



Detection of New Emerging Contaminants in Water

Teen T. Chin, PhD

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What is an “Emerging Contaminant” ?



- May not be a “new” chemical
- Significance only recognised now
- These chemicals have been released into the environments as long as they have been in use
- **“Everything can be Found Everywhere”**



Definitions

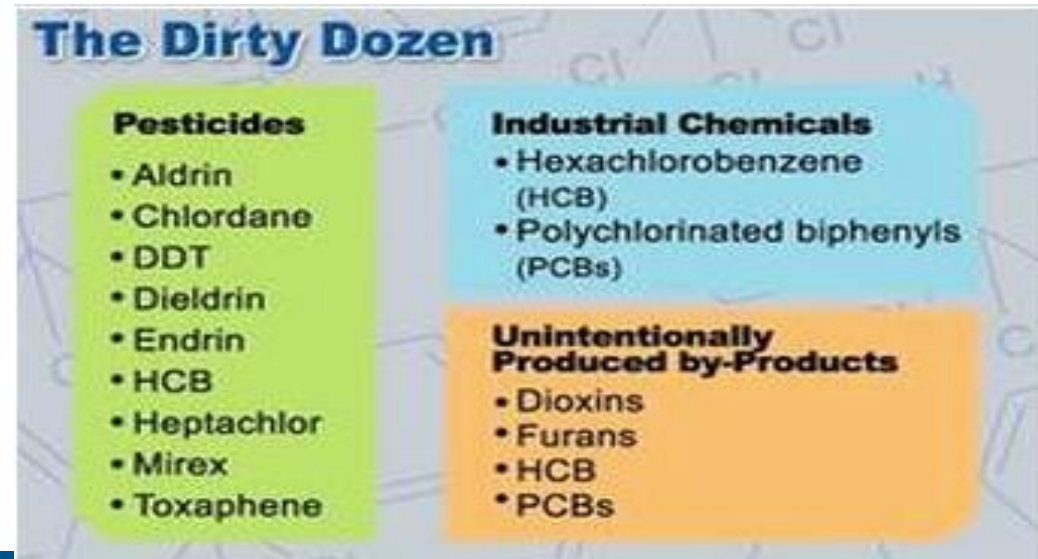


- “Contaminants with a potential threat to health and environment that have no regulatory standard.”
- “A chemical or material that has pathways to enter the environment and presents potential unacceptable human health or environmental risks, and either does not have regulatory peer-reviewed human health standards or the regulatory standards are evolving due to science, detection capabilities, or new pathways.”

“New Emerging Contaminants”... Acronyms...



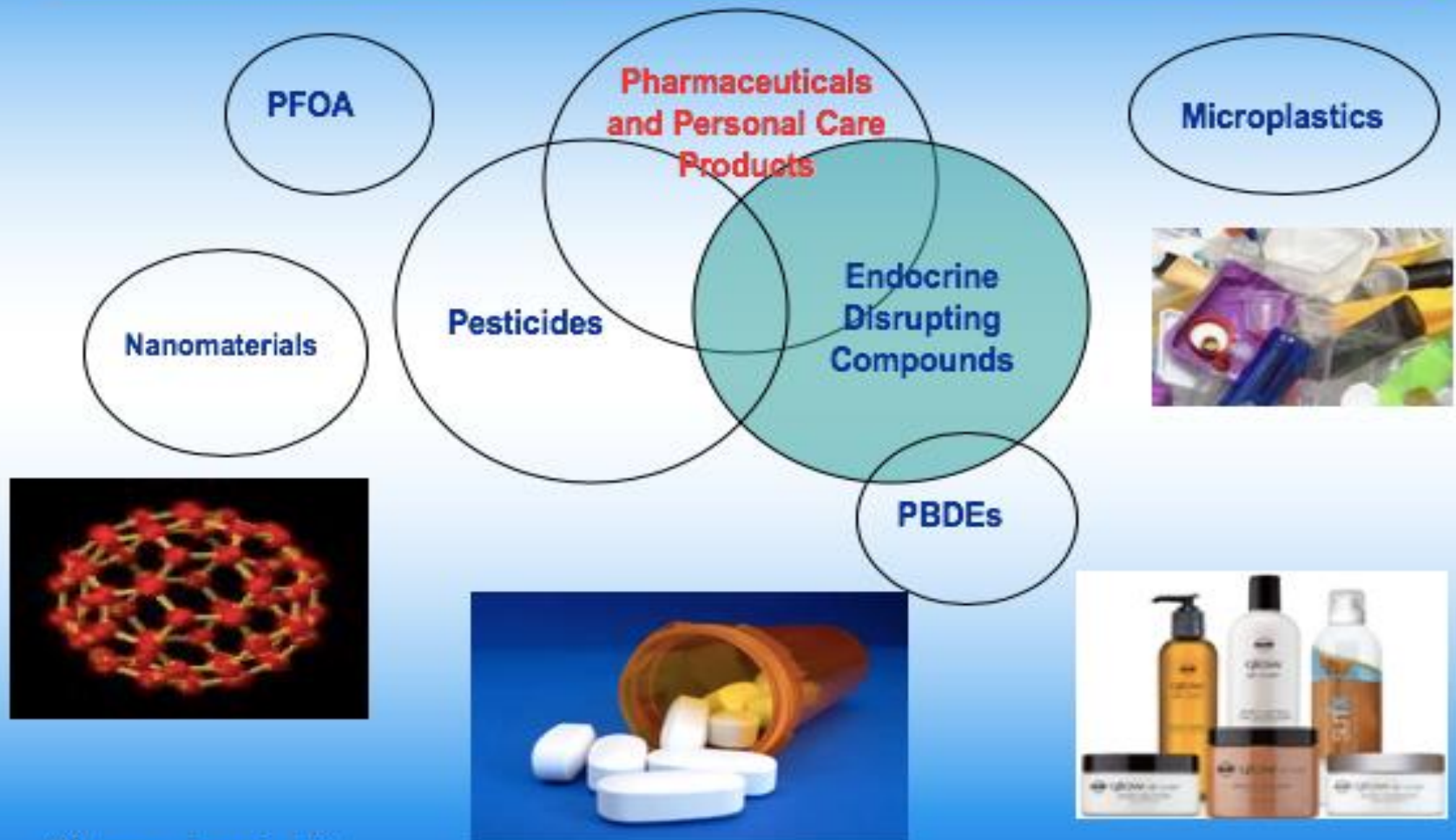
- “Dirty Dozen” – the original list
- POPs - Persistent Organic Pollutants
- PBTs – Persistent Bioaccumulative Toxic
- EDCs – Endocrine Disruptor Chemicals
- PCPPs – Pharmaceutical & Personal Care Products



“Emerging Contaminants”



*Contaminants of Emerging Concern in Water**



*Not an exhaustive list.

Endocrine Disruptor Chemicals



Some Classes of Known or Suspected EDCs



Effluents	WWTP, pulp and paper mills, CAFOs
Flame Retardants	PBDEs
Fungicides	Vinclozolin
Herbicides	Atrazine
Insecticides	Methoxychlor
Metals	Tributyltin
Pharmaceuticals	Ethinyl Estradiol
Phenols	Bisphenol A
Plasticizers	Phthalates
PAHs	PCBs, dioxin
Soy Products	Genistein
Surfactants	Alkylphenol
	Ethoxylates



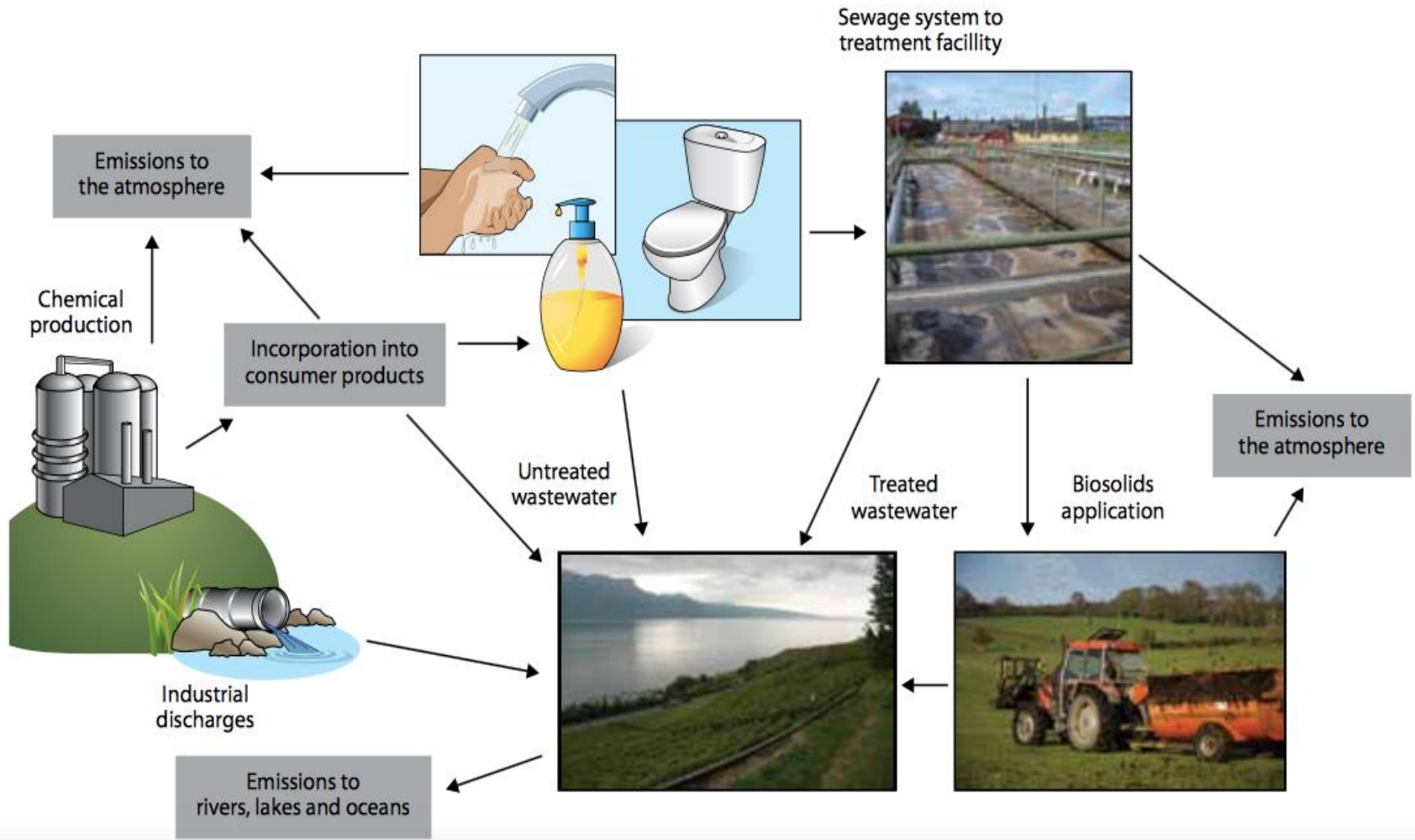
“The Chemical Universe”



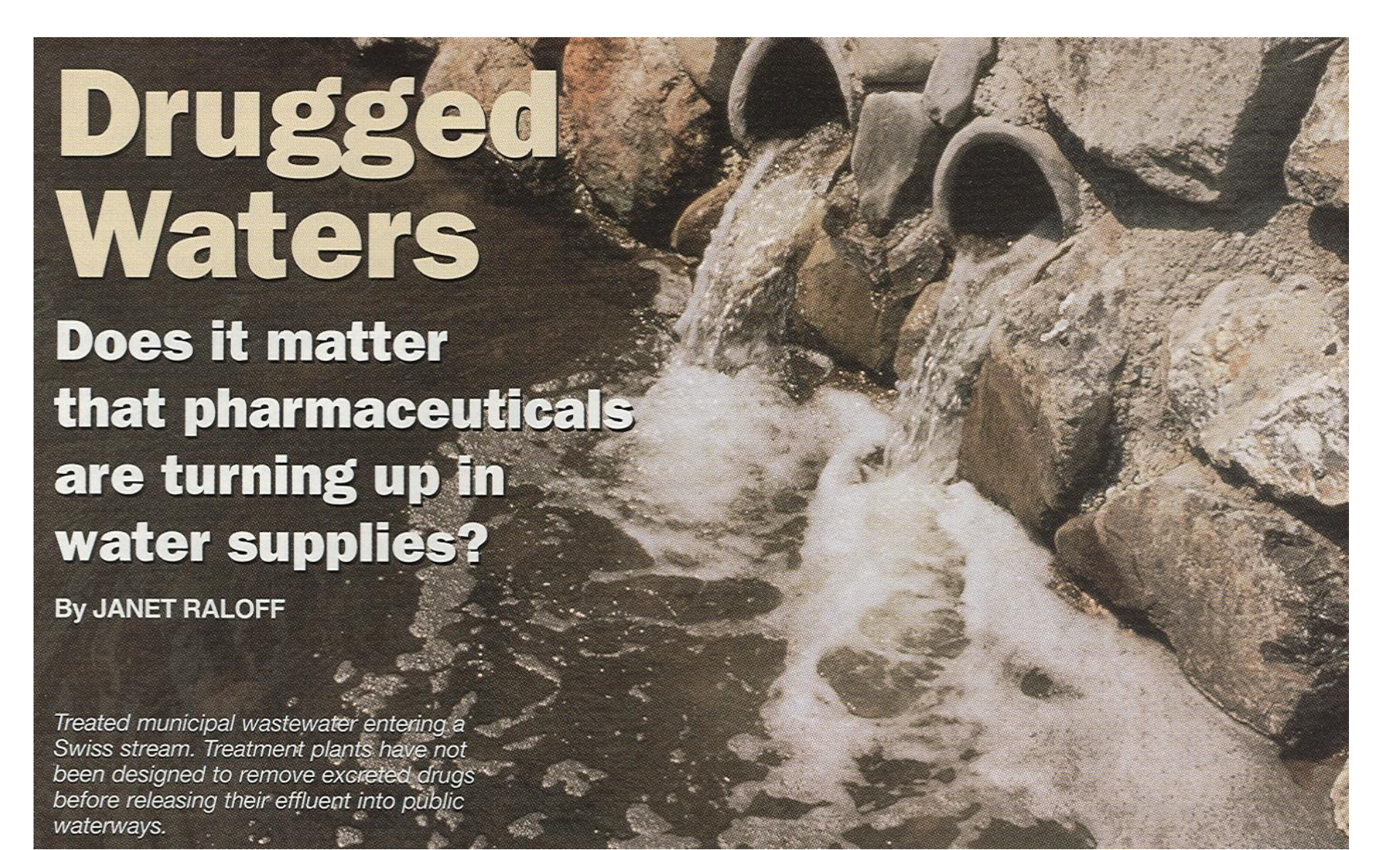
> 30 million chemicals



Emerging Contaminants in Environmental Waters



Drugged Waters



**Does it matter
that pharmaceuticals
are turning up in
water supplies?**

By JANET RALOFF

Treated municipal wastewater entering a Swiss stream. Treatment plants have not been designed to remove excreted drugs before releasing their effluent into public waterways.

MARCH 21, 1998

SCIENCE NEWS, VOL. 153

> *Sci Total Environ.* 2019 Jun 25;671:431-442. doi: 10.1016/j.scitotenv.2019.03.243.

Epub 2019 Mar 16.

Occurrence and risk assessment of multiclass endocrine disrupting compounds in an urban tropical river and a proposed risk management and monitoring framework

Sze Yee Wee ¹, Ahmad Zaharin Aris ², Fatimah Md Yusoff ³, Sarva Mangala Praveena ⁴

PLANNING MALAYSIA:

Journal of the Malaysian Institute of Planners

VOLUME 17 ISSUE 2 (2019), Page 168 – 178

SOURCE WATER PROTECTION FROM PHARMACEUTICAL CONTAMINANTS: ASSESSMENT OF ENVIRONMENTAL QUALITY ACT 1974 AND ITS REGULATIONS

Adillah Othman¹ & Mariani Ariffin²

^{1,2}Faculty of Environmental Studies
UNIVERSITI PUTRA MALAYSIA

> *J Water Health*. 2013 Jun;11(2):311-23. doi: 10.2166/wh.2013.151.

Assessment of endocrine disruptors – DDTs and DEHP (plasticizer) in source water: a case study from Selangor, Malaysia

Santhi Armugam Veerasingam ¹, Mustafa Ali Mohd

Environment International

Volume 106, September 2017, Pages 207-233

Endocrine disrupting compounds in drinking water supply system and human health risk implication

Sze Yee Wee, Ahmad Zaharin Aris*

Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia

What we know and don't know



- Encompasses many classes of chemicals
- Not all are currently regulated
- Unknown or incomplete knowledge of environmental fate and toxicity in tropical countries
- Different consumption behavior, temperature, climate conditions

“Emerging Contaminants”



- “Emerging Awareness”
- Most are not new to the Environment



- New chemicals (new drugs / pesticides)
- New advances in Chemical Analysis
- Ability to detect existing pollutants at lower concentrations

Detection Challenges



Few distinct chemicals at higher concentrations

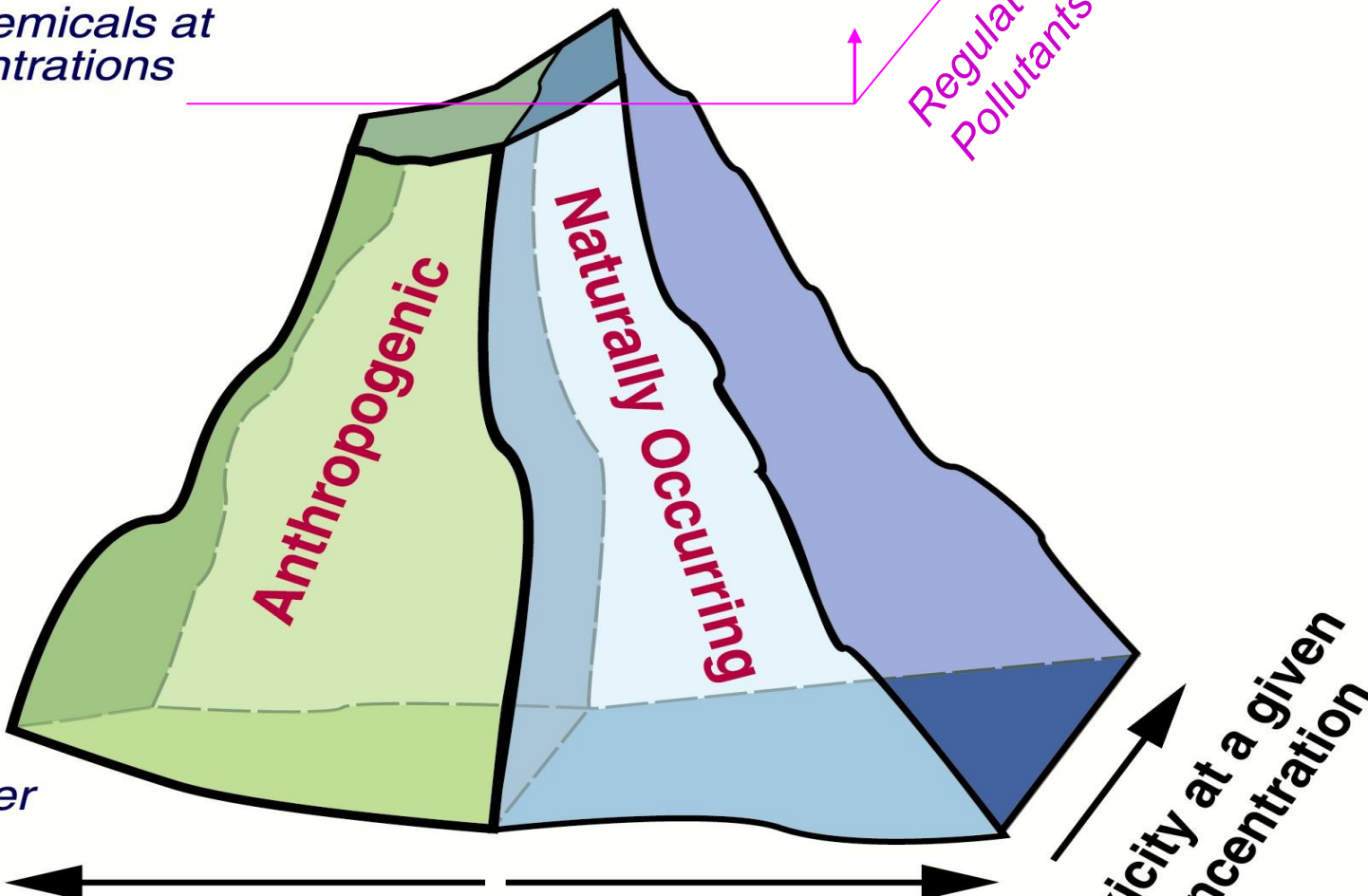
Concentration (log)

Regulated Pollutants

Anthropogenic

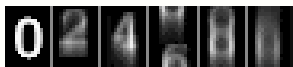
Naturally Occurring

Many distinct chemicals at lower concentrations

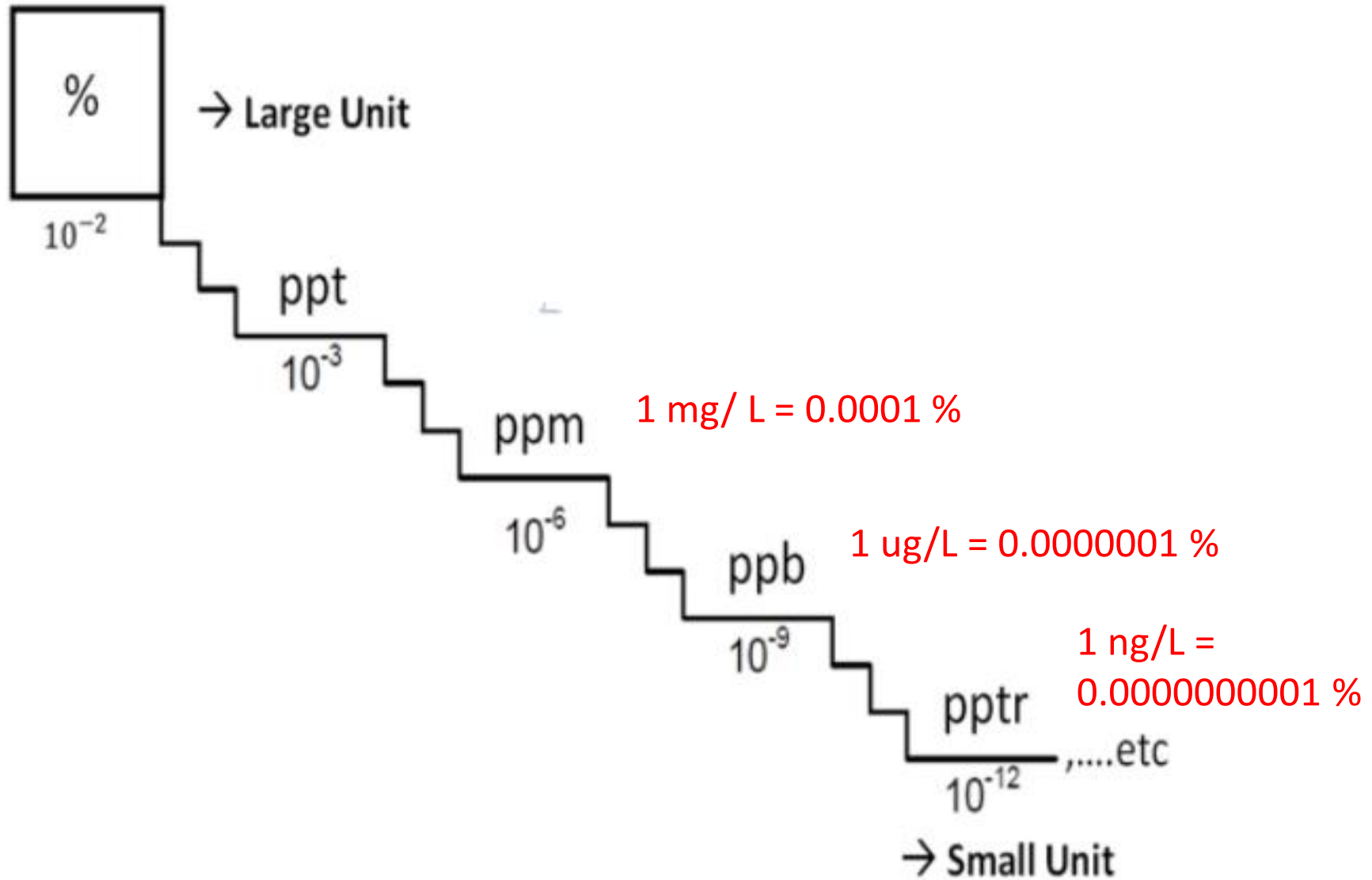


Types of distinct chemicals (log)

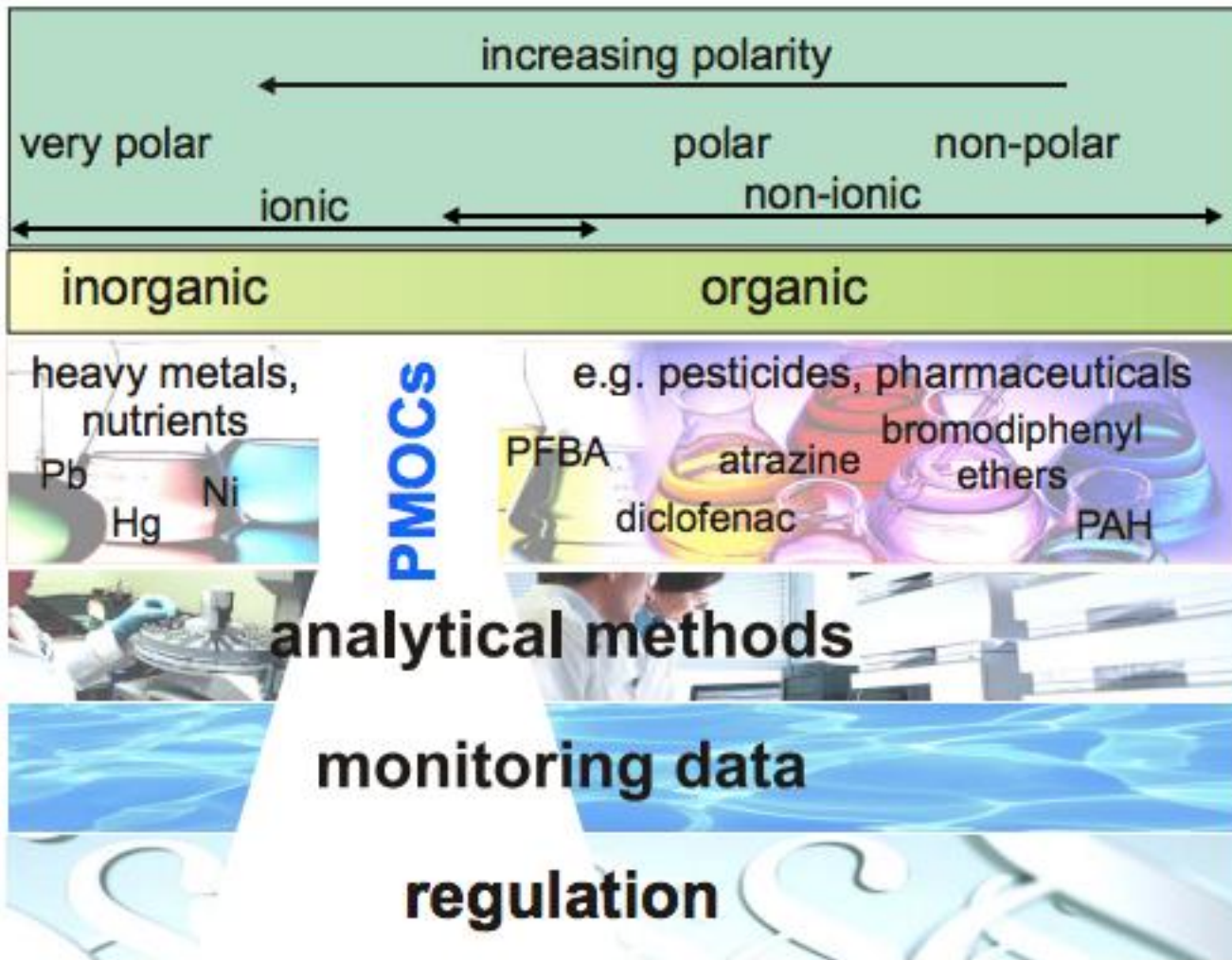
Toxicity at a given concentration

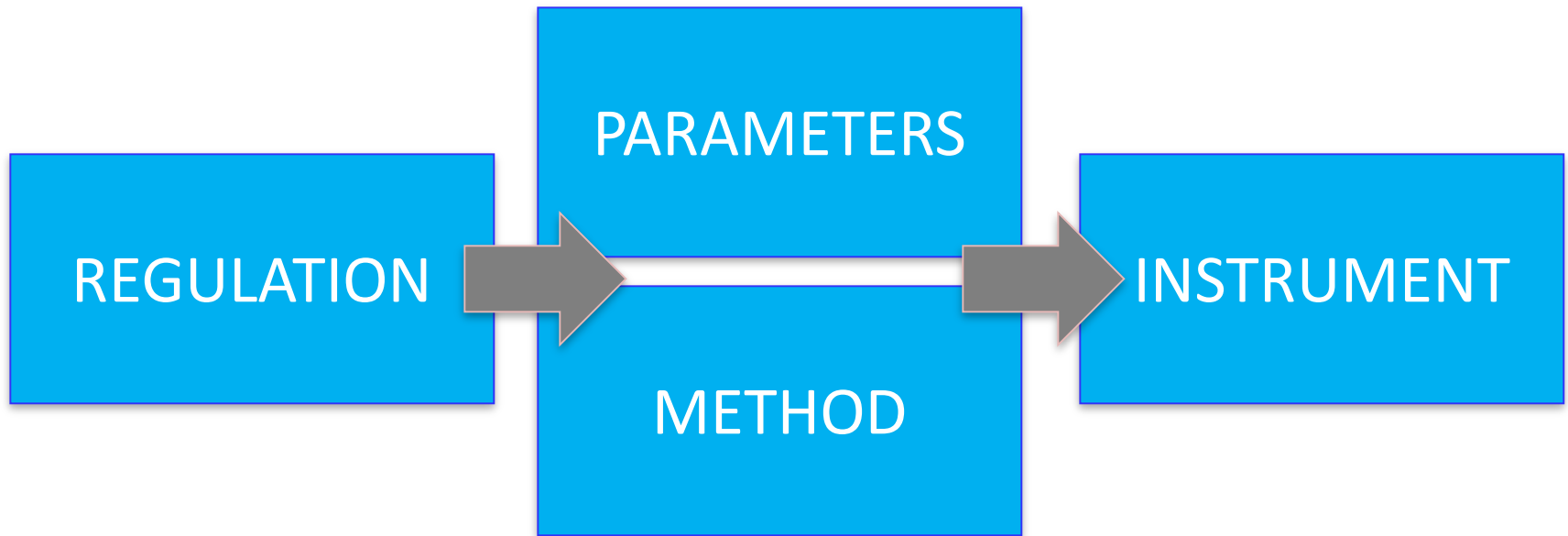


Units of Measurement – in Water

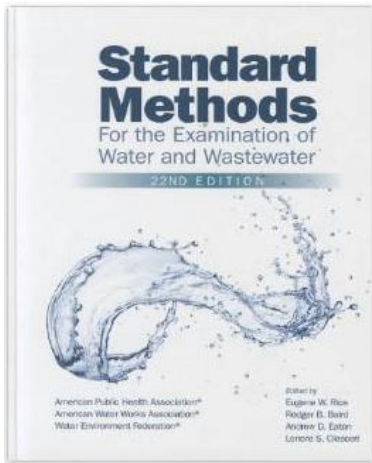


The Chemical Universe





Analytical Method References


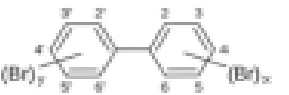
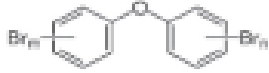





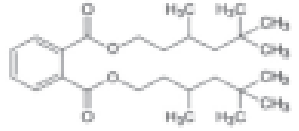


**MALAYSIAN
STANDARD**

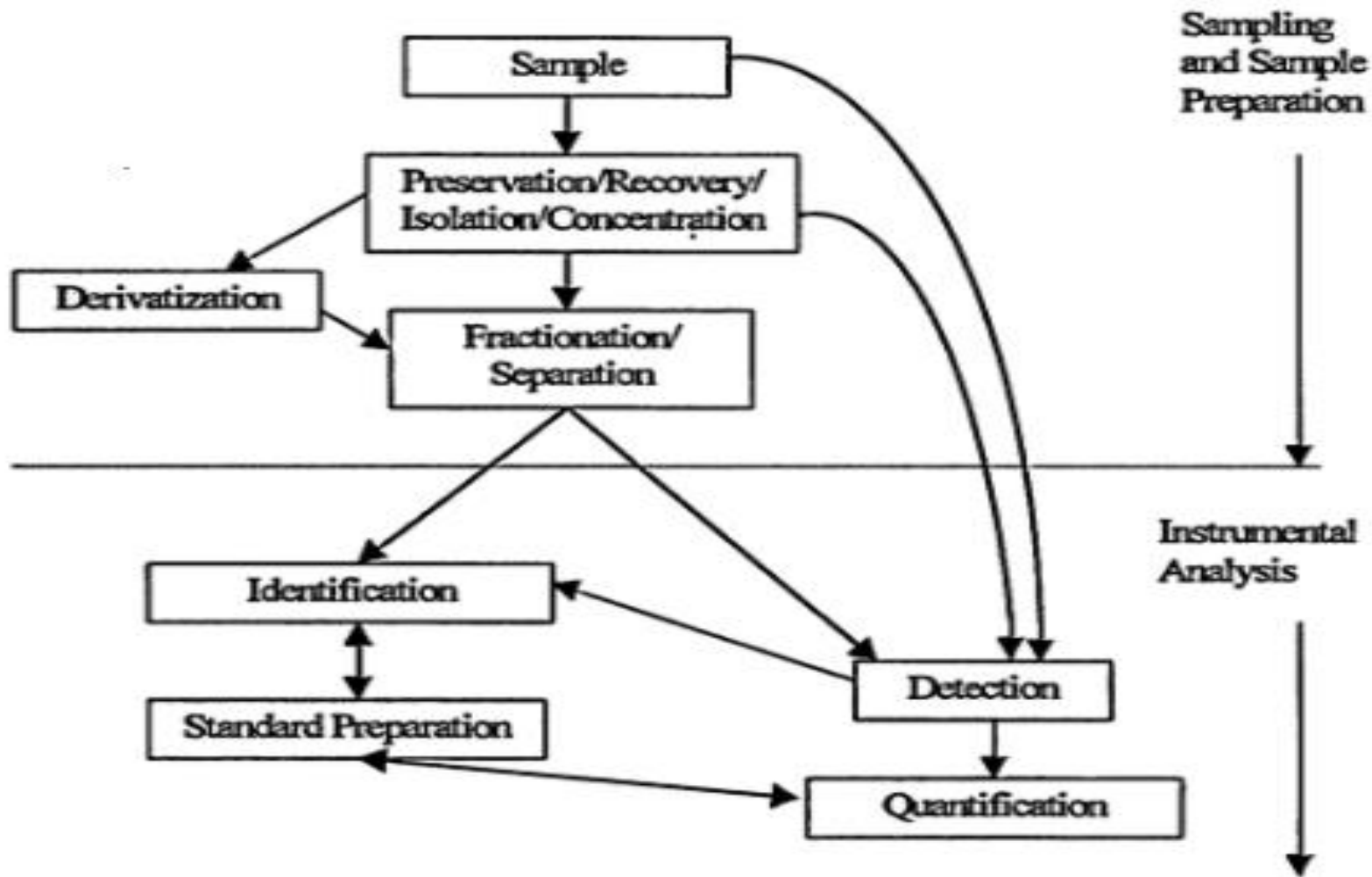


Trace Organic Contaminants - Examples

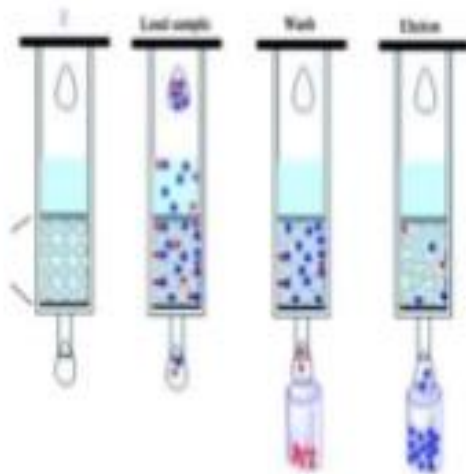


EDC class	Example and structure	Usage
Polyhalogenated compounds	 <p>Polychlorinated biphenyls (PCBs)</p>	<ul style="list-style-type: none"> - Flame retardants - Surfactants
	 <p>Polybrominated biphenyls (PBBs)</p>	
	 <p>Polybrominated diphenyl ethers (PBDEs)</p>	
Phenolic compounds	 <p>Perfluorooctanesulfonic acid (PFOS)</p>	<ul style="list-style-type: none"> - Plasticizers - Surfactants - Lubricants - Fragrances - Antioxidants - Additives
	 <p>Perfluorooctanoic acid (PFOA)</p>	
	 <p>Bisphenol A (BPA)</p>	
	 <p>Nonylphenol (NP)</p>	
	 <p>Octylphenol (OP)</p>	
	Phthalates	
 <p>Di-isononyl phthalate (DINP)</p>		

General Analytical Protocol for Identification



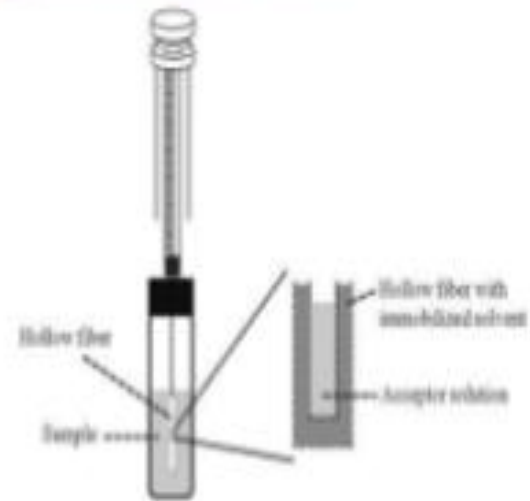
Extraction methods



Solid phase extraction
(SPE)



Solid phase micro-extraction
(SPME)



Liquid phase micro-extraction
(LPME)

- Mostly mass-spectrometry based methods

- GC-MS
- HPLC-MS
- HPLC-UV
- GC-MS/MS
- LC-MS/MS
- LC-MS/TOF



Preparation and Analytical Detection Methods.... Even More Acronyms ...

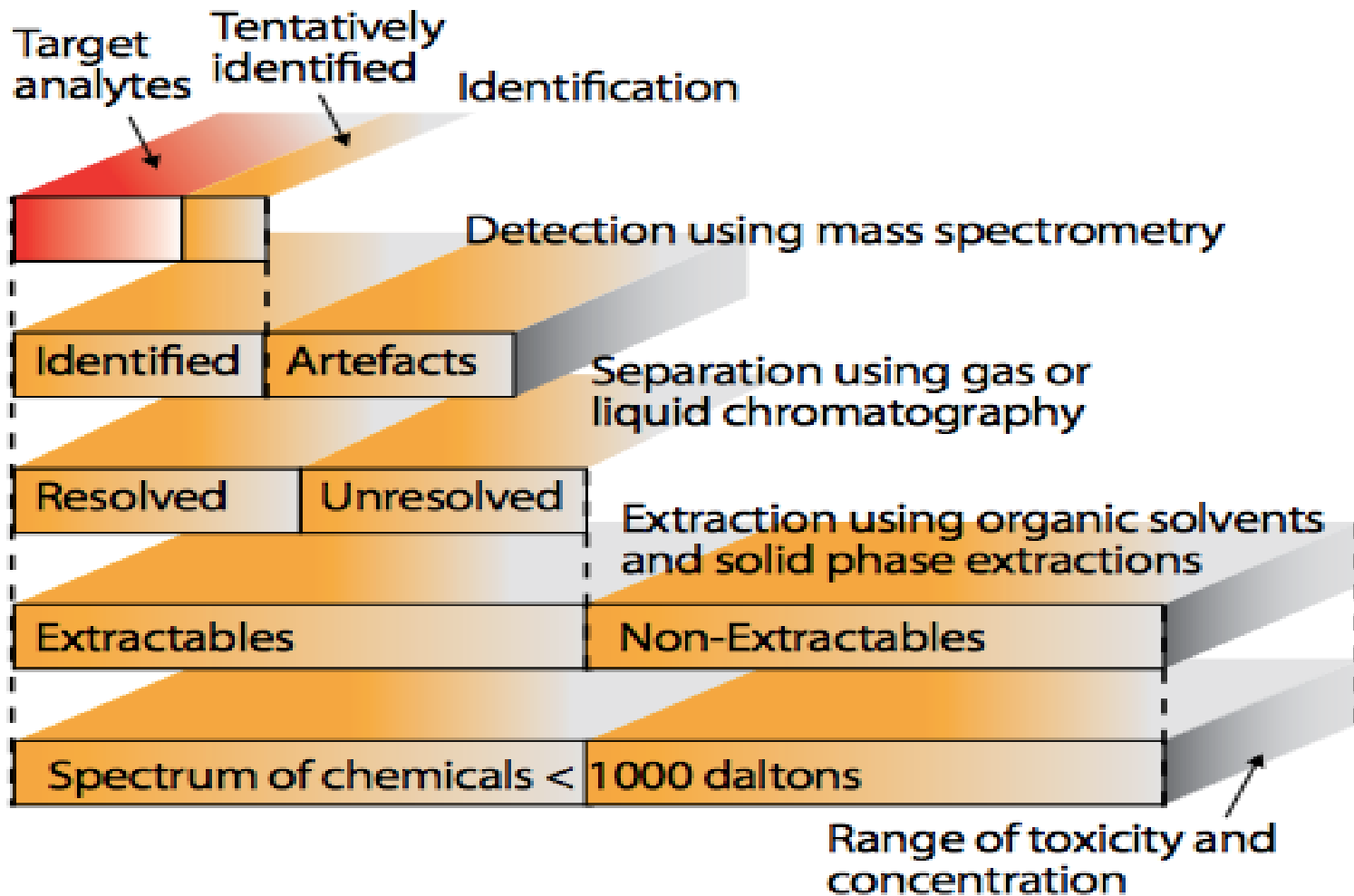


Extract / clean-up / pre-concentrate / analyze

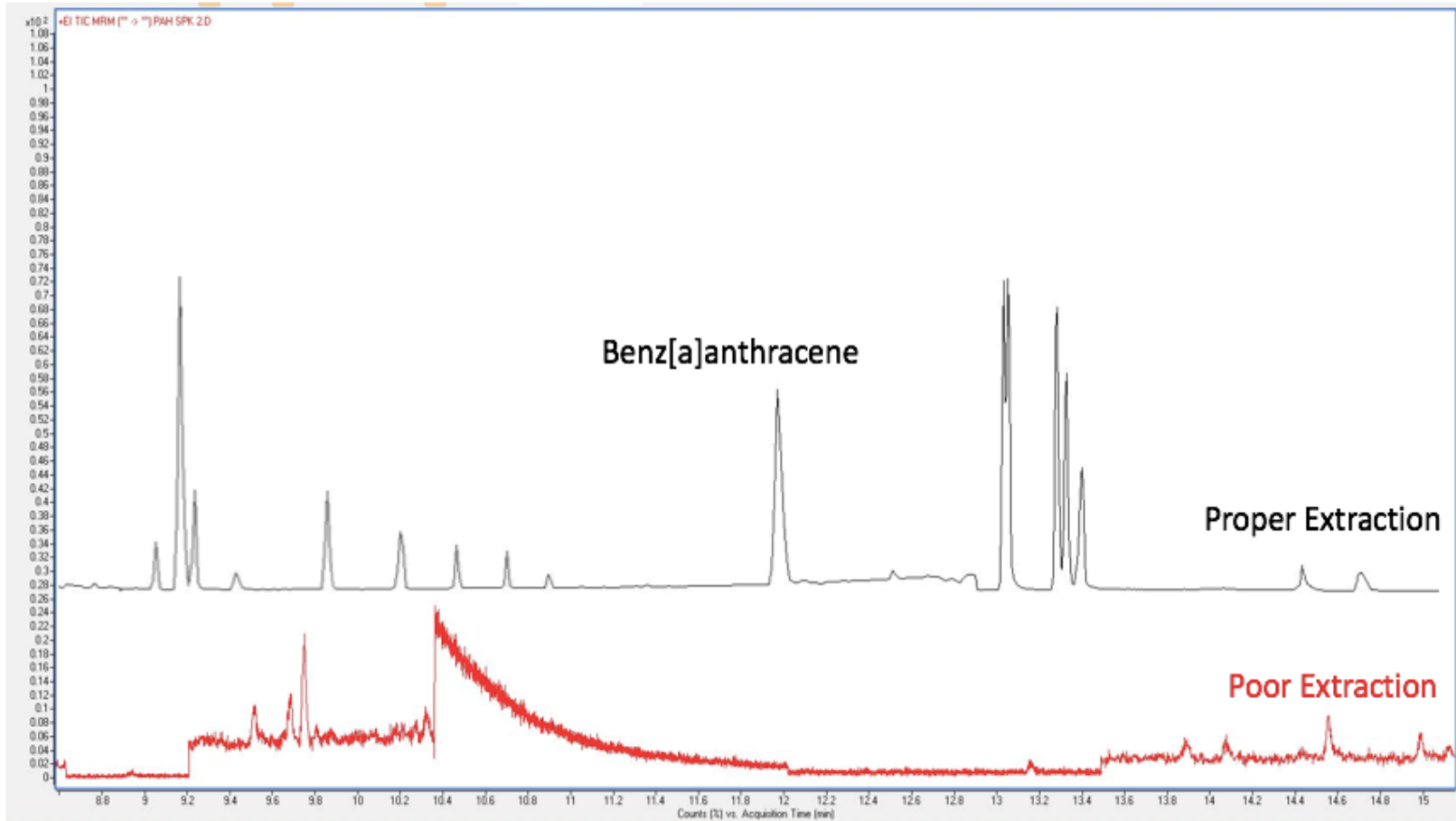
- SPE - GC-MS/MS
- SPME - GC-MS/MS
- SPE - LC-MS/MS



Detection of Ultra-Trace Organic Contaminants



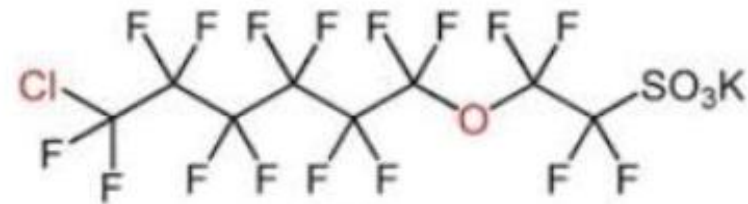
PAH analysis in GC-MS/MS



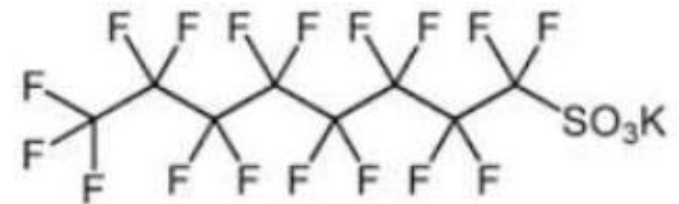
PFAS (Polyfluorinated Alkyl Substances)



- Man-made chemicals
- Thousands of variations
- Chemistry of Fluorocarbons – extensive and complex
- ~ 10,000 types
- Used commercially for 50+ years

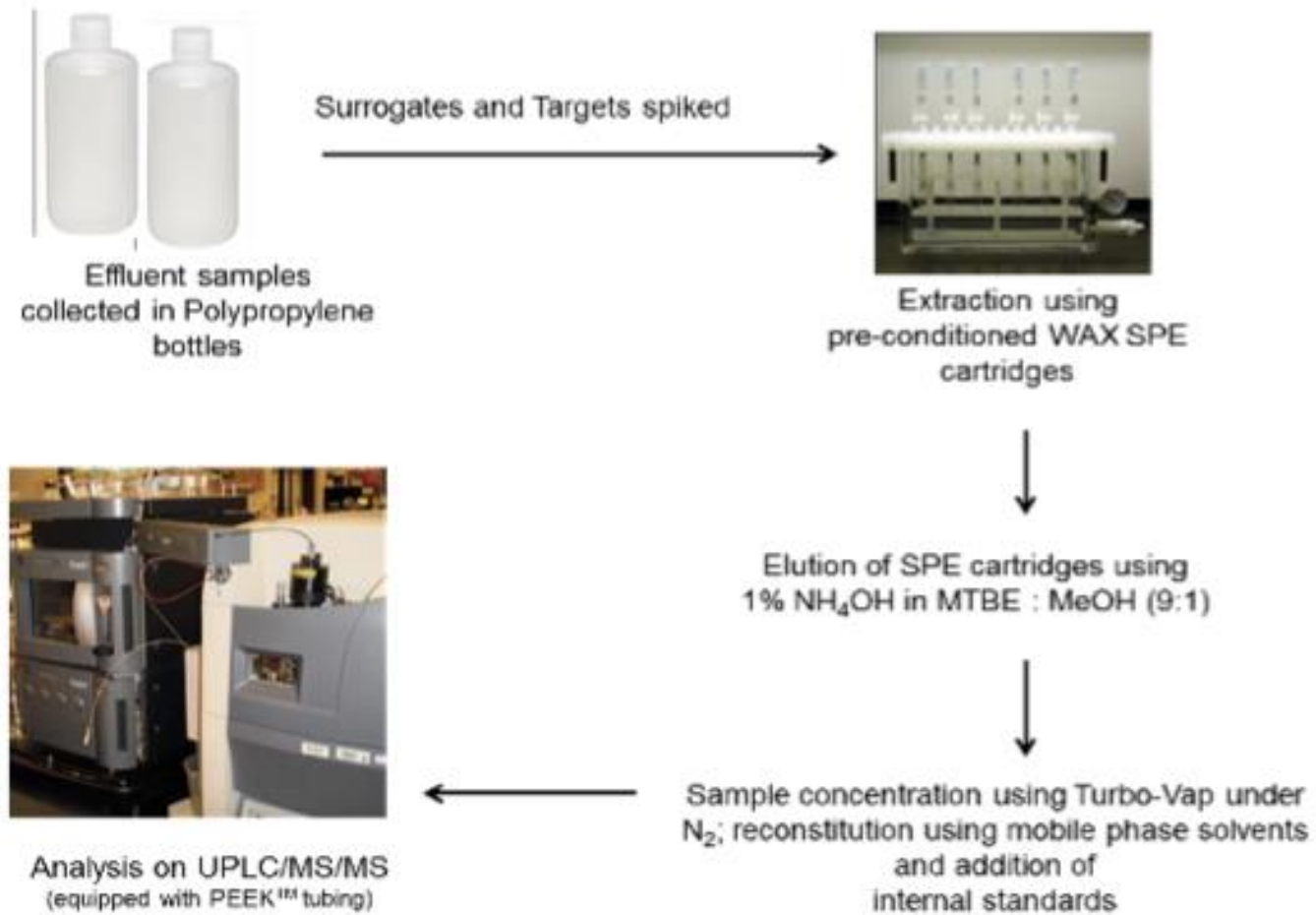


F-53B



PFOS

Detection in Drinking Water – EPA 537.1

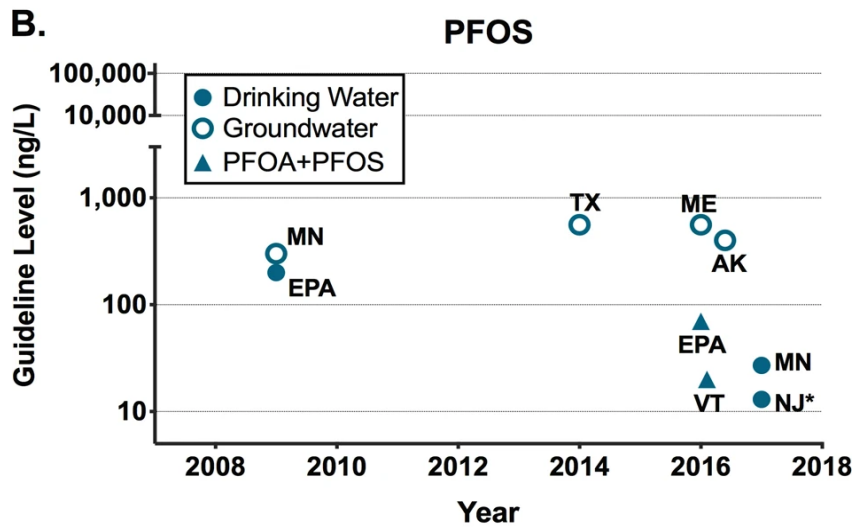
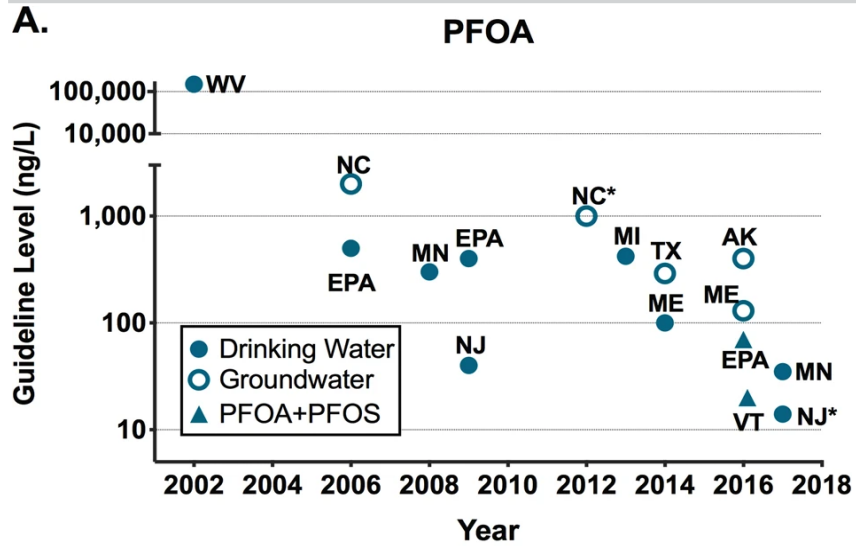


Methodologies - PFAS



Method	EPA 537	EPA 537.1	ASTM D7979-17	ASTM D796 8-17	EPA 8327	EPA 8328	EPA 8329	EPA "Short Chain"
Sample	Drinking Water	Drinking Water	Ground/ Surface/ Waste Water Effluent	Soil Sludge	Ground/ Surface/ Waste Water Effluent	EPA 8327 Soil Sludge	Soil Sludge	Water
Target	14	18	21	21	24 (EPA 537+10)	25 (EPA 8327+ GenX)	24 (EPA 537+ 10)	25

Regulated Tests – in the US



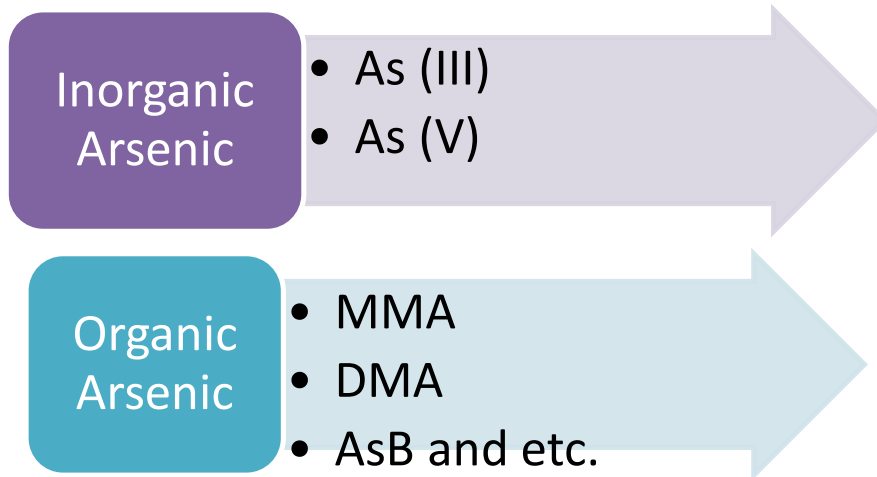
* indicates draft/proposed levels



Inorganics - Arsenic Species

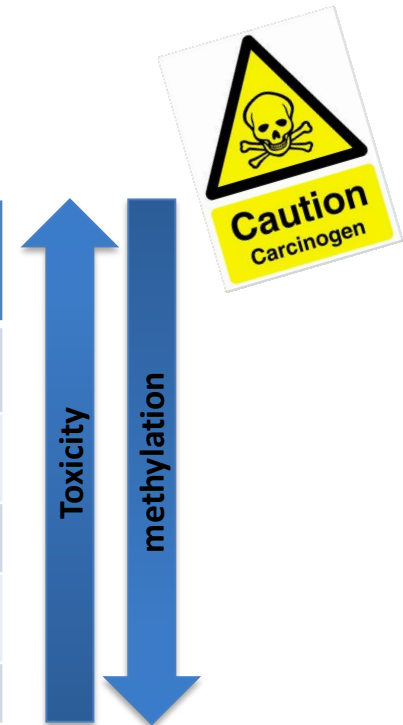


- Arsenic exist in various chemical forms. Classified as 2 major group:



- The toxicity decreases with increasing methylation

As species	LD 50 (mg/kg)
As(III)	34.5
As(V)	41
DMA	1200
MMA	1800
AsB	10,000



Inorganic As > Organic As

Toxicity

As(III) > As(V) > MMA > DMA > Arsenobetaine

Inorganics – Mercury Species



- Mercury exist in 3 chemical forms

Elemental Mercury

- Hg^0

Inorganic Mercury

- Hg^{2+}
- Hg^+

Organic Mercury

- Methyl Mercury
- Ethyl Mercury



Amplification factor in food chain means larger predatory fish contain higher levels of MeHg^+

Elemental Mercury < Inorganic Hg < Organic Hg

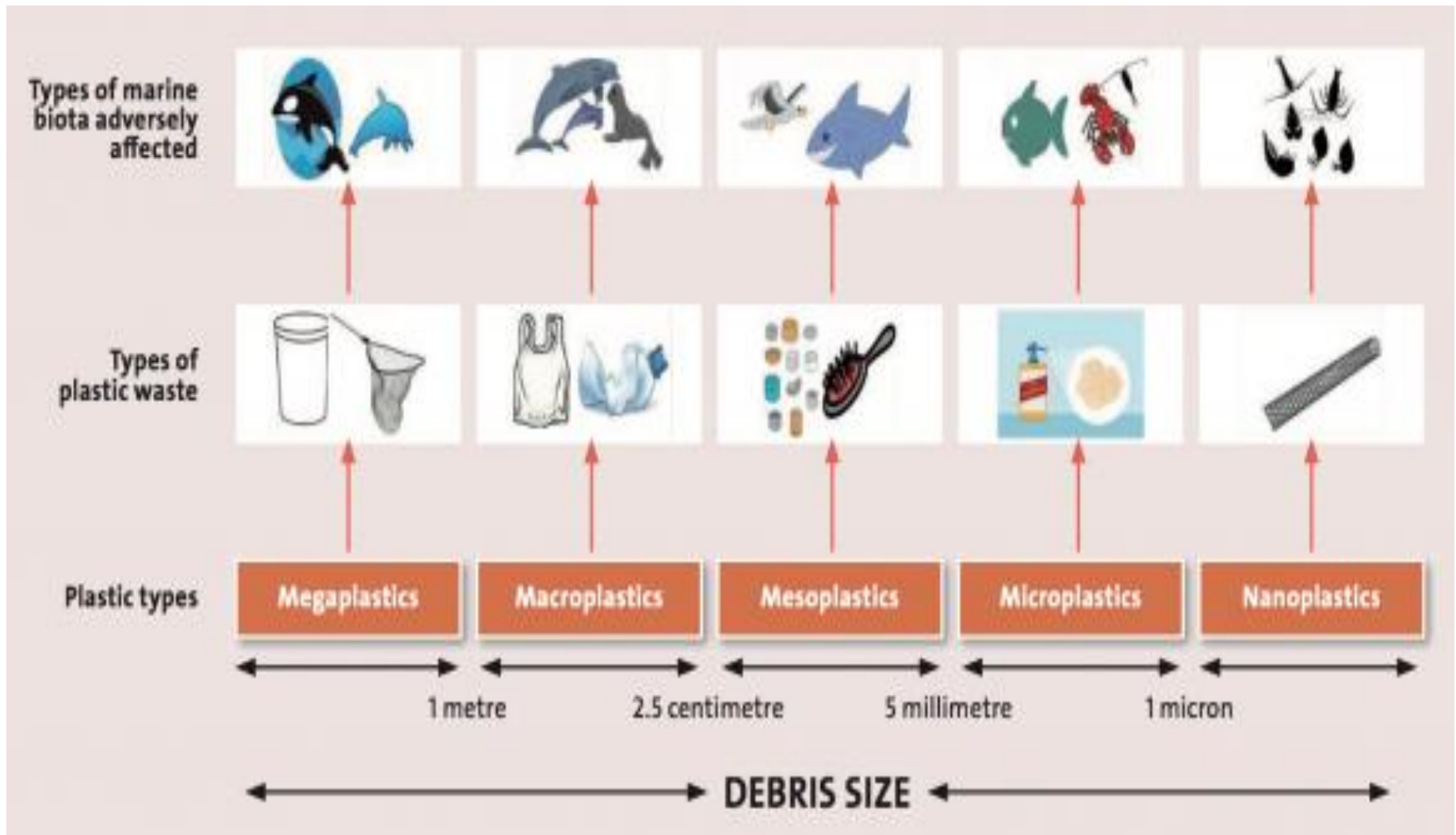
Toxicity



Elemental speciation by LC-ICPMS



Plastics Pollution



Types of plastics



PETE

polyethylene terephthalate

soft drink bottles, mineral water, fruit juice container, cooking oil



HDPE

high-density polyethylene

milk jugs, cleaning agents, laundry detergents, bleaching agents, shampoo bottles, washing and shower soaps



PVC

polyvinyl chloride

trays for sweets, fruit, plastic packing (bubble foil) and food foils to wrap the foodstuff



LDPE

low-density polyethylene

crushed bottles, shopping bags, highly-resistant sacks and most of the wrappings



PP

polypropylene

furniture, consumers, luggage, toys as well as bumpers, lining and external borders of the cars



PS

polystyrene

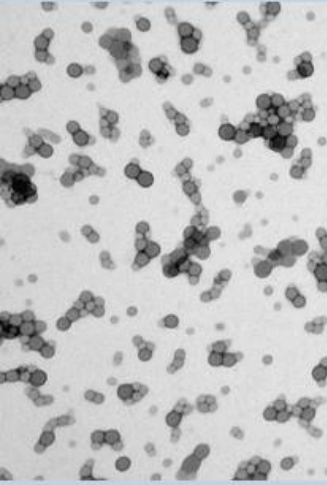



toys, hard packing, refrigerator trays, cosmetic bags, costume jewellery, CD cases, vending cups



OTHER

other plastics, including acrylic, polycarbonate, polyactic fibers, nylon, fiberglass

Microplastics

	< 1 μm	5 mm	2.5 cm	> 1 m
	nano	micro	meso	macro
				

WHO launches health review after microplastics found in 90% of bottled water

Researchers find levels of plastic fibres in popular bottled water brands could be twice as high as those found in tap water



"We urgently need to know more about the health impact of microplastics because they are everywhere – including in our drinking-water,"

Dr Maria Neira, WHO Director of Public Health

HOME / MALAYSIA

WWF-Malaysia report: 'Tapau' culture major contributor to country's plastic waste problems

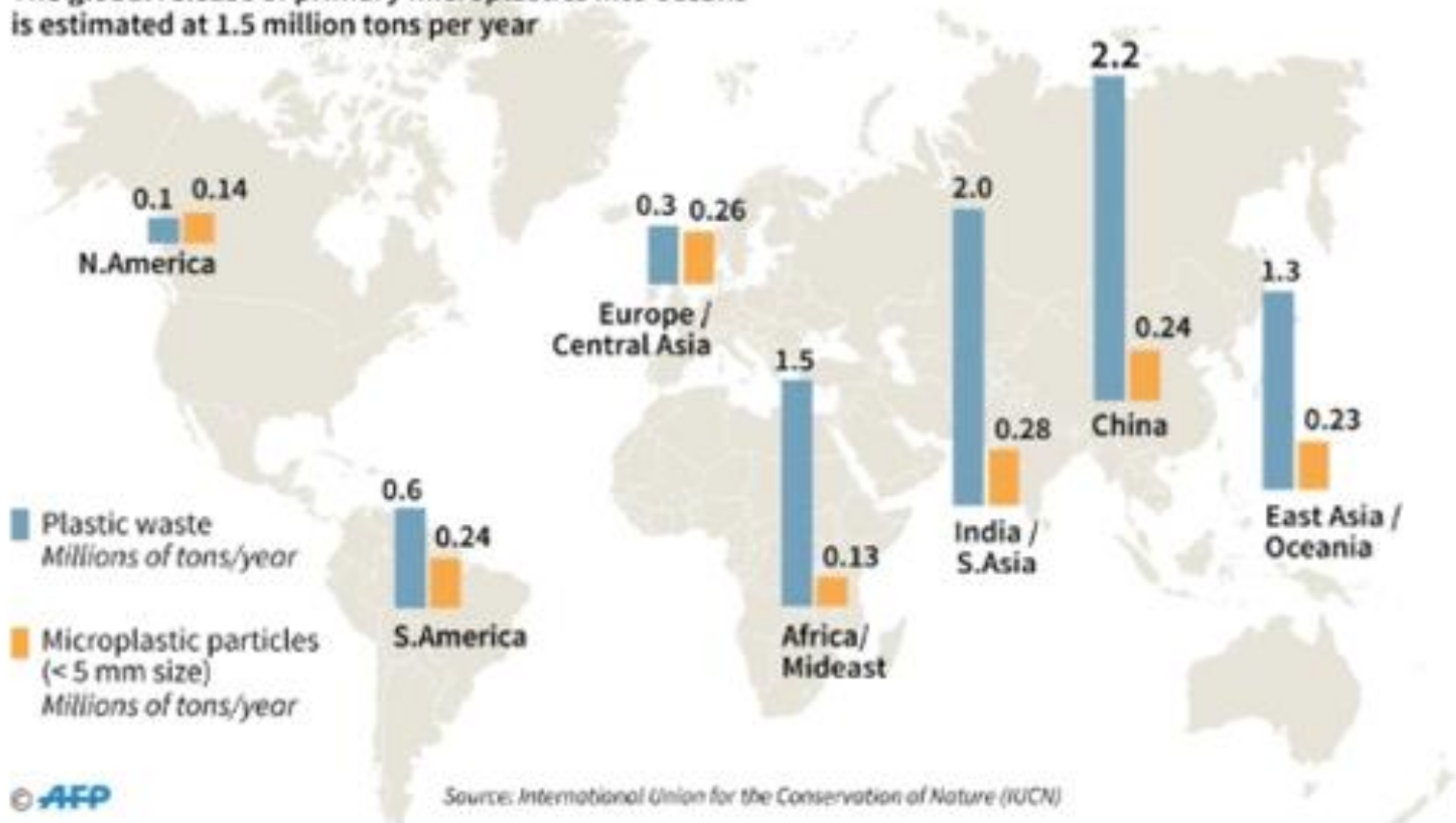
Monday, 21 Sep 2020 08:00 PM MYT

Plastic Pollution - Oceans



Plastic pollution released into the world's oceans

The global release of primary microplastics into oceans is estimated at 1.5 million tons per year



“Plastic Pandemic”



Covid-19: Klang River monitored for contamination after face masks, gloves and sanitiser bottles found during clean-ups

Thursday, 16 Apr 2020 01:53 PM MYT

Conservationists warn Covid waste may result in 'more masks than jellyfish' in the sea

By Francesca Giuliani-Hoffman, CNN

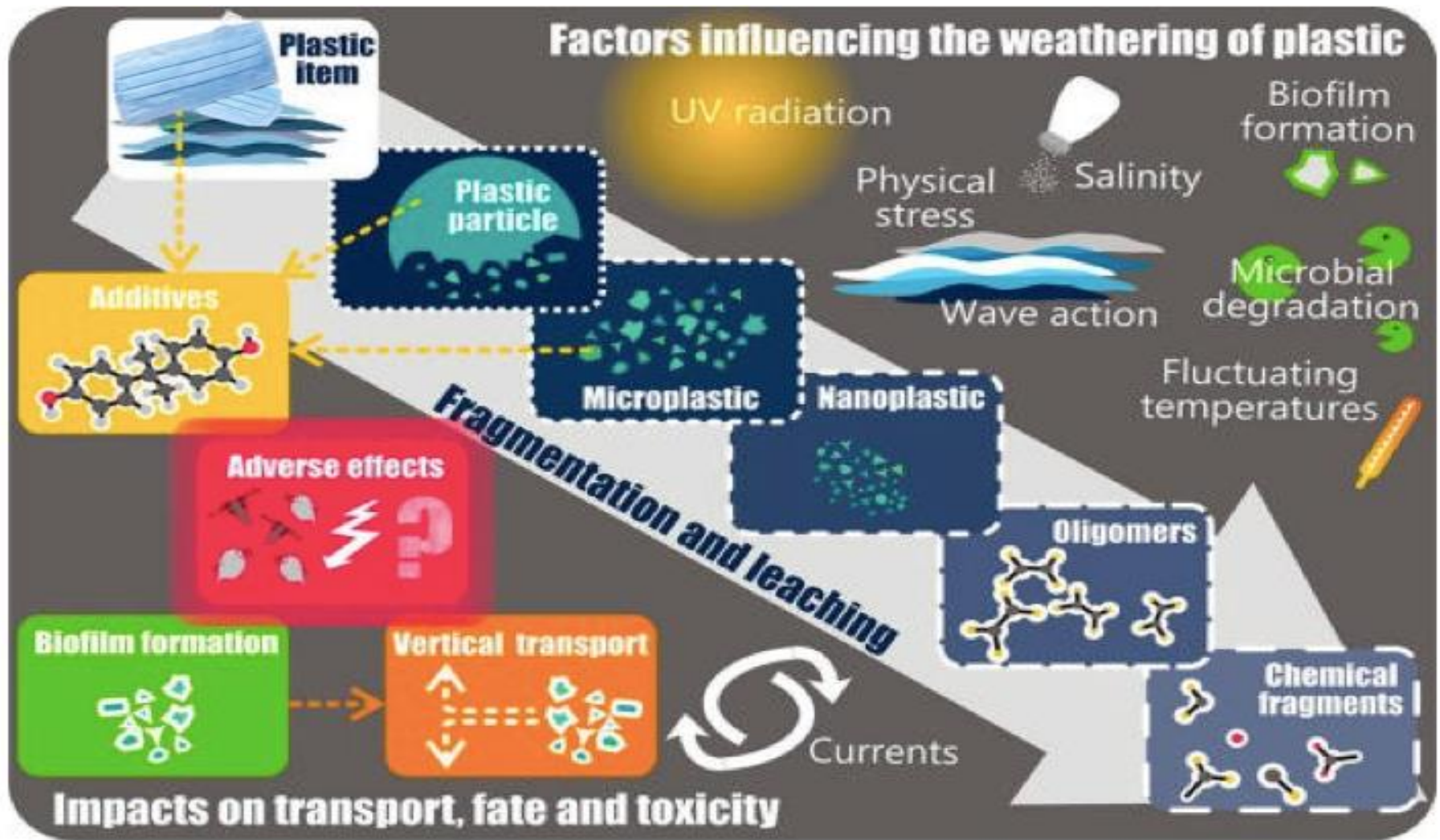
🕒 Updated 2037 GMT (0437 HKT) June 24, 2020

COVID-19 Has Worsened the Ocean Plastic Pollution Problem

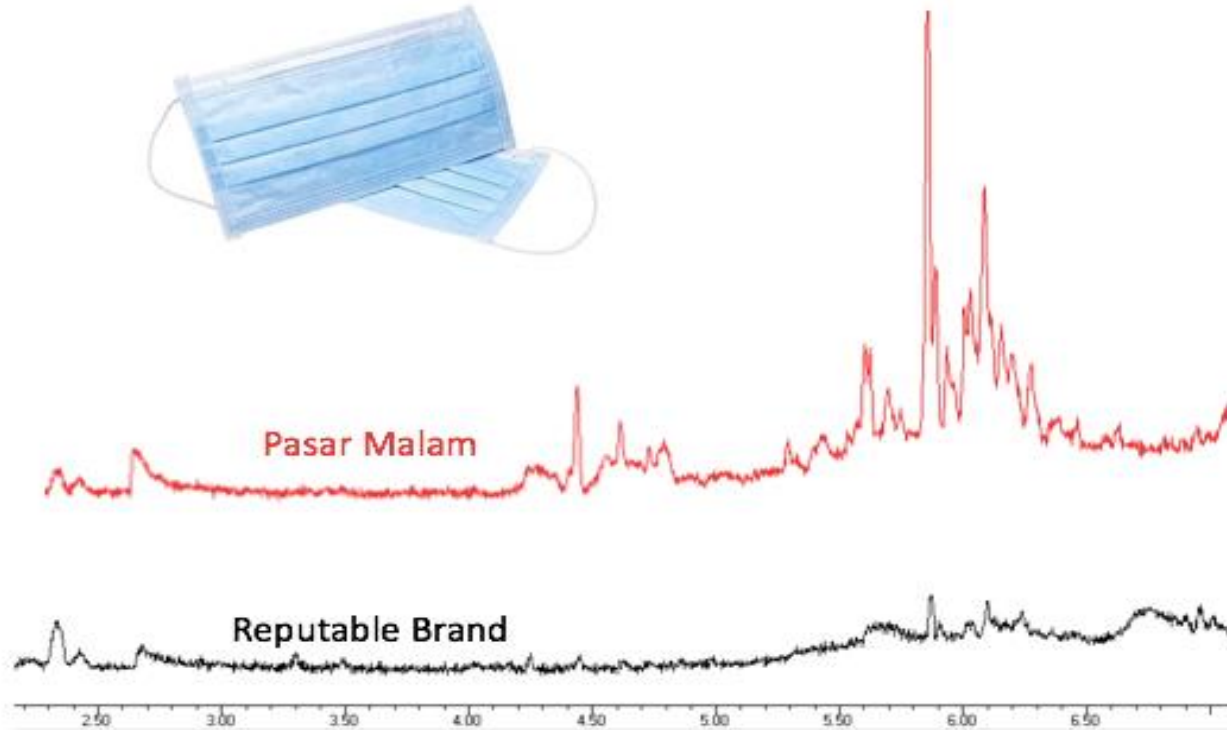


A drastic increase in use of masks and gloves, plus a decline in recycling programs, is threatening the health of the seas

“Plastic Pandemic”



Volatile Organic Compounds Identified



Microplastics Analysis – Challenges



- No established standard method references
- Depends on type and size of microplastic particles
- Huge variation in density, shapes, size
- Cleanup steps are difficult

Macro



$\geq 25\text{mm}$

Meso



$<25 - 5\text{mm}$

Micro



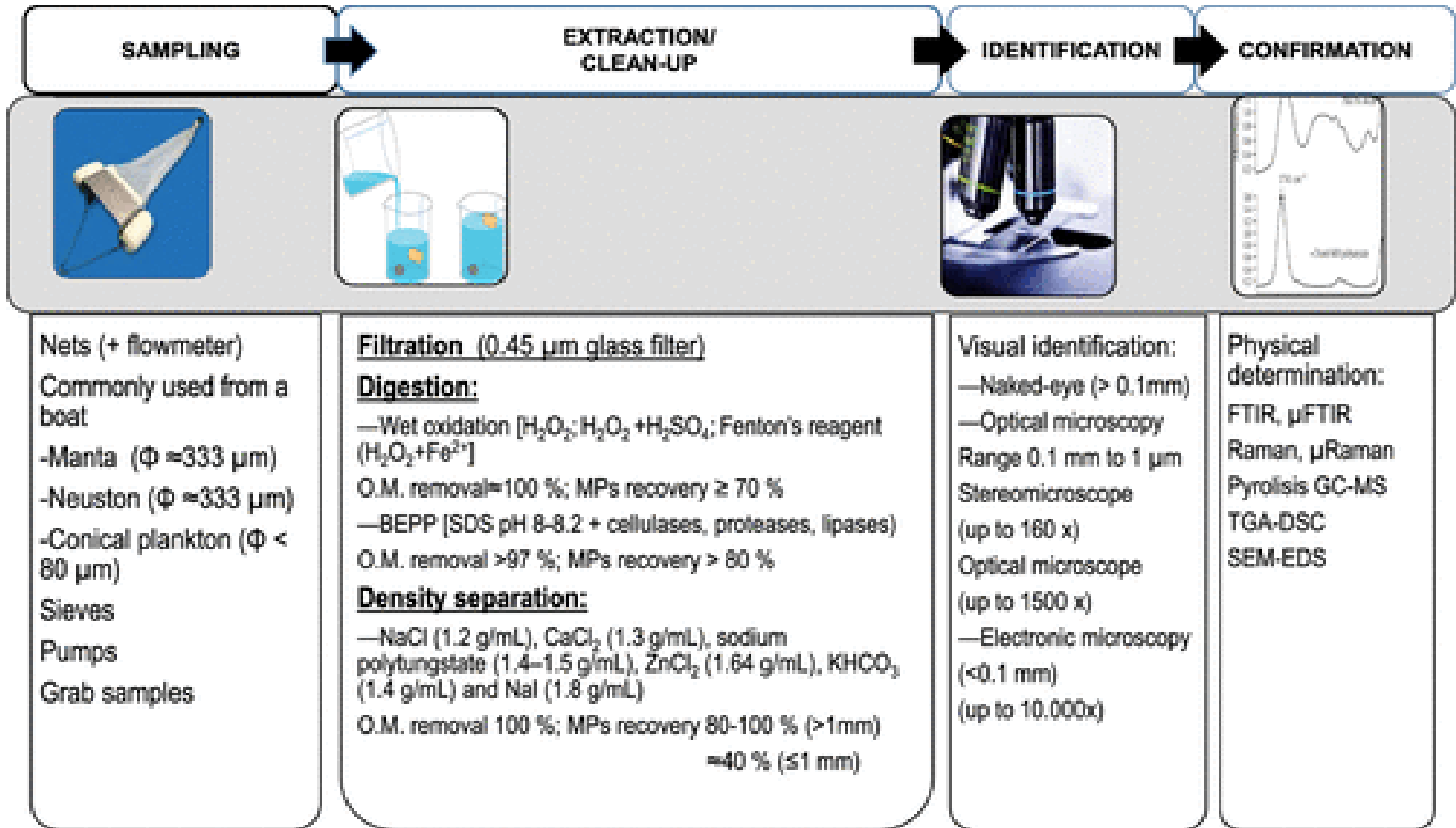
$<5 - 1\text{mm}$

Mini-micro

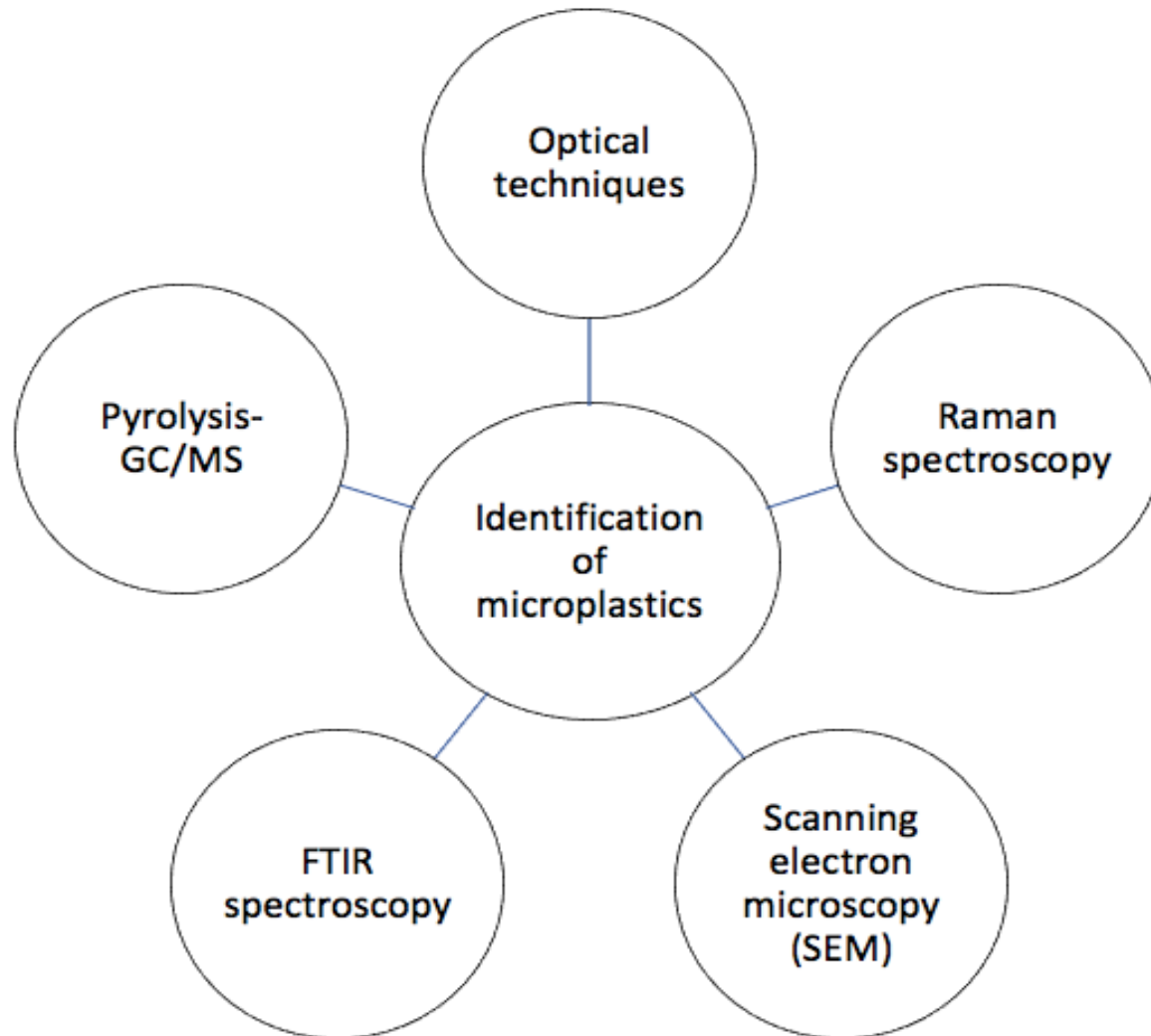


$<1\text{mm} - 1\mu\text{m}$

Microplastics Detection



Microplastics Detection



Abundance of microplastic depends on method used

No standardized method for sampling, clean-up and detection

Combine microscope with analytical instruments to better identify microplastics

Challenge in quantification of smaller-sized plastic particles

Suitable analytical methods should be developed locally

Need to collect more data on MP contamination in our rivers

Where did it come from?

Clinical Infectious Diseases

BRIEF REPORT

A Well Infant With Coronavirus Disease 2019 With High Viral Load

Kai-qian Kam,^{1,2} Chee Fu Yung,¹ Lin Cui,² Raymond Tzer Pin Lin,² Tze Minn Mak,² Matthias Maiwald,³ Jiahui Li,¹ Chia Yin Chong,¹ Karen Nadua,¹ Natalie Woon Hui Tan,¹ and Koh Cheng Thoon¹

¹Infectious Disease Service, Department of Pediatrics, KK Women's and Children's Hospital, Singapore, Singapore, ²National Public Health Laboratory, National Centre for Infectious Diseases, Singapore, Singapore, and ³Department of Pathology and Laboratory Medicine, KK Women's and Children's Hospital, Singapore, Singapore

Asymptomatic/
pre/post-symptomatic
individuals can shed
virus in their feces

Chin Med J (Engl). 2020 May 5; 133(9): 1039–1043.

Published online 2020 May 5. doi: [10.1097/CM9.0000000000000774](https://doi.org/10.1097/CM9.0000000000000774)

PMCID: PMC7147278

PMID: [32118639](https://pubmed.ncbi.nlm.nih.gov/32118639/)

Persistence and clearance of viral RNA in 2019 novel coronavirus disease rehabilitation patients

Yun Ling,¹ Shui-Bao Xu,² Yi-Xiao Lin,³ Di Tian,¹ Zhao-Qin Zhu,¹ Fa-Hui Dai,¹ Fan Wu,¹ Zhi-Gang Song,¹ Wei Huang,¹ Jun Chen,² Bi-Jie Hu,⁴ Sheng Wang,⁵ En-Qiang Mao,⁶ Lei Zhu,⁷ Wen-Hong Zhang,⁸ and Hong-Zhou Lu^{1,2,8,9}

Monitoring Editor: Peng Lyu

In brief, as the clearance of viral RNA in patients' stools was delayed compared to that in oropharyngeal swabs, it is important to identify viral RNA in feces during convalescence. Because of the delayed clearance of viral RNA in the glucocorticoid treatment group, glucocorticoids are not recommended in the treatment of COVID-19, especially for mild disease. The duration of RNA detection may relate to host cell immunity.

JOURNAL OF

MEDICAL VIROLOGY

LETTER TO THE EDITOR | [Free Access](#)

Asymptomatic SARS-CoV-2 infected case with viral detection positive in stool but negative in nasopharyngeal samples lasts for 42 days

Xuejun Jiang, Mei Luo, Zhen Zou, Xu Wang, Chengzhi Chen ✉, Jingfu Qiu

First published: 24 April 2020 | <https://doi.org/10.1002/jmv.25941> | Citations: 2

Wastewater-Based Epidemiology




- Early warning
- Identifying high risk areas
- Estimating infected population
- Assessing the effectiveness of mitigation plans

ScienceNews

NEWS HEALTH & MEDICINE

Wastewater could provide up to a week of warning for a COVID-19 spike

Finding coronavirus RNA in sewage may signal that people in a community are infected



Genetic material from the coronavirus can be detected in patients' stool and wastewater from water treatment plants, like this one just south of Houston. A new study adds to evidence that sewage may serve as an early warning signal for COVID-19 hot spots.

ART WAGER/ISTOCK/GETTY IMAGES PLUS

COVID-19 WBE: What has been done?



Study	City/ Country	Scale	Output
Qualitative			
Medema et al., 2020	Netherlands	7 WWTPs, serving 54,000 - 1,400,000 inhabitants	Presence/absence
Quantitative			
Wurtzer et al., 2020	Paris, France	3 WWTPs, serving >100,000 inhabitants	$10^3 - 10^7$ viral genomes/L
Randazzo et al., 2020	Spain	6 WWTPs, serving 29,133 - 370,593 inhabitants	5.1 -5.1 \log_{10} gc/L
Kocamemi et al., 2020	Istanbul, Turkey	8 WWTPs, serving 7,000 - 1,500,000 inhabitants	$7.35 \times 10^2 - 1.13 \times 10^4$ copies/L
Estimating the infected population			
Ahmed et al., 2020	Australia	1 suburban pumping station, 2 WWTPs, serving 231,643 & 504,529	171 -1,090 infected individuals
Wu et al., 2020	Massachusetts, US	1 major WWTP	0.1% - 5% disease prevalence

COVID-19 Sewage Testing : Singapore



- Study : foreign worker dormitories.
- Findings:
 - **Viral load in wastewater reflects the prevalence of COVID-19 cases**



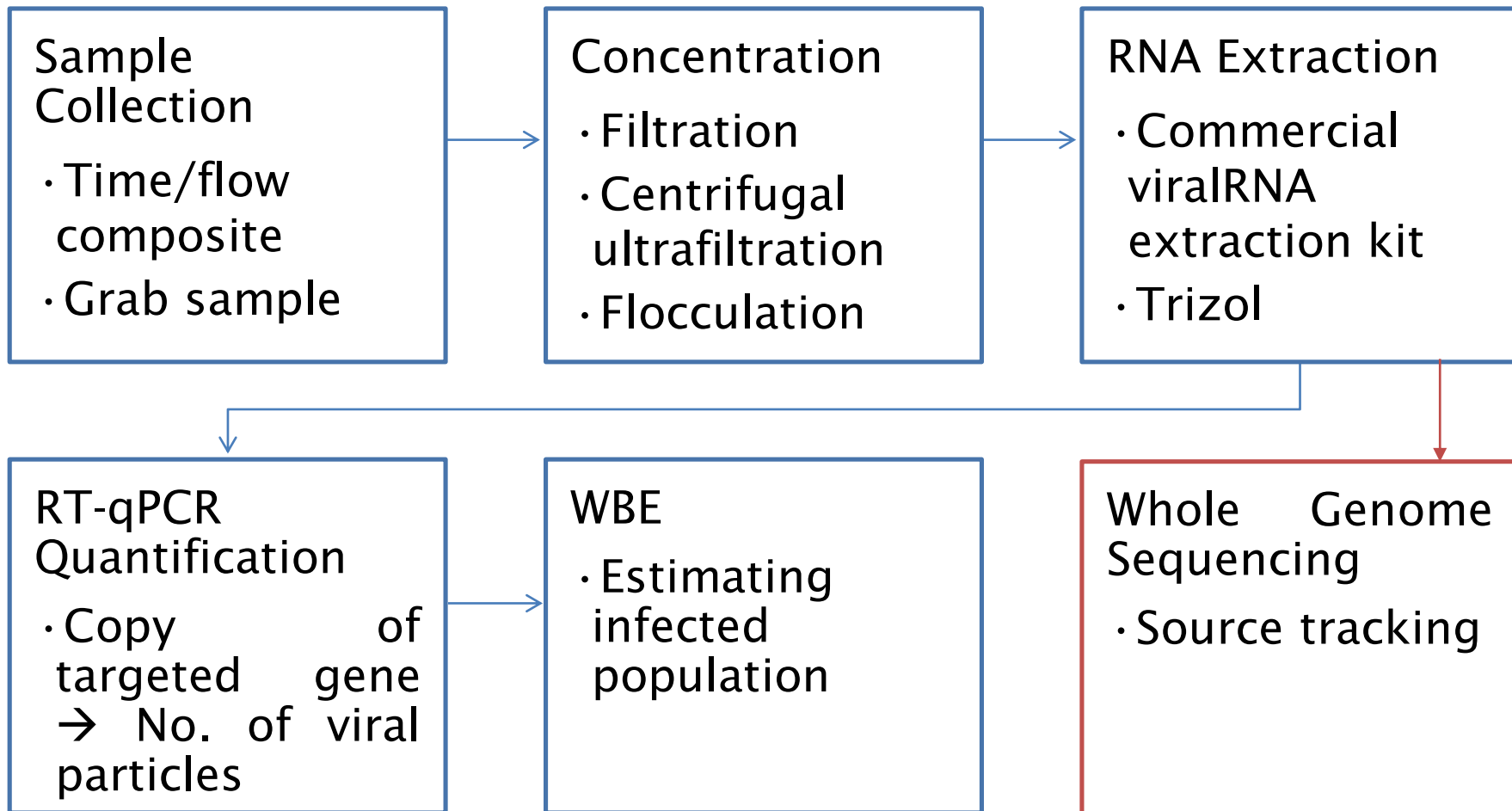
Field work being conducted. (Photo: NEA, PUB, HTX)

More wastewater testing under way in Singapore to tackle COVID-19; pilot launched at foreign worker dormitories

Singapore is expanding its wastewater testing to tackle COVID-19, with a pilot programme launched at 20 large foreign worker dormitories in the country, the National Environment Agency, National Water Agency PUB and Home Team Science and Technology Agency (HTX) said in a joint [news release on Friday \(Jun 19\)](#).

— *Channel NewsAsia*

COVID-19 Sewage Testing Workflow



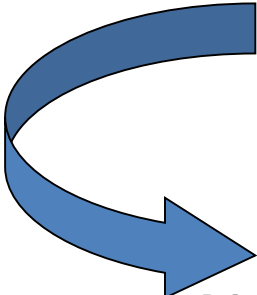
As Technology Gets Better....



- Rapid, Sensitive, and Simplified Analysis
- New developments in analytical methods
- Refinement in extraction and purification procedure
- Improvement in instrument sensitivity
- To support research in the fate, transport, and biological effects of these substances

“Not everything that can be counted counts, and not everything that counts can be counted.”

(attributed to Albert Einstein)

A large, thick blue arrow that starts on the left and curves downwards and to the right, pointing towards the second quote.

Not everything that can be measured is worth measuring, and not everything worth measuring is measurable.

Tip of the Iceberg



- Only a small fraction of hundreds of thousands of chemicals identified in our environmental waters



Key Points



- What one finds usually depends on what one aims to search for.
- Only those compounds targeted for monitoring have the potential for being identified and quantified.
- Those compounds not targeted will elude detection.
- The spectrum of pollutants identified in a sample represent but a portion of those present and they are of unknown overall risk significance.

Avoiding contamination ! False Positives !

- Sources of contamination :
 1. Sampling (Sampling bottles used)
 2. Deionized water used for analysis and preparation of reagent
 3. Contamination from airborne particulate matter
 4. Reagent consumption
 5. Carry over contamination (on the instrument)
 6. Contamination by indirect contact



1. Method Selection
2. Extraction efficiency
3. Cleanup to remove chemical interferences
4. Availability of Calibration Reference Standards
5. Linearity, Repeatability, Selectivity, Sensitivity, Accuracy
6. Selection of instrument – sensitivity, precision \$\$ -
\$\$\$\$\$\$\$\$

False Negatives ! False Positives !

Final Thoughts :



- Strengthen our Scientific Knowledge on ECs Detection
- We need to collect more environmental data ! Still many scientific uncertainties on “old and new contaminants” in our local surface and drinking water supplies
- More studies required on validating analytical methods for detection of Emerging Contaminants
- Greater collaboration between private and public institutions – combine the diverse talents !



THANK YOU

Teenteen.chin@alsglobal.com



Right Solutions • Right Partner
www.alsglobal.com

