

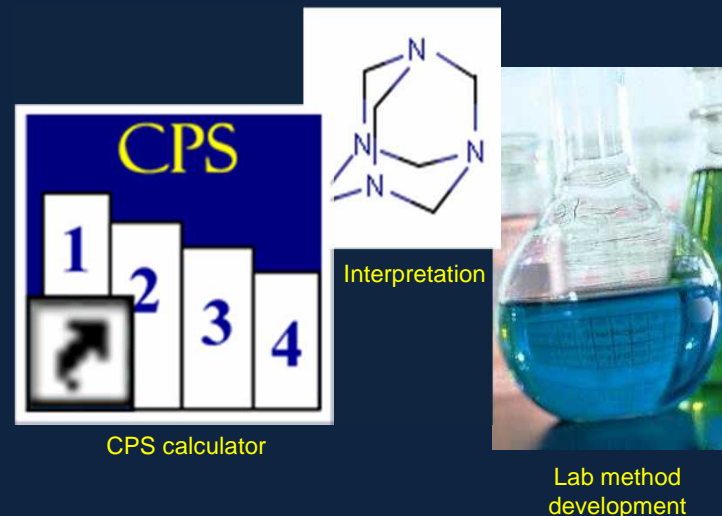
Prioritization of Constituents and Analytical Methods for National Assessment by the U.S. Geological Survey

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U.S. Geological Survey



NAWQA's Unique Approach to National Assessment

- National-scale monitoring of a wide variety of constituents in ambient waters.
- Low levels of detections for laboratory methods to achieve:
 - Contaminant occurrence
 - Long-term trends
 - Human and natural factors controlling spatial and temporal patterns

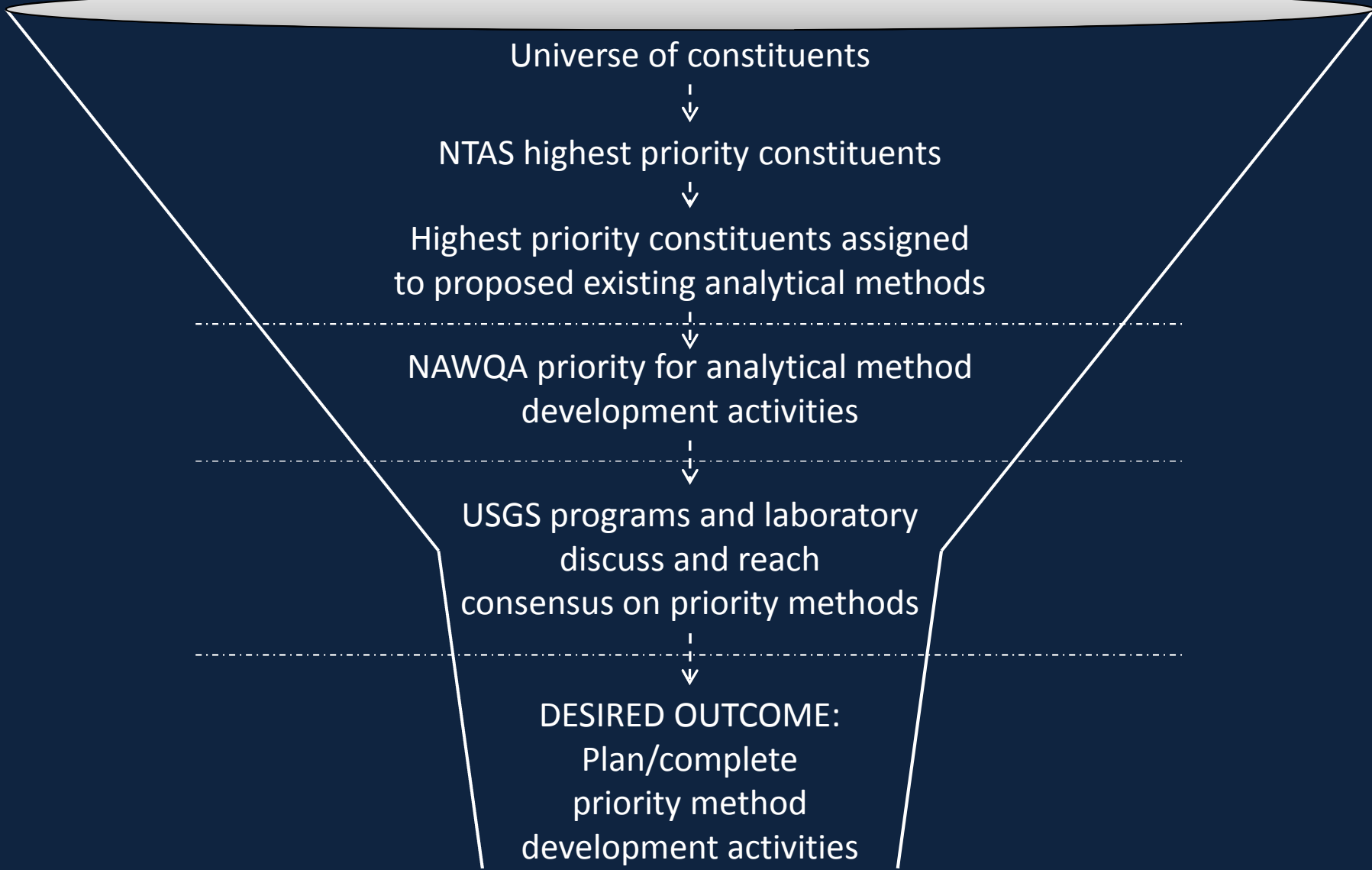
Purpose of the National Target Analyte Strategy (NTAS) Workgroup

- Review and prioritize **constituents currently monitored** by NAWQA and determine the efficacy of existing analytical methods...
- Review and prioritize **new or emerging constituents** that are being considered for monitoring and development of new methods...

Major Take Home Messages

- The review of about three thousand constituents for ambient monitoring of water and/or sediment has been finalized and documented.
- Common and unique screening criteria were used on a wide range of chemical classes.
- Constituent groups of largest interest for implementation in third decade of NAWQA assessments were given priority for development of new analytical methods.

Schematic of Process to Prioritize Constituents and Analytical Methods



Constituent Groups of Interest

Constituent group	Sampling medium and the number of constituents evaluated	Examples from each constituent group
Algal Toxins	Water – 15	Microcystin YR (MCYR)
Disinfection Byproducts	Water – 93	Trichloroacetic acid
High Production Volume (HPV) Chemicals	Water – 318	Chlorodifluoromethane; Benzenamine
Industrial Constituents	Water – 470	Acetamide; 1-Butanol
VOCs	Water – 89	Benzene; Methyl <i>tert</i> -butyl ether
Lipophilic Organics	Sediment– 696	Phenol; 2,2',4,4',6-pentabromodiphenyl ether (PBDE 100)
Pesticides	Water – 615; Sediment – 605	2,4-D; Simazine
Pharmaceuticals / Antibiotics / Hormones	Water – 403; Sediment – 403	17- β -Estradiol; Equilin
Trace Elements	Water – 38; Sediment – 8	Cadmium; Uranium

USGS Report on the Approach and Findings for the Prioritization of Constituents

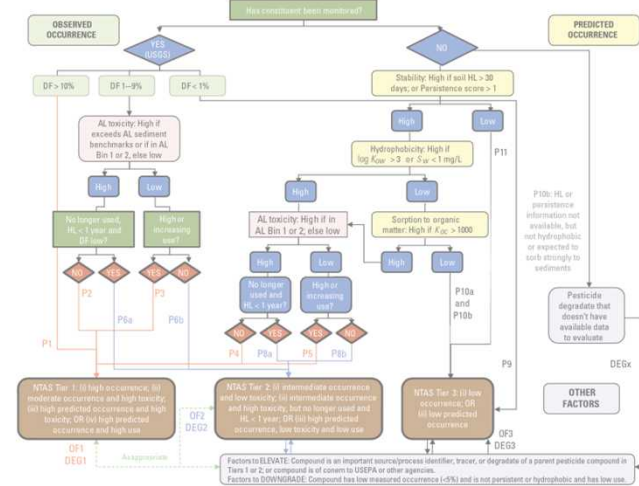
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National Water-Quality Assessment Program

Prioritization of Constituents for National- and Regional-Scale Ambient Monitoring of Water and Sediment in the United States



Labelled flowchart pathways are defined in table B2.1. DF: detection frequency; AL: aquatic life; AL Bin: NTAS Aquatic-Life Toxicity Bin; HL: soil half-life; log K_{ow}: log octanol-water partitioning coefficient; DR: water solubility, mg/L, milligrams per liter; S_w: soil organic carbon-water partitioning coefficient; USEPA: U.S. Environmental Protection Agency; <, less than; >, greater than; %, percent

Scientific Investigations Report 2012-XXXX

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Development of Screening Procedures

- Wherever possible, both occurrence and toxicity information were used in the screening procedures
- Preference for occurrence: National-scale modeling or NAWQA monitoring data > literature summaries > predicted from physiochemical (P-C) properties
- Preference for toxicity: benchmarks > NTAS toxicity bins
- Used common screening criteria, when feasible

Criteria for Tiering Constituents

- Common screening criteria:
 - Benchmark Quotient > 0.01
 - Detection frequency $\geq 10\%$
 - LTMDL ≤ 0.1 of benchmark
 - Byproducts tiered with parent
 - Indicator constituents
 - Priority of other agencies
 - Other constituents of interest and cost effective
- Unique screening criteria:
 - Chemical Prioritization Calculator – HPVs
 - Predicted concentrations – Pesticides
 - Hydrophobicity – Lipophilic Organics
 - Known constituent of a mixture with human-health concerns - VOCs

Priority Tiers

Tier 1. NTAS Constituent of Interest

Constituents that are of **highest regional, national, and/or international interest** based on consideration of human and/or ecological receptors, occurrence and effects information, and other information as appropriate for each constituent.

Tier 2. Constituent of Potential Interest

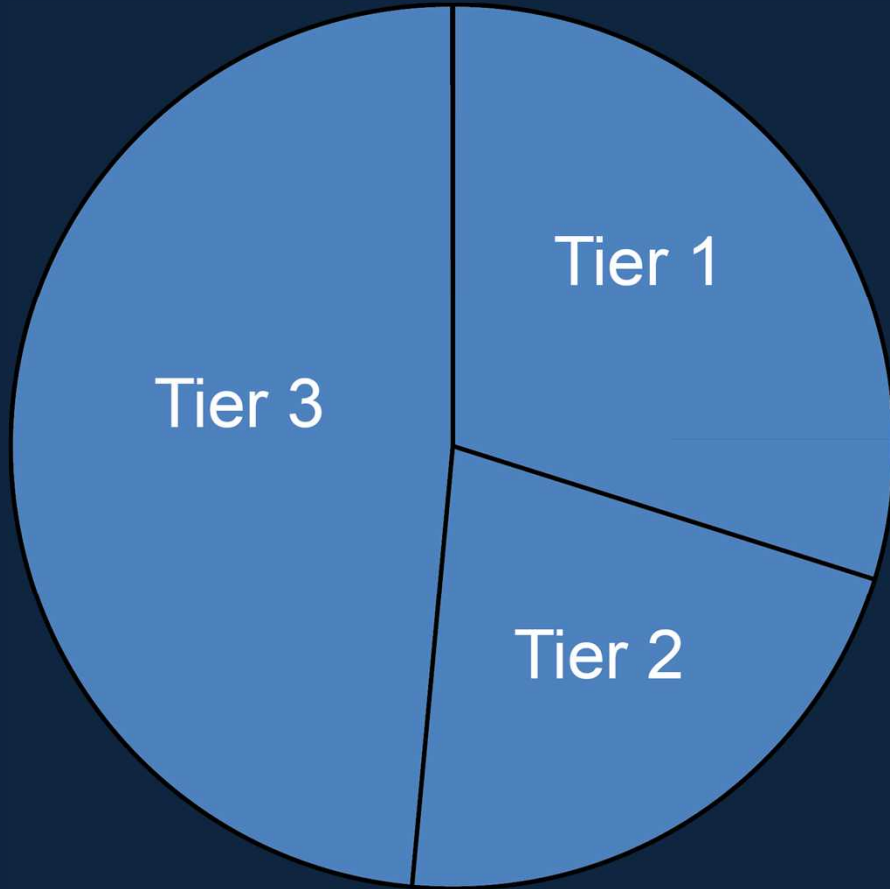
Constituents that are of secondary interest because there is **some indication of actual or potential occurrence and/or health and aquatic-life effects.**

Tier 3. Constituent of Little or No Interest

Constituents that may be of **potential interest in the future however, there is little or no information as a basis for inclusion in Tier 1 or Tier 2**, or for further evaluation as of 2011. Also included in Tier 3 are constituents that have been **monitored but not detected, or very infrequently detected**, in ambient waters.

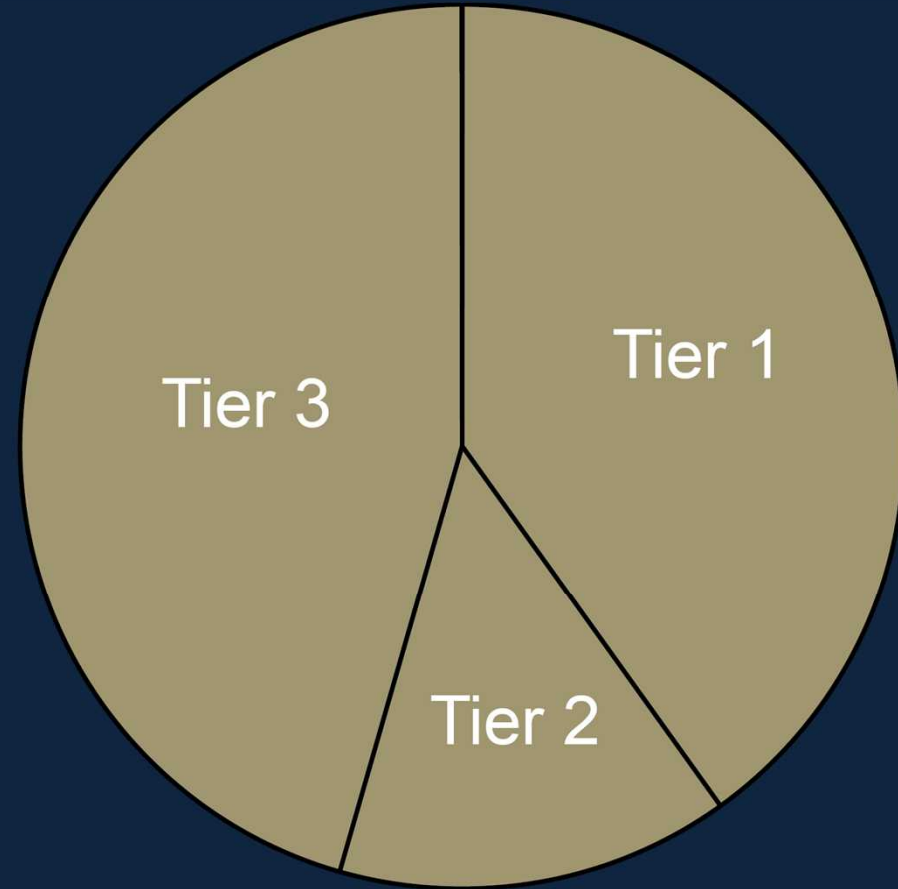
Results of the NTAS Screening

Water (n=2017)



Tier 1 – 602, 30%
Tier 2 – 436, 22%
Tier 3 – 979, 48%

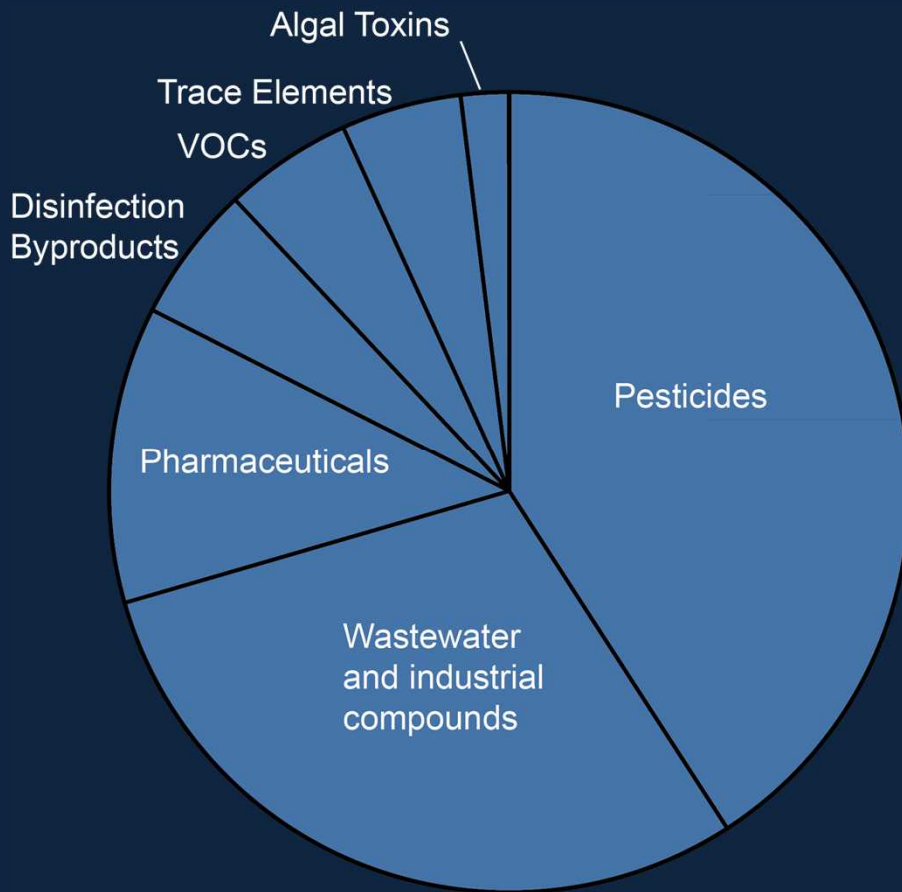
Sediment (n=1711)



Tier 1 – 686, 40%
Tier 2 – 246, 14%
Tier 3 – 779, 46%

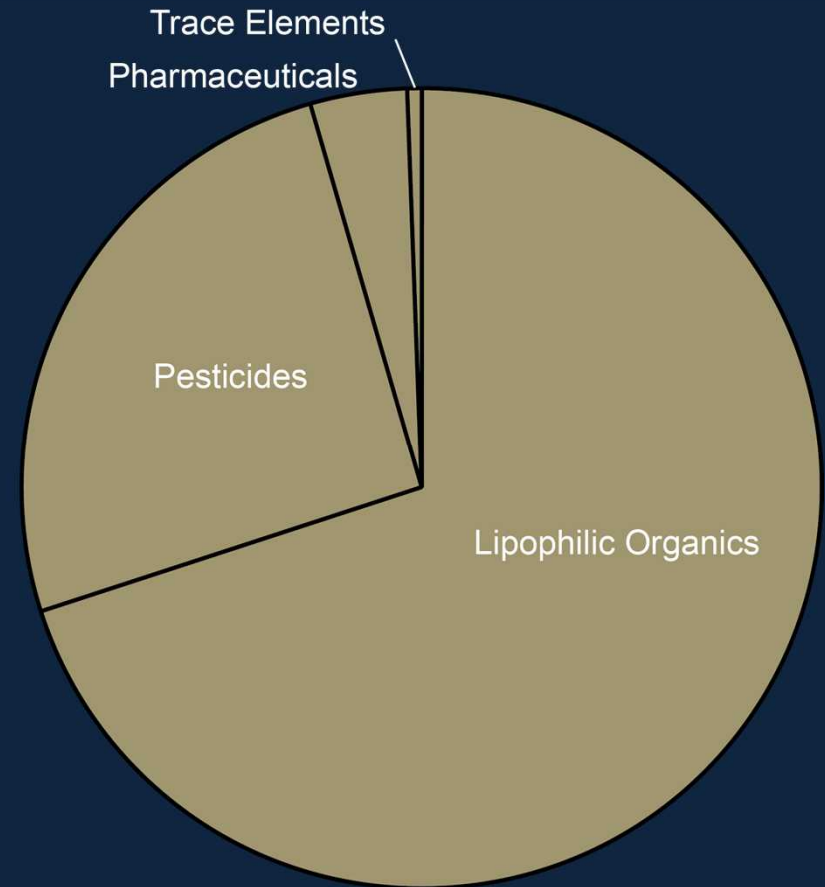
Tier 1 Results of the NTAS Screening

Water



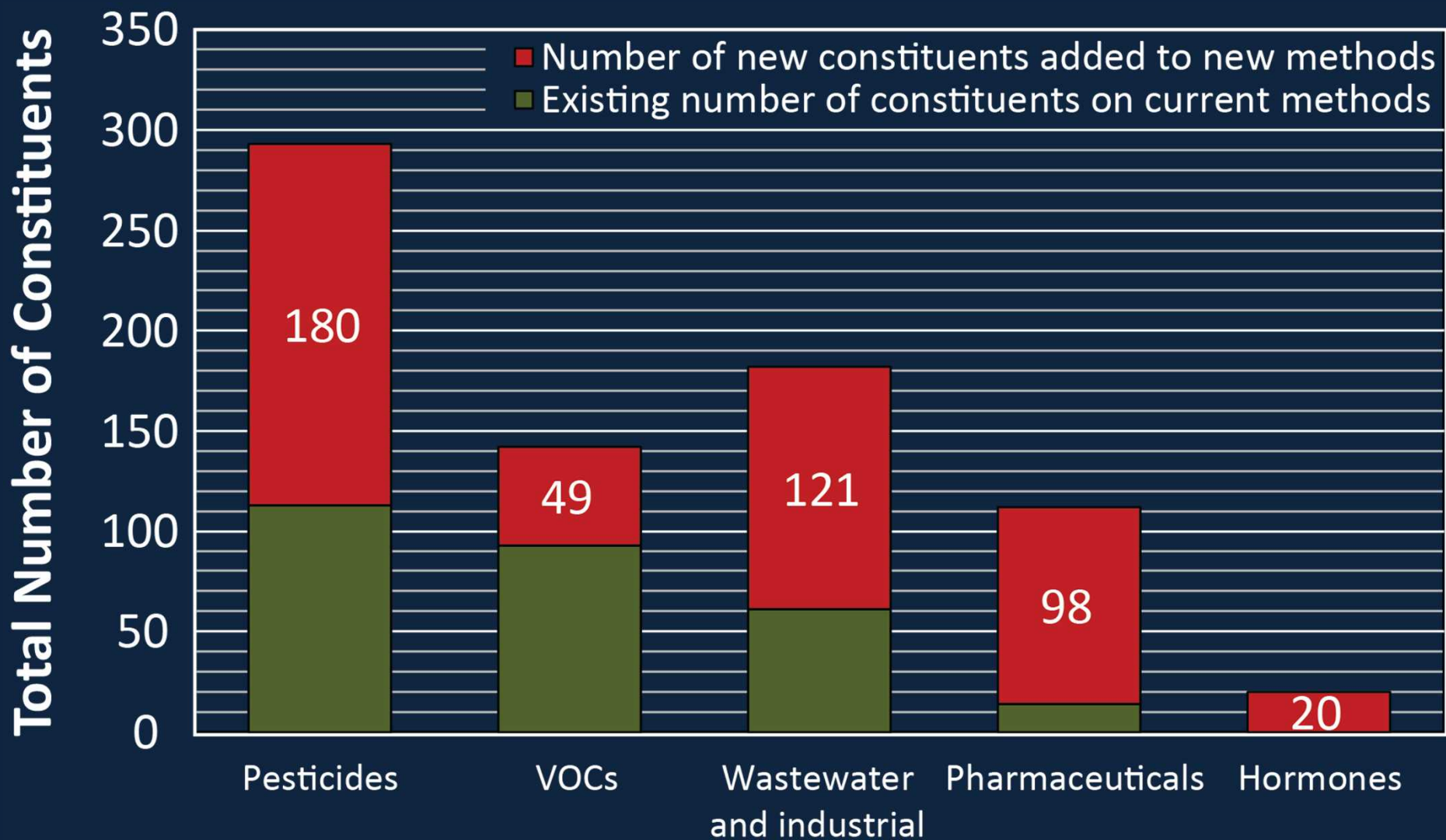
Pesticides – 41%
Wastewater and Industrials – 29%
Pharmaceuticals – 12%
DBPs – 6%
VOCs – 5%
Trace Elements – 5%
Algal Toxins – 2%

Sediment



Lipophilic Organics – 70%
Pesticides – 25%
Pharmaceuticals – 4%
Trace Elements – 1%

NAWQA's Priority for Water Sample Method Development



Analytical Methods for Water Samples

Analytical method	Constituent group	Remarks
DAI HPLC MS/MS	Pesticides	Approximately doubling the number of analytes compared to legacy methods with many of the new constituents being degradates.
GC/MS/MS	Pesticides	The analyte list is not yet final pending DAI validation. Higher specificity from MS/MS.
Ambient P+T GC/MS	VOCs	Similar to current ambient purge and trap GC/MS method, giving emphasis to only tier 1 constituents.
Heated P+T GC/MS SIM	VOCs	New selective ion monitoring method will provide lower reporting limits. Method includes 4 fumigants that need very low reporting levels.
GC/MS	Industrial, commercial and other organics	Replaces three lab schedules. Modified sample prep to achieve cost efficiency. Method development also focused on reduction of blank contamination. Many new analytes including HPVs, industrials, brominated flame retardants .
NCI GC/MS	Halogenated organics	More than 100 halogenated organic analytes are in this method, which have been validated for water, sediment, and tissue.
DAI HPLC MS/MS	Pharmaceuticals	~5X larger analyte list compared to existing method. Improved specificity due to MS/MS, sensitivity retained.
GC/MS/MS	Hormones	Uses isotope dilution standards for 20 constituents to correct for matrix effects.

Application of New Analytical Methods

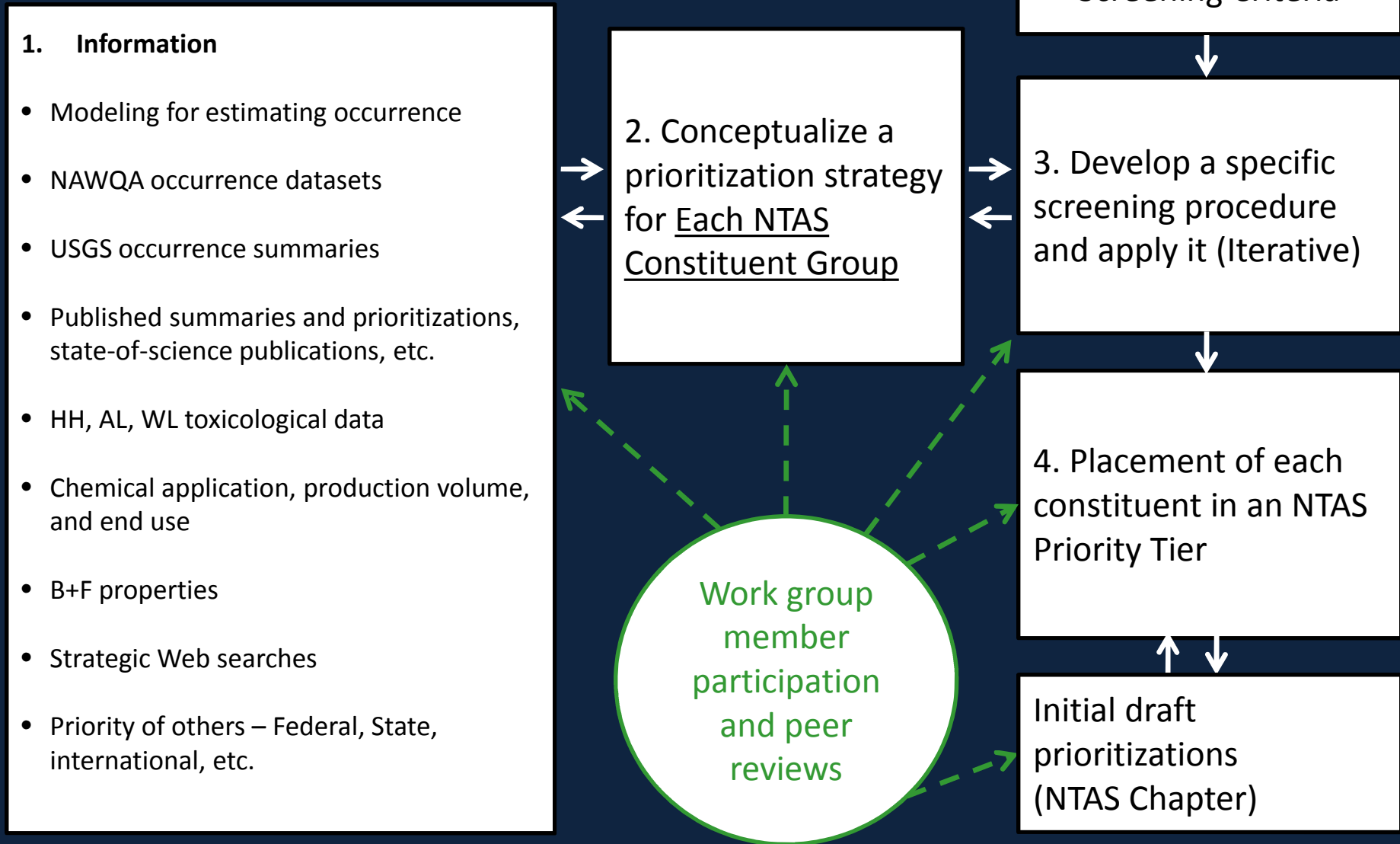
Constituent group	Analytical method	NAWQA study component		
		Surface water fixed station networks	Aquifer networks	Upper mid-west regional synoptic (NAWQA – NARS)
Pesticides	DAI HPLC MS/MS	X	X	X
Pesticides	GC/MS/MS	X (?)	X	X
VOCs	Ambient P+T GC/MS		X	
VOCs	Heated P+T GC/MS SIM		X	
Industrial, commercial and other organics	GC/MS			
Halogenated organics	NCI GC/MS			X (sed)
Pharmaceuticals	DAI HPLC MS/MS		X	
Hormones	GC/MS/MS			

Major Take Home Messages

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Supplemental Information

Variable Information Created the Need for Different Screening Procedures



NTAS Toxicity Bins

NTAS Human-health toxicity bins

NTAS HH toxicity bin	Description
1	Constituents with quantitative HH toxicity information or cancer classification
2	Constituents without quantitative HH toxicity information or cancer classification, but that appear on one of several priority lists related to human health
NIA	Constituents without relevant HH information available in USEPA ACToR database

Aquatic-life toxicity bin

NTAS AL toxicity bin	Toxicity endpoint concentration
1	Acute: <100 µg/L OR Chronic: <10 µg/L
2	Acute: 100–100,000 µg/L OR Chronic: 10–10,000 µg/L
3	Acute: >100,000 µg/L OR Chronic: >10,000 µg/L
NIA	Constituents without ECOTOX data that meet the study selection criteria

Members of the National Target Analyte Strategy (NTAS) Work Group

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