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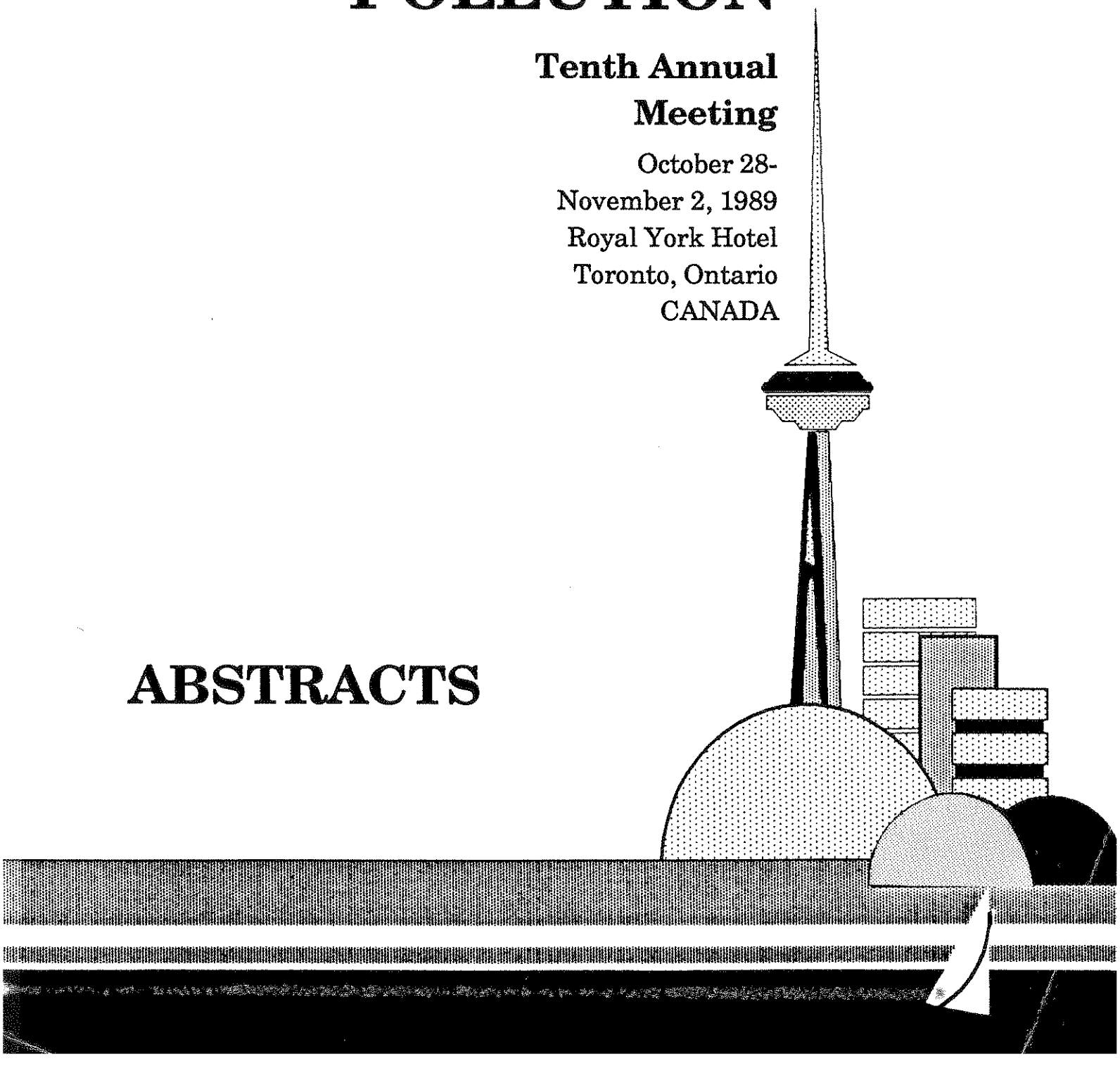

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WEDNESDAY, NOVEMBER 1ST

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EXTRACTION OF ORGANICS FROM GROUNDWATER AND THEIR RAPID TRANSFER TO CAPILLARY G.C. COLUMNS WITH CHEMICALLY MODIFIED FUSED SILICA FIBERS. Janusz Pawliszyn and Robert Belardi, Department of Chemistry and Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario N2L 3G1.

Microscale solid phase extraction procedures based on chemically modified silica fiber dramatically shorten time and lower cost of routine sampling and analysis for organics of water matrix samples such as groundwater, factory effluents or surface waters. This technique involves chemically bonding the organic layer to the surface of the fused silica fibers (optical fibers). After extraction this approach allows convenient "on column" sample introduction by placing the fiber with the absorbed organics directly in front of the capillary column. This method can be made very specific by designing selective organic layers similar to those already reported for chromatographic stationary phases and selective electrodes. In our study we focus on analysis of aromatic molecules present in groundwater. Initial results indicate that the detection limit of this rapid approach to be in the ppb level.

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pH DETERMINATION IN DILUTE GROUNDWATER SYSTEMS. C.J. Hanton and S.L. Schiff, Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, Canada.

Measurement of pH with a classical pH electrode in dilute groundwaters gives imprecise values. Systematic errors as large as 0.5 pH units can arise from CO_2 degassing, low sample ionic strength, or sample stirring. An alternate method for pH determination using carbonate equilibria is presented in which pH is calculated from measurements of dissolved inorganic carbon, CO_2 partial pressure, and buffer capacity (alkalinity).

Groundwater samples were collected at Harp Lake basin near Huntsville, Ontario using an in situ syringe sampler. This minimized sample degassing since the samples were collected at depth, stored, and treated in the same syringe. Results from both field and laboratory electrodic pH measurements are compared with calculated pH values. Different methods for the determination of alkalinity, including fixed endpoint, Gran, and inflection point titrations all yield different values for dilute groundwaters depending on aluminum and dissolved organic carbon concentrations, and the endpoint chosen. Problems with pH and alkalinity determinations observed at landfill leachate monitoring sites are also discussed.

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FRESHWATER BIVALVE TOXICITY TESTING USING AUTOMATED BIOMONITORING. Eric L. Morgan, Tennessee Technological University, Cookeville, TN, USA: R. C. Young, Young-Morgan & Assoc., Inc., Franklin, TN, USA; and Gary Rausina, Chevron Environmental Health Center, Inc., Richmond, CA, USA.

Methods for mature freshwater bivalve toxicity testing have not been developed because these aquatic animals typically respond to developing toxicity by closing their shells to help avoid immediate exposure, thus complicating the observation of when and if mortality occurs. Automated biomonitoring devices were developed to continuously record discrete bioelectric events of unrestrained freshwater mussels maintained under a toxicity test regime. A total of 120 bivalves were evaluated under flow through serial treatments. Each mussel was monitored for cardiac function and time of death. Results support the applicability of using an automated toxicity monitor for measuring critical bivalve physiological functions and time of death validation. Additional advantages include: (1) multiple species applications; (2) direct measure of functional stress response; (3) a nondestructive alternative for detecting sublethal or developing toxicity; and (4) inclusion of mature bivalves in toxicological assessment programs.

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THE USE OF E. complanata SHELLS FOR MONITORING ^{90}Sr CONTAMINATION. **B.P. Bourgoin and R.D. Evans; Dept. Environmental and Resource Studies, Trent University and Jack R. Cornett; Atomic Energy of Canada Ltd., Chalk River Lab.**

In this study, we investigated the feasibility of using the shells of the freshwater mussel, E. complanata, to record ^{90}Sr contamination. Live mussels collected from Perch Lake near the Chalk River nuclear research facility were maintained under natural conditions in a holding system at Trent University. After eight months, the three structural shell components (periostracum, prismatic layer and nacreous layer) and the soft tissues of the mussels were analyzed for stable Sr and ^{90}Sr. These levels were compared to those measured in specimens frozen upon collection. The limitations of using mussel shells in transplants experiments are discussed.

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ACUTE TOXICITY OF SEVERAL METALS AND ORGANIC COMPOUNDS TO THE FRESHWATER MUSSEL ANODONTA IMBECILIS. A.E. Keller and T.L. Crisman, Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL.

Two different toxicity test protocols were used to determine the acute toxicity of Cu, Cd, SDS, PCP, acetone, methanol, Lindane and Hydrothol to the freshwater mussel Anodonta imbecilis. Protocol 1: Juvenile mussels were exposed to toxicants 1-3 days after transformation and survival was monitored for 48-h. Protocol 2: Juvenile mussels were exposed to sediments spiked with toxaphene, chlordane, Cu or Cd for 96-h in chambers that also contained Ceriodaphnia dubia. Relative to Ceriodpahnia sp. and Pimephales promelas, mussels were less sensitive to Lindane, Hydrothol, acetone, methanol, toxaphene and chlordane, and about as sensitive to Cu, Cd, PCP and SDS. Both techniques are useful in determining the impact of various types of pollutants on early life stages of these unionid mussels.

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INCORPORATING BIVALVE TESTING FOR A FIELD DERIVED SITE SPECIFIC CRITERION. J. L. Farris, J. H. Van Hassel and D. S. Cherry, Dept. of Biology, Virginia Tech, Blacksburg, VA.

As a result of special toxics monitoring conditions required by the State of Virginia, Appalachian Power Company has been required to conduct effluent toxicity evaluations involving annual benthic macroinvertebrate surveys, chronic bioassays and evaluation of plant discharge effects on downstream mussel populations in the Clinch River. Benthic surveys (1985-1989) have consistently shown effects attributed to Clinch River Plant effluents are confined to a well-defined mixing zone with no effects noted 0.6 km downstream. However, mollusc instream monitoring has shown effects to occur as far downstream as 5-10 km. Results of 30 day exposures to metals (copper and zinc) and plant effluents in artificial streams indicate that bivalves incorporate a number of changes to react to toxicants. These organism adjustments, in turn, are specific in their affect upon metal uptake, growth, and reproduction. Significant changes in growth, cellulolytic activity and metal uptake in *Corbicula fluminea* and *Lasmigona costata* are compared with sensitivity of benthic monitoring and laboratory derived chronic estimates. The importance of refinement upon a field derived site specific criterion related to molluscan effects is discussed.

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ENVIRONMENTAL AND BIOLOGICAL FACTORS AFFECTING THE BIOACCUMULATION OF METALS BY FRESHWATER MOLLUSCS. André Tessier and Peter G.C. Campbell, INRS-Eau, Université du Québec, C.P. 7500, Sainte-Foy, Québec, Canada G1V 4C7

Trace metals of anthropogenic origin tend to accumulate in aquatic sediments, where they pose a potential danger to benthic organisms and to their predators. The overall objective of the present project is to develop a predictive model for metal bioaccumulation (Cd, Cu, Pb, Zn) in filter-feeding molluscs on the basis of geochemical data. The key hypothesis to be verified is that accumulation from (interstitial) water constitutes the major vector for metal bioaccumulation and that the free-metal ion activity ($[M^{z+}]$) constitutes the best predictor of metal bioavailability. Given the difficulties inherent in determining $[M^{z+}]$ in the interstitial water, the expression $\{S_n\text{-}OM\} \cdot [H^+]^X / \{S_n\text{-}OH\}$ is proposed as a surrogate parameter. The experimental approach involves field studies at lacustrine sites located along spatial geochemical gradients (pH, [M]). Measured variables include metal body burdens in indigenous clams (Elliptio complanata; Anodonta grandis), ambient pH, metals in adsorptive equilibrium with the sediment constituents $\{S_n\text{-}OM\}$, together with the concentrations of the solid phase(s), $\{S_n\text{-}OH\}$, responsible for binding the metal in these forms.

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THE TOXICITY OF METALS TO AN OPERCULATE SNAIL: DEVELOPMENT OF A LABORATORY TEST METHOD. J.A. Burris, C.E. Environmental, Inc., Tallahassee, FL; A.J. Stewart, Oak Ridge National Laboratory, Oak Ridge, TN.

In earlier studies, we showed that the freshwater snail *Elimia clavaeformis* was useful for *in situ* tests of streams: They can be marked, released, and recaptured easily, and their movements upstream or downstream over 24-h to 7-d periods provide useful information about water quality. We developed a 7-d laboratory test method for *Elimia*, and compared the results of this test to results of tests with fathead minnow larvae and *Ceriodaphnia* to determine the relative sensitivities of the 3 species to Ni, Zn, Cu, As, and U. The fraction of snails that were active (80-95% in controls) was easily determined, and was useful as an endpoint in measuring the reported immobilization of snails by metals. Turnover time (the time it takes for a snail to right itself when placed upon its back) was too variable to be a useful endpoint: It ranged from <20 s to >5 min in controls. The snails and the fish proved to be about equally sensitive to the metals, but were not nearly as sensitive as *Ceriodaphnia*. Ni NOECs for the snails, fish and *Ceriodaphnia*, for example, were >0.3 mg/L, >0.3 mg/L, and <30 µg/L, respectively; As NOECs were >7.5 mg/L, >7.5 mg/L, and 1.0 mg/L.

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COMPARISONS OF SENSITIVITY AMONG EARLY LIFESTAGES OF FRESHWATER MUSSELS EXPOSED TO COPPER. Peter J.Jacobson,J.L.Farris,D.S.Cherry, Dept. of Biology and R.J.Neves, Fisheries and Wildlife, Virginia Tech, Blacksburg,VA. 24061.

Three early lifestages of bradytictic freshwater mussels, occurring in southwestern Virginia, were tested for response to copper (0-400 μg Cu/L) in order to compare sensitivity. Static exposures of glochidia, from encystment through metamorphosis upon largemouth bass, *Micropterus salmoides*, were compared with static, short-term (24-48 hrs) tests involving isolated glochidia and juvenile mussels. For encysted glochidia, no impairment of metamorphosis, as measured by juvenile recovery, was noted at concentrations up to 400 μg Cu/L. Tests of isolated glochidia yielded LC50 values in the range of 50- 100 μg Cu/L compared with 100% mortality at 50 μg Cu/L for isolated juveniles of all species tested (water hardness 150-190 mg/L $CaCO_3$). The most sensitive of the stages was the juvenile mussel, the most resistant, the encysted glochidia. Given the presence of newly excysted juveniles in summer, during periods of high water temperature and low flow riverine conditions, copper pollution of 50 μg Cu/L or less will impair population recruitment.

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ACUTE TOXICITY, CHRONIC IMPAIRMENT AND RECOVERY OF THE SNAIL, *LEPTOXIS PRAEROSA* FROM COPPER-DOMINATED EFFLUENT EXPOSURES. D. K. Reed, J. L. Farris, D. S. Cherry and J. Cairns, Jr., Virginia Tech, Blacksburg, VA 24061.

The influence of a power plant effluent and associated copper (Cu) upon *Leptoxis praerosa* (Say), in the Clinch River, Virginia, was examined by delineation of impact zones. Zones were identified where in-river effluent concentratrations produced acute and long-term effects as verified in laboratory and artificial stream exposure studies. No snail mortality occurred during 96-hr static exposure to whole effluent with 105 μg Cu/L. However, effluent containing 148 μg Cu/L produced a 96-hr flow-through LC50 value of 95%. Chronic impairment, measured by cellulolytic enzyme activity impairment, was significant ($P < 0.05$) for snails exposed to 40% effluent (52 ± 2 μg Cu/L) for 20 days or 10% effluent (20 ± 3 μg Cu/L) for 30 days.

Suitability of habitat within zones of effluent impact was evaluated. Measured parameters affecting distribution patterns were location, depth, percent periphyton cover, chlorophyll a, pheophytin a, silt, pH and alkalinity. Areas of measurable impact were delineated from areas of naturally occurring unsuitable habitat by in-river sampling of periphyton and snails as well as caged experiments that restricted snail movement.

In-river avoidance of Cu-laden periphyton by *Leptoxis* along with implicated associations between periphyton Cu concentration and cellulolytic enzyme activity, suggest that snail populations can detect food-quality degradation from effluent impact.

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BIOLOGICAL MARKERS OF HUMAN EXPOSURE. Charles H. Nauman and Jerry N. Blancato, Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Las Vegas, NV 89193.

Biological markers of exposure provide useful monitoring data for the estimation of exposure to human receptors. These markers include body burden (tissue, fluid, or breath concentrations of xenobiotics or their metabolites), adducts to molecular constituents (e.g., DNA or protein adducts), enzyme induction or inhibition (e.g., cytochrome P450 induction; red blood cell cholinesterase inhibition), and others. When detected in the body these markers provide definitive evidence that exposure has occurred, and serve to integrate dose resulting from continuous or intermittent exposure, through all pathways to the receptor, and through all routes of exposure (inhalation, ingestion, and dermal contact). The objectives of the exposure biomarkers research program that will be presented include the development and application of well-characterized and validated biomarkers of exposure, as well as the development of protocols for their detection and quantitation. Pharmacokinetic modeling of biomarker data to estimate effective dose or to backcalculate exposure constitutes a critical tool for more accurately estimating target tissue dose or initial exposure, thus effectively reducing uncertainty in exposure assessments that include biomarker data.

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APPLICATIONS OF GAS CHROMATOGRAPHY/MASS SPECTROMETRY TO BIOMONITORING OF EXPOSURE TO CHEMICALS. L. Wazneh, L. Latriano and A.M. Jeffrey. Division of Environmental Sciences, Columbia University New York, NY 10032.

DNA is the most appropriate molecule in which to study the effects of exposure to genotoxic carcinogens. However, for many of the compounds of interest, methods with adequate sensitivity are not available for human monitoring. A surrogate for DNA damage has been hemoglobin, which is available in larger quantities and is more easily purified. Applications of gas chromatography/mass spectrometry (gc/ms) in the negative ion mode, with single ion monitoring (nci/sim) in several instances provides both the sensitivity and selectivity required. Analysis of N-terminal valine residue alkylation in hemoglobin using a modification of the methods developed by Tornqvist et al. [Anal. Biochem. 154, 255, (1986)] by ethylene, propylene, butadiene and styrene oxides has been applied to animal and human cohorts. Two of the problems with this approach, the relative involatility of the pentafluorphenylthiohydantoins derivatives formed and the preparation of a suitable internal standard, will be discussed and some partial solutions presented. Supported by NIEHS grant 5P01ES03881