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DE LA REPÚBLICA
URUGUAY



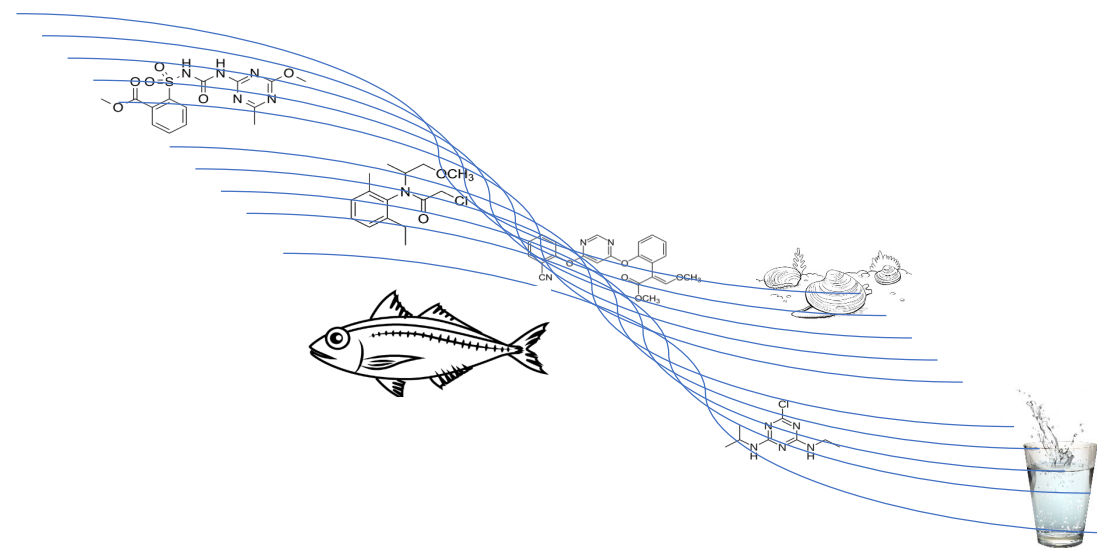
Chemical safety of freshwater for human consumption and aquatic life which also is food

Horacio Heinzen

GACT

Facultad de Química

Uruguay



Who we are



Centro Universitario
de
Paysandú

400km

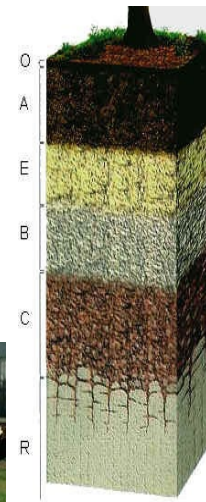
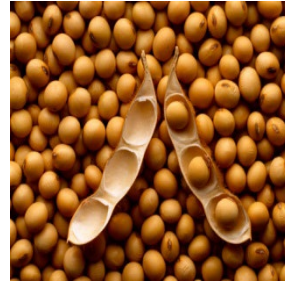
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CURE



Who we are



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de
Paysandú



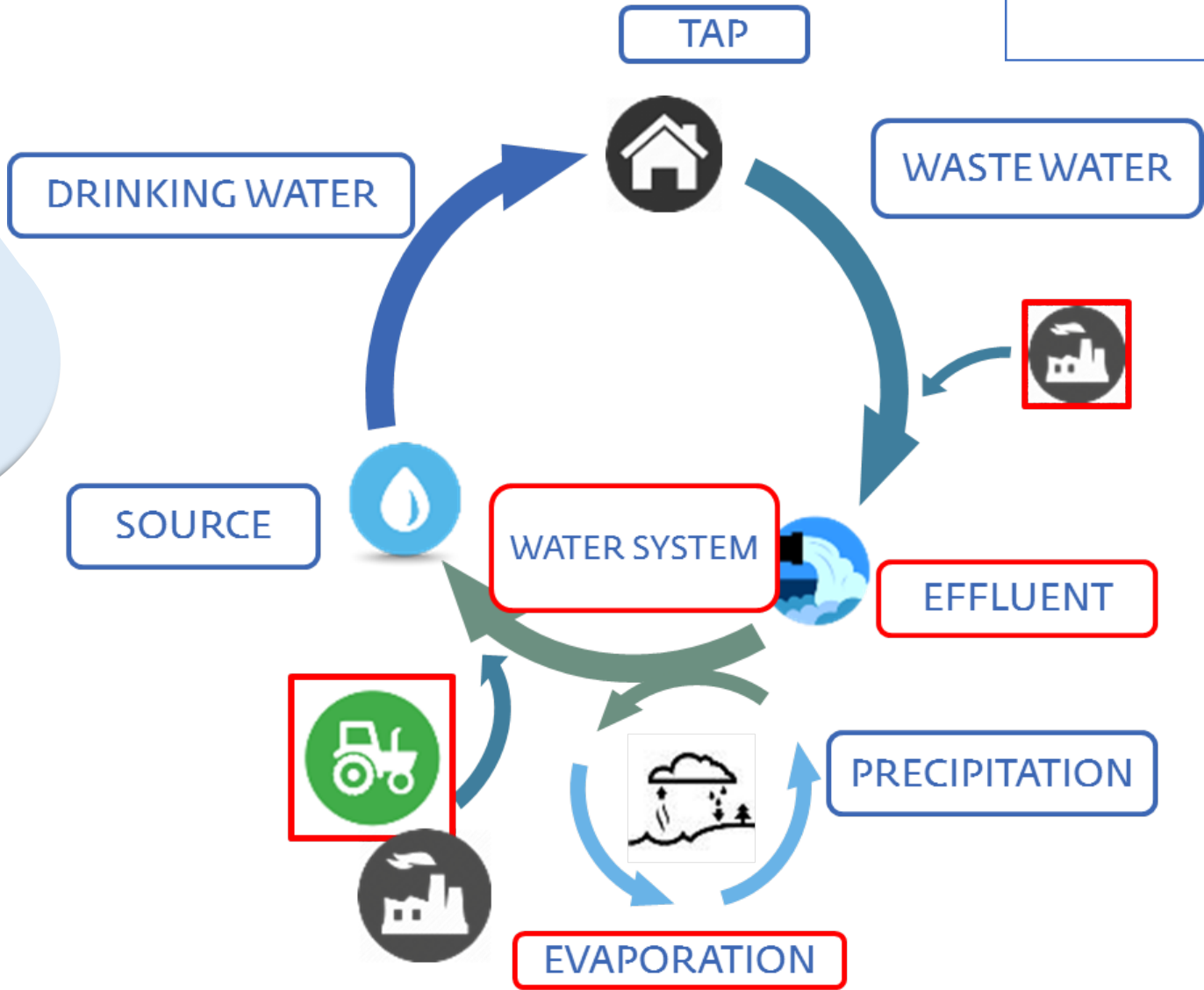
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overview

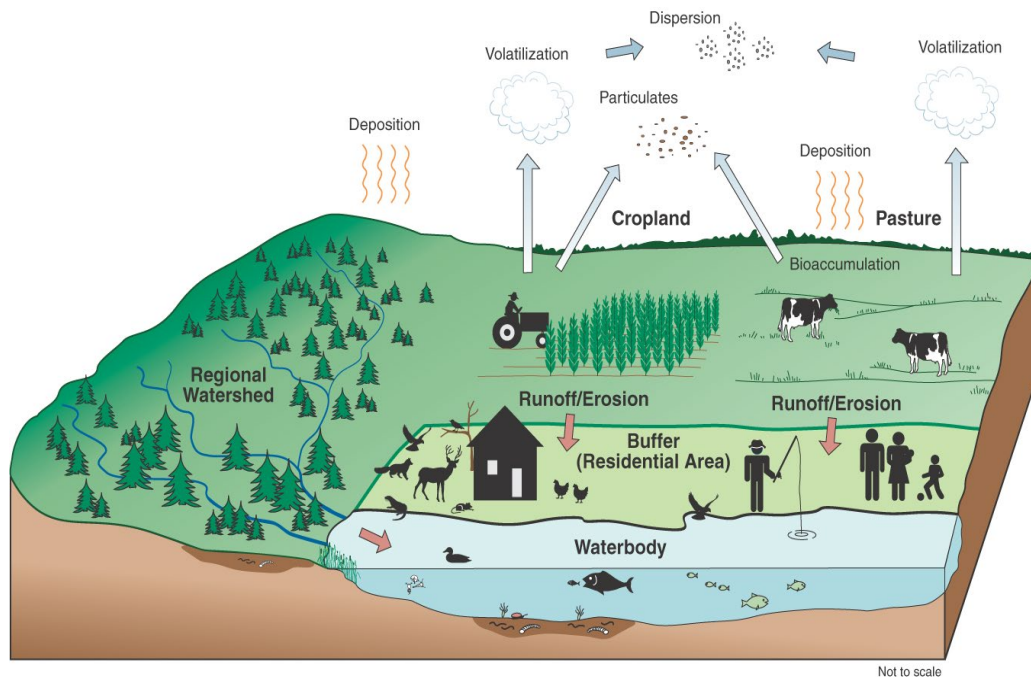
- The water cycle and trace contaminants
- Pesticides in water
 - Sources of contamination
 - Some results
 - Alternatives for the detection of traces
- Emerging contaminants
 - Sources of contamination
 - Some results
- Take home messages

The water cycle

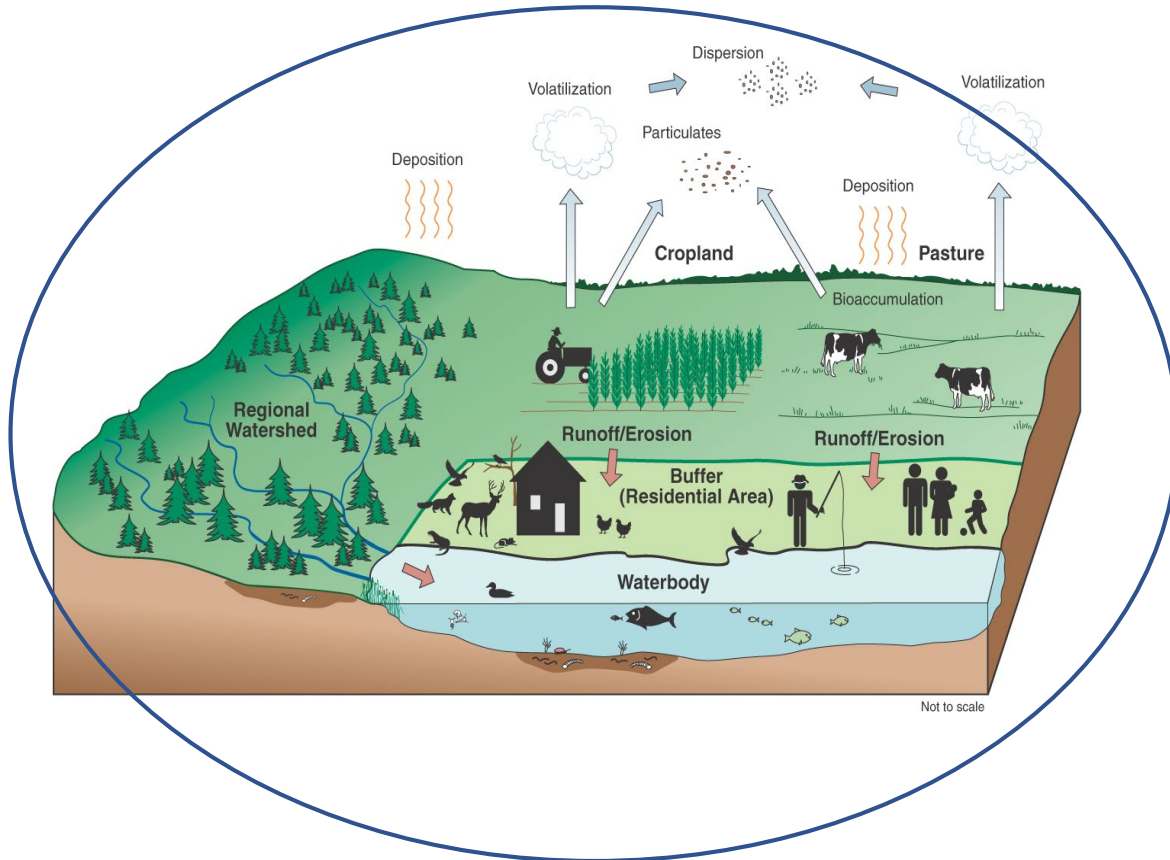


In red sources of ECs pollution

Major sources of water contamination: Anthropogenic activities



Major sources of water contamination: Anthropogenic activities



When a pesticide is applied.....



When a pesticide is applied.....

45%

- Of the applied pesticides, reach crops.

< 0.1 %

- Reach the target pest

?

- The rest is released into the environment, polluting...



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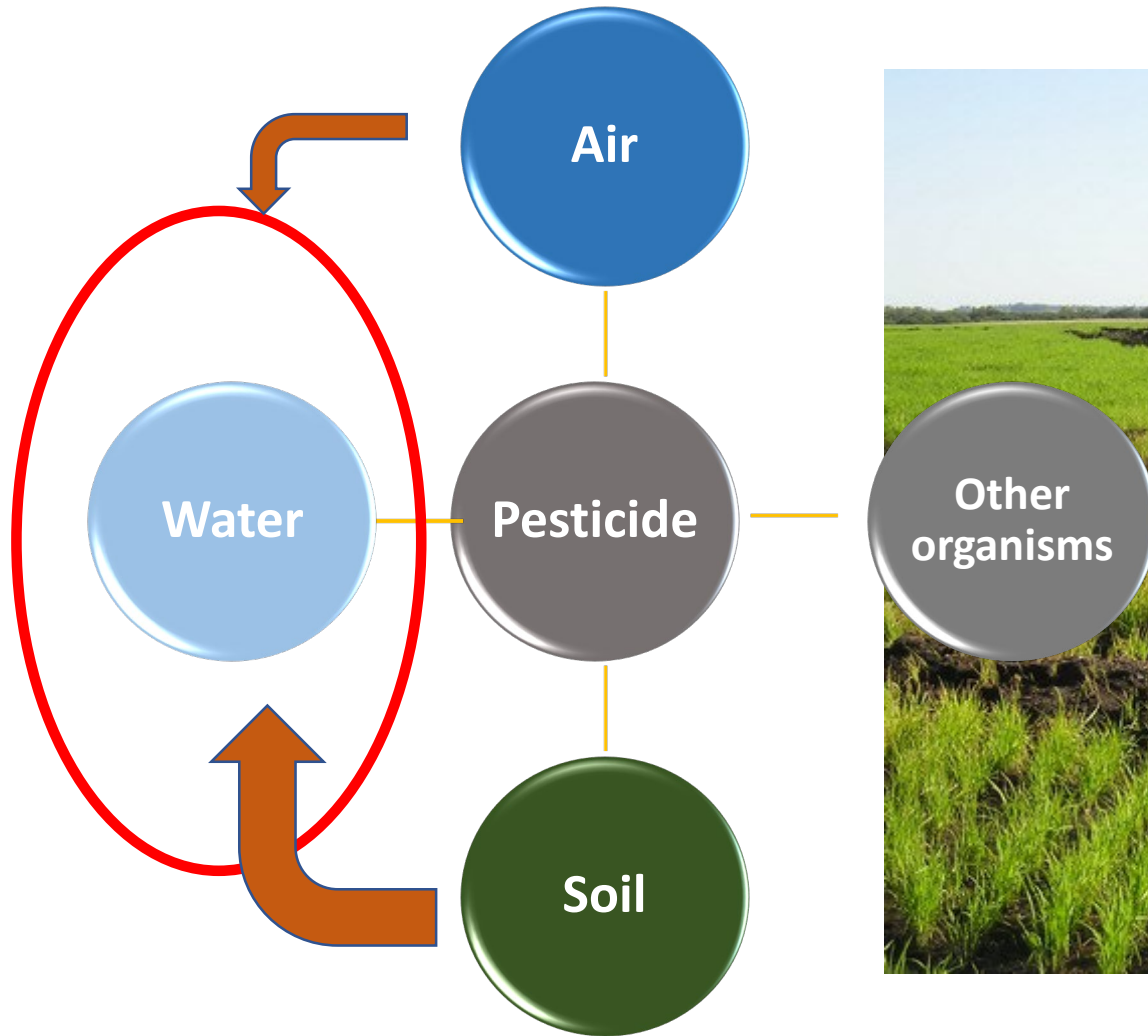
- Reach the target pest

?

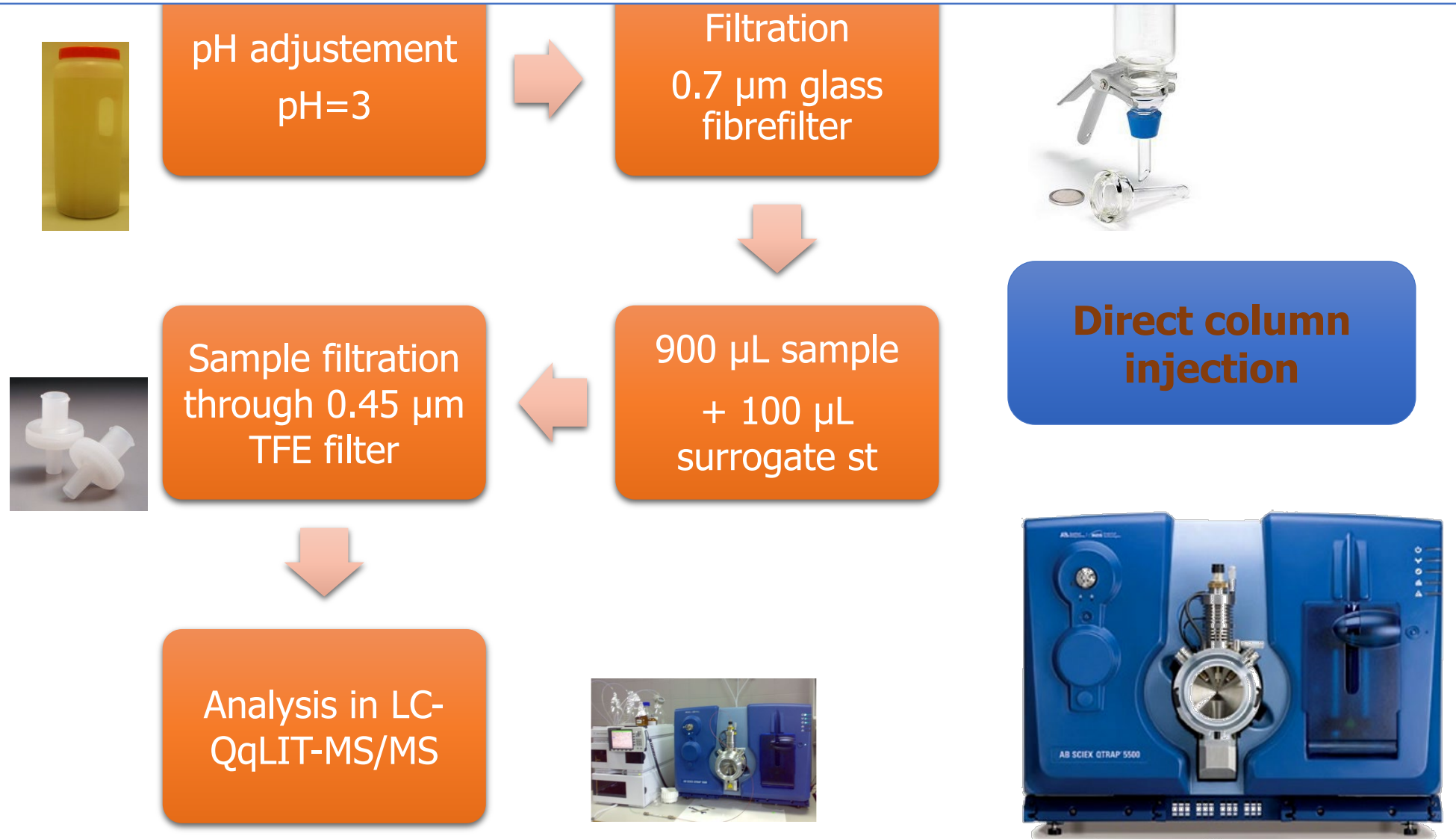
- The rest is released into the environment, polluting...



The way of pesticides into the environment



Pesticide multiresidue análisis by direct injection in the LC-MS/MS



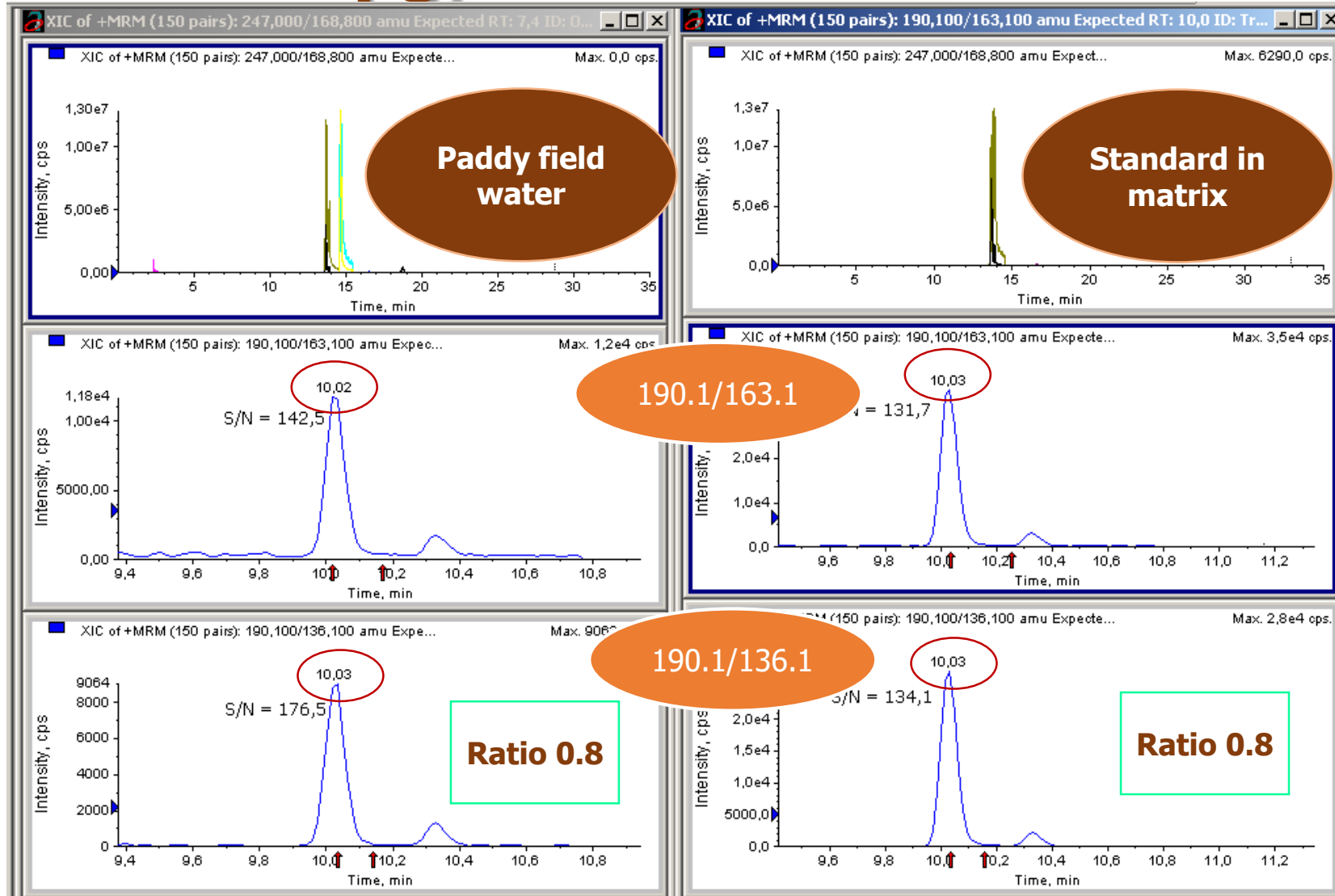
Paddy field water analysis



Water samples were collected from paddy fields in Valencia, Spain and Salto, Uruguay.



Tricyclazole in a real sample and standard solution at 0.1 µg/L level.



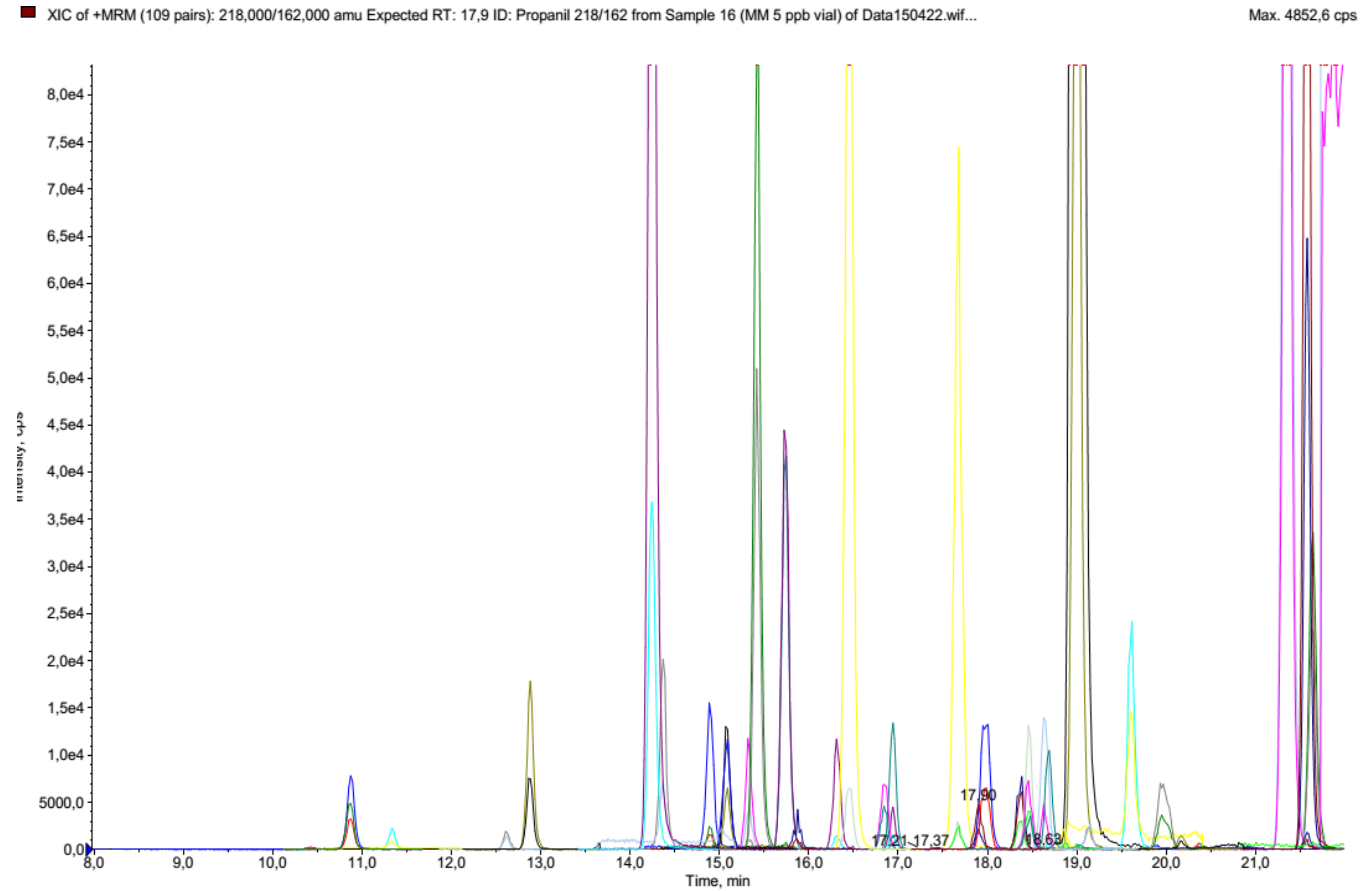
Concentration ranges ($\mu\text{g/L}$) of the detected pesticides in real samples.

Pesticides	LOQ (ng/L)	Valencia	Uruguay
		Concentration range ($\mu\text{g/L}$)	Concentration range ($\mu\text{g/L}$)
Bensulfuron methyl	6	0.20-1.97	N. D
Carbendazim	9	N. D	0.52-0.75
Imidacloprid	4	N. D	0.26-0.36
Tebuconazole	5	0.09-0.65	0.08-0.99
Tricyclazole	2	0.10-1.50	N. D

Citrus plantations by the Uruguay river

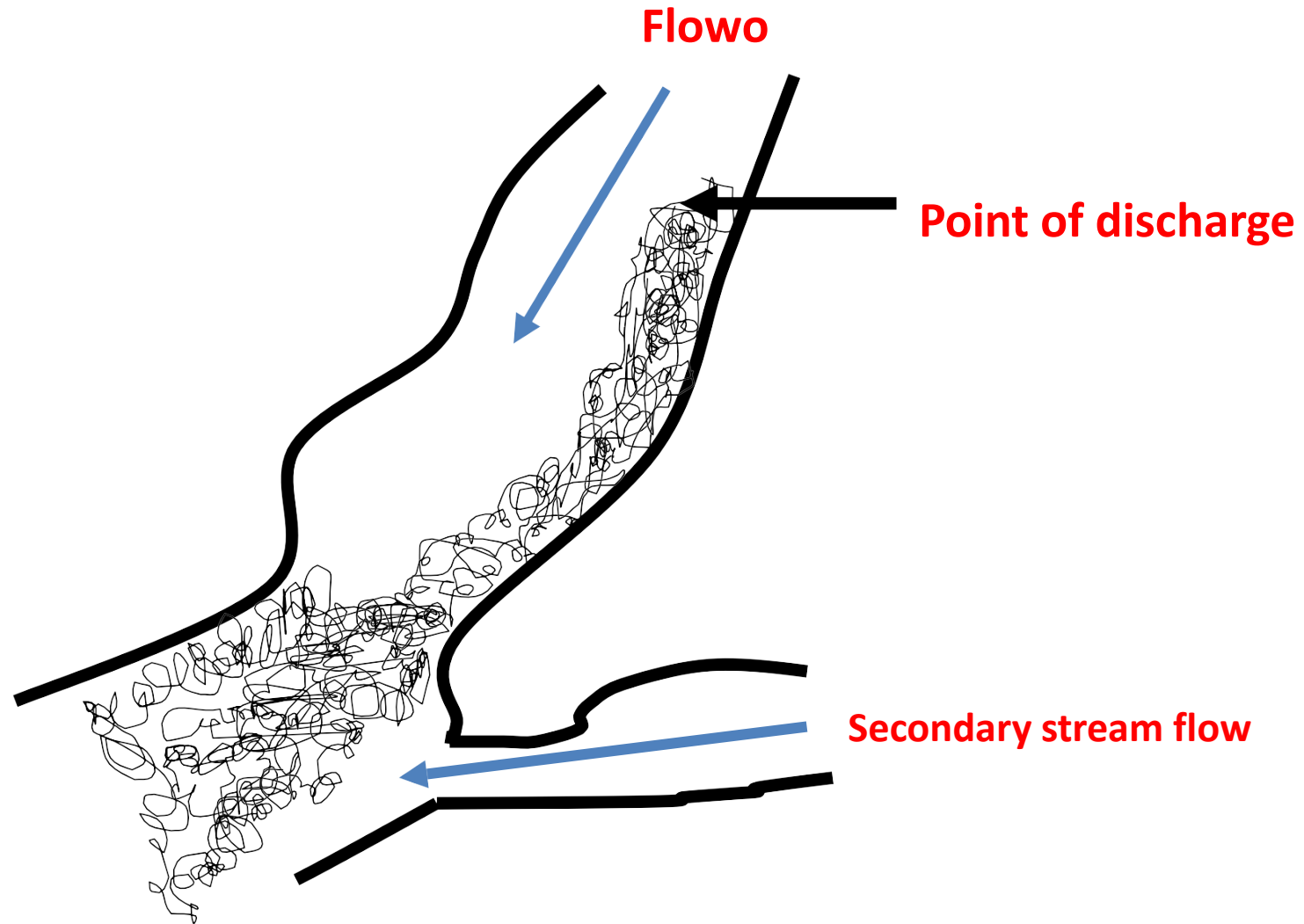


Pesticides in Surface waters

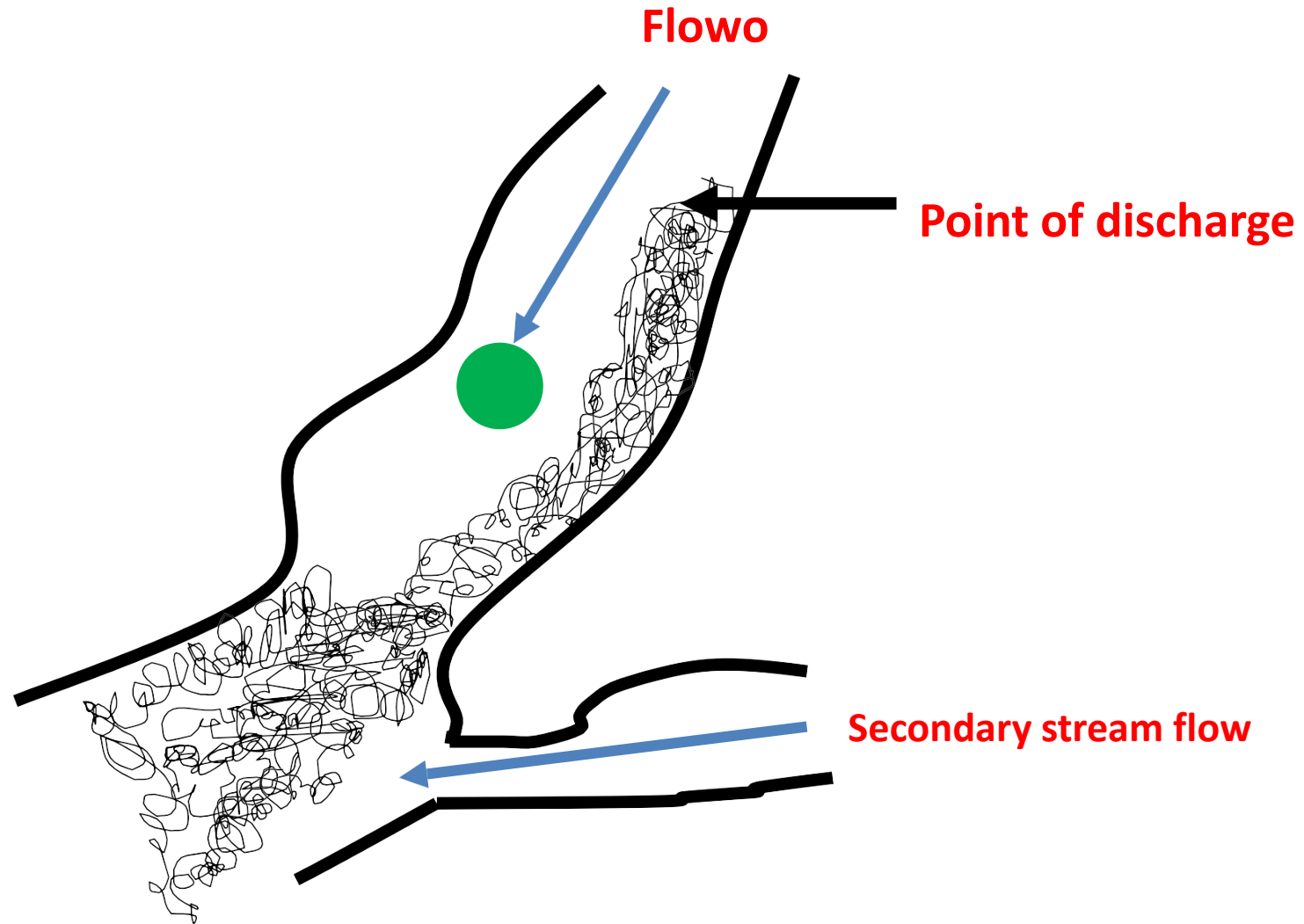


Problem: it is a snapshot!

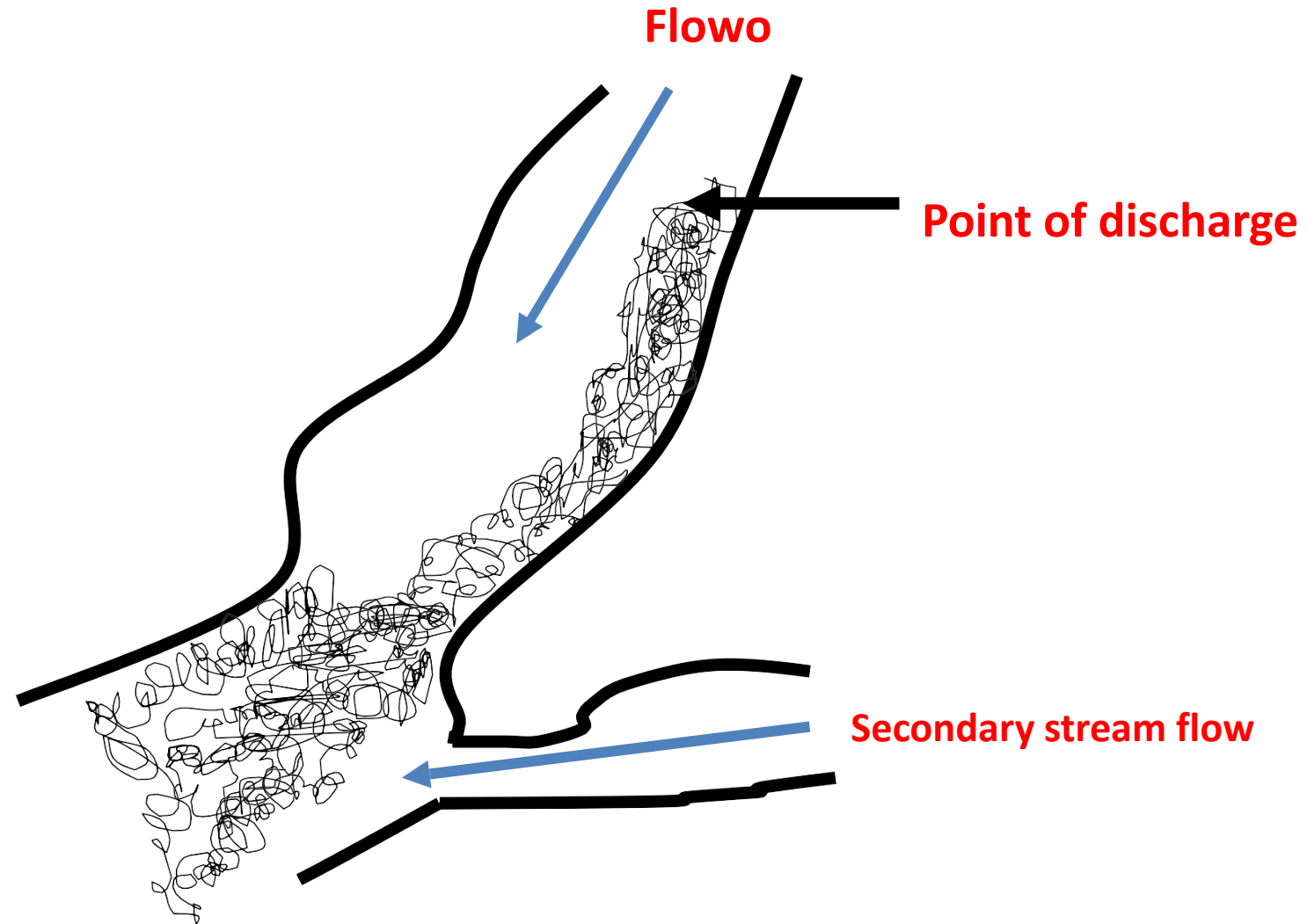
Spatial variations



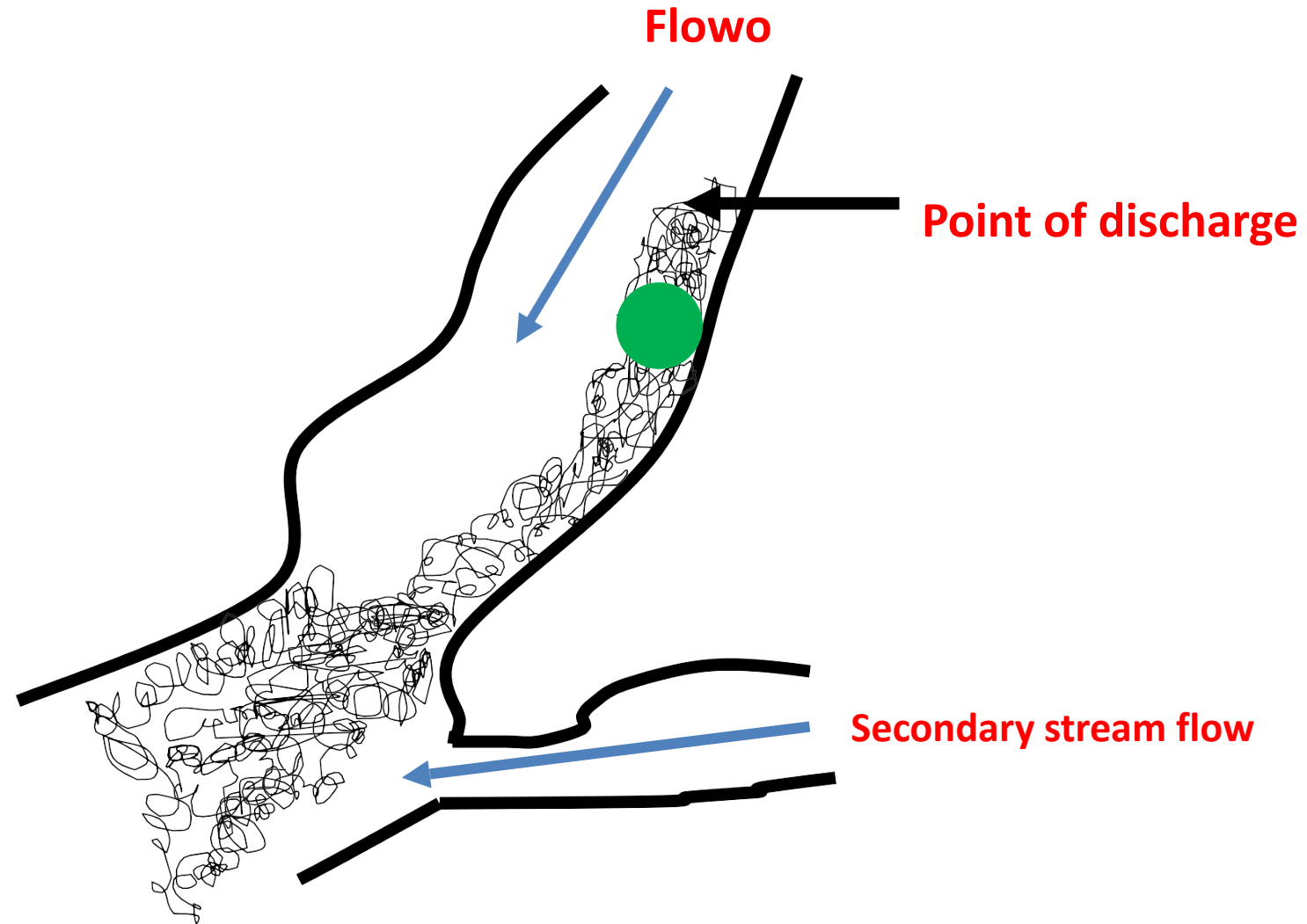
Spatial variations



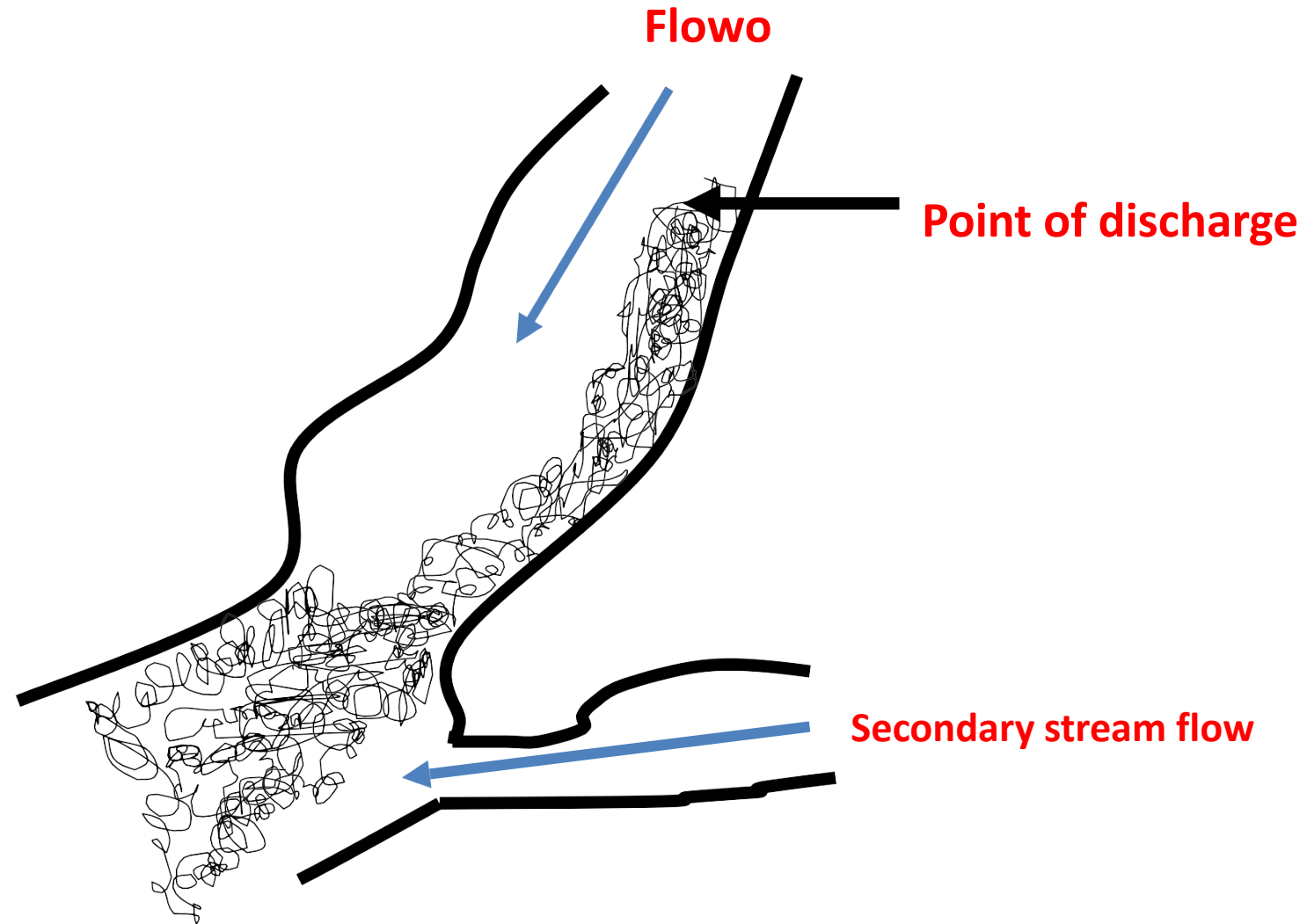
Spatial variations



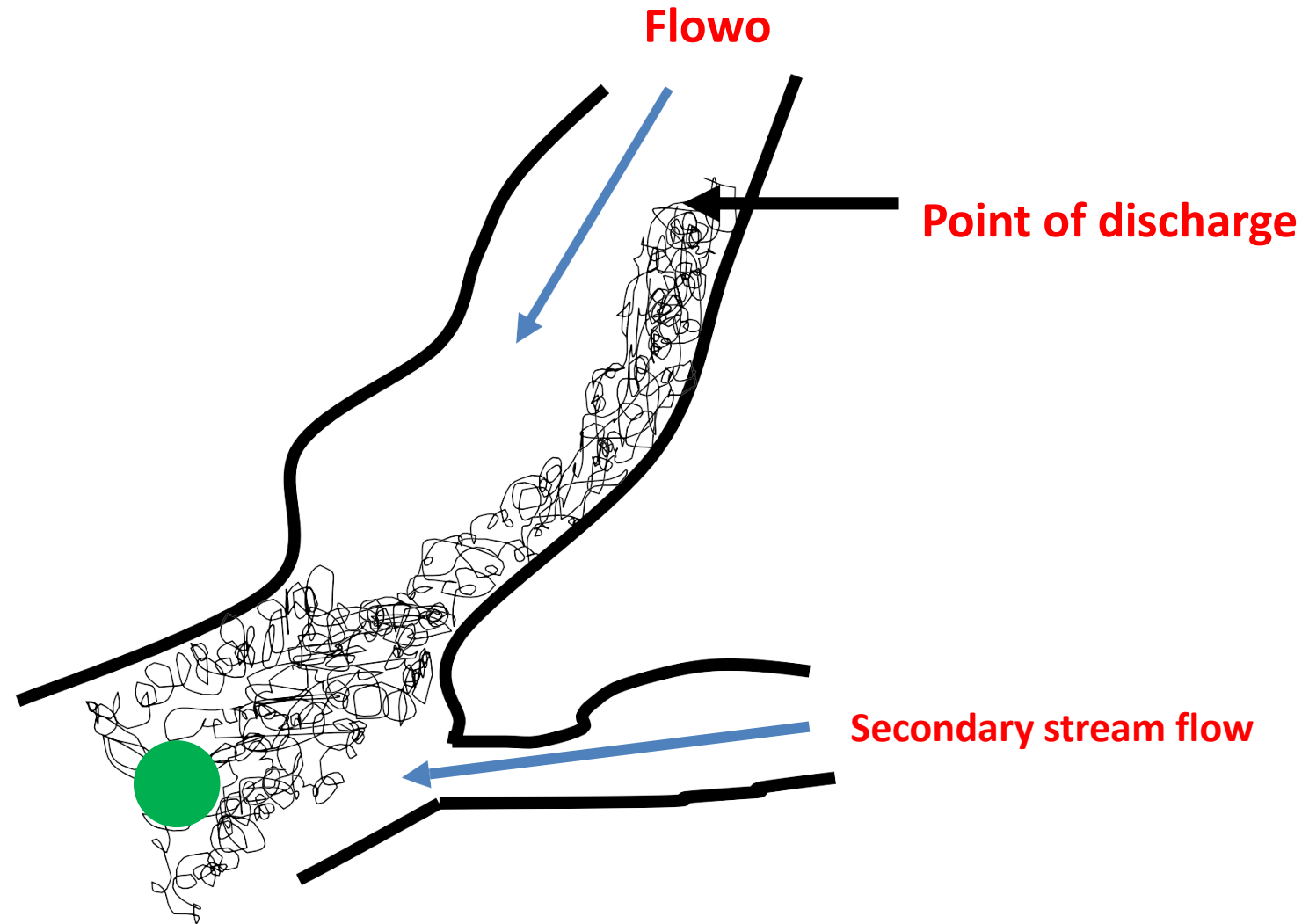
Spatial variations



Spatial variations

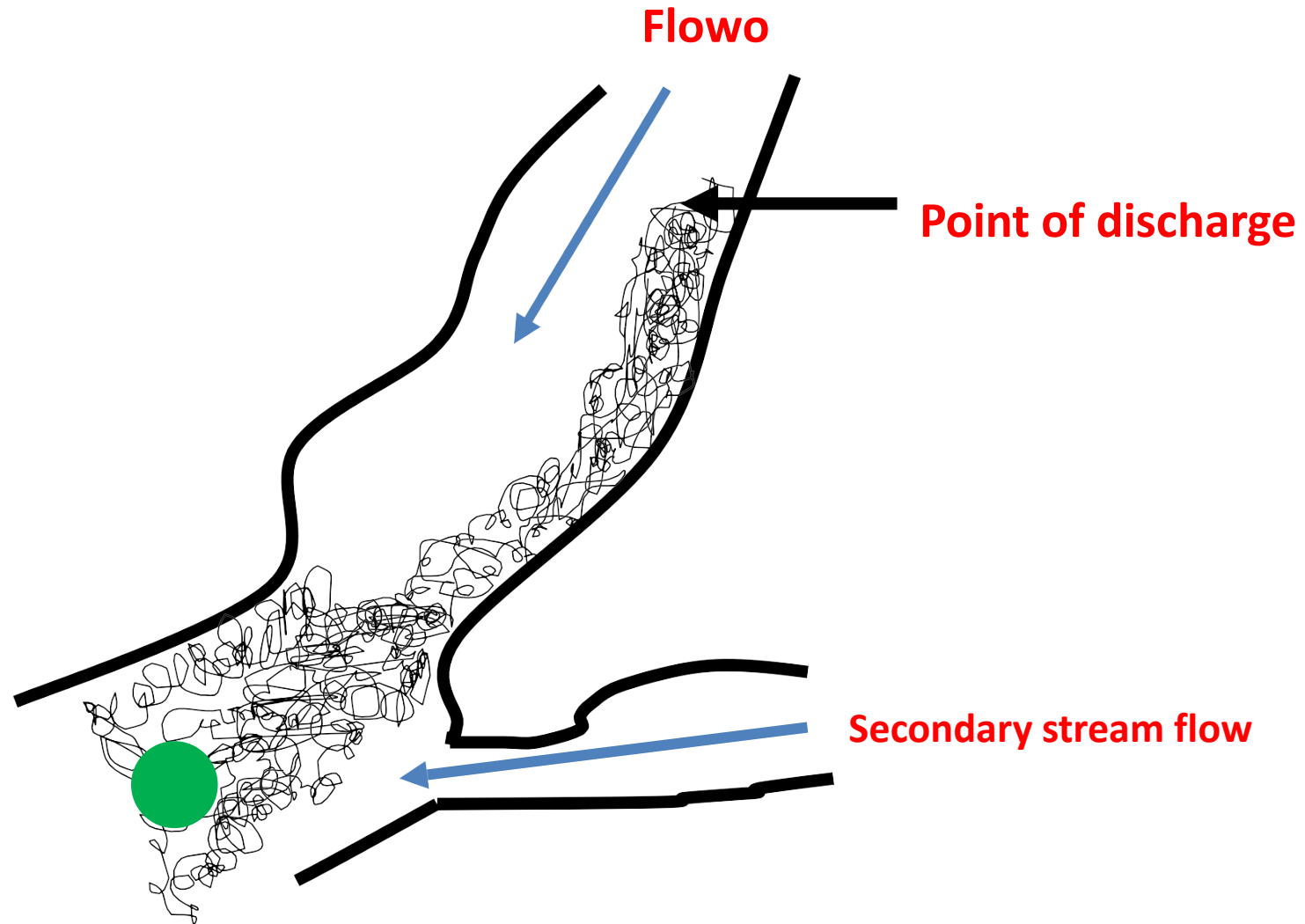


Spatial variations

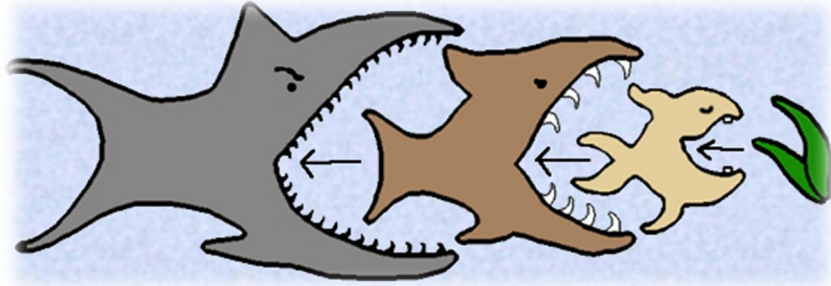


Spatial variations

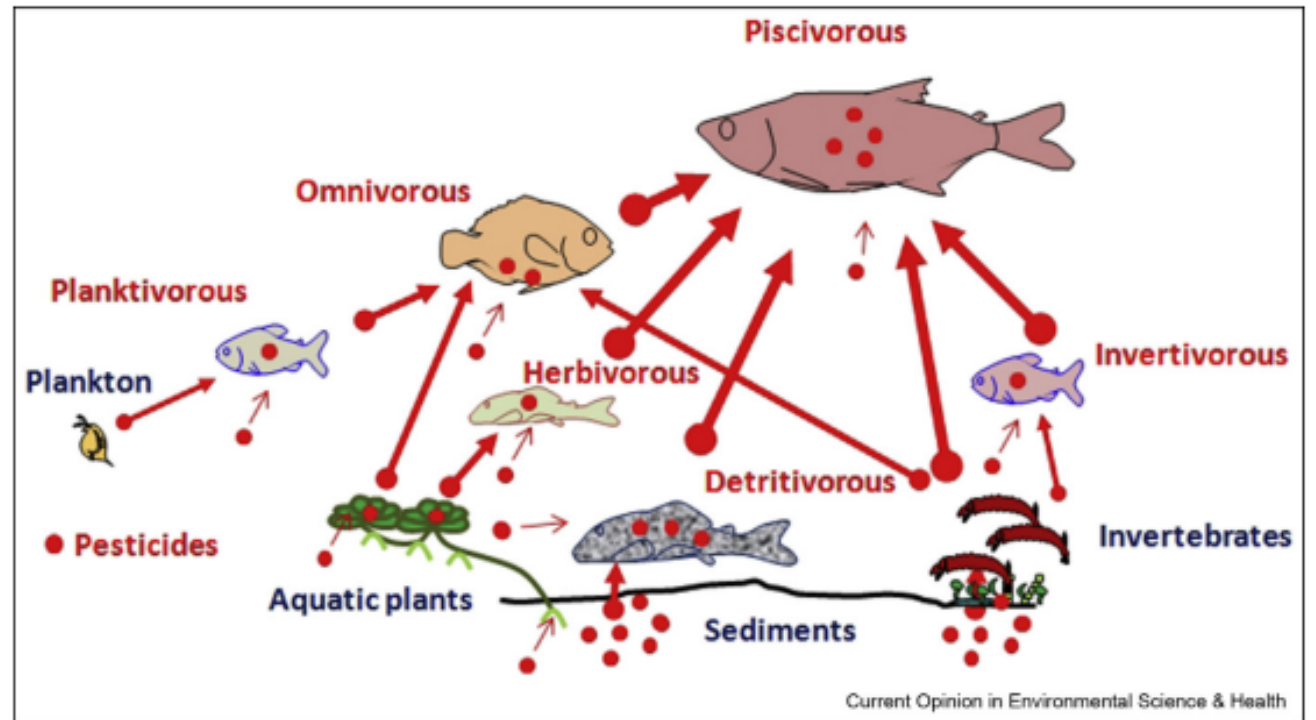
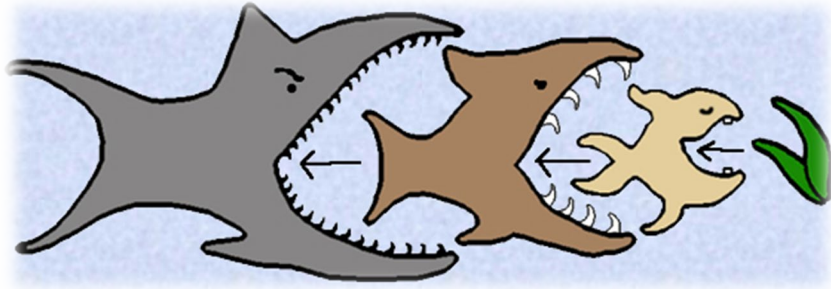
What about a
continuous
sampler?



Fish exposure to pesticides & contaminants



Fish exposure to pesticides & contaminants



Potential interactions of pesticides among fish feeding habits.

60% of the biomass of fish in Rio de la Plata basin
It can swim at 90km/h
food habit **iliophagus**
Production 20.000 t/year



Sabalo
Prochilodus lineatus

Up to 1.20m long
Up to 30kg, 10y old
Carnivorous catfish
Depredated through sport fishing
Third species in economical importance



Pati
Luciopimelodus pati

Small <40cm
4kg average weight
Abundant, very consumed
phytophagous



Boga
Leporinus obtusidens

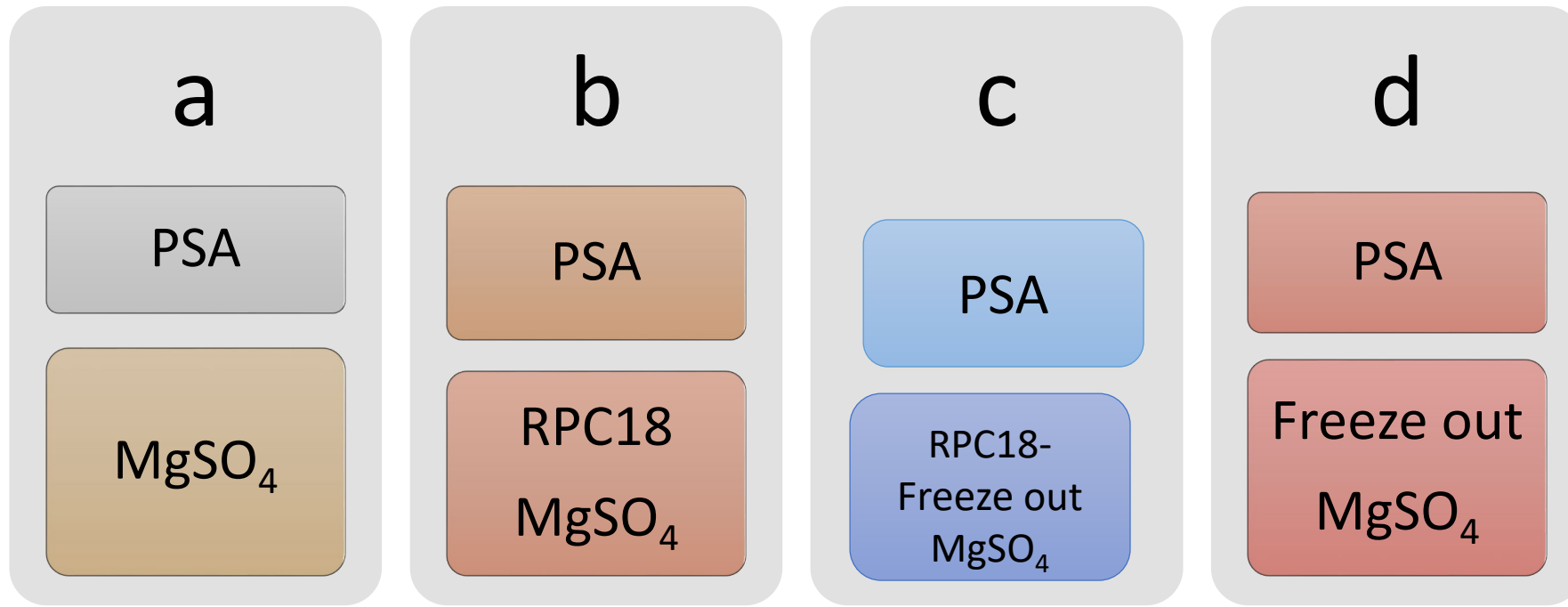


Increasing fat content



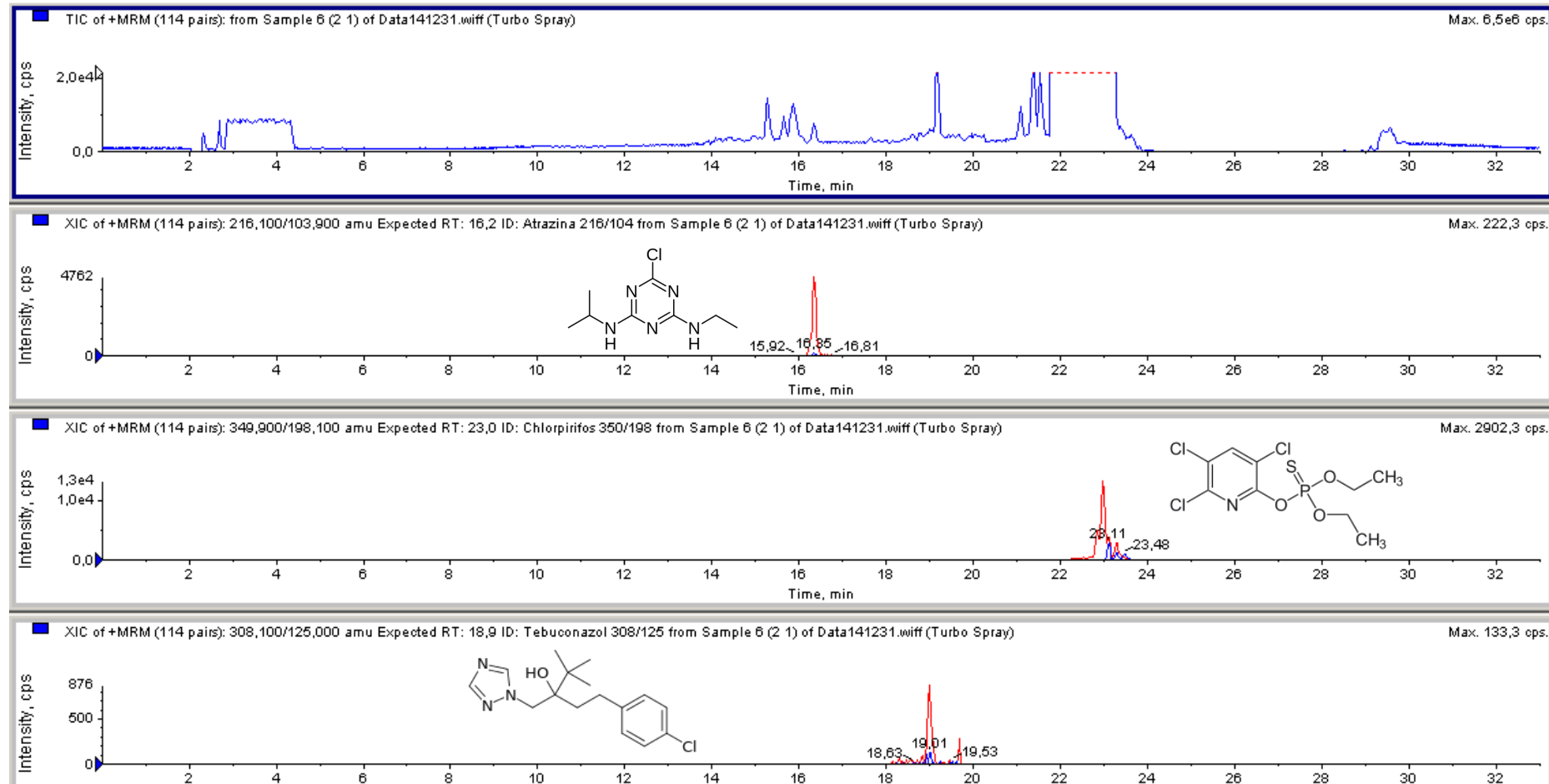
Sample treatments

10g +5mL H₂O/10 mL ACN+MgSO₄ + NaCl



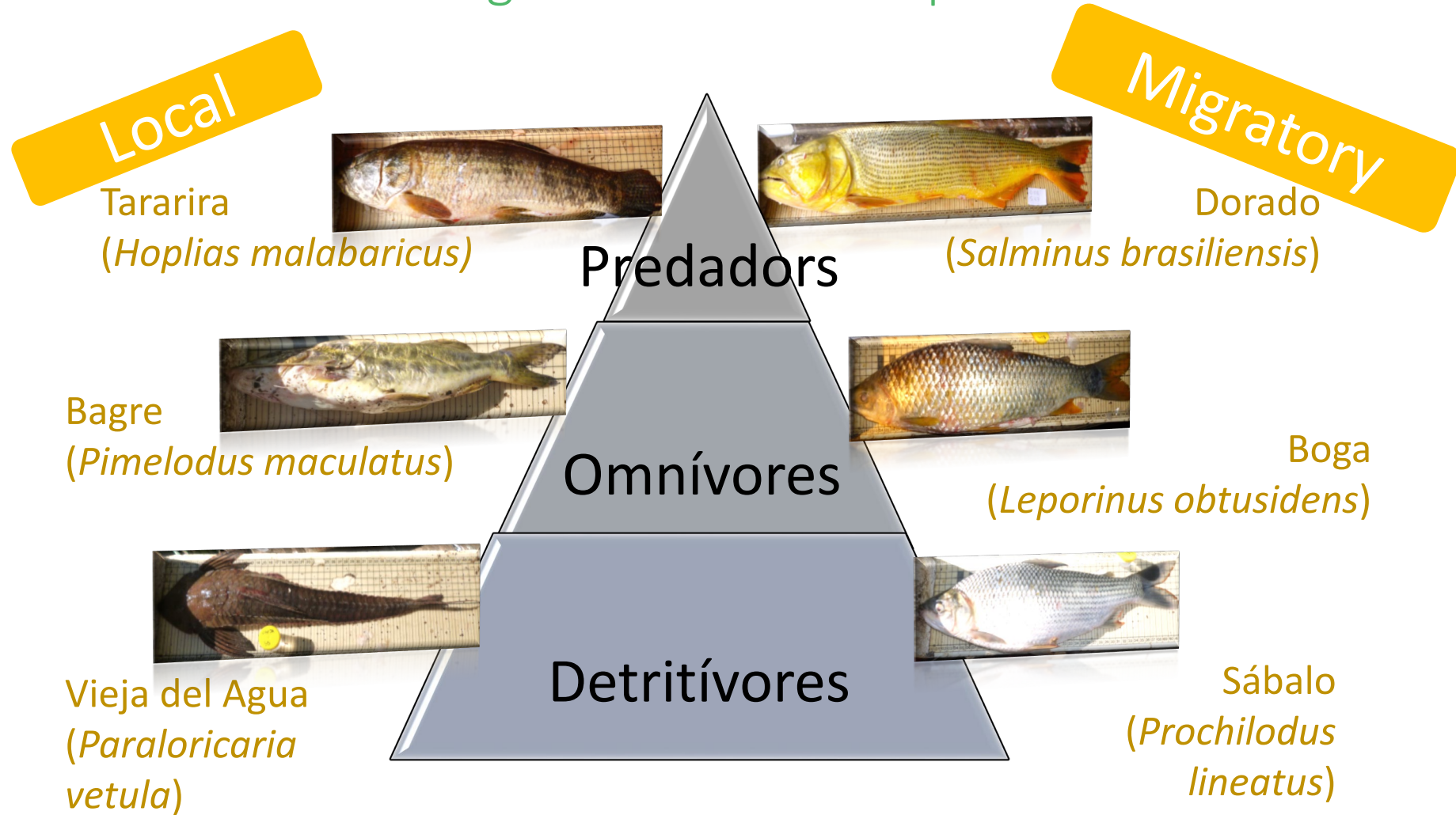
123 GC & LC amenable pesticides

Pati

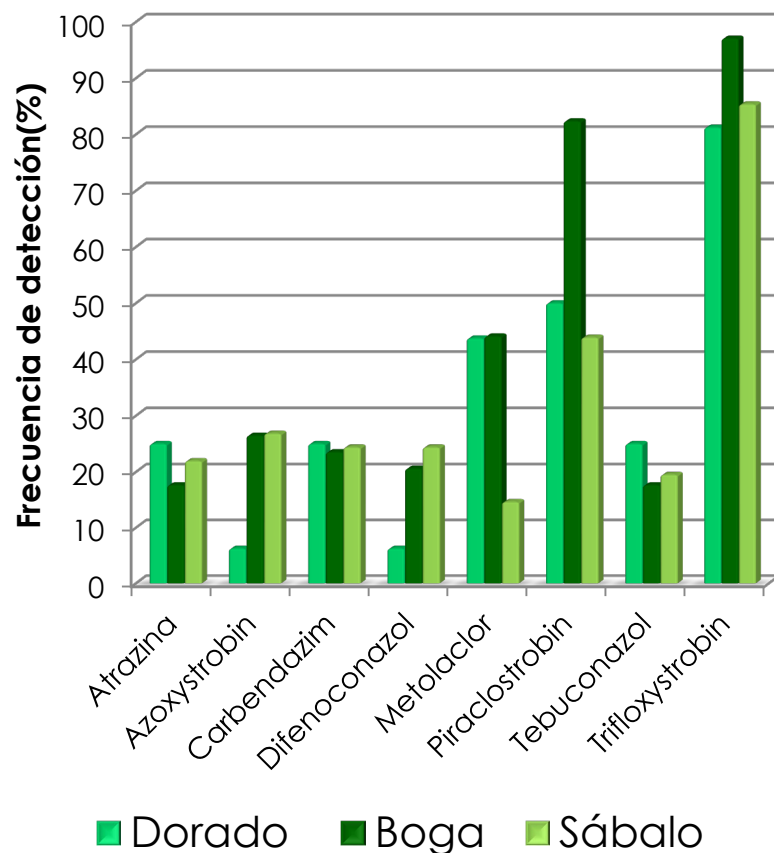


Pesticide Monitoring with fishes

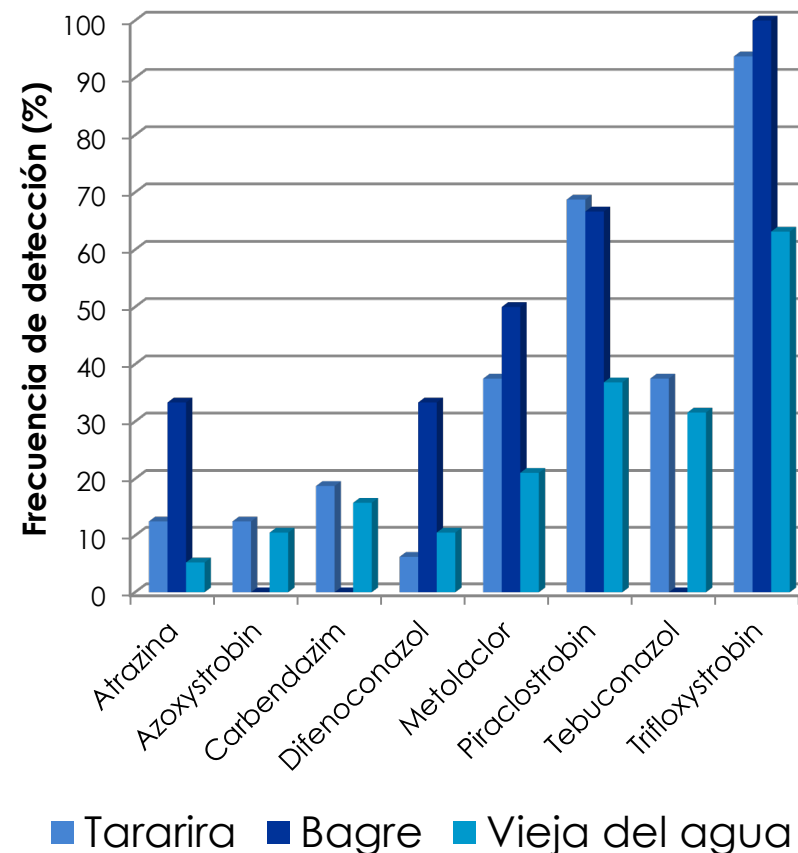
Feeding behavior of the species



Detection frequencies of pesticides in different fish species

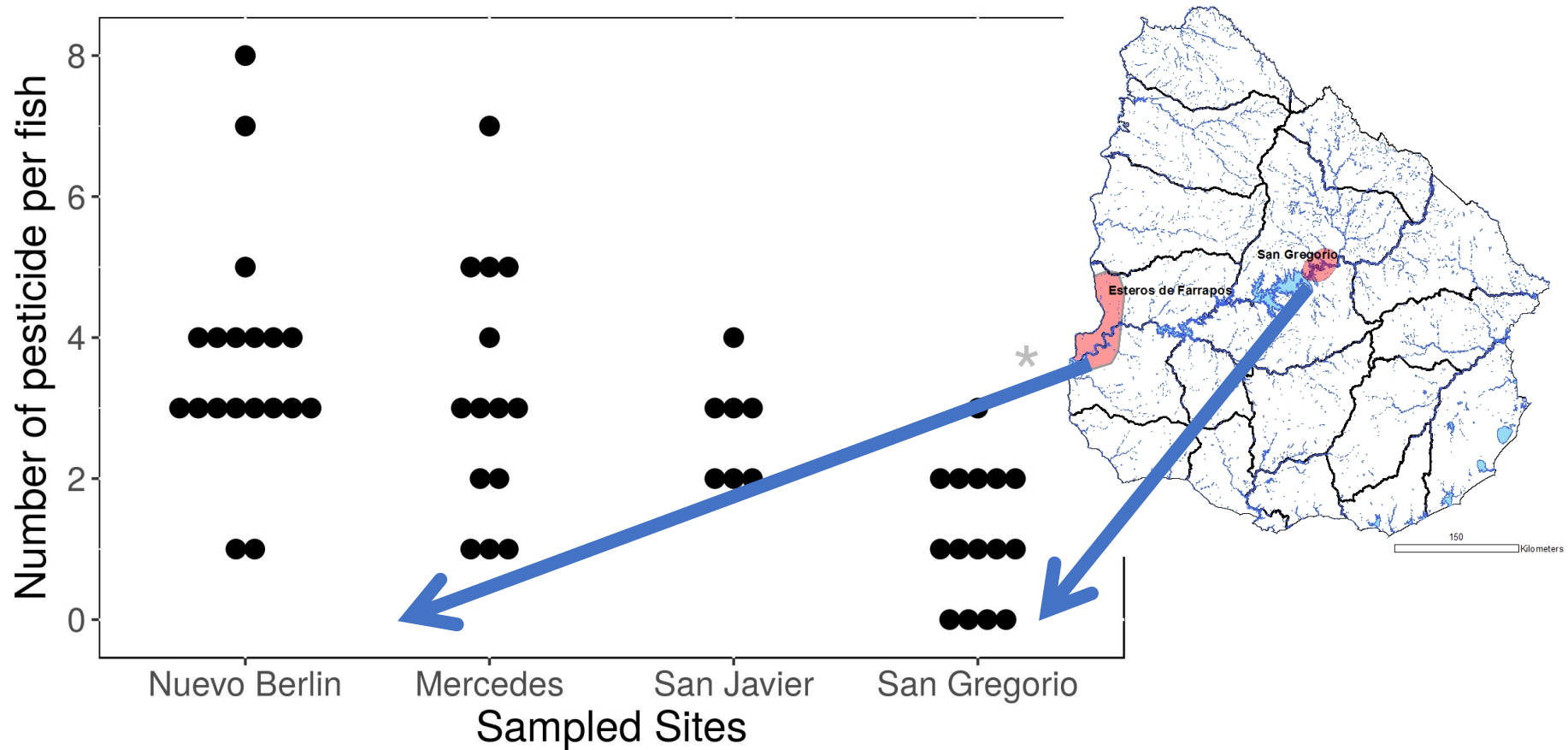


Migratory

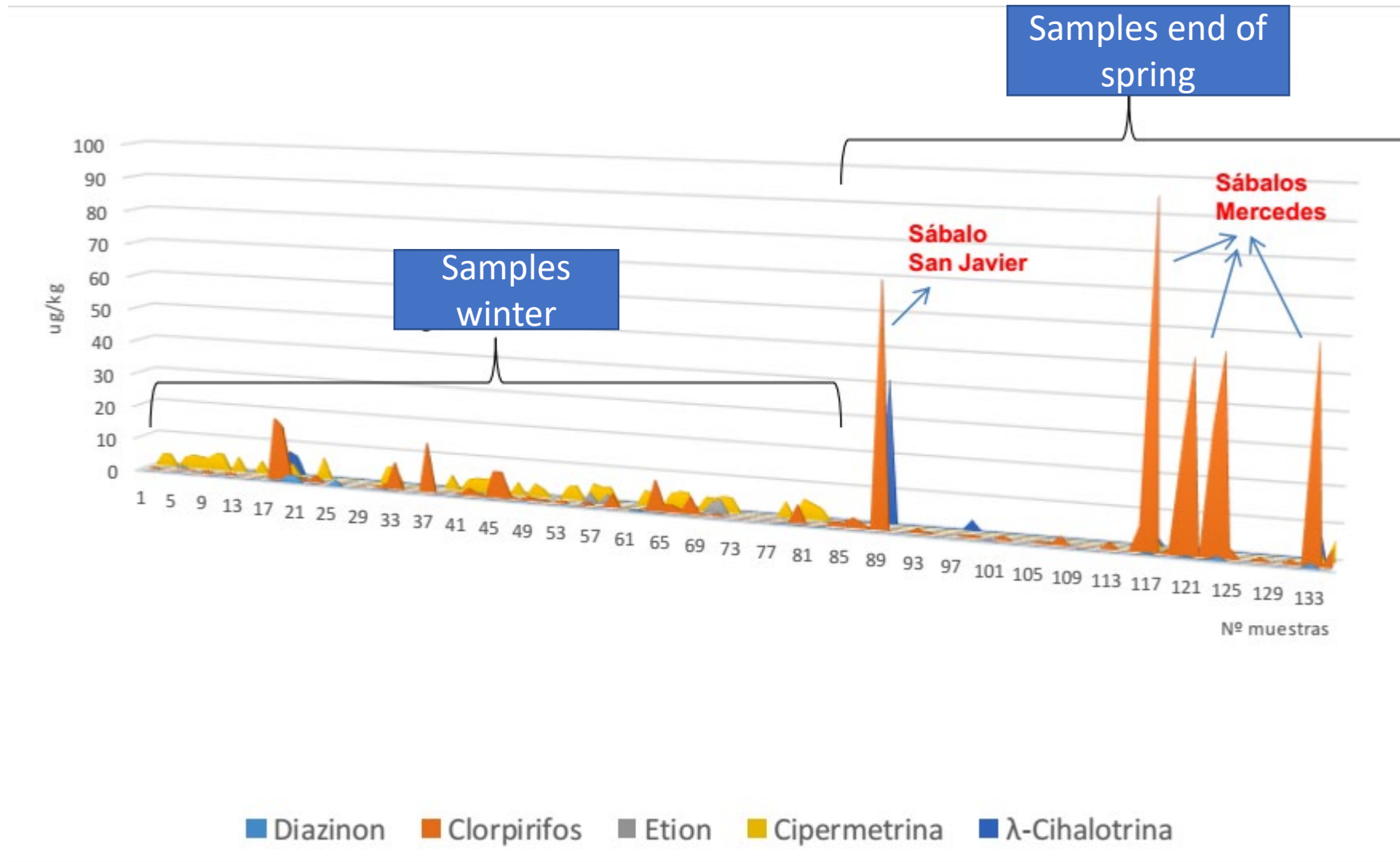


Local

number of pesticides/ sample for non migratory species



Pesticide occurrence in fresh water fish from agricultural regions in Uruguay



Macroinvertebrates, odonates

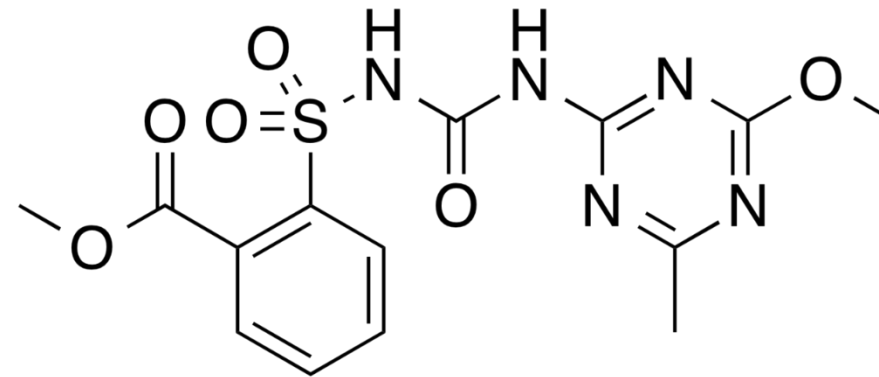
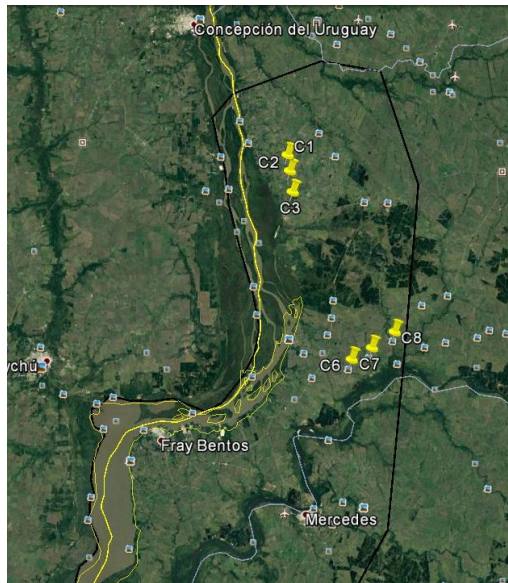


Ecotoxicology and chemistry

Findings in odonate nymphs (macroinvertebrates)



Metsulfuron methyl (label dose : 500g/ha)

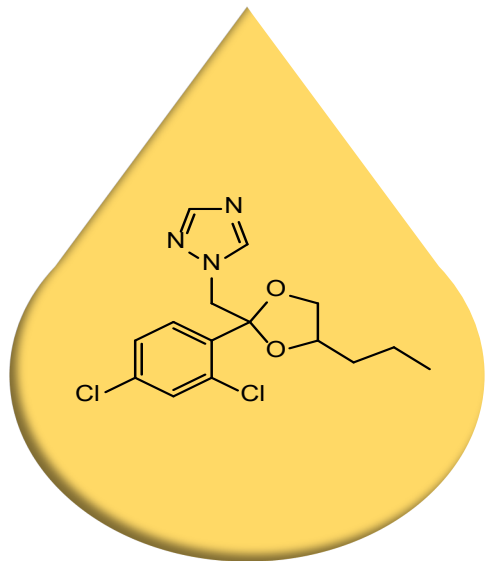


sample	Conc. ($\mu\text{g}/\text{kg}$)
c3	<1
c8	1

Another way of pesticides to water bodies



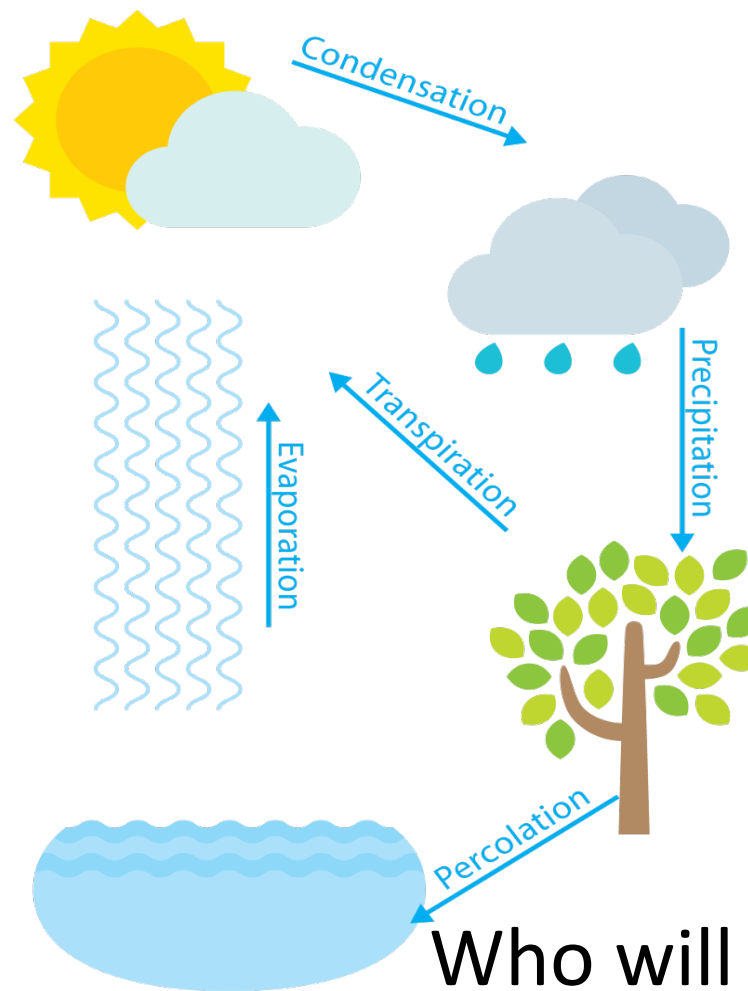
Are pesticides raining ?



¿Co-distillation?

Drift of small droplets to the clouds?

Dragged by the rain?



Who will stop the rain?

Pesticides searched

CARBARILO	ACETAMIPRID	AZINFOS	BUPIRIMATE	BIFENTHRIN
CIPROCONAZOL	ALDICARB	CARBENDAZIN	BUPROFEZIN	CLORANTRALINOPROLE
CLOPIRIFOS METIL	AZOXISTROBIN	CLOMAZONE	CADUSAFOS	FENBUCANAZOL
DIAZINON	BOSCALID	ETHION	CARBOFURAN 3H	IMIDACLOPRID
DIMETOATO	CARBOFURAN	FENHEXAMID	DICONAZOLE	KRESOXIM
EPOXICONAZOL	CLOTIANIDIN	FLUFENUXURON	ETONFENPROX	OMEOTATO
HEXYTIAZOX	DIFENOCONAZOL	FLUOPICOLIDE	FAMOXADONE	FOSALONE
MALAOXON	IMAZALIL	FLUTRIAFOL	FENAZAQU	BUTILAZINE
MALATION	METIOCARB	FLUZILAZOLE	FENTION S	LAZOLE
PENDIMETALIN	METOMILO	HEXACONAZOLE	FENTION	
PIRIFIMIFOS METIL	METHOXYFENOCID	LINURON	METIC	
PROPICONAZOL	OXADIXYL	LUFENURON	ME	
TEBUCONAZOL	PIRACLOSTROBIN	MEPANIPRIM		
TIAMETOXAN	PROCLORAZ	PIRIMICARB		
TIODICARB	PIRIMETANIL	SPIROXAMINE		
TRIFOXISTROBIN	TIACLOPRID	TEFLUBENZURON		

72 PESTICIDES

Experimental design



● ● Sampling from May 2018 to February 2019 ● ● >

Experimental design



● ● **Sampling from May 2018 to February 2019** ● ● ●



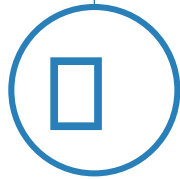
Experimental Design

sampling



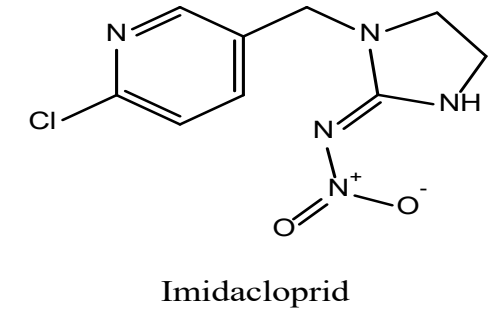
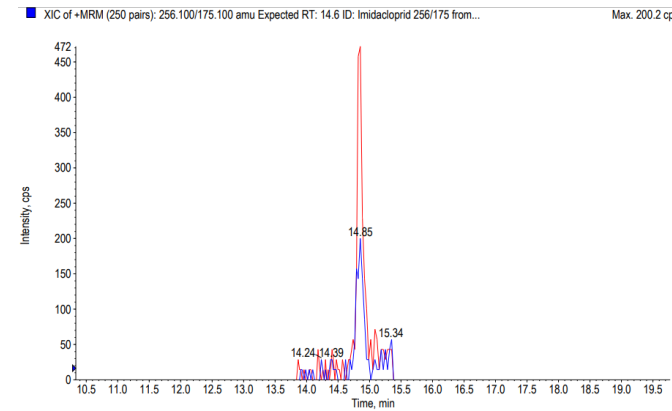
Results

winter



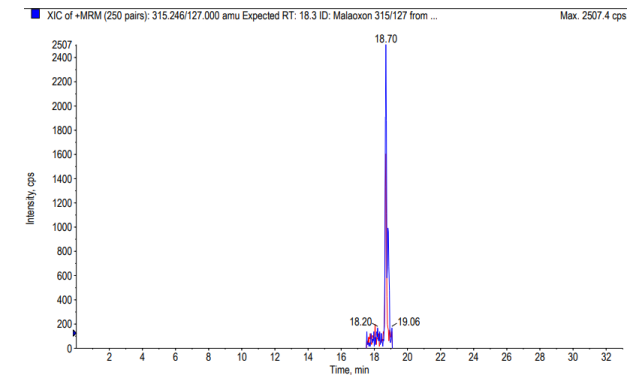
08/07/2018 y 19/07/2018

Imidacloprid
Propiconazol
Malaoxon



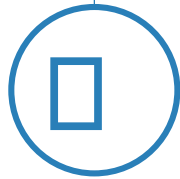
Not longer in use in Uruguay

Malaoxon
found 19/07/18
Conc: 5-7 ng L⁻¹



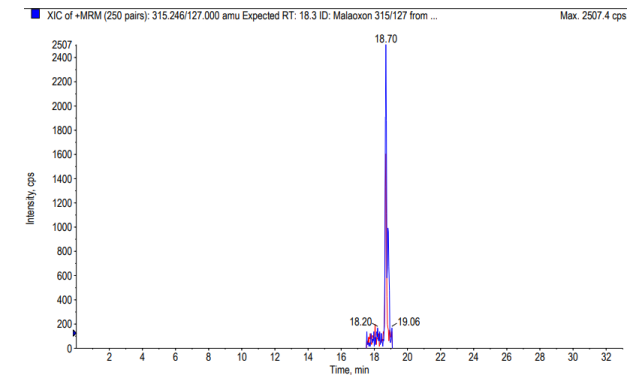
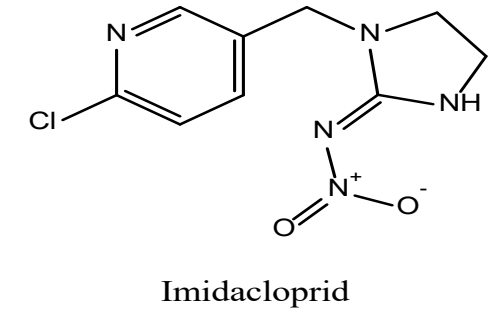
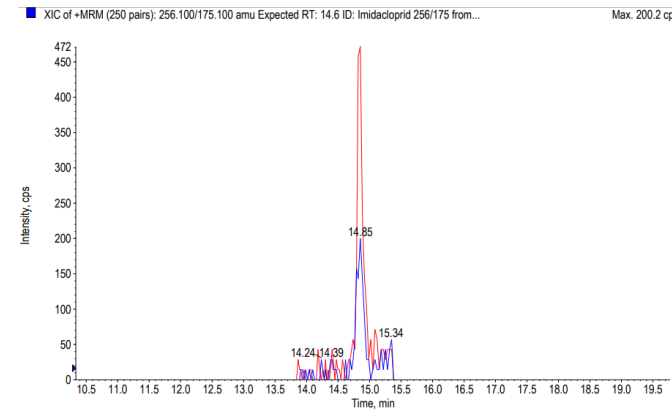
Results

winter



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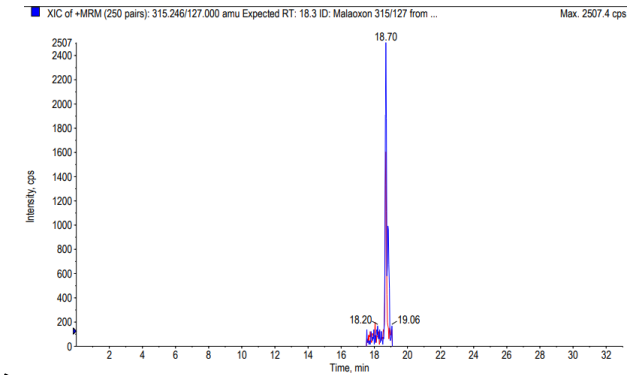
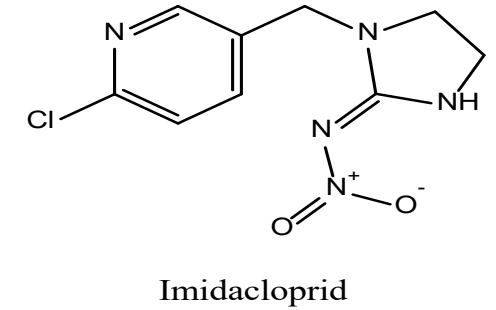
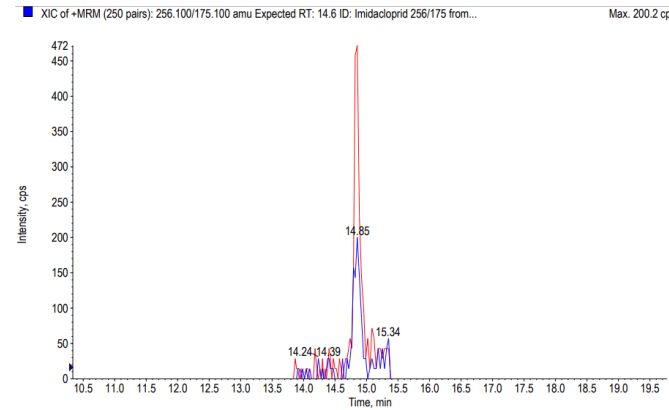
Results

winter



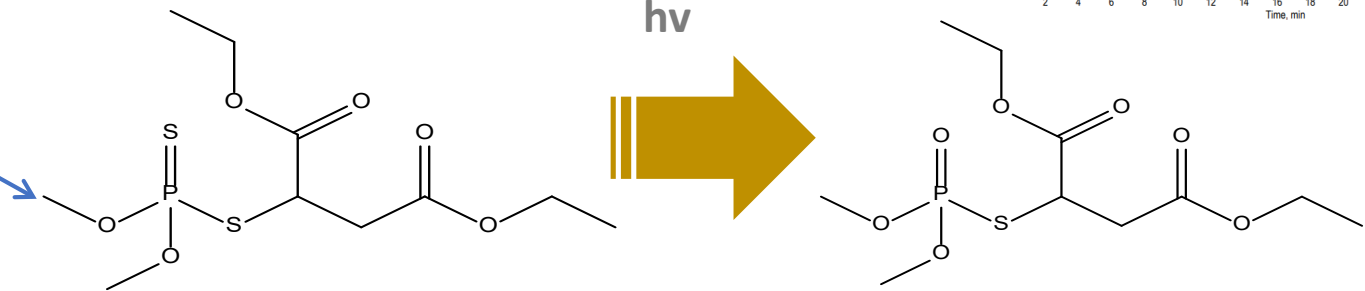
08/07/2018 y 19/07/2018

Imidacloprid
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Rio de la Plata basin



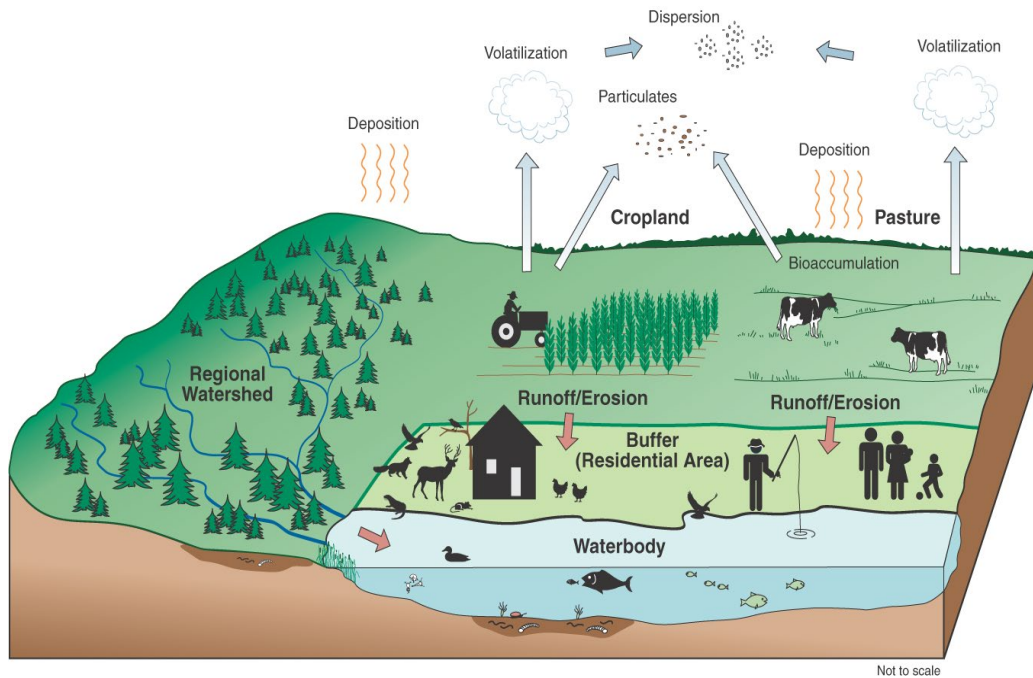
Clouds do
not
recognize
any
borders!!!

Seasonal analysis

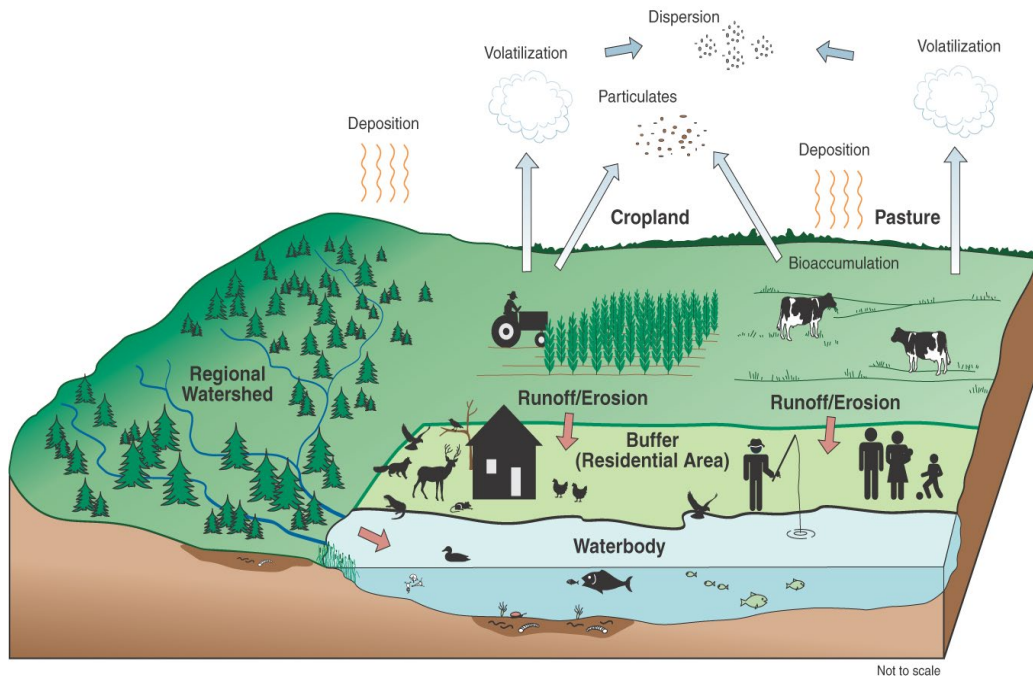
Mayo 2018 a Febrero 2019



Major sources of water contamination: Anthropogenic activities



Major sources of water contamination: Anthropogenic activities





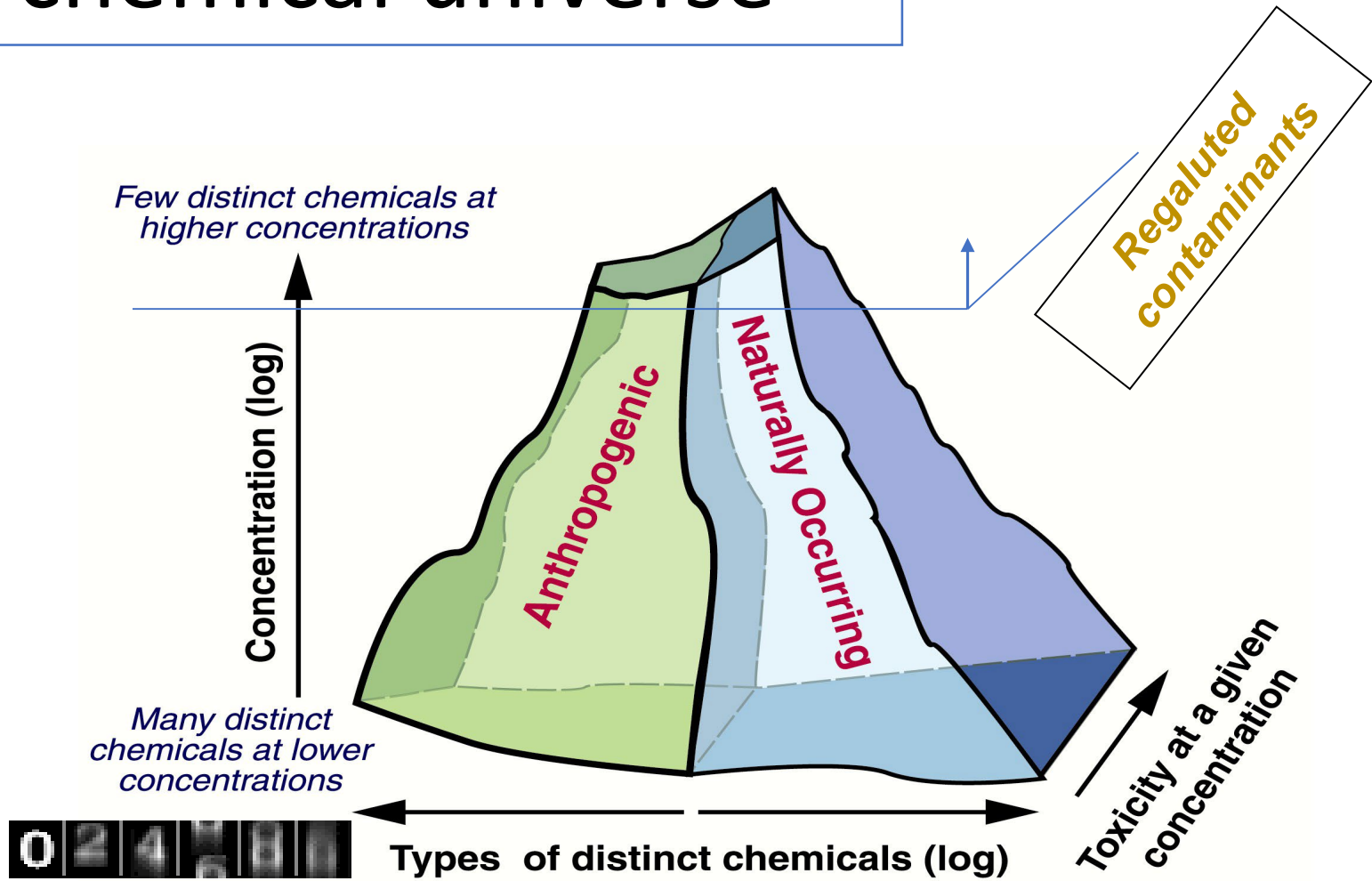
The chemical universe



Emerging Contaminant can be defined as any natural or synthetic chemical compound, any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known, suspected or unknown adverse ecological or human effects.

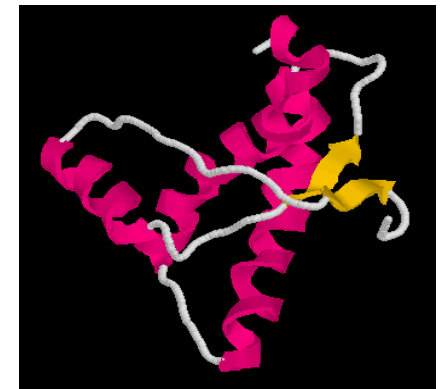
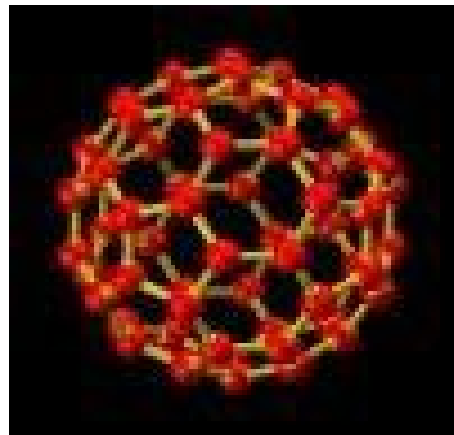
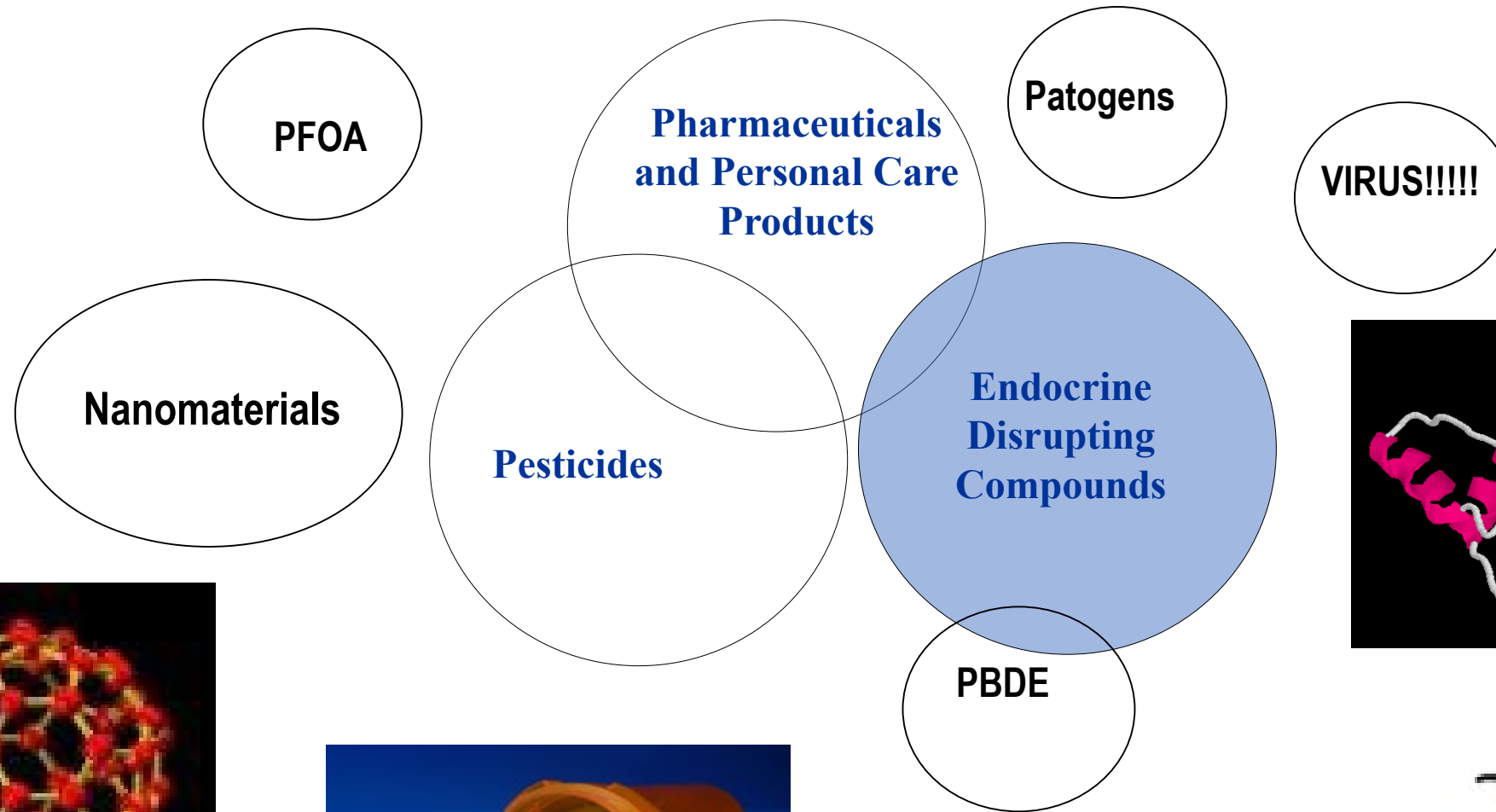


The chemical universe



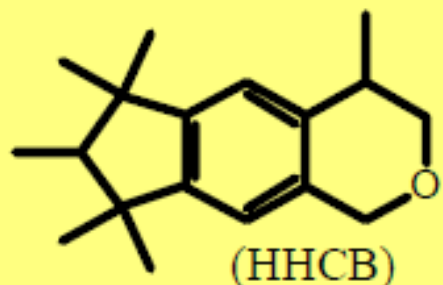
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Emerging Contaminants in Water

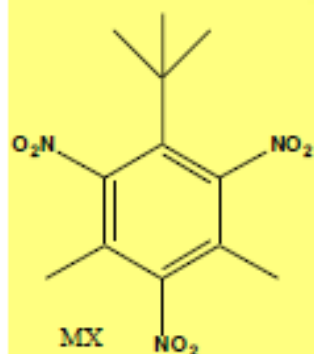
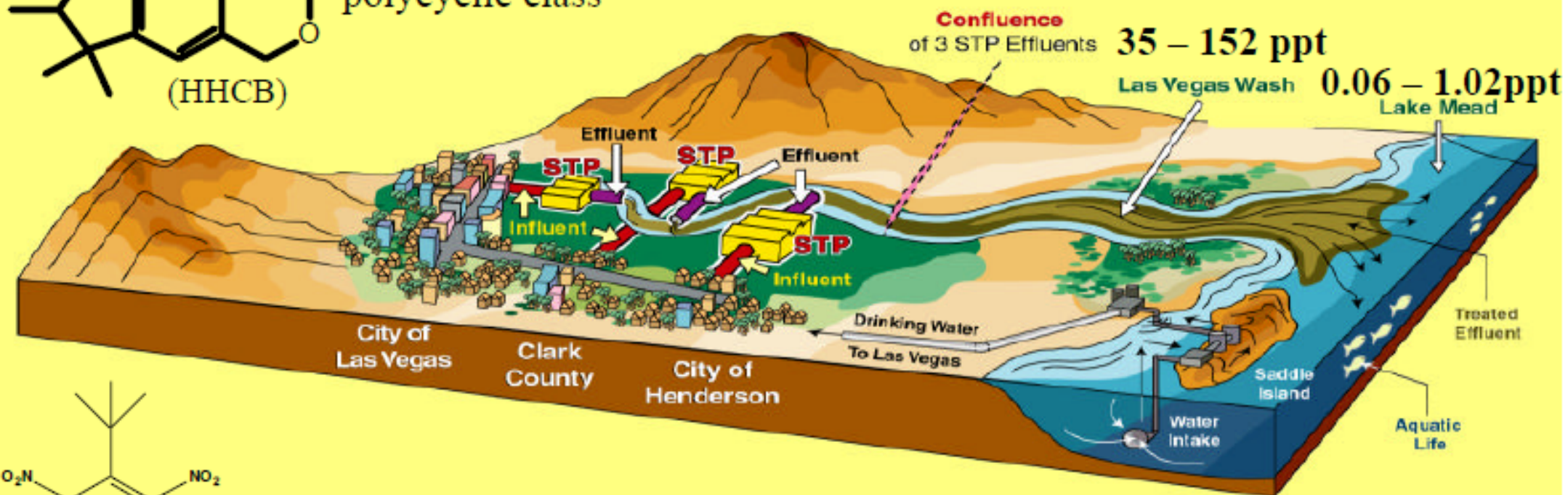


Origin, Transport & Fate of Synthetic Musk Compounds in the Las Vegas Basin

see Osemwengie et al.:
<http://epa.gov/nerlesd1/chemistry/pharma/musks.htm>



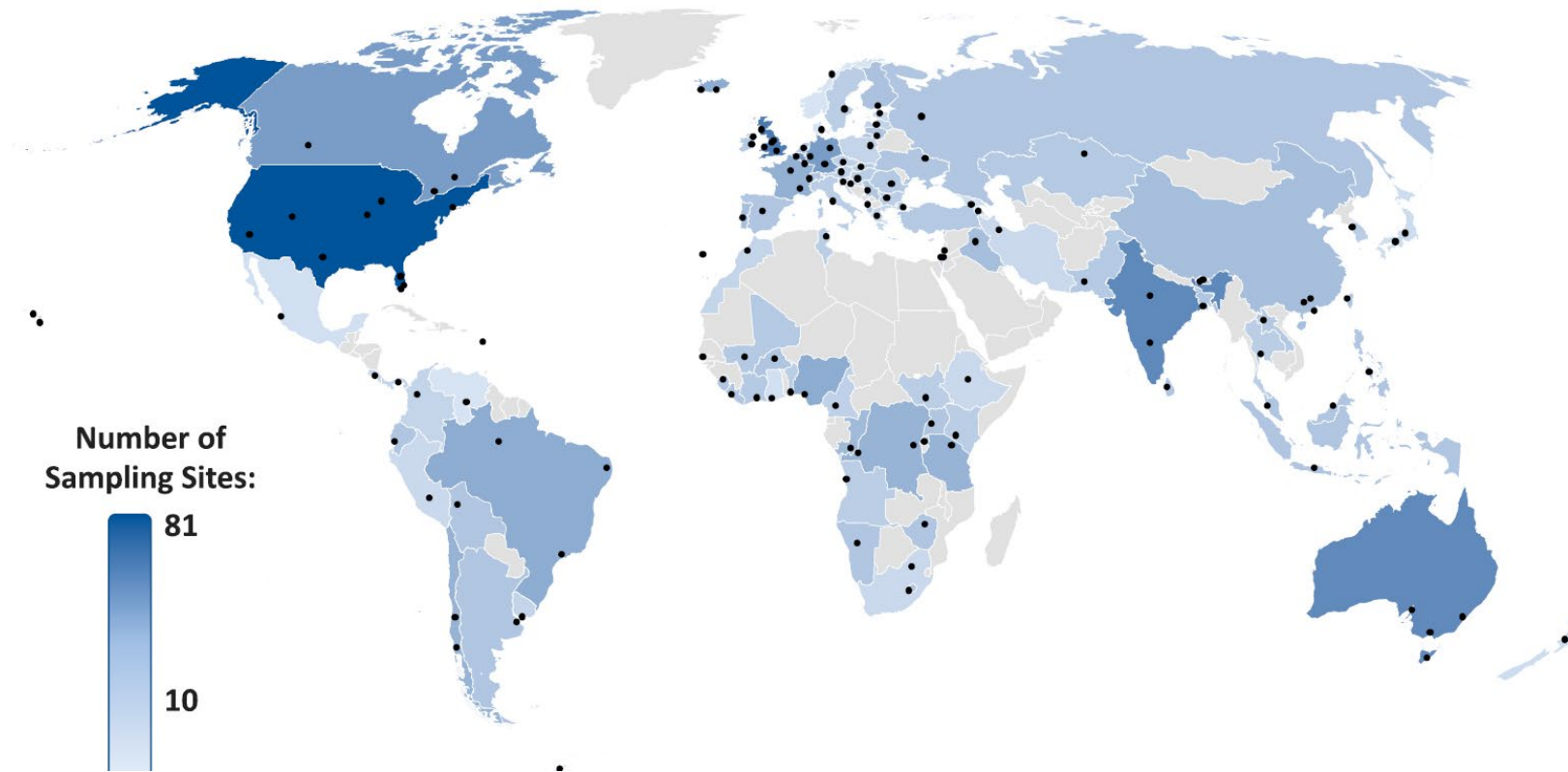
Galaxolide:
polycyclic class



Musk Xylene:
Nitro musk class

1400-4500 ppt

Emerging contaminants: a world survey



258 rivers

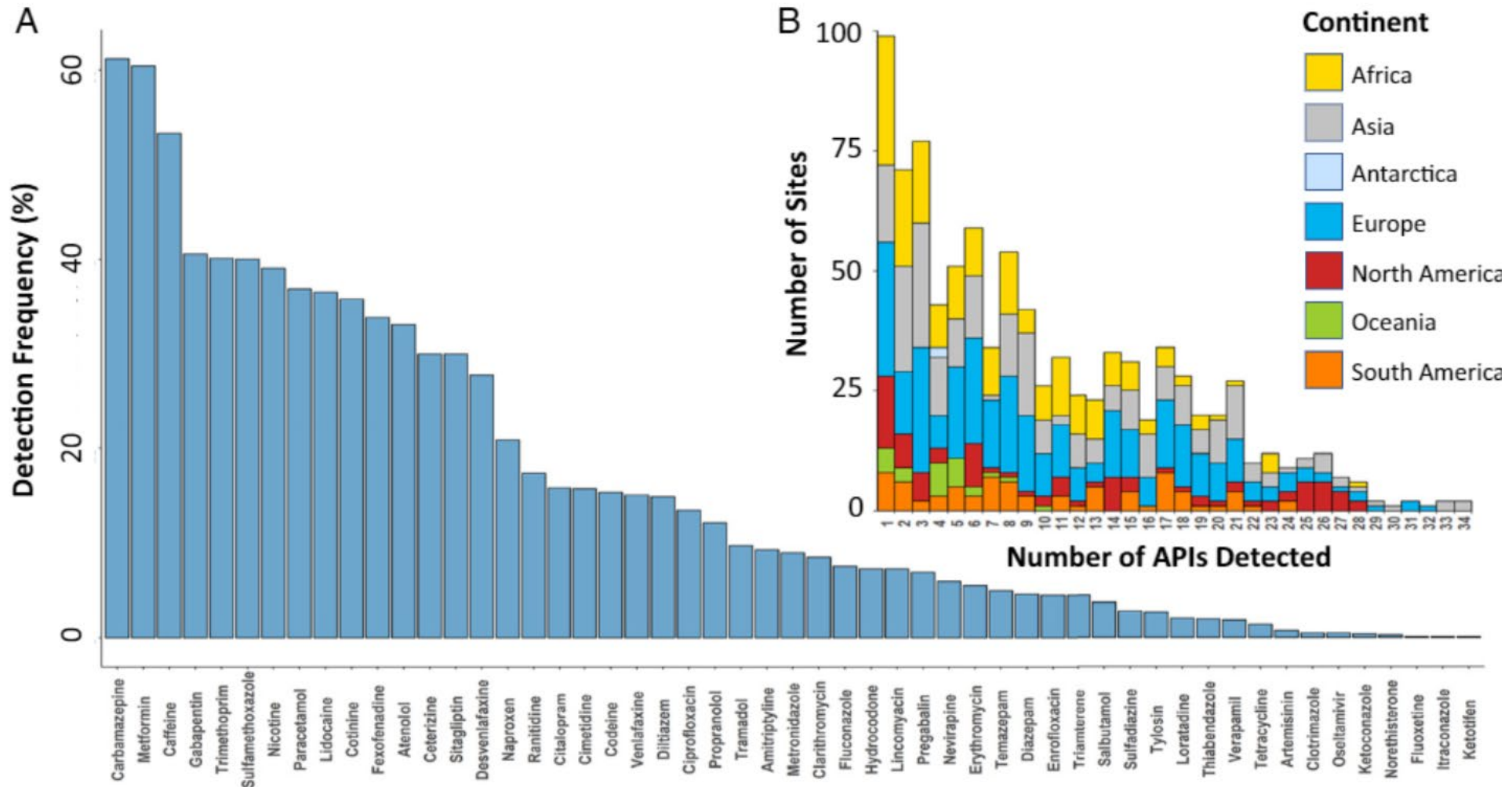
104 countries

137 regions

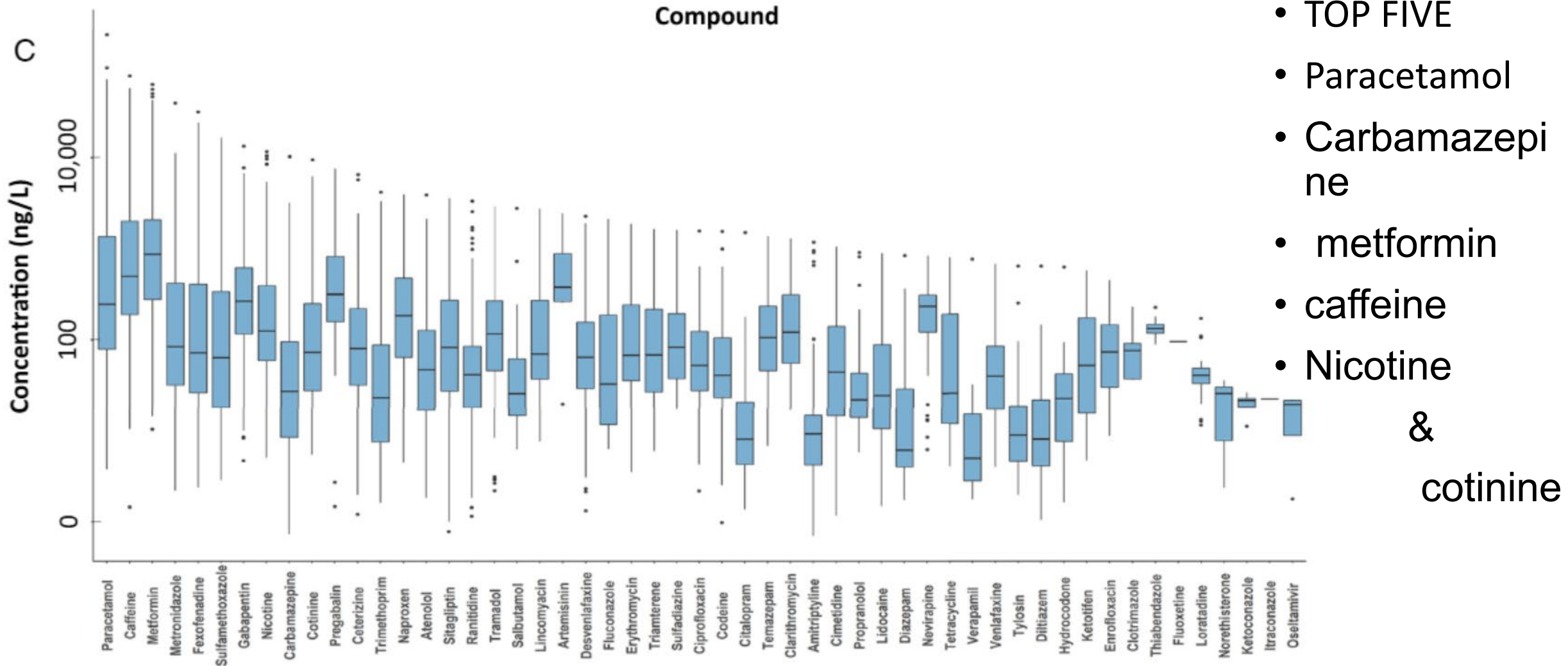
61 countries

6 continents

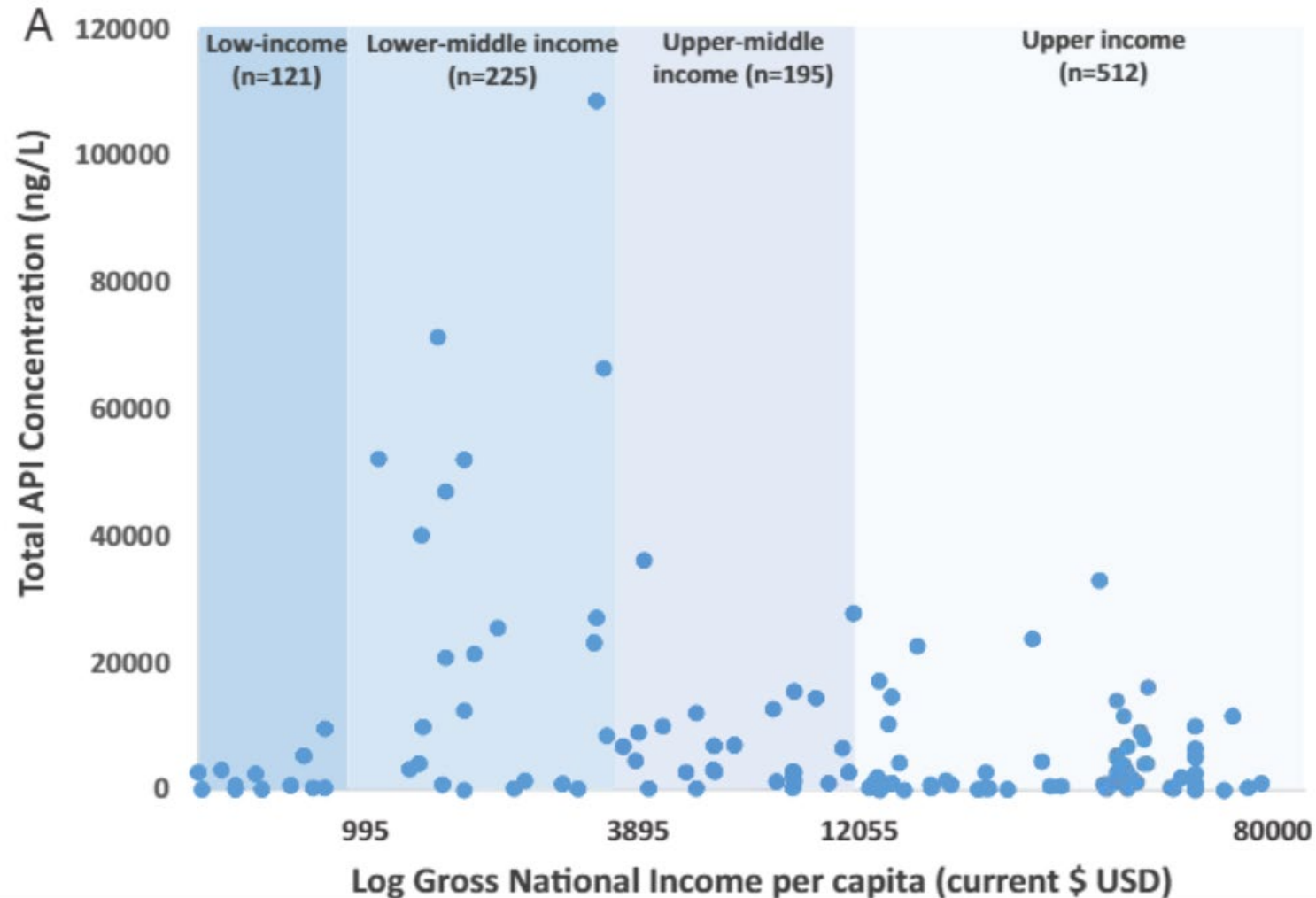
Frequency of detection of 61 pharmaceutical products all over the world



Concentration range of 61 pharmaceutical products found in river waters



Short discussion



Lower frequencies of detection where sewage waters are treated

Specific pharmaceutical were detected according to the región:

Therapetic habits

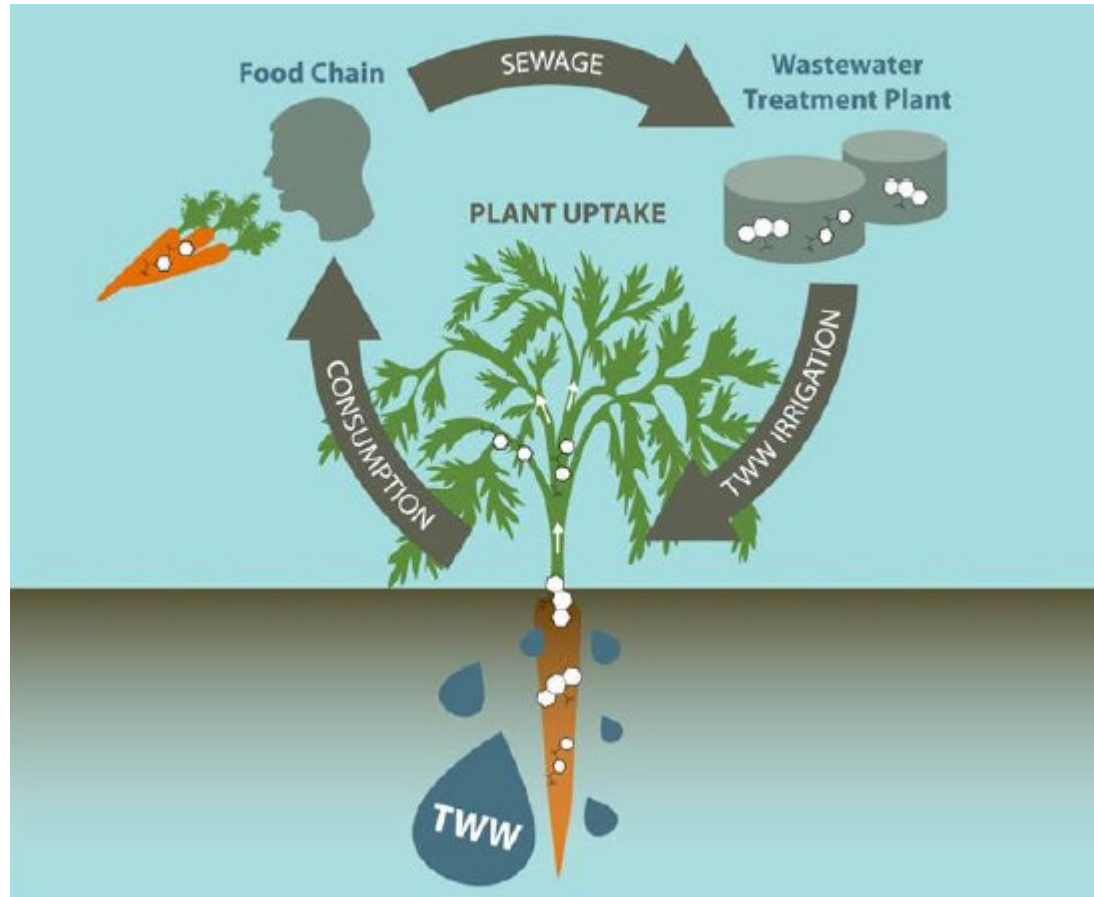
Easyness to reach over the counter remedies (antimicrobials)

Emerging contaminants in Uruguay river



- Samples taken in the bath zone
- Effluents of a nearby stream reach this zone
- Positive for 8 of the 61 compounds searched
- Paracetamol, ranitidine, nicotine, coffee, gabapentin, a.o

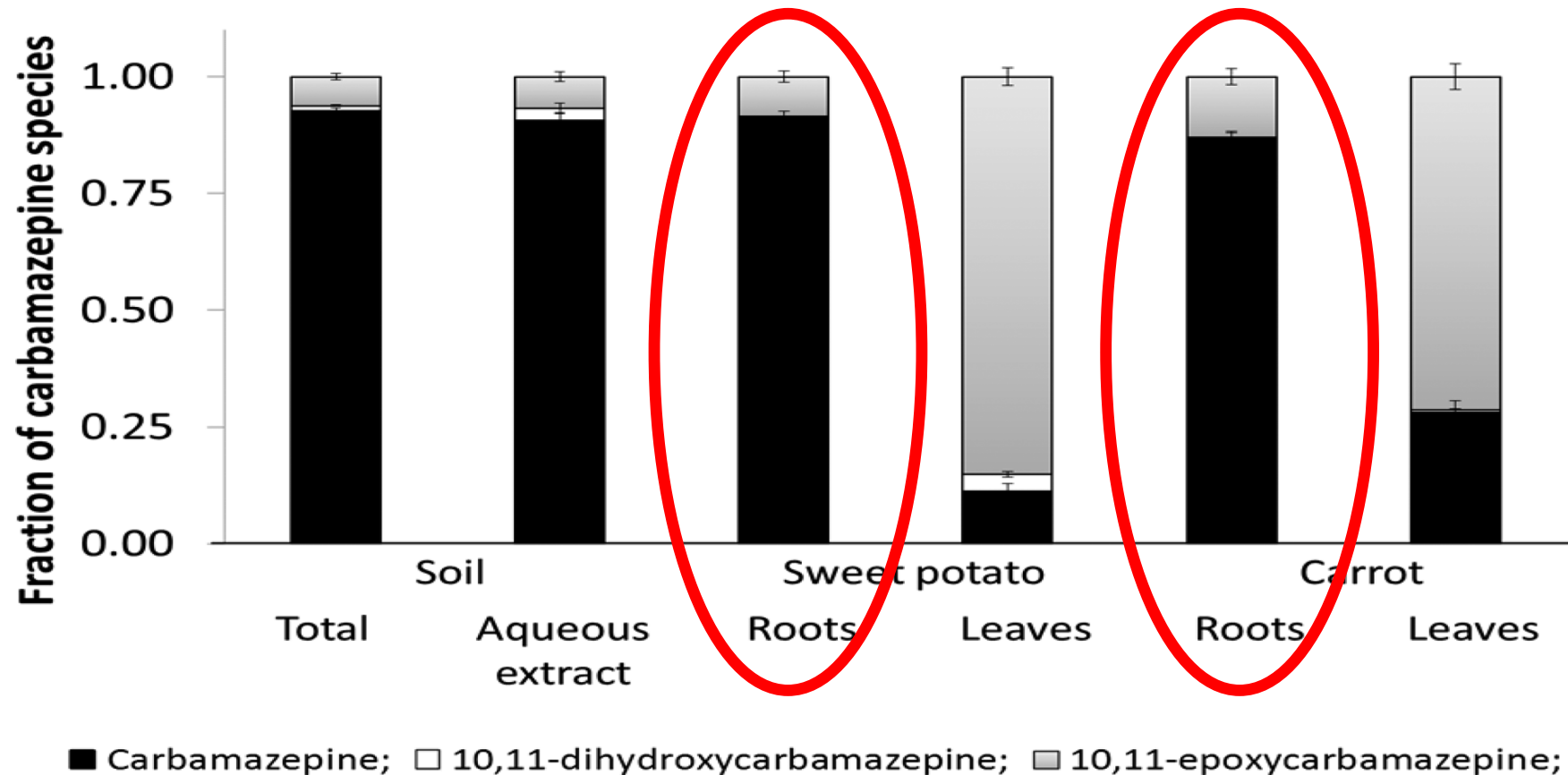
Do emerging contaminants in water enter the food chain?



Vegetables irrigated with reclaimed water containing Personal Care Products can incorporate these products in the edible portion

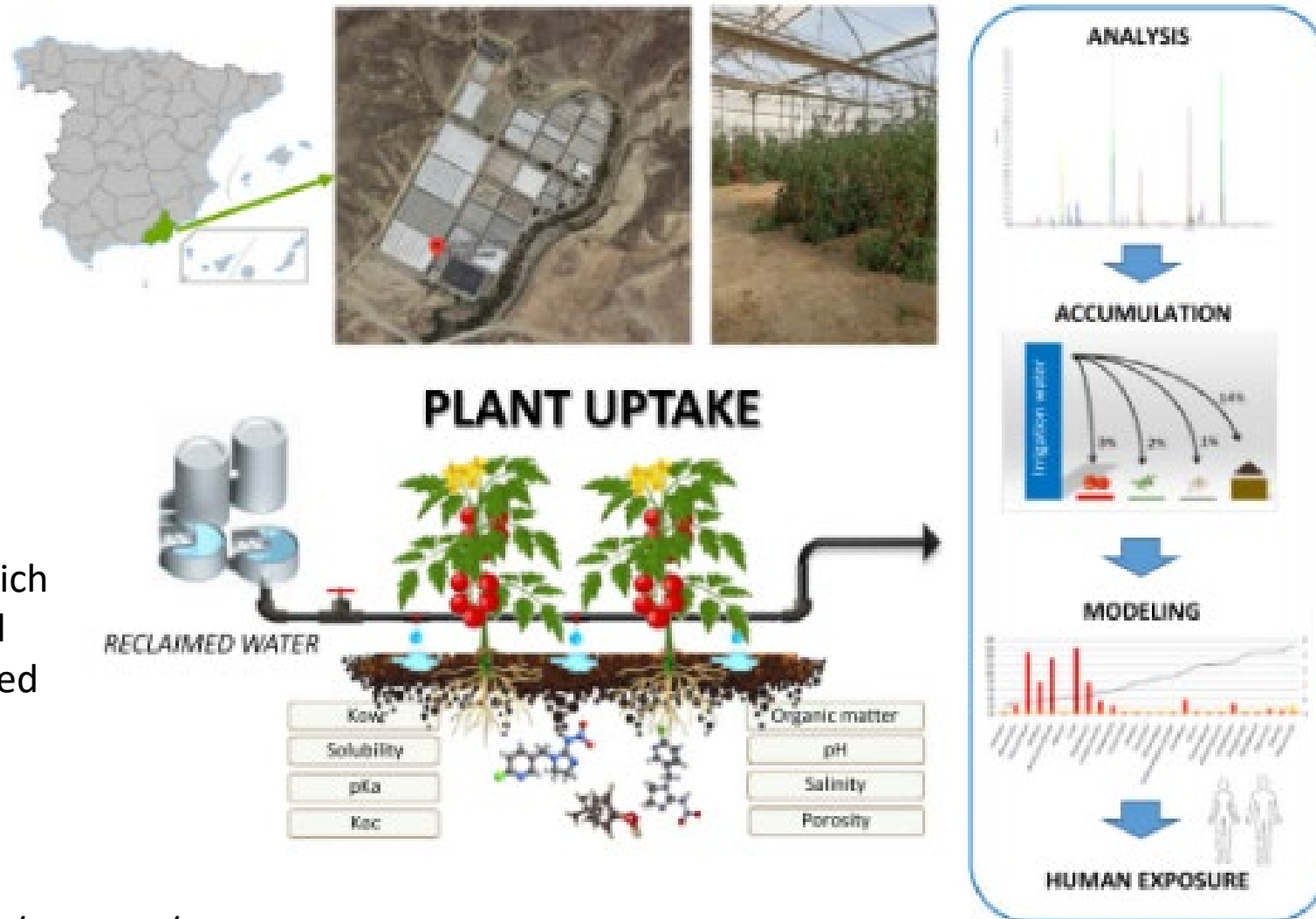
(Zheng, *et al.*, 2014).

Partition of carbamazepine and metabolites in sweet potatoes and carrots irrigated with reclaimed water

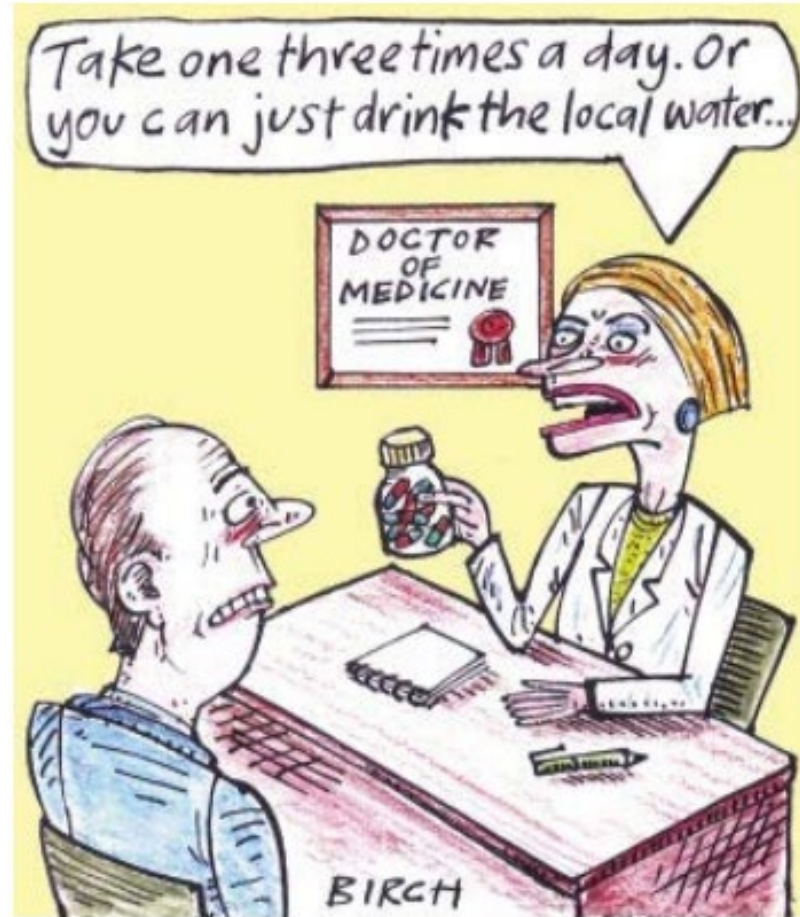


Food safety of irrigated tomatoes with reclaimed water

Risk assesment showed
“Overall, the concentration levels of CECs detected in the tomatoes, which were permanently irrigated with contaminated reclaimed water, do not pose a risk to human health via dietary intake”



Do emerging contaminants reach tap water?

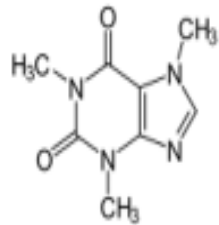


Nature 424, 5 (2003)

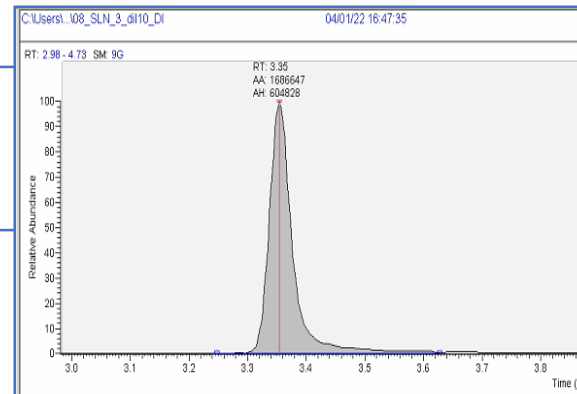
Do emerging contaminants reach tap water?

Do emerging contaminants reach tap water?

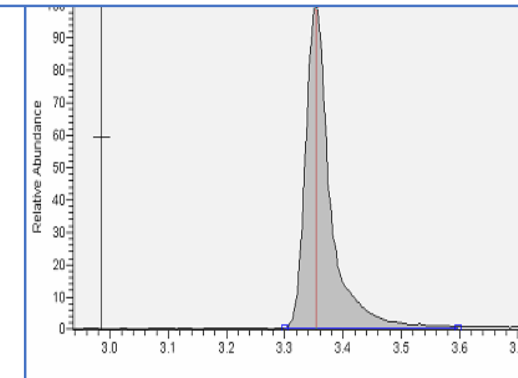
CAFFEINE



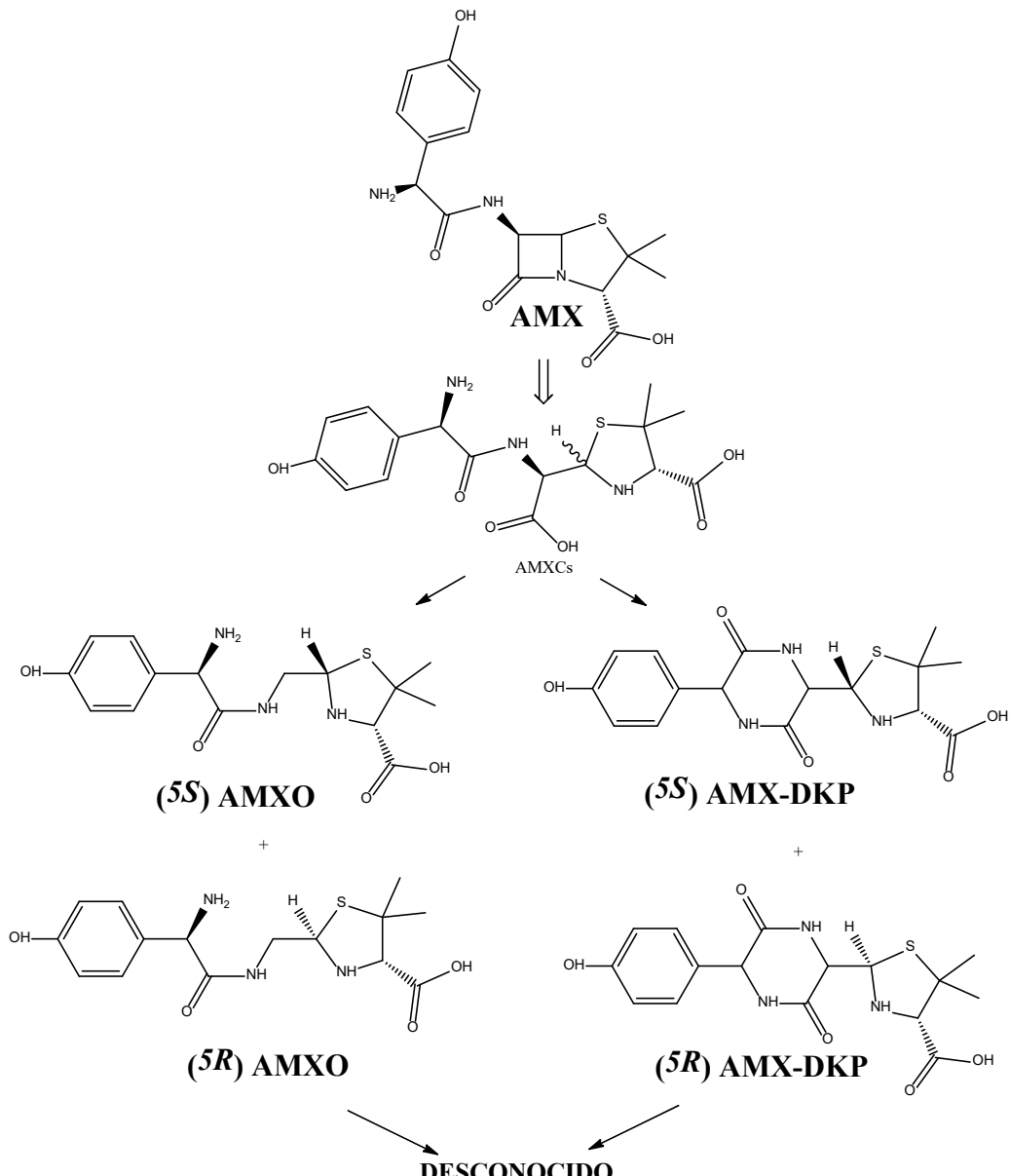
**Natural
raw water**



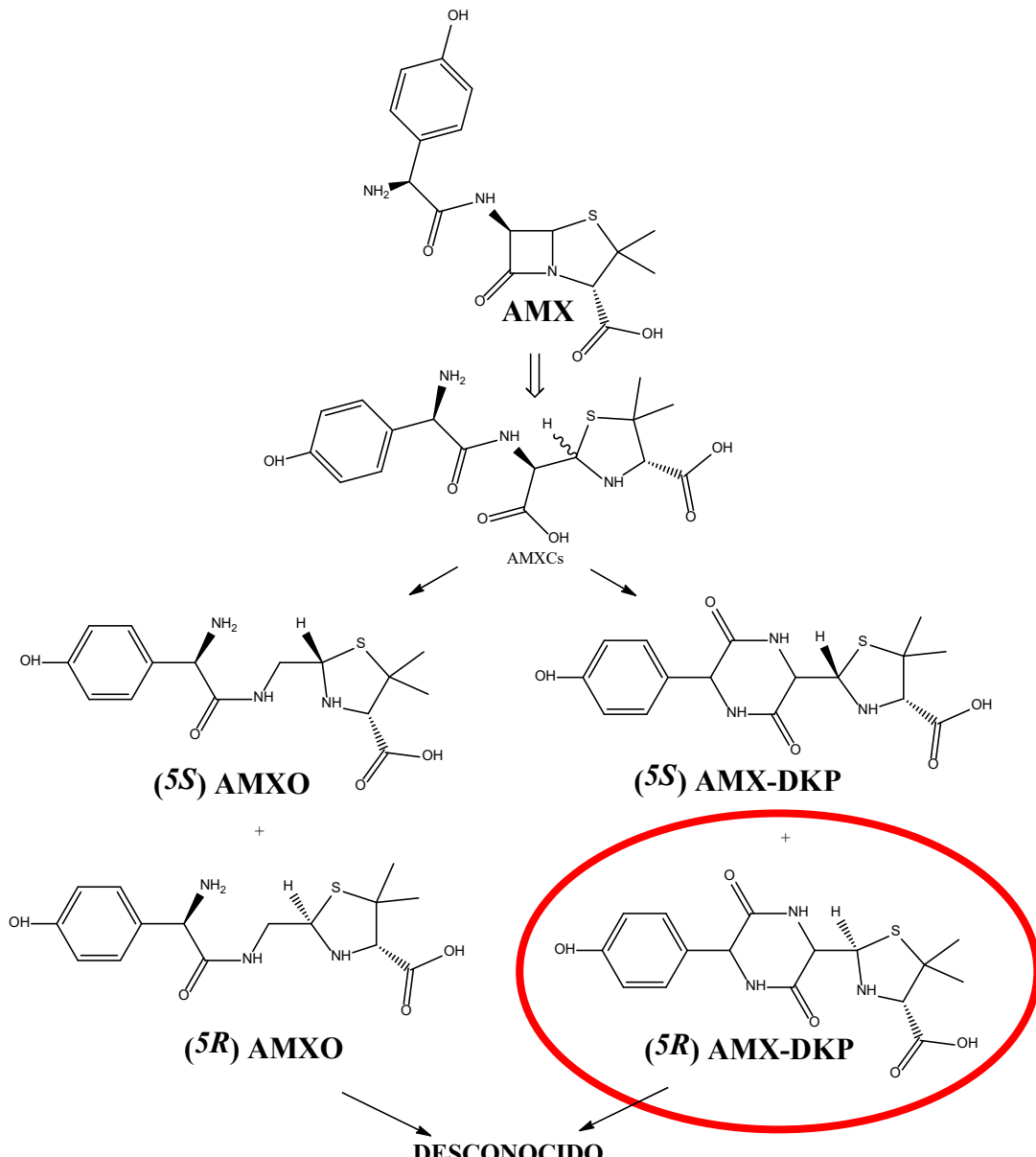
**Treated
Tap water**



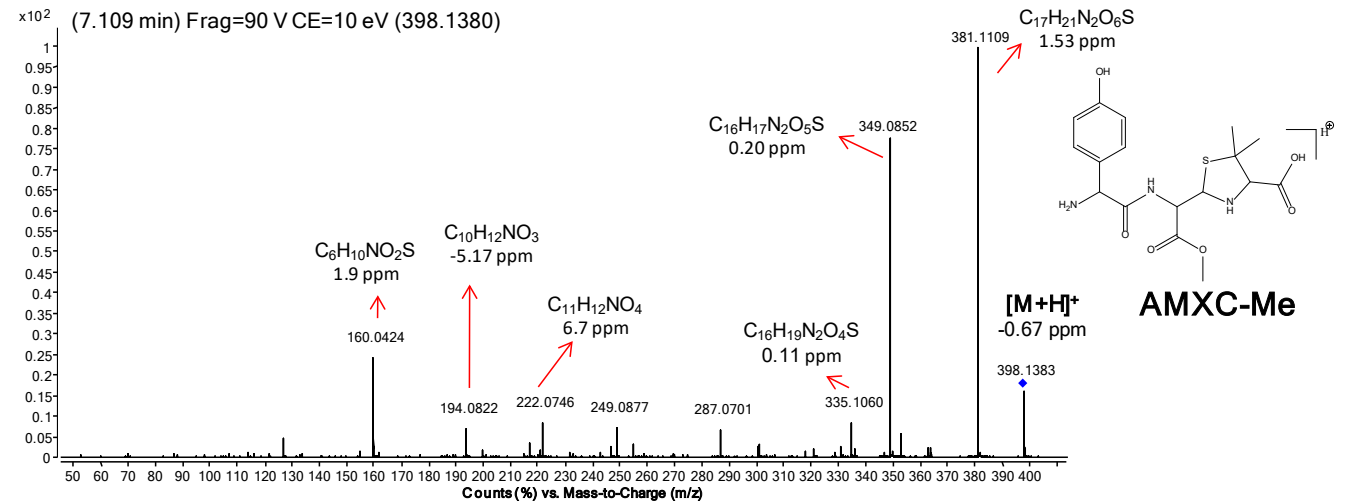
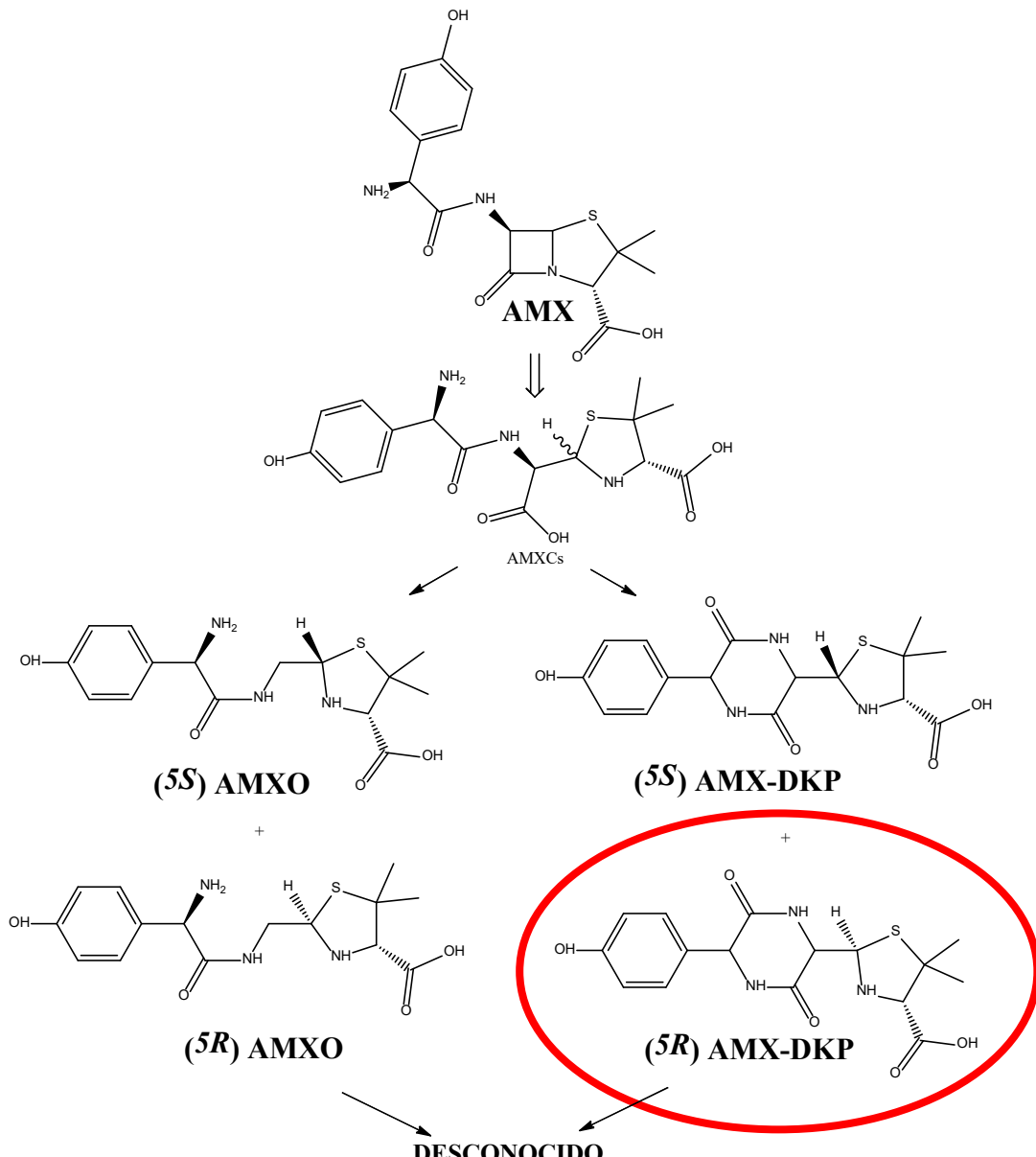
What about the transformation products?

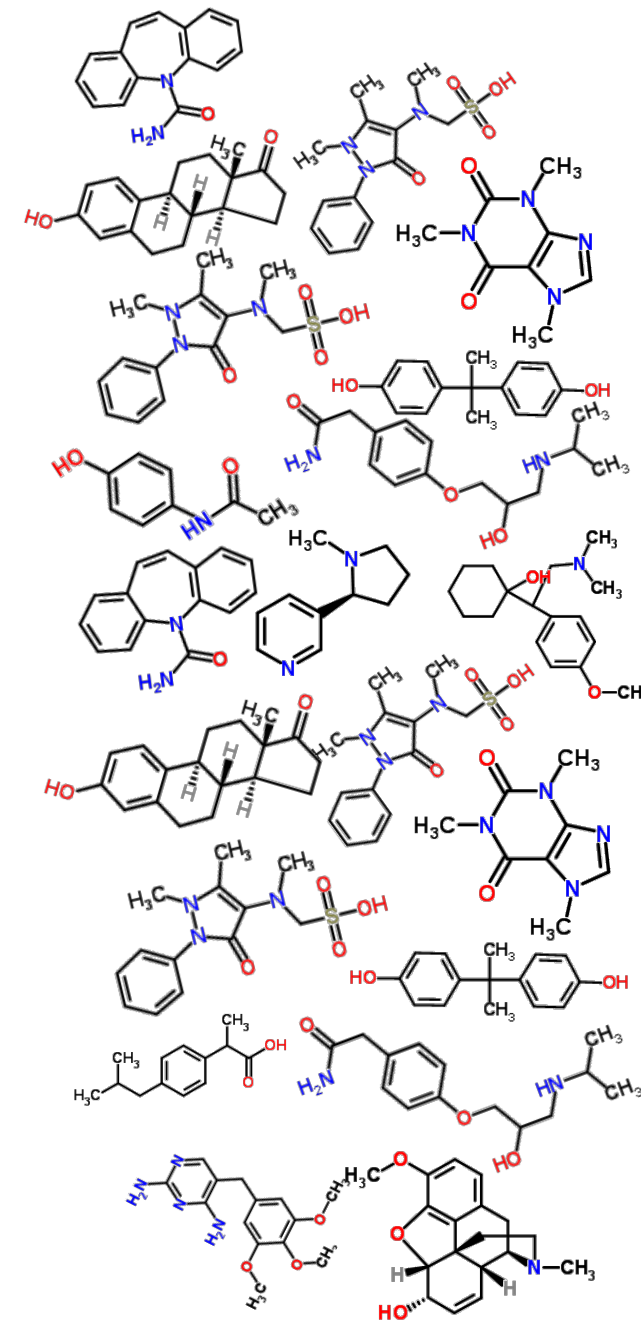


What about the transformation products?



What about the transformation products?







Knowledge



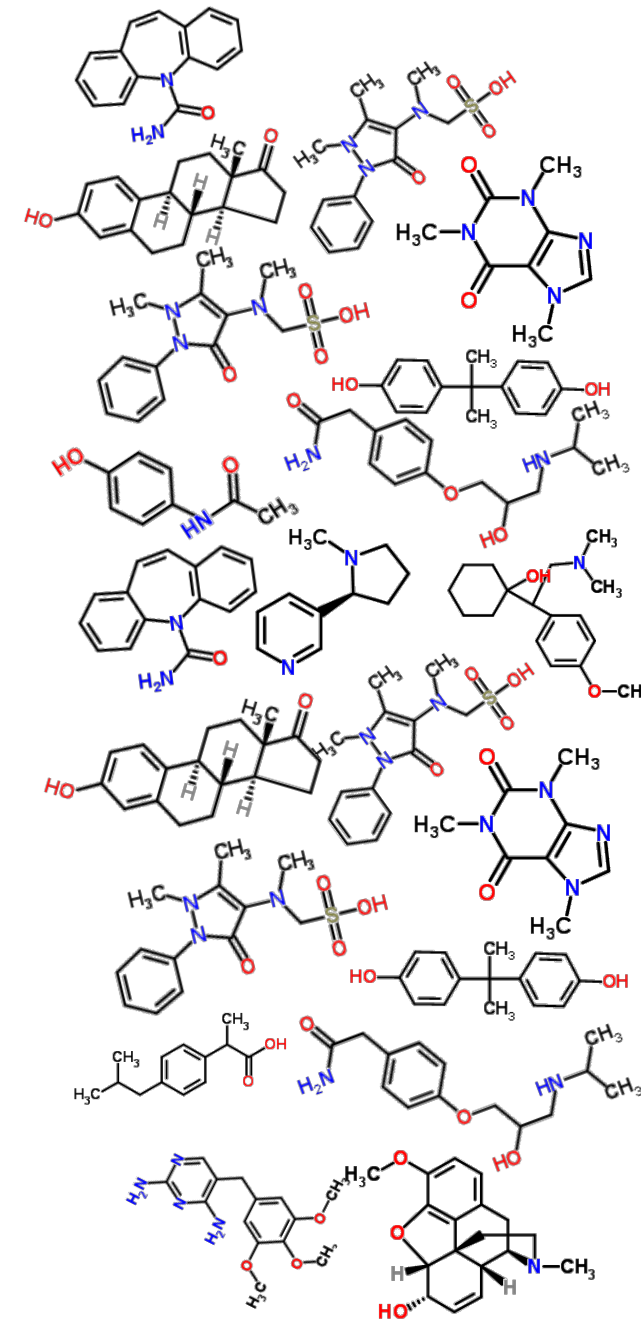
Quality Assurance & Quality Control



Representativity



Regulation



Some take home messages

- Water is being continuously polluted by human activities
- The origin comes from agricultural activities, mainly pesticides but also from the cities and sewage waters but also rain is a source of contaminated water
- These contaminants threaten the biota in aquatic ecosystems and pose a risk for consumers of for instance freshwater fishes
- No specific MRLs are settled for agricultural pesticides in fish, as no GAP is related to wild freshwater fish. The Codex Alimentarius offers the opportunity to settle Extraneous MRLs (E-MRLs)
- The treatment of freshwaters for human consumption must consider the elimination of EC.
- The use of treated sewage Waters must be check in a case by case scenario

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A photograph of a sunset over a body of water. The sun is a bright yellow-orange circle in the center of the horizon, casting a reflection on the water. The sky is a gradient of red and orange. The water is dark with a small boat visible on the horizon. The text "Thank you !!!" is overlaid in white in the upper left, and "Hvala vam!!!" is overlaid in white in the lower right.

Thank you !!!

Hvala vam!!!