PROTOCOL FOR:

SAMPLING FOR RESIDUES OF ARSENIC, CHROMIUM, AND COPPER IN SUBSTRATES (SOILS/BUFFERING MATERIALS) BENEATH/ADJACENT TO CHROMATED COPPER ARSENATE (CCA)-TREATED PLAYGROUND EQUIPMENT

Modification of OPPTS Guidelines:
OPPTS 875.2200 (Soil Residue Dissipation);
OPPTS 840.1100 (Terrestrial Field Dissipation)

STUDY SPONSOR AND COORDINATORS

Office of Pesticide Programs (OPP)
Consumer Product Safety Commission (CPSC)

TESTING FACILITIES

OPP/Contract Laboratories

Protocol For Sampling Of Soil Residues of Arsenic, Chromium, and Copper in Soils Beneath/Adjacent To Chromated Copper Arsenate (CCA)-Treated Playground Equipment

I. General Study Information

A. Study Title

Sampling For Soil Residues Of Arsenic, Chromium, and Copper In Soils Beneath/Adjacent To Chromated Copper Arsenate (CCA)-Treated Playground Equipment

B. Purposes of Study

a. Background:

As part of the reregistration process for the Heavy Duty Wood Preservatives (HDWPs), the U.S. Environmental Protection Agency (USEPA) is evaluating the human and environmental risks of Chromated Copper Arsenate (CCA). CCA pesticide products are mixtures of water-soluble chemicals containing metal oxides of chromium as chromic acid (CrO_3), copper as cupric oxide (CuO), and arsenic as arsenic pentoxide (As_2O_5). These products are used as wood preservatives for vacuum-pressure treatment of dimensional lumber which is marketed to commercial and general consumers via lumberyards, hardware stores, and other retailers. CCA-treated wood dominates the residential consumer market for use in landscape timbers, decks, fences, and fabricated outdoor structures (e.g., gazebos, picnic tables, and playground equipment).

Since CCA-treated wood can be used in both commercial and residential settings, USEPA intends to evaluate all uses of CCA-treated wood. Because of specific concerns associated with use of CCA-treated wood in playground structures, the Agency is presently evaluating available exposure and hazards data in order to determine the risks to children who come in contact with CCA-treated wood and CCA-contaminated soil. These evaluations will be presented to the Science Advisory Panel (SAP) in October, 2001.

b. Specifics:

As part of the CCA-exposure evaluation, the Agency intends to develop a sampling regime that addresses potential residues of arsenic, chromium, and copper in substrates [soils/buffering materials (e.g., wood chips, pea gravel, shredded rubber)] below/adjacent to CCA-treated playground equipment. This sampling regime will involve:

1. Identification of suitable test sites which contain either new or existing CCA-treated playground structures;

2. Obtaining access to identified sites from local, state, or federal authorities;

3. Collection of a specific number of soil and buffering materials samples at each site;

4. Storage in dry ice of subsamples selected for speciation analyses and transport of all soil and buffering materials samples to (a) laboratory (ies) for analyses[1];

5. Soil: Analyses of soil samples for total arsenic, chromium, and copper[2];

6. Soil: If results from the pilot study suggest that further analyses of speciated forms of arsenic and chromium are in order, then analyses of a subsample of soil samples for speciated forms of arsenic (e.g., pentoxide forms, As^{+5}, and trioxide forms, As^{+3}) and chromium (e.g., hexavalent forms, Cr^{+6}, and trivalent forms, Cr^{+3}) may be undertaken;

7. Buffering materials: Analyses of a subsample of buffering materials (10 % of total samples collected) for total arsenic, chromium, and copper[3];

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[1] NOTE: In the pilot study only the Agency plans to analyze a subsample of total samples collected for speciated forms of arsenic and chromium. If such analyses indicate that various speciated forms of arsenic or chromium are significantly present, then further speciation analyses may be undertaken in the field study.

[2] The Agency intends to focus on sampling/analyzing for arsenic and chromium to address human exposures. The Agency will make a determination whether to perform analyses for copper after samples are collected. A determination to do so would involve considerations of environmental (e.g. aquatic) exposures.

[3] For example, if 750 total samples are collected, then 75 samples, or 10 %, would be analyzed for total arsenic and

8. Buffering materials: If results from the pilot study suggest that further analyses of speciated forms of arsenic and chromium are in order, then analyses of a subsample of these samples for speciated forms of arsenic (e.g., pentoxide forms, As^{+5}, and trioxide forms, As^{+3}) and chromium (e.g., hexavalent forms, Cr^{+6}, and trivalent forms, Cr^{+3}) may be undertaken; and

9. Review and reporting of such analyses in (a) report(s) which will support the Agency's exposure deliberations for the children's risk assessment for CCA-treated playground equipment.

Thus, the Agency will use the results of the above analyses, along with other available exposure data, to develop a more complete exposure assessment and risk characterization for children using CCA-treated playground equipment.

C. Test Substances

a. Active Ingredients:

Chromated Copper Arsenate (CCA), which consists of mixtures of water-soluble chemicals containing metal oxides of chromium as chromic acid (CrO_3), copper as cupric oxide (CuO), and arsenic as arsenic pentoxide (As_2O_5).

b. Common Name: CCA- Chromated Copper Arsenicals

c. Chemical Group: Inorganic Arsenicals

d. Case Number: 0132

e. CCA-Pressure Treated Wood:

CCA treatment solutions are typically classified as either type A, B, or C. However, CCA type C is the most commonly used to treat dimensional lumber for above-ground residential applications. CCA-Type A contains 14.7 % - 19.7 % arsenic pentoxide (As_2O_5), 59.4 % - 69.3 % chromic acid

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chromium.

(CrO_3), and 16.0 % - 20.9 % cupric oxide (CuO).[4] CCA-Type B contains 42.0 % - 48.0 % arsenic pentoxide (As_2O_5), 33.0 % - 38.0 % chromic acid (CrO_3), and 18.0 % - 22.0 % cupric oxide (CuO)[4] (Lebow, Stan, 1996). CCA-Type C is composed of 34.0 % arsenic pentoxide (As_2O_5), 47.5 % chromic acid (CrO_3), and 18.5 % cupric oxide (CuO).

The amount of CCA active ingredients that are added to, or retained in, wood is dependent upon the intended end use of the wood. AWPA lists a variety of "retention levels"; typical retention levels are: 0.25 pounds per cubic foot (pcf), 0.40 pcf, 0.60 pcf, 0.80 pcf, and 2.50 pcf, depending on the proposed uses of the treated lumber (Lebow, Stan, 1996).

D. Test Systems

Test systems will be substrates [soils/buffering materials (e.g., wood chips, pea gravel, shredded rubber)] found beneath, or adjacent to, CCA-treated playground structures which are located in public or private playgrounds (e.g., municipal playgrounds, private/public schools).

E. Justification For Experimental Parameters

A number of studies have been conducted on the determination of arsenic, chromium, and copper levels in soils found beneath residential decks found in residential and playground settings (Stilwell, 1997, 1998, Helena Solo-Gabriele et al., 2001). Similar studies were conducted on the soils underneath a wetland boardwalk (Stan Lebow et al., 2000). An earlier study was conducted by the Tasmanian Parks and Forest Service (Comfort, 1993).

Considering the above, the Agency concludes that sampling of soils/buffering materials beneath/adjacent to CCA-treated playground equipment is appropriate. Such sampling would provide data pertinent to an exposure assessment which could then be used in future risk calculations for children playing on CCA-treated playground equipment.

F. Study Sponsor and Coordinators

[4] Expressed as minimum and maximum percentages as specified by the American Wood-Preservers' Association (AWPA) standards.

The Office of Pesticide Programs (OPP) will be sponsoring this sampling effort and will identify coordinators of this project.

G. Testing Facilities

Samples will be collected by CPSC regional staff and stored and shipped to an OPP/contract laboratory which will perform the analytical analyses of soil/buffering material samples taken.

H. Proposed Study Schedule

Dates for starting/ending the field portions of the study when samples will be taken as well as dates for analytical analyses will be determined once the protocol has been approved by OPP. It is likely that the start date for field sampling will be late 2001.

I. Reporting of Results

After collection of soil/buffering material samples at each site by CPSC staff; storage and transport of soil samples to an OPP/contractor laboratory for analyses; and analyses of soil/buffering material samples for total arsenic, chromium, and, when required, copper (with analyses of subsamples for speciated forms of arsenic and chromium):

a. OPP/contractor will finalize a report of all analytical results/findings; and

b. OPP will prepare a report specific to the Agency's exposure deliberations for the children's risk assessment for CCA-treated playground equipment.

J. Deviations From The Protocol

Any deviations from the protocol, along with reasons supporting such deviations, will be documented and approved by both OPP and CPSC. A copy of such deviations will be retained by both programs as well.

II. Pilot Test Procedures

USEPA, with assistance from CPSC, will contact random municipalities (and possibly private/public schools/daycare centers) to obtain permission to sample soil beneath/adjacent to

CCA-treated playground structures. Additionally, every effort will be made to obtain records on installation and maintenance of such CCA-treated equipment.

Specifically, CCA-treated playground structures would be randomly selected in one geographic region of the United States (US): e.g., Northeast (NE). In this geographic region three playgrounds containing CCA-treated structures would be located. And at each selected CCA-treated structure ten soil samples (and ten samples from buffering materials, when present) would be obtained as follows:

Pilot Study Design

Summary of Sampling Plan for Arsenic, Chromium, and Copper From CCA-Treated Playground Structures								
Sample Type	Geog Regions	Number of Play-grounds/ Region	Vert Support	Horiz Support - Outside Edge	Horiz Support - Interior Edge	Play Area	Control Area	Total
Soil	1	3	2	2	2[1]	2	2[1]	30
Buffering Materials	1	3	2	2	2	2	2	30

1/ One of these samples will be a core sample for determining the distribution of arsenic, chromium, and copper, as well as the soil type, organic content, and pH of the soil. Additionally, a comparison of metal concentrations between the playground area and control area will be made.

Thus, a total of thirty soil samples - and possibly thirty samples of buffering materials, when present - would be collected. (Note: Some playgrounds selected for sampling may not contain buffering materials; thus, the number of samples of buffering materials collected may be less than the total estimated here.) Of these samples the Agency plans to analyze:

1. Soil: Thirty samples (100 % of thirty samples collected) for total arsenic and chromium;
2. Soil: Three samples (10 % of thirty samples collected) for speciated forms of arsenic and chromium;
3. Buffering Materials: Three samples (10 % of thirty samples collected) for total arsenic and chromium; and
4. Buffering Materials: Two samples (50 % of three samples analyzed for total arsenic and chromium) for speciated forms of arsenic and chromium.

(Note: The above number of soil/buffering material samples collected may be reduced if USEPA/CPSC have difficulty in gaining access to playground structures.)

The Agency will perform this pilot study to standardize field sampling techniques by identifying potential differences in

sampling procedures between selected sites. Further, the Agency is undertaking speciation analyses to determine if various speciated forms of arsenic or chromium are significantly present in soil and/or buffering materials. If such speciated forms are present, then the Agency, in consultation with CPSC, will determine if further speciation analyses should be undertaken in the full field study. Also, the procedures used in the pilot study will follow those outlined below for the full field study.

III. Field Test Procedures

A. Sample Collection Design

USEPA, with assistance from CPSC, will contact random municipalities (and possibly private/public schools/daycare centers) to obtain permission to sample soil beneath/adjacent to CCA-treated playground structures. Additionally, every effort will be made to obtain records on installation and maintenance of such CCA-treated equipment.

Specifically, CCA-treated playground structures would be randomly selected and replicated in each of three geographic regions of the United States (US): e.g., Northeast (NE), Southeast (SE), and Southwest (SW). In each geographic region twenty-five playgrounds containing CCA-treated structures would be located. And at each selected CCA-treated structure ten soil samples (and ten samples from buffering materials, when present) would be obtained as follows:

Field Test Design

Summary of Sampling Plan for Arsenic, Chromium, and Copper From CCA-Treated Playground Structures								
Sample Type	Geog Regions	Number of Play-grounds/ Region	Vert Support	Horiz Support - Outside Edge	Horiz Support - Interior Edge	Play Area	Control Area	Total
Soil	3	25	2	2	2[1]	2	2[1]	750
Buffering Materials	3	25	2	2	2	2	2	750

1/ One of these samples will be a core sample for determining the distribution of arsenic, chromium, and copper, as well as the soil type, organic content, and pH of the soil. Additionally, a comparison of metal concentrations between the playground area and control area will be made.

Thus, a total of seven hundred and fifty soil samples - and possibly seven hundred and fifty samples of buffering materials, when present - would be obtained. (Note: Some playgrounds selected for sampling may not contain buffering materials; thus, the number of samples of buffering materials collected may be

less than the total estimated here.) Of these samples the Agency plans to analyze:

1. Soil: Seven hundred and fifty samples (100 % of seven hundred and fifty samples collected) for total arsenic and chromium;
2. Buffering Materials: Seventy-five samples (10 % of seven hundred and fifty samples collected) for total arsenic and chromium; and
3. Speciated Forms of Arsenic and Chromium: At this time the Agency does not plan to analyze for speciated forms of arsenic and chromium unless the pilot study indicates that various speciated forms of arsenic and chromium are significantly present in soil and/or buffering materials.

(Note: The above number of soil/buffering material samples collected may be reduced if USEPA/CPSC have difficulty in gaining access to playground structures.)

B. General Information Collection

At each playground a CPSC team will obtain the following information (via a written survey form to be developed by USEPA/CPSC):

a. General Site Data:

1. Date;
2. Time of day;
3. Name of site;
4. Geographic location;
5. Name of scientist performing sampling;
6. Geographic, state, and site number(s);
7. Type of site (e.g., public school playground);
8. Two or more photographs of the playground site taken from several vantage points. (Such photographs are to be labeled and stored in a manner that will allow for adequate identification of the site/structure during analyses of soil samples.);
9. General, written diagram/description of site showing surrounding vegetation and structures (e.g., sandy playground surrounded by turf and trees);

10. Soil types (e.g., pH, organic content);[5]
11. Name(s) of contacts providing permission;
12. Local name of site/school/playground if appropriate;
13. Phone number for site (e.g., school playground);
14. History of site (e.g., what was on the playground site before it was built?);

b. Meteorological/Weather Data:

1. Temperature on day of sampling;
2. General weather conditions (relative humidity, wind direction/speed);
3. Estimated time structure is in sun/shade throughout day;
4. Date of last rainfall;
5. Amount of yearly rainfall for site;
6. Amount of annual snowfall, if applicable;
7. Typical acidity of rainfall for site;

c. Playground Structure Data:

1. Relative size of structure (estimate of dimensions);
2. Type of wood, if known (e.g., southern pine);
3. Relative age of structure (when was structure built?);
4. CCA-treatment level (e.g., level of preservative retention). (If this information cannot be obtained from the municipality or the manufacturer of the equipment, then a stain method, as outlined by Solo-Gabriele et al, 2001, can be utilized.);
5. Retreatments, if any;
6. General condition of structure (e.g., rough surfaces, worn surfaces);
7. Use of paints/sealants, if any, and how often, including date of last treatment;
8. Size of vertical support where soil samples were taken (e.g., 4 x 4);
9. Has any portion of structure been replaced; if so, when?;
10. Typical maintenance schedule;

d. Playground Usage Data:

[5] Additionally, the Agency will determine soil texture and soil classification using available samples and/or soil maps.

1. Number of children who use playground daily;
2. Age ranges of children using playground;
3. Approximate number of hours playground is in use daily or yearly, if known;
4. Known injuries, or illness, of children from use of equipment;

C. Sample Collection/Shipping

Once test sites/structures have been located and permission granted to obtain samples, a team of scientists from the CPSC will perform the soil/buffering material sampling. At each structure ten soil samples, as well as ten buffering materials samples, will be taken as follows:[6]

a. Vertical support:

The sampling scientist should identify the largest vertical support of the playground structure. (If all of the vertical supports are of the same general size, then one vertical support should be randomly selected, but adequately identified on a written diagram and/or via photographs.) For this vertical support the sampling scientist will:

1. Measure and record the dimensions of this vertical support on a written survey form and rough diagram (sampling scientist will create diagram) (e.g., 4x4 that is 6 feet tall);
2. Provide a general description of this support (e.g., of rough appearance)
3. Indicate what this support is attached to (e.g., ladder, decking);
4. Indicate whether it appears this support is used, or handled, during play activities;
5. Soil - Outside Edge: At the base of this support measure out two inches from an outside side and, keeping two inches from the post, obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops,

[6] The following sampling procedures provide an overview of the sampling collection, storage, and transport process.

measuring cups), which is disposed of between samples.[7] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;

6. Soil - Interior Edge: At the base of this support measure out two inches from an interior/inside side and, keeping two inches from the post, obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops or measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the soil core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;
7. Concrete Base: When concrete is found at the base of the vertical support, measure out two inches from the end of the concrete, and keeping two inches from the concrete, perform the sampling. Follow procedures outlined above for sampling.;
8. Buffering Materials: When buffering materials (e.g., wood chips, pea gravel, shredded rubber) are found above the soil sample to be taken, first collect a sample of this buffering material as follows: Buffering samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For cores the buffering materials above the top one inch of the core will be analyzed.)[8] The location of the sample will be identified on the rough

[7] Sample storage stability will be verified before field sampling is done. Additionally, other factors that will be considered include: verification that sampling equipment does not interact with soil samples/buffering materials; verification that samples will not be compromised during storage/transport before analyses can be done; and recording of elapsed time between sample collection, transport, storage, and analyses.

[8] Depending on the analytical technique used a larger sample of buffering materials may need to be taken (e.g., using a shovel).

diagram and/or photograph;
9. Adequately label and identify each sample taken (geographic/site numbers, vertical sample number, replicate number, date of sampling, and initials of scientist who collected the sample.); and
10. Store samples in appropriate media (e.g., plastic bags, plastic core liner) and transport to the laboratory. (For subsamples selected for speciation analyses place such samples in portable insulated coolers with dry ice for transport to the laboratory.)

b. Horizontal Support, Outside Edge:

The sampling scientist will identify a horizontal supporting edge/support, which is on the outside of the structure, and which can be considered to be an outside edge (e.g., horizontal joist/supporting beam which is on the outside edge of the structure). The largest horizontal support on the outside edge should be chosen. However, if all of these supports are of the same general size, then one support should be randomly selected, but adequately identified on a written diagram and/or via photographs.) For this horizontal support the sampling scientist will:

1. Measure and record the dimensions of this horizontal support on a written survey form and rough diagram (sampling scientist will create diagram) (e.g., 4x4 that is 6 feet tall);
2. Provide a general description of this support (e.g., of rough appearance)
3. Indicate what this support is attached to (e.g., vertical supports) and what it supports (e.g., decking);
4. Indicate whether it appears this support is used, or handled, during play activities;
5. Soil - Midpoint: Directly below the midpoint of this support (measure or eyeball distance from each end of the support) obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;
6. Soil - Halfway Between Midpoint and One Edge: On the

same horizontal support locate a point halfway between the midpoint (see above) and one edge (measure or eyeball distance), and directly below this point obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the soil core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;

7. Obstructions: When concrete, or other obstructions, are found at the location where a soil sample is to be taken, select another point along the horizontal supporting structure for sampling and note this on the diagram/photograph. Follow procedures outlined above for sampling.
8. Buffering Materials: When buffering materials (e.g., wood chips, pea gravel, shredded rubber) are found above the soil sample to be taken, first collect a sample of this buffering material as follows: Buffering samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For cores the buffering materials above the top one inch of the core will be analyzed.)[7] The location of the sample will be identified on the rough diagram and/or photograph;
9. Adequately label and identify each sample taken (geographic/site numbers, horizontal sample number, replicate number, date of sampling, and initials of scientist who collected the sample.); and
10. Store samples in appropriate media (e.g., plastic bags, plastic core liner) and transport to the laboratory. (For subsamples selected for speciation analyses place such samples in portable insulated coolers with dry ice for transport to the laboratory.)

c. Horizontal Support, Interior of Structure:

The sampling scientist will identify a horizontal supporting edge/support, which is on the interior of the structure, and which can be considered to be an interior edge (e.g., horizontal joist/supporting beam which is on the interior edge of the structure). The largest horizontal support on

the interior edge should be chosen. However, if all of these supports are of the same general size, then one support should be randomly selected, but adequately identified on a written diagram and/or via photographs.) For this horizontal support the sampling scientist will:

1. Measure and record the dimensions of this horizontal support on a written survey form and rough diagram (sampling scientist will create diagram) (e.g., 4x4 that is 6 feet tall);
2. Provide a general description of this support (e.g., of rough appearance)
3. Indicate what this support is attached to (e.g., vertical supports) and what it supports (e.g., decking);
4. Indicate whether it appears this support is used, or handled, during play activities;
5. Soil - Midpoint: Directly below midpoint of this support (measure or eyeball distance from ends) obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;
6. Soil - Halfway Between Midpoint and One Edge: On the same horizontal support locate a point halfway between the midpoint (see above) and one edge (measure or eyeball distance), and directly below this point obtain a core soil sample of at least seven inches in depth. Samples may be taken by using appropriate soil cores.[6] These soil cores will be analyzed to determine distribution of arsenic, chromium, and copper, as well as the soil type, organic content, and pH of the soil.) The location of the sample will be identified on the rough diagram and/or photograph;
7. Obstructions: When concrete, or other obstructions, are found at the location where a soil sample is to be taken, select another point along the horizontal supporting structure for sampling and note this on the diagram/photograph. Follow procedures outlined above for sampling.
8. Buffering Materials: When buffering materials (e.g., wood chips, pea gravel, shredded rubber) are found

above the soil sample to be taken, first collect a sample of this buffering material as follows: Buffering samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For cores the buffering materials above the top one inch of the core will be analyzed.)[7] The location of the sample will be identified on the rough diagram and/or photograph;

9. Adequately label and identify each sample taken (geographic/site numbers, horizontal sample number, replicate number, date of sampling, and initials of scientist who collected the sample.); and
10. Store samples in appropriate media (e.g., plastic bags, plastic core liner) and transport to the laboratory. (For subsamples selected for speciation analyses place such samples in portable insulated coolers with dry ice for transport to the laboratory.)

d. Play area:

The sampling scientist will identify a general play area adjacent to the playground structure. If possible, the play area which appears to have the most use by children should be chosen. However, one location in a general play area should be randomly selected, but adequately identified on a written diagram and/or via photographs.) For this play area the sampling scientist will:

1. Measure and record the general dimensions of this play area on a written survey form and rough diagram (sampling scientist will create diagram) (e.g., play area is approximately 5x 20 feet square);
2. Provide a general description of this area (e.g., composed of sand, pea gravel, wetness of surface);
3. Soil - Center Point: In the approximate center of this play area (measure or eyeball distance of area) obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;

4. Soil - Second Point: Within this play area, but at a randomly chosen point which lies between the center point chosen above and the side which is adjacent to, or lies between the play area and, the playground equipment, obtain a soil sample from the top one inch of soil. Specifically: (1) if the play area is immediately adjacent to the playground equipment, then obtain a sample that is six inches from the equipment; (2) if the play area is not immediately adjacent to the playground equipment, then take a sample two inches from the edge which is adjacent to, or lies between the play area and, the playground equipment, obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;
5. Obstructions: When concrete, or other obstructions, are found at the locations where a soil sample is to be taken, select another point in the play area for sampling and note this on the diagram/photograph. Follow procedures outlined above for sampling.
6. Buffering Materials: When buffering materials (e.g., wood chips, pea gravel, shredded rubber) are found above the soil sample to be taken, first collect a sample of this buffering material as follows: Buffering samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For cores the buffering materials above the top one inch of the core will be analyzed.)[7] The location of the sample will be identified on the rough diagram and/or photograph;
7. Adequately label and identify each sample taken (geographic/site numbers, point sample number, replicate number, date of sampling, and initials of scientist who collected the sample.); and
8. Store samples in appropriate media (e.g., plastic bags, plastic core liner) and transport to the laboratory. (For subsamples selected for speciation analyses place such samples in portable insulated coolers with dry ice for transport to the laboratory.)

e. Control area:

The sampling scientist will identify an area located away from the playground structure that appears to be a non-playground area or area of minimal play activity (e.g., surrounding field, turf, shrubs, trees). The areas chosen should be at least fifteen to twenty feet away from the playground structure and preferably higher in elevation than the playground structure.

1. Record the general dimensions of this control area on a written survey form and rough diagram (sampling scientist will create diagram) (e.g., control area is located approximately thirty feet from playground structure);
2. Provide a general description of this area (e.g., composed of turf, shrubs);
3. Soil - First Point: Randomly select one point in this control area and obtain a soil sample from the top one inch of soil. Samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For soil cores the top one inch of the core will be analyzed.) The location of the sample will be identified on the rough diagram and/or photograph;
4. Soil - Second Point: Randomly a select second point in this control area and obtain a core soil sample of at least seven inches in depth. Samples may be taken by using appropriate soil cores.[6] These soil cores will be analyzed to determine distribution of arsenic, chromium, and copper, as well as the soil type, organic content, and pH of the soil.) The location of the sample will be identified on the rough diagram and/or photograph;
5. Buffering Materials: When buffering materials (e.g., wood chips, pea gravel, shredded rubber) are found above the soil sample to be taken, first collect a sample of this buffering material as follows: Buffering samples may be taken by using appropriate equipment (e.g., cores, scoops, measuring cups), which is disposed of between samples.[6] (For scoops or cups, a minimum sample size of one-quarter cup (59 ml) will be taken. For cores the buffering materials above the top one inch of the core will be analyzed.)[7] The

location of the sample will be identified on the rough diagram and/or photograph;
6. Adequately label and identify each sample taken (geographic/site numbers, point sample number, replicate number, date of sampling, and initials of scientist who collected the sample.); and
7. Store samples in appropriate media (e.g., plastic bags, plastic core liner) and transport to the laboratory. (For subsamples selected for speciation analyses place such samples in portable insulated coolers with dry ice for transport to the laboratory.)

D. Analyses of Samples

a. Sample Analyses

Analyses of soil samples and buffering materials will be handled by USEPA (OPP/contract laboratory). Samples will be analyzed for total arsenic, chromium, and, when required, copper concentrations. Subsamples of soil and buffering materials samples (see Section I.B.b. above) will also be analyzed to quantify amounts of oxidation states of metals (e.g., arsenic trioxide, As^{+3}; arsenic pentoxide As^{+5}) in soil samples. Quantitative results will be reported in mg/kg (ppm) of metal species (e.g.,As^{+3}, As^{+5}). However, it is recognized that analytical determination of total arsenic and total chromium is much easier than quantitative determination of oxidation states of these elements.

b. Analytical Techniques

Some of the standard analytical techniques that can be used to analyze and quantify the amounts of arsenic, chromium, or copper in the samples are:

1. Electro-Thermal or Graphite Furnace Atomic Absorbance Spectrometry (ETAAS, GFAAS, USEPA Method 7191 or APHA's Standard Method for arsenic and chromium;
2. Flame Atomic Absorbance Spectrometry (USEPA Method 7190);
3. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES or ICP-OES USEPA Method 6010, 200.7);
4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS, USEPA Methods 6020A, # 200.8); and
5. X-Ray Florescence (XRF), OSW, Method 6200, Draft Method, 1996).

Copies of these methods are attached as PDF files. Methods can be found at the following website:

http://www.epa.gov/sw-846/main.htm

c. Validation of Method

Analytical methods for soil/buffering materials will be validated. Validation data will include analysis of control samples for various soil types and buffering materials. Recovery studies will also be needed on such samples and samples will be spiked with known quantities of the residue of concern. These recovery studies will reflect fortification of a variety of different soil/buffering material types. The fortification levels will provide information so that the practical Limits of Detection (LOD) and Limits of Quantitation (LOQ) will be determined.

Recovery values at and above the LOQ should lie between 70 percent and 120 percent for the residues of concern. Residues of concern include arsenic, chromium, and, when required, copper. Validation data will be generated for arsenic at the +3 and +5 valence states and for chromium at the +3 and +6 valence states. Recoveries above and below the 70 - 120 % recovery range will raise questions concerning the validity of data generated by the analytical method.

Guidance for generating validation data for analytical methods, in general, can be found in USEPA Office of Solid Waste (OSW) and OPP 860 Guidelines.

E. Recording Data

Sampling scientists will record all information via appropriate media (field notebooks, still cameras, video cameras). As outlined earlier, information will be adequately identified.

All analytical work will be recorded and will include appropriate correlations with field samples taken. Additionally, all pertinent analytical laboratory data will be recorded: e.g., spike solution log, storage location and condition of samples, log of use.

F. Statistical Methods

Upon completion of sampling and analyses of samples USEPA, with possible assistance from sister agencies, will determine the most appropriate statistical methods to use in examining the available data.

G. Reporting of Results

See discussion in I. above.

H. Data/Samples Retention

All raw field data will be maintained in Agency (OPP/contractor) files. All samples remaining after analytical analyses will be retained in frozen storage in Agency laboratories until OPP has determined such samples can be disposed.

I. Good Laboratory Practice (GLP)/Quality Assurance (QA)/Quality Control (QC)

All field and analytical procedures will be conducted either as per FIFRA Good Laboratory Practices (GLP) Standards, as defined in 40 CFR, Section 160, or as outlined in CPSC GLP or QA/QC standards.

J. References

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