

## **Minutes of the TAG Meeting Held February 22, 2004 in Orlando, Florida**

### Attendees:

Richard Buff, Akzo Nobel Functional Chemicals LLC, Norcross, GA  
Lee Casey, Miami Dade Solid Waste, Miami, FL  
Iben Christensen, Technical University of Denmark, Lyngby, Denmark  
James Cooper, Florida Dept. of Agriculture, Tallahassee, FL  
Dave Deans, PBS&J Engineering, Orlando, FL  
David Dee, Landers & Parson, Tallahassee, FL  
Brajesh Dubey, University of Florida, Gainesville, FL  
Ross Elliot, U.S. EPA Office of Solid Waste, Washington, DC  
Fazel Faqeer, FDUT/State Mof, Gainesville, FL  
Myron Georgiadis, Florida International University, Miami, FL  
Warren Godson, Clean Air Society Aust & NZ, South Australia  
Toshimitsu Hata, Wood Research Institute – Kyoto University, Kyoto, Japan  
Lieve Helsen, Katholieke Universiteit Leuven, Heverlee, Belgium  
Jenna Jembeck, University of Florida, Gainesville FL  
Gary Jacobi, University of Miami, Coral Gables, FL  
Elijah Johnson, Florida A&M University, Tallahassee, FL  
Michelle Lersch, Waste Management Inc., Tampa, FL  
Glenn Malmstrom, Broward Cnty Dept. of Planning and Environ. Protection, Ft. Lauderdale, FL  
Jim McDonald, Orange County Environ. Protection Division, Orlando, FL  
Hugh McNeely, Simien & Simien, Baton Rouge, LA  
Daniel Mourant, University Laval, Ste-Foy, Canada  
Kazem Oskoui, West Central Environmental Consultants Inc., Maple Grove, MN  
Lisbeth Ottoson, Technical University of Denmark, Lyngby, Denmark  
Dave Renz, Akzo Nobel Functional Chemicals LLC, Norcross, GA  
Mike Retigum, Florida Department of Environ. Protection, Tallahassee, FL  
Joseph Sekerke, Florida Dept. of Health, Tallahassee, FL  
Raj Sharma, Arch Chemicals, Norwalk, CT  
Tomoyuki Shibata, University of Miami, Coral Gables, FL  
Mark Simien, Simien & Simien, Baton Rouge, LA  
Helena Solo-Gabriele, University of Miami, Coral Gables, FL  
Gus Staats, Osmose Inc, Griffin, GA  
Rod Stanley, Earthwise Mulch, Stuart, FL  
Dave Stilwell, Connecticut Agricultural Experiment Station, New Haven, CT  
Bollineni Tarakanadha, Institute of Wood Science & Technology, Bangalore, India  
Richard Tedder, Florida Department of Environmental Protection, Tallahassee, FL  
Tim Townsend, University of Florida, Gainesville, FL  
Sermin Unsal, Broward County Dept. of Planning and Environ. Protection, Ft. Lauderdale, FL  
Rick Wilkins, Broward County Dept. of Planning and Environ. Protection, Ft. Lauderdale, FL

**Agenda for TAG Meeting**  
**Wednesday, February 11, 2004, 10 am to 12 noon**  
**(Immediately after the FICCESS Conference)**  
**Location: Orlando Airport Marriott Hotel**

Introduction

1. Welcome
2. Brief History of Florida CCA Research SoloG/Townsend

Florida Center for Solid and Hazardous Waste Sponsored Research (FCSHWM)

3. Background Information Concerning FCSHWM Description of new FICCESS Center Schert
4. Review of “Year 6” Draft Report “As and Cr Speciation of Leachates from CCA-Treated Wood”
  - Overview and Solvent Extraction Study Khan/SoloG/Town
  - Lysimeter Study Jambeck/Khan
  - Groundwater Near C&D Landfills Khan/SoloG
5. Research Plan and Progress on “Year 7” and “Year 8” Studies Focusing on Mulch Jacobi/Solo-Gabriele
6. Research Plan and Progress on “Year 7 – RCRA Study” Focusing on Disposal Options for CCA-treated wood SoloG/Townsend

Research Funded through other Agencies

8. Comparison of Environmental Impacts of Wood Treated with CCA and Three Different Arsenic-Free Preservatives Townsend/Dubey
9. Research to Date for Project Titled, “Impacts of Arsenic from CCA-Treated Wood in Marine and Terrestrial Environments”
  - Arsenic Speciation in Runoff from CCA-Treated Decks SoloG/Khan
  - Arsenic Speciation in Soils Cai/Georgiadis
10. Pilot Epidemiologic Study Evaluating Potential As Exposures to Children from CCA-treated Playgrounds
  - Environmental Study Shibata/SoloG
  - Exposure Study SoloG/ Shibata

Refreshments Will Be Available.

## Transcript of Meeting

Transcripts (below) from TAG Meeting were obtained from a tape recording. Some of the information presented was inaudible due to the fact that speakers (in particular those who asked questions from the audience) may not have used the microphone.

Meeting began at 10:00 am and ended at 12:00 noon.

[Tape 1 Side 1]

*Helena Solo-Gabriele:* Welcome to the CCA Research TAG meeting. As we typically do during these meetings we introduce each of ourselves by stating our names our affiliation and maybe a word or two about our interest in CCA treated wood. So I will go ahead and get started. My name is Helena Solo-Gabriele and I am an Associate Professor of Civil and Environmental engineering at the University of Miami and I have been working on CCA treated wood issues for 8 years.

*Tim Townsend:* I am Tim Townsend, Environmental Sciences at the University of Florida. I have been working with Helena on this product for about the same time.

*Elijah Johnson:* I am Elijah Johnson, Environmental Sciences Institute at Florida A & M University. I am not looking at CCA treated wood at the moment but I have a general interest in environmental risk assessment. Also I have a strong interest in mass transport, which might be my route of entry into some of this treated wood work.

*Fazel Faqeer:* My name is Fazel Faqeer from the Florida Department of Transportation, State Materials Office. I am a metals and timber specialist.

*David Renz:* Hi my name is David Renz and I am with Akzo Nobel. I have a general interest in the wood treatment industry.

*Gus Staats:* Gus Staats, I am with Osmose Inc, which is a preservative producer.

*Daniel Mourant:* Ph.D. candidate Laval University, Quebec Canada. General interest in wood preservation also.

*Glenn Malmstrom:* I am Glenn Malmstrom with Broward Family Planning and Environmental Protection. I am a regulator.

*David Deans:* I am Dave Deans an environmental engineer with PBS & J specializing in waste management and disposal and there is my connection to CCA.

*Mark Simian:* Mark Simian from Baton Rouge, Louisiana. We have had an interest in treated wood for several years.

*Hugh McNeely:* Hugh McNeely also from Baten Rouge, Simian & Simian that interest includes consumer litigation relative to CCA in the residential place.

*Michelle Lersch:* Michelle Lersch with Waste Management Inc. of Florida, obviously you can understand our interest in this subject, so enough said.

*David Dee:* I am David Dee. I am an environmental law attorney in Tallassee. It was one of my facilities that started the problem 8 years ago and I have followed it ever since.

*Tarakanadha, Bollineni:* I am Tarakanadha Institute of Wood Science and Technolgy in Bangalore. Basically I am a toxicologist. I wanted to do a study on the evolution of the impact of different wood preservatives on target and non-target organisms.

*Rod Stanley:* Rod Stanley Earthwise Mulch, Bagger, Mulcher & trying to learn ways of getting CCA out in the public and the work place.

*Mike Retigum:* Mike Retigum with the DEP at the head quarters office for the RCRA program. I help enforce and write the regulations on waste disposal.

*Warren Godson:* My name is Warren Godson from the Clean Air Society in Australia. I am here to look at the emissions and so forth from arsine gas from CCA and so forth and also indoor gasing from treated timber.

*Toshimitsu Hata:* I am Toshimitsu Hata with the research institute at Kyoto University, Japan. My interest is thermal conversion and extraction of CCA compounds from CCA treated wood.

*Tomoyuki Shibita:* Hi, my name is Tomoyuki Shibita, Ph.D. candidate at the University of Miami. My research focuses on arsenic exposure to young children. Thank you.

*Gary Jacobi:* Hi, I am Gary Jacobi. I am a graduate student at the University of Miami and I am doing a study on the extent of CCA treated wood in consumer mulches.

*Myron Georgiadis:* Hi my name is Myron Georgiadis. I am from Florida International University. I am a graduate student there and my interest soil speciation.

*Brajesh Dubey:* Hi I am Brajesh Dubey. I am a Ph.D. candidate at the University of Florida and my research focus on CCA and other alternatives.

*Lee Casey:* Hi I am Lee Casey from Miami Dade County Department of solid waste management. We are interested in disposal issues surrounding CCA wood.

*Dave Stilwell:* Dave Stilwell Connecticut Agricultural Experiment station. I am interested in arsenic in soil and wood surfaces.

*Jim Cooper:* I am Jim Cooper, I'm with the Florida Department of Agriculture, Bureau of Pesticides and we are interested in any pesticide with arsenic in it.

*Richard Tedder:* I am Richard Tedder with the Department of Environmental Protection out in Tallahassee. I am an administrator of the solid waste section.

*Joseph Sekerke:* I don't talk that much. I am Joseph Sekerke. I am with the Florida Department of Health and I do risk assessment on the health affects of arsenic and a bunch of other things.

*Kazem Oskoui:* I am Kazem Oskoui. I am an environmental engineer. I am working on a process to extract arsenic and CCA compounds from wood. Thank you.

*Rick Wilkins:* Good Morning, I am Rick Wilkins. I am the director of the Pollution Prevention Division with Broward County's Department of Planning and Environmental Protection. As a local environmental regulatory agency we are interested in research regarding solid waste matters.

*Sermin Unsal:* I am Sermin Unsal and I am with Broward County Department of Planning and Environmental Protection.

*Lieve Helsen:* Hi I am Lieve Helsen. I am working at the University of Leuven in Belgium.

*Helena Solo-Gabriele:* And in the back we have Lisbeth Ottosen, from the Technical University of Denmark, Iben Christiansen from the Technical University of Denmark and we have one person who just walked in the back. Jim would you like to introduce yourself.

*Jim McDonald:* Hello, I am Jim from the Orange County Environmental Protection.

*Helena Solo-Gabriele:* Talking about lunch we should be having some refreshments at the end of the TAG meeting. I would like to go ahead and get started on the agenda. The agenda is given on these blue sheets here and I would like to provide a 5 to 10 minute summary of what we have accomplished so far on CCA treated wood research. I will give you a little bit of the history of the project. I also like to acknowledge our funding sources. We have received funding through the Florida Center for Solid & Hazardous Waste Management, Florida Power and Light, Sarasota County, the FDEP. We have also received funding through universities, through university centers, the National Institutes of Environmental Health Centers at FIU and at Rutgers University, and through the University of Florida - the National Science Foundation. I want to emphasize that the Florida Center for Solid and Hazardous Waste Management has been what I consider our backbone as far as funding. They have consistently on a yearly basis have provided funding for us to continue this work. I also like to acknowledge the faculty researchers on this project and it includes myself from the University of Miami, Tim Townsend of the University of Florida. We have been working together on CCA treated wood research for the past 8 years or so. As projects have evolved we have also had participation and expertise from others including Gabriele Bitton, a toxicologist from the University of Florida. Yong Cai at Florida International University has provided us with expertise on arsenic speciation. Lora Fleming of the University of Miami and Stuart Sherlat of Rutgers University who are epidemiologists/toxicologists who are the leads in the child exposure studies and David Hahn who is a laser expert from the University of Florida. I would also like to acknowledge our graduate students who have worked extremely

hard throughout the years. I have counted up the students and up to this point in this time we have estimated that 32 students have been supported on our CCA projects both at the University of Miami and the University of Florida and at Florida International University. I would also like to introduce our student presenters today which include Jenna Jembeck and Brajesh Dubey of the University of Florida, Gary Jacobi and Tomoyuki "Shiba" Shibata from the University of Miami and Myron Georgiadis from Florida International University. And for those of you who were here yesterday, there is a little bit of repetition here, but I would like to iterate the original motivation for the project as David Dee mentioned in the back that this whole issue was brought to the for-front due to an ash disposal problem associated with wood co-generation plants predominately located in the central portion of the state which burn bagasse which is a by product of sugar cane manufacture to produce electricity. Once these facilities began accepting recycled construction and demolition wood they started getting high concentrations of arsenic and chromium within their ash which then raised awareness of the CCA treated wood issue. Back in 96-97 we were funded through the Florida Center for Solid and Hazardous Waste Management to determine how CCA treated wood was disposed within the state. Tim's group went to 13 or so recycling facilities throughout the state collecting mulch samples that were either being sold for mulch purposes or as wood fuel and found that on average 6 percent of the CCA in those piles, 6% of the wood in those piles were in fact CCA. Subsequent work since this time has not only confirmed this but indicated that the percentages may be higher. Also early on we were interested in determining how much material was being disposed. This is an updated forecast in comparison to what we provided earlier, but what the forecast indicates is that in 95 we were roughly at this point in the disposal forecast and if we were observing problems in disposal in 95 we anticipated that the problems were going to escalate and spike at around 2008 or 2010 given this particular model. Now given the phase out, we will be probably going back down to similar levels as in back in 1995. That brings us to year 2 of the research. Year 1 we identified the problem, we identified how it is being disposed, the quantity that was being disposed, in year two we were interested in coming up with solutions to the problem. And again our original motivation was an ash disposal problem. We thought well perhaps disposal through incineration is allowable as long as the ash that is produced as part of the residual does not exceed TCLP or is not characterized as hazardous waste. We therefore conducted a series of experiments to determine what mix of treated vs. untreated wood would just past TCLP limits and it turns out that you could just have 5% CCA wood and 95% untreated wood and be right at the boarder line for failing or exceeding hazardous waste criteria. Also during this time we worked with some solvents to extract the metals from the ash, at that point we observed that citric acid worked very well, but given the talks yesterday it seems that oxalic acid may be a better acid to work with. Also during year two we recognized the need to be able to identify treated wood in the disposal sector so that we could assure that a 5% maximum within the wood fuel stream or to assure that the material is removed from mulch for example and at that point in time we began working with technologies including the use of chemical stains to identify the difference between treated and untreated wood with x-ray technology. Since these first two years the projects have evolved and we have received funding from other sources and therefore I have organized the work in terms of two major issues: the first is in-service issues and second are disposal issues. Our historical work on in-service impacts focused on collecting samples of soils below CCA treated structures. These included collecting surface soil samples and cores samples. Results from these samples showed that CCA treated wood structures impact the soil below them. You can observe the elevated levels at the surface, in particularly at the surface portion of

the profile and you can see impacts down to a depth of about 8 inches. That project is completed and the other in-service projects are on going and we will be discussing those as we proceed on in today's presentations. That brings us to disposal issues and I would briefly like to describe work focusing on chemical alternatives as a means of waste minimization, sorting methods and leaching of new and weathered wood. As far as alternatives to leaching, work was done in Tim's lab in collaboration with Gabriel Bitton and what we found with the alternatives, the most common alternative being ACQ, currently on the market, and copper azole - these alternatives although they don't leach arsenic they do leach more copper than CCA indicating that copper releases maybe of concern in particular with respect to aquatic environments because copper is very toxic to aquatic organisms. This brings us to the sorting work which I would like to describe very quickly. Again we had our work with the stains. The stains are specific to copper and not specific to arsenic. We are currently working on methods to identify arsenic specifically in an inexpensive fashion. We have been working with tests kits that are specific to arsenic it takes about 45 minutes to process a sample. More automated methods that can identify, for example the laser can identify chromium very quickly within a fraction of a second in treated wood and x-ray technology which can identify chromium, arsenic and copper within a fraction of a second. The original x-ray unit that we worked with a couple of years ago was very bulky about 25 pounds in weight and they now have these new units that are hand held, small compact and easy to carry around. And we have done some pilot work with them, evaluating them both at the recycling facilities and evaluating playgrounds and we have found that they are outstanding pieces of equipment. They can very quickly analyze 15 different metals but they are very expensive. They are on the order of 30 -40 thousand dollars apiece. As far as the leaching work, the leaching work that has been completed - It has focused on evaluating new wood and used wood. This graph shows that statistically the amount of arsenic leached from used wood is very similar to that of new wood and that both new and used wood consistently failed the TCLP limit. So if there was no exemption at the federal level, exempting CCA treated wood from being characterized as a hazardous waste, it would be disposed as such but we have that exemption. So that is a very brief history. We can open it up for quick questions at this point in time.

*Joe Sekerke:* What is instrument are you using for the X-ray fluorescence?

*Helena Solo-Gabriele:* The instrument that we are using is a manufactured by Niton out of Massachusetts. It is an XL series, they have various model.

*Helena Solo-Gabriele:* At this point in time I would like to go ahead and discuss the status of our most recent report. This report is available on the web. We are accepting comments on this particular report through February 22<sup>nd</sup>, ten days from now and the title of the report, our most recent work is "Arsenic and Chromium Speciation of Leachates from New and Weathered and Treated Wood." And this particular presentation will be series of three different presentations and I will go ahead and start it. The purpose of the study evaluating arsenic and chromium speciation was to quantify the amount of releases in terms of species from CCA treated wood. The reason we were interested in that is because the toxicity and mobility of different species is significantly different and therefore assessing the impacts and toxicity of the wood would require evaluation of species. With respect to arsenic the most common species that are observed range from a valence of negative three to plus five and within the study the valances that we evaluated were predominantly the plus three and the plus five. There are two forms of inorganic arsenic, as

plus three and plus five. Arsenic three versus arsenic five: the toxicity and the mobility of arsenic three is greater than that of arsenic five. In addition to that other species that we have observed in the samples include organic species, including MMA or monomethyl arsenic acid and DMA, dimethyl arsenic acid. When it comes to toxicity and mobility, the inorganic forms are more mobile and toxic and the toxicity of the organic forms is typically lower than that of the inorganic forms. When it comes to chromium, the most common species that are observed in the environment include the plus six and the plus three species and also zero as a metal, but within our studies the plus six and plus three were the most relevant. Both of these are inorganic forms of chromium with chromium six being more toxic and mobile than chromium three. The methods that we utilized for speciation for arsenic included one of two methods both of them included HPLC, high performance liquid chromatography. In one case it was HPLC – ICP-MS, and in the other case it was HPLC, hydride generation atomic fluorescence spectroscopy. Chromium six was analyzed by ion chromatography and total chromium was determined by ICP - atomic emission. Chromium three was determined by difference from the total chromium and the chromium six. As far as the solvent extraction study is concerned, again in the solvent extraction study we evaluated two different types or classes of wood: one is new wood and weathered CCA treated wood. Within the new wood we evaluated several retention levels and within the weathered wood, the weathered came from several different applications in use, applications including utility pole, fences, playgrounds and so on. Each of these samples were subjected to a series of solvents. The solvents included solvents of various pH ranges, ranging from 1, 2, 3 all the way up to 14. Solvents also included TCLP solutions, SPLP, de-ionized water, rainwater and seawater. The general test involves a contact time, besides reducing the sample, the contact time of 18 hours and after the contact time the leachate was separated from the waste, and then that leachate is analyzed. As far as the pH experiment is concerned, these are the results for the weathered wood sample, we also have results for the new wood sample as well. And what we found in the weathered wood sample and also in the new wood, was that the largest amount or the highest concentration of arsenic released from the samples correspond to the extreme pH ranges. Also of interest in this particular pH experiment, we did not observe arsenic three in the new wood, but in the weathered wood we did observe arsenic three being released up to a pH of about nine. Also of significance is the concentration of the releases within the typical environmental pH range, arsenic releases were on the order of about 5, or a little bit higher than five milligrams per liter exceeding TCLP limits. These are the results from the SPLP study and again what the data show is the release of arsenic three from the weathered wood or in higher concentrations or higher relative portion to that from, in comparison to that from the new wood. Also it is difficult to evaluate given the small number of samples that we have, but what the data suggests is the amount of arsenic being released from the weathered wood at a given retention level maybe higher than the amount released from the new wood. So for example, we have a weathered wood sample here of 24 kilogram per meter cubed and here we have another new wood sample of 24 kilograms per meter cubed and a total amount of arsenic released from this sample is higher than this sample. Even more so than a new wood sample of high retention levels of 27 and 46. Also what we found of interest with respect to the solvent extraction study is that the total releases of the arsenic for the new wood, the way in which it was released was different than patterns of release for the weathered wood. For the new wood there seems to have been no relationship between the amount of chemical released and the retention level of the wood. It seemed to be more sporadic. But one thing we did observe from the new wood is apparently the seawater solvent extracted less arsenic than the other solvents such as the SPLP,

and rainwater and the DI-water. So in that case we were able to observe that difference. But the weathered wood showed a particular pattern where the amount of arsenic released seems to be proportional to the retention level with higher or larger concentrations of arsenic in the leachate solution with higher retention levels. This brings us to chromium, so I have been discussing arsenic up to this point in time. The chromium results are similar to the arsenic results in the sense that we have the highest amounts of chromium released at the extreme pH levels at low pH and high pH. Also very interesting with respect to the chromium is the occurrence or the observation that chromium six is observed at high pH values. So there is a tendency for chromium six to form or to be converted over at the high pH values. The concentration of the chromium in the solution within the environmental pH ranges are on the order of 1 mg per liter here. Continuing on with chromium with respect to SPLP, these are retention levels at the bottom, and identification of the different samples. We didn't see a clear relationship between retention levels and chromium concentration in the leachate, in particular with the unburned wood. Now with the burned wood we had some very strange results. Essentially what we were observing with the burned wood, especially when we were only evaluating the total chromium, when we had very little chromium in our samples we had a lot of chromium leaching in the burned wood. We were getting the opposite of what we expected. When we had a lot of CCA in the sample and we would burned that we would get very little chromium leaching off the sample. And it wasn't until speciation was conducted that this became more apparent. Apparently what happened is the conversion of chromium from chromium 3 to chromium 6 is highly pH dependant and if your wood waste is acidic and the CCA solution is acidic, so if you have a lot of CCA chemical in your wood, such as the high retention level, 2.5 pcf is a highest retention level, it has a lot of CCA chemical, therefore the wood itself is acidic so you are going to get relatively little chromium leaching off. But if you have little of the acidic CCA solution in your wood sample the pH of the wood is higher, but this results in a conversion of the chromium from a form that is essentially immobile to a form that is very mobile, chromium six. And therefore this is the primary reason for the higher concentration of chromium coming off the samples that have relatively low total chromium concentrations. So what we found was that low retention level wood leached much more chromium than the high retention level wood.

*Question:* Inaudible

*Helena Solo-Gabriele:* I don't recall if these are TCLP or SPLP results. But part of the process requires that you start out with a solution set at an initial pH. But then due to the chemical characteristics of the ash that pH will adjust itself throughout the duration of the 18-hour extraction period. And these pH values correspond to the pH at end of the extraction period.

*Question:* Inaudible

*Helena Solo-Gabriele:* Yes, so in summary, I want to mention as far as solvent extraction work is concerned, that arsenic and chromium species leaching is pH dependant. At the environmental pH range of 6 –10, the amount of arsenic released was on the order of 5 milligrams per liter whereas for chromium it was on the order of 1 milligram per liter. We also observed enhanced leaching of arsenic from weathered wood and this is presumably due to the presence of arsenic three, which is again more mobile. The observed arsenic leaching in rainwater, TCLP, SPLP was comparable, and however in seawater the amount of arsenic leaching was less. And also with

respect to incineration the chromium results are very important because of the conversion of chromium three to chromium six in particular for samples that contain lower retention levels of wood. At this point I would like to open it up for questions and if Jenna can start converting over. Any questions.

*Question:* How possible is it that the carbon in wood is acting as a reducing agent in forming arsenic plus three?

*Helena Solo-Gabriele:* Very possible and I think Lieve Helsen is our expert in the chemistry and the fundamentals of the conversion process and it is my understanding that it does. Any other questions? Yes, Joe.

*Joe Sekerke:* Is there any way to determine if the weathered wood had a higher arsenic content than the amount specified. You did say that for some of them you did see higher values than the content that had been specified.

*Helena Solo-Gabriele:* That is an interesting point because sometimes we would buy 0.4 pcf wood at the store or 0.25 and you bring it back and you analyze it and it is not consistent with the retention level that is claimed at the store. Actually we have gone out to buy CCA treated wood and we have gotten ACQ treated wood when we come back and analyze it. So trying to keep track of retention is a challenge and we do analyze, once we bring the wood back we do analyze for the retention level. So the retention level that was reported in the solvent extraction study is the measured value, but when we name the sample we name it based on the retention level specified at that store, which is a little confusing.

*Question:* If there is a higher concentration [inaudible].

*Helena Solo-Gabriele:* We looked at the retention level, we don't know the initial retention level of the weathered wood but we can measure the retention level once we have the wood in the lab after it has been weathered. And we do observed that he arsenic leached from the weathered wood. In general, the data suggests that we need more samples, more data points. But the data suggests that the weathered wood at a given retention level leaches more than the new wood. And we believe it is because of the decomposition of the wood and the conversion of the arsenic to a more mobile form.

*Question:* This is different than what Stan Lebow showed.

*Helena Solo-Gabriele:* Yes, yes Stan Lebow. But the question was asked whether or not that was based on experimental data and he did not have experimental data to back that up so it maybe based on some other studies or his long-term work with it. But we are seeing the opposite. Any other questions. Ok Jenna.

*Jenna Jambeck:* I know I have a strict time limit, but I wanted to say one thing quick and that I think this should be the last TAG meeting that I am presenting at because I am graduating soon. But I wanted to say what a pleasure it has been to work with everyone and thank everyone that I worked with especially Dr. Townsend and Dr. Solo-Gabriele for being wonderful mentors and

examples to me. So I am going to talk about the arsenic leaching specifically the speciation in this report from my disposal scenarios. The second thing that I want to do is acknowledge Bernine Khan who actually performed the arsenic speciation work and has graduated with her Ph.D. at the University of Miami. She also composed this picture at a different schematic in my presentation yesterday. But without some simulated landfills and this is a catchment basin for natural precipitation or potentially added de-ionized water if needed. We had 20 feet of waste in here and some drainage material at the bottom to collect the leachate and a port at the bottom where I was able to collect the leachate for analysis. We had three different scenarios: a wood monofill, a C&D waste scenario, and an MSW waste scenario. The wood monofill had a 100 percent CCA and a control lysimeter with no CCA and completely untreated wood. The C&D scenario had a mixture of C&D waste with no CCA and 10% CCA by total weight in the experimental lysimeter and then in the MSW scenario we had a control lysimeter with untreated wood and then 2% CCA. I am going to talk about the total concentrations first which we analyzed for and I presented yesterday and some of the questions came up about comparing some of the scenarios and what I did last night was really quick back-of-the-envelope calculation and I know that Dr. Solo Gabriele looked at this as well in the speciation report but the experiment continued a little bit further and a total of 1.6% of the arsenic of this lysimeter leached during this time period which corresponds to a rate of 0.8% leached per year. And it was on the order of about 40 to 60 milligrams per liter. For the C&D lysimeter the concentrations ranged one to four milligrams per liter. A total of 1.1 % of the arsenic that was available from the CCA leached and that corresponded to a rate of 0.9% per year. So it was a pretty similar rate and as you can see, there is an impact of CCA disposal compared to the control lysimeters. For the MSW scenario as you can see this large leaching of metal at the beginning corresponded to a low pH at the beginning of the scenario, during the volatile fatty acid forming stage of landfill degradation. And what I did was calculate two rates here, this is not necessarily the way it should be done, but for the first five samples rounds since we had such an extreme change here 1.1% of the total arsenic that was available leached during this time which would correspond to a rate of 5.6% per year and during this more consistent time another 1.2% of the arsenic leached and that corresponded to about 1.2% per year. So a total arsenic in the MSW that leached was 2.3%. Now it seemed a little bit more aggressive than the study of the other scenarios however since there is such a small percentage there in the first place we get lower concentrations, a least at this point where you have reached pH stabilization. Ok on to the arsenic speciation, here is the arsenic species in the control lysimeter and here is the arsenic species in the experimental lysimeter and this is for the wood monofill as you can see you have arsenic 5 and arsenic 3, higher in the experimental. Here is the C&D scenario, the control again some more organics here and then more of the arsenic 3 and 5 in the experimental. And of course the difference in the total amount, and this is total amount leaching, cumulative arsenic. And MSW, again some organic some arsenic three, in the control here we have more arsenic 3 and arsenic 5 and so in summary here is a photo of the actual lysimeters with the catchment basins and the 20 feet of waste and leachate was collected here. In the untreated lysimeters, we had relatively low concentrations of arsenic and primarily they were in the organic form, and I mean they actually very low, and comparatively we definitely had impacts from the co-disposal with the CCA and we saw arsenic 3 and arsenic 5 in the CCA monofill and then I think primarily arsenic 5 in the C&D waste but both arsenic 3 and all four species were prevalent there and then in the reducing conditions of the MSW primarily arsenic 3 but again all the different species. I think that is it. Are there any specific questions for me.

*Question:* Comparing the C&D and the municipal waste you said there was a 120 milligrams of [inaudible speech].

*Jenna Jambeck:* Say that again,

*Question:* Did 120 milligrams of total arsenic in C &D....

*Jenna Jambeck:* Were you looking at cumulative graphs or when I when I was just giving the percentage numbers?

*Question:* You said [inaudible] that it was 10% in one and 10% in the other of the [inaudible] the numbers are high but it seems that you are getting a lot higher percentage in the municipal waste than you did [inaudible]

*Jenna Jambeck:* Yes, it was 2.3% of the total arsenic that was in the CCA in the MSW leached over the time period that the experiment was operating. For the C&D it was only 1.2% or 1.1% so it was about double. So does that seem right. Anything else?

*Helena Solo-Gabriele:* Ok I would like to go to discuss the last chapter, the last results chapter of that particular report. And that particular report ended, as far as the results section focusing on ground water analysis from Florida C&D landfills. The purpose of this work was to determine if arsenic concentrations in ground water near C&D facilities were elevated beyond that from background concentrations, and also to determine the species of the arsenic. A total of 21 C&D debris facilities were visited. This did not include the entire list of C&D facilities. We did not go to facilities where the landfills were undergoing enforcement action, those that were exceeding concentrations of whatever contaminants in their ground water wells and therefore were being fined or undergoing some sort of litigation with the FDEP. And therefore these 21 C&D debris facilities are what I consider to be the facilities that are in the middle of the road with respect to the C&D landfills within the state of Florida. At these 21 facilities a total of 23 background samples were collected and 48 samples were collected from compliance and detection wells. As far as the results from the background samples, the background samples were typically, in general typically very low. We have two lines here, one corresponds to the speciation analysis and the other one corresponds to what the commercial lab obtained. We physically went out or the landfill consultant would go out collect samples for us and they would collect their sample and analyze it in the lab for compliance purposes and then they would provide us with a second sample for our speciation analysis. So the purple line corresponds to their results and our results which is the sum of the speciation is given by the data in blue, but overall the data in the background wells tends to be very close or near detection limits, overall average arsenic concentrations were on the order on seven micrograms per liter with the exception of this particular set of samples here. This compares with Florida ground water background concentrations which was obtained from an independent study conducted by the U.S. Geological Survey which found that on average the background concentration of ground water in Florida is on the order of 2 micro grams per liter so they are within the same order of magnitude a little bit higher. Statistically given that we are so close to the detection limit, it is very difficult to show. As far as compliance and detection wells, again the majority of the landfills the concentration of

arsenic within the compliance and detection wells were very close or near detection limits. We had three landfills for which the concentrations were elevated. The first landfill the background well, the corresponding concentration of arsenic in the background well was also high so the arsenic that was observed in the ground water well could not be attributed solely to the C&D landfill. Apparently there is another source of arsenic that is impacting that particular site. The second landfill showed elevated arsenic concentrations. Unfortunately on that particular day the background well was not functioning properly. The consultant couldn't pull water out of it. And so there was no background well sample available for this particular landfill. In the third one, this third one is the only one for which the concentration in the background well was also low, where as we see elevated levels of arsenic in the compliance and detection wells. So in this particular case the arsenic observed in the ground water could be attributed to the C&D facility. As far as speciation is concerned, the speciation was very interesting in comparison. For the well that had an elevated background concentration we found that those particular samples were different with respect to speciation from the others in that we saw also elevated levels of MMA which suggests that perhaps that there is an alternative source. Arsenical pesticides are used in the State of Florida. The arsenical pesticide that is used in golf courses and railroad rights-of-way includes MMA and perhaps given the speciation it may suggest some alternative source of organic arsenic impacting this particular facility. Again the second elevated levels are primarily arsenic three but there was no background well associated with it and then the one landfill that had low background concentrations we see speciation primarily in the inorganic forms, arsenic 5 and arsenic 3. Again indicating that perhaps speciation may provide us with some additional clues as to the ultimate sources of the arsenic at the ground water wells. So in conclusion I would like to summarize that the average concentration of arsenic in the background and compliance detection wells range from about 7-10 micrograms per liter. This is in comparison to the Florida background ground water concentrations for arsenic which is on the order for 2 micrograms per liter. We saw that depending on the landfill you get different species predominating. The results suggestive in that some arsenic contamination maybe occurring from the C&D landfills but the data is not statistically robust. Also it is important to keep in mind that it takes time for arsenic to leach out of C&D landfills, assuming that it is in the wood, it is going to take a long time for it to come out. And although we are not seeing statistically robust data now showing that "yes" there is contamination, it maybe just a matter of time before we start seeing that so we have to be very cautious. Any questions?

*Question:* I have got a couple of comments on this. First of all, is that when you are sampling these wells, these monitoring wells, did you sample them, at the water table depth? Do you have any data for the water table depth because that is very important. Because if the water table depth is low therefore you are going to get high concentration and if the water table is high you are going to get a very low concentration because of the dilution affect. That's one point. The other point is that do you have any idea what went into those landfills, any estimation or whatever. Because in most of them you are saying that there is not much detection, but was there anything there to start with? And third one is water gradient and the water velocity, the aquifer gradient and velocity. How fast is the water moving in the aquifer? There are means of doing those things. We can measure those things and it will dictate what is going in [End of Side 1 Tape 1].... And the third, the last one is that is that arsenic in the form of DNAPL, in other words is it denser than water. It sinks. I am not sure but I have to get that. But if it is a DNAPL, then you have to check the depth of the well. How deep did you go to measure that? Because sometimes

with DNAPL most of the concentration just drops down to the bottom of the aquifer and then the type of aquifer is also important. The first aquifer was the main aquifer. These are important things to actually if you want to evaluate what the level of contamination of the aquifer is in that area. We can help on those.

*Helena Solo-Gabriele:* I think the point of the water level depth is a good one. The wells, the location of the wells are identified by the landfill operators in conjunction with the FDEP and in some cases there were, usually the wells were at one elevation and in some cases depending on the geology of the area they may have had wells screened at two different depths. But also obtaining data on the water level as well to see how, to see what the difference is between the actual measurement depth and the surface of the water is a good point. And also the issue of gradient and velocity, we had that data for multiple wells perhaps you can get an estimate of how fast the water is moving if we have information on the geology of the area. And also the issue of dispersion of where the wells are located, these wells are located very close to the base of the landfill. They are on the property of the landfill owners. I believe they are on the order of about 50 feet from the base of the landfill. As far as DNAPL, non-aqueous phase liquids, it's my understanding that landfill leachate has the same density as water and so I would not expect it to  
....

*Question:* I am not sure [inaudible]. If it is dissolved then you do not have any problem. [inaudible]. Also the well screen, how big is the well screen.

*Helena Solo-Gabriele:* It is an interesting point though. I mean your comments give me some ideas as far as perhaps taking one, well you can't do it for all of them, but maybe taking one landfill and evaluating it in more detail with all the hydrology and well configurations and so on. This may be of interest.

*Question:* It is a complicated process that [inaudible].

*Comment:* What I think you have here today is purely raw data and you do have to do exactly that and put the data into a model. For the landfills where you did not see any arsenic or any decrease in arsenic you should go back and say how old is the landfill, how fast is the groundwater traveling. If it is in the ground water, do I need to expect that it will get into the well in the period of time that it has traveled. For the wells where you have high spikes, I have some experience in North Florida, of trying to collect groundwater samples at landfills, there's a very clayey geology up there. When I had an upgradient well that is dry my downgradient well is usually pretty muddy and I get a high turbidity sample and that makes it just about useless [inaudible] We've had some droughts too. So the data you have should be actually considered as raw data and you do have to put it back into the very site specific setting and analyze it in that context.

*Helena Solo-Gabriele:* Yes, I agree, I think that would be very helpful. Addressing the issue of the high turbidity, we went out at the beginning of the project, we went out and tagged along with the consultants that collect the samples and they have very stringent criteria that they need to follow as far as FDEP sampling criteria, as far as the rate at which the water is pumped and its turbidity limitations and so on. So we received that information as far as turbidity, conductivity,

and so on. There is a lot of data that they are required record and I don't suspect that turbidity is a problem here. I think that may have been a problem with the one landfill that we couldn't get a background well sample for. A turbidity issue there. Yes.

*Question:* [Inaudible]

*Helena Solo-Gabriele:* The focus of this particular study was to speciate the arsenic and we did not look at the data as far as other metals. But that data is available and would be worthwhile. Perhaps any more in depth analysis of one particular landfill to see what is happening. Also it is easy to evaluate the other metals for the other landfills as well so maybe a more comprehensive look at that would be worthwhile. Yes

*Question:* I guess that I am just curious. Were these wells not placed with regards to the direction of water flow in the specific [inaudible].

*Helena Solo-Gabriele:* It is my understanding, and I know Richard Tedder can speak to this better than I can, but it is my understanding that they are required to have a background well. They have to do a site assessment ahead of time to determine the direction of ground water flow and they put a well on the upstream side to represent the background well and then the compliance and detection wells are on the downstream side. Yes.

*Question:* They are placed by a PG?

*Helena Solo-Gabriele:* By a Professional Geologist. Yes.

*Question:* How do you [inaudible] of the rule making possibility that Mr. Tedder has a technical advisory group who is meeting and is undertaking that data that is being looked at as part of the rule making process, for background for the potential rule-making. The research is going on at the same time [inaudible]. I don't think that we Richard or Bill or anybody is planning on doing any rule-making with all the data that you have.

*Helena Solo-Gabriele:* Just to reiterate this is just one set of data. There is a significant amount of additional data that is being evaluated by a committee that's been set up through the FDEP. Any questions? I would like to proceed into our discussion on our results focusing on mulch which we call our year 7 - year 8 studies. And early studies have shown that recycled construction demolition wood from facilities throughout Florida have had elevated levels of arsenic, chromium and copper and contained CCA. As a consequence we received some follow up funding to collect additional samples of mulch. These samples were collected from retail stores, from stores where you pick them up or from nurseries or from residential areas that already have the mulch in service. And during year 7 our focus was on samples collected from south Florida and during year 8 it was on the rest of Florida.

*Gary Jacobi:* This here you can see is the problem. It would normally be a very good idea to recycle C&D wood and make it into mulch. That way you could even buy mulch cheaper but the C&D wood does have CCA wood in it and without any form of sorting it ends up getting into consumer mulches. What we did, we just said, we went through South Florida and then through

the rest of Florida. We collected these samples from large stores like Home Depots to small nurseries to even playgrounds and parks. And we took these samples and we broke them up into four sub samples for visual inspection, size distribution, ash analysis for total metals and SPLP analysis for leachate. And I am mainly going to speak about the ashing and the SPLP analysis. But I am going to mention the visual inspection a little bit because we can see how easy it would be for consumers to possibility spot mulch that may have arsenic in it. First of all we will start with the ashing result. Out of 20 samples 14 were colored and 6 were non-colored. Of the 14 colored, 6 were positive for arsenic and 8 were not. And of the non-colored only 1 was positive for arsenic and 5 were not. Now you will notice which is good for the visual inspection all 6 of the red samples that were positive for arsenic did contain some form of engineered wood. Now this is the concentration range for the sample. You can see how there are many samples that have high concentrations of arsenic. And many of these samples came from playgrounds and parks. And this is just a graph that shows the correlation between the chromium and the arsenic for the ashing sample. Now moving on to the SPLP results, we have out of 32 samples, 17 were colored and 15 were not colored. Of the colored, 8 were positive for arsenic and 9 were not. And then of the non-colored 5 were positive for arsenic and 10 were not. And you will notice again, all 8 of the positive samples that were red colored had engineered wood which would be good for the visual inspections. This is another graph of the concentration range of just the SPLP results and you can see that there are many results that have high concentrations of the arsenic. And again many of these came from playgrounds and parks. Here is another graph of the arsenic vs. chromium, the correlation for the chromium and arsenic for just the SPLP analysis. And in conclusion 28% of the engineered wood was found in consumer mulches in Florida and 35% of these had arsenic. With the SPLP test 37% leached arsenic and 26% of these were above 50 micrograms per liter.

*Helena Solo-Gabriele:* And just to mention a study that is currently ongoing as well as part of the year 8 study. We are looking at the affect of iron oxides on the leachability of the metals of the CCA treated wood. We have in the back untreated wood, uncolored and colored, we have treated wood, colored and uncolored, and in the front we have a mixture of treated and untreated wood, colored and uncolored. But we recently initiated that study in January. Are there any questions?

*Question:* [inaudible]

*Helena Solo-Gabriele:* What we are looking at here is ..

*Comment:* Ok, I am not saying [inaudible]

*Helena Solo-Gabriele:* No this is even newer than the other work so we have not yet written it up.

*Question:* [inaudible]

*Gary Jacobi:* I don't remember any. I can confirm that later on though, but I don't remember any that had engineered wood that did not leak arsenic.

*Question:* [inaudible] total arsenic

*Gary Jacobi:* With the ashing I believe we did.

*Comment:* These estimates of total arsenic are acting [inaudible] are really not in part with the [inaudible] ashing process [inaudible].

*Gary Jacobi:* Yes, eventually yes.

*Question:* [inaudible] What concentrations of arsenic are found in mulch that is found in [inaudible]?

*Gary Jacobi:* Up to almost 200 milligrams per kilograms with some of them.

*Question:* Milligrams per kilograms, but I mean in what percentage? [inaudible].

*Gary Jacobi:* I don't have any off the top of my head, percentages, but most of the samples from playgrounds did leach quite a bit of arsenic.

*Helena Solo-Gabriele:* I would like to go ahead and proceed to discuss a project that we have initiated. We have written a very rough draft report but it is not yet available and the title of the project is, "Management and Disposal Options for CCA-treated Wood Waste." The purpose of this project is to prioritize feasible management and disposal options for CCA treated wood in Florida. Ideally the approach is to not conduct additional laboratory work, not collect additional data, and just look at the data already available in the literature. The intent is also to use the information gathered at the conference that preceded this TAG meeting as a way in which we can start identifying what, recommending options for disposal for the State of Florida. There are many options that are available. These options include the traditional demolition process where you have the commingled C&D waste which may go to an unlined landfill or continue on for recycling purposes. For the wood that is recycled - there is various options available for it and to evaluate which one of these pathways are feasible there is also the possibility of sorting at the source and then what is the ultimate disposition of the material. Given the information that we have received at today's workshop, earlier during the conference, it appears as if landfilling and waste-to-energy and incineration maybe the ways to go. The relative distribution of that is yet to be determined though. So that is a report that is coming, if anyone has questions.

*Brajesh Dubey:* Good morning everybody, since the last few days we have been talking on CCA and alternatives and it has been pointed out by various experts that we don't have much information on the alternatives. So this research which is going to focus on alternatives and it will compare CCA with alternatives under similar settings. The research will focus on four preservatives, one is CCA, ACQ alkaline copper quaterline, CBA, and DOT, which is sold in Florida has EnviroSAFE Plus. The objective of this research is to compare and contrast the potential environmental impacts of CCA treated wood with that from the wood treated with ACQ, CBA, and DOT. Three specific scenarios will be evaluated, one is the impact on soil and this will be done using a deck study, the second scenario is the impact of pressure treated wood on natural aquatic systems. And the third one is the impact of pressure treated wood on disposal

and MSW landfills. In the first scenario which is the deck study, I have a deck built up and it will have, it will be on soil in a control environment and the leachate will be subject to natural precipitation and the leachate will be collected at the bottom and will be characterized for preservatives components. And I will also have an element for collecting run off at the top which is not shown here on the sketch as well as the soil. At the beginning of the experiment, will be characterized and at the end of the experiment the soil surface samples and the core samples will be analyzed for the preservatives components. In the second scenario as I mentioned it will be on the impact on natural water bodies. It will be something similar to the AWWA block test. It will have treated wood blocks and natural water collected from different parts of Florida and the leaching will be studied. And the main focus of the study will be to see how the different water bodies will affect the leaching of copper, like whether the copper is bioavailable or not. In the third scenario the leachate characterization will be done for the heavy metals and the leachate produced from co-disposal of pressure treated wood with municipal solid waste. There are two different approaches for this one is to leach the treated wood with landfill leachate like we do the TCLP. Rather than using the TCLP leaching fluid, we leach the sawdust with the landfill leachate. Similar results I have presented in the poster in the conference before which was focusing on CCA treated wood. So this is kind of the result we got for the CCA. The CCA one and the CCA two is the new wood and as you can see here the TCLP leaches more compared to the MSW and similar for chromium. And if you look at the other treated wood with the ACQ and the CBA for the copper, we see the MSW leaches more copper. And in MSW leachate we saw the leaching of copper more compared to the TCLP. And the second approach which is going to be a simulated lab scale lysimeter study which will have MSW, treated wood co-disposed with MSW. And these columns will be set up in the lab in a water body to control the temperature so that the microbial activity doesn't get affected by the wood. In the field, the temperature in the landfill is controlled by the surrounding waste. This way the temperature of the waste in the lysimeters can be held to values that are typical of landfill conditions. Any questions?

*Helena Solo-Gabriele:* Just to go over the agenda. Under item number four there is already a report available on the web. That is the speciation, chromium and arsenic speciation of leachates from CCA treated wood. Under item number five which is a mulch work, this is a work in progress, we are not done with work, but a report will be available I would assume within 8 months, 8-10 months. Under item number 6, that is more of a literature review and recommendations for the state of Florida. There will be a report posted as well I would assume within a few months. Item number 8,9, 10 are different from each other in that our reporting requirements are different in that we are not required to necessarily prepare interim reports or post the information on the web. The way in which those projects are evaluated are based on manuscripts that are submitted so our focus is to, under items 8,9,10, is to prepare journal articles which will then be available, but of course when it comes to the journal review process it takes time in order for the material to go through that particular process. So Dubey's work is a work in progress, it will be available through his Ph.D. dissertation earlier, but the ultimate objective of that work is to develop journal manuscripts. Under item number 9, this project focuses in on arsenic speciation, it is funded by, it is synergistically funded through the Florida Center but also through the National Institute of Environmental Health Sciences with a subcontract through Florida International University and again under item number 9, which is the item I am going to cover now, it focuses in on arsenic speciation. The goal is to look solely at arsenic speciation. We have evaluated arsenic speciation in deck and fields scale decks, but also developed

techniques and technologies which Myron will describe in a few minutes on how do you speciate arsenic in soil, from the solid medium. What I would like to iterate Jenna's acknowledgement. All the arsenic speciation work was conducted by a Ph.D. student who has just recently completed her work, Bernine Khan. And I am here summarizing the work for her and also I want to acknowledge the assistance obtained through Yong Cai's laboratory at Florida International University. We're about 20 minutes from each other. And she would take samples, she would drive over to FIU to run her analysis there. So the original motivation for the deck study came from our early work looking the impacts of CCA treated structures on the soils located below them. This early work resulted in this particular profile where we had high concentrations of arsenic near the surface of the soil and then a decrease as you proceed downwards. One of the interpretations of this profile was that all the arsenic is being retained in the soil and none of it is passing through. And we were concerned about that interpretation. We were interested in determining with certainty whether or not arsenic is making its way down through the soil profile. So we set up a series of field scale experiments, these are 6 by 6 foot decks located in what we call "sand boxes." We have 2 sand boxes. One sand box for CCA treated wood and one sand box for a deck constructed of untreated wood. The samples that we collected from these decks include surface run off samples that are collected before they come in contact with the soil. The remaining run off flows into the soil and then ultimately down through a drainage collection system where we also collect the samples of the infiltrated water. As far as what is happening at the run off at the surface, the water that does not touch the soil, what we observe is that early on during the project, during the first few months we see a lot of variability in the arsenic releases. We get concentrations of arsenic in the run off in the order of milligrams per liter with occasional spikes of the order of 2 or maybe even up to 8 milligrams per liter. Whenever we see these spikes, these spikes are not correlated with rainfall events and they are not correlated with seasonal conditions. What we do observe is arsenic 3 coming off in correlation with these spikes. So there is something going on in the chemistry of the wood that makes arsenic more mobile that converts it over to the more mobile form. Perhaps there is checking of the wood, wood cracks open making other areas of the wood that were not previous exposed, exposed. After this initial time period of variability the concentrations of arsenic in the run off seem to have stabilized at lower levels on the order of about 0.5 milligrams per liter. And we hypothesize that the level to which it stabilizes is a function of the retention level of the wood. Also in comparison with the untreated wood samples or the untreated deck, the concentration of arsenic in the run off is very low on the order of 2 micro grams per liter whereas we have over 700 micrograms per liter coming off the CCA treated deck. Within the soil, what we observed was consistent with our earlier deck study where higher concentration of arsenic were observed in the surface layers and we also apparently observed an increase in the arsenic concentrations in the surface layers with the age of the deck, from 6 months to 13 months. Also the speciation work that Myron will be describing in a few minutes, FIU developed a new method my which arsenic species can be analyzed in soils, and the results from that analysis indicate that the predominant form of arsenic in the soil is arsenic 5 and with smaller amounts of arsenic 3. Going down through the soil now into the infiltrated water and again the units here are different than the units on the run off water. Here we are working in units per micrograms per liter whereas in the previous graph, the run off graph, they were in milligrams per liter so there is a difference of a factor of a 1000. What we find early on during the first two weeks or so, the concentrations of arsenic in the infiltrated water is similar to what was observed from the untreated deck of the order of 2 to 3 micrograms per liter. But after the first to two weeks or so we start seeing increases in the arsenic

concentrations in the infiltrated water. And I believe the last set of samples that I observed, Shiba is running these but we are not doing speciation after this point in time, - We are continuing to run total arsenic and the latest numbers I have observed are up on the order of 25, 24 micrograms per liter. So in summary as far as the deck study, we have observed arsenic in the deck run off at an average of over 700 micrograms per liter. The maximum spike observed is on the order of 8 milligram per liter or 8000 micro grams per liter. Arsenic was found predominantly in the surface soil layers and the concentration in the soil layers increase with the age of the deck. And also arsenic was found in elevated concentrations in the water that infiltrated below the 2 feet of sand. Ok Myron would you like to bring up your presentation while we are changing over. Are there any questions?

*Question:* [inaudible] per liter, how is that [inaudible] change the design?

*Helena Solo-Gabriele:* The [inaudible].

*Question:* When you look at the timeline [inaudible] by total arsenic [inaudible].

*Helena Solo-Gabriele:* We have our [inaudible].

*Question:* [inaudible] did you do an analysis [inaudible].

*Helena Solo-Gabriele:* We did an analysis [inaudible] deck [inaudible].

*Myron Georgiadis:* Ok we found it. Basically I am doing arsenic speciation in the soil and sediments. Let me give you a little background. We know that leaching does occur from CCA treated wood into soil and sediments. Now traditional methods for arsenic analysis is to do a soil acid leach or a total digestion. Now these methods are considered too harsh because you might convert the species while you are doing that. So we wanted to develop an extraction method for arsenic in soils and sediments while preserving the chemical species. Now in order to do that unfortunately there is no arsenic reference standard for speciation work so we had to go to the next best thing which we used a reference soil standard where we know the total concentration of arsenic in there and we use that as a model soil to start from. As in this case we chose PACS2, which is a marine sediment reference material purchased from the National Research Council in Canada. Now once we have the soil we need to figure out what kind of extraction media or solution we are going to use in order to extract the arsenic species. But in order to do that you need to consider a variety of different parameters that might affect your speciation work. One of the things is pH, the buffer capacity and what kind of chemical interactions that your solution might have. Then what we did was we went ahead and extracted PACS2, we choose a phosphate buffer to extract. So we went ahead and extracted PACS2. Then the solution was analyzed by HPLC, hydride generation with atomic fluorescence. Now what this graph shows is that we went ahead and extracted PACS2 with 10 milli-molar phosphate solution for a period of one hour all the way to 24 hours and within certain time intervals 1,3,5, 12 and 24. And one of the things you will notice, and this is speciation work, so the arsenic three is in the blue and arsenic 5 is in the red. Now you will notice that arsenic 3 decreases over a period of time while arsenic 5 increases slightly over extraction time period. Now there are two possible things that might be happening. One is species interconversion between arsenic 3 and arsenic 5. And the others are absorption

back into the soil over the higher extraction time periods. Now in order to do that, we first decided to treat the conversion of arsenic species. One possible thing we tried to do is that there might be some metals extracted along with arsenic that might catalyze the reaction of the conversion. So we wanted to use a complexing agent to complex with those metals possibly that are extracted. The other thing is providing a reducing, a slightly reducing environment to keep arsenic 3 in as arsenic 3 form by use of hydroxylamine. Now to address the absorption of arsenic since PAC2 has a large concentration of iron and manganese, there is great potential for it to reabsorb. So we went and saw possibilities of chelating agents that will bind to arsenic, such as sodium DDC and APDC. We didn't use APDC because it interfered with our analytical procedure so we went ahead and used sodium DDC, which is sodium diethyl dithiocarbamate. Now we went ahead to address the conversion issue, we went ahead, and this is again PAC2. We used phosphate plus EDTA to see if we noticed any different trend and unfortunately arsenic 3 decreased while arsenic 5 slightly increased. Now to use hydroxylamine to provide a reducing environment, a slightly reducing environment, we had pretty good results up to 12 hours but after that again we noticed the same trend. Now to address the absorption issue we went ahead and used 0.5 % sodium DDC and this case you will notice that we don't notice any of that trend we noticed before with EDTA and just the phosphate and things like that. So this was very encouraging we just increase arsenic 5 and arsenic 3 over a larger extraction time period. Now since we tried to develop the method we wanted to see how it would react with actual soils and sediments and things like that. And in this case we choose an uncoated sand. Now here is the spiked amount on this side you have arsenic three spike and this side you have an arsenic 5 spike. In this case it's an uncoated sand extracted with 10 millimolar phosphate and on the other side its 10 millimolar phosphate plus the addition of sodium DDC. And you notice that we get very good recovery for that and again the with arsenic 5. We chose another a naturally coated sand with a little bit of peat, and you'll notice that we get very results with that too. So we wanted to apply this method and see if it works with the soil used in the deck study described in the previous presentation. So we went ahead and extracted the deck soil and again we got good recoveries for those. Now this is a picture of the deck on top. And we actually sampled the soil that is inside. We took core samples. We have noticed....[End of Tape 1 Side 2]

*Question:* ...the total amount of arsenic. Our extraction efficiency is about 10%. .

*Question:* [inaudible]

*Question:* What do you mean by how stable?

*Question:* [inaudible]

*Myron Georgiadis:* Yes, with phosphate. Yes we have to. Now you might use another extraction media but you will have to take into account that you might get a higher extraction but you might get conversion. If you increase the time period you might get a species change over during that time period so you need to be careful with that.

*Question:* [inaudible]

*Myron Georgiadis:* We haven't because there is some complication with those. Some of the extraction procedures require for it to reach equilibrium and once you reach equilibrium you get a different response of your arsenic concentrations in there. So it is a little bit difficult to do that. You might use one solution where you extract a large amount, but you might get on your second time absorption from somewhere else. So you have to be careful when you use multiple extractions.

*Helena Solo-Gabriele:* This is the last presentation for the day and this presentation focuses on a pilot epidemiological study to evaluate the potential arsenic exposure to young children from CCA treated playgrounds. This project is a collaborative project through Rutgers University, Stewart Shalat, is the lead investigator on this. He is a toxicologist. Lora Fleming is an epidemiologist at the University of Miami who is the lead that the University of Miami. The responsibilities that we have at the University of Miami are to collect data, the environmental data to support that the playgrounds are in fact CCA treated. As far as what we would like to discuss our work focuses on evaluating the distribution of CCA within the playgrounds, evaluating the factors that contribute to dislodgeable arsenic and then the biomonitoring study which includes the collection of hand wipe samples and urine samples from children. Funding for this project was received through NIEHS Centers located at Rutgers University and the University of Miami. And the specific aims of this project are to determine the amount of arsenic present in playgrounds from CCA treated wood. To do an environmental characterization of the playgrounds to determine if the amount of arsenic, dislodgeable arsenic, from CCA treated playgrounds is present on children's hands and correlates with wipe samples and also to determine if the levels of arsenic on children's hands are associated with the levels of arsenic measurable in the children's urine.

*Tomoyuki Shibata:* We have visited many families, those of whom have a playground in their back yard. Before we conduct any environmental studies we conducted confirmation tests, we start collecting environmental samples including sawdust, soil, mulch, and wipes. Speaking of our human subject study, it is approved by the Internal Review Board and we collect hand traces, hand rinses, and urine samples. And we also collect a bunch of epidemiological data including a questionnaire administered to the mothers. First we conduct the confirmation test using PAN indicator test. This PAN indicator stain reacts with copper, therefore, the color of the stain changed into a magenta color. It means that the wood contains copper. So we can identify that the wood is treated with copper. Then we conduct another confirmation test using a commercially available arsenic test kit. This test kit requires a small piece of wood or sawdust in order to react. If the wood contains some arsenic the color of the white paper will turn to brown as you see. Then after the two confirmation tests finally we can identify that the playground is treated with CCA-treated wood. Today there is an innovative technology available, an XRF analyzer. This technology, Dr. Solo already mentioned, is quite simple. The analyzer can detect 12 different metals in a second. It is very useful in the field; however it is pricey. This is a picture of Dr. Solo-Gabriele collecting a soil sample underneath a playground and also Dr. Solo-Gabriele collecting mulch and we found a small piece of plywood in the red-dyed mulch as Gary said if you find plywood it means that the mulch came from the recycled C&D route. We have conducted wipe tests based upon the method developed by the US Consumer Product and Safety Commission. We collected wipes from wood treated at various retention levels and from the long time weathering deck and also private playgrounds. First we measured the children's hand in

order to calculate the surface areas of their hand and then we let children play on the playground for a while. After playing for a while we rinsed their hand using de-ionized water then we analyzed the sample water for arsenic. We provided the mother with a sample bottle and also a cotton diaper insert. In the case that a child is potty trained we asked the mother to collect urine first thing in the morning. However so far, in many cases, children just pee on the diaper so in that case we extract the urine, we squeeze physically, then extract the urine from the diaper insert. This a picture of me, this is my happiest moment, holding a diaper insert and the urine. This is just one example of the data. Because we enjoy so much using the handy XRF analyzer we went back to the playground then we collected more than 200 hundred samples from within playgrounds. Relatively there was a higher concentration of arsenic found in the vertical boards and lower concentrations in the horizontal boards. The retention level was twice as high as the lowest concentrations. The amount of dislodgeable arsenic can be affected by many factors for example the period of weathering. Retention level affects the amount of dislodgeable arsenic, for example for the 0.25 pcf samples we collected 74 micrograms per wipe of arsenic and 1200 micrograms per wipe of arsenic was collected from the 2.5 pcf samples. The amount of dislodgeable arsenic from sapwood is higher than that from heartwood. So far we have monitored five children and as you can see, we found arsenic in the playground soil and wipe. And during the collection of the samples we observed the children's hand-to-mouth behavior. Also there was a child who bit the mulch which was from the C&D wood. And currently we are evaluating the data. Thank you.

*Question:* How long were the children playing on the playground?

*Tomoyuki Shibata:* We asked the children to play for at least one hour or until they get tired so 30 – 45 minutes so far. Most children played for 30-45 minutes.

*Question:* [Inaudible] did you collect the urine from the playground separate.

*Tomoyuki Shibata:* No only after.

*Question:* [Inaudible] I would be very surprised if you did not find arsenic given the background.

*Tomoyuki Shibata:* Actually we analyzed arsenic species so if you find inorganic arsenic in the urine, and also there is a half life for the arsenic in your body. So we collect urine the next day in the morning. So if you find inorganic arsenic in the urine, we could assume it is from CCA treated wood.

*Question:* Inorganic arsenic [inaudible] with 5 micrograms per liter. You have to do pre-exposure analysis of the urine [inaudible].

*Helena Solo-Gabriele:* Ok this study is pilot scale study and unfortunately we do not have the resources to do pre and post urine analysis. But we do recognize that low levels of arsenic will be....

*Question:* [inaudible]

*Helena Solo-Gabriele:* The purpose of this study is just to collect very preliminary data, this is not the study that is going to answer the overall question of how much arsenic children ingest while they play on the playground. It is just pilot data to find whether or not we can even observe the arsenic in the urine of the children. This is not the end-all project, this is a very preliminary pilot scale project.

*Question:* The data based on the absorption of arsenic [inaudible]

*Helena Solo-Gabriele:* The question was the absorption of arsenic through skin. At the last scientific advisory panel back in October of 2001 we did, I learned for the first time, that arsenic could be absorbed through the skin. There are questions about the rate at which it is absorbed through the skin. It does happen, I know the EPA has done a comparative risk assessment looking at hand-and-mouth behavior versus absorption through skin versus soil ingestion and I believe that their conclusion was that skin absorption is small in comparison to the hand-and-mouth source of arsenic.

*Question:* [Inaudible] If there is any data of any other arsenic stays in the body like in the blood stream or like in organs rather than being extricated through urine or other means that would be important.

*Comment:* [Inaudible].

*Question:* [Inaudible] wipe test from marine treated pilings. Obviously children are not playing on the ....

*Helena Solo-Gabriele:* Our focus was to look at the effects of retention level on the amount of dislodgeable arsenic. And as far as whether not children come in contact with marine wood, the pilings are structures which are typically treated to the highest retention levels. Those are the structures that are vertical and precede upwards above the deck. Whereas one would imagine that contact on a playground would be more frequent. There could be occasional contact of any individual and people who work with boats and docks with the vertical components of the pilings. So that data, as far as evaluating children at playgrounds may not be directly relevant, it would be relevant for exposures in marine environments. Yes David.

*David Stilwell:* I think you were using de-ionized water right.

*Tomoyuki Shibata:* Which extraction?

*David Stilwell:* When you extracted from the hand wipes, you used just water right? You are getting only the soluble component which is almost 100% bioavailable, and there are other components which would be like the wood residue which would have some bioavailability but it would be less. You did find arsenic in the de-ionized water right.

*Tomoyuki Shibata:* Yes correct.

*Joe Sekerke:* I know that you [inaudible] are any of the hand rinsate or the urine samples positive for arsenic?

*Tomoyuki Shibata:* Yes they were positive.

*Helena Solo-Gabriele:* If you would like to get to that data as early as possible I recommend that you contact Stewart Shalat. He makes the decision as far when we will be releasing the data.

*Question:* [Inaudible] ... for arsenic I would be surprised .... pre-exposure assessment [inaudible] yet to find inorganic arsenic...

*Question:* How would you conduct a pre-exposure assessment if the child has a playground in their backyard that has been there for a long time?

*Comment:* Because the half-life of arsenic pretty short so you take it away from the playground before you do the pre-exposure urine sample and then you do...[in audible] otherwise you don't know your baselines..... [inaudible]... you can do that too.

*Helena Solo-Gabriele:* Any additional questions? There are some sandwiches outside and some refreshments. I would like to thank everyone for their participation and the feedback at this meeting and again thank you very much, and thank you to all the students. [End of Tape].