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Prioritization of High-Production Volume (HPV*) Chemicals for Assessing Water Resources

2010 National Water-Quality Monitoring Conference

April 28, 2010

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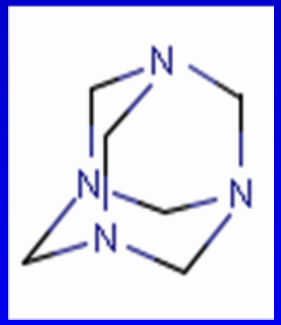
Calculator



Analysis of results


Lab development

***HPV = ≥10^6 pounds/year**

Talk Overview

1. *Current USGS Study Cycle…*
2. *HPVs in Current NAWQA Efforts…*
3. *Which HPVs Should be Added in the Next Study Cycle?*
4. *Analytical Considerations…*
5. *Summary / Conclusions…*

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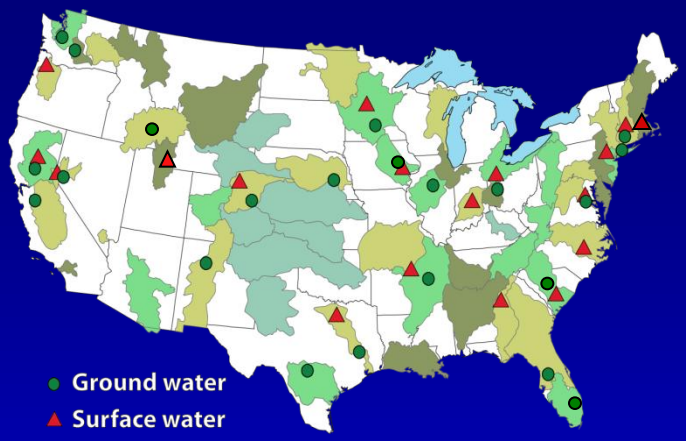
1. Current USGS Study Cycle…

USGS National Water Quality Assessment (NAWQA) Program

Cycle 2 (2001-2012)



http://water.usgs.gov/nawqa/

⋮

Source-Water Assessments

- Characterize occurrence of 277 man-made organic compounds in source water used by community water systems
- Understand occurrence patterns in source water and determine if the patterns also occur in finished drinking water

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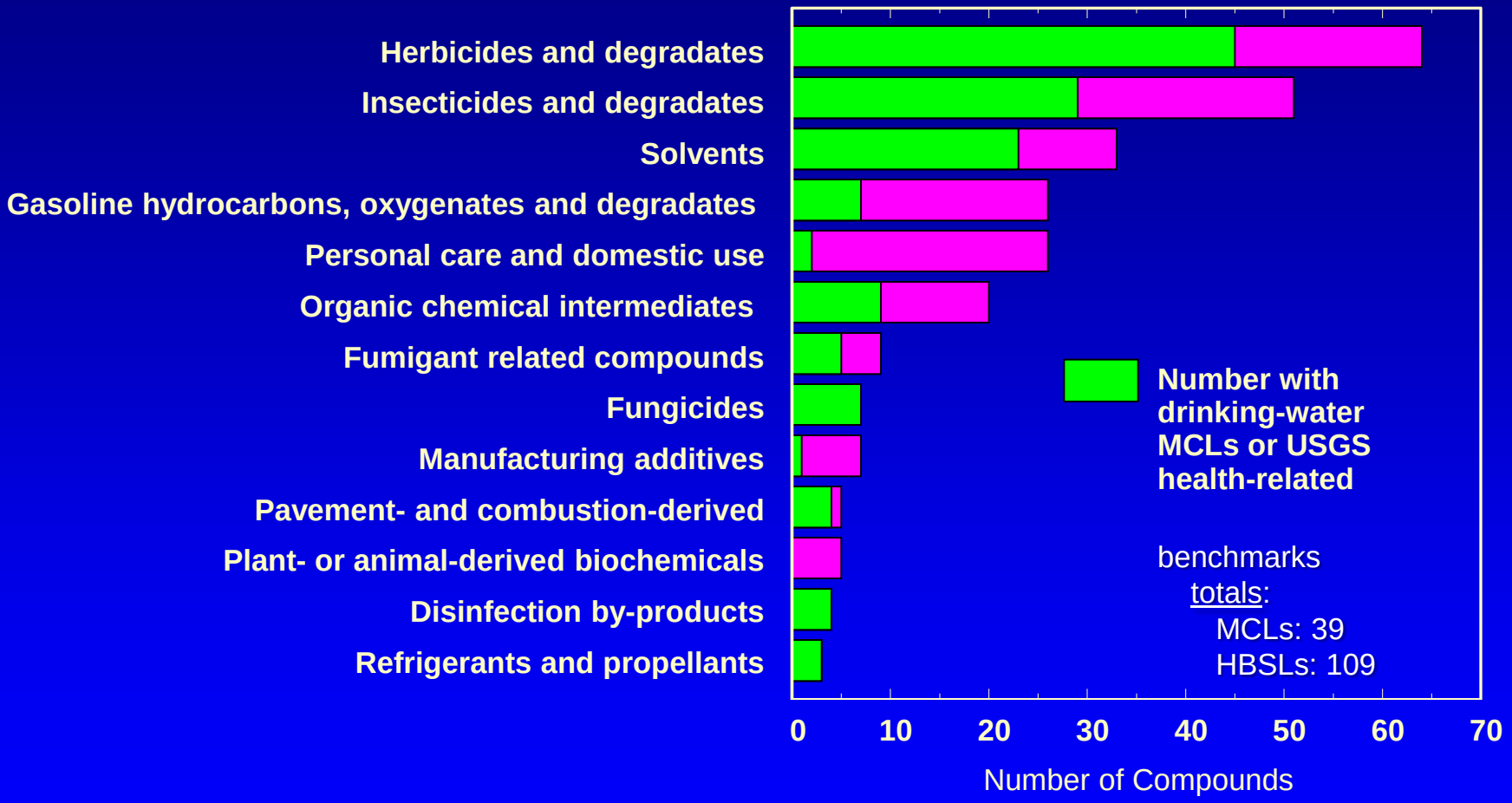
1. Current USGS Study Cycle…

277 Compounds Monitored in Cycle 2

(95 are HPVs)



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Key Findings

- Diversity of compounds (non-HPVs and HPVs) present in source waters at low concentrations;
- Occurrence and concentrations in a source water and its finished water often similar;
- Samples frequently contain certain groups of co-occurring compounds ("co-travelers")

  e.g.: atrazine and deethylatrazine;
  perchloroethylene and trichloroethylene;
  chloroform and bromodichloromethane

95 HPVs in Cycle-2 Studies

- HPV status *per se* had not been a selection criterion but several HPVs were frequently detected in groundwater:

NAWQA Detection Frequencies (%) in Surface Water – Cycle 2	
Perchloroethylene	47
MTBE	40
1,1,1-Trichloroethane	18
1,2,4-Trimethylbenzene	17
Chloromethane	16

- On the other hand, recent re-prioritization suggests 18 of the 95 may be dropped because there are no occurrence or toxicity concerns.

3. Which HPVs Should be Added in the Next Study Cycle?

…there are a lot more than 95 HPVs…

Numbers of HPVs

U.S. 3,300 ≥10^6 pounds/y

→ *in aggregate: 4 – 7 x 10^{13} pounds/y*

~18,000 pounds/person-y

Europe 5,235 ≥2.2 x10^6 pounds/y

OECD = European Org. Econ. Coop. & Development

→ Some of the compounds not currently measured are expected to occur in source waters and drinking water.

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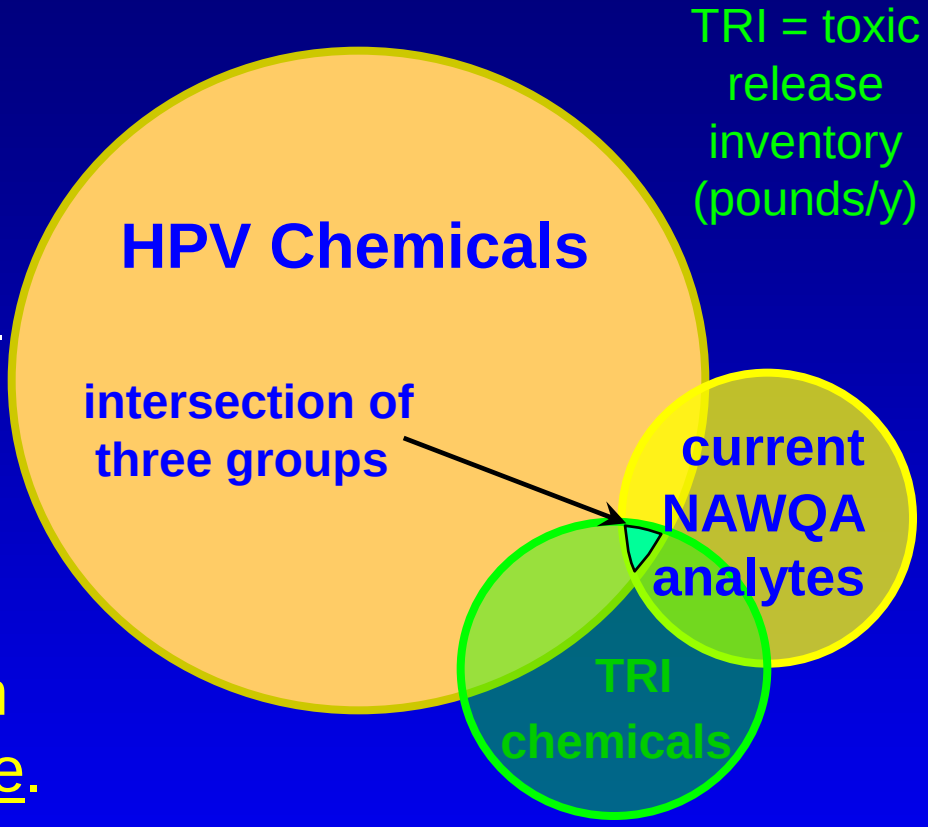
3. *Which HPVs Should be Added in the Next Study Cycle?*

- Needed a way to prioritize HPVs for monitoring.
- Hypothesis:
  a) production/release; &
  b) persistence
  as Predictors of Occurrence
- For the compounds in the intersection, test whether the frequency of USGS detection (% of samples) is correlated with TRI values and persistence.



$$\log [DF, \%] = 0.514 \log [TRI, \#/y] + 0.573 \log [HL, days] - 4.715$$

highly significant correlation ($p = 0.00064$)

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3. Which HPVs Should be Added in the Next Study Cycle?

Proceed with Ranking Work

a) Toxic Release Inventory (TRI) values

or

b) <u>actual</u> annual production volumes

Unfortunately, NOT AVAILABLE for most HPVs.

<u>Information of Initial Interest</u>:

together, TRI surrogate

- Low-end prod. volume range (lbs/y) — e.g., phosgene
- End-use info → score 3 to 1 — e.g., EDTA
- Persistence info → score 3 to 1
- Log K_{ow}

Chemical Prioritization System (CPS) Calculator

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3. Which HPVs Should be Added in the Next Study Cycle?

Scoring End-Use

High End Use ~70+% use in final products in manners that preserve the chemical structure ..... 3 e.g., EDTA

Low End Use ~30% or less use in manners that preserve chemical structure..... 1 e.g., phosgene

All Others..... 2 e.g., chloroethane

Scoring Persistence

Used BIOWIN model from EPI Suite

- 3 very persistent
- 2 moderately persistent
- 1 not persistent

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Chemical Prioritization System (CPS) Calculator

Features:

- User control of ranking algorithm
- Handles up to 3000 compounds and 25 ranking parameters
- Useable with different types of databases containing the user-chosen ranking parameters
- Numerous ways to view and analyze rankings
  outputs: a) rankings (spreadsheet)
  b) distributions of rank values

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Ranking for Detection in Natural Waters

Total Score = 0.5 x log [Low-End HPV Production]

+ 1.0 x End Use (3 to 1)

+ 1.0 x Persistence (3 to 1)

- 0.5 x $\underbrace{\log K_{ow}}_{\text{binned with 5 fencelines}}$ (partition out of water)

K_{ow} = octanol/water partition coefficent

high $K_{ow} \rightarrow$ less likely to be found in water

$K_{ow\ bin}$ = selected range of K_{ow} values

high score = more likely to be detected

low score = less likely to be detected

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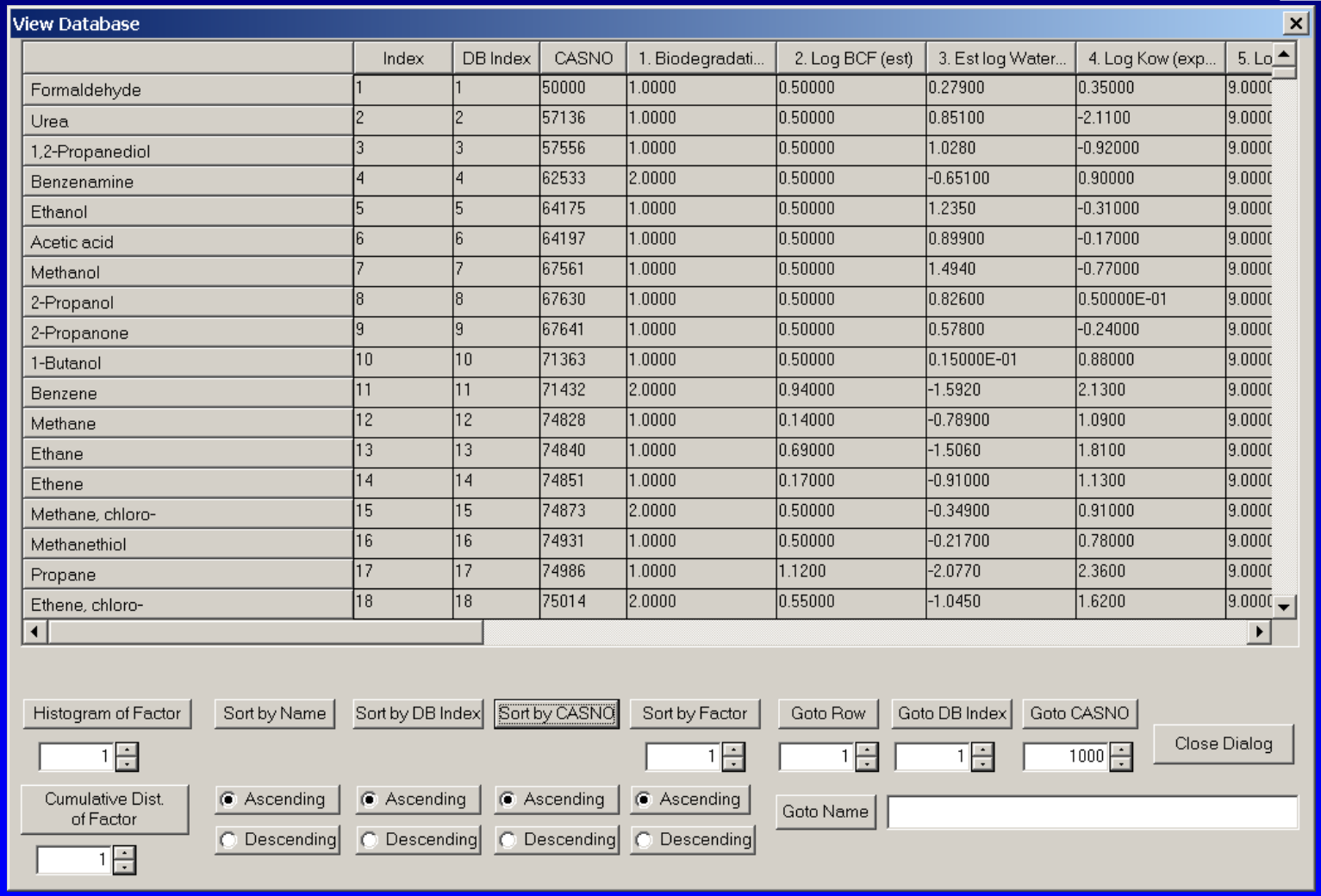
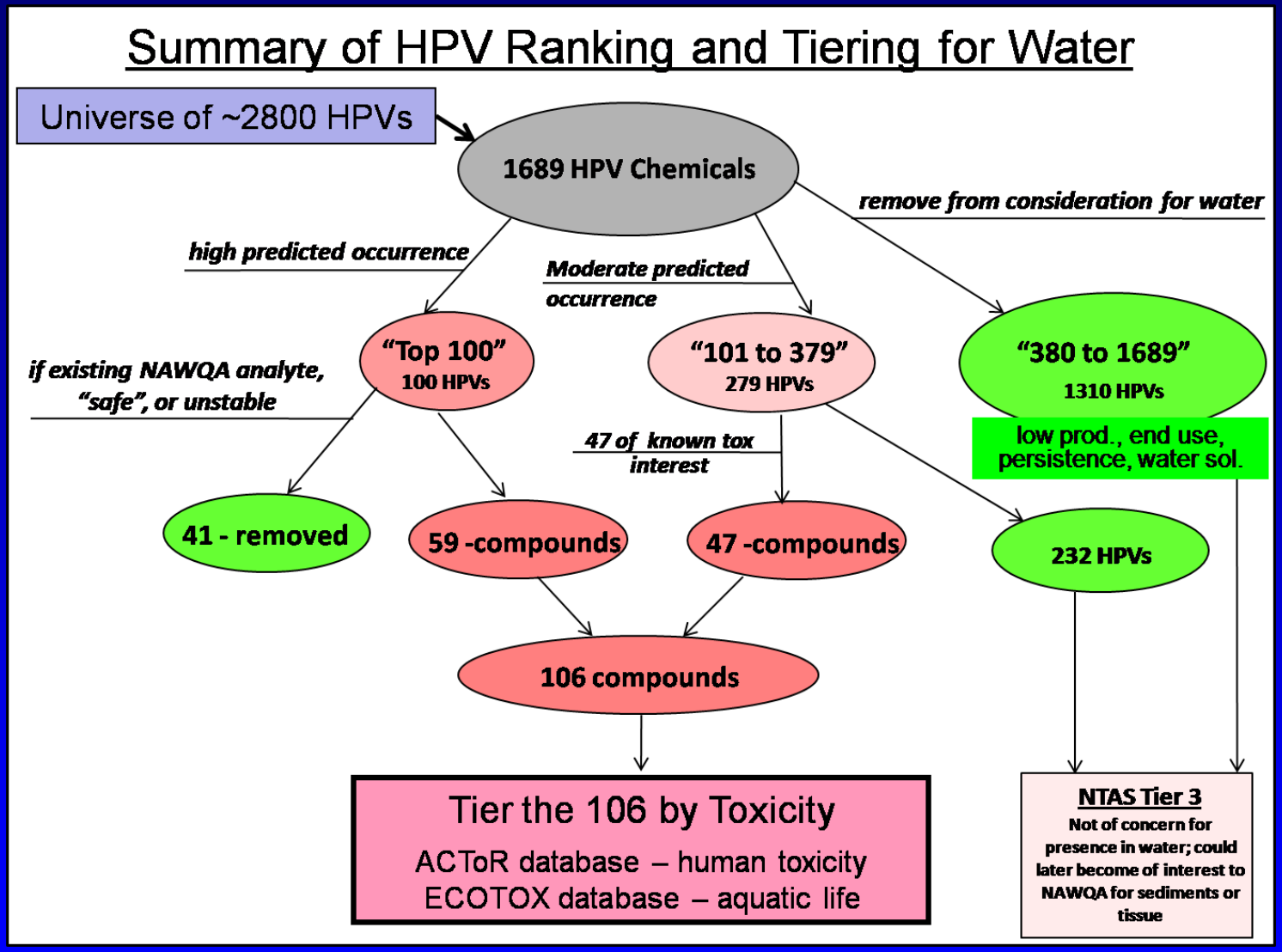
3. *Which HPVs Should be Added in the Next Study Cycle?*

Screenshot of Database



	Index	DB Index	CASNO	1. Biodegradati...	2. Log BCF (est)	3. Est log Water...	4. Log Kow (exp...	5. Lo
Formaldehyde	1	1	50000	1.0000	0.50000	0.27900	0.35000	9.0000
Urea	2	2	57136	1.0000	0.50000	0.85100	-2.1100	9.0000
1,2-Propanediol	3	3	57556	1.0000	0.50000	1.0280	-0.92000	9.0000
Benzenamine	4	4	62533	2.0000	0.50000	-0.65100	0.90000	9.0000
Ethanol	5	5	64175	1.0000	0.50000	1.2350	-0.31000	9.0000
Acetic acid	6	6	64197	1.0000	0.50000	0.89900	-0.17000	9.0000
Methanol	7	7	67561	1.0000	0.50000	1.4940	-0.77000	9.0000
2-Propanol	8	8	67630	1.0000	0.50000	0.82600	0.50000E-01	9.0000
2-Propanone	9	9	67641	1.0000	0.50000	0.57800	-0.24000	9.0000
1-Butanol	10	10	71363	1.0000	0.50000	0.15000E-01	0.88000	9.0000
Benzene	11	11	71432	2.0000	0.94000	-1.5920	2.1300	9.0000
Methane	12	12	74828	1.0000	0.14000	-0.78900	1.0900	9.0000
Ethane	13	13	74840	1.0000	0.69000	-1.5060	1.8100	9.0000
Ethene	14	14	74851	1.0000	0.17000	-0.91000	1.1300	9.0000
Methane, chloro-	15	15	74873	2.0000	0.50000	-0.34900	0.91000	9.0000
Methanethiol	16	16	74931	1.0000	0.50000	-0.21700	0.78000	9.0000
Propane	17	17	74986	1.0000	1.1200	-2.0770	2.3600	9.0000
Ethene, chloro-	18	18	75014	2.0000	0.55000	-1.0450	1.6200	9.0000

3. Which HPVs Should be Added in the Next Study Cycle?



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3. Which HPVs Should be Added in the Next Study Cycle?

Binning for Human Toxicity Using ACToR Database

Table H.2. NTAS Human-Health Toxicity Bins. Toxicity bins for high-production-volume (HPV) chemicals of interest based on human-health (HH) data available in the ACToR database (http://actor.epa.gov/actor/faces/ACToRHome.jsp)

[CERCLA, Comprehensive Environmental Response, Compensation, and Liability Act of 1980; EPA, Environmental Protection Agency; NIA, no information available; USEPA, U.S. Environmental Protection Agency]

NTAS Toxicity Bin	Criteria	Comments
1	**Compounds of Greatest HH Concern** • Compounds with Federal or State recognized Reference Dose (RfD); Reference Concentration (RfC), Slope Factor (SF), Cancer Classification, or Food and Drug Administration (FDA) intake limits. Compounds with data of this nature are of increased priority and interest due to their recognized human-health effects.	For compounds with more than one listed relevant exposure limit, Federal listings were given preference over State listings. RfD, SF, RfC, Cancer Class, and FDA intake limits were given priority in that order. Data from: • USEPA • FDA • State of California
2	**Other Compounds of HH Concern** • Compounds that have been listed as priority substances by agencies tasked with protection of human health. • Compounds with data indicating negative human- health consequences following exposure, but have not been recognized by adoption of a formal RfD, SF, RfC or Cancer Classification.	Data from: • Clean Water Act List of Hazardous Substances • CERCLA Hazardous Substances • Danish EPA • USEPA HPV Information System • European Union Detergent Ingredient Database • Health Canada

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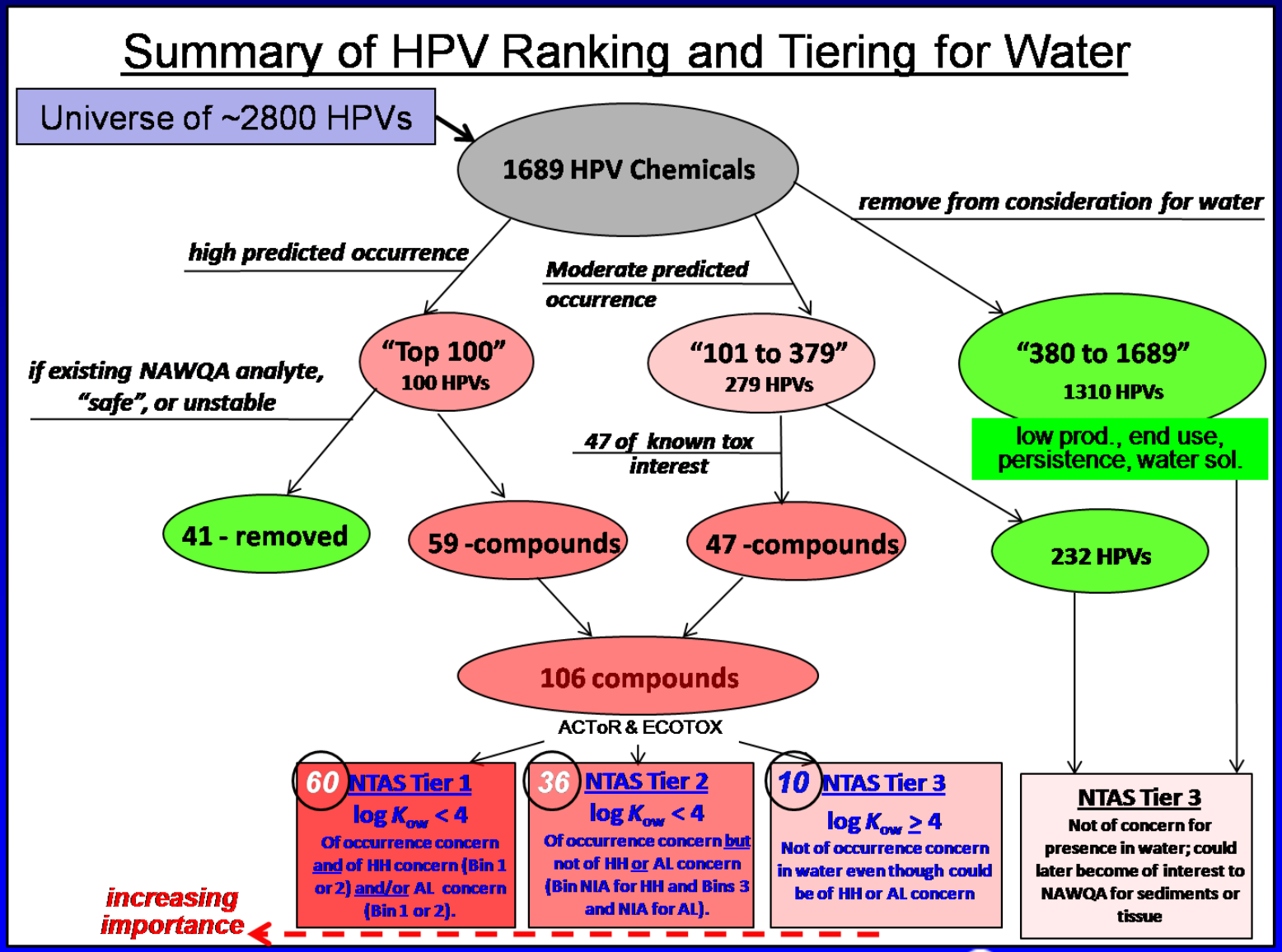
3. Which HPVs Should be Added in the Next Study Cycle?



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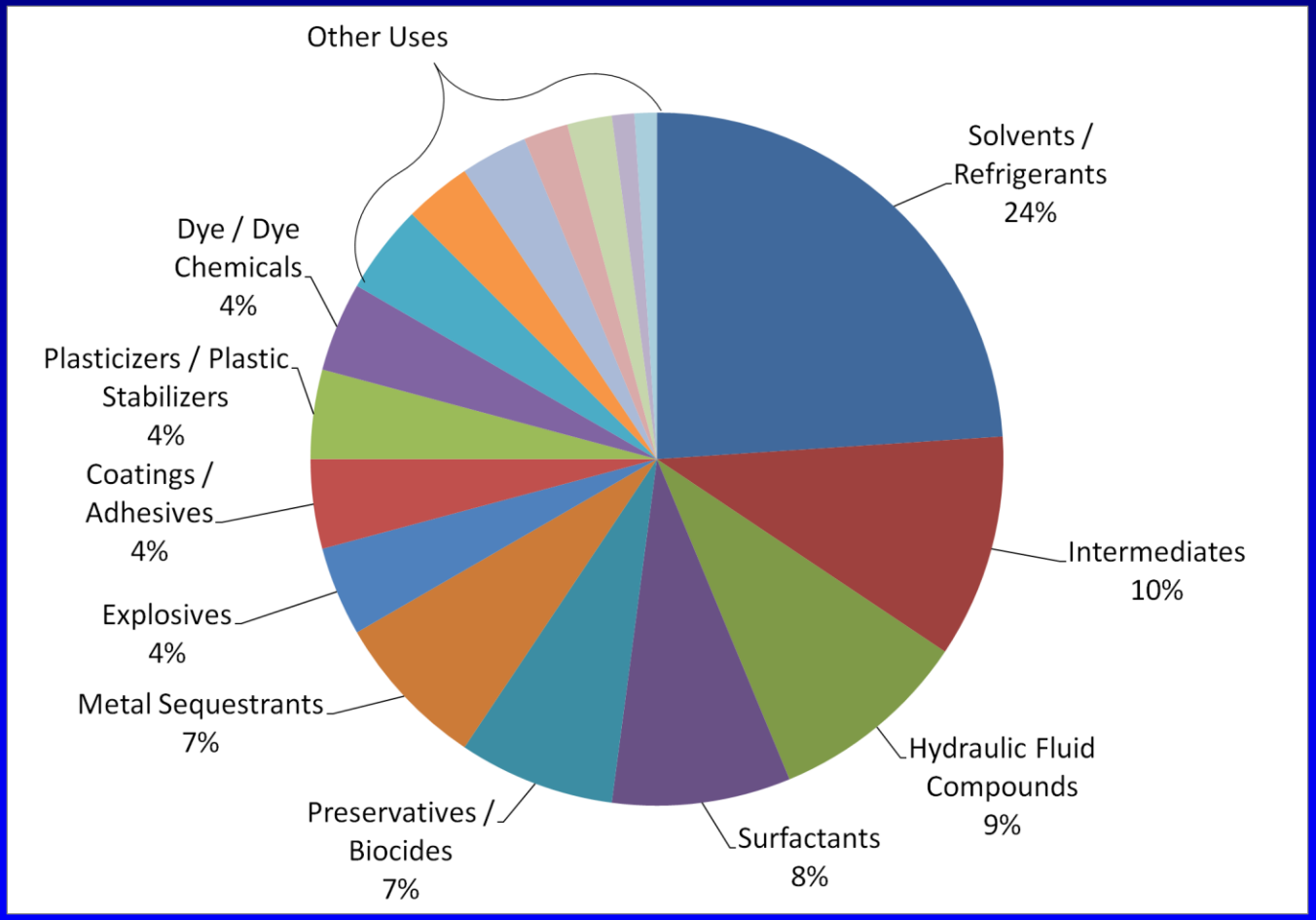
3. Which HPVs Should be Added in the Next Study Cycle?

Primary Uses of the 96 HPVs in Priority Tiers 1 & 2



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3. Which HPVs Should be Added in the Next Study Cycle?

Examples of Tier 1 HPVs

(60 total)

Chemical name	CAS No.
1,2,3-Propanetriol, trinitrate	55-63-0
Glycine, N,N'-1,2-ethanediylbis N-(carboxymethyl)-	60-00-4
Benzenamine	62-53-3
Thiourea	62-56-6
Formamide, N,N-dimethyl-	68-12-2
Acetonitrile	75-05-8
Oxirane	75-21-8
Methane, chlorodifluoro-	75-45-6
Oxirane, methyl-	75-56-9
Ethane, 1-chloro-1,1-difluoro-	75-68-3
Propanenitrile, 2-hydroxy-2-methyl-	75-86-5
Propane, 2-nitro-	79-46-9
1,1'-Biphenyl -2-ol	90-43-7
3-Cyclohexene-1-methanol, .alpha.,.alpha.,4-trimethyl-	98-55-5

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10 Tier 1 HPVs on the CCL3 List

(24 HPVs on CCL3 list not in Group of 96)

Name	CAS no.
1,2,3-Propanetriol, trinitrate	55-63-0
Benzenamine	62-53-3
Oxirane	75-21-8
Methane, chlorodifluoro-	75-45-6
Oxirane, methyl-	75-56-9
Ethanol, 2-methoxy-	109-86-4
Hexane	110-54-3
Ethanamine, N,N-diethyl-	121-44-8
1,3,5-Triazine, hexahydro-1,3,5-trinitro-	121-82-4
1-Methyl-2-pyrrolidone	872-50-4

Analytical Options

Separation

GC = gas chromatography (high separation power)

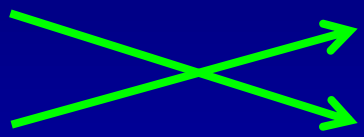
LC = liquid chromatography (lower separation power but can determine less volatile constituents)

Detection

MS = mass spectrometry (good specific detection)

MS/MS = second MS focused on a particular ion from the first MS (better specific detection)

Separation		Detection specificity	
high	GC	high	MS/MS
lower	LC	lower	MS



Major options: USGS National Water Qual. Lab.

GC/MS

LC/MS/MS*

*Note: advantage of LC/MS/MS: can directly inject a water sample: "Direct Aqueous Injection"

→with a 250 μL injection and sensitive instruments, can achieve ng/L sensitivity with little sample work-up

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Method Approaches for the 96 Compounds

- 29 – "purgeable" from water
  → will use purge & trap with GC/MS
- 11 – volatile enough for GC
  → can use GC/MS but will likely use LC/MS/MS because of Direct Aq. Injection advantage
- 53 – feasible by LC/MS/MS (including 5 chelates)
- 3 – yet to be determined (properties to be investigated)

96

Feasibility testing now underway at USGS and PSU

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Summary + Conclusions

1. 277 Organics measured in source and finished waters in NAWQA Cycle 2 (2001–2013) → 95 are HPVs;
2. Detection frequencies of the HPV compounds correlated with release and persistence values;
3. Other HPVs ranked for possible inclusion in NAWQA → 96 compounds identified for possible inclusion in Cycle 3 of NAWQA → broad mix compound types;
4. Efforts begun to develop + test analytical methods for determination of the 96 at the ng/L level;
5. Significant emphasis being given to LC/MS/MS (even for "GC-able" compounds) because of possibly reduced analytical costs provided by Direct Aqueous Injection.

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