Agenda for TAG Meeting
Friday, January 10, 2003, 11 am to 3 pm
McArthur Engineering Building Annex, Room MCA 202
University of Miami Campus, Coral Gables, Florida

Introduction

1. Welcome
2. History of Florida CCA Research — Solo-G/Townsend

Florida Center for Solid and Hazardous Waste Sponsored Research (FCSHWM) 3.
Background Information Concerning FCSHWM — Schert
Description of new FICESS Center

4. Review of "Year 4" Second Draft of Report Titled, "Leaching and Toxicity of CCA-Treated and Alternative-Treated Wood Products"
   - Brief review of project results — Townsend
   - Additional analyses to confirm initial retention levels — Solo-Gabriele
   - Updates to text — Townsend

5. Review of "Year 5" First Draft of Report Titled, "Quantities of Arsenic in Florida" — Solo-Gabriele

6. Progress to Date on "Year 6" Study Focusing on As and Cr Speciation
   - Review of Cr Speciation Data — Townsend
   - As Speciation of CCA-Treated Wood Samples — Khan
   - As Speciation of Groundwater Samples from C&D Facilities — Khan/Szuri
   - Lysimeter Results, Cr and As Speciation plus other results — Jambeck

7. Research Plan and Progess on "Year 7" Study focusing on Mulch — Solo-Gabriele

8. Research Plan and Progress on "Year 7 – RCRA Study" Focusing on Disposal Options for CCA-treated wood. — Solo-Gabriele

Research Funded by the National Institutes of Environmental Health Sciences with contracts through Florida International University and Rutgers University

9. Research Plan for Project Titled, "Impacts of Arsenic from CCA-Treated Wood in Marine and Terrestrial Environments"
   - Arsenic Speciation in Runoff from CCA-Treated Decks — Solo-G/Khan
   - Arsenic Speciation in Soils and Marine Environments — Cai/Georgiadis

10. Pilot Epidemiologic Study Evaluating Potential As Exposures to Children from CCA-treated Playgrounds
   - Environmental Study — Laas/Vega/Solo-G
   - Exposure Study — Fleming/Shibata

Refreshments Will Be Available.

Minutes of the January 10, 2003
Meeting Held at the University of Miami
Coral Gables, Florida

Attendees:
Advincula, Gene, Florida Wood Recycling, Medley, FL
Aleman, Gonzalo, Montenay Power Corp, Miami, FL
Bingham, Mark, BFI Waste System of North America, Inc., Davie, FL
Buff, Richard, Akzo Nobel Functional Chemical LLC, Norcross, GA
Cai,Yong, Florida International University, Miami, FL
Chen, ZhangRong, FIU Dept. of Chem., Miami, FL
Dee,David, Landers & Parsons, Tallahassee, FL
DiVita, Louis, Delta Recycling Co., Pompano Beach, FL
Dombrowski, Leo, Wildman, Harrold, Allen & Dixon, Chicago, IL
Dubey,Brajesh, University of Florida, Gainesville, FL
Eldan, Michal, MAA Research Task Force, Memphis, TN
Fleming, Lora, University of Miami, Miami, FL
Freudenthal, Dr. Ralph, Toxicology Consultant, West Palm Beach, FL
Freudenthal, Susan, Toxicology Consultant, West Palm Beach, FL
Georgiadis,Myron, Florida International University, Miami, FL
Hinkley,Bill, Florida Dept. of Environ. Protection, Tallahassee, FL
Hosein, Naila, Westhorp and Assoc., Miami Shores, FL
Jambeck,Jenna, University of Florida, Gainesville, FL
Khan, Bernine, University of Miami, Coral Gables, FL
Krumbholz, Bill, FDEP, Ft. Myers, FL
Marra, Dominic, Montenay Power Corp., Medley, FL
Marwede, Marcia, Fl. Center for Solid & Haz. Waste Mgt., Gainesville, FL
Mason, Dave, Dept. of Environmental Protection, Tallahassee, FL
McMinn, Bryan, Maher etal, Winter Park, FL
McNeely, Hugh, Simien & Simien, Baton Rouge, LA
Messer, James M., Levin Papanfonia Law Firm, Pensacola, FL
Moretzsohn, Jose A., Residue Recovery Systems, Inc., Aventura, FL
Nahari, Yoram, Residue Recovery Systerms, Inc., Miami, FL
Renz, Dave, Akzo Nobel Functional Chemicals LLC, West Palm Beach, FL
Rogers, Rhonda, Florida Center for Solid and Haz. Waste Mgt., Gainesville, FL
Salisbury, Penny, Koppers Industries, Inc., Gainesville, FL
Schert, John, Florida Center for Solid and Haz. Waste Mgt., Gainesville, FL
Schneider, Harvey, Florida Wood Recycling, Medley, FL
Simien, Jimmy, Simien & Simien, Baton Rouge, LA
Simien, Mark, Simien & Simien, Baton Rouge, LA
Solo-Gabriele, Helena, University of Miami, Coral Gables, FL
Stetter, Diana, Florida Center for Solid and Haz. Waste Mgt., Gainesville, FL
Surrency, Don, Koppers Industries Inc., Gainesville, FL
Szuri, Sheena P, FIU Dept. of Chem., Miami, FL
Tewari, Ram, Broward County Wood, Plantation, FL
Townsend, Timothy, University of Florida, Gainesville, FL

Unsal, Sermin, Broward Co. Dept.Planning & Environ. Protection, Ft. Lauderdale, FL
Wilkins, Rick, Broward Co. Dept. Planning & Environ. Protection, Ft. Lauderdale, FL
Zavodska, Anita, Barry University Sch. Adult & Continuing Ed., Miami, FL

The meeting began at 11:05 am and adjourned at 3:10m. The participants took a 45 minute break for lunch at approximately 12:30 pm.

1. Welcome

Helena Solo-Gabriele welcomed the meeting attendees. Each attendee introduced themselves by stating their name and affiliation. Helena Solo-Gabriele reviewed the agenda.

2. History of Florida CCA Research

Helena Solo-Gabriele described the history of the CCA-treated wood research. She mentioned that primary funds for this research have been obtained from the Florida Center for Solid and Hazardous Waste Management. Funds have also been obtained from Florida Power and Light, Sarasota County/Florida Department of Environmental Protection, and Florida International University/National Institutes for Environmental Health Science. Active faculty researchers on the project include herself and Dr. Lora Fleming of the University of Miami, Dr. Timothy Townsend of the University of Florida, and Dr. Yong Cai of Florida International University. She also acknowledged the work of numerous students who have been supported on the project. Background information concerning CCA-treated wood was provided including a description of the original motivation for research. The original motivation was due to an ash contamination problem from cogeneration plants located in Florida that burned recycled construction and demolition (C&D) wood. Due to this problem, research was initiated during year 1 (1996-1997) to develop a disposal forecast for CCA-treated wood and to determine the disposal routes for the waste. Research has shown that CCA-treated wood is disposed through C&D recycling facilities. Markets for C&D waste wood include wood for cogeneration and for use as mulch. Given the problems associated with the disposal of CCA-treated wood identified during year 1, the focus of year 2 (1997-1998) was to develop potential solutions to the disposal problems. The focus of research during year 2 was to conduct leaching studies of CCA-treated wood ash and to identify sorting methods for separating CCA-treated wood within the waste stream. During year 3 (1998-1999), research again focused on disposal-end management plus evaluating an option for waste minimization in the form of utilizing alternative-chemical treated wood. The 4 most promising alternatives to CCA identified in this study included ACQ, CBA, CC, and CDDC. During the year 3 project, the research team was invited to the Minnesota Proceedings which focused on a potential ban on CCA-treated wood within that particular State. One of the observations from this meeting was the lack of scientific data. As a result, the research team applied for supplemental funds to evaluate: the impacts of CCA-treated wood during its in-service use, to quantify use sectors for CCA-treated wood, to evaluate leaching of CCA-treated wood and C&D wood mulch, and to conduct a literature review on laboratory analytical methods for evaluating arsenic/chromium species and for evaluating alternative chemicals in solution. The results of the "year 3 supplemental" were briefly reviewed. In addition to the Center funded research, a study focusing on sorting CCA-treated wood from untreated wood was funded through the Sarasota County/FDEP Innovative Recycling Grants Program. The sorting study focused on the use of laser and x-ray technologies for identifying CCA-treated wood within the waste stream. Results from this study indicate that both technologies are very promising. Research reports currently under review include the report for the year 4 study focusing on leaching and toxicity of CCA-treated wood and alternative chemical treated wood, and the report for the year 5 study focusing on quantities of arsenic within the State of Florida. On-going research includes evaluation of arsenic and chromium species in CCA-treated wood, a new deck study funded by FIU/NIEHS, and a children's playground exposure study. Projects that have been recently funded include a mulch study and a study that focuses on disposal options for the State of Florida.

2. <u>Background Information Concerning FCSHWM and FICESS</u>

John Schert indicated that the Florida Center for Solid and Hazardous Waste Management (FCSHWM) is a statewide research center whose mandate is to sponsor funded research. During his presentation he introduced his staff and the Center's advisory board. He described several of the research projects sponsored by the Center and mentioned that the CCA project is one of the longest projects funded. John Schert also emphasized that he is now the director of a new Center called the Florida Interdisciplinary Center for Environmentally Sound Solutions (FICESS). The objective of this Center is to develop partnerships among interested parties to solve environmental problems. He listed the many FICESS partner organizations and emphasized that one of the first activities of the FICESS Center is to host a conference on CCA-treated wood. The title of this conference is, "Treated Wood: Environmental Impacts of In-Service Use and Disposal." This conference will be held in February 2004 in Orlando, Florida. More information about this Center is available at www.ficess.org.

3. <u>Review of "Year 4" Report Titled, "Leaching and Toxicity of CCA-Treated and Alternative-Treated Wood Products</u>"

Tim Townsend mentioned that the rationale for conducting this portion of the study was because the aquatic toxicity of chemical alternatives to CCA was of concern. The objectives of the study was to conduct side-by-side comparisons of CCA-treated wood and alternative-chemical treated wood with respect to chemical leaching and aquatic toxicity of the leachates. Experiments were conducted with untreated wood and with CCA-, ACQ-, CBA-, CC-, and CDDC-treated wood. Leaching tests included the SPLP, TCLP, and leaching tests with synthetic seawater and deionized water. Each component of each chemical preservative was measured. Leaching data indicated that the amount of arsenic leached was a function of the leaching solution used. For the CCA samples, more copper was leached using the TCLP and the seawater extraction fluid than with de-ionized water and the SPLP fluid. Similar results were observed for the CBA-treated wood. General observations include that for copper, the TCLP solution and saltwater extract the most. When considering the alternative chemical treated wood it was found that copper concentrations were greater in the leachates from the alternative-chemical treated wood samples than from the CCA-treated wood samples.

Aquatic toxicity tests conducted in this study included the MetPLATE^{TM} test, the Microtox test, an algal assay (*Selenastrum capricornutum*), and an invertebrate assay (*Ceriodaphnia dubia*). In general it was found that the invertebrate and algal assays were the most sensitive test methods. For the invertebrate assay it was found that CCA-treated wood was less toxic than the alternative-chemical treated wood. The toxicity of the wood samples is correlated with the copper concentration in the leaching solution. Overall results show that alternative-chemical treated wood products are expected to leach more copper. This observation raises concern since copper is a potent aquatic biocide. Additional factors including dilution, sedimentation, and complexation should be considered when evaluating the potential toxicity of treated wood. Data were evaluated in terms of relative risk. CCA-treated wood is considered to pose a greater relative risk with respect to human toxicity and waste management. Results from this work indicate that relative risk from alternative-chemical treated wood is greater with respect to aquatic toxicity.

Helena Solo-Gabriele mentioned that the remainder of this presentation focused on discussing changes to the last draft of the report. These changes focused on re-analyzing the initial retention levels of wood and adding text to the interpretation of the results. The initial retention levels were measured by Timber Products Inspections (TPI) during September and November 2000. A letter was then received from TPI on May 2002 indicating that the results for one of the samples were in error. It was then decided to reanalyze the initial retention levels of the wood samples. This was addressed by generating 40 grams of sawdust for each sample. This sawdust was then split among 4 laboratories which included the Southern Pine Inspections Bureau (SPIB), the University of Florida (UF), the University of Miami (UM), and Spectrum Laborotories. The results were consistent among TPI and the 4 additional laboratories for CCA-treated wood. Data were more variable for the analyses on the alternatives. The average results for the 5 laboratories were used for incorporation within the final report. The % mass values as a result were modified but these modifications were not large enough to alter the overall conclusions. Tim Townsend described the recommended changes by the groups that provided comments on the report. He mentioned that the updated report maintained the same overall structure but a considerable amount of text was added to explain the significance of the results and urging caution concerning how the aquatic toxicity data should be evaluated. Efforts focused on adding language that would help educate the reader so that the results would not be mis-used.

<u>Questions</u>

Yong Cai: The leachability should be a function of the type of wood. How was the wood selected for this study?

Tim Townsend: All of the wood used in this study was untreated Southern Yellow Pine. The original wood was purchased from a batch of wood samples. Bundles were as homogeneous as possible.

Yong Cai: Were comparisons made with other types of wood?

Tim Townsend: Comparisons with other types of wood was beyond the scope of this study. However, the results that were obtained from Southern Yellow Pine used in this study were consistent with those found in the literature.

5. Review of "Year 5" First Draft of Report Titled, "Quantities of Arsenic in Florida."

Helena Solo-Gabriele mentioned that the purpose of the arsenic mass balance research was to evaluate the relative magnitude of arsenic from CCA-treated wood versus the amounts from other arsenic sources for the State of Florida. Arsenic quantities were evaluated in terms of inputs, outputs, and reservoirs. Inputs/outputs/reservoirs evaluated included CCA-treated wood, non-CCA pesticides, geologic sources, fuels, fertilizers, food sources, waste disposal, and the hydrosphere. Sample computations were provided for the input of CCA-treated wood and the MSMA use in golf courses. Computations were also described for the amount of MSMA stored in golf courses. Results included a bar graph for the concentration of various arsenic sources and the input fluxes for arsenic. Tabular data was provided for the input of arsenic, output, and arsenic within the "accessible" reservoirs. Overall it is estimated that 2,500 metric tons of arsenic are imported per year. CCA-treated wood represents 60% of this value, non-CCA arsenical pesticides (MSMA) represent 20%, and geologic sources represent 15%. Of the imported quantity only 10% is exported which indicates that the majority of the arsenic imported into the state accumulates over time. In order to limit the impacts due to arsenic within the State of Florida, it is recommended that the use of MSMA be reduced, CCA-treated wood be disposed in a proper fashion, and that the impacts of CCA-treated wood currently in service be minimized. A draft report is available at www.ccaresearch.org

Questions

John Schert: It appears as though limestone used in road building is not accessible.

Mark Bingham: Every home pad uses limerock. It is ironic that the residential standard for arsenic for residential applications is 0.8 mg/kg whereas limerock has an average arsenic concentration of 3 mg/kg.

David Dee: Was the ash number shown as an input?

Helena Solo-Gabriele: The ash number corresponded to a concentration value. Arsenic from ash would be considered a form of "cycled" arsenic. Arsenic that is lost to the atmosphere through air emissions would be considered an output.

Yong Cai: Was the concentration of 1,350 mg/L for arsenic in golf courses a value observed for soil?

Helena Solo-Gabriele: The 1,350 mg/L value corresponded to the concentration of the liquid pesticide added to golf courses. It corresponds to the dilution as stated on the product label.

6. <u>Progress to Date on "Year 6" Study Focusing on As and Cr Speciation</u>

<u>Chromium Speciation</u>

Tim Townsend mentioned that the chromium speciation study was funded by the FDEP RCRA Program. He described the different chemical species of chromium. It was emphasized that Cr(VI) is much more toxic and mobile than Cr(III). The predominance of different species was reviewed in the context of an Eh-pH diagram. The fate of chromium during the treatment process was discussed. Chromium is present as Cr(VI) in the raw CCA treating solution. Once it is impregnated into the wood it is converted to Cr(III) as part of the fixation process. The objective of the chromium speciation study was to examine the fate and behavior of hexavalent chromium in various environmental media impacted by CCA. Methods used for analyzing chromium species included an alkaline solvent extraction followed by total chromium analysis. The alkaline solvent extraction is designed to prevent a change in the distribution of chromium between its different species. Cr(VI) is measured in the extract using either a colorimetric method or ion chromatography (SW-846 Method 7199). The first set of experiments was designed to examine the fate of Cr(VI) in soils spiked with CCA solution. The soils were subjected to the alkaline solvent extraction procedure to measure total Cr(VI) and were also subjected to SPLP test to measure leachable Cr(VI). Three soil types were evaluated: a clay soil, an organic soil, and a sandy soil. Results indicate that the total Cr(VI) concentration remained elevated in the sandy and clay soils whereas it decreased significantly in the organic soil. A similar trend was observed for the leachable Cr(VI) fraction. However, even for the organic soil, the leachable Cr(VI) concentration was above Florida's GWCTL of 0.1 mg/L for a considerable amount of time. Experiment number 2 focused on evaluating how much Cr(VI) is in CCA-treated wood. Results from the alkaline digestion of CCA-treated wood showed that Cr(VI) concentrations ranged from 7 to 250 mg/kg, which represents less than 3% of the total-total chromium. SPLP leachates showed no detectable Cr(VI) concentrations. The focus of experiment 3 was to evaluate the conditions during which Cr(VI) would form. Data indcates that Cr(VI) predominates under alkaline pH values. High alkaline leachates can be generated in C&D wastes that contain significant amounts of concrete, in particular if the waste is under saturated conditions. It is also recognized that some ash is characterized by a high pH. Experiment 4 focused on using an alkaline leachate to determine if Cr(VI) can be formed. It was found that Cr(VI) is leached from CCA-treated wood when subjected to a concrete leachate solution. Experiment 5 focused on evaluating whether Cr(VI) is formed during the combustion of CCA-treated wood. Ash formed from the combustion of CCA-treated wood and from recycled C&D wood indicate that Cr(VI) is the predominate chromium species leached for the 0.25 pcf sample, the weathered wood sample, and the C&D wood samples evaluated. Chromium leaching was not observed for the untreated wood sample and the 0.6 pcf and 2.5 pcf CCA-treated wood samples. It is hypothesized that the reason for the presence of Cr(VI) in some CCA ash samples is due to the presence of other chemicals within the samples.

Question

Yong Cai: Why is Cr(VI) used in CCA?

Tim Townsend: The chromium is not used as a pesticide, it does not serve as a fungicide nor as an insecticide. The chromium is added to "fix" the chromium within the wood.

Arsenic Speciation of CCA-Treated Wood Samples

Bernine Khan explained that the purpose of this portion of the study was to identify and quantify the arsenic species (As(III), As(V), MMAA, and DMAA) leached from CCA-treated wood. Speciation is of interest because the toxicity of the leachate depends upon the species of arsenic. She explained that the speciation is the quantification of the individual parts that make up the whole. Speciation can be based upon element valence and inorganic/organic forms which is the focus of her research or it can be based upon particle size or molecular weight size which is the focus of the next presenter's research (Sheena Szuri). She described the relative toxicity of various arsenic species which typically follows the order AsH_3 gas>AsIII>AsV>MMAA>DMAA>TMAO>AsB>AsC. With AsH_3 gas being the most toxic and AsC being the least toxic. Arsenic leaching from CCA-treated wood was evaluated through a set of solvent extraction experiments. These experiments included TCLP, SPLP, extractions with other solvents (de-ionized water, rain water, and seawater), and a pH stat experiments. Results from the TCLP test for unburned CCA-treated wood indicates that the highest concentrations of As(III) were leached from the weathered wood sample. The highest concentrations of As(V) were leached from the 2.5 pcf sample. Data indicates that all samples exceeded TCLP limits for arsenic with the exception of untreated wood and the unburned 0.25 pcf sample and the unburned C&D samples. Results for the SPLP extraction again showed that weathered wood extracted greater amounts of arsenic as a whole and greater proportion of As(III). All samples exceeded SPLP guidelines for arsenic with the exception of untreated wood (unburned and ash) and one unburned C&D sample. Results from the de-ionized water and rainwater leaching experiments using unburned wood were also similar to the results from the TCLP and SPLP test. Leachates created with de-ionized or rainwater water indicate that As(III) represents a significant fraction of the total arsenic for weathered wood and the concentration of arsenic within the leachates was between 2.5 and 5 mg/L. The amount of arsenic leached from wood ash samples was much higher than the amount leached from unburned wood. The 2.5 pcf sample leached the most As(III) and As(V) for the wood ash samples. Results from the pH stat experiment showed that arsenic leaching is enhanced at the extreme pH values. For new wood, As(V) was the only species detected. Both As(III) and As(V) were detected in weathered wood. More arsenic was leached from weathered wood in the near neutral pH ranges. The reason for increased leaching from weathered wood can be due to the higher retention of the weathered wood sample, the age of the wood, and the finding that the arsenic in the wood has been converted to the +3 valence which is more mobile than arsenic in the +5 valence.

<u>Questions</u>

Bill Hinkley: The 0.05 mg/L value for SPLP is a guideline not a standard. The 5 mg/L value for TCLP is a regulatory standard.

John Schert: Arsenic toxicity varies with each species. Why is As(III) retained in the body more readily than As(V)?

Yong Cai: The mechanisms of toxicity are different for each species. As(III) attaches to the thio groups of proteins causing damage to the enzyme system. As(V) replaces phosphate in the production of ATP. Some As(V) may also be converted to As(III) in the body.

Dave Mason: Why is there more As(III) in weathered wood?

Bernine Khan: We are currently conducting experiments to evaluate this. We believe that it could be due to microbial processes or due to the breakdown of the wood over time.

David Dee: CCA-treated wood can be disposed in MSW and C&D landfills.

Bernine Khan: The last slide was in error, it should have stated CCA-treated wood ASH.

Bill Hinkley: It is surprising that new 0.4 pcf wood that was purchased measured at 0.21 pcf and that old wood measured at 0.38 pcf.

Bernine Khan: The high value may be due to over-treatment of the wood.

Tim Townsend: The retention level analysis was based upon the outer 0.6 inch and there tends to be variability in the results along the length of a board.

Don Surrency: The 0.25 pcf is recommended for above ground applications and the 0.4 pcf is recommended for ground contact. The old wood was probably rated for ground contact.

Bill Hinkley: What is the fate of arsenic in various valence states?

Bernine Khan: The fate depends upon the environment. For an oxidizing environment we would expect As(V) and for a reducing environment we would expect As(III).

Bill Hinkley: Are the conditions reducing enough within a landfill environment.

Bernine Khan: We would expect As(III) to predominate near the bottom of the landfill.

Yong Cai: Conditions do not have to be very reducing in order to get the conversion of arsenic between As(V) and As(III). Under very reduced conditions, such as those within landfills, arsine gas can be generated.

Tim Townsend: Within landfills one would expect to have conditions where the valence of arsenic is lowered. The reactions with the wood would promote a reducing environment.

John Schert: It would be of interest to speciate the arsenic in contaminated mulch.

Arsenic Speciation of Groundwater Samples from C&D Landfills

Bernine Khan mentioned that the purpose of this study was to measure the species of arsenic for groundwater in the vicinity of C&D landfills. A total of 26 C&D landfills have been identified. Groundwater has been collected from 18 of these facilities. Four of the facilities are currently undergoing enforcement action with either FDEP or DERM and so samples will not be collected at these facilities. There are still 4 landfills pending. At each landfill a sample is collected from a background well and from two compliance or detection wells. Water from a total of 56 wells have been sampled and analyzed to date. Results show that the concentration of arsenic in the groundwater is very low, with most samples either at or below the quantification limit. The highest arsenic concentration was observed for a sample collected from a background well.

Questions

Tim Townsend: Are the totals provided the sum of the different arsenic species?

Bernine Khan: Yes.

Bill Hinkley: It is interesting to note that the Limit of Quantification (0.01 mg/L) is the new groundwater standard.

Bernine Khan: The Limit of Quantification is a function of the matrix.

David Dee: In the final report, will the location of the samples be identified.

Helena Solo-Gabriele: As part of our agreement with the C&D owners, we will not disclose the precise location of each landfill from where samples were collected. The landfills will be coded by number or letter. The coded data will be provided in the final report.

Arsenic Speciation of Groundwater Samples from C&D Landfills (con'd)

Sheena Szuri presented results from an equilibrium dialysis method which speciates arsenic based upon molecular weight of the molecule to which it is bound. She emphasized that arsenic can form complexes with compounds of different molecular weights which is an indication of particle size. Size of complexes affect bioavailability and mobility through soil. Once samples were subjected to equilibrium dialysis they were analyzed by either ICP-MS or HG-AFS. The physical characteristics of the dialysis membranes and the experimental design were described. The first set of experiments focused on determining the equilibration time for the 3 membrane sizes used in this study. These sizes included a 500, 3500, and a 12000 kiloDalton size membrane. Data indicate that the equilibration time for the 500 kD membrane was 3 days whereas for the 3500 and 12000 kD membrane it was less than 1 day. For samples of C&D and MSW leachate, results show that the majority of the arsenic is associated with molecules that are smaller than 3500 kD. Future studies will focus on the analysis of additional leachate samples. The influence of matrix elements (dissolved organic matter, Fe, Mn, Ca, and Al) and physical parameters (pH, Eh, salinity) will be also evaluated.

Questions

John Schert: What's a kiloDalton?

Sheena Szuri: It is the measurement of the size of a molecule. A 500 kD size corresponds to a molecule characterized by a molecular weight of 500.

David Dee: Are there C&D landfills from which true leachate can be collected?

Bill Hinkley: There are a few C&D landfills in Florida that are fitted with liners.

Bernine Khan: The samples provided to Sheena for analysis were C&D leachate samples.

Bill Krumbholz: Will iron tie-up the arsenic in the leachate?

Sheena Szuri: Certain valence states of iron are capable of tie-ing up arsenic.

Bill Hinkley: Lena Ma postulates that soils high in iron and aluminum should be capable of sorbing arsenic.

Yong Cai: Binding of arsenic by soils is well documented. In terms of leachate, soil binding of arsenic is not well known. Quite different results have been obtained with golf courses and leachates, for examples.

Lysimeter Study

Jenna Jambeck reviewed the design of the 6 lysimeters to be used. The lysimeters are constructed of 22 ft high, 1 ft diameter, PVC columns. The leachate is produced from natural rainfall that is captured in the cap and from deionized water that is added. The contents of the lysimeters are designed to simulated a CCA monofill, a C&D landfill, and a MSW landfill. The lysimeters are designed to capture gases that are released. The contents of the lysimeters were described. Lysimeter 1 contains untreated wood; lysimeter 2 contains 50% weathered CCA-treated wood and 50% new (0.4 pcf) CCA-treated wood. Lysimeter 3 contains a typical C&D mix without CCA; lysimeter 4 contains a typical C&D mix with CCA-treated wood; lysimeter 5 contains MSW with untreated wood; and lysimeter 6 contains MSW with CCA-treated wood. Lysimeters began operation during August and September 2002. Monitoring includes a local weather station and weekly temperature readings inside the lysimeters. Leachate is collected twice monthly an analyzed for general water quality parameters and As, Cu, and Cr. Preliminary results show that the temperature in the lysimeter fluctuates in relation to ambient temperature. Methane was detected in the MSW lysimeters and leachate has been generated from all lysimeters. Arsenic, chromium, and copper concentrations were measured in lysimeters containing CCA. Concentration of arsenic in lysimeter 2 reached 50 mg/L. Copper and chromium concentrations were generally lower at about 10 mg/L at their highest level to date. Arsenic and chromium concentrations in lysimeter 4 were in the 2 mg/L range at their highest concentrations. As and Cr in lysimeter 6 was measured in the 4 mg/L range. The pH of the lysimeters varied between 5 and 8. Comparative results between the lysimeters suggest that the concentration of arsenic within the CCA only lysimeter is increasing whereas the concentration of arsenic within MSW and C&D waste is generally decreasing. Operation of the lysimeters will continue through the summer. Measurements of temperature, gas, and metals will continue.

Questions

Bill Hinkley: Was speciation of chromium conducted?

Jenna Jambeck: Yes but no Cr(VI) was observed.

John Schert: Can arsine gas be formed under MSW conditions?

Jenna Jambeck: Yes. There are references which indicated that arsine gas can be formed. Methane was formed in the lysimeters indicating extreme reducing conditions; however, over the winter the amount of methane generated has dropped during the winter. A gas filter will be installed to capture gases from the lysimeters once the methane begins to be regenerated.

Yong Cai: How often was the leachate from the lysimeters collected and is the leachate produced from rain only or was water added?

Jenna Jambeck: The leachate was collected once every two weeks and the leachate is produced from both rain and added water.

Yong Cai: It would be helpful to plot the data as cumulative arsenic because the amount of water introduced to the lysimeters will affect the concentration.

Bill Hinkley: What would be ultimate fate of the arsine gas? Would it precipitate out once it is released into the atmosphere?

Yong Cai: The boiling point of arsenic is very low. In air it would likely oxidize and would thus change valence and possibly get sorbed to aerosols or particulates.

7. <u>Research Plan for Project Titled, "Impacts of Arsenic from CCA-Treated Wood in Marine and Terrestrial Environments</u>."

Helena Solo-Gabriele mentioned that this project was funded through Florida International University with ultimate funding through the National Institutes of Environmental Health Sciences. She reviewed the objectives of the project which included developing methods for arsenic speciation in the particulate phase and evaluating the impacts of arsenic from CCA-treated wood by measuring the species of arsenic that are leached from different einvironmental samples. The project is separated into two phases: phase I, laboratory evaluation and phase II, field evaluation. Phase I focuses on a series of leaching experiments which have been previously described by Bernine Khan. Method development for arsenic speciation in the particulate phase will be described by Myron Georgiadis. Results from marine dock sampling will be described by Yong Cai and Bernine Khan will summarize the results to date focusing on the deck sampling effort. The deck sampling consists of two decks: one CCA treated and one untreated Southern Yellow Pine. The decks are fitted with a leachate collection system. Rainwater, rainwater runoff, and infiltrated water are collected from the deck twice a week. Results indicate that the arsenic concentration in rainwater runoff was initially above 1 mg/L but the concentrations appear to be declining. The corresponding concentrations from the untreated deck were less than 0.01 mg/L. The concentration of arsenic in the infiltrated water from both decks was less than 0.01 mg/L. Most of the arsenic in the rainwater runoff is in the As(V) form; however a measurable amount of As(III) is also observed. Data are currently being compiled in terms of cumulative arsenic. Bernine Khan also described the experimental set up for a series of soil column experiments which are intended to augment the results from the field deck study.

<u>Questions</u>

Tim Townsend: Is the runoff measured from one panel?

Bernine Khan: Yes.

Bill Hinkley: Do you plan to analyze a clay soil?

Bernine Khan: Possibly yes, assuming that I can get a representative sample.

Bill Hinkley: Some soils, in particular organic soils, have high concentrations of arsenic up to 18 to 50 ppm. It is also interesting to note that there was no arsenic observed in the infiltrated water.

Bernine Khan: The sand probably absorbed the arsenic. A preliminary test showed that much of the arsenic is absorbed.

Tim Townsend: There is a possibility for small amounts of arsenic to leach through the soil.

<u>Method Development for As Speciation in the Particulate Phase and Marine Dock Sampling</u>

Myron Georgiadis described the methods used to develop a protocol for arsenic speciation in the particulate phase. Experimentation is currently being conducted on a reference soil called PACS-2. Results from spiking the PACS-2 standard with As(III) indicates that As(III) is converted to As(V) during the extraction process. This conversion may be due to the presence of Fe and Mn. The chemical EDTA was also tested along with the phosphate solution. It was found that EDTA does enhance the extraction of the arsenic from the soil, however the As(III) appears to be converting to As(V) as time progresses. Hydroxylamine appears to stabilize the As(III) after extraction. Future work will focus on the use of complexing agents, sodium diethyldithiocarbamate and ammonium pyrrolidine dithiocarbamate.

Yong Cai mentioned that the organisms analyzed in the marine study included a wide variety of organisms including soft coral species, hydroids, crabs, barnacles, oysters, tube worms, starfish, etc… Results to date indicate that the hydroids and amphipods showed elevated arsenic concentrations for organisms collected from CCA-treated wood. Arsenic speciation standards were available for AsB, As(III), DMA, MMA, and As(V). The following species were observed within hydroids on concrete pilings: AsC, AsB, As(III), DMA, MMA, As(V), plus several unknown arsenic species. The "Old Wood Pier" sample showed similar species but at slightly higher concentrations.

<u>Questions</u>

Gene Advincula: Sea animals have high concentrations of arsenic so are they safe to eat? Are these animals resistant to arsenic?

Yong Cai: It is safe to consume seafood because the form of arsenic (AsC and AsB) found in them is generally non-toxic to people.

Gene Advincula: Have there been analyses of the employees who work at wood treatment plants?

Don Surrency: There are no adverse effects found in employees who work at wood treatment plants. I am not aware of general tests but specific tests conducted locally show no adverse effects.

Bill Hinkley: It is likely that the handyman working at home would be subjected to higher exposures because many are not aware that the wood contains arsenic. Employees at modern wood treatment plants would be educated of the dangers.

Richard Buff: The monitoring of employees at wood treatment plants would fall under OSHA. OSHA should provide recommendations for their protection.

Lora Fleming: Was a wood control included in the marine study?

Yong Cai: Yes, marine organism samples were collected from a concrete pier, a CCA-treated wood dock and from wood pilings not treated with CCA.

Lora Fleming: Concerning the occupational question, it is important to emphasize that there are not many occupational studies and more are needed, in particular those studies that focus on end-users.

8. <u>Pilot Epidemiologic Study Evaluating Potential As Exposures to Children from CCA-treated Playgrounds</u>

Lora Fleming emphasized that funding for this project was received through NIEHS Environmental Health Center (Rutgers Robert Wood Johnson NJ Medical College) and from the NIEHS Marine & Freshwater Biomedical Sciences Center (University of Miami). She emphasized that exposure routes include arsenic that is “dislodged” by touching the wood with subsequent hand-to-mouth ingestion and through transdermal routes in which arsenic is absorbed through the skin. Different species of arsenic have different toxicities. The type of arsenic in seafood is generally non-toxic. The health affects from arsenic ingestion vary from acute to chronic. Chronic low level ingestion is more relevant for playground exposures. In this case, the nervous system, dermal, hepatic, and peripheral vascular systems are most affected. In some cases this can lead to cancer. Childhood exposure to CCA-treated wood is age and behavior dependent. Children are especially vulnerable because of their developing neurologic system. Although CCA-treated wood will be phased out by the end of 2003 for residential applications, the problem is that it is currently everywhere and will likely remain so for some time. Helena Solo-Gabriele mentioned that all of the playgrounds owned by Miami-Dade Parks Department were visited to confirm CCA-treatment, with the ultimate goal of identifying one playground for the exposure study. About 13 playgrounds were visited and CCA-treated wood was confirmed through 3 different methods: an arsenic test kit, a chemical stain, and through laboratory analysis of a sawdust sample. The protocol for the wipe test has been also developed. Lora Fleming mentioned that the project has received "Human Subject Approval" from both the University of Miami and Rutgers University. The methods for exposure analysis will involve obtaining hand tracing and rinses and urine samples. Urine samples will be speciated to determine the relative contribution of arsenic from seafood versus that from other sources. A questionnaire has been developed to ask the parents of possible household arsenic exposure, demographics, and child behavior. The pilot study will consist of 10 children. Incentives are provided for participation and parents will be provided education materials and will be informed if their child is positive for arsenic exposure. The study that is currently funded is considered to be very preliminary. In order to develop conclusive data the study population would have to be increased. It is also recommended that children be video-taped to better assess hand-to-mouth behavior.

<u>Questions</u>

Bill Hinkley: Playgrounds vary in design. Was this considered when chosing the playground?

Helena Solo-Gabriele: We did not find the Leather's-type playground in Miami-Dade County. The CCA-treated playgrounds in Miami-Dade had a very similar design and consisted of CCA-treated wood posts.

Bill Hinkley: The "Dorito Effect" is interesting. It is also of interest that there are cases where children eat on CCA-treated decks. They place their food or sandwich down on the deck, play, and then return to each their sandwich.

Bill Hinkley: What kinds of pesticides were evaluated in the earlier studies?

Lora Fleming: They were organo-phosphates, not arsenical pesticides. These studies evaluated the importance of household dust and child hand-to-mouth behavior.

Bill Hinkley: Is the study designed to include the Pica child?

Lora Fleming: The project will take into account the Pica child, by default, especially given that the age group chosen for the study is in the 15 month range, in which case all of these children would have a tendency to consume soil if given the opportunity.

<u>Research Plan and Progess on "Year 7" Study focusing on Mulch and "Year 7 – RCRA Study" Focusing on Disposal Options for CCA-treated wood</u>

Helena Solo-Gabriele described the research plan on the two projects funded as part of year 7 (2002-2003) of the research project. The first project focuses on evaluating mulch samples purchased from retail stores, playgrounds, and 1 school for leachable metals and the fraction of CCA-treated wood contained within them. The purpose of this study is to document the quality of mulches sold and used in South Florida and to evaluate the adequacy of visual identification methods (i.e. presence of engineered wood) in identifying suspect mulch samples. The second study focuses on identifying disposal options for CCA-treated wood in Florida. This project will be conducted primarily in the form of a literature review.

Bill Hinkley: Is the SPLP test an indirect measure of dislodgeable arsenic?

Helena Solo-Gabriele: Samples are ground-up in the SPLP test whereas dislodgeable arsenic is affected by the amount of chemical on the surface of the wood. Each test would measure different quantities.

John Schert: The quality of the mulch may be associated with the particle size of the mulch.

Helena Solo-Gabriele: Yes, it has been mentioned to me by those in the mulching industry that mulches with a greater quantity of fines may have a higher likelihood of containing CCA.

Harvey Sneider: Iron will likely serve as a binder for the arsenic in the mulch.

Helena Solo-Gabriele: Yes. We have a proposal submitted to evaluate that possibility.

David Dee: The lysimeter II leachate exceeded the TCLP criteria for chromium. Lysimeter II simulates a monofil. This leachate would thus be considered a hazardous waste. Such a result may deter the disposal of CCA-treated wood within monofils.

Bill Hinkley: Even if the wood is disposed in a Class I landfill, the metals would eventually leach out. This will also be a problem.

David Dee: Right now it appears as though CCA-treated wood should not be burned and should not be placed in a solid waste landfill. Monofils result in a hazardous leachate. There does not seem to be many options available.

Harvey Sneider: When wood is recycled it does not necessarily contain CCA-treated wood. The presence of plywood does not necessarily indicate the presence of CCA.

Tim Townsend: Data indicates that recycled C&D wood usually contains CCA-treated wood. Recycled C&D wood also contains plywood. One of the objectives of the study is to determine if the presence of plywood is indicative of the presence of CCA. We will be able to determine the significance of the plywood only after we obtain the results of the study.