Progress Report (PIRE Work: 2013)

3 Major Projects:

1) Surface Microlayers as Contaminant Hotspots in LID Systems

2) Spatial & Temporal Variability of Pesticides in Stormwater Runoff

3) Tradeoffs in Pollutant Removal Efficiency by Biofilters: optimized WSUD systems

Surface Microlayers in LID Systems: pollutant partitioning hotspots?

The surface microlayer is a naturally occurring thin-film (~ 60 um thick) on the surface of aquatic systems

Microlayers can concentrate some pollutants:
- heavy metals (Pb, Zn, & Cu),
- polycyclic aromatic hydrocarbons
- petroleum hydrocarbons, &
- some triazine pesticides

Little is known about freshwater microlayers (research has focused on sea and estuarine microlayers)

In particular, microlayer – bulk water contaminant partitioning in freshwater, urban, LID systems is understudied

Contaminant partitioning affects pollutant removal and thus LID function

Contaminants in surface microlayers might:
- form films on plants or soils that negatively impact wildlife
- experience enhanced photodegredation (and thus enhanced removal)
- volatilize (thereby avoiding treatment)
- be efficiently removed by a rotating drum or skimmer prior to treatment (⬆LID longevity)

Project Goals

Evaluate the following:

Do surface microlayers form in freshwater LID systems like constructed wetlands and biofilters?

Do contaminants partition preferentially into the microlayer?

Can excitation-emission fluorescence spectroscopy be used as a cost-effective proxy for detecting;

1) surface microlayer presence, and/or

2) the partitioning of anthropogenic contaminants between microlayer and bulk water?

LID Field Sites

BAN

BP

NP

HRW

4 LID systems were sampled in Melbourne, AU

- **BAN**: wetland-biofilter treatment train
- **BP**: ornamental pond
- **NP**: a stormwater retention basin
- **HRW**: a constructed wetland

Sampling:

- Paired subsurface (bulk) water and microlayer samples were collected at each site
- Samples were analyzed for:
    - → **Micropollutants**: Total Petroleum Hydrocarbons & Trihalomethanes
    - → **Fluorescent compounds**: EEM fluorescence microscopy

Micropollutant Measurements

Both types of micropollutants were detected:

- **Total Petroleum Hydrocarbons** (C10-C14 - C29-C36)
  - → road runoff
  - → sewage

- **Trihalomethanes** (Chloroform)
  - → industrial waste (refrigerator manufacture)
  - → pools/hot-tubs (disinfectant byproduct)
  - → recycled water / treated effluent (disinfectant byproduct)

Microlayer

Chemical Type	Analytes Detected	Detect Lim. (ug/L)	BAN S (ug/L)	BP S (ug/L)	NP S (ug/L)	HRW S (ug/L)
Total Petroleum Hydrocarbons	**TPH** C10-C14	164	--	492	--	--
	TPH C15-C28	410	--	17220	410	--
	TPH C29-C36	410	--	1230	--	--
Trihalomethanes	Chloroform	4.1	--	--	4.1	7.8
	Total Trihalomethanes	4.1	--	--	4.1	7.8

Bulk

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Micropollutants were NEVER detected in bulk water

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BAN has no evidence of a chemically defined surface microlayer

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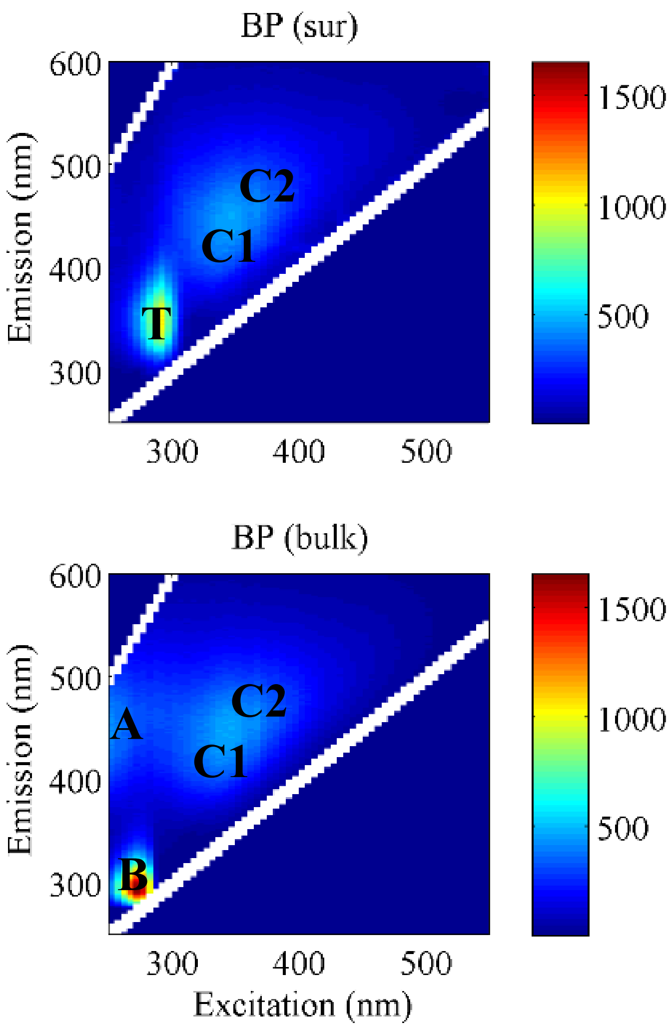
Microlayer Detection using Fluorescence: Excitation-Emission Spectra



5 different peaks were identified

A: UV Humic-like

C1: Fulvic-like (ubiquitous)

C2: VIS Humic-like (terrestrial)

B: Tyrosine-like (microbial)

T: Tryptophan-like (microbial)

Peak composition was different in bulk vs. microlayer waters at all sites except BAN consistent with micropollutant results

The surface microlayer can be detected by fluorescence in LID systems

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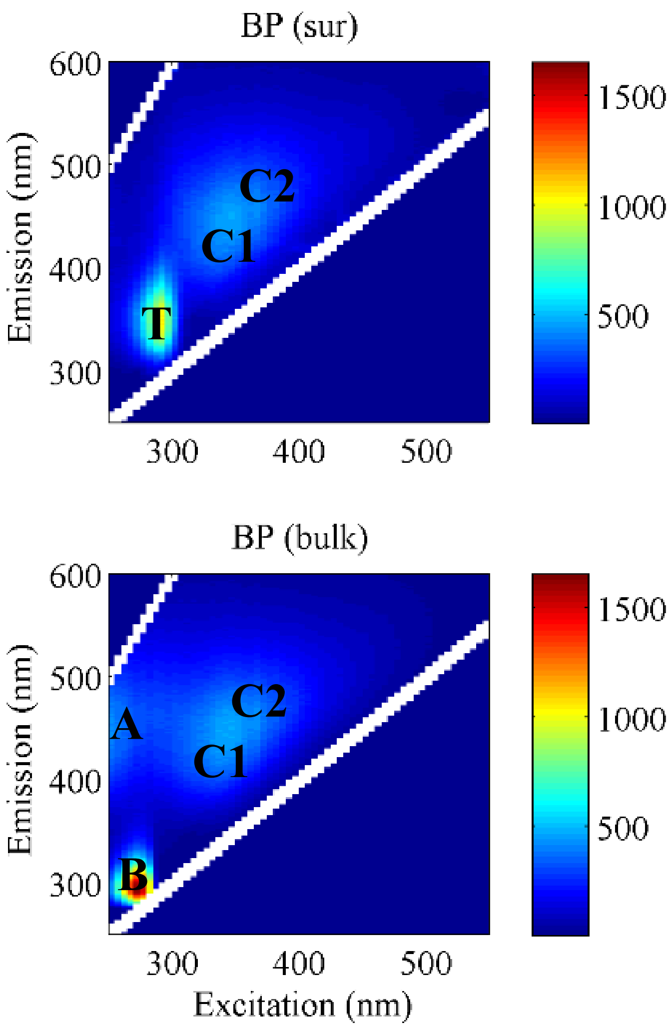

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} anthropogenic inputs

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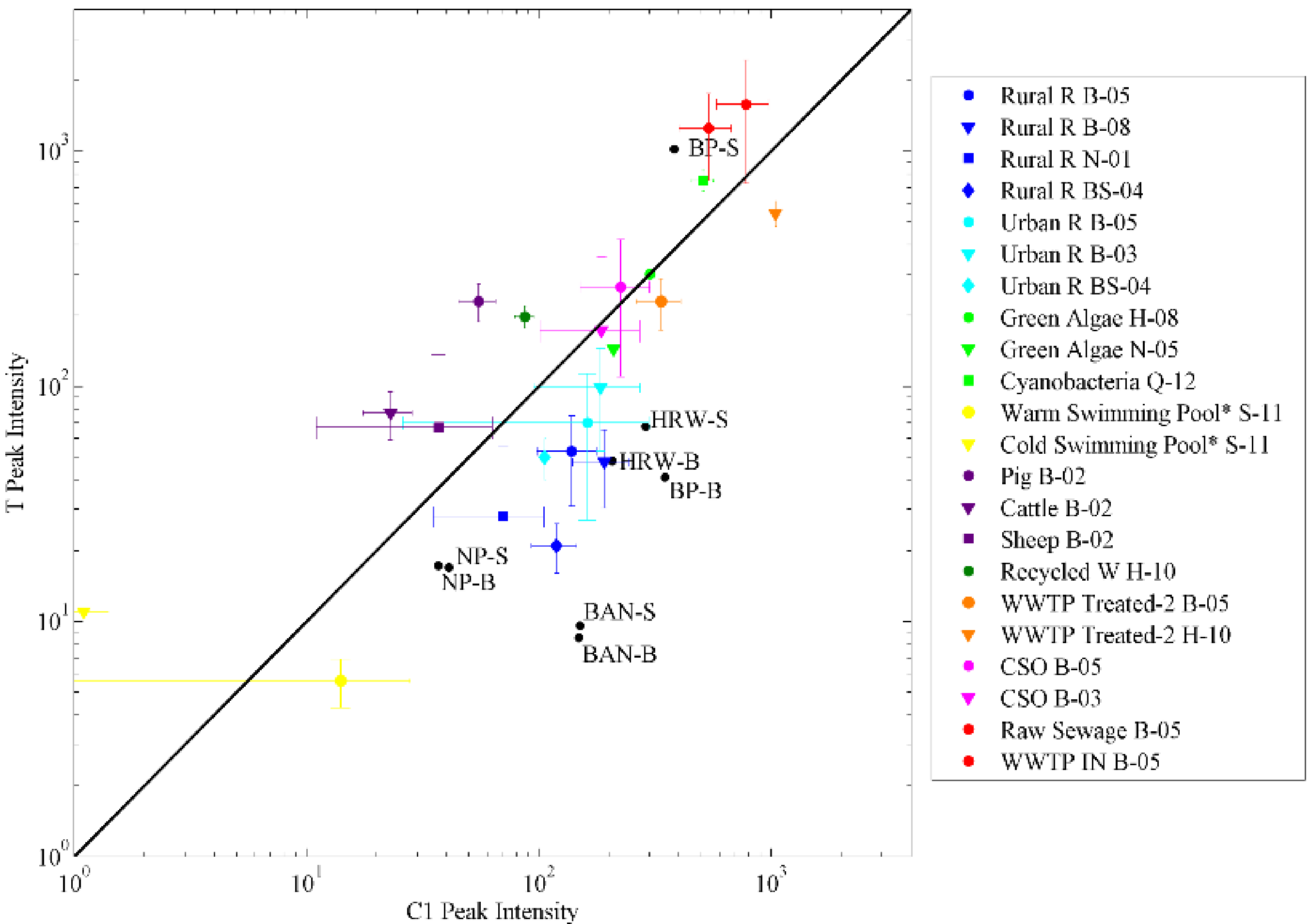
<u>consistent with micropollutant results</u>

Can we detect pollutant partitioning into microlayer vs. bulk waters using fluorescence?

Tracking Anthropogenic Inputs Using Fluorescence



- Microlayer and bulk samples for most sites group together
- HRW looks like urban river water
- BAN is extremely clean
- NP also looks like clean river water
- BP microlayer and bulk waters are different

Major differences in fluorescence between microlayer and bulk waters may be biological rather than anthropogenic → may make tracking anthropogenic signals difficult

Future Work & Conclusions

- Chemical surface microlayers are observed in LID systems in Melbourne, Australia

- These microlayers concentrate pollutants (petroleum hydrocarbons and trihalomethanes)
  → **surface skimmers like rolling-drums might be effective for 1st order pollutant removal (extending the life of the biofilter)**

- Excitation-emission spectroscopy can detect differences between surface and microlayer waters in LID systems
  → **these fluorescent differences may reflect biological processes like algal growth rather than anthropogenic inputs**

- Further work is needed to evaluate the utility of the B (tyrosine-like) peak as a tracer for anthropogenic inputs

- The study could also benefit by being expanded (geographically – US) and/or in terms of the micropollutants assessed (estrogenic compounds, pesticides, etc)

- It would be interesting to evaluate the constituents in microlayer vs bulk waters over a diurnal cycle and/or along a treatment train (sed. basin - wetland – biofilter)

- Mixing effects on microlayer stability & pollutant concentrations should be explored

Spatial and Temporal Variability in Urban Stormwater Pesticide Conc.

Ana Deletic *et al.*
(Monash University)

Wolfgang Gernjak *et al.*
(U of Queensland)

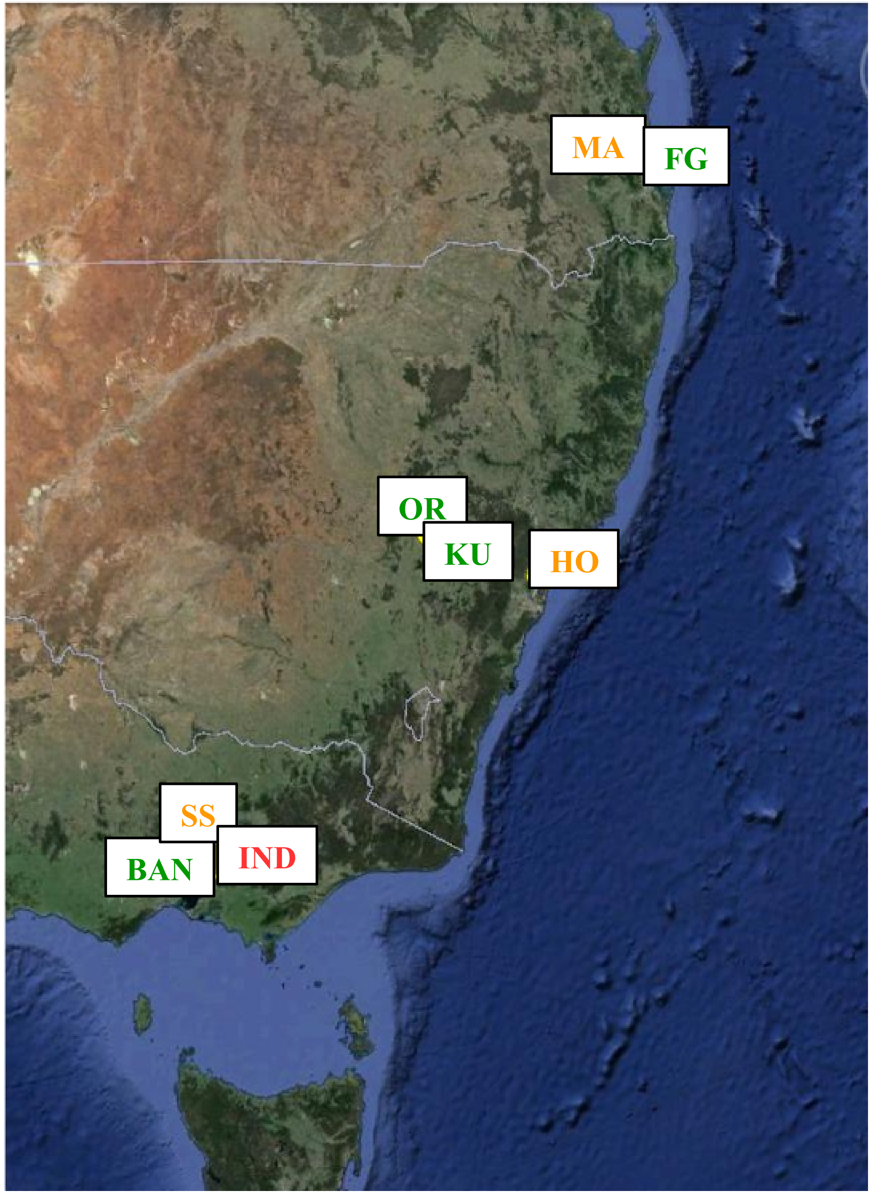
Meg Rippy *et al.* (UCI)

Part of a Large Dataset: many other variables

Multi-year sampling effort (2011 – 2013 … still ongoing)

Wide geographic footprint (8 catchments across 3 Australian states)

Sampling Locations:
Stormwater Pesticide Conc.



8 Sites: sampled 2011-2013

Queensland (QLD):
- **Makerston (MA)**
  commercial: SD near high-rises
- **Fitzgibbon (FG)**
  residential MD: SD receives animal waste

New South Whales (NSW):
- **Orange (OR)**
  residential: stormwater
  (indirect potable reuse)
- **Ku-ring-gai (KU)**
  residential LD: SD near sports oval
- **Hornsby (HO)**
  commercial: shops and restaurants

Victoria (VIC):
- **Industrial site (IND)**
  industrial: petrol depot
- **Smith Street (SS)**
  commercial: shops + industrial history
- **Banyan Creek (BAN)**
  residential: newer (1970's)

Pesticide Variability in Stormwater

Stormwater samples were analyzed for 37 pesticides

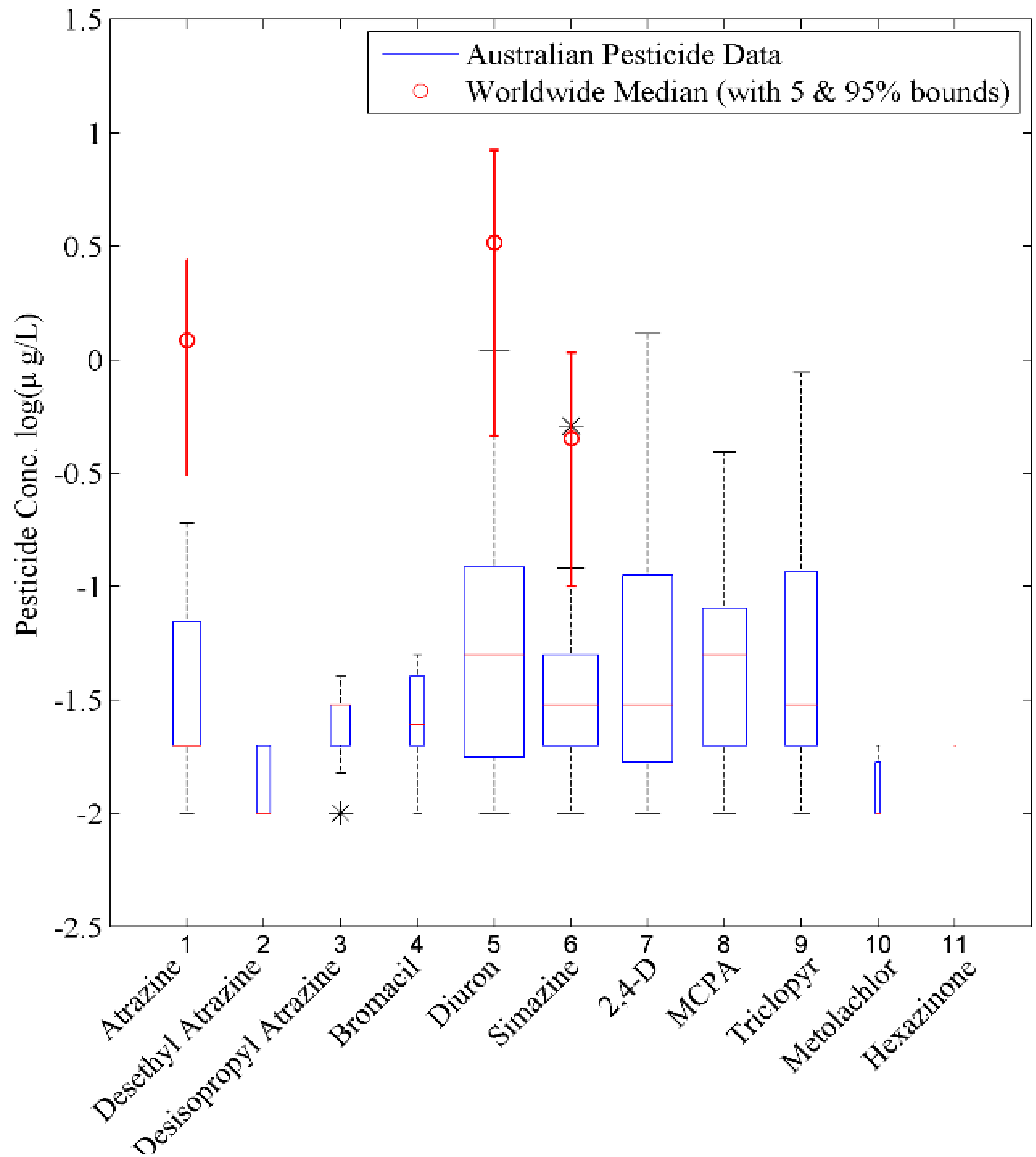
9 were tested for infrequently (not evaluated here)

17 were never detected

Final Dataset: 11 pesticides were measured (and occasionally detected) across all sites

Box widths represent the number of samples with pesticide detects

AU pesticide concentrations are low relative to global averages



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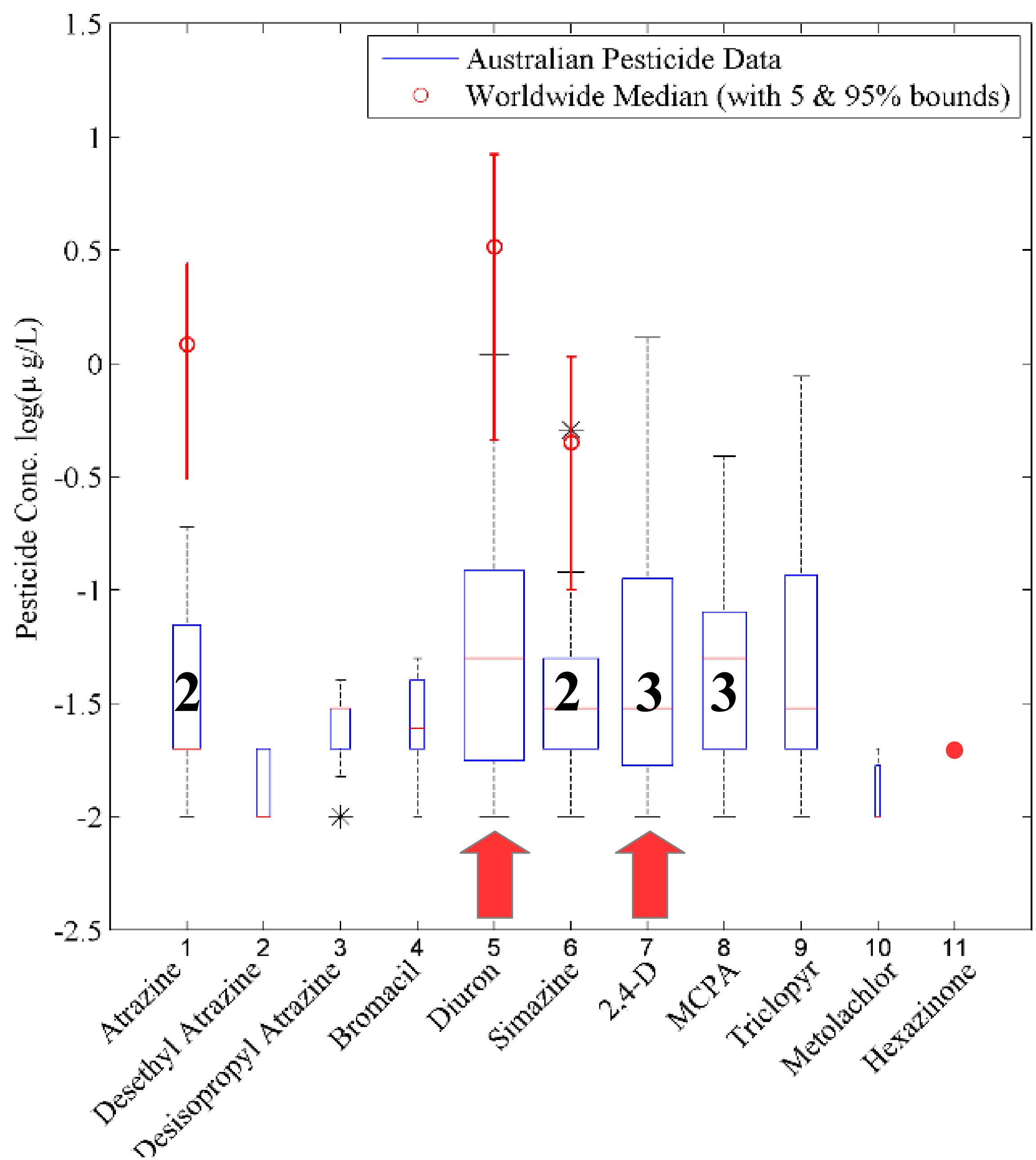

Project Goals

Evaluate the following:

Is variability in pesticide detection and/or conc. in stormwater:

- catchment specific?

    Are specific catchment features (land use, catchment area, total imperviousness, etc.) linked to particular pesticide fingerprints?

- time dependent?

    Do we see shifts in pesticide fingerprints reflecting bans or changes in usage preference?

- related to pesticide chemistry?

    (e.g. K_{ow}, recalcitrance, etc.)

Based on conc. data and reported toxicities for different pesticides can we predict toxicity hotspots? (Compare findings with published toxicity bio-assays?)

Are there proxies for pesticides that are cost effective and can be used for routine monitoring? (fluorescence, TSS, etc)

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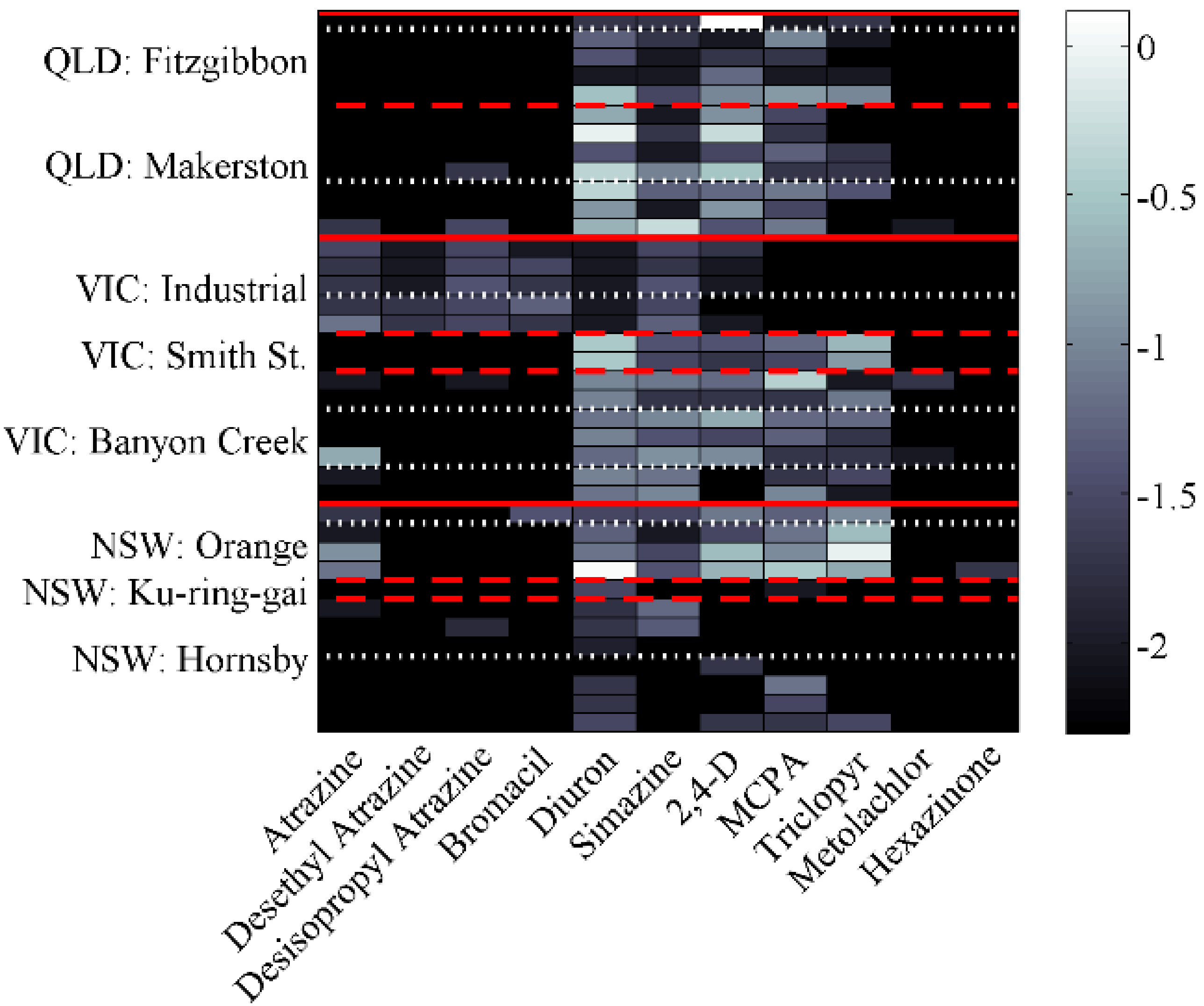
Is Variability Catchment or Time (year) Specific?

Heat Map of Pesticide Conc. (color: log ug/L)
-- Site Location & ... Year



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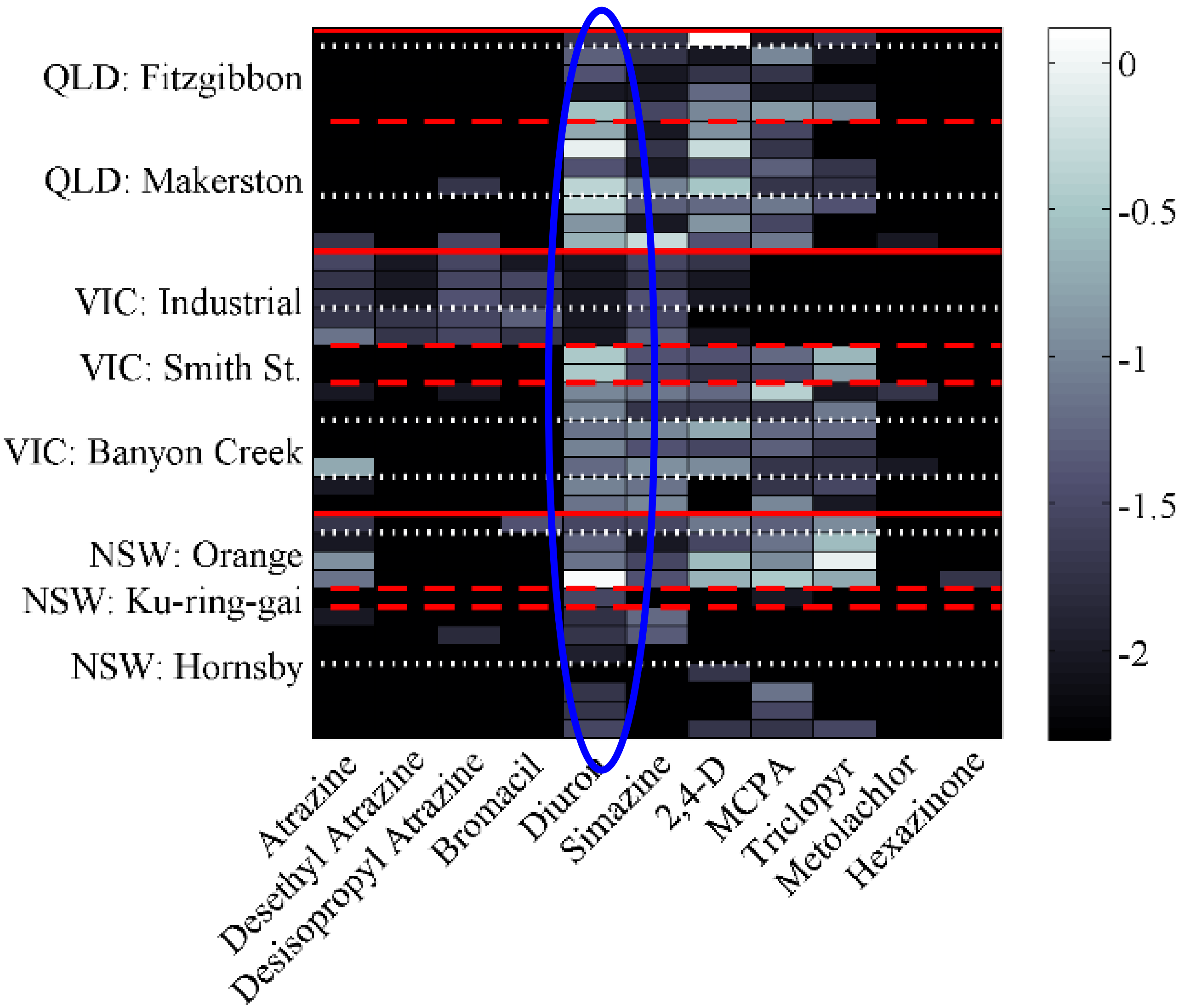

Diuron is present at almost all sites

Used for many applications

Recalcitrant (years - decades)

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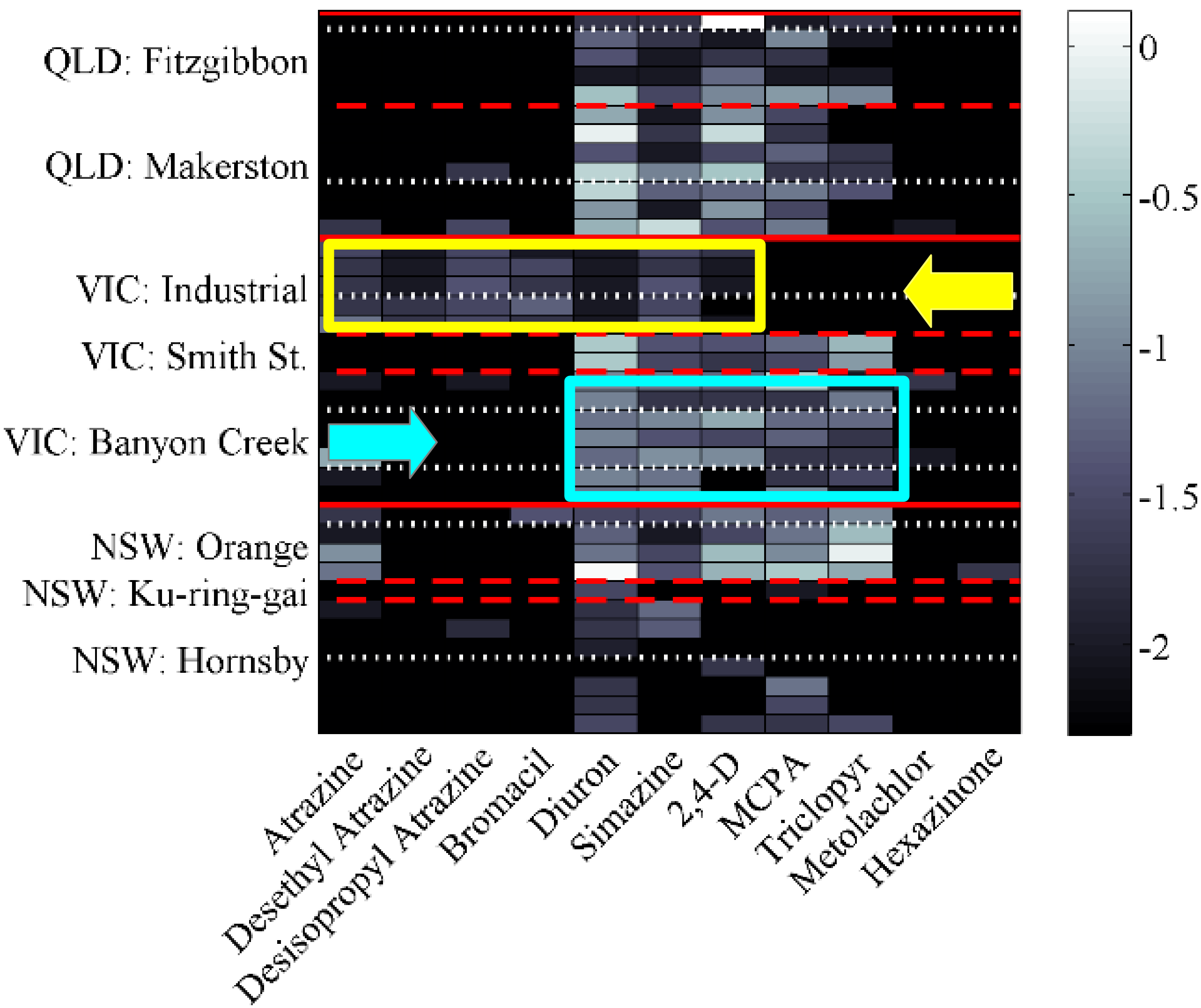

Pesticide fingerprints vary by catchment

IND is triazine rich & MCPA/Triclopyr poor

BAN is Atrazine poor & MCPA/ Triclopyr rich

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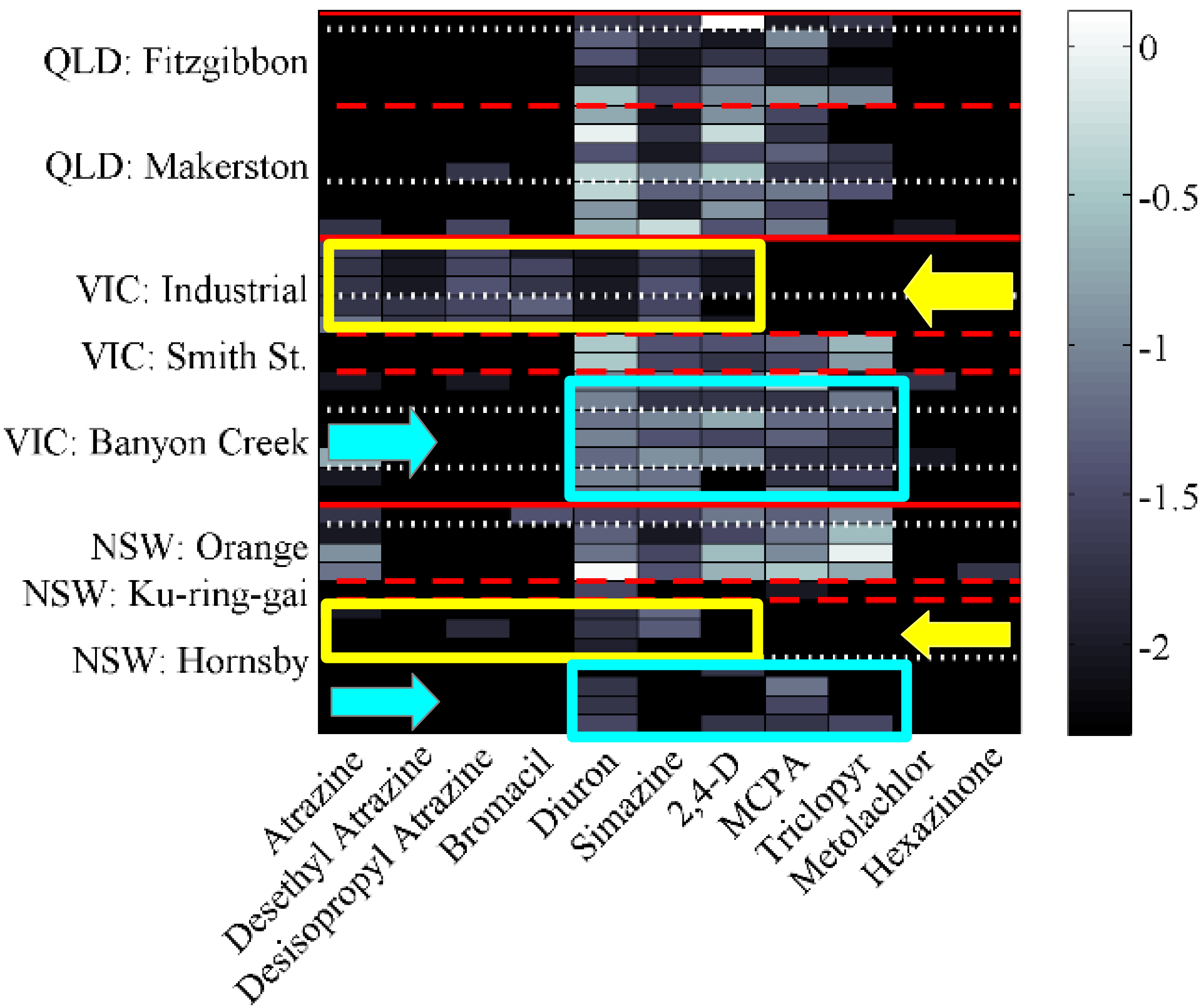

Pesticide fingerprints vary by catchment

- IND is triazine rich & MCPA/Triclopyr poor
- BAN is Atrazine poor & MCPA/ Triclopyr rich

Sometimes they vary by year

- HO (2011) has triazines & is MCPA/Triclopyr poor
- HO (2012) is atrazine poor & has MCPA/ Triclopyr

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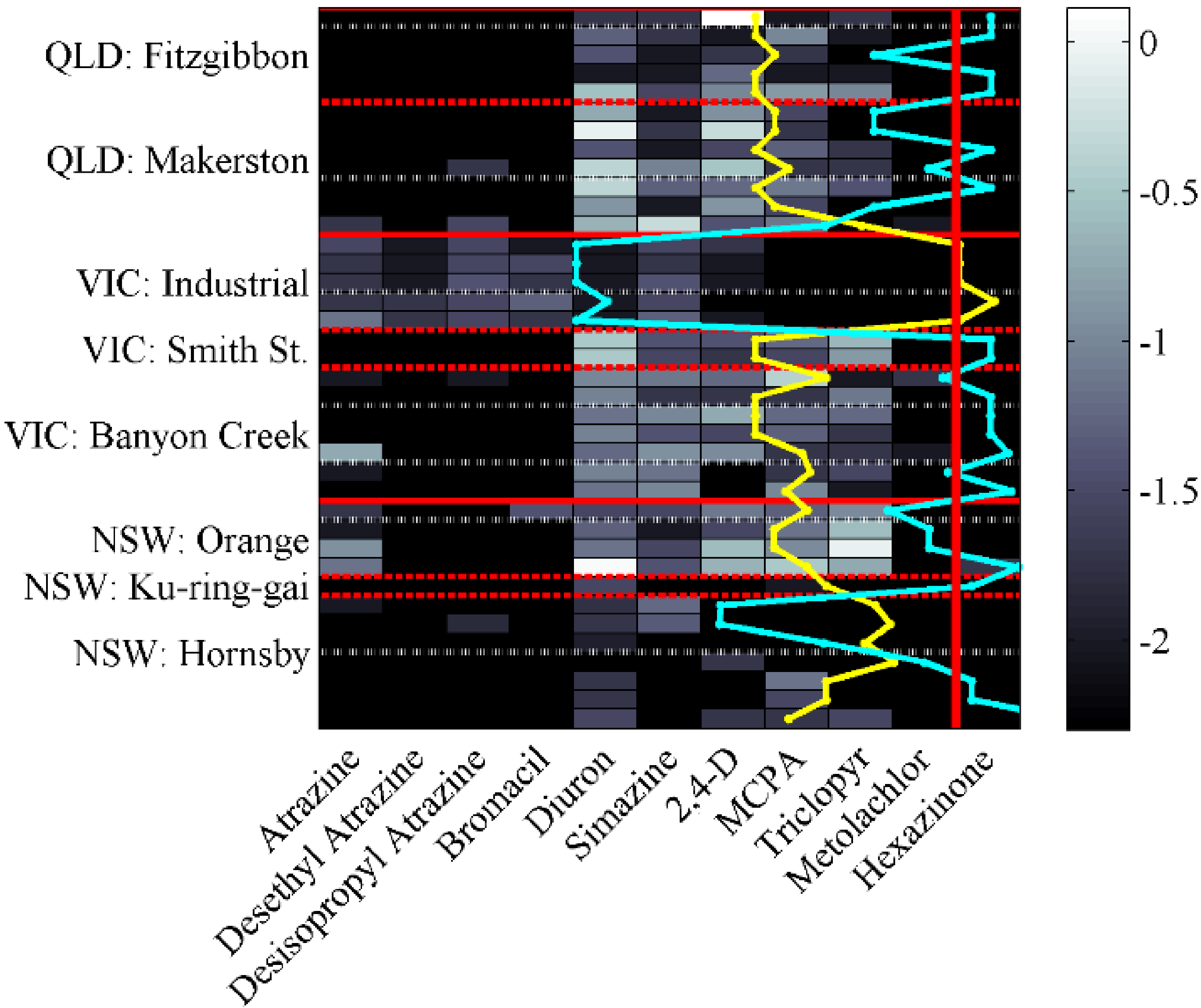

2 EOF modes explain **> 70%** of the variability in pesticide conc. data

M1: ⬇ Atrazines
⬆ MCPA, Tricopyr Diuron, 2-4D, Simazine

Most Sites

M2: ⬆ Triazines
⬇ MCPA, Tricopyr

Sites: IND, HO (2012)

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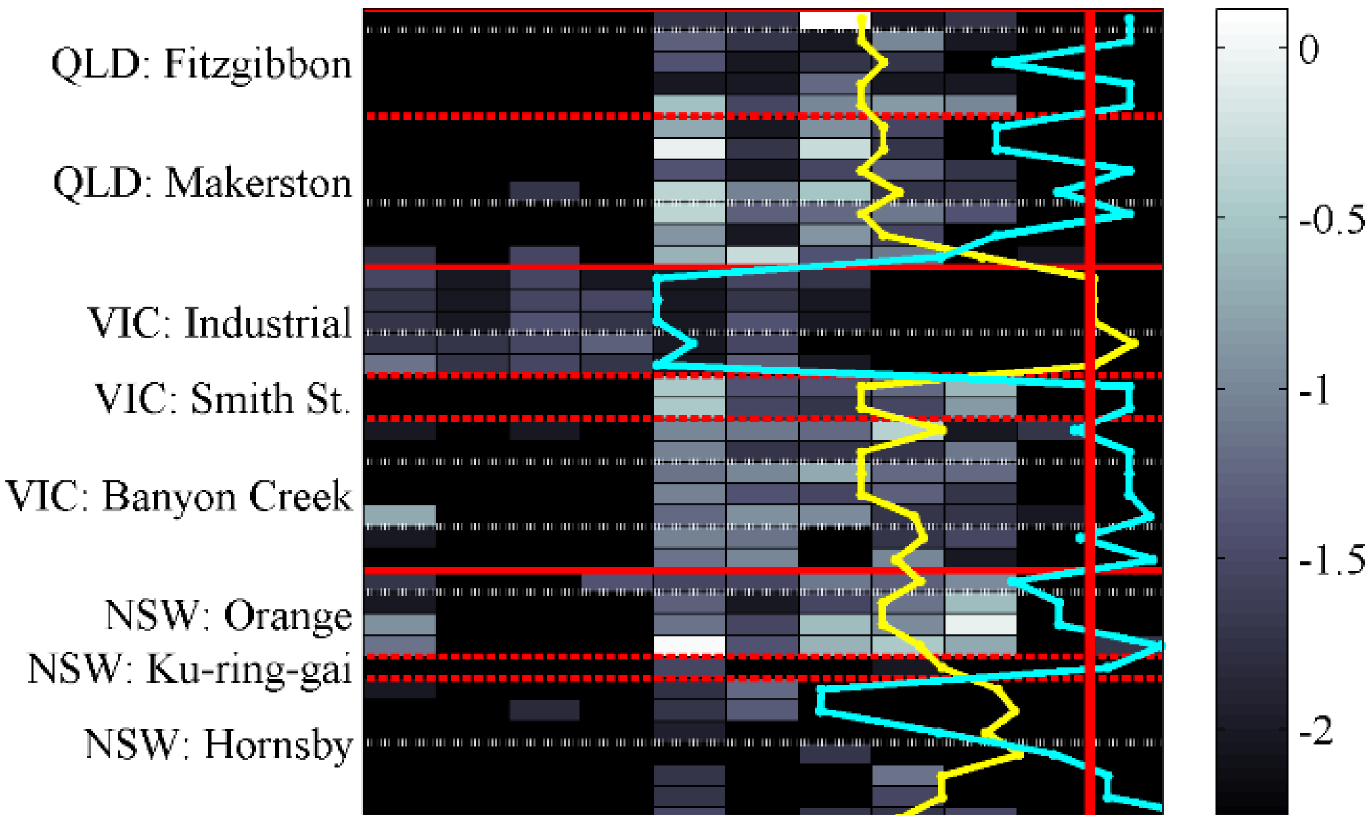

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A significant fraction of pesticide variability is either catchment (M1) or catchment and time (M2) specific

Future Work & Conclusions

- Stormwater pesticide variability is strongly linked to sample catchment and sample year (> 70% variability explained)
  - → There were no significant state specific or month specific patterns

- Catchment characteristics and use patterns should be evaluated to identify possible correlates with observed spatial and temporal patterns (M1 and M2)

- Develop a timeline of local/regional pesticide management decisions (HO)
  - → Did HO management change roadside pesticide use in 2012?
  - → Could this reflect an earlier change that is only manifesting in 2012?
  - → Were there infrastructure changes that could have caused the shift?

- Pesticide heatmaps weighed by toxicity to evaluate potential toxicity hotspots

- Explore possible, cost effective, proxies for detecting pesticides in stormwater across all catchments