HAVING YOUR CAKE AND EATING IT TOO:
MICRO EXTRACTION PLUS LARGE VOLUME INJECTION GC/MS
SAVES TIME, LOWERS EXPENSES, AND MAINTAINS DETECTION LIMITS

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NATIONAL ENVIRONMENTAL MONITORING CONFERENCE

BELLEVUE, WA

August 18, 2011

WATER POLLUTION CONTROL FACILITIES PERMIT
FOR CLASS V STORMWATER UNDERGROUND INJECTION CONTROL SYSTEMS

Department of Environmental Quality
Northwest Region
2020 SW Fourth Avenue, Suite 400, Portland, OR 97201
Telephone: (503) 229-5263

Issued pursuant to ORS 468B.050 implementing the Federal Safe Drinking Water Act requirements

ISSUED TO:
City of Portland
Bureau of Environmental Services
1120 SW 5th Avenue, Suite 1000
Portland, OR 97204

SYSTEM TYPE:
Class V Underground
Injection Control Systems
Owned, operated and under the
Jurisdiction of the City of Portland

SYSTEM LOCATIONS:
City of Portland, Oregon and other
City of Portland owned or operated
UIC Systems within Oregon.

SOURCES COVERED BY THIS PERMIT:
Type of Waste: Storm Water and Incidental Non-Stormwater Fluids
Outfall: Multiple
Method of Disposal: Class V Underground Injection Systems

RIVER BASIN INFORMATION:
Basin: Willamette
Subbasin: Lower Willamette River
Streams: Lower Columbia River
LLID: 1227618456580
Latitude: 45.5231
Longitude: -122.6681
County: Multnomah
River Mile: Not applicable
Waters of the State: Ground Water
Nearest surface stream which would receive waste if it were to discharge: Willamette and Columbia Rivers

Effective Permit Issuance Date: June 1, 2005
WPCF APPLICATION NO.: 985599
Date Application Received: July 1, 2002
DEQ Northwest Region File Number: 111885
This permit is issued based on the Land Use Compatibility Statement in the permit record.

Neil Mullane
Neil Mullane, Manager Water Quality Source Control Program
Northwest Region

6/1/05
Date

PERMITTED ACTIVITIES

The City of Portland (Permittee) is classified as a large municipality with more than 50 Permittee owned or operated (public) Class V Underground Injection Control systems (UICs). The Permittee must comply with the provisions, limitations, and conditions of this permit, including Oregon Administrative Rules (OAR) 340-040, OAR 340-044, and 40 Code of Federal Regulations (CFR) Parts 136, 141, 144 and 146, as applicable, either expressly or by reference, which are not specifically enumerated within this permit. The Permittee shall have the burden of showing that the requirements of this permit are met.

Public UICs are individual point sources. As provided by 40 CFR 144.33, this is an area permit which allows inclusion of all individual public UIC point sources on an area basis, rather than a permit for each individual public UIC. Therefore, this permit coverage is inclusive of all public UICs for storm water and non-motor vehicle floor drains.

UIC PERMIT SPECIFICS

- 250 SURFACE WATER FIELD SAMPLES: 5 SAMPLING EVENTS WITHIN 8 MONTHS
- ~ 100 FIELD & LAB QC SAMPLES
- ANALYTES INCLUDE 6 METALS, 4 VOAs, PENTA, NITRATE, ONE PAH, & ONE PHTHALATE (ALL ON 8270 LIST ARE REPORTED)
- LOW DETECTION LIMITS FOR PAH & PHTHALATE

DETECTION LIMITS RELEVENT TO UIC PERMIT (ug/L)

COMPOUND	PERMIT MRL	EPA 8270	EPA 8270-SIM
benzo(a)pyrene	0.01	1.0	0.01
bis(2-ethylhexyl)phthalate	0.5	1.0	0.5

MRL = method reporting limit
SIM = single-ion monitoring


PURPLE NITRILE
VWR INTERNATIONAL
W11B141-02 E
W11B141-02 F
W11B141-03 F
W11B141-04 F
W11B141-04 K
W11B141-04 L

EXTRACTION BY EPA 3510C: TWO LITER SEPARATORY FUNNEL

ADVANTAGE:

- LARGE SAMPLE SIZE (1,000 mL)

DISADVANTAGES:

- LARGE VOLUME OF SOLVENT (~ 300 mL)
- 2 L SEP FUNNELS AWKWARD & DANGEROUS
- K-D CONCENTRATOR + SOLVENT RECOVERY or
- TURBOVAP and maybe MICRO-SNYDER
- **~ 6 HRS TO RUN A 10-SAMPLE BATCH)**

OTHER EXTRACTION METHODS

HAVE ADVANTAGE OF 1 LITER SAMPLE SIZE

ALL HAVE DISADVANTAGES OF

- EQUIPMENT TO BUY, CLEAN, STORE, BREAK
- SIGNIFICANT SOLVENT USE
- **THEY ALL TAKE A LOT OF TIME**

MICRO EXTRACTION VIA EPA 3511

ADVANTAGES:

- SOLVENT USE DROPS TO **5 mL**
- USES ONLY A 40 mL VOA VIAL
- TIME DROPS TO **≤ 2 HRS** FOR 10 SAMPLE BATCH

DISADVANTAGE:

- 37 mL SAMPLE SIZE RAISES DETECTION LIMITS BY A FACTOR OF ~ 54 (2 mL FINAL VOLUME)

DETECTION LIMITS RELEVENT TO UIC PERMIT (ug/L)

COMPOUND	PERMIT MRL	EPA 8270	EPA 8270-SIM	EPA 8270-SIM + ME
benzo(a)pyrene	0.01	1.0	0.01	~ 0.5
bis(2-ethylhexyl)phthalate	0.5	1.0	0.5	~ 27

MRL = method reporting limit
SIM = single-ion monitoring
ME = micro extraction (2 mL final extract volume)

WHAT'S OLD IS NEW AGAIN

"APPLICATION OF SMALL SCALE EXTRACTIONS TO LARGE VOLUME INJECTIONS FOR ENVIRONMENTAL GC/MS ANAYSIS"

By

Rick McMillin, Diane Gregg, Mike Daggett

U.S. EPA Region VI Laboratory, Houston, TX

1998

AT-Process The Journal of Process Analytical Chemistry: **VI** (1,2), 48-55. (http://www.epa.gov/region6/6lab/lvinject.pdf)

ATAS OPTIC 3 GL-8270 LARGE VOLUME INJECTOR

OPTIC 3

High Performance GC Injector

PROGRAMMABLE TEMPERATURE VAPORIZATION

- MULTIPLE INJECTIONS
- DIRECT (GLASS WOOL PACKING)
- SPEED CONTROLLED
- ON-COLUMN

DETECTION LIMITS RELEVENT TO UIC PERMIT (ug/L)

COMPOUND	PERMIT MRL	EPA 8270	EPA 8270-SIM	EPA 8270-SIM + ME	EPA 8270-SIM + ME/LVI
benzo(a)pyrene	0.01	1.0	0.01	~ 0.5	~ 0.01
bis(2-ethylhexyl)phthalate	0.5	1.0	0.5	~ 27	~ 0.3

MADL = maximum allowable discharge limit
SIM = single-ion monitoring
ME = micro extraction (2 mL final extract volume)
LVI = large volume injection

ME-LVI EQUIPMENT & CONSUMABLES

EQUIPMENT & CONSUMABLES	VENDOR	MODEL/PART NUMBER
Equipment		
gas chromatograph	Agilent Technologies (Santa Clara, CA, USA)	6890N
mass selective detector	Agilent Technologies (Santa Clara, CA, USA)	5973N
large volume injector	ATAS International (Eindhoven, The Netherlands)	Optic 3-GL-8270
centrifuge	Hermle Labortechnik (Wehingen, Germany)	Z400
Consumables		
chromatography column	Restek (Bellefonte, PA, USA)	Rxi-5Sil MS, 30m, 0.25mm ID
packed injector liner	Restek (Bellefonte, PA, USA)	565665 (3x5.0x80mm, deactivated)
VOA vials, 40 mL	I-Chem (Rockwood, TN, USA)	C236-0040
Injector vials, 2 mL	Restek (Bellefonte, PA, USA)	32009E-1232

OVERALL COMPARISON W/ "REGULAR" METHODS

PROCEDURAL ELEMENT	EPA 3510C + 8270-SIM	WPCL ME + LVI 8270-SIM	EPA 625	WPCL ME + LVI 625
sample volume (mL)	1,000	37	1,000	33
final extract volume (mL)	1	2	5	4
extract injected (uL)	0.5	50	0.5	25*
solvent used (mL)	~ 300	5	~ 450	5
solvent reduction	---	98.3%	---	98.9%
MDL relative to EPA method	1	0.54	1	0.76
extraction time, 10 samples (hr)	~ 6	2	~ 7	2.5

MADL = maximum allowable discharge limit
SIM = single-ion monitoring
ME = micro extraction
LVI = large volume injection
*after 1:1 split

RECEIVED APPROVAL FROM EPA REGION 10 TO USE ME-LVI WITH EPA METHOD 625 FOR CITY'S NPDES PERMITS (TWO TREATMENT PLANTS, MS4) IN 2009

- REQUIRED BECAUSE EPA METHOD 3511 IS NOT APPROVED AT 40 CFR 136
- TWO EXTRACTIONS (NEUTRAL & ACIDIC)
- 1:1 SPLIT INJECTION
- APPROVAL REQUIRED MDL & IPR STUDIES
- ONGOING APPROVAL REQUIRES SATISFACTORY OPR RESULTS

FURTHER WORK

- VALIDATING CONCURRENT SOLVENT RECONDENSATION LVI (W/O ATAS INJECTOR)
- COMBINE WITH MICRO EXTRACTION FOR PCBs BY EPA METHOD 8082 & PETROLEUM HYDROCARBON SCAN BY WA DOE/OR DEQ NWTPH METHOD
- COMBINE WITH WPCL “SECRET” MICROWAVE SOILS EXTRACTION FOR PCBs???


OPTIC 3


WPCL
QUESTIONS ?