

An Overview of Methods Used to Analyze Raw and Finished Drinking Water for USDA's Pesticide Data Program

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*- CDA's *Analytical Laboratory* analyzes feed mixes, fertilizers, ground water and variety of matrices involved in pesticide violation cases.

*- On Sept. 11, 2001 Martha Lamont and her staff from USDA's Monitoring Program Office (*MPO*) toured the CDA lab and approved our admission into the Pesticide Data Program (PDP).

*- CDA agreed to analyze drinking water and became one of three labs which included NY and CA, that initially made up PDP's Water Program.

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- *- Method development started and CDA began analyzing finished drinking water samples from five municipalities (2-CO, 2-KS and 1-TX) in January 2002 and continued until December 2003. Samples were taken on a weekly basis.
- *- Analyzed for a number of commonly used pesticides including organophosphates (OPs), triazines, phenoxy acids, imidazolinones, sulfonyleureas, and carbamates.
- *- Analytes residues that were found in these samples included atrazine and its desethyl and desisopropyl metabolites, and metolachlor.

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- *- In January 2004, CDA began analyzing samples from five new sites: 3-OR, 1-WA, 1-PA.
- *- From these sites, samples were taken prior to (“Raw”) and just after (“Finished”) water passage through these treatment plants. Two sets of water samples from these municipalities were taken every other week.
- *- After one year, no pesticide residues were detected.

However!!!

- *- \$\$ was not approved to continue PDP’s Water Program for the federal FY 2005 so the program was scheduled to be discontinued after Sept 2004.

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*- In October of 2004, MPO announced that funding had been obtained to keep the Water Program going through FY 2005.

*- In January 2005 CDA started analyzing untreated and finished drinking water samples from four new sites: CA, PA, LA and FL. After 2 months, the FL site was discontinued and a ND site was initiated.

*- These sites were chosen at the request of EPA. To help with their dietary risk assessments for carbamates.

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*- In addition to field samples, MPO required that CDA participate in a quarterly proficiency testing program.

*- In-house samples are fortified with a mix prepared by an outside party, containing known amounts of pesticides.

*- Results from these proficiency samples were sent to MPO and compared to other PDP labs in the Water Program.

Field Samples and Method Validation

*- At each raw and finished water site, three samples were collected in 1-L amber glass bottles, shipped directly to CDA overnight, and are extracted within 96 hours from collection.

Great Lakes Environmental Center prepares the sample kits.

GC Sample: Water was combined with 1g of sodium thiosulfate (dechlorination agent).

LC Sample: Water was combined with 1 mL of a 1% hydroxylamine solution (dechlorination agent).

Acetamide Herbicides and Metabolites (AHM) Sample: Water was combined with 1g of sodium thiosulfate (dechlorination agent).

Field Samples and Method Validation

*- Method validation was done under criteria set up by the MPO. Each target analyte is evaluated for:

Method Limit of Detection (LOD)

Method Limit of Quantitation (LOQ) = (10/3) x LOD

Method Performance: Evaluate analyte recoveries from water samples fortified @ (1,5,10) x LOQ. (Three per level)

Method Repeatability: Evaluate analyte recoveries from seven water samples fortified @ 2 x LOQ.

Instrument Response: Evaluate analyte response from standards prepared @ (1,2,5,10) x LOQ. (Linearity)

Field Samples and Method Validation

*- All validation data generated for each target analyte is sent to MPO for evaluation.

If the results meet the established criteria for all five areas, then the analyte is termed “validated” for the sample extraction process and instrumentation used.

If one or more of the criteria are not met, MPO has the option to either accept the submitted data and consider the target analyte “validated”, or reject the data and term the analyte “unvalidated” for the methodology used.

PDP Method: LC Samples (A)

*** Raw water samples:**

- Pass sample through a 75 mm x 0.45 μm polyethersulfone (PES) membrane, 500 mL bottle top filter.

*** Filtered raw and finished water samples:**

- Measure out 1000 mL of the sample and discard any remaining water. Pour the measured aliquot back into the empty sample bottle.

- Add 1 gram of $\text{NaCl}_{(s)}$ followed by 250 μL of process control solution containing propoxur and 2,4-dichlorophenylacetic acid (DCAA) at a 20xLOQ level.

- Prior to sample extraction, add 500 μL of $\text{H}_3\text{PO}_{4(\text{con})}$. Cap and shake bottle.

PDP Method: LC Samples (A)

*** QC samples:**

- *For matrix control (MC)*: Measure out 1000 mL of cold tap water and pour into a 1-L amber glass sample bottle.

- Add 1 gram of $\text{NaCl}_{(s)}$ followed by 1 mL of a 1% hydroxylamine solution.

- *For matrix spike (MS)*: prepared a second MC sample and add 250 μL of the process control solution and 100 μL of a 20xLOQ fortification solution.

- Prior to sample extraction, add 500 μL of $\text{H}_3\text{PO}_{4(\text{con})}$ to both MC and MS samples. Cap and shake bottles.

PDP Method: LC Samples (A)

*** Solid Phase Extraction (SPE) Cartridges:**

- Attach an Oasis[®] HLB SPE cartridge (6 cc, 200 mg) to a vacuum manifold system

- Rinse the sorbent bed with: 2 x 5mL of a CH_2Cl_2 :MeOH:HOAc (80:20:0.2 v/v) followed by 1 mL of MeOH using vacuum if needed.

- Gravimetrically elute 2x5mL of a 0.05% $\text{H}_3\text{PO}_{4(\text{aq})}$ solution through the sorbent bed.

- Once conditioned, place the SPE cartridge onto one of the sample loading stations on the Zymark Auto Trace workstation.

PDP Method: LC Samples (A)

For each QC, raw or finished water sample:

*** Sample Loading and Elution:**

- Place the water sample into the metal rack and insert the appropriate transfer line into the bottle.
- Insert the "LC/MS Method" disk into the workstation and load the sample extraction program. Load the sample onto the SPE column at 20mL/min. After loading, the sorbent bed is rinsed with 10 mL of water and dried for 10 minutes with N_{2(g)}.
- Remove the cartridge and place on a Supelco® Visidry manifold and further dry the sorbent bed under vacuum with N_{2(g)} for another hour. (Stopping point if necessary.)
- Elute the sorbent bed with 2 mL of MeOH, followed by 2x5 mL of the CH₂Cl₂:MeOH:HOAc and 2x5 mL of hexane into a 30 mL glass tube.

PDP Method: LC Samples (A)

*** Sample Concentration:**

- Place the collection tube into a TurboVap LV concentrator and reduce the extract volume to 2 mL using N_{2(g)} at a pressure of 15 psi, and a water bath at 38°C.
- Transfer the concentrate to a 10-mL Kuderna-Danish (KD) tube calibrated for a 1.00 mL volume. Rinse the 30-mL tube with a small amount of MeOH (1-2 mL) and transfers the rinsate to the K-D tube.
- Place the K-D tube into the concentrator and evaporate the liquid to a volume of 0.1 mL. Rinse the inner surfaces of the K-D tube with 1 mL of MeOH and evaporate the solution to 0.1 mL a second time.
- Remove the tube from the concentrator, add 200 µL of MeOH and vortex mix. Dilute to sample to 1.00 mL with water then sonicate.

PDP Method: LC Samples (A)

*** Extract Analysis:**

- Vortex mix the resulting extract solution and filter through a 0.45 µm polyvinylidene fluoride (PVDF) membrane into an amber sample vial, and seal.

- The resulting extract is injected three times into the LC/MS system and target analyte contents are evaluated using one of three instrument methods: *LC/MS/MS (+) ion*, *LC/MS/MS (-) ion* and *LC/MS/MS (+) ion carbamate screen*.

PDP Method: LC Samples (A)

*** LC/MS/MS (+) Ion Analysis:**

- Instrument Parameters:

Mobile Phase: A: 0.05% HOAc_(aq)

B: 4% IPA, 0.05% HOAc_(aq) in MeOH

Flow: 300 µL/min

Run time: 29 min

Gradient: 90% A -----> 27% A-----> 5%A-----> 90%A

(Hold time) 0 min 12 min 18 min 22 min
(5 min) (2 min) (7 min)

Column: Agilent Zorbax SB-C18, 2.1x150 mm, 3.5 µm, 40 °C

Injection Volume: 20 µL Tray Temp: 15 °C

Liquid Chromatograph: Thermo-Finnigan Surveyor

Mass Spectrometer: Thermo-Finnigan LCQ Duo Ion Trap. Mode: (+) polarity, MS/MS SRM

Tuning Compounds: *3-OH Carbofuran* (0-10.5 min), *Monuron* (10.5 to 13.25 min),

Imazamethabenz Methyl (13.25 to 16.5 min), *Propiconazole* (16.5 to 22.0 min),

3-OH Carbofuran (22.0 to 29.0 min).

PDP Method: LC Samples (A)

*** LC/MS/MS (+) Ion Analysis:**

Confirmation Criteria: (Ion area ratio)_{sample} is $\pm 20\%$ of (Ion area ratio)_{standard}

Analytes (19):

3-OH Carbofuran	Linuron
Bensulfuron Methyl	Methiocarb
Carbofuran	Monuron
Chlorimuron Ethyl	Neburon
DM-Norflurazon	Norflurazone
Fenuron	Propiconazole
Imazamethabenz methyl	Sulfometuron Methyl
Imazaquin (Scepter)	Tebuconazole
Imazethapyr	Tebuthiuron
Imidacloprid	

LODs: 4.2 to 189 ng/L LOQs: 14.0 to 630 ng/L

PDP Method: LC Samples (A)

*** LC/MS/MS (-) Ion Analysis:**

- Instrument Parameters:

Mobile Phase: A: 0.05% HOAc_(aq)

B: 4% IPA, 0.05% HOAc_(aq) in MeOH

Flow: 300 μ L/min

Run time: 25 min

Gradient: 90% A -----> 27% A-----> 5% A-----> 90% A

(Hold time) 0 min 8 min 14 min 17 min
(5 min) (1.5 min) (8 min)

Column: Agilent Zorbax SB-C18, 2.1x150 mm, 3.5 μ m, 40 °C

Injection Volume: 20 μ L Tray Temp: 15 °C

Liquid Chromatograph: Thermo-Finnigan Surveyor

Mass Spectrometer: Thermo-Finnigan LCQ Duo Ion Trap, Mode: (-) polarity, MS/MS SRM

Tuning Compounds: *Dicamba* (0-9.5 min), *Triclopyr* (9.5 to 12.0 min), *MCPB* (12.0 to 17.5 min), *Dicamba* (17.5 to 22.0 min).

PDP Method: LC Samples (A)

*** LC/MS/MS (-) Ion Analysis:**

Confirmation Criteria: (Ion area ratio)_{sample} is $\pm 20\%$ of (Ion area ratio)_{standard}

Analytes (14):

2,4,5-T	Dicamba
2,4-D	Flumetsulam
2,4-DB	MCPA
Acifluorfen	MCPB
Bentazon	MCPB
Bromoxynil	Picloram
Clopyralid	Triclopyr

LODs: 22 to 447 ng/L LOQs: 73.3 to 1490 ng/L

PDP Method: LC Samples (A)

*** LC/MS/MS (+) Carbamate Screen:**

- Instrument Parameters:

Mobile Phase: A: 0.05% HOAc_(aq)

 B: 4% IPA, 0.05% HOAc_(aq) in MeOH

 Flow: 300 μ L/min

 Run time: 29 min

 Gradient: 95% A -----> 27% A-----> 5% A-----> 95% A

 (Hold time) 0 min 12 min 18 min 22 min
 (4 min) (5 min) (2 min) (7 min)

Column: Agilent Zorbax SB-C18, 2.1x150 mm, 3.5 μ m, 40 °C

Injection Volume: 20 μ L Tray Temp: 15 °C

Liquid Chromatograph: Thermo-Finnigan Surveyor

Mass Spectrometer: Thermo-Finnigan LCQ Duo Ion Trap, *Mode:* (+) polarity, MS/MS Full Scan

Tuning Compounds: *Oxamyl* (0-12.5 min), *Thiodicarb* (12.5 to 19.3 min),
Oxamyl (19.3 to 29.0 min).

PDP Method: LC Samples (A)

*** LC/MS/MS (+) Carbamate Analysis:**

Confirmation Criteria: (Ion area ratio)_{sample} is $\pm 20\%$ of (Ion area ratio)_{standard}

Analytes (11):

- 3-OH Carbofuran
- Aldicarb Sulfone
- Aldicarb Sulfoxide
- Aldicarb
- Benomyl
- Carbaryl
- Carbofuran
- Methiocarb
- Methomyl
- Oxamyl
- Thiodicarb

LODs: 0.50 to 1500 ng/L LOQs: 1.7 to 5000 ng/L

Method is currently being validated.

PDP Method: GC Samples (B)

*** Raw water samples:**

- Pass sample through a 75 mm x 0.45 μm PES membrane, 500 mL bottle top filter.

*** Filtered raw and finished water samples:**

- Measure out 1000 mL of the sample and discard any remaining water. Pour the measured aliquot back into the empty sample bottle.

- Add 5 mL of MeOH followed by 100 μL of process control solution containing tolclofos methyl at a 20xLOQ level.

- Cap and shake bottle.

PDP Method: GC Samples (B)

*** QC samples:**

- *For matrix control (MC):* Measure out 1000 mL of cold tap water and pour into a 1-L amber glass sample bottle.
- Add 1 gram of $\text{Na}_2\text{S}_2\text{O}_3(\text{s})$ followed by 5 mL of MeOH.
- *For matrix spike (MS):* prepared a second MC sample and add 100 μL of the process control solution and 100 μL each of a 20xLOQ fortification solution for GC/MS and GC/PFPD analytes.
- Cap and shake bottles.

PDP Method: GC Samples (B)

*** Solid Phase Extraction (SPE) Cartridges:**

- Attach an Oasis[®] HLB SPE cartridge (6 cc, 200 mg) to a vacuum manifold system
- Gravimetrically elute 5 mL of a hexane:IPA (3:1) solution through each sorbent bed then dry for 20 minutes under vacuum (~10 mm Hg).
- Place the rinse SPE cartridge onto one of the sample loading stations on the Zymark Auto Trace workstation.
- Fill Solvent Bottle #1 half full with water and half fill solvent bottle #2 with MeOH.

PDP Method: GC Samples (B)

For each QC, raw or finished water sample:

*** Sample Loading and Elution :**

- Place up the sample into the metal rack and insert the appropriate transfer line into bottle.
- Insert the “Organophosphate Method” disk into the workstation and load the sample extraction program. Loads the sample onto the SPE column at 20mL/min. After loading, the sorbent bed is rinsed with 10 mL of water and dried for 10 minutes with N_{2(g)}.
- Remove the cartridge and place on a Supelco® Visidry manifold and further dried the sorbent bed under vacuum with N_{2(g)} for another 35 minutes. (Stopping point if necessary.)
- Gravimetrically elute the bed with 2x5 mL of the Hexane:IPA solution followed by 5 mL of MeOH into a 30 mL glass tube.

PDP Method: GC Samples (B)

*** Sample Concentration:**

- Add 10 mL of acetone and place the collection tube into a TurboVap LV concentrator. Reduce the extract volumes to 0.5 mL using N_{2(g)} at a pressure of 8 psi and a water bath at 45°C.
- Transfer the concentrate to a 10-mL Kuderna-Danish (KD) tube calibrated for a 0.500 mL volume. Rinse the 30-mL tube with 2x5 mL aliquots of acetone and transfer the rinsates to the K-D tube.
- Place the K-D tube into the concentrator and evaporate the extract to a volume of less than 0.500 mL.
- Dilute the extract with acetone to a volume of 0.5 mL and vortex mix. Transfer the final extract into 3 amber glass vials containing 250 µL inserts: 2-for GC/PFPD analysis, 1-one for GC/MS analysis.

PDP Method: GC Samples (B)

* Sample Analysis: GC/PFPD w/ Dual Column Injections

Instrument Parameters: (Agilent 6890 Gas Chromatograph, OI 5380 Pulsed Flame Photometric Detectors)

Oven: Temperature: 80 °C (hold time) $\xrightarrow[27.2\text{ °C/min}]{1\text{ min}}$ 178 °C (4 min) $\xrightarrow[2.0\text{ °C/min}]{}>$ 205 °C $\xrightarrow[10.0\text{ °C/min}]{}>$ 310 °C (8 min) (Total: 41 min)

	<u>Front</u>	<u>Back</u>
Inlet:		
Injection (µL):	2.0	2.0
Temp (°C):	270	270
Mode:	Pulsed/Splitless (30 psi)	Pulsed/Splitless (30 psi)
Purge Time (min):	1.00	1.00
Total Flow (mL/min):	65.8	65.8
Liner:	< Siltek Single Goose Neck w/ deactivated glass wool (4mm) >	
Column:	Restek-OP-Pes2 (30 m x 250 µm I.d. x 0.25 µm)	Restek-OP-Pest (30 m x 250 µm I.d. x 0.40 µm)
He Flow (mL/min):	1.2	1.3
Detector:		
Temp (°C):	310	310
Gas Flows (mL/min) H ₂ :	10.0	11.5
Air:	14.0	14.0
Make-Up (He):	8.8	10.7

PDP Method: GC Samples (B)

* Sample Analysis: GC/PFPD w/ Dual Column Injections

Confirmation Criteria: Evaluate retention time (RT) ratios based on tolclofos retention time.

- Analyte RT ratios were determined for both front and back columns during validation.
- Mix #1 Analytes (27):

Carbophenothion	Oxydemeton-methyl
Chlorfenvinphos	Parathion-OA
Chlorpyrifos	Phorate
Chlorpyrifos methyl	Phorate-OA
Coumaphos	Phosalone-OA
Diazinon	Phosdrin (Mevinphos)
Disulfoton	Pirimiphos-methyl
Ethion dioxon	Propetamphos
Fenamiphos	Sulfotep
Fenitrothion	Sulprofos-OA
Imidan (Phosmet)	Terbufos
Isofenfos-OA	Terbufos-OA
Isofenphos	Tetrachlovinphos
Malathion	

LODs: 2.4 to 255 ng/L LOQs: 8.0 to 850 ng/L

PDP Method: GC Samples (B)

*** Sample Analysis: GC/PFPD w/ Dual Column Injections**

Confirmation Criteria: Evaluate retention time (RT) ratios based on tolclofos retention time.

- Analyte RT ratios were determined for both front and back columns during validation.
- Mix #2 Analytes (19):

Chlorpyrifos -OA	Methidathion-OA
Dichlorvos	Methyl Parathion-OA
Dicrotophos	Phosalone
Dimethoate	Prophos (Ethoprop)
Ethion	SSS Tributylphosphoros thioate
Ethion monoxon	Sulprofos
Fenamiphos Sulfone	Tebupirimphos
Fenthion	Tebupirimphos-OA
Fenthion-OA	Terbufos Sulfone
Methidathion	

LODs: 4.5 to 915 ng/L LOQs: 15 to 3050 ng/L

PDP Method: GC Samples (B)

*** Sample Analysis: GC/PFPD w/ Dual Column Injections**

Confirmation Criteria: Evaluate retention time (RT) ratios based on tolclofos retention time.

- Analyte RT ratios were determined for both front and back columns during validation.
- Mix #3 Analytes (5):

Diazinon-OA
Phorate Sulfone
Phorate Sulfoxide
Phosphamidon
Profenofos

LODs: 16 to 297 ng/L LOQs: 53 to 990 ng/L

PDP Method: GC Samples (B)

* Sample Analysis: GC/MSD

Instrument Parameters: (Agilent 5890 Gas Chromatograph)

Oven: Temperature: 55 °C_(hold time) $\xrightarrow{10.0\text{ }^\circ\text{C/min}}$ 230 °C_(10 min) $\xrightarrow{5.0\text{ }^\circ\text{C/min}}$ 275 °C_(8 min) (Total: 44.5 min)

Inlet: Injection (μL): 5.0 Mode: Splitless
Temp (°C): 270 Purge Time (min): 1.00
Total Flow (mL/min): 65.8 Liner: Siltek Single Goose Neck w/ deactivated glass wool (4 mm)

Column: Phenomenex® Zebron ZB-5, 30 m x 250 μm I.d. x 0.25 μm He Flow (mL/min): 1.2

Detector: Agilent 5972 MSD Temperature (°C): 280 Mode: Full Scan and SIM

PDP Method: GC Samples (B)

* Sample Analysis: GC/MSD

Confirmation Criteria: (Ion area ratio)_{sample} is \pm 20% of (Ion area ratio)_{standard}

-Analytes (57):

Aldrin	Cypermethrin	Metalaxyl	Propanil
Alpha-Chlordane(cis)	Dacthal	Methoxychlor	Propargite
Alpha-Endosulfan	Devrinol	Metribuzin	Propoxur
Atrazine	Dichlobenil	Molinate	Propyzamide
Atrazine (Desisopropyl)	Dieldrin	Myclobutanil	S-2(OH)propyl EPTC
Atrazine Desethyl	Endrin	o-p'-DDE	Simazine
Benfluralin	EPTC	Oxadiazon	Tefluthrin
Beta - Endosulfan	Esfenvalerate	Oxyflufen	Tralomethrin
Beta-Chlordane	Ethalfuralin	Pebulate	Triadimefon
Bifenthrin	Heptachlor	Pendimethalin	Tri-allate
Butylate	Heptachlor epoxide	p-p' - Dicofof	Trifluralin
Chlorothalonil	Hexachlor	p-p'-DDE	Vinclozolin
cis-Permethrin	Hexachlorobenzene	Prometon	
Cyanizine (Bladex)	Lambda Cyhalothrin	Prometryn	
Cyfluthrin	Lindane	Propachlor	

LODs: 2.5 to 300 ng/L LOQs: 8.3 to 999 ng/L

PDP Method: AHM Samples (C)

*** Raw water samples:**

- Pass sample through a 75 mm x 0.45 μm PES membrane, 500 mL bottle top filter.

*** Filtered raw and finished water samples:**

- Measure out a 100 mL aliquot of the sample into a clean 100-mL glass graduated cylinder.

- Add 0.3 mL of a 5% $\text{H}_3\text{PO}_{4(\text{aq})}$ followed by 100 μL of process control solution containing propoxur at a 20xLOQ level.

- Cap and shake the cylinder.

PDP Method: AHM Samples (C)

*** QC samples:**

- *For matrix control (MC):* Measure out 1000 mL of cold tap water and pour into a 1-L amber glass sample bottle.

- Add 1 gram of $\text{Na}_2\text{S}_2\text{O}_{3(\text{s})}$ and dissolve.

- Measure out a 100 mL of the resulting solution into a clean 100-mL glass graduated cylinder and add 0.3 mL of a 5% $\text{H}_3\text{PO}_{4(\text{aq})}$ solution. Cap cylinder and shake.

- *For matrix spike (MS):* prepared a second MC sample and add 100 μL of the process control solution and 100 μL each of a 20xLOQ fortification solution for the ESA analytes.

- Cap and shake the cylinder.

PDP Method: AHM Samples (C)

*** Solid Phase Extraction (SPE) Cartridges:**

- Attach a Supelco® LC-18 SPE cartridge (6 cc, 500 mg) to a vacuum manifold system. Attach a 70-mL reservoir to the top of the cartridge.

- Gravimetrically elute 5 mL of MeOH through the sorbent bed followed by 5 mL of a 5% $\text{H}_3\text{PO}_{4(\text{aq})}$ solution. Discard the resulting eluate and keep the sorbent bed moistened prior to sample extraction.

PDP Method: AHM Samples (C)

For each QC, raw or finished water sample:

*** Sample Loading and Elution :**

- Close the valve on the SPE manifold and carefully pour the sample into the SPE reservoir. Open the valve and gravimetrically elute the sample through the sorbent bed.

- Once all the sample has eluted through the SPE column, remove the reservoir and dry the sorbent bed for 15 minutes under full vacuum.

- Attach a Teflon needle on the manifold, underneath the SPE column and place a 10-mL K-D tube under the needle.

- Elute 3 x 2 mL aliquots of a 80:20 MeOH:water solution through the sorbent bed into the K-D tube. Dry the sorbent for 1 minute under full vacuum.

PDP Method: AHM Samples (C)

*** Sample Concentration and Analysis :**

- Place the K-D tube containing the SPE eluate into a TurboVap LV concentrator and reduce the volume of the extract to less than 1.0 mL using N_{2(g)} at 15 psi and a 40 °C water bath.

- Remove the K-D tube from the concentrator and rinse the inner tube surfaces with a small amount of the 80:20 MeOH:water solution.

- Place the K-D back into the concentrator and reduce the liquid volume to less than 0.5 mL. Dilute to 0.5 mL with a matrix control solution.

- Dilute the extract to a final volume of 1.00 mL with aqueous mobile phase (0.05% HOAc_(aq)) and vortex mix. If needed, pass the resulting solution through a 0.45 mm PVDF filter into an amber glass sample vial. Otherwise, transfer the resulting extract to an amber glass sample vial.

PDP Method: AHM Samples (C)

*** LC/MS/MS (+,-) Ion Analysis:**

- Instrument Parameters:

Mobile Phase: A: 0.05% HOAc_(aq)
B: 4% IPA, 0.05% HOAc_(aq) in MeOH

Flow: 150 µL/min

Run time: 20 min

Isocratic: 30% - A 70% - B

Column: Waters Xterra MS C₁₈, 2.1x150 mm, 3.5 µm, 40 °C

Injection Volume: 10 µL Tray Temp: 15 °C

Liquid Chromatograph: Thermo-Finnigan Surveyor

Mass Spectrometer: Thermo-Finnigan LCQ Duo Ion Trap, Mode: (+/-) polarity, MS/MS Full Scan

Tuning Compounds: Propoxur (+) (0-4.82 min), Metolachlor ESA (-) (4.82 to 20.0 min)

PDP Method: AHM Samples (C)

*** LC/MS/MS (+,-) Ion Analysis:**

Confirmation Criteria: (Ion area ratio)_{sample} is $\pm 20\%$ of (Ion area ratio)_{standard}

Analytes (14):

Acetochlor
Acetochlor-ESA
Acetochlor-OA
Alachlor
Alachlor-ESA
Alachlor-OA
Dimethenamid
Dimethenamid-ESA
Dimethenamid-OA
Flufenacet
Flufenacet-ESA
Metolachlor
Metolachlor-ESA
Metolachlor-OA

LODs: 45 ng/L LOQs: 150 ng/L

CDA's PDP People

Technicians: *Becky Crabb and Alan Haywood*

Chemist: *Dan Hurlbut*

Technical Program Manager: *Eric Petty*

Quality Assurance Officer: *Heidi Phillips*

Lab Supervisor: *Charlie Hagburg*

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