Monitoring Strategy, Annual Fluxes and Risk Assessment of Emerging Contaminants in a Catchment Scale

Zulin Zhang

The James Hutton Institute

Chemicals Overview

- Chemicals are an integral part of modern daily life.
- Global production: 1 MT/a to 400 MT/a between 1930 and 2000.
- Over 143,000 chemicals registered in EU REACH of 2011 (>1T, REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals).
- Global chemical output value: US$4.12 trillion in 2010.
- Globally, the growing rate is over 25% between 2012 and 2020 (Table 1).
- Over 70% are organic chemicals.
- Over 50% of total production with environmentally harmful compounds.

Table 1: Chemical Production: Predicted Annual Growth Rates, 2012-2020

	Percent change, 2012-2020	
North America	**25%**	
United States		25%
Canada		27%
Mexico		28%
Latin America	**33%**	
Brazil		35%
Other		31%
Western Europe	**24%**	
Emerging Europe	**35%**	
Russia		34%
Other		36%
Africa & Middle East	**40%**	
Asia-Pacific	**46%**	
Japan		22%
China		66%
India		59%
Australia		23%
Korea		35%
Singapore		35%
Taiwan		39%
Other		44%

Source: Percentages calculated based on projections in Thomas Kevin Swift et al., "Mid-Year 2011 Situation & Outlook." American Chemistry Council, June 2011.

Emerging Contaminants (ECs)

The James Hutton Institute

New and more sensitive analytical and biological methods

Def: Newly developed/identified or discovered pollutants

Little or no investigated

Scarcity or lack of environmental data and analytical methods

Not regulated

(Gavrilescu et al., 2015; Petrovic and Barceló, 2006; Richardson and Ternes, 2011)

Emerging Contaminants: POPs and EDCs

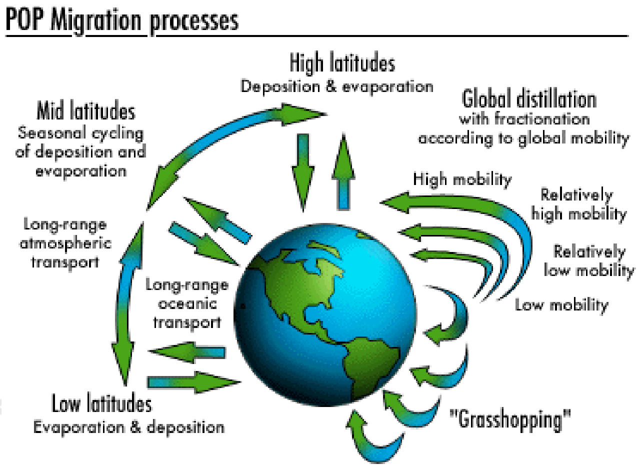
Persistent Organic Pollutants (POPs):

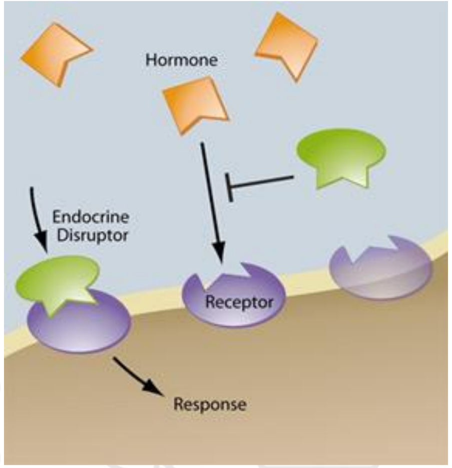
- Persist in the environment.
- Long-range transport.
- Bio-accumulate through the food web.
- Pose a risk of causing adverse effects to human health and the environment.

2001, UNEP: 《Stockholm Convention on POPs》
2017: 181 parties (180 states + EU) to the Convention

Endocrine disrupting chemicals (EDCs):

- Substances may interfere with normal function of the endocrine (hormone) system of humans and animals.

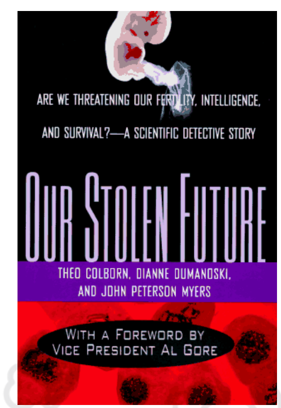




(Erbach , 2013; Greenpeace , 1999)

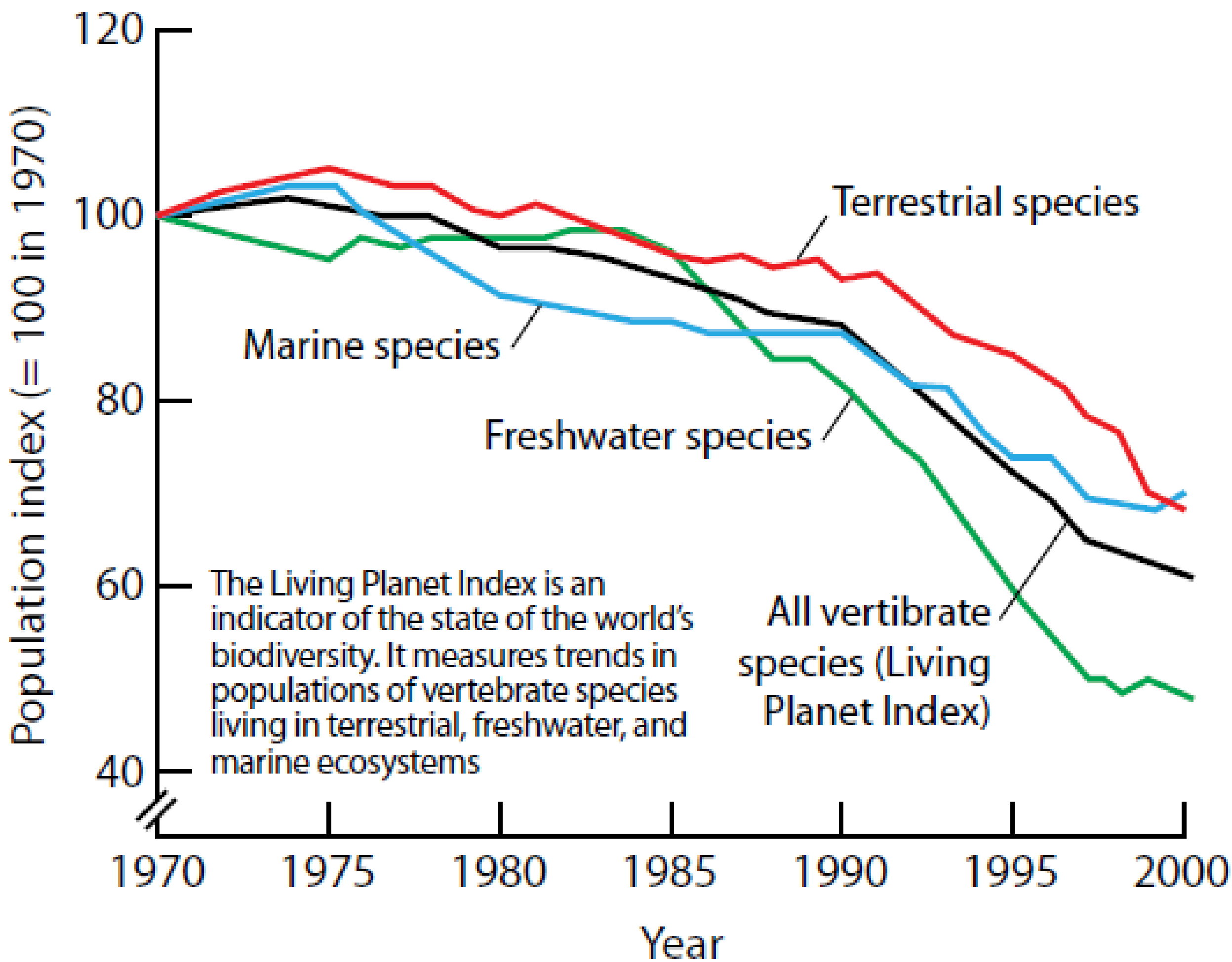
Adverse Effects on Animal and Human

- Eggshell thinning in birds of prey
- Reduction in frog population
- Adverse effects on fish reproduction and development
- Development of male sex organs in female marine animals such as whelks and snails
- Declines in the numbers of males born
- Reductions in male fertility
- Female reproductive diseases
- Earlier puberty
- ……



Population declines in wildlife (>50%) over 30 years, 1970-2000
One of important reasons: Chemical Pollution?

The James Hutton Institute



(WHO, 2012)

Our Work on Emerging Contaminants

- Monitoring Strategy of Emerging Organic Contaminants
- Fluxes and Risk Assessment of EOCs in the Catchment
- Isotope Techniques Applied for Organic Pollutant Study
- Geochemical behavior and Fate of Organic Contaminant
- Long Term Changes of EOCs in the Sludge Treated Soils
- Sustainable Removal of Organic Pollutants from Water

Target Emerging Contaminants in this Work

- Pharmaceutical and Personal Care Products (PPCPs):

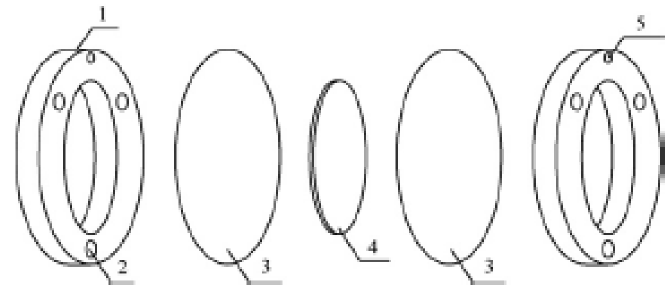
  Diclofenac (NSAID), **Paracetamol** (Analgesics), **Carbamazepine** (Antiepileptic), **Ibuprofen** (NSAID), **Trimethoprim** (Antibiotics), Triclosan (Antibacterial)

  (**Most frequently detected > 15countries**).

- Steroid Hormones: **E1** (estrone), **E2** (17β-estradiol), **E3**(estriol), **EE2** (17α-ethinylestradiol) and BPA. (Watch list, EU2015)

- Pesticides: Metaldehyde, Isoproturon, Simazine, Chlorotoluron, Atrazine, Epoxiconazole, Chlorpyrifos, Cypermethrin and Permethrin (Priority Substances, EU 2013).

in situ Monitoring Technique for Emerging Contaminants



The schematic diagram of the POCIS device (1) PTEE holder, (2) screw, (3) membrane, (4) sorbent and (5) hole.

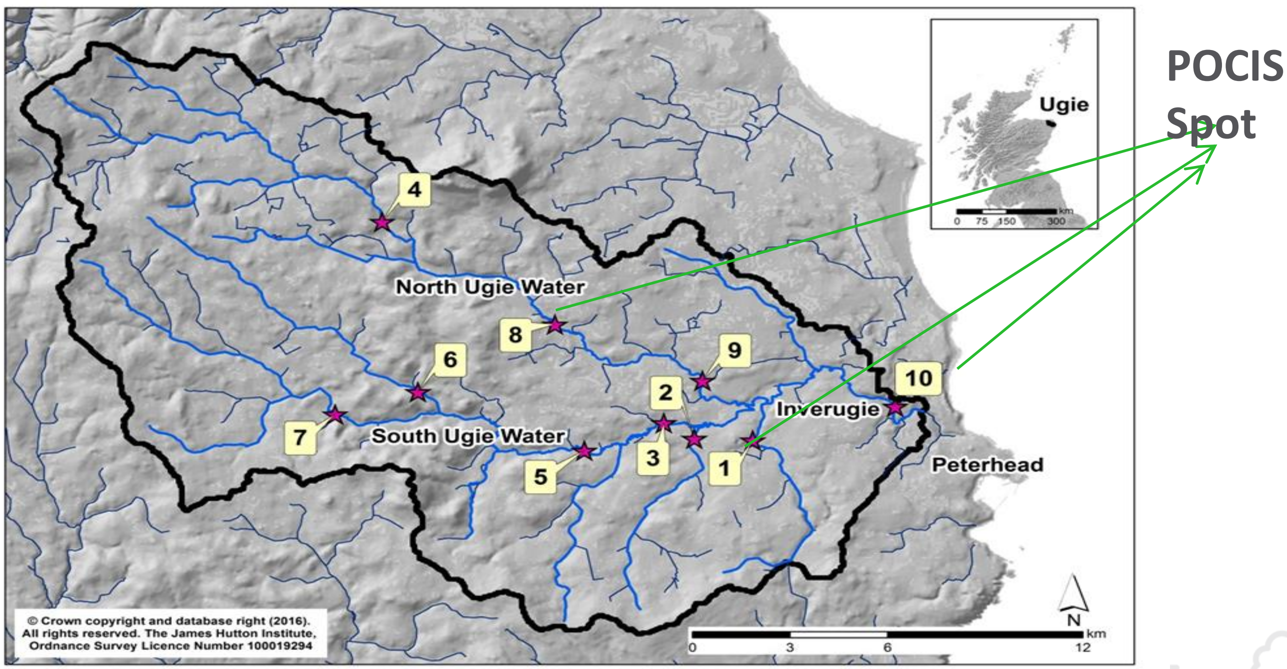
Spot sampling
Instantaneous measurement

Passive sampling
Time-weighted Measurement

Zhang et al., (2016) Sci Total Environ
Zhang et al., (2018) Environ Geochem Health

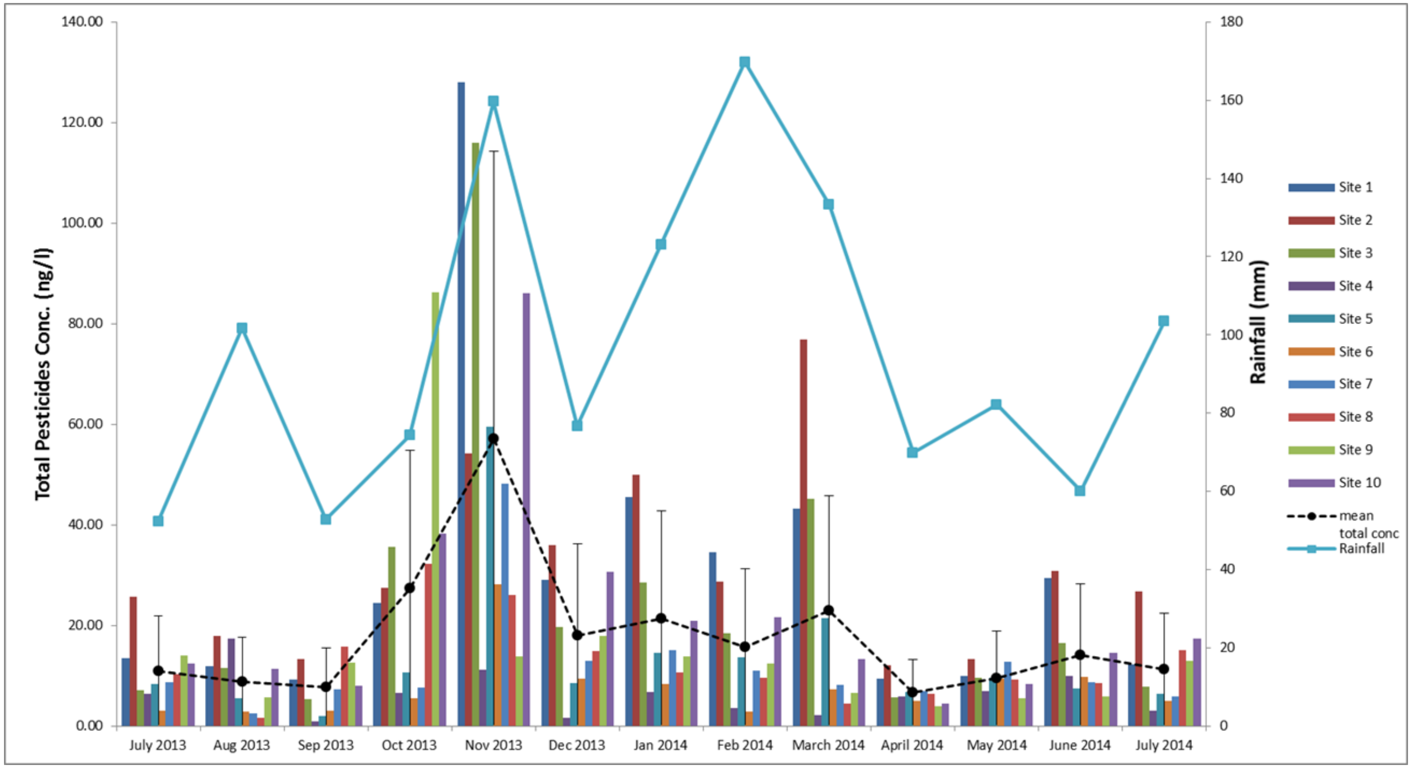
Monthly Monitoring in a priority catchment (SEPA) - River Ugie, Scotland (12 months)

- Ugie catchment:
  - Used by SW as drinking water source for Peterhead, Aberdeen
  - Organic Contaminants in the river have exceed drinking water standards (e.g. pesticides, individual: 0.1 μg/l ; total 0.5 μg/l)
  - SEPA priority catchment of WFD 'good ecological status', 335 km^2.



Zhang et al., (2016) Sci Total Environ

Temporal Changes of pesticides in the River Ugie, Scotland

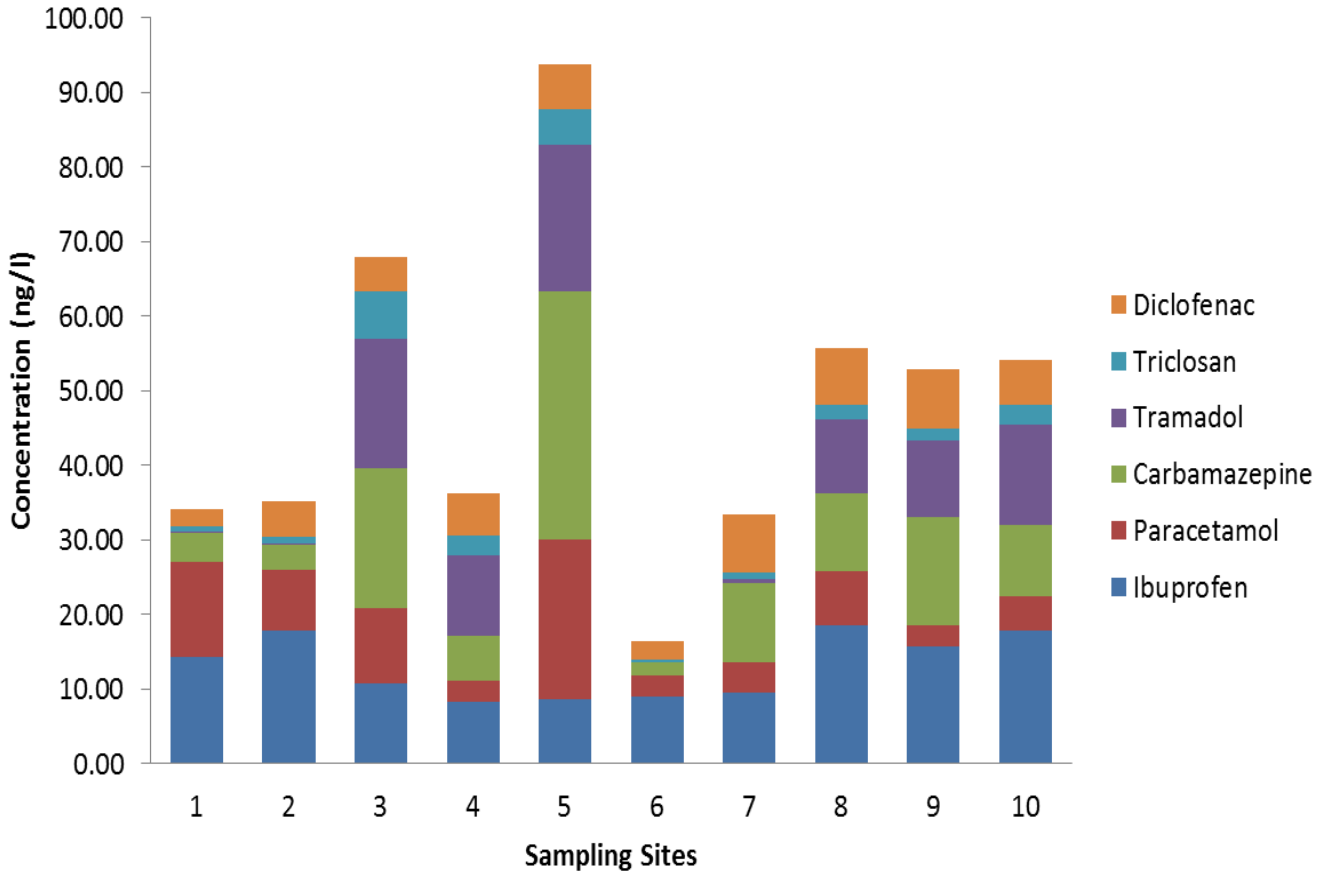


Agreement with pesticides usage data - good volume in the Autumn.

Surface runoff contribution (Rainfall) to the pesticides pollution.

Zhang et al., (2016) Sci Total Environ

Spatial Changes of PPCPs in Ugie, Scotland



Site 5: Close to WWTP and largest village of the catchment; Site 3: located just downstream of Site 5.

Zhang et al., (2018) Environ Geochem Health

PPCPs and EDCs level in the River Ugie, Scotland

Compound	LOD ng/l	Compound Class	Water (ng/l)			
			Range	Mean	DF (%)	Literature values
E1	0.15	Natural hormone	<0.15–19.51	1.65	90	<0.4–33 (Europe, Pal et al. 2010)
E2	0.10	Natural hormone	<0.10–3.74	0.17	45	<0.1–3.6 (Europe, Pal et al. 2010)
E3	0.17	Natural hormone	<0.17–8.08	0.42	47	<LOD–3.1 (Denmark, Bachmann-Christiansen et al. 2002)
BPA	0.03	Chemical additive	<0.03–53.08	2.71	48	0–21.9 (USA, Padhye et al. 2014)
Diclofenac	0.17	NSAID	<0.17–33.87	5.53	88	2.5–35 (Germany, Mompelat et al. 2009)
Ibuprofen	0.18	NSAID	<0.18–91.46	13.06	75	14–44 (Europe, Pal et al. 2010)
Paracetamol	0.28	Analgesic	<0.28–119.4	7.66	76	<0.5–71 (France, Vulliet et al. 2011)
Tramadol	0.35	Analgesic	<0.35–54.05	8.25	73	7–51 (The Netherlands, de Jongh et al. 2011)
Carbamazepine	0.12	Antiepileptic	<0.12–192.7	11.23	40	9–157 (Europe, Pal et al. 2010)
Triclosan	0.10	Antiseptic	<0.10–25.35	2.27	80	<0.5–74 (Switzerland, Singer et al. 2002)

<LOD to 193 ng/l, comparable level to the other countries in EU.

Zhang et al., (2018) Environ Geochem Health

Measured Concentration Compared between Spot Sampling (SS) and Passive Sampling (PS)

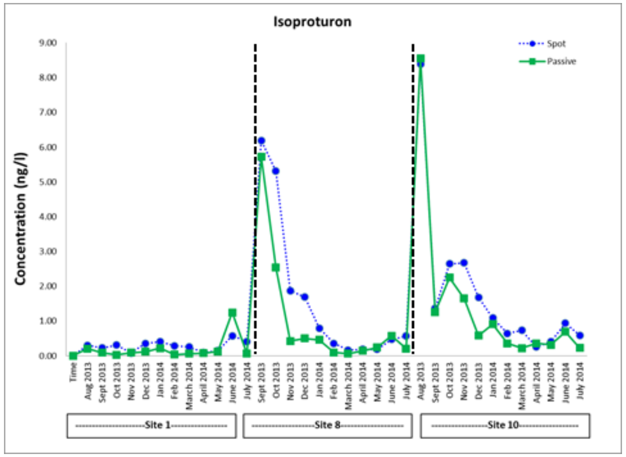


Fig.1 In a Good Agreement

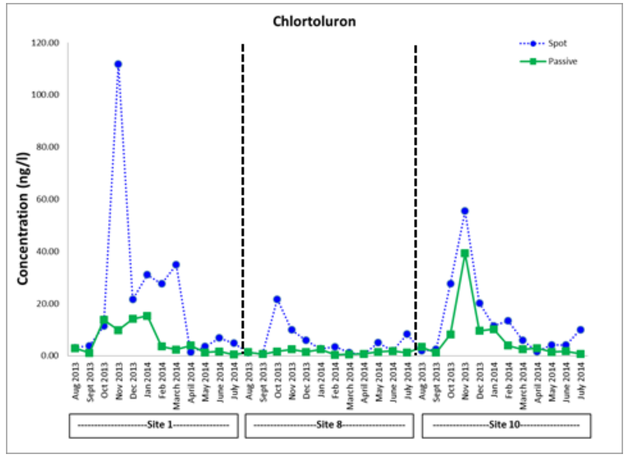


Fig.2 Peak Conc. Integrated

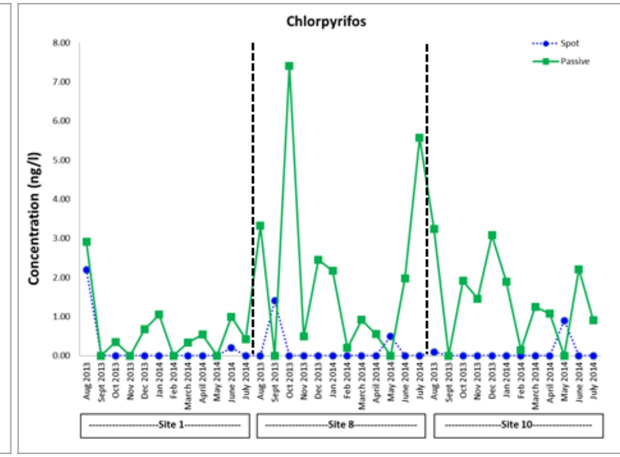


Fig.3 Quant. At Lower LOD

Fig.1 In general, SS are slightly higher/close to PS, and are in good agreement.

Fig.2 Spiked concentrations (e.g. after flood event) integrated over sampling time.

Fig.3 *in situ* accumulation allows quantification at lower LOD.

Zhang et al., (2016) Sci Total Environ

Flux calculation: different sampling strategies

$$F_{w,i} = K \times C_{w,i} \times Q_{m,i} \times t_i$$

$$F_{POCIS,i} = K \times C_{TWA,i} \times Q_{m,i} \times t_i$$

K – conversion factors for unifying the units

$C_{TWA,i}$ – TWAC measured with the POCIS sampling (ng/l)

$Q_{m,i}$ – average water flow (l/d)

t_i – time exposure (days)

Annual flux – summing the flux of the successive periods

Richard et al, 1999; Poulier et al., 2015; Zhang et al., 2016

Pesticides Monthly and Annual fluxes estimated by SS and PS in the River Ugie, Scotland

Monthly	Ave. flow	Isoproturon		Simazine		Chlortoluron		Atrazine		Epoxiconazole		Chlorpyrifos		∑ 6pesticides	
	m^3/s	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive
08/2013	1.49	33.55	34.17	2.17	2.33	7.60	13.34	0.00	10.16	1.48	12.59	0.40	12.97	45	86
09/2013	1.35	4.77	4.39	ND	ND	8.57	4.07	2.81	2.95	0.82	0.84	ND	ND	17	12
10/2013	2.66	18.83	16.01	ND	5.87	197.0	58.43	19.37	14.42	5.57	8.54	ND	13.61	241	117
11/2013	5.52	38.20	23.59	22.98	18.42	794.2	561.6	14.85	22.29	24.36	14.90	ND	20.90	895	662
12/2013	4.35	19.60	6.80	11.64	3.60	236.0	111.0	19.47	6.82	ND	5.52	ND	35.92	287	170
01/2014	10.10	29.34	24.52	23.43	8.99	309.9	277.2	28.14	14.02	ND	43.11	ND	51.35	391	419
02/2014	11.73	18.30	10.18	29.01	10.18	381.0	110.9	32.95	10.11	50.43	26.06	ND	4.15	512	172
03/2014	5.16	10.09	3.01	14.07	5.09	83.06	33.99	20.42	7.17	20.92	9.53	ND	17.29	149	76
04/2014	2.83	1.87	2.62	4.34	1.93	11.50	21.66	9.33	9.77	5.90	4.28	ND	7.86	33	48
05/2014	2.43	2.63	2.03	4.65	1.98	27.45	9.49	13.67	5.88	ND	2.76	5.88	ND	54	22
06/2014	2.24	5.43	4.01	4.33	0.92	23.98	10.12	12.69	5.02	6.77	5.78	ND	12.85	53	39
07/2014	1.50	2.37	0.91	2.50	1.32	40.47	2.97	8.08	3.11	5.64	3.51	ND	3.67	59	15
Yearly		**185**	**132**	**119**	**61**	**2121**	**1215**	**182**	**112**	**122**	**137**	**6**	**181**	**2735**	**1837**

Fluxes estimated by SS are close/slightly higher than by PS, the exception is Chlorpyrifos, due to concentration below LOD or pollutants missed for SS while being captured by PS.

Zhang et al., (2016) Sci Total Environ

EDCs and PPCPs Monthly and Annual fluxes estimated by SS and PS in the River Ugie, Scotland

Monthly	Ave. flow	E1		E2		E3		BPA		∑ 4EDCs	
	m^3/s	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive
07/2013	1.49	9.13	2.10	ND	0.15	1.06	0.69	ND	2.66	10.18	5.61
08/2013	1.35	8.94	1.00	ND	0.79	1.48	1.76	5.41	0.98	15.83	4.52
09/2013	2.66	14.60	23.48	ND	ND	1.48	1.42	10.02	2.76	26.10	27.66
10/2013	5.52	39.17	52.51	5.54	ND	21.87	11.49	8.56	6.40	75.1	70.4
11/2013	4.35	74.94	22.87	ND	ND	6.51	11.64	ND	3.87	81.5	38.4
12/2013	10.10	102.7	65.27	ND	ND	ND	6.34	ND	14.54	102.7	86.1
01/2014	11.73	26.90	5.02	16.77	3.32	ND	0.40	ND	16.50	43.68	25.24
02/2014	5.16	7.24	5.83	12.72	0.29	2.87	1.29	ND	ND	22.83	7.41
03/2014	2.83	3.08	4.18	ND	0.21	ND	ND	ND	ND	3.08	4.38
04/2014	2.43	6.36	ND	1.65	0.09	ND	ND	4.57	6.39	12.59	6.48
05/2014	2.24	5.57	4.76	1.48	0.75	ND	ND	1.92	5.38	8.96	10.89
06/2014	1.50	6.04	2.26	ND	0.11	ND	1.65	ND	2.56	6.04	6.59
Yearly		305	189	38	6	35	37	30	62	409	294

Monthly	Ave. flow	Ibuprofen		Paracetamol		Carbamazepine		Tramadol		Triclosan		Diclofenac		∑ 6PPCPs	
	m^3/s	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive	Spot	Passive
07/2013	1.49	365.7	16.48	8.88	8.10	226.2	33.31	97.77	21.23	13.25	6.95	17.80	2.97	729.6	89.0
08/2013	1.35	ND	1.09	1.34	5.35	ND	23.35	59.07	50.20	3.35	40.15	40.91	10.05	104.7	130.2
09/2013	2.66	3.56	34.10	14.54	16.45	240.6	93.04	207.7	81.36	28.55	36.41	26.30	20.16	521.2	281.5
10/2013	5.52	50.61	66.46	150.2	203.9	ND	319.1	136.3	132.5	62.75	68.68	62.04	7.09	461.9	797.8
11/2013	4.35	257.1	11.47	110.5	ND	4.29	3.41	219.7	7.39	43.85	1.01	9.61	11.03	645.1	34.3
12/2013	10.10	17.24	26.61	16.42	475.3	ND	ND	34.04	8.93	28.51	1.93	41.78	61.01	138.0	573.8
01/2014	11.73	ND	148.2	36.33	703.3	ND	53.50	19.56	48.86	31.64	0.78	156.9	83.38	244.4	1038
02/2014	5.16	70.53	57.79	287.1	736.7	20.22	142.6	63.49	13.65	29.38	2.38	56.95	7.69	527.6	960.8
03/2014	2.83	14.05	21.08	49.17	64.55	ND	40.56	61.86	8.77	12.10	0.31	24.07	7.84	161.3	143.1
04/2014	2.43	83.84	28.32	ND	64.22	51.12	ND	67.08	13.78	19.67	0.24	81.76	11.82	303.5	118.4
05/2014	2.24	328.5	206.0	ND	21.49	55.76	39.90	107.5	9.54	36.82	0.16	30.75	21.92	559.4	299.0
06/2014	1.50	79.74	22.10	2.43	10.69	23.10	36.91	74.25	21.80	ND	34.33	59.48	13.91	239.0	139.8
Yearly		1271	623	677	2302	621	752	1148	397	310	186	608	256	4636	4517

Zhang et al., (2018) Environ Geochem Health

Rough Estimating Example: Global Pesticides Fluxes (F_G)

The James Hutton Institute

$$F_G = F_U / Q_U \times Q_G$$

- Q_U : 0.134 km^3 Water Volume to Ugie Estuary and North Sea

- Q_G: 40k km^3 from the global rivers to the ocean

- F_U: 2735g pesticides (6) flux to Ugie Estuary and North Sea

F_G: 520 Tons?

Based on: (1) 6 pesticides only; (2) one small Scottish catchment;

(3)Total Prod. 2.4 MT, 0.02% leaching, how about all chemicals, >>?

Ecological Risk Assessment

$$RQ = \frac{MEC}{PNEC}$$

RQ – risk quotient

MEC – measured environmental concentration

PNEC – predicted no-effect concentration

Risk – $RQ<0.01$: minimal risk; $0.01\leq RQ<0.1$: low risk; $0.1\leq RQ<1$: medium risk; $RQ\geq1$: high risk

Assessment factors (AF) used to derive PNEC data

Available data	Assessment factor
At least one short-term assay L(E)C50 at one trophic level (algae, aquatic invertebrates and fish)	1000
One long-term assay(NOEC) with either aquatic invertebrates or fish	100
Two long-term assays(NOEC) at two trophic levels (algae and/or aquatic invertebrates and/or fish)	50
Three long-term assays at three trophic levels (algae, aquatic invertebrates and fish)	10

$$PNEC = \frac{NOEC}{AF}$$

NOEC – No observed effect concentration

Van Leeuwen et al, 2003; Paulier et al., 2015

Environmental risk of pesticides, EDCs and PPCPs detected in the River Ugie, Scotland

Compound	NOEC µg/l			Critical conc.	AF	PENC	Minimal risk	Low risk	Medium risk	High risk
	Fish	Aquatic invertebrates	Algae	µg/l		µg/l	≤0.01 (%)	0.01–0.1 (%)	0.1–1 (%)	≥1 (%)
Metaldehyde	37,500	90,000	–	37,500	50	750	100	–	–	–
Isoproturon	1000	120	52	52	10	5.2	100	–	–	–
Simazine	700	2500	600	600	10	60	100	–	–	–
Chlorotoluron	400	16,700	1	1.0	10	0.1	16.1	60.8	22.3	0.8
Atrazine	2000	250	100	100	10	10	100	–	–	–
Epoxiconazole	10	630	7.8	7.8	10	0.78	98.5	1.5		
Chlorpyrifos	0.14	4.6	43	0.14	10	0.014	76.9	7.7	13.9	1.5
Cypermethrin	0.03	0.04	1300	0.03	10	0.003	96.1	–	3.1	0.8
Permethrin	0.12	–	0.9	0.12	50	0.0024	97.7	0.8	1.5	–

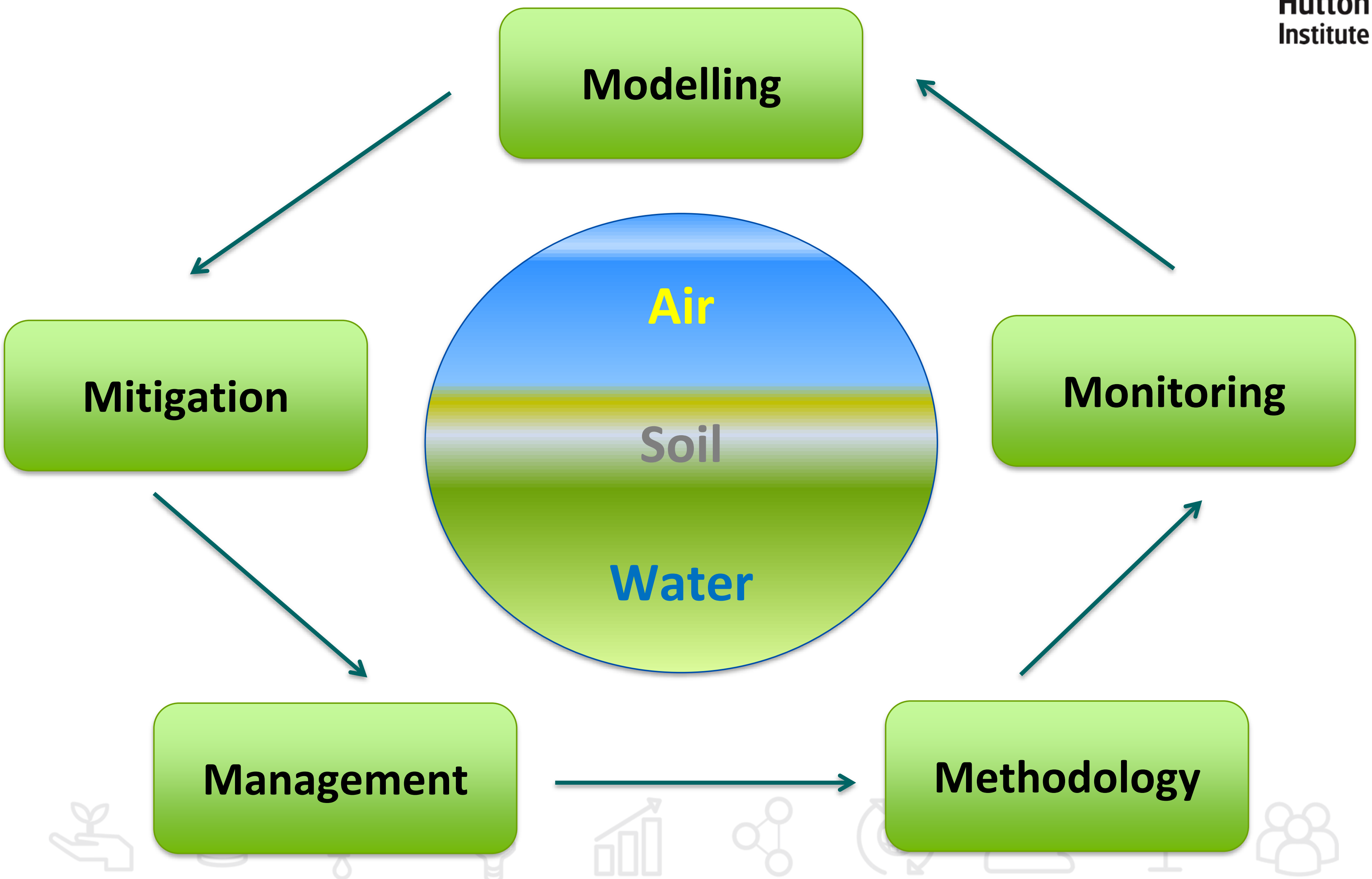
Compound	PENC	minimal risk	low risk	medium risk	high risk
	ng/l	≤0.01 (%)	0.01 - 0.1(%)	0.1-1(%)	≥1(%)
E1	6.0	10.0	19.2	67.7	3.1
E2	2.0	55.4	17.7	26.2	0.8
E3	60	81.5	17.7	0.8	0
BPA	3.1	51.6	3.8	23.1	21.5
Ibuprofen	5000	89.8	10.2	0	0
Paracetamol	9200	99.2	0.8	0	0
Carbamazepine	6400	95.3	4.7	0	0
Tramadol	57000	100	0	0	0
Triclosan	50	28.3	63.8	7.9	0
Diclofenac	300	98.4	1.6	0	0

Zhang et al., (2016) Sci Total Environ
Zhang et al., (2018) Environ Geochem Health

Conclusion

- Human activities (e.g. medication and farm usage) are mainly responsible for these contaminants.
- *in situ* accumulation in PS allows quantification at lower LOD and integrating spiked conc. over sampling time, which is a complementary strategy to SS (e.g. fluxes and risk estimation).
- Annual fluxes to Ugie catchment were estimated (e.g. PPCPs 4.6 kg, pes: 2.7kg), however, when looking into the global input to the aquatic environment, seems enormous?
- Risk assessment suggested medium/high risk of 6 considered target contaminants (Chlortoluron, chlorpyrifos, cypermethrin, E1, E2 and BPA) in this studied catchment.
- However in real environment, there are over T/M chemicals, what is the consequence of these mixtures combined?

‘5M’ Study of Environmental Pollutants



Acknowledgements

Mark Osprey

Christine Kerr

Melanie Lebleu

Estelle Courtot

Yuan Li

Thibault Lefebvre

Nikki Baggaley

Kyari Yates

Scottish Government's Rural and Environment Science and Analytical Services (RESAS) Division

Thank You!