of SOC models in the tropics. We observed SOC content changes in a 16-year continuously cropped agroforestry experiment in Ibadan, south-western Nigeria. SOC levels declined in all treatments. The decline was most pronounced in the no-tree control treatments with continuous maize and cowpea cropping, where SOC levels dropped from the initial 15.4 to 7.3–8.0 Mg C ha⁻¹ in the 0–12 cm topsoil in 16 years. In the two continuously cropped alley cropping (AC) systems, one with *Leucaena leucocephala* and one with *Senna siamea* trees, SOC levels dropped to 10.7–13.2 Mg C ha⁻¹. Compared to the no-tree control treatments, an annual application of an additional 8.5 Mg ha⁻¹ (dry matter) of plant residues, mainly tree prunings, led to an extra 3.5 Mg C ha⁻¹ (~0.2% C) in the 0–12 cm top soil after 11 years, and 4.1 Mg C ha⁻¹ after 16 years. The addition of NPK fertilizer had little effect on the quantities of above-ground plant residues returned to the soil, and there was no evidence that the fertilizer affected the rate of SOC decomposition. The fact that both C₃ and C₄ plants returned organic matter to the soil in all cropping systems, but in contrasting proportions, led to clear contrasts in the ¹³C abundance in the SOC. This ¹³C information,

together with the measured SOC contents, was used to test the ROTHC model. Decomposition was very fast, illustrated by the fact that we had to double all decomposition rate constants in the model in order to simulate the measured contrasts in SOC contents and ^{13}C between the AC treatments and the no-tree controls. We hypothesized (1) that the pruning materials from the legume trees and/or the extra rhizodeposition from the tree roots in the AC treatments accelerated the decomposition of the SOC present at the start of the experiment (true C-priming), and/or (2) that the physical protection of microbial biomass and metabolites by the clay fraction on this site, having a sandy top soil in which clay minerals are mainly of the 1:1 type, is lower than assumed by the model.

Trophic niche differentiation in soil microarthropods (Oribatida, Acari): evidence from stable isotope ratios ($^{15}\text{N}/^{14}\text{N}$)

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The large number of animals that coexist in soil without any clear niche differentiation has puzzled biologists for a long time. We investigated stable isotope ratios ($^{15}\text{N}/^{14}\text{N}$) in a diverse group of soil microarthropods, oribatid mites, to evaluate trophic niche differentiation. The natural variation of the stable isotopes $^{15}\text{N}/^{14}\text{N}$ was measured in 36 species/taxa from four beech and beech-oak forests. Signatures of ^{15}N formed a gradient spanning over 12 units suggesting that (a) different species occupy different trophic niches and (b) oribatid mites span three to four trophic levels. This study for the first time documented strong trophic niche differentiation in decomposer microarthropods. The results suggest that trophic niche differentiation within taxonomic groups significantly contributes to the high diversity of soil animal taxa.

Functional and molecular responses of soil microbial communities under differing soil management practices

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The effects of soil management on some microbiological properties and soil bacterial community structure were evaluated. Two field sites with the same soil type, located on the same geographic area adjacent to one other, have received different soil management practices and cultivation. One site has been subjected for 20 years to intensive horticulture under conventional tillage and irrigation with low quality salt-rich water; the second field site has been uncultivated for a long period and was turned to organic farming practices over the last 5 years and is currently cultivated with fruit orchard. Total bacterial counts, microbial ATP, microbial community metabolic (BIOLOG[®]) profiles, and DNA fingerprinting by PCR-DGGE were determined. Two-way ANOVA revealed that total bacterial counts were not significantly ($P>0.3$) affected by the two different management practices; ATP content was consistently and significantly ($P<0.001$) lower in salt-water irrigated soil than in organic soil at the three sampling times. The cluster analysis of community level physiological profiles indicated that microbial communities were much more uniform in organic soil than in irrigated one, suggesting that salt-water irrigation could have affected the size of the microbial population, its metabolic activities, as well as its composition. Molecular patterns fitted the BIOLLOG[®] profile diversity. In particular, at any sampling time, PCR-DGGE patterns of bacterial DNA, extracted by an indirect method, significantly discriminated irrigated from organic soil samples. The PCR-DGGE patterns of total soil DNA, extracted by a direct method, showed a moderate to significant variation among irrigated and organic soil samples. Biochemical, microbiological and molecular data contributed to evidence a significantly different response of indigenous microflora to soil management by using saline water or organic farming.

RIVER GEOCHEMISTRY

Solute sources and processes in the Achankovil River basin. Western Ghats. South India

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Preliminary studies on the water chemistry of the high altitude river basin with relatively homogeneous lithology with pristine ecosystem in Western Ghats region has been carried out. A time series survey has been carried out to understand the hydrogeochemical processes taking place in the Achankovil River of the Western Ghats range in 2002. The water is neutral with pH and EC ranges from 6.32-7.56 and 24 – 54 $\mu\text{S}/\text{cm}$. Chloride and sodium are the dominant anion and cation in the water respectively. Correlation analysis of the chemical parameters of the water shows that some ions have additional sources such as sea spray, soil conditioners and evaporates. This study shows that the majority of carbonate is derived from carbonate weathering followed by silicate weathering. Cation concentrations show decreasing trend from upstream to downstream in contrast to the increasing trend in the major world rivers. Dissolved silica in premonsoon water is low. This is due to the silica uptake by diatoms. The Gibbs plot indicates that the river chemistry is dominated by rock weathering induced by precipitation. The partial pressure of CO_2 in water is high and is in equilibrium with the atmosphere. Thermodynamic plots show that dolomite, kaolinite, albite and chlorite are in equilibrium with the river water. The additional sources which influence the water chemistry are sea spray leaching of evaporates and anthropogenic inputs. Chemical weathering is predominant here compared to physical weathering. The annual discharge of the Achankovil River is $1.48 \text{ km}^3/\text{yr}$ and transports a significant amount of solute flux ($1389 \times 10^6 \text{ t}/\text{yr}$) and suspended flux ($27 \times 10^6 \text{ t}/\text{yr}$) to the Vemband estuarine lake. The overall material transport seems to be lower compared to the other Indian rivers nevertheless the solute loads are comparable to certain large rivers like Cauvery in the south India. The solute flux including the nutrient flux is very high among the Western Ghats Rivers in comparison to its size, which will certainly supplement the productivity of the lake/estuary and the coastal waters. Since this study is restricted to one-year period. long-term data procurement and analysis along with micro nutrients studies are needed. which are lacking in the present study. to gain insight into the material flux by this river into the Arabian Sea.

A river water quality management model for optimising regional wastewater treatment using a genetic algorithm

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To achieve water quality goals and wastewater treatment cost optimisation in a river basin, a water quality management model has been developed through the integration of a genetic algorithm (GA) and a mathematical water quality model. The developed model has been applied to the Youngsan River, where water quality has decreased due to heavy pollutant loads from Kwangju City and surrounding areas. Pollution source, land use, geographic features and measured water quality data of the river basin were incorporated into the Arc/View geographic information system database. With the database, the management model calculated treatment type and treatment cost for each wastewater treatment plant in the river basin. Until now, wastewater treatment policy for polluted rivers in Korea has been, first of all, to construct secondary treatment plants for untreated areas, and secondarily, to construct advanced treatment plants for the river sections whose water quality is impaired and for which the water quality goal of the Ministry of Environment is not met. Four scenarios that do not use the GA were proposed and they were compared with the results of the management model using the GA. It became clear that the results based on the GA were much better than those for the other four scenarios from the viewpoint of the achievement of water quality goals and cost optimisation.

**The impact of land use change on soil water holding capacity and river flow modelling
in the Nakambe River, Burkina-Faso**

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The annual hydrological regime of the Nakambe River shows substantial changes during the period 1955–1998 with a shift occurring around 1970. From 1970 to the mid-1990s, despite a reduction in rainfall and an increase in the number of dams in the basin, average runoff and maximum daily discharges increased. This paper reviews the hydrological behaviour of the Nakambe River from 1955 to 1998 and examines the potential role of land use change on soil water holding capacity (WHC) in producing the counter-intuitive change in runoff observed after 1970. We compare the results of two monthly hydrological models using different rainfall, potential evapotranspiration and WHC data sets. Model simulations with soil WHC values modified over time based upon historical maps of land use, are compared against simulations with a constant value for WHC. The extent of natural vegetation declined from 43 to 13% of the total basin area between 1965 and 1995, whilst the cultivated areas increased from 53 to 76% and the area of bare soil nearly tripled from 4 to 11%. The total reduction in WHC is estimated to range from 33 to 62% depending on the method used, either considering that the WHC values given by the FAO stand for the environmental situation in 1965 or before. There is a marked improvement in river flow simulation using the time-varying values of soil WHC. The paper ends with a discussion of the role of other factors such as

surface runoff processes and groundwater trends in explaining the hydrological behaviour of the Nakambe River.

Impact of informal regulation of pollution on water quality in rivers in India

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In this paper an attempt is made to assess the impact of informal regulation of water pollution on water quality in Indian rivers. For this purpose, an econometric analysis of determinants of water quality in Indian rivers is carried out using water quality (water class) data for 106 monitoring points on 10 important rivers for five years, 1995–1999. To explain variations in water quality, an Ordered Probit model is estimated, in which poll percentage in parliamentary elections, a proxy for the intensity of informal regulation, is taken as one of the main explanatory variables. Rainfall, industrialization, irrigation intensity and fertilizer use are some of the other explanatory variables used in the model to control for the influence of these factors. As expected, river water quality is found to be positively related with rainfall, and negatively related with industrialization, irrigation intensity and fertilizer use. A significant positive relationship is found between poll percentage and water quality, and also between the rate of increase in literacy level in a district and the water quality in rivers flowing through the district. These results point to a significant favorable effect of informal regulation of pollution on water quality in rivers in India.

Determination of Shallow Aquifer Parameters in Kodaganar River Basin, Dindigul and Karur Districts, Tamil Nadu

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Kodaganar river basin is a hard rock terrain where the upper shallow weathered part followed by deep fractured rocks form the aquifer system. The area is drought prone and indiscriminate exploitation of groundwater over decades has resulted in depletion of water level. Therefore, assessment of groundwater potential is warranted which in turn requires the knowledge of aquifer parameters. The common practice of determining the aquifer parameters is by carrying out pumping test on wells and further by interpreting the time drawdown data. In the present study the aquifer parameters are determined through pumping tests on dug wells duly taking into account the actual field conditions while interpreting the data. Numerical method has been adopted to carry out forward modelling of pumping test data to estimate aquifer parameters.

Modelling the transport of suspended particulate matter by the Rhone River plume (France). Implications for pollutant dispersion

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A model to simulate the transport of suspended particulate matter by the Rhone River plume has been developed. The model solves the 3D hydrodynamic equations, including baroclinic terms and a 1-equation turbulence model, and the suspended matter equations including advection/diffusion of particles, settling and deposition. Four particle classes are considered simultaneously according to observations in the Rhone. Computed currents, salinity and particle distributions are, in general, in good agreement with observations or previous calculations. The model also provides sedimentation rates and the distribution of different particle classes over the sea bed. It has been found that high sedimentation rates close to the river mouth are due to coarse particles that sink rapidly. Computed sedimentation rates are also similar to those derived from observations. The model has been applied to simulate the transport of radionuclides by the plume, since suspended matter is the main vector for them. The radionuclide transport model, previously described and validated, includes exchanges of radionuclides between water, suspended matter and bottom sediment described in terms of kinetic rates. A new feature is the explicit inclusion of the dependence of kinetic rates upon salinity. The model has been applied to ^{137}Cs and $^{239,240}\text{Pu}$. Results are, in general, in good agreement with observations.

A model has been developed to simulate transport of suspended particulate matter in the Rhone River plume.

Groundwater Quality of Pageru River Basin, Cuddapah District, Andhra Pradesh

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The study was undertaken to assess the water quality in relation to agricultural and domestic uses in parts of Pageru river basin, Andhra Pradesh. The rock formation of study area is Cuddapah Supergroup and Kurnool Group. The important lithounits consist chiefly of quartzite, limestone and shale. The results of chemical analyses of ninety-nine water samples were collected from bore wells. The quality analysis is made through the estimation of silica, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulphate, chloride, total dissolved solids, Hydrogen ion concentration (pH) and specific conductance. Based on the analyses, certain parameters like non-carbonate hardness, sodium adsorption ratio, percent sodium, potential salinity, residual sodium carbonate, Kelly's ratio, magnesium ratio, index of base exchange and permeability were calculated. From the evaluation, it is known that the water quality is suitable for both domestic and irrigation purposes. According to Gibb's diagram all the samples in both the seasons fall in the rock dominance field. Assessment of water samples from various methods proved that majority of the water samples are good either for drinking or for agriculture in both seasons. The overall quality of waters in the study area in post-

monsoon season in all constituents are high because of rock-water interaction and rules out any pollution from extraneous sources.

Impact of a flood disaster on sediment toxicity in a major river system – the Elbe flood 2002 as a case study

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The ecotoxicological implications of a flooding disaster were investigated with the exceptional Elbe flood in August 2002 as an example. Sediment samples were taken shortly after the flood at 37 sites. For toxicity assessment the midge *Chironomus riparius* (Insecta) and the mudsnail *Potamopyrgus antipodarum* (Gastropoda) were exposed to the sediment samples for 28 days. For a subset of 19 sampling sites, the contamination level and the biological response of both species were also recorded before the flood in 2000. The direct comparison of biological responses at identical sites revealed significant differences for samples taken before and immediately after the flood. After flood sediments of the river Elbe caused both higher emergence rates in the midge and higher numbers of embryos in the mudsnail. Contrary to expectations the toxicity of the sediments decreased after the flood, probably because of a dilution of toxic substances along the river Elbe and a reduction in bioavailability of pollutants as a result of increasing TOC values after the flood. The extraordinary Elbe flood in August 2002 did not result in an overall increase of environmental contamination.

Fluvial Response to Late Quaternary Tectonic Changes in the Dhadhar River Basin, Mainland Gujarat

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The study aims at reconstruction of the Dhadhar drainage system during Late Quaternary applying geomorphic and stratigraphic criteria. Remote sensing data show occurrence of palaeodrainages in the area between the Dhadhar and Orsang Rivers. The exposed sediment records of these river basins, lakes and ponds mainly in the areas where there is no drainage help in reconstructing the palaeodrainage. The exposed sediment succession in the lakes and ponds show a thick fluvial sequence (Gm and Sh) overlain by a 4-5 m thick black organic rich finely laminated lacustrine clays (FC). The sedimentary records and mineralogy of the Dhadhar and Orsang basins are quite similar and correlatable. The course of Orsang River which flowed through the Dhadhar River during Late Pleistocene was changed during Early Holocene due to tectonic uplift along the major faults in the area.

PAH dissipation in a contaminated river sediment under oxic and anoxic conditions

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A batch experiment was conducted to compare PAH degradation in a polluted river sediment under aerobic and anaerobic conditions, and to investigate whether input of fresh organic material (cellulose) could enhance such degradation. All measurements were checked against abiotic control treatments to exclude artifacts of sample preparation and non-biological processes like aging. Three- and four-ring PAHs could be degraded by the indigenous microbial community under aerobic conditions, but anaerobic metabolism based on iron and sulphate reduction was not coupled with PAH degradation of even the simplest 3-ring compounds like phenanthrene. Cellulose addition stimulated both aerobic and anaerobic respiration, but had no effect on PAH dissipation. We conclude that natural attenuation of PAHs in polluted river sediments under anaerobic conditions is exceedingly slow. Dredging and biodegradation on land under aerobic conditions would be required to safely remediate and restore polluted sites.

Natural attenuation of PAHs under anaerobic conditions is exceedingly slow.

Palaeohydrology and River Channel Management

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Palaeohydrology has continued to develop during the GLOCOPH period (1991-2003) so that it is now appropriate to consider how its research contributions can relate to global change. Palaeohydrology is just one multi-disciplinary research field that can make a contribution to the study of global change, achieved through deriving data, elucidating the mechanics of change; identifying spatial contrasts; assisting the coupling of global change models to hydrological models, and eventually providing new models of palaeohydrological change. Palaeohydrology can contribute to river channel management, which has now progressed from hard engineering, to ecological and thence to sustainable approaches. Inputs from palaeohydrology can inform river channel hazards, although necessarily varying according to the engineering, working with the river, or sustainable approaches. Research on temporal change can provide information for river management to complement periods of continuous instrumental records. Contributions can be made from palaeohydrology for the elaboration of flow records, especially of palaeofloods; demonstration of the sensitivity of reaches and their role within a basin context; provision of hydrological and sedimentological histories to provide a temporal context; and elucidating the question of what is 'natural'. It is possible to extend protocols for river

channel management by a provisional protocol from palaeohydrology. Although palaeohydrology may not readily provide analogues for future sequences it can provide insight into the scenarios and mechanisms that may occur, and offers experience that requires river management to be undertaken within the framework of a long-term perspective.

Concentration and fate of trace metals in Mekong River Delta

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In the Mekong River delta and its associated coastal zone trace elements concentrations (Cd, Cu, Ni and Pb) were measured in the dissolved phase (DP) during dry (March 1997) and wet (October 1997) seasons. As, Co, Cr, Ni, Pb, and Al were also measured in suspended matter (SM) and total and organic carbon, trace elements (Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn) and macro elements in superficial sediments (S). Trace metal concentrations in DP and SM during the contrasting hydrological conditions were generally found within the range observed for uncontaminated environment. The average DP concentrations (nM) in the river for March and October are: Cd 0.03 and 0.09, Cu 15 and 14, Ni 7.8 and 8.4, Pb 0.51 and 0.50, respectively. In general there is no significant difference between the concentrations observed during dry and wet season. The evolution of the DP trace metal concentration in the surface water within the salinity gradient suggests no noticeable exchange between the particulate and dissolved phase. This result is in good agreement with those observed in most plume structures studied so far. The average concentrations in the SM (g/g) (March, October) at the river end-member are: As (24; 11), Co (17; 9), Cr (49; 29), Ni (32; 18), Pb (42; 19) and Al (113 000; 67 000), respectively. All trace elements show higher concentrations in March than in October, with an average increase of two times. This is essentially related to grain size effect since smaller particles were supplied during dry season. These differences are not reflected in the mixing zone, which integrates the seasonal variations. The concentration of major elements (C total, C organic, Si, Al, Ca, K, Fe, Mg, Ti), trace elements (Pb, Zn, Cu, Ni, Mn, Cr, Cd, Hg) in superficial sediments, show similar values during the two seasons and does not show any important variation with depth, indicating either a very fast sedimentation rate and/or the absence of any significant contamination.

River networks and groundwater flow: a simultaneous solution of a coupled system

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Coupled hydrologic modeling of surface and subsurface systems are necessary to obtain a better understanding of hydrologic pathways in a watershed. In early studies, the coupling is achieved by linking the two systems through an iterative process in which convergence of parameters linking the two domains are defined as the criteria for an acceptable solution. In this study, we propose a new

approach based on the simultaneous solution of coupled channel and groundwater flow systems. The proposed method is based on the idea of solving a single global matrix at once rather than solving separate matrices for each flow domain while improving the solution iteratively. The proposed solution technique is implemented by coupling a one-dimensional channel network flow model that uses the complete form of the St Venant equation with a two-dimensional vertically averaged groundwater flow model. The proposed approach provides a more efficient solution strategy for the coupled flow problem and demonstrates an effective process of integrating the two hydrologic systems.

Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain)

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This paper intends to analyse seasonal variations of the quality of the water of the Odiel River. This river, together with the Tinto River, drains the Iberian Pyrite Belt (IPB), a region containing an abundance of massive sulphide deposits. Because of mining activity dating back to prehistoric times, these two rivers are heavily contaminated. The Odiel and Tinto Rivers drain into a shared estuary known as the Ría of Huelva. This work studies dissolved contaminant data in water of the Odiel River collected by various organisations, between October 1980 and October 2002, close to the rivers entry into the estuary. Flow data for this location were also obtained. The most abundant metals in the water, in order of abundance, are zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu). Arsenic (As), cadmium (Cd) and lead (Pb) are also present but in much lower quantities. The quality of the river water is linked to precipitation; the maximum sulphate, Fe, Zn, Mn, Cd and Pb concentrations occur during the autumn rains, which dissolve the Fe hydroxysulphates that were precipitated during the summer months. In winter, the intense rains cause an increase in the river flow, producing a dilution of the contaminants and a slight increase in the pH. During spring and summer, the sulphate and metal concentration (except Fe) recover and once again increase. The Fe concentration pattern displays a low value during summer due to increased precipitation of ferric oxyhydroxides. The arsenic concentration displays a different evolution, with maximum values in winter, and minimum in spring and summer as they are strongly adsorbed and/or coprecipitated by the ferric oxyhydroxides. Mn and sulphates are the most conservative species in the water. Relative to sulphate, Mn, Zn and Cd, copper displays greater values in winter and lower ones in summer, probably due to its coprecipitation with hydroxysulphates during the spring and summer months. Cd and Zn also appear to be affected by the same process, although to a lower degree than Cu, experiencing a slight reduction in summer with respect to Mn and sulphates.

Late Quaternary History of the Ganga Plain

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Flexural subsidence of the Indian lithosphere created the Ganga Plain foreland basin in front of the Himalayan orogen, which attained its present configuration during the late Quaternary. Climate change, neotectonics and base level changes influenced the evolution of the present landforms of the Ganga Plain. The regional geomorphic surfaces are: (1) Upland Interfluve Surface (T_2); (2) Marginal Plain Upland Surface (MP); (3) Megafan Surface (MF); (4) Piedmont Fan Surface (PF); (5) River Valley Terrace Surface (T_1) and (6) Active Flood plain Surface (T_0). The Upland Interfluve Surface (T_2) is widespread reference surface; other surfaces are either incised or overlie this surface. Formation of these surfaces is essentially related to the climate cycles of late Pleistocene-Holocene (128 ka BP). These surfaces are depositional and have a succession of overlying sediments, younger than the time of formation of the respective surfaces. The sediments coming from the Himalaya undergo significant chemical weathering in the alluvial plain where much Na, Ca, Sr, K, Mg, is removed; while As, Cr, Ni and Th are enriched. In suitable conditions smectite and kaolinite are formed. These sediments are partly eroded and transported to the delta region and beyond. The Ganga Plain consists of a large number of river systems; originating in different parts of the Himalaya, Peninsular Craton, and alluvial plain formed at different times during the late Pleistocene-Holocene. Surface runoff and groundwater are the main sources of water. It is difficult to make meaningful scheme of classification of channels. Based on the sediment-water transfer patterns, the channels are classified into three broad categories. The river systems are in different stages of evolution. The active perennial rivers are incised within the alluvium, and show avulsion on a scale of 10^4 - 10^5 years; some channels, part of the ancient anastomosing network, act as flood channels and show avulsion on a scale of 10^1 - 10^2 years.

The Upland Interfluve Surface (T_2) exhibits a number of microgeomorphic features which have helped in the reconstruction of the history of the Ganga Plain during the last ~20 ka BP: 20-13 ka BP - new drainage of low density; 13-8 ka BP - extension of drainage system, high rainfall; 8-6 ka BP - channel disruption due to base-level rise and tectonics and formation of large lakes which retained most water-sediment of T_2 -Surface; 6-4 ka BP - dry climate, increased terrigenous clastic sediments in lakes; 4-2 ka BP - increased siltation of the lakes, moderate rainfall; 2-0 ka BP - fragmentation and drying of lakes, strong anthropogenic influence. The basin exhibits active tectonism, which is mostly in the form of contractional system in the piedmont zone, and prominent extensional system in the southern part of the basin. One of the most significant events in Ganga Plain history is tectonics of 8-5 ka BP, which produced areas of centripetal drainages and changed the fluvial landscape into a landscape of ponds and lakes with few high grounds. It was helped by the climate change from humid to dry around 5 ka BP.

Seasonal nutrient dynamics in a chalk stream: the River Frome, Dorset, UK

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Chalk streams provide unique, environmentally important habitats, but are particularly susceptible to human activities, such as water abstraction, fish farming and intensive agricultural activity on their fertile flood-meadows, resulting in increased nutrient concentrations. Weekly phosphorus, nitrate, dissolved silicon, chloride and flow measurements were made at nine sites along a 32 km stretch of the River Frome and its tributaries, over a 15 month period. The stretch was divided into two sections (termed the middle and lower reach) and mass balances were calculated for each determinant by totalling the inputs from upstream, tributaries, sewage treatment works and an estimate of groundwater input, and subtracting this from the load exported from each reach. Phosphorus and nitrate were retained within the river channel during the summer months, due to bioaccumulation into river biota and adsorption of phosphorus to bed sediments. During the autumn to spring periods, there was a net export, attributed to increased diffuse inputs from the catchment during storms, decomposition of channel biomass and remobilisation of phosphorus from the bed sediment. This seasonality of retention and remobilisation was higher in the lower reach than the middle reach, which was attributed to downstream changes in land use and fine sediment availability. Silicon showed much less seasonality, but did have periods of rapid retention in spring, due to diatom uptake within the river channel, and a subsequent release from the bed sediments during storm events. Chloride did not produce a seasonal pattern, indicating that the observed phosphorus and nitrate seasonality was a product of annual variation in diffuse inputs and internal riverine processes, rather than an artefact of sampling, flow gauging and analytical errors.

Modeling river/reservoir system management, water allocation, and supply reliability

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The state of Texas has implemented a modeling system for assessing the availability and reliability of water resources that consists of a generalized simulation model called the Water Rights Analysis Package (WRAP) and input datasets for the state's 23 river basins. Reservoir/river system management and water allocation practices are simulated using historical naturalized monthly streamflow sequences to represent basin hydrology. Institutional systems for allocating streamflow and reservoir storage resources among numerous water users are considered in detail in evaluating basinwide impacts of water management decisions. The generalized WRAP model is a flexible tool that may be applied to river basins anywhere. The Texas experience in implementing a statewide modeling system illustrates issues that are relevant to water management in many other regions of the world.

**Radiocarbon Dating and Holocene Episodes of Alluvial Sedimentation in the
Koratallaiyar-Cooum River Basin, Chennai, South India**

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The near coastal areas of the landscape around Chennai, Tamil Nadu, preserve younger fluvial deposits than the ferricretes, which are of the late Neogene-Pleistocene age. Two major rivers meandering parallel to one another drain in this area. They are: the Korattalayar, and the Cooum. The interfluves are less dynamic and preserve an older record. Satellite imagery and aerial photographs have been used in this study for understanding the large floodplain areas. Investigations from remote sensing data, borehole lithologs, and field observations in the Korattalayar and Cooum Basin, indicate that channel migration through cut-off, overbank flooding and structural control are the most important factors controlling the floodplain structure in the study area. Many older and palaeo-levees exist in the form of ridges (2-3 m high) in the Korattalayar floodplain. Well-developed river terrace points to late Pleistocene-early Holocene sedimentation. Presently the river is incising in its own sediments.

Organic-rich sediments and peat have been dated by radiocarbon method to understand the phases of sedimentation processes. The Korattalayar and the Cooum River deposits can be divided into three groups based on radiocarbon calibrated ages: 9,710-8,430 yrs BP, 5,910-5,490 yrs BP and ~900 yrs BP. Rates of net sediment accumulation calculated using these radiocarbon dates, span a period of the order 10^2 - 10^3 yrs BP. Change in grain size and process of sedimentation relates to structural configuration of the basin, minor changes in winter monsoon climate and varying magnitude of flood events.

Lead, cadmium, and zinc concentrations in plaster and mortar from structures in Jasper and Newton Counties, Missouri (Tri-State Mining District)

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The primary goal of this study was to evaluate anecdotal evidence that within Jasper and Newton Counties, Missouri, two counties within the Tri-State Mining District, granular mine tailings were commonly used in place of river sands in wall plasters and mortar. Interior wall plaster and mortar samples from structures in this mining district were analyzed for lead, cadmium, and zinc, and compared to samples from Springfield, MO (comparison site). The Jasper and Newton County samples showed elevated concentrations of the three elements, consistent with the inclusion of mine tailings, with a number of samples containing lead and cadmium at concentrations greater than EPA remediation targets for yard soil. X-ray diffraction studies showed the presence of the zinc ore minerals, sphalerite and hemimorphite, in high level samples. Thin section optical studies identified the major component of the aggregate as chert, a mineral abundant within the tailing piles. Because dust from crumbling plaster and mortar could represent an avenue for significant heavy metal exposure to building occupants, we suggest that there may be associated health consequences that should be further evaluated.

The water quality of the River Carnon, west Cornwall, November 1992 to March 1994: the impacts of Wheal Jane discharges

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In January 1992, there was a major pollutant event for the River Carnon and downstream with its confluence to the River Fal and the Fal estuary in the west Cornwall. This incident was associated with the discharge of several million gallons of highly polluted water from the abandoned Wheal Jane tin mine that also extracted Ag, Cu and Zn ore. Later that year, the Centre for Ecology and Hydrology (CEH; then Institute of Hydrology) Wallingford undertook daily monitoring of the River Carnon for a range of major, minor and trace elements to assess the nature and the dynamics of the pollutant discharges. These data cover an 18-month period when there remained major water-quality problems after the initial phase of surface water contamination. Here, a summary is provided of the water quality found, as a backdrop to set against subsequent remediation. Two types of water-quality determinant grouping were observed. The first type comprises the determinants B, Cs, Ca, Li, K, Na, SO₄, Rb and Sr, and their concentrations are positively correlated with each other but inversely correlated with flow. This type of water-quality determinant shows variations in concentration that broadly link to the normal hydrogeochemical processes within the catchment, with limited confounding issues associated with mine drainage. The second type of water-quality determinant comprises Al, Be, Cd, Ce, Co, Cu, Fe, La, Pb, Pr, Nd, Ni, Si, Sb, U, Y and Zn, and concentrations for all this group are positively correlated. The determinants in this second group all have concentrations that are negatively correlated with pH. This group links primarily to pollutant mine discharge. The water-quality variations in the River Carnon are described in relation to these two distinct hydrogeochemical groupings.

Environmental Changes during Late Pleistocene in the Orsang River Basin, Western India

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Chronometric and sedimentological data generated from the exposed Quaternary sequences of the Orsang River basin indicate close correspondence between the environmental changes and fluvial aggradation. The oldest and regionally extensive fine silty-clay occurring at the base of the successions is dated to >97 ka suggesting prevalence of high sinuosity suspended load fluvial regime. Its stratigraphic position suggests that the deposition occurred during the enhanced southwest monsoon corresponding to the Marine Isotopic Stage-5 (MIS-5). The gravel deposits that overlie provide an age of ~60 ka indicating dominance of braided system (MIS-4) during the reduced southwest monsoon. The pluvial interstadial (MIS-3) is represented by flood plain facies that was deposited

under the persistent fluvial system strengthened by enhanced southwest monsoon and assigned ages ranging between 50 and 30 ka. An extensive aeolian sand sheet that blankets the topography, is luminescence dated to 21 ka suggesting the onset of Last Glacial Maximum in the Orsang River basin.

Geochemistry and mineralogy of the NW Aegean Sea surface sediments: implications for river runoff and anthropogenic impact

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Surface sediments of the NW Aegean Sea were analyzed for clay mineral composition (94 samples), organic C and carbonate content, and major and minor elements (112 samples). Illite is the most abundant clay mineral, followed by smectite, chlorite and kaolinite. Clay minerals are preferentially deposited within the continental shelf and slope environment, due to the prevailing cyclonic circulation and the formation of flocs in the rivers' pro-delta areas. The spatial distribution of major lithogenic elements (Si, Al, Ti, Fe) is substantially biased by the presence of relict sands located in the central-eastern part of the Thermaikos Gulf continental shelf. Biogenic elements (Ca, Sr) are noticeably pronounced on the northern flank of the North Sporades Islands. Organic C content and minor elements Cu, Zn, As and Pb are enriched markedly over the Thessaloniki Bay and Gulf suggesting substantial human impact, deriving largely from untreated or partly treated domestic and industrial effluents. The terrigenous component of the elements is preferentially contributed from the Axios River (Zn and Pb), the Aliakmon River (Cr, Co, Ni, Cu and As), and to a lesser extent from the Pinios River (V, Co, Ni and Cu); a considerable part of the metals originates in ultra-mafic and volcanic formations, which are abundant in the rivers' catchment basins. Carbonate content exhibits great variability, with the highest values observed in biogenic sediments of the Sporades Basin. In the latter area, Mn (and Fe) oxides and hydroxides were found as coatings on calcite. The coatings were enriched in Cr, Co, Ni, Zn, As, Mo and Pb, due to adsorption or ion-exchange during early diagenesis. The combined influence of the river systems, the Thessaloniki metropolis, and the diverse sedimentological background, generates great patchiness in the distribution of major and minor elements.

Statistical Modelling of Rainfall and River Flow in Thailand

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Thailand experiences severe floods and droughts that affect agriculture. New techniques, such as Data-Based-Mechanistic modelling are being developed to study rainfall and river flow to improve

flood and drought alleviation policies and practices. Dynamic Harmonic Regression models are used to analyze rainfall and discharge time series across Thailand to define seasonality, trends and to forecast rainfall and discharge and their spatial distribution. Statistical patterns in the frequency of extreme rainfall and flow periods are identified with a view to improving predictions of medium and longer-term rainfall and river flow patterns. The results show temporal and spatial variation within the annual rainfall pattern in the study catchments. For example, the seasonality of the rainfall in the south is less pronounced (more equatorial). The discharge seasonal pattern shows stronger semi-annual cycles, with the weakest pattern in the south of country, whereas the strongest discharge seasonality is observed in the far north. The overall areal rainfall trend has not changed significantly over the last 20 years. Dry years can be associated with ENSO events. The discharge trend also tended to dip in ENSO years. The DHR forecasts of rainfall and river flow data for 1998-1999 using data up to 1997 have low prediction errors.

Identification and regional quantification of hydrochemical processes at the contact zone between anoxic groundwater and surface water in poldered floodplains (Oderbruch polder, Germany)

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The hydrochemistry in the largest polder of the Oder River, named Oderbruch, is affected by long-term infiltration of water from the Oder into the aquifer below an alluvial loamy top layer of the polder. These exceptional hydraulic conditions are a result of dyke constructions which were built more than 250 a ago. The objective of this investigation is a better understanding and a characterisation of the contact zone between the anaerobic groundwater and the surface water of a vast drainage system. Induced by changing water levels, different hydraulic conditions occur, which strongly influence the hydrochemistry of the shallow aquifer and therefore the natural sink function of the polder area.

Field investigations with a hydrochemical and hydraulic characterisation of selected drainage ditch locations show considerable chemical interactions between groundwater and surface water. Depending on the drainage ditch type, which is defined by the hydraulic situation, the redox processes create a chemical gradient combined with a distinct enrichment of Fe and Mn. The source of the high amounts of Fe and Mn in the groundwater are reduced Fe- and Mn-hydroxides from the aquifer sediments.

Under exfiltrating conditions interrupted by dry phases, more than 50 g kg⁻¹ Fe and 0.25 g kg⁻¹ Mn have accumulated in the drainage ditch floor sediments since the construction of the drainage ditches 35 a ago. The results show a very effective fixation of trace metals in the drainage ditch sediments under these conditions. Under permanent exfiltration conditions, the enrichment of Fe and Mn is relatively low. The maximum Fe content was 4 g kg⁻¹ sediment and the Mn content reached only 0.4 g kg⁻¹. This is less than 10% of the mobile Fe²⁺ and less than 1% of the Mn²⁺ which migrates from the aquifer into the surface water.

The Mekong River: Morphology, Evolution and Palaeoenvironment

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The Mekong, the largest river in Southeast Asia, shows striking variations in channel form and behaviour along its course. It appears to link several different types of channel rather than continuing in an orderly progression. Eight different river units have been identified along the lower 2000+ km of the river from the Chinese border to the sea across Southeast Asia. The exercise was carried out using satellite images, field visits, topographical maps, and various publications of the Mekong River Commission including large-scale river maps. The boundaries between such units are sharp and not gradual. They are different from each other depending on their morphological characteristics, their behaviour and whether the channel is bedrock-controlled. The Mekong flows for nearly 4000 km before being a freely-moving river with overbank flooding and course changes across the wide plain of Cambodia. Prior to that the channel is essentially structure-guided. It is a seasonal river with high flows during the southwestern monsoon and periodic floods late in the wet season. This linkage of several identifiable river units and the location of the present course of the river have not been properly explained. The estimated stream power of the Mekong in large floods seems to be very low when compared to what is required to erode a large channel in rock even along geological lineations. The opening of the South China Sea and the lowlands of Southeast Asia are associated with extrusion tectonics resulting from the Indian Plate colliding with the Eurasian Plate and building of the Himalaya Mountains from Eocene onwards. The present course of the river is likely to have been determined at least primarily from this event, and possibly also associated with stronger monsoon systems in the Early Holocene as recognised for South Asia. Morphology comparable to that of the Mekong seems to exist in several other major rivers of Southeast Asia and there could be a regional pattern, but investigation on this topic has hardly started.

Geochemistry of the Kola River, northwestern Russia

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The Kola River in the northern part of the Kola Peninsula, northwestern Russia, flows into the Barents Sea via the Kola Bay. The river is a unique place for reproduction of salmon and an important source of drinking water for more than 500,000 people in Murmansk and the surrounding municipalities. To evaluate the environmental status of the Kola River water, sampling of the dissolved

(<0.22 μm) and suspended (>0.22 μm) phases was performed at 12 sites along the Kola River and its tributaries during 2001 and 2002. Major (Ca, K, Mg, Na, S, Si, HCO_3 and Cl) and trace (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, and Zn) elements, total and particulate organic C (TOC and POC), N and P were analysed. Comparison with the boreal pristine Kalix River, Northern Sweden, shows that, except for Na, Cl, Al, Cu and Ni, which exceed the concentrations in the Kalix River by as much as 2–3 times, the levels of other major and trace elements are close to or even below the levels in the Kalix River. However, the results also demonstrate that pollutants from the three major sources: (1) the Cu–Ni smelter in Monchegorsk, (2) the open-pit Fe mine and ore concentration plant in Olenegorsk, and (3) the Varlamov, the Medveziy and the Zemlanoy creeks, draining the area of the large agricultural enterprises in the lower part of the watershed, have a major influence on the water quality of the Kola River.

Long-range downstream effects of urban runoff and acid mine drainage in the Debed River, Armenia: insights from lead isotope modeling

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Lead concentrations and isotopic compositions measured along 80 km of the Debed River in the Republic of Armenia provide new insights into the geochemical and physical controls on riparian Pb transport by allowing comparison of the long-range, downstream impacts of acid mine drainage with runoff from an industrialized city. The modern background Pb concentration in Armenian surface waters is estimated to be ~0.01 g/L, based on analyses of remote alpine rivers in Armenia. The lead concentration in the Debed River is 8 g/L (800 times background) after passing through Vanadzor, the second largest industrial city in Armenia; it then decreases to 1 g/L before the Debed River flows into the Alaverdi mining district. There, the Debed River receives waters from two mining drainage streams with Pb concentrations >3000 g/L, but those concentrations decrease 3 orders of magnitude to ~3 g/L by the time the river exits Armenia and flows into the Republic of Georgia.

Isotope mixing plots show shifts in Pb isotope composition as the river flows out of Vanadzor, evidencing the mixture of an average terrestrial Pb composition ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.17$; $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.45$) with past leaded gasoline and other industrial Pb emissions retained in the river's sediments within that region ($^{208}\text{Pb}/^{207}\text{Pb} \sim 2.45$). The isotopic composition again shifts (e.g., $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.46$) as the river passes through the Alaverdi mining district, where isotopic ratios in the water are characteristic of Pb in the area's massive sulfide deposits.

Modeling both downstream elemental concentrations and Pb isotopic compositions further resolves the physical and chemical behavior of the contaminants in the river system. A multi-element model of concentration gradients in the acid mine drainage streams indicates Pb is attenuated by $\text{Al}(\text{OH})_3$ precipitation (54% of the loss) and by adsorption onto other particles settling out of the water column (46% of the loss). Modeling of Pb transport in the Debed River indicates the natural outflow of Pb is ~10 kg/a, while the contributions from industrial runoff and acid mine drainage are each ~ 10^3 kg/a, two orders of magnitude greater than the natural flux. Thus, the total annual flux of Pb from the Debed River as it leaves Armenia and flows into Georgia is calculated to be 2500 kg/a.

This value is consistent with the average annual Pb flux of 2360 kg/a estimated for the last 20 a. The predicted effects of local climate change over the next 100 a may reduce annual Pb flux by 10–15%, slowing the removal of contaminant Pb and maintaining the two order of magnitude increase over the natural flux.

Input determination for neural network models in water resources applications. Part 2.

Case study: forecasting salinity in a river

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This paper is the second of a two-part series in this issue that presents a methodology for determining an appropriate set of model inputs for artificial neural network (ANN) models in hydrologic applications. The first paper presented two input determination methods. The first method utilises a measure of dependence known as the partial mutual information (PMI) criterion to select significant model inputs. The second method utilises a self-organising map (SOM) to remove redundant input variables, and a hybrid genetic algorithm (GA) and general regression neural network (GRNN) to select the inputs that have a significant influence on the model's forecast. In the first paper, both methods were applied to synthetic data sets and were shown to lead to a set of appropriate ANN model inputs. To verify the proposed techniques, it is important that they are applied to a real-world case study. In this paper, the PMI algorithm and the SOM–GAGRNN are used to find suitable inputs to an ANN model for forecasting salinity in the River Murray at Murray Bridge, South Australia. The proposed methods are also compared with two methods used in previous studies, for the same case study. The two proposed methods were found to lead to more parsimonious models with a lower forecasting error than the models developed using the methods from previous studies. To verify the robustness of each of the ANNs developed using the proposed methodology, a real-time forecasting simulation was conducted. This validation data set consisted of independent data from a six-year period from 1992 to 1998. The ANN developed using the inputs identified by the stepwise PMI algorithm was found to be the most robust for this validation set. The PMI scores obtained using the stepwise PMI algorithm revealed useful information about the order of importance of each significant input.

Water mixing in a St. Lawrence river embayment to outline potential sources of pollution

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Water mass balances on an isolated embayment (Hoople Bay) in the St. Lawrence River revealed a small stream (Hoople Creek), local groundwater and the St. Lawrence Main Channel as the 3 principal water sources. The latter had an average evaporative isotope signal that was inherited from the Great Lakes ($^{18}\text{O}_{\text{H}_2\text{O}}=-7.0\text{‰}$) and an average Cl^- content of 0.55 mmol/l. Hoople Creek and Hoople Bay waters were more variable in their isotopic composition and Cl^- contents, while local groundwater was assumed to have a homogeneous composition year around. These parameters constituted an equation system that was solved with matrix operations to yield monthly contributions of the 3 endmembers. Influx of groundwater and Hoople Creek dominated the embayment only after higher snowmelt discharges, while the Main Channel contributed more than 50% during the remainder of the year. Preliminary results suggest that potential pollution in the Main Channel would strongly affect Hoople Bay and similar ecosystems along the river. Nevertheless, more detailed data are needed for a better water balance over longer time periods. The 3-component mixing technique serves as a good tool to evaluate seasonal water fluxes and may also become useful in other mass balances.

Lead isotope signatures of Holocene fluvial sediments from the Loire River valley

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The distribution of Mn, V, Th, Pb and isotopes of Pb in the labile fraction of sediments from a channel infill in the Middle Loire alluvial plain are used to highlight some aspects of the basin evolution over the period from 0 to 10 ka BP. The acid extractable matter (AEM) in the sediment samples is variable in amount and in trace element contents. Iron-Mn oxyhydroxides are the principle trace element carrying phase in the labile fraction and carbonates are a secondary carrier. Vanadium and Pb originate from the weathering of silicates and are used as a silicate erosion rate index in the fluvial record. Most of the AEM data plot along a general trend between 3 endmembers (basalts, Cretaceous carbonate rocks and granites) in the relationship between $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{206}\text{Pb}$. These endmembers have been mixed in various proportions depending on natural Holocene inputs (erosion, volcanic events) or human influences (mining and smelting of ore).

Reductive dissolution of Mn oxides in river-recharged aquifers: a laboratory column study

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River-recharged aquifers are developed for drinking water supplies in many parts of the world. Often, however, dissolved organic carbon (DOC) present in the infiltrating river water causes

biogeochemical reactions to occur in the adjacent aquifer that create elevated Mn and Fe. Mn concentrations in groundwater from some of the production wells installed in the aquifer at Fredericton, New Brunswick exceed the Canadian Drinking Water Guideline of 9.1×10^{-4} mmol/l by up to 5.5×10^{-2} mmol/l. It has previously been hypothesized that the influx of DOC from the Saint John River is causing bacterially mediated reductive dissolution of Mn oxides in the aquifer system, leading to elevated aqueous Mn concentrations. Previous work was limited to the collection of water samples from production wells and several observation wells installed in the glacial outwash aquifer. The objective of this study was to investigate the biogeochemical controls on Mn concentrations using sand-filled columns. One column was inoculated with bacteria while a second column was treated with ethanol in order to decrease the microbial population initially present in the system. Both columns received the same influent solution that contained acetate as a source of DOC. The results of the experiments suggested that the two main controls on Mn concentrations in the columns were microbially mediated reductive dissolution of Mn oxides and cation exchange. The conceptual model that was developed based on the experimental data was supported by the results obtained using a one-dimensional reactive-transport model. The reductive dissolution of Mn oxides in the aquifer sands could be adequately simulated using dual-Monod kinetics. Similar trends are observed in the experimental data and field data collected from Production Well 5, located in the Fredericton Aquifer. From the experiments, it is evident that cation-exchange reactions may be an important geochemical control on Mn concentrations during the initial stages of pumping; however, the reductive dissolution of Mn oxides may represent a long-term source of Mn in the drinking water supply.

Water toxicity and metal contamination assessment of a polluted river: the Upper Vistula River (Poland)

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In aquatic systems, the bioavailability of an element to microorganisms is greatly influenced by its chemical speciation. The goal of this work was to assess metal toxicity to a green algae (*Pseudokirchneriella subcapitata*) and a bacterium (*Vibrio fischeri*) as a function of size fractionation and chemical speciation (using the program MINTEQA2) in contaminated water of the Upper Vistula River. Water samples were collected at 1 reference site, 4 polluted sites and one polluted site on the Vistula's main tributary, the Przemsza River. Toxicity measurements were performed on unfiltered samples and, total dissolved (<1.2 m), and truly dissolved (<1 kDa) fractions. Trace metal (Cd, Co, Cr, Cu, Mn, Pb, Zn) concentrations were measured in these samples and also in the colloidal fraction (1 kDa–1.2 m). At the reference site, the low metal concentrations were in agreement with the absence of measurable toxicity. In the polluted section of the river, free metal concentrations were largely below the potential toxic levels for bacteria, which was in agreement with the absence of toxicity. Although Zn^{2+} was at potentially toxic-level concentrations in total

dissolved and truly dissolved fractions in the polluted riverine section, toxicity for algae was observed, only in truly dissolved fractions from two stations. The absence of toxicity in most samples was related to metal association with particles and with low molecular weight ligands as well as the presence of organic ligands (phenol). The reason for toxic effects in two ultrafiltered samples is not clear, but may be related to the elimination of the colloidal organic fraction and thus the eradication of its protective effect occurring in natural samples.

WATER CHEMISTRY

Treatment of sulphide containing wastewater with sulphur recovery in a novel reverse fluidized loop reactor (RFLR)

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A novel aerobic bioreactor, the reverse fluidized loop reactor (RFLR) was tested for recovering sulphur from aqueous sulphide in this study. The RFLR contained buoyant carrier particles on which chemolithotrophic sulphide oxidizing bacteria formed a biofilm, which oxidized sulphide to sulphur and separated from the aqueous phase. The redox potential of the RFLR was regulated to control the oxygenation of sulphide for sulphur production. The RFLR was operated without any pH control and under various controlled pHs. The sulphide removal and nature of products formed under various sulphide loading rates and pH were examined. Under pH uncontrolled state, 95% of sulphur was recovered up to 11 kg sulphide/m³ d. The maximum sulphide loading supplied to the reactor was 30 kg sulphide/m³ d at pH 8, of which 90% was completely oxidized and 65% recovered as sulphur. The decline in bacterial sulphide oxidation leads to chemical oxidation of sulphide and subsequent accumulation of intermediary products such as thiosulphate and polysulphide in the reactor.

Interaction between shallow groundwater, saline surface water and contaminant discharge at a seasonally and tidally forced estuarine boundary

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This paper presents findings from a 2-year field investigation of a dissolved hydrocarbon groundwater plume flowing towards a tidally and seasonally forced estuarine river system in Perth, Western Australia. Samples collected from transects of multiport wells along the riverbank and into the river,

enabled mapping of the fine scale (0.5 m) vertical definition of the hydrocarbon plume and its longitudinal extent. Spear probing beneath the river sediments and water table, and transient monitoring of multiport wells (electrical conductivity) was also carried out to define the zone of mixing between river water and groundwater (the hyporheic zone) and its variability. The results showed that groundwater seepage into the estuarine surface sediments occurred in a zone less than 10 m from the high tide mark, and that this distance and the hyporheic transition zone were influenced by tidal fluctuations and infiltration of river water into the sediments. The dissolved BTEXN (benzene, toluene, ethylbenzene, the xylene isomers and naphthalene) distributions indicated the behaviour of the hydrocarbon plume at the groundwater/surface water transition zone to be strongly influenced by edge-focussed discharge. Monitoring programs and risk assessment studies at similar contaminated sites should therefore focus efforts within the intertidal zone where contaminants are likely to impact the surface water and shallow sediment environments.

Water chemistry and nutrient budgets in an undisturbed evergreen rainforest of southern Chile

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In a pristine evergreen rainforest of *Nothofagus betuloides*, located at the Cordillera de los Andes in southern Chile (41°S), concentrations and fluxes of nutrients in bulk precipitation, cloud water, throughfall water, stemflow water, soil infiltration and percolation water and runoff water were measured. The main objectives of this study were to investigate canopy–soil–atmosphere interactions and to calculate input–output budgets. From May 1999 till April 2000, the experimental watershed received 8121mm water (86% incident precipitation, 14% cloud water), of which the canopy intercepted 16%. Runoff water volume amounted 9527mm. Bulk deposition of inorganic (DIN) and organic (DON) nitrogen amounted 3.6kg $\text{gha}^{-1}\text{year}^{-1}$ and 8.2kg $\text{gha}^{-1}\text{year}^{-1}$ respectively. Occult deposition (clouds+fog) contributes for 40% to the atmospheric nitrogen input (bulk+occult deposition) of the forest. An important part of the atmospheric ammonium deposition is retained within the canopy or converted to nitrate or organic nitrogen by epiphytic bacteria or lichens. Also the export of inorganic (0.9kg $\text{gha}^{-1}\text{year}^{-1}$) and organic (5.2kg $\text{gha}^{-1}\text{year}^{-1}$) nitrogen via runoff is lower than the input to the forest floor via throughfall and stemflow water (3.2kgDIN $\text{ha}^{-1}\text{year}^{-1}$ and 5.6kgDON $\text{ha}^{-1}\text{year}^{-1}$). The low concentrations of NO_3^- and NH_4^+ under the rooting depth suggest an effective biological immobilization by vegetation and soil microflora. Dry deposition and foliar leaching of base cations (K^+ , Ca^{2+} , Mg^{2+}) was estimated using a canopy budget model. Bulk deposition accounted for about 50% of the total atmospheric input. Calculated dry and occult deposition are both of equal value (about 25%). Foliar leaching of K^+ , Ca^{2+} , and Mg^{2+} accounted for 45%, 38% and 6% of throughfall deposition respectively. On an annual basis, the experimental watershed was a net source for Na^+ , Ca^{2+} and Mg^{2+} .

**Wastewater treatment with multilayer media of waste and natural indigenous materials
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Wastewater treatment using waste materials (refuse concrete, waste paper and charcoal) and natural indigenous rocks (andesite, limestone, granite and nitrolite) in the form of multilayer media was investigated. The removal of suspended solids (SS), phosphate ion, nitrate ion, ammonium ion, toxic metals and chemical oxygen demand (COD) were evaluated for the multilayer wastewater treatment system. Effective removal of heavy metals such as cadmium, chromium, mercury and lead was demonstrated. SS and phosphate ion were removed with relatively high efficiency and the COD after treatment was lessened using certain combinations of media. The present wastewater treatment system is simple, convenient and low cost. Therefore, this method can be applied in small scale plants for wastewater treatment in local and nonexclusive areas.

**Removal of direct red 12B and methylene blue from water by adsorption onto Fe (III)/
Cr (III) hydroxide, an industrial solid waste
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Removal of direct red 12B and methylene blue by adsorption onto Fe (III)/Cr (III) hydroxide was studied using various parameters such as agitation time, dye concentration, adsorbent dose and pH. Equilibrium adsorption data followed both Langmuir

**Wetland ecological and compliance assessments in the San Francisco Bay Region,
California, USA**

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The San Francisco Bay Region of the California Regional Water Quality Control Board (SFB CRWQCB) and the San Francisco District of the US Army Corps of Engineers (US ACOE) are looking for an expeditious means to determine whether regulated wetland projects produce ecologically valuable systems and remain in compliance with their permits (i.e. fulfill their legal requirements) until project completion. A study was therefore undertaken in which 20 compensatory wetland mitigation projects in the San Francisco Bay Region were reviewed and assessed for both permit compliance and habitat function, and this was done using a rapid assessment method adapted for this purpose. Thus, in addition to determining compliance and function, a further goal of this study was to test the efficacy of the assessment method, which, if useful, could be applied not only to mitigation projects, but also to restoration projects and natural wetland systems.

Survey results suggest that most projects permitted 5 or more years ago are in compliance with their permit conditions and are realizing their intended habitat functions. The larger restoration sites or those situated between existing wetland sites tend to be more successful and offer more benefits to wildlife than the smaller isolated ones. These results are consistent with regulatory experience suggesting that economies of scale could be realized both with (1) large scale regional wetland restoration sites, through which efforts are combined to control invasive species and share costs, and (2) coordinated efforts by regulatory agencies to track project information and to monitor the increasing number and size of mitigation and restoration sites. In regard to the assessment methods, we find that their value lies in providing a consistent protocol for evaluations, but that the ultimate assessment will rely heavily on professional judgment, regulatory experience, and the garnering of pre-assessment information.

Roofing as a source of nonpoint water pollution

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Sixteen wooden structures with two roofs each were installed to study runoff quality for four commonly used roofing materials (wood shingle, composition shingle, painted aluminum, and galvanized iron) at Nacogdoches, Texas. Each roof, either facing NW or SE, was 1.22 m wide×3.66 m long with a 25.8% roof slope. Thus, there were 32 alternatively arranged roofs, consisting of four roof types×two aspects×four replicates, in the study. Runoff from the roofs was collected through galvanized gutters, downspouts, and splitters. The roof runoff was compared to rainwater collected by a wet/dry acid rain collector for the concentrations of eight water quality variables, i.e. Cu²⁺, Mn²⁺, Pb²⁺, Zn²⁺, Mg²⁺, Al³⁺, EC and pH.

Based on 31 storms collected between October 1997 and December 1998, the results showed: (1) concentrations of pH, Cu, and Zn in rainwater already exceed the EPA freshwater quality standards even without pollutant inputs from roofs, (2) Zn and Cu, the two most serious pollutants in roof runoff, exceeded the EPA national freshwater water quality standards in virtually 100% and more than 60% of the samples, respectively, (3) pH, EC, and Zn were the only three variables significantly affected by roofing materials, (4) differences in Zn concentrations were significant among all roof types and between all roof runoff and rainwater samples, (5) although there were no differences in Cu concentrations among all roof types and between roof runoff and rainwater,

all means and medians of runoff and rainwater exceeded the national water quality standards, (6) water quality from wood shingles was the worst among the roof types studied, and (7) although SE is the most frequent and NW the least frequent direction for incoming storms, only EC, Mg, Mn, and Zn in wood shingle runoff from the SE were significantly higher than those from the NW; the two aspects affected no other elements in runoff from the other three roof types. Also, Zn concentrations from new wood-shingle roofs were significantly higher than those from aged roofs of a previous study. The study demonstrated that roofs could be a serious source of nonpoint water pollution. Since Zn is the most serious water pollutant and wood shingle is the worst of the four roof types, using less compounds and materials associated with Zn along with good care and maintenance of roofs are critical in reducing Zn pollution in roof runoff.

Effects of golf course construction and operation on water chemistry of headwater streams on the Precambrian Shield

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To investigate the effects of golf course construction and operation on the water chemistry of Shield streams, we compared the water chemistry in streams draining golf courses under construction (2) and in operation (5) to streams in forested reference locations and to upstream sites where available. Streams were more alkaline and higher in base cation and nitrate concentrations downstream of operational golf courses. Levels of these parameters and total phosphorus increased over time in several streams during golf course construction through to operation. There was evidence of inputs of mercury to streams on two of the operational courses. Nutrient (phosphorus and nitrogen) concentrations were significantly related to the area of unmanaged vegetation in a 30 × 30 m area on either side of the sampling sites, and to River Bank Quality Index scores, suggesting that maintaining vegetated buffers along the stream on golf courses will reduce in-stream nutrient concentrations.

Golf course construction and operation had a significant impact on alkalinity, nitrogen and base cation concentrations of streams.

Priority volatile organic compounds in surface waters of the southern North Sea

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The occurrence of 25 volatile organic compounds (VOCs) was studied from April 1998 to October 2000 in the southern North Sea. Target VOCs were selected from lists of priority pollutants for the marine environment and included, e.g., chlorinated short-chain hydrocarbons (CHCs), monocyclic aromatic hydrocarbons (MAHs), and chlorinated monocyclic aromatic hydrocarbons (CMAHs).

Water samples were taken from the Channel, the Belgian Continental Shelf, the mouth of the Scheldt estuary and the Southern Bight, and were analysed by purge-and-trap and high-resolution gas chromatography–mass spectrometry. All data were produced by analyses deemed ‘in control’ by a rigorous quality assurance/quality control program provided by QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe). Chloroform and trichloroethene were commonly detected at concentrations up to 1900 and 270 ng l⁻¹, respectively. The other CHCs were generally found below 5 ng l⁻¹, and rarely exceeded 10 ng l⁻¹. Concentrations of MAHs were at least one order of magnitude higher than those of the CHCs. The higher levels were attributed to anthropogenic emissions from oil-related activities in coastal areas. CMAHs, except chlorobenzene and 1,4-dichlorobenzene, were hardly detected in North Sea waters. The levels of several CHCs and MAHs were shown to decrease compared to previous investigations in 1994–1995, probably as a result of on-going emission reduction efforts. The occurrence of 1,1,1-trichloroethane, for instance, was substantially reduced since the Montreal Protocol was implemented in 1995. Volatile aromatics are a major group of volatile organic compounds in the North Sea, and are attributed to discharges from shipping and oil related activities.

Do tubificid worms influence the fate of organic matter and pollutants in stormwater sediments?

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In urban area, management of stormwater leads to the accumulation of polluted sediments at the water–sediment interface of various aquatic ecosystems. In many cases, these sediments are colonised by dense populations of tubificid worms. However, the influence of tubificid worms on the fate of stormwater sediments has never been tackled. The aim of this study was to measure in sediment columns the influence of tubificid worms on sediment reworking, organic matter processing (O₂ uptake and release of NH₄⁺, NO₃⁻, PO₄³⁻, and dissolved organic carbon), release of hydrocarbons and heavy metals, and microbial characteristics. Results showed that tubificid worms increased the release of NH₄⁺, PO₄³⁻, and dissolved organic carbon by 2-, 4-, and 3-fold, respectively. O₂ uptake also increased by more than 35% due to tubificid activity. The increase in the percentages of active bacteria and hydrolytic activity in the presence of worms indicated that the higher sediment respiration was caused by the stimulation of microbial communities. A reduction of the number of sulphate-reducing bacteria in the uppermost layers of the sediment was attributed to the penetration of O₂ due to worm activity. These significant effects of tubificid worms were probably linked to the dense network of burrows, which enhanced the exchange surface between the water column and the sediment. No release of heavy metals and hydrocarbons to the water phase was detected in the sediment columns. Understanding the fate and effect of organic stormwater sediments in the natural environment requires the integration of the role of bioturbation in urban pollution studies. Tubificid worms significantly increased the organic matter mineralization and the release of nutrients from stormwater sediments.

Ammonium content and buoyancy in midwater cephalopods

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The majority of squid families (Teuthoidea: Cephalopoda) exchange sodium for ammonium, creating a low-density fluid that imparts lift for neutral buoyancy. However, previous methods for measuring ammonium did not distinguish between NH_4^+ and various other amine compounds. The present study, using single column ion chromatography, reassessed the cation concentrations in several midwater cephalopod species. High NH_4^+ levels were confirmed for histioteuthid, cranchiid, and chiroteuthid and related squids. A strong relationship is reported between ammonium content and body mass in *Histioteuthis heteropsis*, suggesting a gradual accumulation of ammonium coincident with an ontogenetic migration to greater depths. The bathypelagic squids *Bathyteuthis abyssicola* and *Bathyteuthis berryi*, on the other hand, contained very little ammonium but rather contained large quantities of an as yet unidentified cation. The ecological significance of this compound is not yet known. Morphology in Bathyteuthid squids suggests that the unknown cation is contained intracellularly and so, unlike sequestered ammonia, does not diminish the space available for muscle tissue. Accordingly, protein measurements in *B. berryi* mantle muscle are on par with shallower-living muscular squids, and in situ submersible observations reveal strong locomotory abilities relative to other deep-water squids.

Hydrodynamic and morphodynamic response to river engineering documented by fixed-discharge analysis, Lower Missouri River, USA

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This research detects long-term trends in flow conveyance on the Lower Missouri River, and uses equal-discharge analysis of channel-gaging time series to assess the mechanisms driving these trends. Five long-term gaging stations along the Lower Missouri were examined using specific-gage analysis, which is a technique that holds discharge constant in order to observe trends in water-surface elevation (or stage) over time. This analysis reveals that for all flood conditions on the Lower

Missouri River, stages have systematically risen for equal discharge volumes over the period of record. Flows that were fully contained within the Missouri channel in the early 20th century now create floods, and extreme high flows today are associated with stages as much as 3.7 m higher than at the start of the record. Equal-discharge analysis also can be used for analyzing time series of other parameters that co-vary strongly with discharge and that change systematically over time. On the Lower Missouri, long-term records of river gaging measurements, including cross-sectional area, flow velocity, and channel width, have been collected for the past 70 years. Equal-discharge analysis of these parameters illustrates the mechanisms of channel change driving flood magnification. At three stations, decreased flow velocity has been the dominant mechanism driving stage changes. At two other stations, constriction in channel cross-sectional area has increased flood stages. These changes in channel geometry and flow dynamics correlate with wing-dam construction and other engineering of the Lower Missouri River, but the changes occur progressively over the duration of record as a gradual and reach-scale re-equilibration of the fluvial system. Magnification of flood stages should be recognized on the Missouri River and incorporated into current estimates of flood hazard and into strategies for river management and flood mitigation in the future.

Water quality characteristics of vegetated groundwater-fed ditches in a riparian peatland

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The Environmental Ministry of Schleswig–Holstein (Northern Germany) has implemented a novel peatland rehabilitation programme to utilise the high denitrification potential of degenerated, minerotrophic peatlands for the reduction of nitrate input into aquatic ecosystems, and to simultaneously improve the habitat conditions. Realisation of both goals requires changes to the water management adapted to the site-specific geohydrological conditions. The effect of raised groundwater levels and extensive land use on the water quality of heavily vegetated and groundwater-fed ditches was investigated in a riparian peatland located in the River Eider Valley (a nationally important wetland case study area). The water quality of the selected representative ditches was regularly assessed at different discharge levels during different flow obstruction cover periods. The hydraulic residence time was predominantly a function of the ditch geometry and the overall flow obstruction. A better understanding of the effect of ditch vegetation on the temporal flow patterns and the hydraulic residence times is of high environmental interest, especially for improving nutrient standards in lowland rivers such as the River Eider. Within-ditch vegetation and other hydraulic flow obstructions such as accumulated silt and organic debris increased the hydraulic residence time and led to an improvement of the water quality (e.g. reduction in nitrate content) along the ditch. While orthophosphate and ammonia concentrations were acceptable to German water quality standards, nitrate–nitrogen concentrations were frequently elevated due to high discharges despite high flow obstruction cover. Further findings show that the lower stretches of the ditches were flooded by the River Eider

due to the absence of a macrophyte-mowing scheme that led to increased water levels during late summer.

Organophosphorus flame retardants and plasticisers in surface waters

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Organophosphates used as flame retardants, plasticisers and lubricants such as tris-(2-chloro-, 1-methyl-ethyl)-phosphate (TCPP), tris-(2-chloroethyl)-phosphate (TCEP) or tris-(2-chloro-, 1-chloromethyl-ethyl)-phosphate (TDCP), tri-*n*-butylphosphate (TnBP), tri-*iso*-butylphosphate (TiBP), triphenylphosphate (TPP) and tris-(butoxyethyl)-phosphate (TBEP) have been analysed in several rivers and sewage treatment plant (STP) effluents. The concentrations in the River Ruhr are 20–200 ng/l TCPP, 13–130 ng/l TCEP, about 50 ng/l TDCP, 10–200 ng/l TBEP and up to 40 ng/l TPP. The STP effluents exhibit concentrations up to 400 ng/l TCPP, 130 ng/l TCEP, about 120 ng/l TDCP and 500 ng/l TBEP, respectively. The main sources for the load of organophosphates are sewage treatment plants, but not all contribute equivalent to the amount of inhabitants they serve.

Determination of biodegradable dissolved organic carbon in waters: comparison of batch methods

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An effect of different types of bacterial inocula upon the final biodegradable dissolved organic carbon (BDOC) result was investigated in samples of both low and high BDOC concentrations. Stream water and leaf leachate samples were incubated either with free, suspended bacteria or with bacteria attached to the stream sediment particles or attached to artificial substrata. The time course of dissolved organic carbon (DOC) decomposition was observed using absorbance analysis of DOC. BDOC determination by means of commonly used suspended bacteria as the inoculum made for an underestimation of BDOC between 5% and 25%, compared with attached bacterial community (biofilm). The reason for these findings could be the higher microbial diversity, higher metabolic activity of attached bacteria and abiotic adsorption of organic molecules to inorganic support and biofilm matrix surfaces. Adsorbed DOC is easily hydrolyzed and utilized by biofilm bacteria.

Comet and micronucleus assays in zebra mussel cells for genotoxicity assessment of surface drinking water treated with three different disinfectants

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The aim of this research was to study the influence of classic (sodium hypochlorite and chlorine dioxide) and alternative (peracetic acid [PAA]) disinfectants on the formation of mutagens in surface waters used for human consumption. For this proposal, *in vivo* genotoxicity tests (Comet and micronucleus assay) were performed in an experimental pilot plant set up near Lake Trasimeno (Central Italy). The effects were detected in different tissues (haemocytes for the Comet assay and gills for the micronucleus test [MN]) of *Dreissena polymorpha* exposed in experimental basins supplied with lake water with/without the different disinfectants. Specimen collection was performed before disinfectant input for both tests and after the start of disinfection (3 h and 20 days for the Comet assay and 10 and 20 days for micronucleus test, respectively) to assess short- and long-term exposure effects during three sampling campaigns (October 2000, February 2001, and June 2001). Seasonal differences in baseline levels of DNA migration and micronucleus frequency were observed. Raw water quality modulation on disinfection by-product formation was shown. The results of the micronucleus and Comet assays on zebra mussel cells after *in situ* exposure to water disinfected with the two chlorinated compounds clearly indicate DNA/by-product interaction. PAA did not induce either clastogenic/aneugenic effects or DNA damage on this bioindicator.

Monitoring of selected estrogenic hormones and industrial chemicals in groundwaters and surface waters in Austria

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In order to address the Austrian situation concerning endocrine disrupting substances (EDS), a consortium called Austrian Research Cooperation on Endocrine Modulators (ARCEM) was established in 1999. Among several other issues that were investigated, ARCEM monitored more than 400 ground- and surface water samples for selected estrogenic hormones and industrial chemicals. Appropriate analytical methods were established using GC-HRMS for the detection of hormones and LC/MSMS for the detection of industrial chemicals. Since analytical results were forwarded for toxicological assessments within the programme, quantification limits below 0.1 ng/l (ethinyl estradiol) and 10 ng/l (industrial chemicals) were required depending on the NOEL of the individual compound.

Results indicate that both hormones and industrial chemicals occur in the selected ground- and surface water sites in detectable concentrations. Three river sites were identified as being charged

with noticeable concentrations of EDS. These results were verified by biological indications within the part of the ARCEM programme dealing with bio-indications.

Lead isotopes in tap water: implications for Pb sources within a municipal water supply system

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Residential tap waters were investigated to examine the feasibility of using isotopic ratios to identify dominant sources of water Pb in the Columbus (Ohio, USA) municipal supply system. Overall, both the concentrations, which are generally low (0.1–28 µg/L), and isotopic compositions of tap water Pb show wide variations. This contrasts with the situation for a limited number of available service lines, which exhibit only a limited Pb-isotope variation but contain Pb of two very different types with one significantly more radiogenic than the other. Most tap water samples in contact with Pb service lines have Pb-isotope ratios that are different from the pipe Pb. Furthermore, the Pb isotope compositions of sequentially drawn samples in the same residence generally are similar, but those from separate residences are different, implying dominant Pb sources from domestic plumbing. A separate pilot study at two residences without Pb service lines shows isotopic similarity between water and solders in each house, further suggesting that the major Pb sources are domestic in these cases and dominated by Pb from solder joints. Although complicated by the broad range of overall Pb-isotope variations observed and limited by sample availability, the results suggest that Pb isotopes can be used effectively to constrain the sources of Pb in tap waters, especially for individual houses where multiple source candidates can be identified.

The spatial distribution of groundwater age for different geohydrological situations in the Netherlands: implications for groundwater quality monitoring at the regional scale

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The spatial distribution of groundwater age is a key factor determining the distribution of dissolved contaminants in the subsurface when contamination loadings have increased in time. The effects of surficial drainage and aquifer heterogeneity on the spatial distribution of groundwater age in unconsolidated aquifers in flat areas were investigated, and consequences were presented for the monitoring of contaminants from diffuse sources. First, the effects were assessed using model simulations. Second, the groundwater age distribution was evaluated in the two regional monitoring networks of Noord-Brabant and Drenthe using tritium measurements. Theoretically, a simple spatial distribution of groundwater age is present in homogeneous aquifers with natural groundwater recharge, characterized by a horizontal pattern of residence time isochrones and a gradual increase of groundwater age with depth. The model simulations show that the isochrone pattern becomes

distorted in areas with a surficial drainage network, resulting in relatively old groundwater at shallow depth and larger spatial variation in groundwater age at a specific depth. This drainage effect on the spatial distribution of groundwater age is relatively large compared with effects of regional scale aquifer heterogeneity or spatially varying groundwater recharge. The effects of surficial drainage on the spatial distribution of groundwater age were confirmed by tritium measurements made in the regional monitoring networks of two provinces in the Netherlands. At about 24 m depth, the proportion of post-1950 groundwater in drained areas was significantly less and the spatial variation of groundwater age was larger than in recharge areas that lack a drainage network. The age of the groundwater appeared to be related to the drainage network density and the water table regime. A preliminary survey showed that contamination patterns in the two networks agree well with the proportion of post-1950 groundwater.

Controls on water chemistry of the Pilcomayo river (Bolivia, South-America)

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In order to reveal the intra-annual variability of the major ion composition of the Pilcomayo river, a dryland river, and its relationship to discharge, water samples were taken at regular time intervals from May 1998 until February 1999 at the town of Villa Montes (Bolivia). Water chemistry of the Pilcomayo river was highly variable during the year and strongly influenced by differences in discharge between the wet and the dry season. Halite dissolution appeared to play an important role and both Cl and Na concentrations became very high (± 10 mmol L⁻¹) during the dry season. Pyrite weathering and dissolution of gypsum, dolomite and calcite determined Ca, Mg, CO₃ and SO₄ chemistry. At the onset of the rainy season ‘rinse out’ effects occurred, resulting in marked concentration peaks especially for the least soluble ions. Possible effects on biota, such as consequences for trace metal toxicity, are discussed briefly.

Investigating surface water–well interaction using stable isotope ratios of water

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Because surface water can be a source of undesirable water quality in a drinking water well, an understanding of the amount of surface water and its travel time to the well is needed to assess a well's vulnerability. Stable isotope ratios of oxygen in river water at the City of La Crosse, Wisconsin, show peak-to-peak seasonal variation greater than 4‰ in 2001 and 2002. This seasonal signal was identified in 7 of 13 city municipal wells, indicating that these 7 wells have appreciable surface water contributions and are potentially vulnerable to contaminants in the surface water. When looking at wells with more than 6 sampling events, a larger variation in $\delta^{18}\text{O}$ compositions correlated with a larger fraction of surface water, suggesting that samples collected for oxygen isotopic composition over time may be useful for identifying the vulnerability to surface water influence even if a local meteoric water line is not available.

A time series of $\delta^{18}\text{O}$ from one of the municipal wells and from a piezometer located between the river and the municipal well showed that the travel time of flood water to the municipal well was approximately 2 months; non-flood arrival times were on the order of 9 months. Four independent methods were also used to assess time of travel. Three methods (groundwater temperature arrival times at the intermediate piezometer, virus-culture results, and particle tracking using a numerical groundwater-flow model) yielded flood and non-flood travel times of less than 1 year for this site. Age dating of one groundwater sample using ^3H - ^3He methods estimated an age longer than 1 year, but was likely confounded by deviations from piston flow as noted by others. Chlorofluorocarbons and SF_6 analyses were not useful at this site due to degradation and contamination, respectively. This work illustrates the utility of stable hydrogen and oxygen isotope ratios of water to determine the contribution and travel time of surface water in groundwater, and demonstrates the importance of using multiple methods to improve estimates for time of travel of 1 year or less.

FRESH WATER ECOSYSTEM

Estimation of natural recharge and its dependency on sub-surface geoelectric parameters

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Natural groundwater recharge is estimated using the injected tracer technique in the Bairasagara watershed of Kolar district, Karnataka (India) comprising of medium grained granite and granitic gneiss with weathering/fracturing up to 46 m depth. On a macroscopic scale, it is estimated that the weathered granites act as a uniform body having a recharge capacity of about 6–200 mm per annum for an average value of rainfall of 968 mm. Marked differences of infiltration rates (nil to 130 cm/year) were observed under cultivated and dry areas. The water level fluctuation and recharge are found to be minimum in the ayacut area as compared to the catchment area. Studies helped in demarcating recharge and discharge areas. Qualitative correlation studies of estimated natural groundwater recharge have been carried out with depth to basement, resistivity of subsurface layers, and water level fluctuations.

An attempt has been made to get empirical relationships between recharge vs. depth to basement, and recharge vs. water level fluctuations. The paper discusses the studies carried out, the result obtained, and the importance of such studies in the evaluation of groundwater resources.

Reducing risks of maintenance dredging on freshwater mussels (Unionidae) in the Big Sunflower River, Mississippi

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In response to proposed dredging in a 122-km reach of the Big Sunflower River, Mississippi, we studied freshwater mussels (family: Unionidae) using qualitative, semi-quantitative, and quantitative (0.25 m² total substratum removal) methods in 1987, 1993, 1994, 2001, 2002, and 2003. Our objectives were to identify important mussel resources, to devise methods for minimizing dredging risks, and to identify habitat improvement features. Approximately 60% of the fauna was located on two high-density shoals characterized by extreme dominance of the commercially valuable threeridge (*Amblema plicata*). Shallow nearshore and main channel areas comprised approximately 10 and 88% of the aquatic habitat in the project area; however, these areas were of less importance for mussels and supported densities of approximately 5 and 0.5 individuals/m², respectively. Throughout the project area the mussel fauna exhibited little or no evidence of recent recruitment, dominance

of relatively few species (either *A. plicata*, or the bank climber *Plectomerus dombeyanus*), and low species diversity (*H'*) and evenness.

No federally listed endangered or threatened mussels were found, although the pyramid pigtoe (*Pleurobema pyramidatum*), a species listed as endangered in Mississippi, was collected in and upstream of the project area. Two other state-listed species, *Plethobasus cyphus* (sheepnose) and *Quadrula cylindrica* (rabbitsfoot), were only found on gravelly shoals upriver of the project area. Maintenance plans were redesigned to minimize environmental damage; a hydraulic cutterhead dredge will be used in most of the mainstem to reduce risk to nearshore habitats. High-density assemblages on four shoals will not be dredged and 150 and 100 m buffer zones will be left immediately up and downriver. Enhancements for aquatic biota will be created with gravel substratum and wing dams.

Circulation of copper in the biotic compartments of a freshwater dammed reservoir

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This study concerns a chronic copper release in an aquatic ecosystem: Mirgenbach reservoir; which is characterized by high salinity, conductivity and hardness, a eutrophic state and a high temperature. To study the bioavailability of copper in the biotic compartments, the sampling covered the entire food chain (phyto- and zooplankton, macroalgae, aquatic plants, crustaceans, mollusks, and fish). Of the organisms present, the filter feeder *Dreissena polymorpha*, the detritivorous *Bithynia tentaculata* and *Orconectes limosus* were most contaminated by copper. The level of copper found in fish was the lowest. Body copper concentrations recorded in the present study show large variability between species even in some that are closely related. In most cases, however, the metal handling strategy, feeding habits, morphology and ecology can, at least partially, explain the metal content recorded. Pollution factors have been used to assess the state of contamination of the food chain. This study showed finally that the copper in the lake is bioavailable and bioaccumulated by organisms up to high levels and some effects of long-term toxicity of copper on benthic community and planktonic biomass were pointed out.

Water striders (family Gerridae): mercury sentinels in small freshwater ecosystems

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To circumvent some of the previous limitations associated with contaminant-monitoring programs, we tested the suitability of the water strider (Hemiptera: Gerridae) as a mercury sentinel by comparing total mercury concentrations in water striders and brook trout (*Salvelinus fontinalis*) from a variety of stream sites in New Brunswick, Canada. There was a strong association between the two variables across sites ($r^2 = 0.81$, $P < 0.001$) in systems where both atmospheric deposition and a point source (an abandoned gold mine) were likely contributing to ambient mercury levels. In a small stream draining the gold mine tailings pile, water striders had mercury concentrations an order of magnitude higher than those from reference locations. Temporal variation at three southern New Brunswick stream sites was non-significant. These results suggest that water strider mercury levels accurately quantify food chain entry of the element. The use of sentinel species holds great potential for expanding contaminant-monitoring programs.

Water striders accurately reflect the entry of mercury in food chains of small freshwater systems.

Mobility of heavy metals within freshwater sediments affected by motorway stormwater

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The assessment of the mobility and bioavailability of heavy metals in sediment samples requires the use of sequential extraction procedures. Results for sediments taken from an unmanaged motorway detention pond showed heavy metals to be associated with the carbonate and residual fractions. In particular, nickel and cadmium showed a high percentage association, compared with other geochemical fractions, such as carbonates and residual fractions. Copper and zinc were shown to be associated with carbonates and iron–manganese oxides, whereas lead showed the strongest association (72%) with the Fe–Mn oxides. When compared to a groundwater-fed lake on the same site, all heavy metals contained within this sediment were found to be at much lower concentrations and strongly associated with the residual fraction (>50%) and are therefore strongly bound within the sediment. Following discharge via a wet detention pond, stormwater then flows through a series of interconnecting lake systems. Heavy metal fractionation of these interconnecting lakes is discussed and shows changes in fractionation through the lake system for copper, nickel, lead and zinc. The main concern in these lakes is the continued use of calcium carbonate to maintain freshwater pH for coarse fishing. This practice, used until 1999, may present an enhanced risk to the freshwater environment, causing greater mobility of these metals.

Hydrogeochemical evolution of confined groundwater in northeastern Osaka Basin, Japan: estimation of confined groundwater flux based on a cation exchange mass balance method

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A confined aquifer system has developed in argillaceous marine and freshwater sediments of Pliocene–Holocene age in the northeastern Osaka Basin (NEOB) in central Japan. The shallow groundwater (<100 m) in the system is recharged in a northern hilly to mountainous area with dominantly Ca-HCO₃ type water, which changes as it flows toward the SW to Mg-HCO₃ type and then to Na-HCO₃ type water. Comparison of the chemical and Sr isotopic compositions of the groundwater with those of the bulk and exchangeable components of the underground sediments indicates that elements leached from the sediments contribute negligibly to the NEOB aquifer system. Moreover, model calculations show that contributions of paleo-seawater in the deep horizon and of river water at the surface are not major factors of chemical change of the groundwater. Instead, the zonal pattern of the HCO₃-dominant groundwater is caused by the loss of Ca²⁺ from the water as it is exchanged for Mg²⁺ in clays, followed by loss of Mg + Ca as they are exchanged for Na + K in clays between the Ca-HCO₃ type recharge water and the exchangeable cations in the clay layers, which were initially enriched in Na⁺. Part of this process was reproduced in a chromatographic experiment in which Na type water with high ⁸⁷Sr/⁸⁶Sr was obtained from Mg type water with low ⁸⁷Sr/⁸⁶Sr by passing it through marine clay packed in a column. The flux of recharge water into the confined aquifer system according to this chromatographic model is estimated to be 0.99 mm/day, which is compatible with the average recharge flux to unconfined groundwater in Japan (1 mm/day).

Exsolution of nitrogen and argon by methanogenesis in Dutch ground water
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Dutch ground water was sampled under high pressure in stainless steel vessels and analysed by gas chromatography for Ar, N₂, CH₄ and O₂. Results show a deficit N₂ and Ar concentrations combined with a high CH₄ concentration that are attributed to the occurrence of exsolution of Ar and N₂ during methanogenesis (the focus of this article). They also show N₂ and Ar in concentrations exceeding the concentration in equilibrium with atmospheric air that are caused by the entrapment and subsequent (partial) dissolution of excess air; in recent ground water, N₂ excesses also are caused by denitrification. PHREEQC model runs of methanogenesis at different pressures, with different amounts of organic matter decomposition and different amounts of initial dissolved N₂ show five features. Firstly, methanogenesis under lower hydrostatic pressures causes more N₂ and Ar exsolution than methanogenesis under higher hydrostatic pressures. Secondly, when little organic matter is decomposed (e.g. 1 mmol/l), the value taken for the fixed total pressure (between 1.05 and 3.0 atm.) influences mostly the N₂ and Ar concentration, and when much organic matter is decomposed (e.g. 16 mmol/l), the value taken for the fixed total pressure influences mostly the CH₄ concentration. Thirdly, in order to explain the observed gas concentrations, not more than 27 mmol of organic matter should be decomposed per litre of soil. Fourthly, the PHREEQC run with initial denitrification (initial N₂ pressure=1.0 atm.) fits the data better than the PHREEQC run without initial denitrification. Fifthly, the maximum total pressure of bubble formation is 3.0 atm. Analysed

gas concentration profiles show that the greatest source of CH₄ is found up to approximately 20 m below surface. However, samples with CH₄ partial pressures >0.25 atm. were found up to a maximum average sampling screen depth of 81 m below surface.

Factors controlling tungsten concentrations in ground water, Carson Desert, Nevada

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An investigation of a childhood leukemia cluster by US Centers for Disease Control and Prevention revealed that residents of the Carson Desert, Nevada, are exposed to high levels of W and this prompted an investigation of W in aquifers used as drinking water sources. Tungsten concentrations in 100 ground water samples from all aquifers used as drinking water sources in the area ranged from 0.27 to 742 µg/l. Ground water in which W concentrations exceed 50 µg/l principally occurs SE of Fallon in a geothermal area. The principal sources of W in ground water are natural and include erosion of W-bearing mineral deposits in the Carson River watershed upstream of Fallon, and, possibly, upwelling geothermal waters. Ground water in the Fallon area is strongly reducing and reductive dissolution of Fe and Mn oxyhydroxides may be releasing W; however, direct evidence that the metal oxides contain W is not available.

Although W and Cl concentrations in the Carson River, a lake, and water from many wells, appear to be controlled by evaporative concentration, evaporation alone cannot explain the elevated W concentrations found in water from some of the wells. Concentrations of W exceeding 50 µg/l are exclusively associated with Na-HCO₃ and Na-Cl water types and pH > 8.0; in these waters, geochemical modeling indicates that W exhibits <10% adsorption. Tungsten concentrations are strongly and positively correlated with As, B, F, and P, indicating either common sources or common processes controlling their concentrations. Geochemical modeling indicates W concentrations are consistent with pH-controlled adsorption of W.

The geochemical model PHREEQC was used to calculate IAP values, which were compared with published K_{sp} values for primary W minerals. FeWO₄, MnWO₄, Na₂WO₄, and MgWO₄ were undersaturated and CaWO₄ and SrWO₄ were approaching saturation. These conclusions are tentative because of uncertainty in the thermodynamic data.

The similar behavior of As and W observed in this study suggests ground water in areas where elevated As concentrations are present also may contain elevated W concentrations, particularly if there is a mineral or geothermal source of W and reducing conditions develop in the aquifer.

The impact of freshwater and wastewater irrigation on the chemistry of shallow groundwater: a case study from the Israeli Coastal Aquifer

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Differences in the impact of irrigation with freshwater versus wastewater on the underlying shallow groundwater quality were investigated in the Coastal Aquifer of Israel. Seven research boreholes were drilled to the top-most 3–5 m of the saturated zone (the water table region-WTR) in the agricultural fields. The unsaturated zone and the WTR below the irrigated fields consist mainly of clayey sands, while the main aquifer comprises mainly of calcareous sandstones and sands. We show that the salinity and composition of the groundwater at the WTR are highly variable over a distance of less than 1 km and are controlled by the irrigating water and the processes in the overlying unsaturated zone. Tritium data in this groundwater (4.6 tritium units (TU)) support that these water are modern recharge. The water at the WTR is more saline and has a different chemical composition relative to the overlying irrigation water. High SAR values (sodium adsorption ratio) in wastewater irrigation lead to absorption of Na⁺ onto the clay and release of Ca²⁺ into the recharging water, resulting in low Na/Cl (0.4 compared to 1.2 in the wastewater) and high Ca/Cl ratios. In contrast, in the freshwater-irrigated field the irrigation water pumped from the aquifer (Na/Cl=0.9; SAR=0.6) is modified into Na-rich groundwater (Na/Cl=2.0) due to reverse base-exchange reactions. The high NO₃ concentration (>100 mg/l) in the WTR below both fields is derived from the agricultural activities. In the freshwater field, the source of NO₃ is fertilizer leachates, whereas in the wastewater field, where less fertilizers are applied, nitrate is probably derived from nitrification of the NH₄ in the wastewater. Some of the original inorganic nitrogen in the wastewater is consumed by the agricultural plants, resulting in a lower inorganic-N/Cl ratio in the WTR as compared to that in the wastewater. This study demonstrates the important role of the composition of irrigation water, combined with lithology and land use, in determining the quality of the water that recharge the aquifer below agricultural fields.

The evolution of alkaline, saline ground- and surface waters in the southern Siberian steppes

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Groundwaters, river and lake waters have been sampled from the semi-arid Siberian Republic of Khakassia. Despite the relatively sparse data set, from a diversity of hydrological environments, clear salinity-related trends emerge that indicate the main hydrochemical evolutionary processes active in the region. Furthermore, the major ion chemistry of the evolution of groundwater baseflow, via rivers, to terminal saline lake water, can be adequately and simply modelled (using PHREEQCI) by invoking: (i) degassing of CO₂ from groundwater as it emerges as baseflow in rivers (rise in pH); (ii) progressive evapoconcentration of waters (parallel accumulation of Cl⁻, Na⁺, SO₄²⁻, and increase in pH due to common ion effect); and (iii) precipitation of calcite (depletion of Ca from waters, reduced rate of accumulation of alkalinity). Dolomite precipitation is ineffective at constraining Mg accumulation, due to kinetic factors. Silica saturation appears to control dissolved Si in low salinity waters and groundwaters, while sepiolite saturation and precipitation depletes Si from the more saline surface waters. Gypsum and sodium sulphate saturation are only approached in the most saline environments. Halite remains unsaturated in all waters. Sulphate reduction processes are important in the lower part of lakes.

Modelling urban snowmelt runoff

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Few investigations have been made into modelling snowmelt in urban areas; hence, current urban snowmelt routines have adopted parameters and approaches intended for rural areas that are not appropriate in an urban environment. This paper examines problems with current urban snowmelt models and proposes a model that uses parameters developed from field studies focusing exclusively on urban snow. The Urban Snow Model (USM) uses an energy balance scheme at an hourly time step, changes in urban snow albedo, and incorporates eight different types of redistributed snow cover. USM is tested against observed flow data from a small residential community located in Calgary, Alberta. The degree-day method for snowmelt, the SWMM model, and a modified version of USM that incorporates a partial energy budget scheme relying only on net radiation, are also tested against the observed flow data. The full energy budget version of USM outperformed all other models in terms of time to peak, peak flowrate and model efficiency; however, the modified version of USM fared quite well and is recommended when a lack of data exists. The degree-day method and the SWMM models fared poorly and were unable to simulate peak flowrates in most cases. The tests also demonstrated the need to distribute snow into appropriate snow covers in order to simulate peak flowrates accurately and provide good model efficiency.

Geochemistry of shallow ground water in coastal plain environments in the southeastern United States: implications for aquifer susceptibility

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Ground-water chemistry data from coastal plain environments have been examined to determine the geochemical conditions and processes that occur in these areas and assess their implications for aquifer susceptibility. Two distinct geochemical environments were studied to represent a range of conditions: an inner coastal plain setting having more well-drained soils and lower organic carbon (C) content and an outer coastal plain environment that has more poorly drained soils and high organic C content. Higher concentrations of most major ions and dissolved inorganic and organic C in the outer coastal plain setting indicate a greater degree of mineral dissolution and organic matter oxidation. Accordingly, outer coastal plain waters are more reducing than inner coastal plain waters. Low dissolved oxygen (O₂) and nitrate (NO₃⁻) concentrations and high iron (Fe) concentrations indicate that ferric iron (Fe (III)) is an important electron acceptor in this setting, while dissolved O₂ is the most common terminal electron acceptor in the inner coastal plain setting.

The presence of a wide range of redox conditions in the shallow aquifer system examined here underscores the importance of providing a detailed geochemical characterization of ground water when assessing the intrinsic susceptibility of coastal plain settings. The greater prevalence of aerobic conditions in the inner coastal plain setting makes this region more susceptible to contamination by constituents that are more stable under these conditions and is consistent with the significantly ($p < 0.05$) higher concentrations of NO₃⁻ found in this setting. Herbicides and their transformation products were frequently detected (36% of wells sampled), however concentrations were typically low (<0.1 g/L). Shallow water table depths often found in coastal plain settings may result in an increased risk of the detection of pesticides (e.g., alachlor) that degrade rapidly in the unsaturated zone.

Impacts of parametric and radar rainfall uncertainty on the ensemble streamflow simulations of a distributed hydrologic model

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We diagnose the manner with which rainfall input and parametric uncertainty influence the character of the flow simulation uncertainty in a validated distributed hydrologic model. An extensive Monte Carlo numerical experiment was undertaken for several study watersheds in the southern Central Plains of the United States. It examined the sensitivity of ensemble flow simulations produced by the distributed model HRCDHM to uncertainty in parametric and radar rainfall input. The watersheds are associated with the Distributed Model Intercomparison Project (DMIP) organized by the US National Weather Service Office of Hydrologic Development. The model validated well in DMIP both for watershed outlets and interior points on various scales with Nash-Sutcliffe efficiencies of 0.6–0.9 for hourly flow simulations [J. Hydrol. (2004) 14504, this issue], and we expect that the qualitative nature of the results of this study are of greater applicability than for this model alone. The uncertainty scenarios included: parametric uncertainty involving multiple soil model parameters simultaneously, routing model parameter uncertainty, rainfall uncertainty under two different error distributions, and combined uncertainty in both parameters and input. The flow sensitivities are summarized in terms of a relative measure of the dispersion in the flow ensembles computed for each event, and for several watershed locations consisting of the watershed outlet and additional interior locations. The results consistently show that the flow simulation uncertainty is strongly

dependent on catchment scale for all cases of prescribed parametric and radar-rainfall input uncertainty. Simulation uncertainty is significantly reduced for larger scales of distributed model resolution. The consistency of this result across the selected watershed locations allows for the development of scaling relationships between catchment size and the flow uncertainty measure. The derived scaling relationship may be used to infer pronounced small-scale simulation uncertainties in distributed hydrologic model applications. Several fruitful future research directions are identified including the incorporation of model structure uncertainty in the analysis.

Distribution and mineralogical controls on ammonium in deep groundwaters

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Compositional data from published sources, environmental monitoring and new analyses demonstrate that for a wide range of water types (oilfield water, coal mine water, landfill leachate) NH_4^+ is present in amounts up to 2200 mg/L. Oilfield waters from Alberta, Canada contain 1–1000 mg/L NH_4^+ , coal mine water (UK) surface discharges 1–45 mg/L NH_4^+ , and landfill leachates (UK) up to 2200 mg/L NH_4^+ . Ammonium contents generally show a positive correlation with K, and increase with increasing salinity. Geochemical modelling of sufficiently complete data using SOLMINEQ88 demonstrates that NH_4^+ activities vary systematically, and are consistent with a mineralogical control. Sodium–K exchange divides the entire sample suite into at least 4 groups, controlled by reaction temperature and reaction with either albite/K-feldspar or illitic clay minerals. In contrast, comparison of NH_4^+ and K divides the sample suite into 2 groups. On the basis of geological setting, these correspond to K– NH_4^+ exchange involving illitic (illite-muscovite) clays (and possibly feldspars) for samples from natural sources, and to exchange involving smectitic clays for samples from landfill sites. This study demonstrates the importance of NH_4^+ as a constituent of natural groundwaters, requiring that this reservoir of N is taken into account in detailed discussion of hydrological components of the N cycle.

Near-natural stormwater management and its effects on the water budget and groundwater surface in urban areas taking account of the hydrogeological conditions

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Near-natural stormwater infiltration can cause rising groundwater tables in urban areas. In order to assess these effects, the area-differentiated groundwater recharge in a real investigation area in Germany and their effects on the groundwater table are modelled using three different computer programs. The first program determines the natural area-differentiated groundwater recharge for the whole study area without considering the infiltration facilities. The second program is used to localise infiltration processes and it calculates the groundwater recharge below the infiltration facilities. The groundwater recharge rates calculated with these two programs are incorporated in the numerical groundwater model. It is used to simulate the groundwater surface level development. By varying the size of additional development areas, the degree of sealing, the infiltration rate and the precipitation different simulation scenarios were conducted. It was found that both the precipitation and the infiltration rate are the most influencing factors concerning the groundwater surface. Further, problems have to be expected especially in areas with low hydraulic conductivities. To ensure sustainable depths to groundwater table calculating the water budget can be recommended, as to name just one of the recommendations presented in this paper.

Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia

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Combined hydrogeological and hydrogeochemical data allow flow systems and the origins of solutes in the Honeysuckle Creek area of the southeastern Murray Basin, which is an area affected by dryland salinity, to be constrained. Recharge occurs both on the uplands that are composed of fractured Violet Town Volcanic rocks and the Riverine Plain that comprises sediments of the Shepparton and Coonambidgal Formations. Groundwater from the Violet Town Volcanics has low salinity (<20 mmol/L Cl) and major ion geochemistry that is controlled largely by dissolution of silicate minerals. Low Cl/Br ratios (as low as 281 molar) suggest that this groundwater has not dissolved halite. Groundwater that recharged through the Riverine Plain sediments has higher Cl/Br ratios (up to 1146) and Cl concentrations of <20 mmol/L, consistent with it dissolving minor halite. Higher salinity (>20 mmol/L) groundwater has intermediate Cl/Br ratios (600–1000), which indicate that the high salinities do not simply result from halite dissolution. Rather, mixing of groundwater homogenises Cl/Br ratios, and evaporation as a consequence of a shallow water table is the dominant process that increases salinity. Oxygen and H isotopes also indicate that mixing and

evaporation have occurred. These results indicate that land use over the whole region, not just the uplands, needs to be considered in any salinity management plans. Additionally future development of salinity is controlled by depth to the water table on the plains and the efficiency of recharge rather than by salt stores (halite or brines) in the unsaturated zone.

Calibration of a semi-distributed hydrologic model for stream flow estimation along a river system

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An important goal of spatially distributed hydrologic modeling is to provide estimates of streamflow (and river levels) at any point along the river system. To encourage collaborative research into appropriate levels of model complexity, the value of spatially distributed data, and methods suitable for model development and calibration, the US National Weather Service Hydrology Laboratory (NWSHL) is promoting the distributed modeling intercomparison project (DMIP). In particular, the project is interested in how spatially distributed estimates of precipitation provided by the next generation radar (NEXRAD) network, high resolution digital elevation models (DEM), soil, land-use and vegetation data can be integrated into an improved system for distributed hydrologic modeling that provides more accurate and informative flood forecasts.

The goal of this study is to explore four questions: Can a semi-distributed approach improve the streamflow forecasts at the watershed outlet compared to a lumped approach? What is a suitable calibration strategy for a semi-distributed model structure, and how much improvement can be obtained? What is the minimum level of spatial complexity required, above which the improvement in forecast accuracy is marginal? What spatial details must be included to enable flow prediction at any point along the river network?

The study compares lumped, semi-lumped and semi-distributed versions of the SAC-SMA (Sacramento Soil Moisture Accounting) model for the Illinois River basin at Watts (OK). A kinematic wave scheme is used to rout the flow along the river channel to the outlet. A Multi-step Automatic Calibration Scheme (MACS) using the Shuffled Complex Evolution (SCE-UA) optimization algorithm is applied for model calibration. The calibration results reveal that moving from a lumped model structure, driven by spatially averaged NEXRAD data over the entire basin, to a semi-distributed model structure, with forcing data averaged over each sub-basin while having identical parameters for all the sub-basins, improves the simulation results. However, varying the parameters between sub-basins does not further improve the simulation results, either at the outlet or at an interior testing point.

Biogeochemical processes controlling midday ferrous iron maxima in stream waters affected by acid rock drainage

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The biogeochemical cycling of Fe in acid rock drainage (ARD) streams has presented ongoing challenges to reactive solute transport modeling. Previous studies have relied on the pH-dependent solubility of Fe oxides as the main control of the mid-day Fe(II) maxima concentration in ARD streams. In this study, the authors assess the potential for Fe(II)-oxidizing reactions, including the Fenton and microbial oxidation reactions, to constrain the mid-day Fe(II) maxima concentration. At mid-day, pseudo-equilibrium between Fe(II) oxidizing reactions and photoreduction was assumed in order to evaluate the observed Fe(II) maxima and develop an equation to represent this steady state scenario. This steady state condition is assumed only while light intensity, reactivity of oxides and dissolved organic matter (DOM), and microbial populations remain approximately constant. Three Rocky Mountain ARD streams with known values for Fe(II) were evaluated and average photoreduction rates ranging from 5.56×10^{-4} to 1.39×10^{-3} M/s were found during mid-day steady state Fe(II) maxima. Application of Fe redox biogeochemistry to reactive solute transport modeling may improve predictive capabilities of various trace metal and solute interactions incorporated with the cycling of Fe within ARD streams. Further, model improvement of Fe cycling may enable more accurate remediation predictions for ARD streams.

LAKES BIOGEOCHEMISTRY

Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China

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Contamination by persistent organochlorines (OCs), such as DDTs, hexachlorocyclohexane isomers (HCHs), chlordane compounds (CHLs), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) were examined in sediments, soils, fishes, crustaceans, birds, and aquaculture feed from Lake Tai, Hangzhou Bay, and in the vicinity of Shanghai city in China during 2000 and 2001. OCs were detected in all samples analyzed, and DDT and its metabolites were the predominant contaminants in most sediments, soils and biota. Concentrations of *p,p'*-DDT and ratio of *p,p'*-DDT to Σ DDTs were significantly higher in marine fishes than those in freshwater fishes. While the use of DDTs has been officially banned in China since 1983, these results indicate a recent input of technical DDTs into the marine environment around Hangzhou Bay. Comparison of organochlorine concentrations in fishes collected from Lake Tai and Hangzhou Bay suggests the presence of local sources of HCHs, chlordanes and PCBs at Lake Tai. Higher proportions of penta- and hexa-PCB congeners in fishes at Lake Tai may suggest the use of highly chlorinated PCB product, such as PCB₅, around this lake. To our knowledge, this is a first comprehensive study to examine the present status of organochlorine contamination in various environmental media, such as sediments, soils and wildlife, in China.

Elevated concentrations of DDTs were detected in sediments, soils, and wildlife collected from China.

Maternal exposure to Great Lakes sport-caught fish and dichlorodiphenyl dichloroethylene, but not polychlorinated biphenyls, is associated with reduced birth weight

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Fish consumption may be beneficial for a developing human fetus, but fish may also contain contaminants that could be detrimental. Great Lakes sport-caught fish (GLSCF) are contaminated with polychlorinated biphenyls (PCBs) and dichlorodiphenyl dichloroethylene (DDE), but the effects of these contaminants on birth outcome are not clear. To distinguish potential contaminant effects, we examined (1) whether the decrease over time in contaminant levels in GLSCF is paralleled by an increase in birth weight of children of GLSCF-consuming mothers and (2) the relation between maternal serum concentrations of these contaminants and birth weight. Mothers ($n=511$) were interviewed from 1993 to 1995, and maternal serum was collected from 1994 to 1995 ($n=143$). Potential confounders considered were child gender, maternal age at delivery, maternal prepregnancy body mass index, maternal cigarette and alcohol use during pregnancy, maternal education level, maternal parity, and maternal breastfeeding. Children born during 1970–1977, 1978–1984, and 1985–1993 to mothers who ate more than 116 meals of GLSCF before pregnancy were, on average, 164 g lighter, 46 g heavier, and 134 g heavier, respectively, than children of mothers who ate no GLSCF before pregnancy (P TREND=0.05). GLSCF-consuming mothers had higher serum PCB and DDE concentrations, but only increased DDE was associated with lower birth weight. The data suggest that fetal DDE exposure (as indicated by maternal serum DDE concentration) may decrease birth weight and that decreased birth weight effects associated with GLSCF consumption have decreased over time.

**Reconstruction of Ice-Dammed Lake Outburst Floods in the Altai Mountains, Siberia –
A Review**

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Seven independent approaches to estimate the Pleistocene ice-dammed lake outburst floods in the Altai-Mountains were applied. More detailed studies form the basis of this review. Different methods

are briefly presented and discussed. The peak discharge is estimated as about 10,000,000 m³s⁻¹. This estimate is based on three independent calculations, considering numerous locations with palaeostage indicators along the flood's pathway. Run-up sediments are found in front of the local valley obstructions. Their characteristics and their relation to giant bars nearby is considered to calculate the velocity head of the flow, which is interpreted as indicator of the mean flow velocity. Due to the dynamics of the investigated flood, related features, such as gravel dunes and obstacle marks, provide data on unspecified stages of the decreasing flood. An attempt to estimate peak discharge by using flow competence approach failed due to missing evidence of associated macroturbulence effects.

Compared with previous estimates the peak discharge calculated with several conservative assumptions seems to be smaller than expected. The new calculations are based on a significantly increased number of palaeostage indicators, which support the plausibility of the results.

Metal burdens in surface sediments of limed and nonlimed lakes

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Acidification has been shown to increase the concentrations of many metals in lake water as a result of increased mobility at lower pH, whereas liming has been found to decrease lake water metal concentrations. We hypothesise that increased sedimentation as a result of liming increases the metal burdens in the sediments of limed lakes, but especially those that have been treated directly on the lake surface. We also hypothesise that acidification results in decreased metal burdens in the sediments, whereas near neutral reference lakes and lakes where the lime has been applied on wetlands or upstream have intermediate metal burdens in the sediments.

In order to test the hypothesis, we statistically compare the areal metal and P burdens in the sediments of four groups of lakes: (1) Mainly surface limed lakes, (2) Mainly upstream/wetland limed lakes, (3) Near neutral reference lakes and, (4) Acidified reference lakes. The statistical analysis reveals that the surface limed group have significantly higher areal burdens of As, Cd, Co and Zn in the sediment compared to the acidified reference group, despite large variations within the groups. The investigation indicates that surface liming increases the areal burdens in the sediments of Cd and Pb, probably of As, Ca and Mn and possibly Co and Zn, whereas acidification decreases the areal burdens in sediments of Cd, Fe, Mn and possibly Co, P and Zn. The results of the study confirm the hypothesis.

Water chemistry of high elevation Colorado wilderness lakes

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High elevation alpine and subalpine Rocky Mountain lakes in Colorado and southeastern Wyoming were examined to determine regional variability in water chemistry and their sensitivity to atmospheric deposition. Acid neutralizing capacity, pH, conductivity and concentrations of major anions and cations were compared. Regional differences in water chemistry are evident. The south-eastern most lakes have significantly higher pH, conductivity, ANC, and sums of acid and base concentrations than lakes in the other regions of the state. In contrast the north-western most lakes are significantly more dilute than those from other regions. Despite these two regional differences, most regions are similar in having a wide range of variability in potential sensitivity of their lakes to acidification and nitrogen export. Many wilderness areas in western and eastern regions contains lakes that are extremely sensitive and other lakes not susceptible to deposition. Overall, 70% of the Colorado lakes are sensitive to acidification and 15% are extremely sensitive to acidification. All of the regions had lakes that are classified as susceptible or sensitive to acidification, with 12 of the 17 areas having all of their sampled lakes susceptible or sensitive. Generally NO concentration in surface waters decreased from mid-season to late season; yet a large number of the lakes export NO late in the season, suggesting nitrogen saturation. The results confirm the sensitivity of high elevation wilderness aquatic ecosystems in all regions of Colorado to acidification and nitrogen deposition.

**The Hydrogeology of a Catchment Area and an Artificially Divided Dystrophic Lake –
Consequences for the Limnology of Lake Fuchskuhle**

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The hydrogeology between the catchment area and the divided dystrophic Lake Fuchskuhle with respect to the genesis and the land–water interactions were investigated. Water levels at numerous locations in the catchment area were measured in order to characterize the hydrology. The water balance of the area was calculated based on long term climatic investigations. The geology of the peat was documented at 25 sampling points by cores collected with a peat drill. Chemical parameters including pH, total phosphorus and total nitrogen concentrations, DOC concentration, colour (SAK 436 m⁻¹) and the UV₂₅₄/DOC ratio in the catchment area and in two compartments (NE and SW compartment) were determined. The chemical fluxes of DOC, nitrogen and phosphorus from the catchment area into one compartment (SW compartment) were determined. During the genesis of the Lake Fuchskuhle area two aquifer systems (local peat aquifer, regional sandy main aquifer) developed. Both aquifers are largely independently with almost no lateral interactions. Two compartments are supplied with water from the local peat aquifer. From the other two compartments, however, water is flowing out into the peat body. During high groundwater inflow into the SW compartment higher concentration of DOC, nitrogen and phosphorus in the SW compartment were detected. The fen can be divided in two parts: in the meso – to eutrophic fen northwest and the mainly meso – to oligotrophic – acid fen in the southeast. The significant differences in parameters such as pH, conductivity and DOC concentration gave a clear picture of the heterogeneity of the two compartments and their dependence on the catchment area with the two aquifers.

Selenium mobilization during a flood experiment in a contaminated wetland: Stewart Lake Waterfowl Management Area, Utah

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Constructed and natural wetlands can accumulate elevated levels of Se; however, few data are available on cost-effective methods for remobilization and removal of Se from these areas. A field experiment was conducted to assess the effectiveness of flooding on the removal of Se from dry surface sediments. The 83-m² flood-experiment plot contained 10 monitoring wells, a water-quality minimonitor (continuous measurement of pH, specific conductance, water temperature, and dissolved O₂), a down-hole Br electrode, and 2 pressure transducers. Flooding was initiated on August 27, 2002, and a Br tracer was added to water delivered through a pipeline to the flood plot during the first 1.2 h. Standing water depth in the flood plot was maintained at 0.3 m through September 1, 2002. The Br tracer data indicate a dual porosity system that includes fracture (mud cracks) and matrix flow components. Mean vertical water velocities for the matrix flow component were estimated to range from 0.002 to 0.012 m/h. Dissolved (less than 0.45 μm) Se increased from pre-flood concentrations of less than 10 μg/L to greater than 800 μg/L during flooding in samples from deep (2.0 m below land surface) ground water. Selenium concentrations exceeded 5500 μg/L in samples from shallow (0.8 m below land surface) ground water. Ratios of Se to Br in water samples indicate that Se moved conservatively during the experiment and was derived from leaching of near-surface sediments. Cumulative Se flux to the deep ground water during the experiment ranged from 9.0 to 170 mg/m². Pre- and post-flood surface soil sampling indicated a mean Se flux of 720 mg/m² through the top 15 cm of soil. Ground-water samples collected 8 months after termination of the flood experiment contained Se concentrations of less than 20 μg/L. The minimonitor data indicate a rapid return to chemically reducing conditions in the deep ground water, limiting the mobility of the Se dissolved in the water pulse introduced during the flood experiment. Ratios of Se to Br in deep ground-water samples collected 8 months after the experiment confirmed the removal of Se from the aqueous phase. Based on the median Se flux rate estimated during the experiment of 0.65 mg/h/m² ($n = 52$), 7 flooding cycles would be required to meet the 4 μg/g remediation goal in surface soils from the SLWMA wetland.

Efficiency of natural calcite precipitation compared to lake marl application used for water quality improvement in an eutrophic lake

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Since the 1980s, several in-lake restoration methods for eutrophied lakes have been developed based on artificially induced calcite precipitation and lime additions. The aim of these measures is to improve water quality and reduce the incidence of cyanobacterial blooms by increasing P adsorption and removal through natural calcite precipitation. The authors compared the relative efficiencies of lake marl application and natural calcite precipitation in immobilizing P, Mn and Fe in Lake Arendsee, northeastern Germany, and their subsequent value as a tool for managing eutrophication.

Microprobe investigations of element distributions in calcite minerals of laminae precipitated annually during several years before and two years following the restoration suggest that recently grown biogenic calcites were more efficient at the co-precipitation and immobilization of P, Fe and Mn. The lake marl applied as 16% calcite/water mixture proved unsuitable as a restoration tool because of its coarse grain size mainly in the range of 20–1000 μm and associated organic matter which reduced its suspension time and sorption reaction rates in the water column. In Lake Arendsee or in similar eutrophic hardwater lakes with fast internal P recycling by rapid degradation of autochthonous organic matter in the water column and at the sediment surface (sedimentary TOC:TP ratios of 200 or more), biogenic calcites provide almost permanent P, Fe and Mn retention in the sediments. The study shows that epilimnetic additions of pure CaCO_3 seed crystals comparable to natural calcite precipitation are the most effective for improving water quality. Small CaCO_3 crystals exhibit a larger reactive surface, and thus, incorporate adsorbed dissolved nutrients and trace metals more rapidly during growth. However, in-lake water quality management strategies work best only if external point and non-point nutrient sources are reduced or diverted.

Sediment capping in eutrophic lakes – efficiency of undisturbed calcite barriers to immobilize phosphorus

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The application of a calcite barrier was investigated to prevent P release from eutrophic lake sediments. For this, different calcite materials varying in grain size, specific surface area (SSA) and roughness of the surface were applied. Rohrbach calcite (RB) is a crushed Jurassic limestone with an SSA of $4.3 \text{ m}^2 \text{ g}^{-1}$ and a microporosity of 7%. Merck calcite (M2066) is an analytical reagent with an SSA of $1 \text{ m}^2 \text{ g}^{-1}$ and a microporosity of 17%. The industrially manufactured calcites U1 and U3 have higher SSAs of 20 and $70 \text{ m}^2 \text{ g}^{-1}$ and a microporosity of 20% and 9%, respectively. Short-term batch experiments and long-term sediment incubation experiments showed that the calcite saturation of the water ($\text{SI}_{\text{CaCO}_3}$) predetermines the P fixation mechanisms. In waters supersaturated with respect to calcite ($\text{SI}_{\text{CaCO}_3} > 0$), adsorption and simultaneous co-precipitation with calcite are the predominant processes for P fixation. In addition, precipitation of Ca–P compounds occurs on the surface of calcite seed crystals due to the decrease in the interfacial nucleation energy.

The capacity of P fixation was greatly influenced by the physical properties of calcite grains. An increase in the SSA from 1 (M2066) and 4 m² g⁻¹ (RB) to 67 m² g⁻¹ (U3) improves the efficiency of P removal from about <5% (RB, M2066) to 90% (U3). The grain size affects the P fixation especially in waters close to equilibrium and of weak supersaturation, where small calcite grains dissolve and initiate supersaturation with respect to Ca–P compounds. Under these conditions SRP concentrations decrease by 30% (M2066), 60% (RB) and about 95% (U3) relative to their initial concentrations. At $SI_{CaCO_3} < 0$, calcite dissolution causes an increase in the dissolved Ca concentration and initiates Ca–P precipitation lowering the SRP concentrations by about 65% (M2066, RB) and about 100% (U3). This process is significantly enhanced by the surface roughness of the calcite grains (M2066) due to numerous micropores of <2 nm in diameter.

The results showed that calcite barriers could be optimized individually in accordance to the hydrochemical conditions in lakes to increase the efficiency of P retention in sediments. An application of a 1 cm thick RB barrier resulted in an 80% reduction of the P flux from the sediment for at least 2–3 months, whereas a quartz sand barrier of 2–4.5 cm thickness containing 2 wt% of highly active calcite such as U3 and U1 quantitatively prevents release of P from eutrophic lake sediments for at least 7 and 10 months, respectively.

The springs of Lake Pátzcuaro: chemistry, salt-balance, and implications for the water balance of the lake

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Lake Pátzcuaro, the center of the ancient Tarascan civilization located in the Mexican altiplano west of the city of Morelia, has neither river input nor outflow. The relatively constant lake-salinity over the past centuries indicates the lake is in chemical steady state. Springs of the south shore constitute the primary visible input to the lake, so influx and discharge must be via sub-lacustrine ground water. The authors report on the chemistry and stable isotope composition of the springs, deeming them representative of ground-water input. The springs are dominated by Ca, Mg and Na, whereas the lake is dominated by Na. Combining these results with previously published precipitation/rainfall measurements on the lake, the authors calculate the chemical evolution from spring water to lake water, and also calculate a salt balance of the ground-water–lake system. Comparing Cl and ¹⁸O compositions in the springs and lake water indicates that 75–80% of the spring water is lost evaporatively during evolution toward lake composition. During evaporation Ca and Mg are lost from the water by carbonate precipitation. Each liter of spring water discharging into the lake precipitates about 18.7 mg of CaCO₃. Salt balance calculations indicate that ground water input to the lake is 85.9 × 10⁶ m³/a and ground water discharge from the lake is 23.0 × 10⁶ m³/a. Thus, the discharge is about 27% of the input, with the rest balanced by evaporation. A calculation of time to reach steady-state *ab initio* indicates that the Cl concentration of the present day lake would be reached in about 150 a.

Control mechanisms for dissolved phosphorus and arsenic in a shallow lake

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This study investigated P and As sediment remobilisation in Lake Yangebup, a shallow lake with an overlying floc layer that covers the consolidated sediment. This floc is frequently resuspended into the water column, a process that was postulated to produce high P and As lakewater concentrations. Rate investigations using deionised water showed that P and As remobilisation reached steady state after 20 h in the consolidated sediment and within 1 h for the floc. Floc resuspension in lakewater showed no net release of either P and As, indicating that the floc was in constant equilibrium with the water column. A protocol to distinguish between desorption and dissolution was applied to both sediments and the response of remobilisation to varying slurry density and As addition measured. For the consolidated sediment, the concentration of Fe(II), P and As were unaffected above a slurry density $\sim 30 \text{ g L}^{-1}$ and added arsenate ($10\text{--}100 \text{ g L}^{-1}$) did not significantly change As and P remobilisation. It is shown that these results do not fit an adsorption/desorption equilibrium formulation for P and As remobilisation. Instead, the evidence suggests that the solubility of a thin, non-stoichiometric $\text{FeP}_x\text{FeAs}_y$ oxyhydroxide surface coating determined the remobilisation process. Data scatter lead to some uncertainty in the floc results but suggest that dissolved P is controlled by dissolution, while dissolved As is controlled by adsorption/desorption. The results conclusively show that P and As remobilisation was lower from the floc than from the consolidated sediment and that the removal of the floc would not lower P and As lakewater concentrations. Implications of these results for the management of As in Lake Yangebup are outlined.

ARSENIC PROBLEMS

Value of arsenic-free drinking water to rural households in Bangladesh

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Using contingent valuation survey data for about 2700 households in rural Bangladesh, and applying a multinomial logit model, the paper estimates the value of arsenic-free drinking water to the rural people. The estimates indicate that the rural people in arsenic-affected areas of Bangladesh place a low value on arsenic-free drinking water. It is about 10–14 percent of the amount they are willing to pay for piped water and only about 0.2–0.3 percent of the average household income. The implication of the result is that robust but costly arsenic reduction technologies such as activated alumina technology may find little social acceptance, unless heavily subsidized.

Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications

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In order to investigate the mechanism of As release to anoxic ground water in alluvial aquifers, the authors sampled ground waters from 3 piezometer nests, 79 shallow (<45 m) wells, and 6 deep (>80 m) wells, in an area 750 m by 450 m, just north of Barasat, near Kolkata (Calcutta), in southern West Bengal. High concentrations of As (200–1180 g L⁻¹) are accompanied by high

concentrations of Fe (3–13.7 mg L⁻¹) and PO₄ (1–6.5 mg L⁻¹). Ground water that is rich in Mn (1–5.3 mg L⁻¹) contains <50 g L⁻¹ of As. The composition of shallow ground water varies at the 100-m scale laterally and the metre-scale vertically, with vertical gradients in As concentration reaching 200 g L⁻¹ m⁻¹. The As is supplied by reductive dissolution of FeOOH and release of the sorbed As to solution. The process is driven by natural organic matter in peaty strata both within the aquifer sands and in the overlying confining unit. In well waters, thermo-tolerant coliforms, a proxy for faecal contamination, are not present in high numbers (<10 cfu/100 ml in 85% of wells) showing that faecally-derived organic matter does not enter the aquifer, does not drive reduction of FeOOH, and so does not release As to ground water.

Arsenic concentrations are high (>>50 g L⁻¹) where reduction of FeOOH is complete and its entire load of sorbed As is released to solution, at which point the aquifer sediments become grey in colour as FeOOH vanishes. Where reduction is incomplete, the sediments are brown in colour and resorption of As to residual FeOOH keeps As concentrations below 10 g L⁻¹ in the presence of dissolved Fe. Sorbed As released by reduction of Mn oxides does not increase As in ground water because the As resorbs to FeOOH. High concentrations of As are common in alluvial aquifers of the Bengal Basin arise because Himalayan erosion supplies immature sediments, with low surface-loadings of FeOOH on mineral grains, to a depositional environment that is rich in organic matter so that complete reduction of FeOOH is common.

Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan

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In 49 samples of groundwater, sampled in Muzaffargarh District of south-western Punjab, central Pakistan, concentrations of As exceeded the World Health Organisation provisional guideline value, and United States Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL), of 10 µg L⁻¹ in 58% of samples and reached up to 906 µg L⁻¹. In this semi-arid region canal irrigation has led to widespread water-logging, and evaporative concentration of salts has the potential to raise As concentrations in shallow groundwater well above 10 µg L⁻¹. In fact, in rural areas, concentrations stay below 25 µg L⁻¹ because As in the oxic shallow groundwater, and in recharging water, is sorbed to aquifer sediments. In some urban areas, however, shallow groundwater is found to contain elevated levels of As. The spatial distribution of As-rich shallow groundwater indicates either direct contamination with industrial or agricultural chemicals, or some other anthropogenic influence. Geochemical evidence suggests that pollutant organics from unconfined sewage and other sources drives reduction of hydrous ferric oxide (HFO) releasing sorbed As to shallow groundwater. The situation is slightly less clear for seven wells sampled which tap deeper groundwater, all of which were found with >50 µg L⁻¹ As. Here As concentrations seem to increase with depth and differing geochemical signatures are seen, suggesting that As concentrations in older groundwater may be governed by different processes. Other data on parameters of potential concern in drinking water are discussed briefly at the end of the paper.

Arsenic levels in the soils and macrophytes of the 'Entremuros' after the Aznalcóllar mine spill

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In April 1998, a holding lagoon containing pyrite ore processing waste rich in arsenic, failed and released 5–6 million m³ of highly polluting sludge and acidic water. Over 2700 ha of the internationally important Doñana National and Natural Parks were contaminated. The area of Natural Park to sustain the greatest impact was known as the Entremuros. This paper presents 0–5 cm soil monitoring data from the Entremuros, from sampling campaigns 6 and 18 months after the disaster; as well as macrophyte root, rhizome and stem data from samples taken 18 months after the spill. Results show a clear, decreasing, north–south arsenic soil pollution trend, both 6 and 18 months after the spill, and suggest a small reduction in total soil arsenic levels occurred over time; although a significant increase in extractable arsenic is also noted. The two macrophytes (*Typha dominguensis* and *Scirpus maritimus*) studied herein are not accumulating arsenic in stem parts, however, accumulation of arsenic on iron plaque on the roots of these plants may be occurring. Further work is recommended in order to determine the ecotoxicological significance of this process in relation to the avian food-chains of Doñana, and elsewhere.

Arsenic drinking water exposure and urinary excretion among adults in the Yaqui Valley, Sonora, Mexico

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The objective of this study was to determine arsenic exposure via drinking water and to characterize urinary arsenic excretion among adults in the Yaqui Valley, Sonora, Mexico. A cross-sectional study was conducted from July 2001 to May 2002. Study subjects were from the Yaqui Valley, Sonora, Mexico, residents of four towns with different arsenic concentrations in their drinking water. Arsenic exposure was estimated through water intake over 24 h. Arsenic excretion was assessed in the first morning void urine. Total arsenic concentrations and their species arsenate (As V), arsenite (As III),

monomethyl arsenic (MMA), and dimethyl arsenic (DMA) were determined by HPLC/ICP-MS. The town of Esperanza with the highest arsenic concentration in water had the highest daily mean intake of arsenic through drinking water, the mean value was 65.5 g/day. Positive correlation between total arsenic intake by drinking water/day and the total arsenic concentration in urine ($r=0.50$, $P<0.001$) was found. Arsenic excreted in urine ranged from 18.9 to 93.8 g/L. The people from Esperanza had the highest geometric mean value of arsenic in urine, 65.1 g/L, and it was statistically significantly different from those of the other towns ($P<0.005$). DMA was the major arsenic species in urine (47.7–67.1%), followed by inorganic arsenic (16.4–25.4%), and MMA (7.5–15%). In comparison with other reports the DMA and MMA distribution was low, 47.7–55.6% and 7.5–9.7%, respectively, in the urine from the Yaqui Valley population (except the town of Cocorit). The difference in the proportion of urinary arsenic metabolites in those towns may be due to genetic polymorphisms in the As methylating enzymes of these populations.

A survey of arsenic in foodstuffs on sale in the United Kingdom and imported from Bangladesh

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Arsenic is a highly toxic element and its presence in food composites is a matter of concern to the well being of both humans and animals. Arsenic-contaminated groundwater is often used in Bangladesh and West Bengal (India) to irrigate crops used for food and animal consumption, which could potentially lead to arsenic entering the human food chain.

In this study, we used graphite furnace atomic absorption spectroscopy to determine the total arsenic concentrations in a range of foodstuffs, including vegetables, rice and fish, imported into the United Kingdom from Bangladesh. The mean and range of the total arsenic concentration in all the vegetables imported from Bangladesh were 54.5 and 5–540 $\mu\text{g}/\text{kg}$, respectively. The highest arsenic values found were for the skin of Arum tuber, 540 $\mu\text{g}/\text{kg}$, followed by Arum Stem, 168 $\mu\text{g}/\text{kg}$, and Amaranthus, 160 $\mu\text{g}/\text{kg}$. Among the other samples, freshwater fish contained total arsenic levels between 97 and 1318 $\mu\text{g}/\text{kg}$. The arsenic content of the vegetables from the UK was approximately 2- to 3-fold lower than those observed for the vegetables imported from Bangladesh.

The levels of arsenic found in vegetables imported from Bangladesh in this study, in some cases, are similar to those previously recorded for vegetables grown in arsenic-affected areas of West Bengal, India, although lower than the levels reported in studies from Bangladesh. While the total arsenic content detected in our study in vegetables, imported from Bangladesh, is far less than the recommended maximum permitted level of arsenic, it does provide an additional source of arsenic in the diet. This raises the possibility that the level of arsenic intake by certain sectors of the UK population may be significantly higher than the general population and requires further investigations.

Arsenic fractionation in a fine soil fraction and influence of various anions on its mobility in the subsurface environment

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The degree to which anions can affect As mobility in subsurface environments depends on As speciation and fractionation in the soil. In this study, the fine soil fraction of an acidic soil was deliberately contaminated with arsenate (As(V)) and adequately aged for more than 220 days. A selective sequential extraction (SSE) scheme was developed to fractionate As in the soil into 6 fractions, while the influence of various anions on As mobility was assessed by evaluating its extractability by various salts such as Na_3PO_4 , Na_2CO_3 , Na_2SO_4 and NaCl . The variables of the extraction experiment were type of salt, salt concentration and reaction time. Fractionations of As in soil samples after extraction with the salts were also examined and the results compared against the initial As fractionation. The SSE results showed that the majority of the As was strongly adsorbed via surface complexation in the fine soil. A considerable amount of As was also associated with the exchangeable fraction, amorphous Fe oxyhydroxides, and the residual fraction. Abilities of the anions in mobilizing As bound in the fine soil followed the order of $\text{PO}_4^{3-} \rightarrow \text{CO}_3^{2-} \rightarrow \text{SO}_4^{2-} \sim \text{Cl}^-$. Arsenic mobilization by PO_4^{3-} was believed to be due primarily to a ligand exchange mechanism, through which the strongly bound As was replaced by the PO_4^{3-} -anion. Anion exchange might also contribute to the mobilization of As in this study. Increase in the PO_4^{3-} concentration of the anions tested did not further mobilize As from the soil, with the exception of. The kinetics of As release in the solution could be best described by the Elovich model, which represents an exponential decrease in As desorption rate as more As was extracted from the soil.

Spatial variability of arsenic in some iron-rich deposits generated by acid mine drainage

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Potential contamination of rivers by trace elements can be controlled, among others, by the precipitation of oxyhydroxides. The streambed of the studied area, located in “La Châtaigneraie” district (Lot River Basin, France), is characterised by iron-rich ochreous deposits, acidic pH (2.7–4.8) and SO_4 –Mg waters. Beyond the acid mine drainage, the presence of As both in the dissolved fraction and in the deposits is also a problem. Upstream, at the gallery outlet, As concentrations are high ($\text{As}_{\text{max}} = 2.6 \text{ imol/l}$ and up to 5 wt% locally, respectively, in the dissolved and in the solid fractions). Downstream, As concentrations decrease below 0.1 imol/l in the dissolved fraction and to 1327 mg/kg in the solid fraction. This natural attenuation is related to the As retention within ochreous precipitates (amorphous to poorly crystalline Fe oxyhydroxides, schwertmannite and goethite), which have great affinities for this metalloid. Upstream, schwertmannite is dominant while downstream, goethite becomes the main mineral. The transformation of schwertmannite into goethite is observed

in the upstream deposits as schwertmannite is unstable relative to goethite. Furthermore, thermodynamic calculations indicate that the downstream goethite is not able to precipitate in situ according to the water chemistry. Goethite mainly results from the transformation of schwertmannite and its solid transport downstream.

Moreover, as highlighted by leaching experiments carried out on the ochreous precipitates, this transformation does not seem to affect the As-retention in solids as no release of As was observed in the solution. Arsenic may either be strongly trapped by co-precipitation in the present minerals or it may be quickly released and re-adsorbed on the precipitate surface.

Geochemical and hydrodynamic controls on arsenic and trace metal cycling in a seasonally stratified US sub-tropical reservoir

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The phase distribution of trace metals and oxyanions, including U and As, in 2 surface water bodies was investigated within a South Texas watershed hosting a high density of surface U mine pits and tailings. The objectives of the study were to evaluate the environmental legacy of U mining, with particular emphasis on the spatial and temporal variability of water quality in Lake Corpus Christi, a downstream reservoir that serves as the major water resource to a population of ~350,000 people in the region. Lyssy Pond, a livestock pond bordered by U mine tailings, was used as a model case-study site to evaluate the cycling of U mine-derived oxyanions under changing redox conditions. Although the pond showed seasonal thermal and chemical stratification, geochemical cycling of metals was limited to Co and Pb, which was correlated with redox cycling of Mn mineral phases, and U, which suggested reductive precipitation in the pond's hypolimnion. Uranium levels, however, were too low to support strong inputs from the tailings into the water column of the pond. The strong relationships observed between particulate Cr, Cs, V, and Fe suggest that these metals are associated with a stable particulate phase (probably allochthonous aluminosilicates) enriched in unreactive Fe. This observation is supported by a parallel relationship in sediments collected across a broad range of sediment depositional processes (and histories) in the basin. Arsenic, though selectively enriched in the pond's water column, was dominated by dissolved species throughout the depth of the profile and showed no sign of geochemical cycling or interaction with Fe-rich particles. Arsenic (and other oxyanions) in the water columns of Lake Corpus Christi and Lyssy pond were not affected by the abundant presence of Fe-rich particles but instead behaved conservatively. No evidence was found of anthropogenic impacts of U mines beyond the purely local scale. Arsenic's presence within the Nueces drainage basin is related to interactions between surface and groundwaters with U- and As-rich geological formations rather than large-scale transport

of contaminants downstream of the U mine pits and tailings. A quantitative mass balance model, constructed using monthly hydrological data for the reservoir, provides quantitative evidence of seasonal evaporative concentration of As in surface waters demonstrating the predominance of hydrodynamic over geochemical constraints, on the cycling of this element.

Arsenic mobility in groundwater/surface water systems in carbonate-rich Pleistocene glacial drift aquifers (Michigan)

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Within the Lower Peninsula of Michigan, groundwaters from the Marshall Formation (Mississippian) contain As derived from As-rich pyrites, often exceeding the World Health Organization drinking water limit of 10 g/L. Many Michigan watersheds, established on top of Pleistocene glacial drift derived from erosion of the underlying Marshall Formation, also have waters with elevated As. The Huron River watershed in southeastern Lower Michigan is a well characterized hydrogeochemical system of glacial drift deposits, proximate to the Marshall Fm. subcrop, which hosts carbonate-rich groundwaters, streams, and wetlands (fens), and well-developed soil profiles. Aqueous and solid phase geochemistry was determined for soils, soil waters, surface waters (streams and fens) and groundwaters from glacial drift aquifers to better understand the hydrogeologic and chemical controls on As mobility. Soil profiles established on the glacial drift exhibit enrichment in both Fe and As in the oxyhydroxide-rich zone of accumulation. The amounts of Fe and As present as oxyhydroxides are comparable to those reported from bulk Marshall Fm. core samples by previous workers. However, the As host in core samples is largely unaltered pyrite and arsenopyrite. This suggests that the transformation of Fe sulfides to Fe oxyhydroxides largely retains As and Fe at the oxidative weathering site. Groundwaters have the highest As values of all the waters sampled, and many were at or above the World Health limit. Most groundwaters are anaerobic, within the zones of Fe³⁺ and As(V) reduction. Although reduction of Fe(III) oxyhydroxides is the probable source of As, there is no correlation between As and Fe concentrations. The As/Fe mole ratios in drift groundwaters are about an order of magnitude greater than those in soil profiles, suggesting that As is more mobile than Fe. This is consistent with the dominance of As(III) in these groundwaters and with the partitioning of Fe²⁺ into carbonate cements. Soil waters have very low As and Fe contents, consistent with the stability of oxyhydroxides under oxidizing vadose conditions. When CO₂ charged groundwaters discharge in streams and fens, dissolved As is effectively removed by adsorption onto Fe-oxides or carbonate marls. Although Fe does not display conservative behavior with As in groundwaters, a strong positive correlation exists between As and Sr concentrations. As water-rock interactions proceed, the As/Fe and Sr/Ca ratios would be expected to increase because both As and Sr behave as incompatible elements. Comparisons with groundwater chemistries from other drift-hosted aquifers proximate to the Marshall sandstone are consistent with these relations. Thus, the Sr content of carbonate-rich groundwaters may provide useful constraints on the occurrence, origin and evolution of dissolved As in such systems.

Study of the precipitation equilibria of arsenate anion with calcium and magnesium in sodium perchlorate at 25 °C

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The stabilities of solid Ca and Mg arsenates were established by solubility experiments from the pH and total aqueous Ca, Mg and As concentrations. The experimental data were consistent with the following solid phases defined as a function of the pH range: $\text{Ca}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$ ($7 < \text{pH} < 10$), $\text{CaNaAsO}_4 \cdot 7.5\text{H}_2\text{O}$ ($10 < \text{pH} < 12$), $\text{MgHAsO}_4 \cdot 4\text{H}_2\text{O}$ ($6.5 < \text{pH} < 7.1$) and $\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ($7.2 < \text{pH} < 9$). All the experimentation was performed at constant ionic strength in aqueous NaClO_4 solutions and at 25 °C, where the stoichiometric solubility products of the different solids were calculated. The corresponding thermodynamic solubility products of all the precipitates were computed by means of the Modified Bromley's Methodology (MBM) that considers the variation of the activity coefficients of the ions involved in the precipitation equilibria with the medium and ionic strength. Moreover, all the solid arsenates obtained were characterised by FT-IR and FT-Raman spectroscopies and the hydration of each precipitate was confirmed by X-Ray Diffraction data.

Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments

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Arsenic is present in aqueous environments in +III and +V oxidation states. In oxidizing environments, the principle attenuation mechanism of As migration is its adsorption on Fe(III) oxide and hydroxides. The adsorption affinity is higher for As(V) under lower pH conditions and for As(III) under higher pH conditions. Ferric oxide and hydroxides can dissolve under low Eh and pH conditions releasing adsorbed As. Oxidation-reduction processes often involve high organic matter content in sediments and also contamination by organics such as BTEX. Arsenic may desorb under high pH conditions. Changes of pH can be related to some redox reactions, cation exchange reactions driving dissolution of carbonates, and dissolution of silicates. In very reducing environments, where SO_4 reduction takes place, secondary sulfide minerals like As-bearing pyrite and orpiment, As_2S_3 , can incorporate As. Geochemical modeling can be divided into two principal categories: (a) forward modeling and (b) inverse modeling. Forward modeling is used to predict water chemistry after completion of predetermined reactions. Inverse modeling is used to suggest which processes take place along a flowpath. Complex coupled transport and geochemistry programs, which allow for simulation of As adsorption, are becoming available. A common modeling approach is based on forward modeling with surface complexation modeling (SCM) of As adsorption, which can incorporate the effect of

different adsorbent/As ratios, adsorption sites density, area available for adsorption, pH changes and competition of As for adsorption sites with other dissolved species such as phosphate. The adsorption modeling can be performed in both batch and transport modes in codes such as PHREEQC. Inverse modeling is generally used to verify hypotheses on the origin of As. Basic prerequisites of inverse modeling are the knowledge of flow pattern (sampling points used in model have to be hydraulically connected) and information about mineralogy including As mineral phases. Case studies of geochemical modeling including modeling of As adsorption are presented.

Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview

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Arsenic in the groundwater of Bangladesh is a serious natural calamity and a public health hazard. Most groundwater from the shallow alluvial aquifers (<150 m), particularly in the Holocene plain lands, are vulnerable to As-enrichment. Delta plains and flood plains of the Ganges–Brahmaputra river system are moderately to severely enriched and more than 60% of the tube wells are affected. Shallow aquifers in the Meghna river basin and coastal plains are extremely enriched with more than 80% of the tube wells affected. Aquifers in the Pleistocene uplands and Tertiary hills are low in As. The vertical lithofacies sequence of the sediments from highly enriched areas of the country show two distinct lithofacies associations—a dominantly sandy channel-fill association and a fine-grained over bank association. The sediments can be grouped into 4 distinct lithofacies, viz. clay, silty clay, silty sand and sand. Thin section petrography of the As-enriched aquifer sands shows that the sands are of quartzolithic type and derived from the collision suture and fold thrust belt of the recycled orogen provenance. Groundwater is characterized by circum-neutral pH with a moderate to strong reducing nature. The waters are generally of Ca–Mg–HCO₃ or Ca–Na–HCO₃ type, with HCO₃⁻ as the principal anion. Low SO₄²⁻ and NO₃⁻, and high dissolved organic C (DOC) and NH₄⁺ concentrations are typical chemical characteristics of groundwater. The presence of dissolved sulfides in these groundwaters indicates reduction of SO₄. Total As concentration in the analyzed wells vary between 2.5 and 846 g l⁻¹ with a dominance of As(III) species (67–99%). Arsenic(III) concentrations were fairly consistent with the DOC and NH₄⁺ contents. The HNO₃ extractable concentrations of As in the sediments (0.5–17.7 mg kg⁻¹), indicate a significant positive correlation with Fe_{NO₃}, Mn_{NO₃}, Al_{NO₃} and P_{NO₃}. The concentrations of S_{NO₃} (816–1306 mg kg⁻¹) peaked in the clay sediments with high organic matter (up to 4.5 wt.%). Amounts of oxalate extractable As (As_{ox}) and Fe (Fe_{ox}) ranged between 0.1–8.6 mg kg⁻¹ and 0.4–5.9 g kg⁻¹, respectively. Arsenic_{ox} was positively correlated with Fe_{ox}, Mn_{ox} and Al_{ox} in these sediments. Insignificant amounts of opaque minerals (including pyrite/arsenopyrite) and the presence of high As contents in finer sediments suggests that some As

is incorporated in the authigenically precipitated sulfides in the reducing sediments. Moreover, the chemical extractions suggest the presence of siderite and vivianite as solid phases, which may control the aqueous chemistry of Fe and PO_4^{3-} . Reductive dissolution of Fe oxyhydroxide present as coatings on sand grains as well as altered mica (biotite) is envisaged as the main mechanism for the release of As into groundwater in the sandy aquifer sediments.

A preliminary geochemical map for arsenic in surficial materials of Canada and the United States

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Over the past 30 a, regional and national solid-phase geochemical surveys have been conducted by the United States Geological Survey and the Geological Survey of Canada. In the present paper the authors have examined the distribution of As in stream-sediment and soil samples of the US and Canada in terms of geologic and anthropogenic components. The results of the compilations indicate that the distribution of As in stream sediments, lake sediments, and soils in Canada and the US shows that most of the variability is controlled by the bed rock characteristics.

Redox control of arsenic mobilization in Bangladesh groundwater

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Detailed hydrochemical measurements, $^{34}\text{S}_{\text{SO}_4}$ and ^3H analyses were performed on 37 groundwater samples collected during February 1999, January and March 2000 from 6 locations in eastern and southeastern Bangladesh to examine redox processes that lead to As mobilization in groundwater. The study sites were chosen based on available nation-wide As surveys to span the entire spectrum of As concentrations in Bangladesh groundwater, and to represent 3 of 5 major geological units of the Ganges-Brahmaputra Delta: uplifted Pleistocene terrace, fluvial flood plain and delta plain.

Arsenic was found to be mobilized under Fe-reducing conditions in shallow aquifers (<35 m depth), presumably of Holocene age. It remained mobile under SO₄-reducing conditions, suggesting that authigenic sulfide precipitation does not constitute a significant sink for As in these groundwaters. The redox state of the water was characterized by a variety of parameters including dissolved O₂, NO₃⁻, Mn²⁺, Fe²⁺ concentrations, and SO₄²⁻/Cl⁻ ratios. High dissolved [As] (> 50 g/l; or > 0.7 M) were always accompanied by high dissolved [HCO₃⁻] (> 4 mM), and were close to saturation with respect to calcite. Groundwater enriched in As (200–800 g/l; or 2.7–10.7 M) and phosphate (30–100 M) but relatively low in dissolved Fe (5–40 M) probably resulted from re-oxidation of reducing, As and Fe enriched water. This history was deduced from isotopic signatures of ³⁴S_{SO4} and ³H₂O (³H) to delineate the nature of redox changes for some of the reducing groundwaters. In contrast, As is not mobilized in presumed Pleistocene aquifers, both shallow (30–60 m) and deep (150–270 m), because conditions were not reducing enough due to lack of sufficient O₂ demand.

Mineralogical and geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh

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Sources of As in the Ganges sediments and microbial mechanisms of its release in groundwater were examined in the present study, where the authors have systematically examined the pertinent mineral species present in the sediments using XRD, TEM-EDS and EPMA techniques. The results show several As-bearing minerals in the Ganges sediments, in western Bangladesh. Iron-sulfide minerals consist of near-amorphous and/or crystalline precursors of framboidal pyrite and pyrite both of which contain As. Several types of Fe oxyhydroxides (oxides), which contain variable amounts of As were also found in muddy sediments. The content of As increases from Fe-oxides to the precursors of framboidal pyrite and pyrite. Four different chemical forms of As from the core sediments were determined. The sequentially extracted chemical forms are as follows: (1) acid soluble form (As mainly fixed in carbonates), (2) reducible form (As fixed in Fe- and/or Mn-oxides), (3) organic form, (4) insoluble form (As fixed mainly in sulfide and rarely in silicate minerals). Arsenic is dominantly sorbed on to Fe- and/or Mn-oxides, organic forms and sulfide minerals in most samples, although their relative abundances differ in different samples. Geomicrobial culture experiments were carried out to test the hypothesis that microbial processes play a key role in the release of As in groundwater. Batch culture and circulating water system experiments were designed using the sediments from Bangladesh. In the batch experiments, As was released at low

Eh values a few days after adding nutrients containing glucose, polypepton and yeast extract, urea and fertilizer under a dominantly N₂ atmosphere. This contrasts with the control experiments without nutrients. Circulating water experiments with sand layer in a N₂ atmosphere showed similar results. These results support the hypothesis that microbial processes mediate the release of As into groundwater under reducing conditions. Glucose and polypepton used in the experiments may correspond to C and N sources, respectively. Younger sediments contain abundant organic matter, which is easily used by bacteria. So, the enhanced bacterial activity may correspond to simulation of accelerated natural diagenetic process using organic matter, or some fertilizer/wastewater effects.

Groundwater arsenic variations: the role of local geology and rainfall

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High concentrations of As were detected in the aquifer system of Zimapán Valley, Mexico. Arsenic is related to a multisource system, both natural and anthropogenic. The main source is As bearing-rocks. Groundwater As variations were detected in the more polluted urban deep well. Variations were correlated with the precipitation regime and with the hydrogeologic and geologic framework. An induced As transport mechanism related mainly with the rainfall regime is proposed.

MERCURY RELATED ISSUES

Potential anthropogenic mobilisation of mercury and arsenic from soils on mineralised rocks, Northland, New Zealand

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Eroded roots of hot spring systems in Northland, New Zealand consist of mineralised rocks containing sulfide minerals. Marcasite and cinnabar are the dominant sulfides with subordinate pyrite. Deep weathering and leached soil formation has occurred in a warm temperate to subtropical climate with up to 3 m/year rainfall. Decomposition of the iron sulfides in natural and anthropogenic rock exposures yields acid rock drainage with pH typically between 2 and 4, and locally down to pH 1. Soils and weathered rocks developed on basement greywacke have negligible acid neutralisation capacity. Natural rainforest soils have pH between 4 and 5 on unmineralised greywacke, and pH is as low as 3.5 in soils on mineralised rocks. Roads with aggregate made from mineralised rocks have pH near 3, and quarries from which the rock was extracted can have pH down to 1. Mineralised rocks are enriched in arsenic and mercury, both of which are environmentally available as solid solution impurities in iron sulfides and phosphate minerals. Base metals (Cu, Pb, Zn) are present at low levels in soils, at or below typical basement rock background. Decomposition of the iron sulfides releases the solid solution arsenic and mercury into the acid rock drainage solutions. Phosphate minerals release their impurities only under strongly acid conditions (pH<1). Arsenic and mercury are adsorbed on to iron oxyhydroxides in soils, concentrated in the C horizon, with up to 4000 ppm arsenic and 100 ppm mercury. Waters emanating from acid rock drainage areas have arsenic and mercury below drinking water limits. Leaching experiments and theoretical predictions indicate that both arsenic and mercury are least mobile in acid soils, at pH of c. 3–4. This optimum pH range for fixation of arsenic and mercury on iron oxyhydroxides in soils is similar to natural pH at the field site of this study. However, neutralisation of acid soils developed on mineralised rocks is likely to decrease adsorption and enhance mobility of arsenic and mercury. Hence, development of farmland by clearing forest and adding agricultural lime may mobilise arsenic and mercury from underlying soils on mineralised rocks. In addition, arsenic and mercury release into runoff water will be enhanced where sediment is washed off mineralised road aggregate (pH 3) on to farm land (pH>6). The naturally acid forest soils, or even lower pH of natural acid rock drainage, are the most desirable environmental conditions to restrict dissolution of arsenic and mercury from soils. This approach is only valid where mineralised soils have low base metal concentrations.

Mercury burdens in Chinese mitten crabs (*Eriocheir sinensis*) in three tributaries of southern San Francisco Bay, California, USA

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Chinese mitten crabs (*Eriocheir sinensis*), endemic to Asia, were first reported in the San Francisco Bay in 1992. They are now established in nearly all San Francisco Bay tributaries. These crabs accumulate more metals, such as mercury, than crustaceans living in the water column. Because their predators include fish, birds, mammals and humans, their mercury burdens have an exceptional potential to impact the ecosystem and public health. We sought to elucidate the potential threat of mitten crab mercury burdens in three adjacent streams in southern San Francisco Bay, one of which is known to be contaminated with mercury. Mitten crabs had hepatopancreas concentrations of total mercury and methylmercury that did not differ among streams. The maximum burden we measured was below the action level of 1 ppm recommended by the USEPA. Hepatopancreas concentrations of methylmercury declined with increasing crab size, suggesting a mechanism for mercury excretion and that predators might reduce mercury exposure if they select larger crabs. Because mercury may be heterogeneously distributed among tissues, estimation of the impacts of crab mercury burdens on the environment requires more data on the feeding preferences of predators. Hepatopancreas concentrations of mercury decline with crab size, which may have important consequences for bio-magnification in food webs.

Mercury transfer from fish carcasses to scavengers in boreal lakes: the use of stable isotopes of mercury

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Scavengers play an important role in the flow of energy, matter and pollutants through food webs. For methylmercury (MeHg), which biomagnifies along food chains, the movement of this metal from fish carcasses to aquatic scavengers has never been demonstrated. We measured the transfer of

MeHg from fish carcasses to scavenging leeches in two lakes and in the laboratory. The results of a field experiment indicated that leeches were attracted to fish carcasses and that their Hg concentrations increased by as much as a factor of 5 during the time that Hg-rich fish were available for consumption. Under controlled conditions, we exposed leeches to ^{202}Hg -labelled fish that had been marked in situ following a whole lake ^{202}Hg addition. Leeches rapidly accumulated Hg from carcasses, and within two weeks assumed the isotopic signature of the carcasses. Necrophagous invertebrates could therefore return Hg from fish carcasses to other trophic levels in lakes. Scavengers such as leeches accumulate mercury from fish carcasses which then may return into the food web.

Mercury contamination in human hair and fish from Cambodia: levels, specific accumulation and risk assessment

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Mercury (Hg) concentrations in human hair and fish samples from Phnom Penh, Kien Svay, Tomnup Rolork and Batrong, Cambodia, collected in November 1999 and December 2000 were determined to understand the status of contamination, and age- and sex-dependent accumulation in humans and to assess the intake of mercury via fish consumption. Mercury concentrations in human hair ranged from 0.54 to 190 $\mu\text{g/g}$ dry wt. About 3% of the samples contained Hg levels exceeding the no observed adverse effects level (NOAEL) of WHO (50 $\mu\text{g/g}$) and the levels in some hair samples of women also exceeded the NOAEL (10 $\mu\text{g/g}$) associated with fetus neurotoxicity. A weak but significant positive correlation was observed between age and Hg levels in hair of residents. Mercury concentrations in muscle of marine and freshwater fish from Cambodia ranged from <0.01 to 0.96 $\mu\text{g/g}$ wet wt. Mercury intake rates were estimated on the basis of the Hg content in fish and daily fish consumption. Three samples of marine fish including sharp-tooth snapper and obtuse barracuda, and one sample of sharp-tooth snapper exceeded the guidelines by US EPA and by Joint FAO/WHO Expert Committee on Food Additives (JECFA), respectively, which indicates that some fish specimens examined (9% and 3% for US EPA and JECFA guidelines, respectively) were hazardous for consumption at the ingestion rate of Cambodian people (32.6 g/day). It is suggested that fish is probably the main source of Hg for Cambodian people. However, extremely high Hg concentrations were observed in some individuals and could not be explained by Hg intake from fish consumption, indicating some other contamination sources of Hg in Cambodia.

Mercury baseline levels in Flemish soils (Belgium)

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It is important to establish contaminant levels that are normally present in soils to provide baseline data for pollution studies. Mercury is a toxic element of concern. This study was aimed at assessing baseline mercury levels in soils in Flanders. In a previous study, mercury contents in soils in Oost-Vlaanderen were found to be significantly above levels reported elsewhere. For the current study, observations were extended over two more provinces, West-Vlaanderen and Antwerpen. Ranges of soil Hg contents were distinctly higher in the province Oost-Vlaanderen (interquartile range from 0.09 to 0.43 mg/kg) than in the other provinces (interquartile ranges from 0.7 to 0.13 and 0.7 to 0.15 mg/kg for West-Vlaanderen and Antwerpen, respectively). The standard threshold method was applied to separate soils containing baseline levels of Hg from the data. Baseline concentrations for Hg were characterised by a median of 0.10 mg Hg/kg dry soil, an interquartile range from 0.07 to 0.14 mg/kg and a 90% percentile value of 0.30 mg/kg. The influence of soil properties such as clay and organic carbon contents, and pH on baseline Hg concentrations was not important. Maps of the spatial distribution of Hg levels showed that the province Oost-Vlaanderen exhibited zones with systematically higher Hg soil contents. This may be related to the former presence of many small-scale industries employing mercury in that region.

Increased mercury levels may reflect human activity.

Absence of Hg transpiration by shoot after Hg uptake by roots of six terrestrial plant species

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In this paper we investigated if, and to what extent, six different plant species accumulate, translocate and emit mercury (Hg) into the air. The Hg uptake by roots, distribution of Hg to the shoot and release of Hg via shoots of garden pea, spring wheat, sugar beet, oil-seed rape, white clover and willow were investigated in a transpiration chamber. The airborne Hg was trapped in a Hopcalite trap or a gold trap. Traps and plant materials were analysed for content of Hg by CVAAS. The results show that all plant species were able to take up Hg to a large extent from a nutrient solution containing 200 $\mu\text{g L}^{-1}$ Hg. However, the Hg translocation to the shoot was low (0.17–2.5%) and the Hg that reached the leaves was trapped and no release of the absorbed Hg to the air was detected.

Mercury translocation to shoots was low.

Mercury persistence in indoor environments in the Amazon Region, Brazil
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We evaluated the indoor atmospheric Hg contamination in gold trade shops in two Brazilian cities of the Legal Amazon area using the Spanish moss (*Tillandsia usneoides*, Bromeliaceae) as a sentinel species. Plants inside plastic cages were exposed to a controlled atmosphere to evaluate the rate of Hg retention over time and then distributed in several stores with different characteristics to enable a relative comparison. Hg concentrations were determined by cold vapor atomic absorption spectrophotometry. Plants exposed in active stores with good air circulation exhibited lower levels. Ex-gold trade shops that were kept closed for long periods exhibited higher values. Stores that have been restored before being transformed into new businesses exhibited lower values than nonrestored ones. Direct measurements suggest that indoor Hg air concentrations were below the threshold limit recommended by the World Health Organization to occupational exposure; nevertheless, restoring ex-gold trade shops could ensure a healthier working environment.

**Hair mercury levels versus freshwater fish consumption in household members of
Swedish angling societies**

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Hair mercury levels were determined in 143 individuals from households of members in angling societies in an area of Sweden with many lakes that have freshwater fish with relatively high mercury levels. Thus, the individuals had a potentially high intake of methyl mercury. The mean mercury concentration of pike and perch was approximately 0.7 g/g. One-third of the subjects consumed these freshwater fish at least once a week. As could be expected, there was a clear increase in hair Hg with reported freshwater fish consumption ($P < 0.001$). The median mercury level in hair was 0.9 g Hg/g for the whole group, and for those who reported consumption of freshwater fish at least once a week it was 1.8 g/g. The highest hair mercury level was 18.5 g/g, in a man who consumed pike and perch several times per week. Men had higher hair Hg than women, also when stratified for fish consumption. This was verified in 32 couples, of which the man and woman consumed the same fish and reported the same consumption. The median hair mercury level in these 32 couples was 1.3 g/g for men and 0.8 g/g for women ($P = 0.002$). About half of the subjects had hair mercury

exceeding 1 g/g, corresponding to the reference dose (RfD) of 0.1 g of mercury per kilogram body weight set by the US Environmental Protection Agency. Although the RfD applies to all populations, the most at-risk group at these levels is pregnant women. There were only 2 women (of 12) of fertile age with hair mercury above 1 g/g. In Sweden pregnant women are advised not to eat perch and pike at all during pregnancy. Since fish is rich in many important nutrients, it is unsatisfactory that fish consumption must be restricted, and thus there is a need to reduce mercury levels in fish.

Hair mercury (signature of fish consumption) and cardiovascular risk in Munduruku and Kayabi Indians of Amazonia

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Fish is an important natural resource in the diet of inhabitants of the Amazon rain forest and a marker of its consumption (hair Hg) was used to compare selected cardiovascular risk parameters between tribes of Eastern Amazonia. Three Munduruku (Terra Preta, Kaburuá, Cururu) villages and one Kayabi village at the banks of head rivers (Tapajós, Tropas, Kabitutu, Cururu, Cruzinho, Teles Pires) of the Tapajós Basin were studied in relation to fish Hg concentrations, mercury in hair (fish consumption) and erythrocytes, body mass index (height/weight, kg/cm²), and blood pressure. The mean fish Hg concentrations were higher in predatory (578.6 ng/g) than in nonpredatory species (52.8 ng/g). Overall only 26% of fish Hg concentrations were above 500 ng/g, and only 11% were above 1000 ng/g. There was no systematic trend in fish Hg concentrations from rivers with a history of gold-mining activities. The biomarker of fish consumption (hair Hg) was significantly associated with erythrocyte-Hg ($r=0.5181$; $P=0.0001$) and was significantly higher in Kayabi (12.7 ig/g) than in the Munduruku (3.4 ig/g). Biomarker-assessed fish consumption rate was higher in the Kayabi (110 g/day) than in the Munduruku villages (30 g/day). Although no significant differences in body mass index (BMI) were observed between tribes, there was a trend of lower increase in blood pressure with age among the higher fish consumers (Kayabi). Summary clinical evaluation did not detect neurologic complaints compatible with Hg intoxication (paraparesis, numbness, tremor, balancing failure), but endemic tropical diseases such as clinical history of malaria showed a high prevalence (55.4%). Fish is an abundant natural resource, important in the Indian diet, that has been historically consumed without perceived problems and can easily be traced through hair Hg. The exposure to freshwater fish monomethyl mercury is less of an issue than endemic infectious diseases such as malaria and lack of basic medical services.

Mutagenic effects of mercury pollution as revealed by micronucleus test on three Amazonian fish species

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Genotoxic effect of mercury pollution over Amazonian fish species was evaluated by using the micronucleus test (MNT). Distinct mean frequencies of micronuclei (MN) were observed in three trophically distinct characin fish species collected in two riverine environments in the Amazon Basin: the Madeira (polluted area) and the Solimões (unpolluted area) rivers. Mean frequencies of MN observed in *Prochilodus nigricans* (detritivore), *Mylossoma duriventris* (omnivore), and *Hoplias malabaricus* (piscivore) from the Madeira River were significantly higher compared to the frequencies from the same species from the Solimões River. In addition, mean frequencies of MN from piscivore species were almost fivefold higher than the detritivore and/or omnivore species. We conclude that MNT in fish erythrocytes may be useful for indicating genotoxicity of mercury in Amazon rivers.

Baleen as a biomonitor of mercury content and dietary history of North Atlantic Minke Whales (*Balaenoptera acutorostrata*): combining elemental and stable isotope approaches

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Baleen is an incrementally-growing tissue of balaenopteran whales which preserves relatively well over time in museums and some archeological sites, and, therefore might be useful for studies examining long-term changes of metal levels in whales. This study examined Hg and stable C and N isotopic composition of baleen plates of the North Atlantic minke whale (*Balaenoptera acutorostrata*), which continues to be a food source for people in Greenland and elsewhere. We compared the Hg levels and stable isotopes of major tissues (kidney, liver and muscle) with those of baleen plates to see whether baleen could be used as a biomonitor of variations of Hg intake and diet both between individuals and within individuals over time. Mercury was significantly correlated with concentrations in all tissues (kidney, liver and muscle). Stable C and N isotopes in baleen were generally similar to those of muscle, which reflects the recent (approximately one month) feeding of the whale, but in some individuals there were significant differences between baleen and muscle.

Sectioning of baleen into 1 cm longitudinal increments showed that these differences were due to marked dietary shifts by some individuals over time that had been recorded in the baleen but were lost from the muscle record. Whole baleen C and N isotopes were better correlated with tissue Hg levels, suggesting that baleen may provide a more reliable indicator of long-term average diet, which in turn may be better related to Hg accumulation in tissues than the shorter-term diet record contained in muscle.

Preservation and storage techniques for low-level aqueous mercury speciation

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Although researchers today generally employ appropriate techniques for the storage and preservation of aqueous samples for ambient-level mercury (ppb) speciation, these methods continue to be poorly documented. Numerous experiments were thus conducted to investigate the effects of acidification and bottle type on holding time for various mercury species [elemental mercury (Hg^0), ionic mercury ($\text{Hg}(\text{II})$), dimethyl mercury (DMHg), monomethyl mercury (MMHg), and dissolved-to-particulate ratio] as well as total mercury (THg). We documented that THg is stable for at least 300 days when stored at 0.4–0.5% acidity in either Teflon or glass bottles. In cases where THg is adsorbed to bottle walls, the addition of BrCl at least 24 h before analysis allowed all Hg to be quantitatively recovered. Polyethylene bottles allowed diffusion of Hg^0 through the bottle walls to or from the sample, depending on the Hg concentration of the sample and storage atmosphere. MMHg in freshwater samples can be stored refrigerated and unacidified for days to weeks with no observed degradation of MMHg. For long-term storage (at least 250 days), samples should be acidified with 0.4% HCl (v/v) and kept in the dark to avoid photodegradation (approximate $t_{1/2}$ =6 months). For saltwater samples, preservation with 0.2% (v/v) H_2SO_4 is preferred to avoid exceeding the optimal chloride concentration if the distillation procedure is used for MMHg determination. For volatile species (Hg^0 and DMHg), samples should be collected in completely full glass bottles with Teflon-lined caps, as these species are lost rapidly ($t_{1/2}$ =10–20 h) from Teflon and polyethylene bottles. Because acids can enhance the rapid oxidation of volatile species, these samples should be stored refrigerated and unacidified and processed within 1–2 days if they cannot be purged and trapped in the field. $\text{Hg}(\text{II})$ and the dissolved-to-particulate ratio are more stable and can be stored for a period of days to weeks without preservation.

Characterization and recovery of mercury from spent fluorescent lamps

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Fluorescent lamps rely on mercury as the source of ultraviolet radiation for the production of visible light. Partitioning of mercury among vapor phase, loose phosphor powders produced during breaking

and washing steps, glass matrices, phosphor powders attached on the glass and aluminum end caps was examined from simulated laboratory lamp recycling tests for different types of spent and new fluorescent lamps. Mercury concentrations in lamp glasses taken from commercial lamp recyclers were also analyzed for comparison with the simulated results of spent and new lamps of different types. The mercury content of the glass from spent lamps was highly variable depending on the lamp type and manufacturer; the median values of the mercury concentration in glasses for spent 26- (T8) and 38-mm (T12) diameter fluorescent lamps were approximately 30 and 45 $\mu\text{g/g}$, respectively. The average mercury concentration of samples taken from recycler A was 29.6 $\mu\text{g/g}$, which was about 64% of median value measured from the spent T12 lamps. Over 94% of total mercury in lamps remained either as a component of phosphor powders attached inside the lamp or in glass matrices. New T12 lamps had a higher partitioning percentage of elemental mercury in the vapor phase (0.17%) than spent T12 lamps (0.04%), while spent lamps had higher partitioning percentages of mercury resided on end-caps and phosphor powders detached from the breaking and washing steps. The TCLP values of simulated all lamp-glasses and samples obtained from recyclers were higher than the limit of LDR standard (0.025 mg/L). After investigating acid treatment and high temperature treatment as mercury reclamation techniques, it was found that heating provided the most effective mercury capture. Although the initial mercury concentrations of individual sample were different, the mercury concentrations after 1 h exposure at 100 °C were below 4 $\mu\text{g/g}$ for all samples (i.e., <1% remaining). Therefore, it is recommended that heating be used for recovering mercury from spent fluorescent lamps.

Complexation between Hg(II) and dissolved organic matter in stream waters: an application of fluorescence spectroscopy

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Complexation between Hg(II) and dissolved organic matter (DOM) collected from streams in Ontario, Canada, was studied using three-dimensional excitation emission matrix (3DEEM) fluorescence spectroscopy. The results show that DOM reacted with Hg(II) rapidly, and the complexation reached pseudo-equilibrium within 20 s. Maximum excitation/emission (Ex/Em) wavelengths shifted towards the longer wavelengths, indicating that DOM structure changed during its interaction with Hg(II). Using fluorescence quenching titrations, complexing parameters, conditional stability constants and the percentage of fluorophores participating in the complexation, were estimated by the modified Stern–Volmer equation. The experimental and field survey results suggest that the Hg–DOM complexation in various streams was related to water quality parameters, e.g. DOC, Cl^- , and cation concentrations, and was strongly affected by UV irradiation.

Complexation - Dissolved organic matter - Fluorescence - Mercury - Kinetics - Streams

Spatial and temporal simulation of soil CO₂ concentrations in a small forested catchment in Virginia

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The question of how to extrapolate point measurements of soil CO₂ processes to coarser scales remains unanswered because we know little about the spatial and temporal variability in the CO₂ concentration of soil air. In this work, we describe a series of simple physically-based models that simulate soil temperature, soil tension, and soil CO₂ processes. We apply these models to simulate the spatial and temporal dynamics of soil CO₂ concentrations throughout a small catchment in the Virginia Blue Ridge. Output from the simulations is compared with field measurements. We find that despite some model deficiencies, we are able to simulate the gross patterns through space and time of soil air CO₂ concentration. During the growing season when soil temperature is high, we find that soil water status is the limiting control on soil respiration and CO₂ concentration. We also find that soil CO₂ concentration can be high despite low respiration values due to decreased soil diffusivity as moisture fills pore spaces.

Historical deposition and fluxes of mercury in Narraguinnep Reservoir, southwestern Colorado, USA

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Narraguinnep Reservoir has been identified as containing fish with elevated Hg concentrations and has been posted with an advisory recommending against consumption of fish. There are presently no point sources of significant Hg contamination to this reservoir or its supply waters. To evaluate potential historical Hg sources and deposition of Hg to Narraguinnep Reservoir, the authors measured Hg concentrations in sediment cores collected from this reservoir. The cores were dated by the ¹³⁷Cs method and these dates were further refined by relating water supply basin hydrological records with core sedimentology. Rates of historical Hg flux were calculated (ng/cm²/a) based on the Hg concentrations in the cores, sediment bulk densities, and sedimentation rates. The flux of Hg found in Narraguinnep Reservoir increased by approximately a factor of 2 after about 1970. The 3 most likely sources of Hg to Narraguinnep Reservoir are surrounding bedrocks, upstream inactive Au–Ag mines, and several coal-fired electric power plants in the Four Corners region. Patterns of Hg flux do not support dominant Hg derivation from surrounding bedrocks or upstream mining sources. There are 14 coal-fired power plants within 320 km of Narraguinnep Reservoir that produce over 80 × 10⁶ MWH of power and about 1640 kg-Hg/a are released through stack emissions, contributing significant Hg to the surrounding environment. Two of the largest power plants, located within 80 km of the reservoir, emit about 950 kg-Hg/a. Spatial and temporal patterns of Hg fluxes for sediment cores collected from Narraguinnep Reservoir suggest that the most likely

source of Hg to this reservoir is from atmospheric emissions from the coal-fired electric power plants, the largest of which began operation in this region in the late-1960s and early 1970s.

Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China

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Concentrations of total Hg and methylmercury (MMHg) in riparian soil, mine-waste calcine, sediment, and moss samples collected from abandoned Hg mines in Wanshan district, Guizhou province, China, were measured to show regional dispersion of Hg-contamination. High total Hg and MMHg concentrations obtained in riparian soils from mined areas, ranged from 5.1 to 790 mg kg⁻¹ and 0.13 to 15 ng g⁻¹, respectively. However, total Hg and MMHg concentrations in the soils collected from control sites were significantly lower varying from 0.1 to 1.2 mg kg⁻¹ and 0.10 to 1.6 ng g⁻¹, respectively. Total Hg and MMHg concentrations in sediments varied from 90 to 930 mg kg⁻¹ and 3.0 to 20 ng g⁻¹, respectively. Total Hg concentrations in mine-waste calcines were highly elevated ranging from 5.7 to 4400 mg kg⁻¹, but MMHg concentrations were generally low ranging from 0.17 to 1.1 ng g⁻¹. Similar to the high Hg concentrations in soil and sediments, moss samples collected from rocks ranged from 1.0 to 95 mg kg⁻¹ in total Hg and from 0.21 to 20 ng g⁻¹ in MMHg. Elevated Hg concentrations in mosses suggest that atmospheric deposition might be an important pathway of Hg to the local terrestrial system. Moreover, the spatial distribution patterns of Hg contamination in the local environment suggest derivation from historic Hg mining sites in the Wanshan area.

The geochemical characteristics of mine-waste calcines and runoff from the Wanshan mercury mine, Guizhou, China

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Mercury and other geochemical parameters were measured in mine-waste calcines, stream sediments and surface waters from the Wanshan Hg district in the Guizhou Province of China to evaluate adverse effects of Hg to the surrounding environment. Wanshan ore is dominantly cinnabar, and lacks other sulfide minerals and as a result, heavy metals other than Hg are rare in the calcines and mine-water runoff. Host rocks in the Wanshan area are dominantly carbonates, which upon weathering, produces alkaline-water runoff. Surface waters emanating from calcine piles have water pH varying from 10.6 to 11.8, contain high EC values, and variable major element geochemistries. Dissolved Hg concentration decreases from 300 to 1900 ng/l in mine water to 72 ng/l in stream water

collected significantly downstream from the mine. High concentrations of Hg in mine-waste calcines and alkaline surface water are the major threats to the surrounding environment. Alkalinity is also naturally attenuated downstream from the Wanshan mine. However, erosion and transport of Hg in sediment and water and highly alkaline mine-water runoff, may adversely affect sediment, aquatic and biological columns downstream from the Wanshan mine area.

Mercury removal from water using activated carbons derived from organic sewage sludge

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Various types of activated carbons were developed from organic sewage sludge (SS) using H₂SO₄, H₃PO₄ and ZnCl₂ as chemical activation reagents, and the removal of Hg(II) from aqueous solution by these carbons was effectively demonstrated. The quality of the activated carbons was dramatically improved owing to chemical activation. ZnCl₂ activated carbon had the highest capability for Hg(II) adsorption, followed by H₃PO₄ and H₂SO₄ activated carbons. The adsorption was greatly affected by Hg(II) concentration, solution pH and carbon dosage, and followed Lagergren first order rate equation and Freundlich isotherm model. Desorption results indicated that around 60% to 80% of the adsorbed Hg(II) could be recovered from the carbons to 0.1 M HNO₃ solution by sonication treatment. Accordingly, it is believed that the activated carbons developed in this study are effective and practical for utilization in industrial wastewater treatment for mercury removal.

Mercury assessment and evaluation of its impact on fish in the Cecina river basin (Tuscany, Italy)

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This paper reports the results of mercury contamination monitoring in the Cecina river basin (Tuscany, Italy). Mercury was measured in the waters, sediments and fish species of the river and its most important tributaries. In fish specimens the organic form was also determined. The results showed high mercury levels in most of the samples analysed. Particularly high concentrations were found in the sediments of the S. Marta canal flowing into the Cecina, where a chlor-alkali plant discharges its wastes, and high levels were still detectable 31 km downstream from the confluence. Near the S. Marta confluence many fish specimens were very contaminated and a study on *Leuciscus cephalus cabeda* growth suggested that at this site mercury accumulation occurs in these organisms since they are very young. Mercury entering water from a chlor-alkali plant near Tuscany has led to contamination of river food webs.

Asian Journal of Water, Environment and Pollution

On behalf of the international editorial board, we welcome all readers to the issue of the Asian Journal of Water, Environment and Pollution. As was mentioned in the circular inviting manuscripts for the new journal, the need to focus on developing countries particularly those located in Asia and Africa has long been felt by researchers from the region. At present, most of the literature on the diverse aspects of water and environment is spread across more than 200 international journals not all of them accessible easily by the reading public. Since high growth economies and growing ones are located in this region, it is appropriate to have an international journal in English with emphasis in the region. By no means, the Journal is intended to be exclusive to authors from the region since with the electronic age, scientists from different parts of the world but working on some related problems of interest to this region have also a forum to voice their views.

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