PRESÈNCIA I COMPORTAMENT DELS CONTAMINANTS ORGÀNICS EMERGENTS (COEs) ALS AQÜÍFERS DE BARCELONA

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EMERGING ORGANIC CONTAMINANTS

What are EOCs??

New and more sensitive analytical methods

EOCs are compounds previously unknown or unrecognized contaminants

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New and more sensitive analytical methods

EOCs are compounds previously unknown or unrecognized contaminants
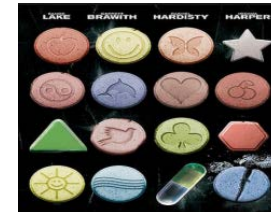
Pharmaceuticals
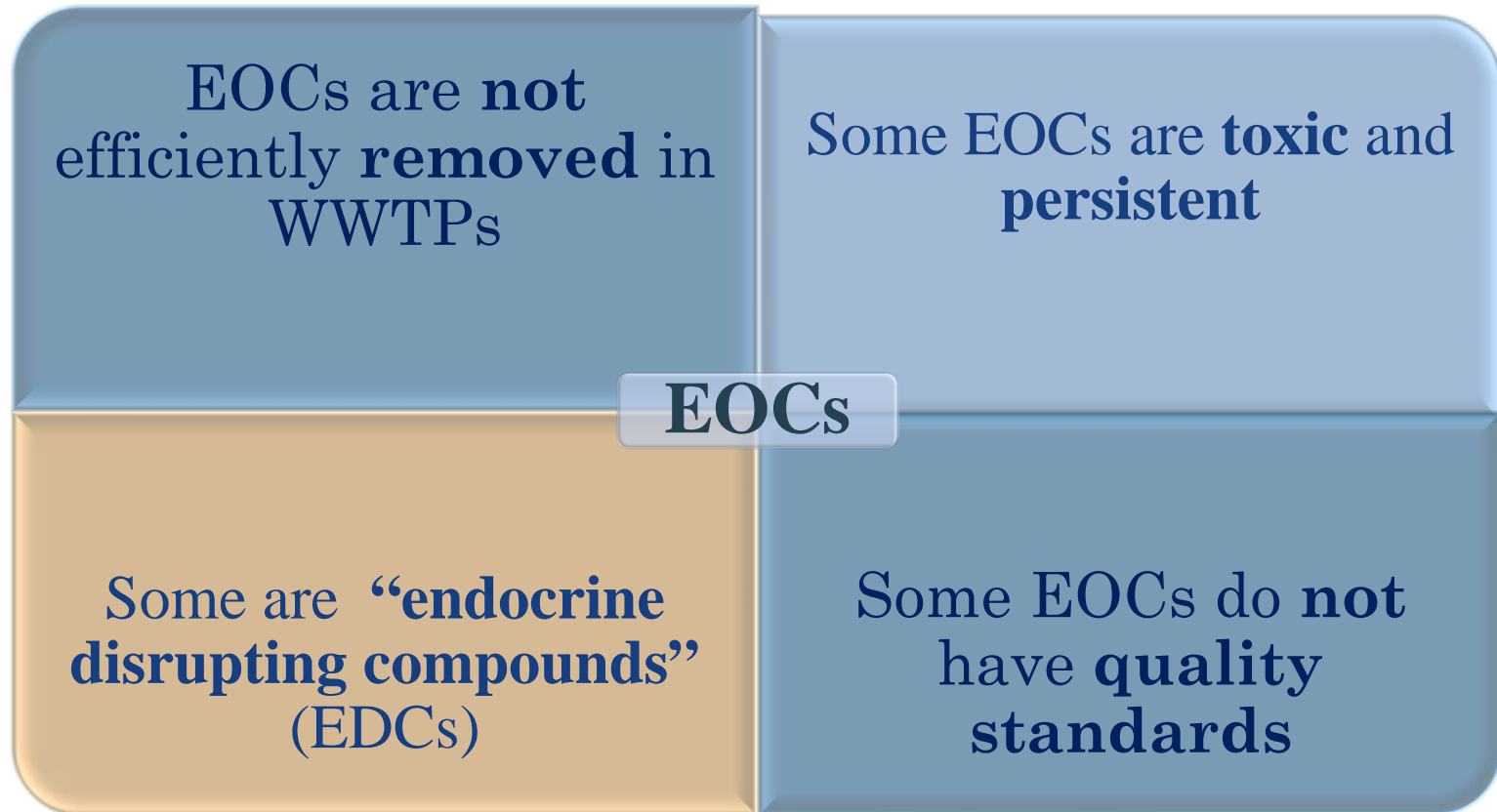
Personal care products

Industrial Products

Drugs of abuse

EMERGING ORGANIC CONTAMINANTS

Why to study EOCs??

EOCs are **not** efficiently **removed** in WWTPs

Some EOCs are **toxic** and **persistent**

EOCs

Some are **"endocrine disrupting compounds"** (EDCs)

Some EOCs do **not** have **quality standards**

EMERGING ORGANIC CONTAMINANTS

Why to study EOCs??

GW has been less characterized than surface water and sewage.

It is necessary to define quality standards in GW:

Pharmaceutical products

Drugs of abuse (DAs)

Industrial products

Personal Care Products (PCPs)

Estrogens / hormones

> Non-legislated
> Insufficent data

- -

Pesticides (polars) $0,1$ µg / L → individual compounds
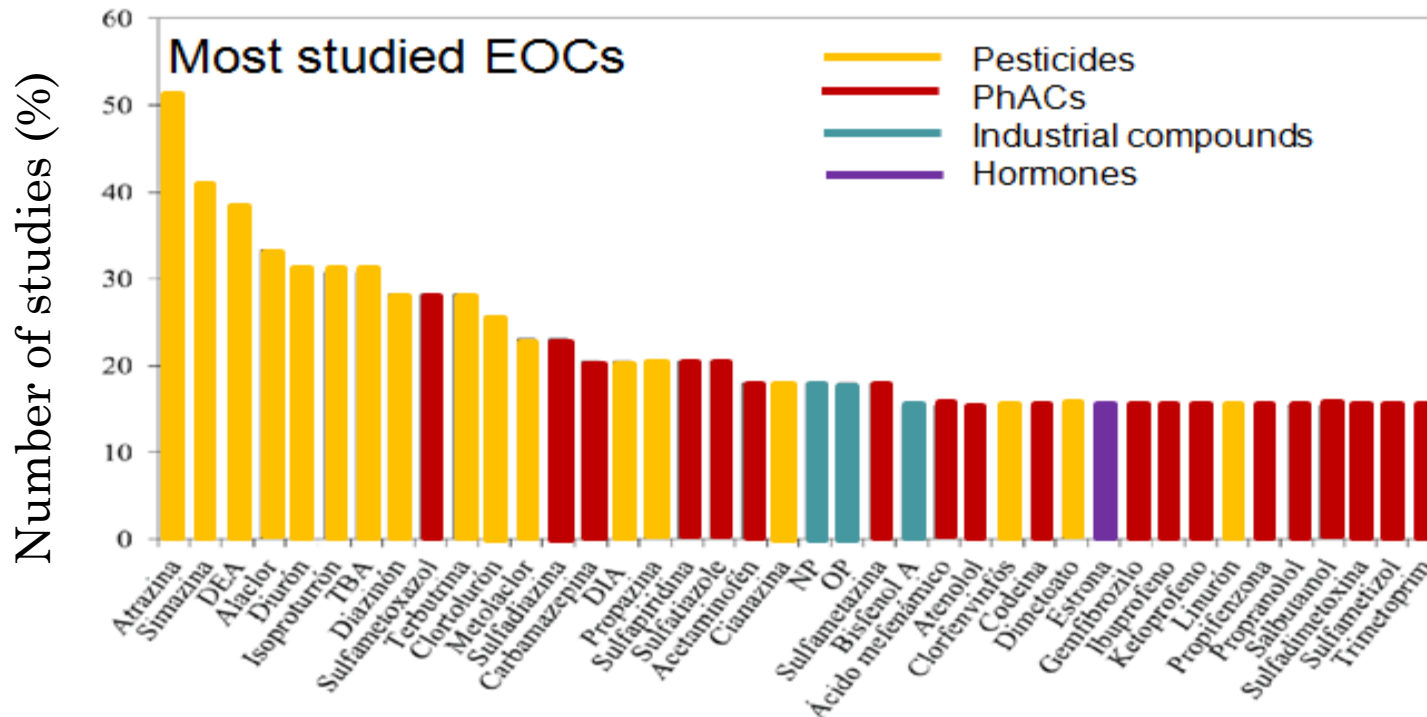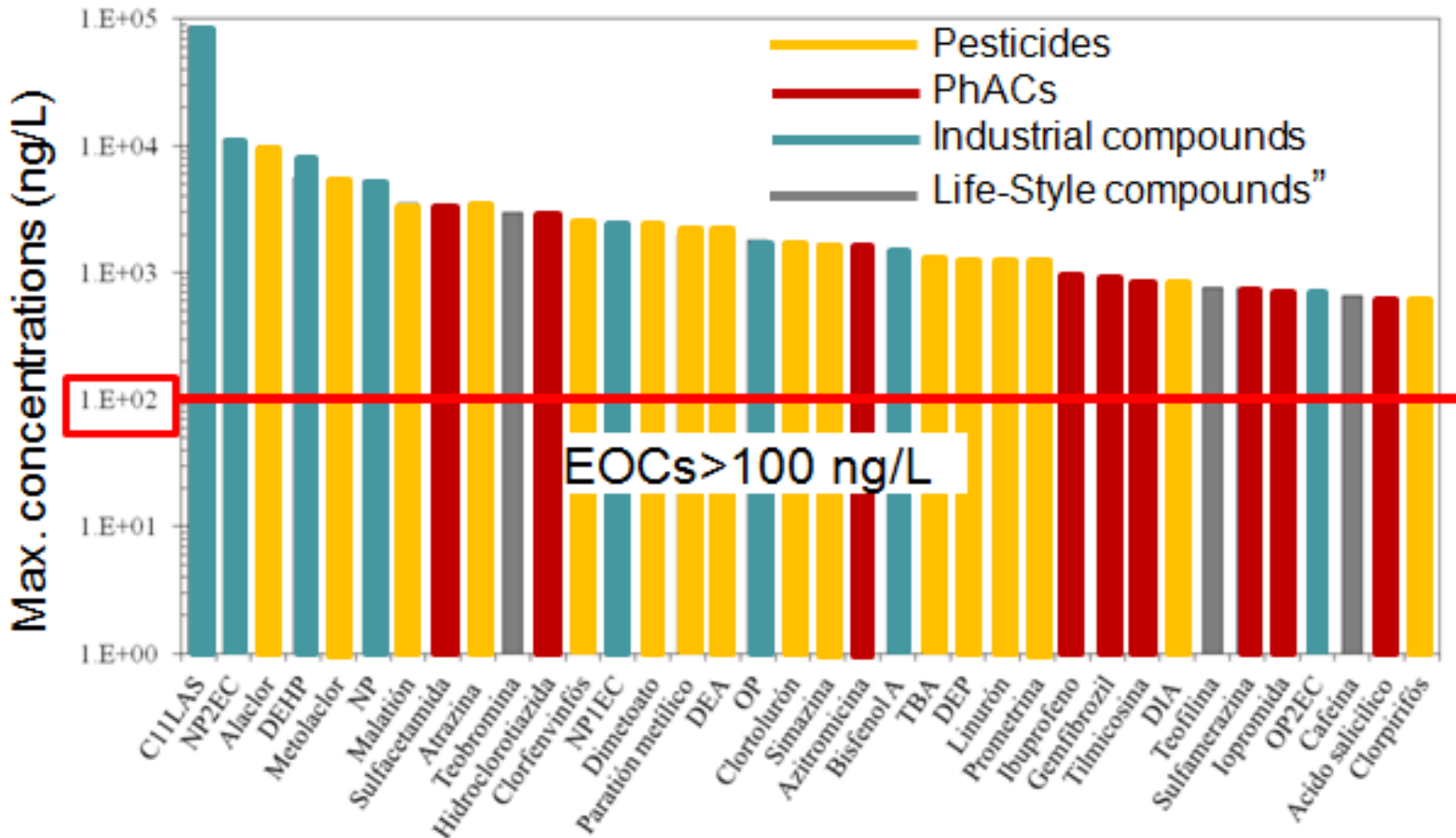(Directive 2006/118/CE) $0,5$ µg / L → sum of compounds

EOCs in Spanish aquifers

Around 40 studies (published in scientific journals) have been reviewed on EOCs in AASS in Spain. (Jurado et al., 2012a)

EOCs in Spanish aquifers

Many EOCs> 100 ng / L→ Need to understand their behavior in groundwater.

Investigate the occurrence and to asses the fate of selected EOCs in an urban aquifer

Drugs of abuse (DAs)

Personal care products

Occurrence of drugs of abuse in urban groundwater. A case study: Barcelona

Jurado, A., Mastroianni, N., Vázquez-Suñé, E., Carrera, J., Tubau, I., Pujades, E., Postigo, C., de Alda, M.L., Barceló, D., (2012). Drugs of abuse in urban groundwater. A case study: Barcelona. Science of the Total Environment 424, 280-288.
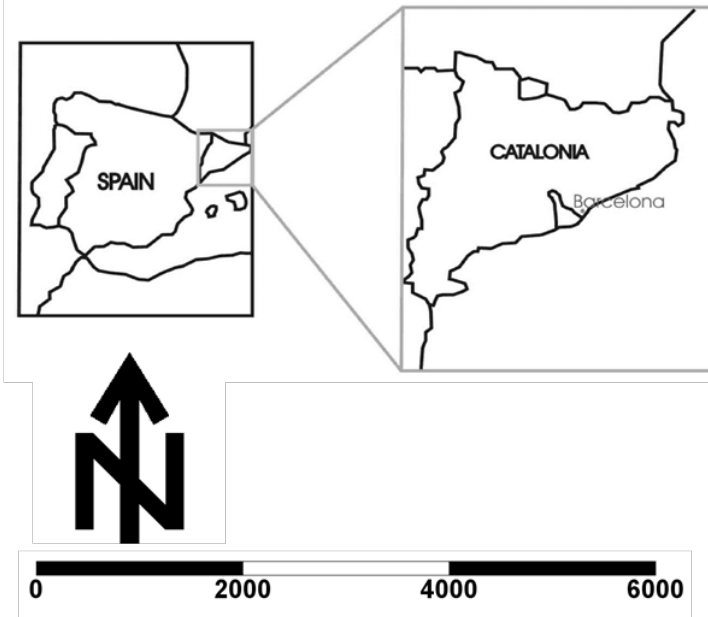
DRUGS OF ABUSE (DAs)

THE AIMS OF THE STUDY:

Occurrence and fate of drugs of abuse (DAs) in urban aquifers of the city of Barcelona.

❖ the spatial distribution of the groundwater samples.

❖ the depth of the groundwater samples.

❖ processes affecting DAs in groundwater.

STUDY AREA

🟩	**Holocene**		Sands, gravels, silt, clays	Llobregat Delta
🟨	**Holocene**	**Quaternary**	Sands, gravels, silt, clays	Besós Delta
⬜	**Pleistocene**		Carbonated clays	Barcelona Plain
🟧	**Tertiary**		Marls, sands, sandstones	Barcelona Plain
🟪	**Paleozoic**		Shale and granites	Collserola Range
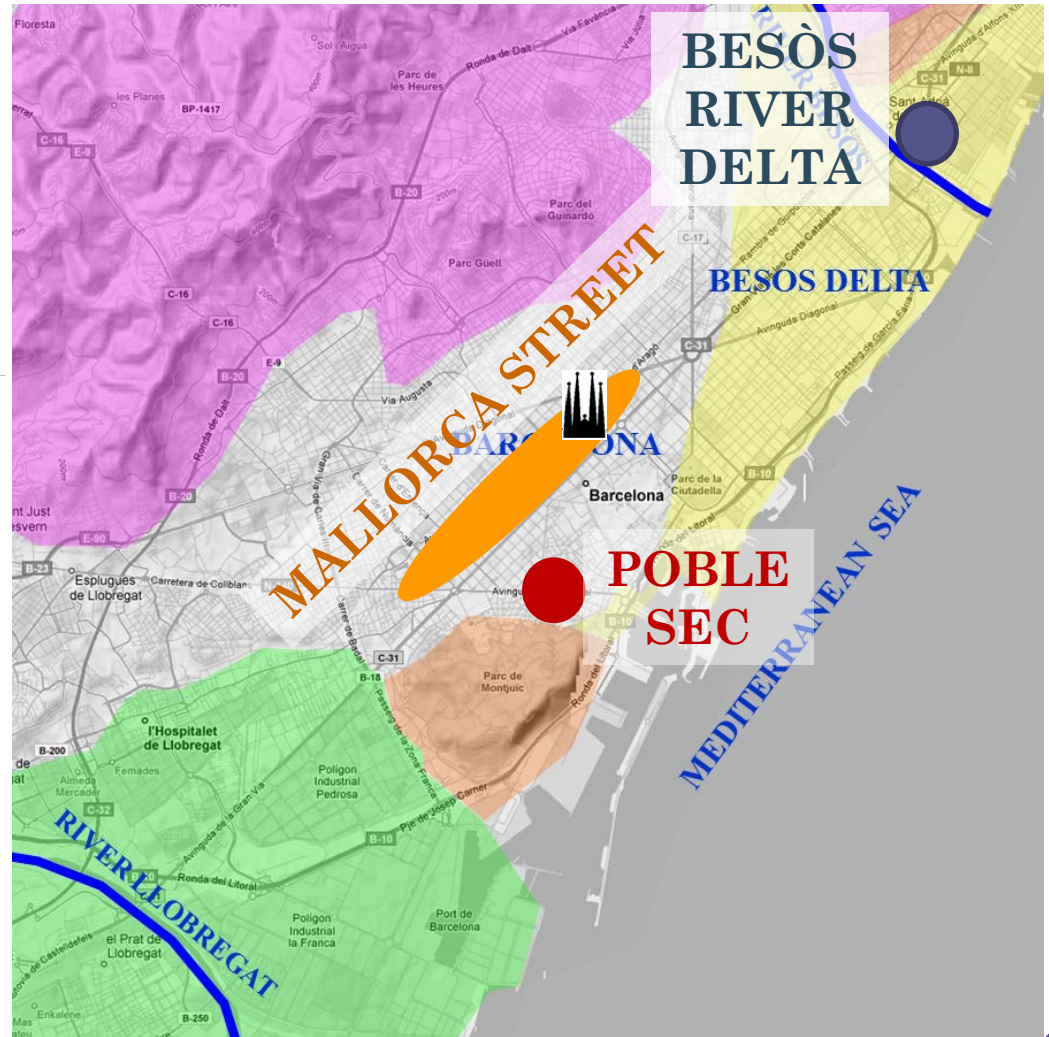
DRUGS OF ABUSE (DAs)

STUDY AREA-Pilot zones

BARCELONA PLAIN
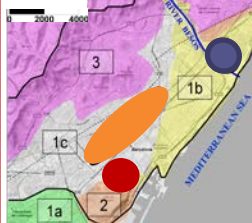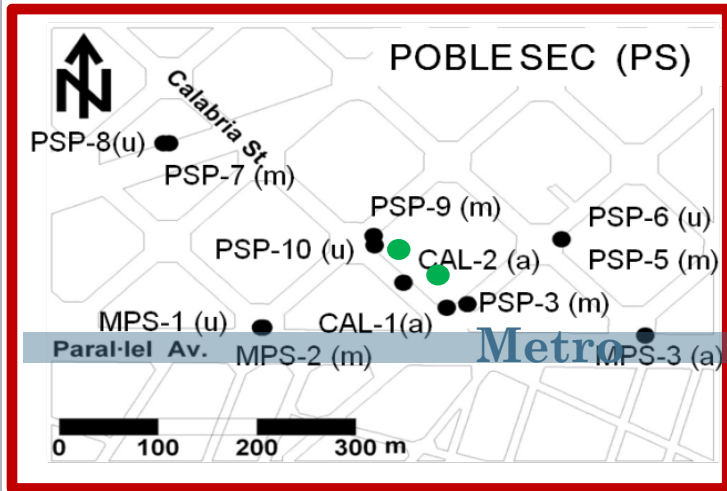
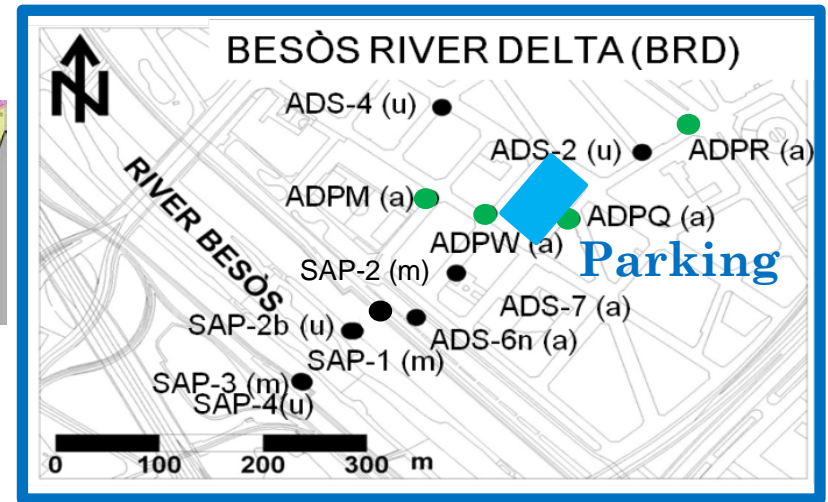### BESÒS RIVER DELTA

- ❖ Urban aquifer
- ❖ 13 observation points
- ❖ Sewage water is the main source of contamination
- ❖ Metro has seepage problems
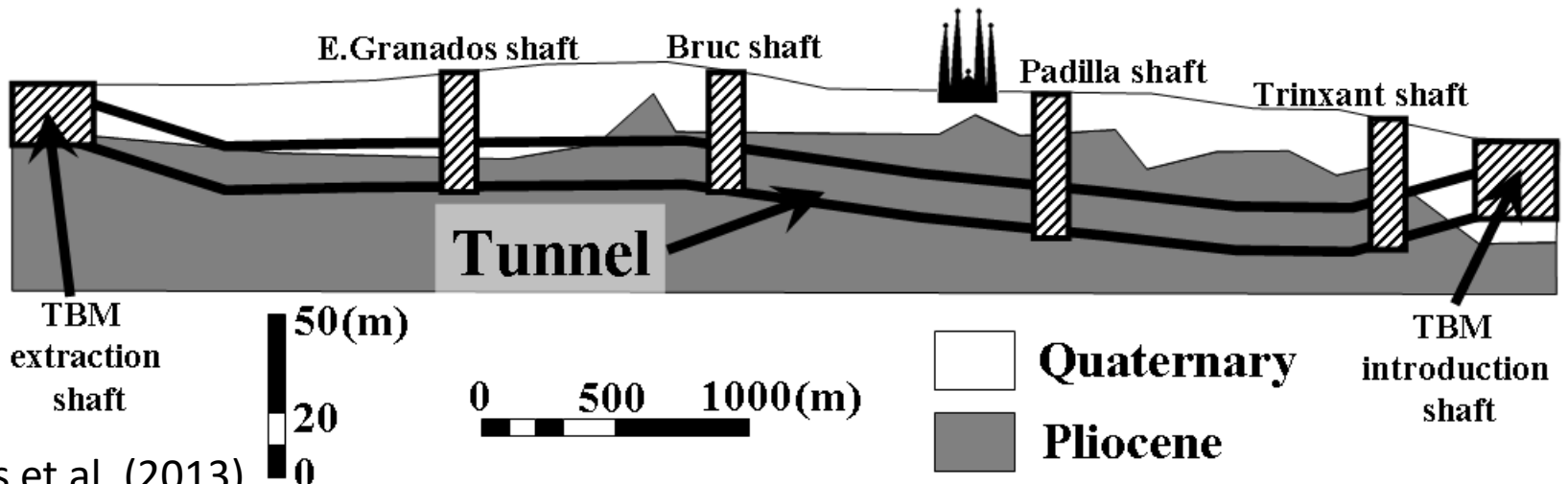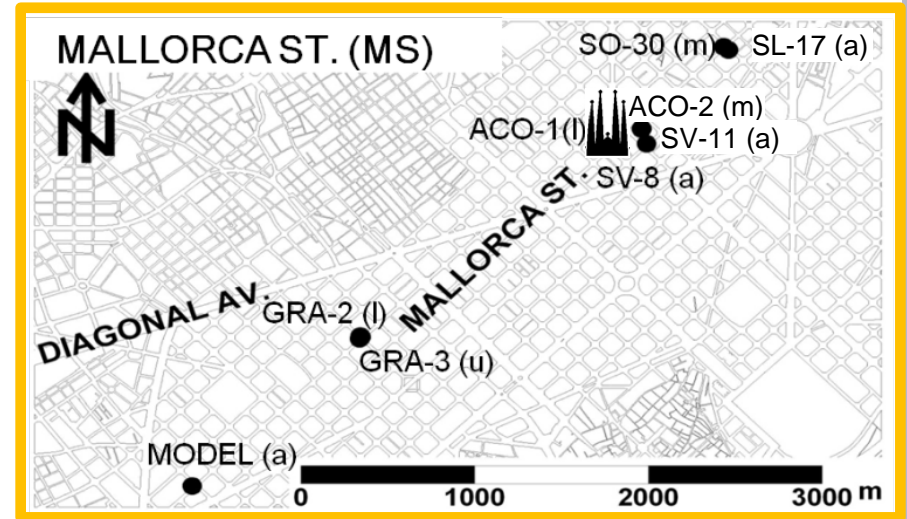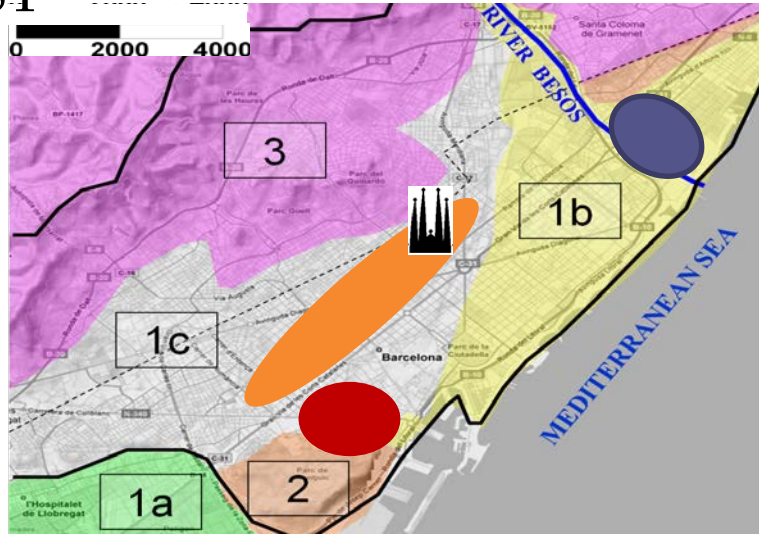- ❖ Supplied by River Llobregat
- ❖ **Oxic environment**

- ❖ Urban aquifer
- ❖ 13 observation points
- ❖ Underground parking pumping 150 l/s
- ❖ River Besòs is the main aquifer recharge source.
- ❖ Supplied by River Ter water
- ❖ **Reducing environment**

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STUDY AREA

Mallorca street → Monitoring system for the construction of the HST

Pujades et al. (2013)

Sampling campaign

General analysis

Drugs of abuse (or illicit drugs)

- ❖ Cocainic compounds
- ❖ Opioids
- ❖ Cannabinoids
- ❖ Amphetamines like compounds
- ❖ Lysergic compounds
- ❖ Benzodiazepines

DRUGS OF ABUSE (DAs)

Analysed compounds

- **Cocaine compounds:** cocaine (CO, original product), benzoylecgonine (BE, main metabolite CO), cocaethylene (CE, metabolite)

- **Cannabinoids:** Δ9-tetrahydrocannabinol (THC), cannabinol (CBN), cannabidiol (CBD), 11-nor-9-carboxyΔ9-tetrahydrocannabinol (THC-COOH metabolite), 11-hydroxy-Δ9-tetrahydrocannabinol (OH-THC, Metabolite)

- **Opioids:** morphine (MOR), heroin (HER), methadone (METH), 6-acetylmorphine (6ACM, HER metabolite), 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP, HER metabolite)

- **Amphetamine like compounds:** Amphetamine (AM), Methamphetamine (MA), Ecstasy (MDMA), Ephedrine (EPH)

- **Lysergic compounds:** lysergic acid diethylamide (LSD)

- **Benzodiazepines:** alprazolam (ALP), diazepam (DIA), lorazepam (LOR)

DRUGS OF ABUSE (DAs)

Results

CHEMICAL CLASS	ANALYTE	FREQUENCY OF DETECTION (%) n=36	CONCENTRATION (ng/L)	
			AVERAGE ± STD	MAX
COCAINICS	CO	31	3.8±12.8	60.2
	BE	19	1.5±4.5	19.6
	COC	3	0.05±0.30	1.8
CANNABINOIDS	THC	0	-	-
	CBN	0	-	-
	CBD	0	-	-
	THC-COOH	0	-	-
	OH-THC	0	-	-
OPIOIDS	MOR	8	1.4±5.2	27.2
	HER	0	-	-
	6ACM	0	-	-
	METH	86	7.4±15.3	68.3
	EDDP	44	0.7±1.7	8.2
AMPHETAMINE LIKE	AM	0	-	-
COMPOUNDS	MA	0	-	-
	MDMA	64	3.9±6.7	36.8
	EPH	8	0.3±1.3	7.3
LYSERGIC COMPOUNDS	LSD	0	-	-
BENZODIAZEPINES	DIA	39	5.92±7.9	19.4
	ALP	14	0.8±2.1	6.4
	LOR	14	3.1±9.1	39.7

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DRUGS OF ABUSE (DAs)

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Spatial distribution of the groundwater samples

Mallorca street: COCAINE and METH

ng/L

DAs effects

Methadone   Cocaine

LOR   ALP   DIA   EPH   MDMA   EDDP   METH   MOP   CE   BE   CO

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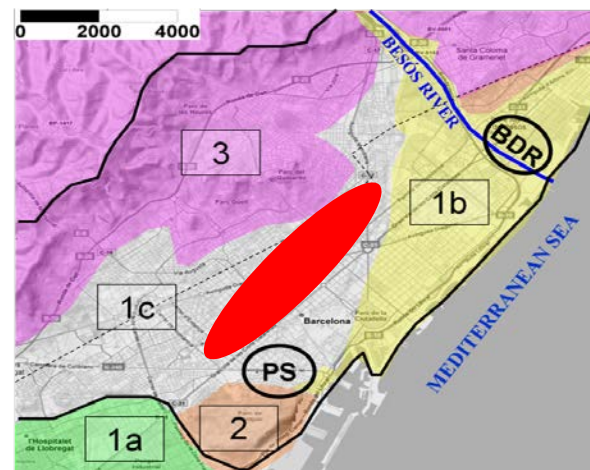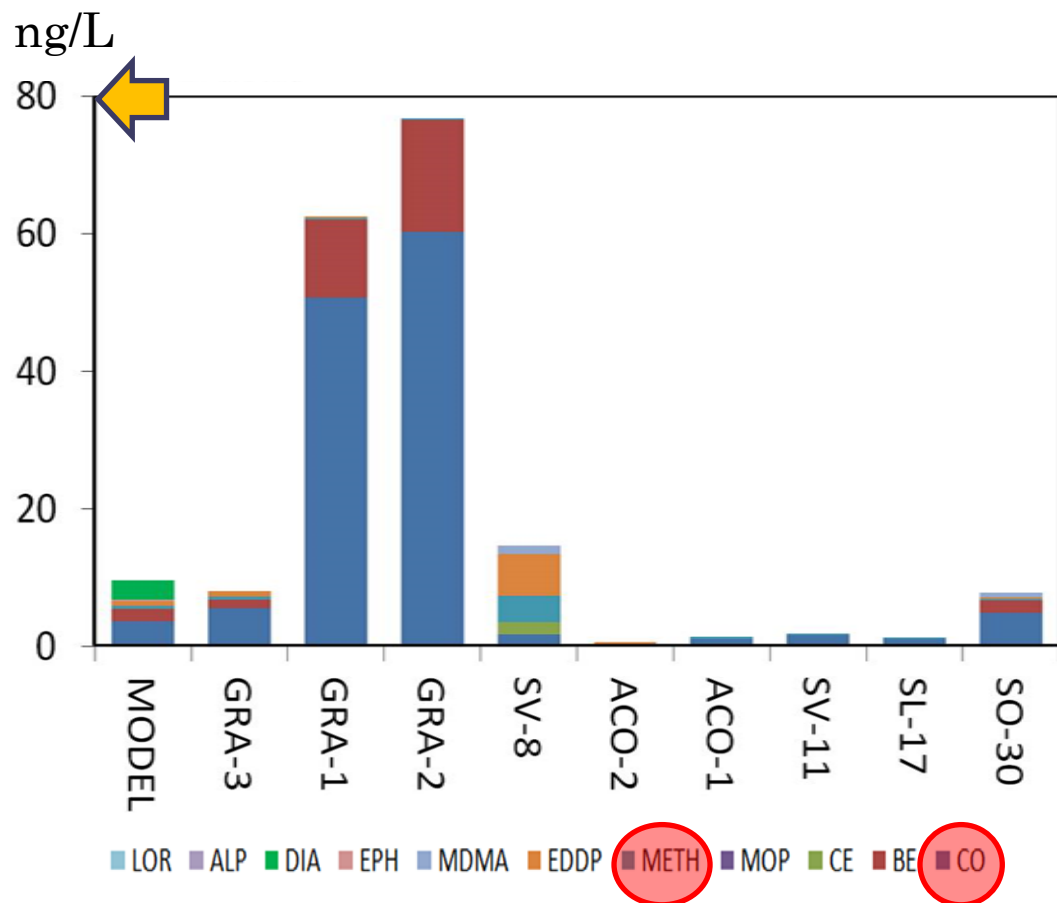
DRUGS OF ABUSE (DAs)

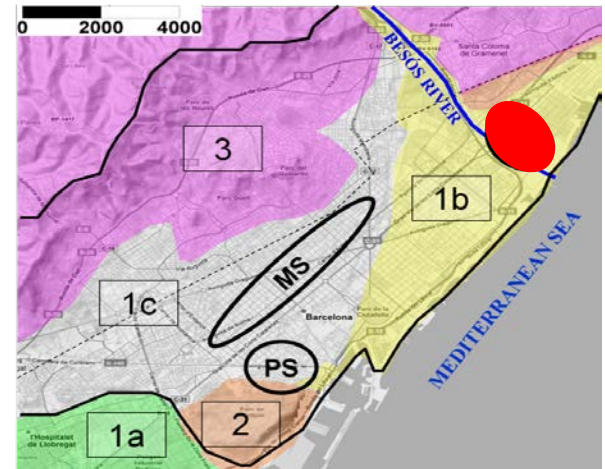## Spatial distribution of the groundwater samples

Poble Sec: MDMA (or ecstasy)

DAs effects

Spatial distribution of the groundwater samples
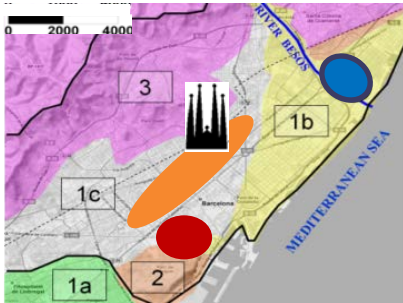
Besòs River Delta: Mixture of DAs

ng/L

DAs effects

Methadone   Ecstasy

LOR · ALP · DIA · EPH · MDMA · EDDP · METH · MOP · CE · BE · CO

Spatial distribution of the groundwater samples

✓MS: Most frequently detected compound CO
✓PS: Most frequently detected compound MDMA
✓BRD: Mixture of DAs (DIA, METH, MDMA)
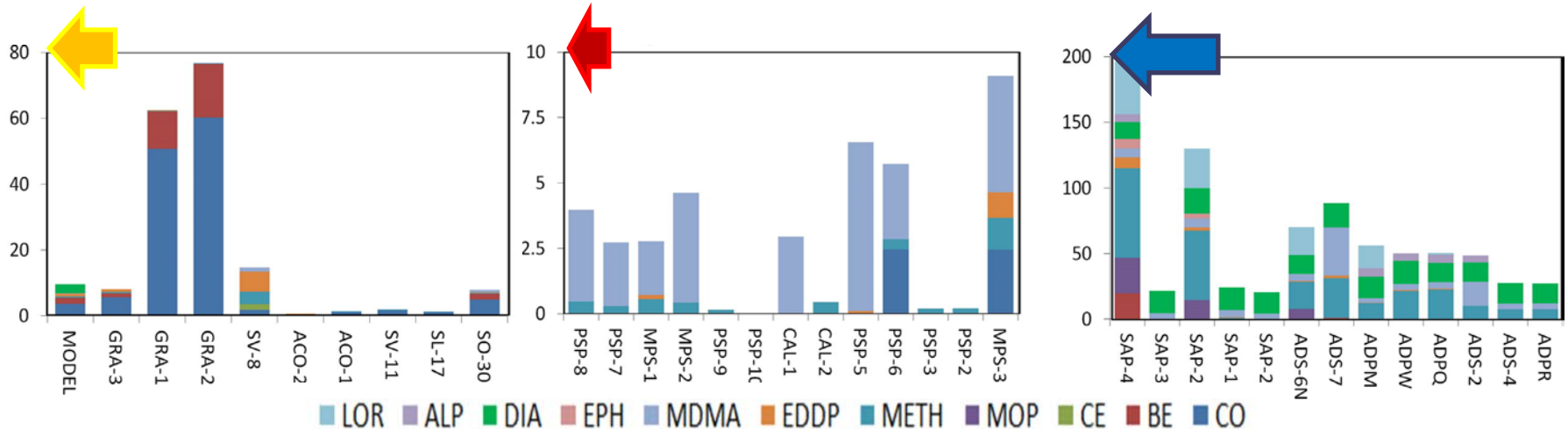
DRUGS OF ABUSE (DAs)

DAs profile according to groundwater depth

❖The **concentration** of most **DAs decreased** with the **depth**

Attenuation processes related to: longer residence time, mixing with deeper waters and clean, adsorption, degradation, etc.

❖**Excepting** for the **cocainic compounds in MS**

DAs profile according to groundwater depth
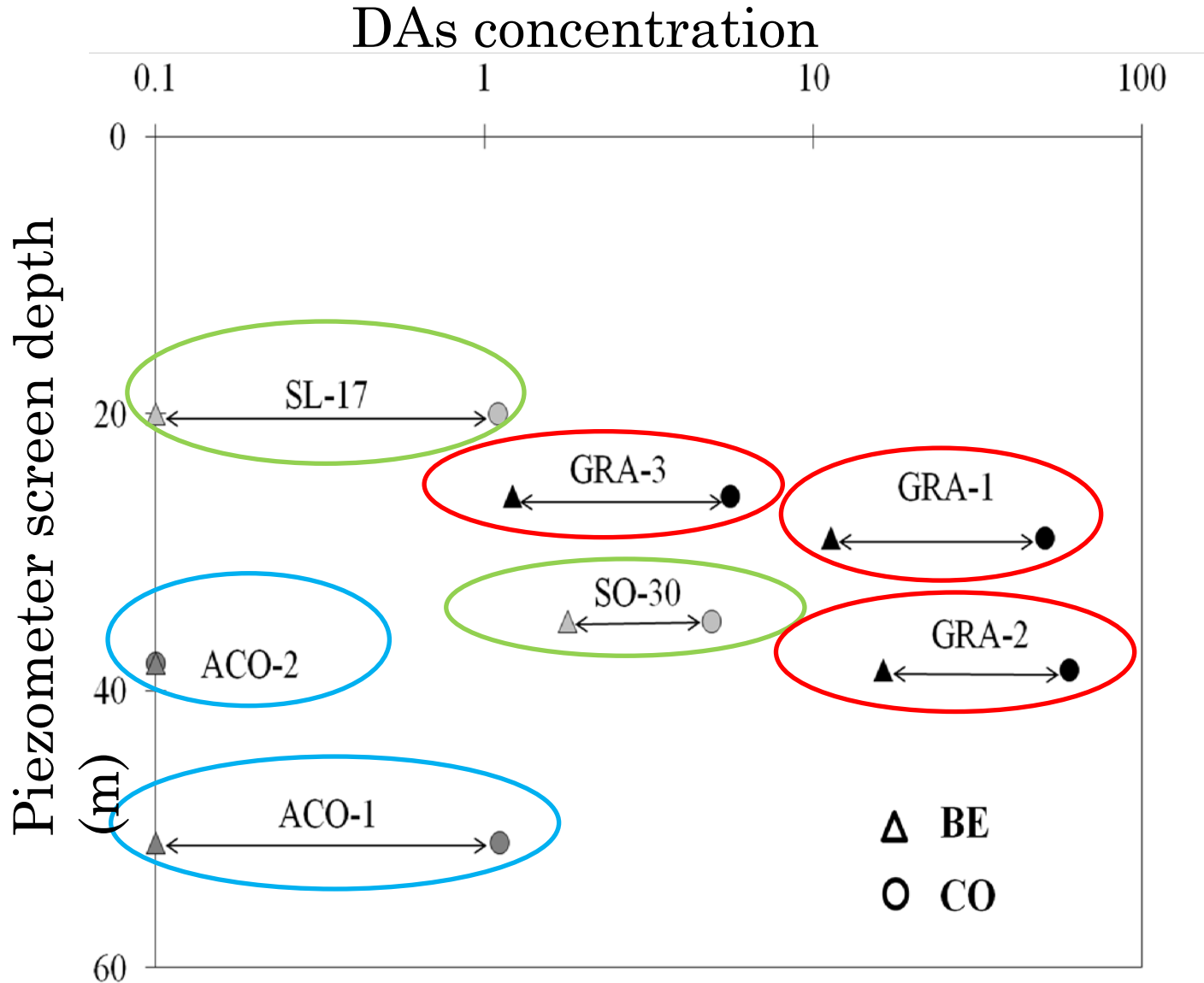
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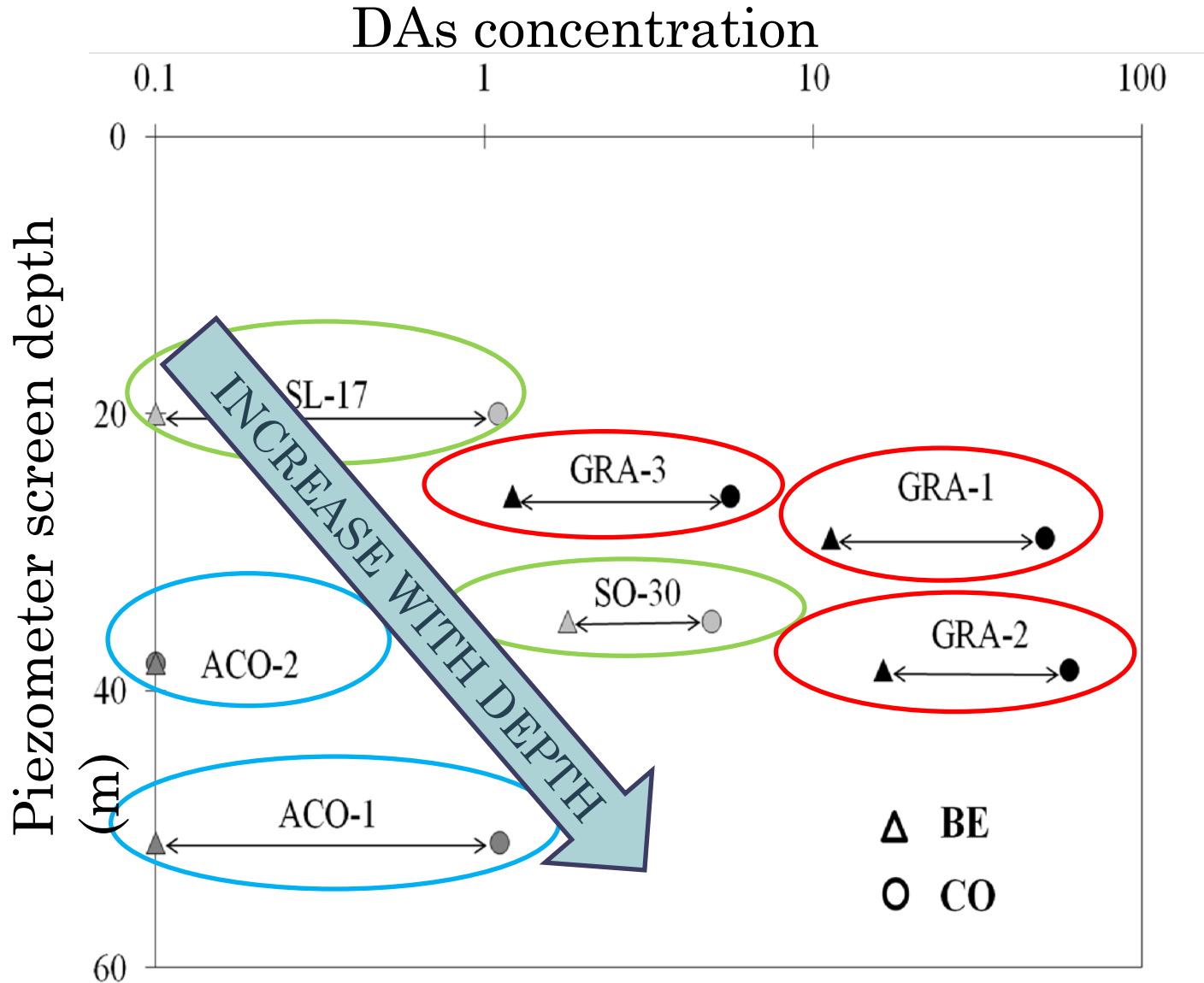
DAs profile according to groundwater depth

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>   Attenuation processes related to: longer residence time, mixing with deeper waters and clean, adsorption, degradation, etc.

❖**Excepting** for the **cocainic compounds in MS**

>   BE was more degraded than CO

>   An illicit or intentional disposal of CO near to GRA's.

DRUGS OF ABUSE (DAs)

Fate of the DAs in groundwater

We have proposed a methodology that uses the mixing proportions (MIX, Carrera et al., 2004)
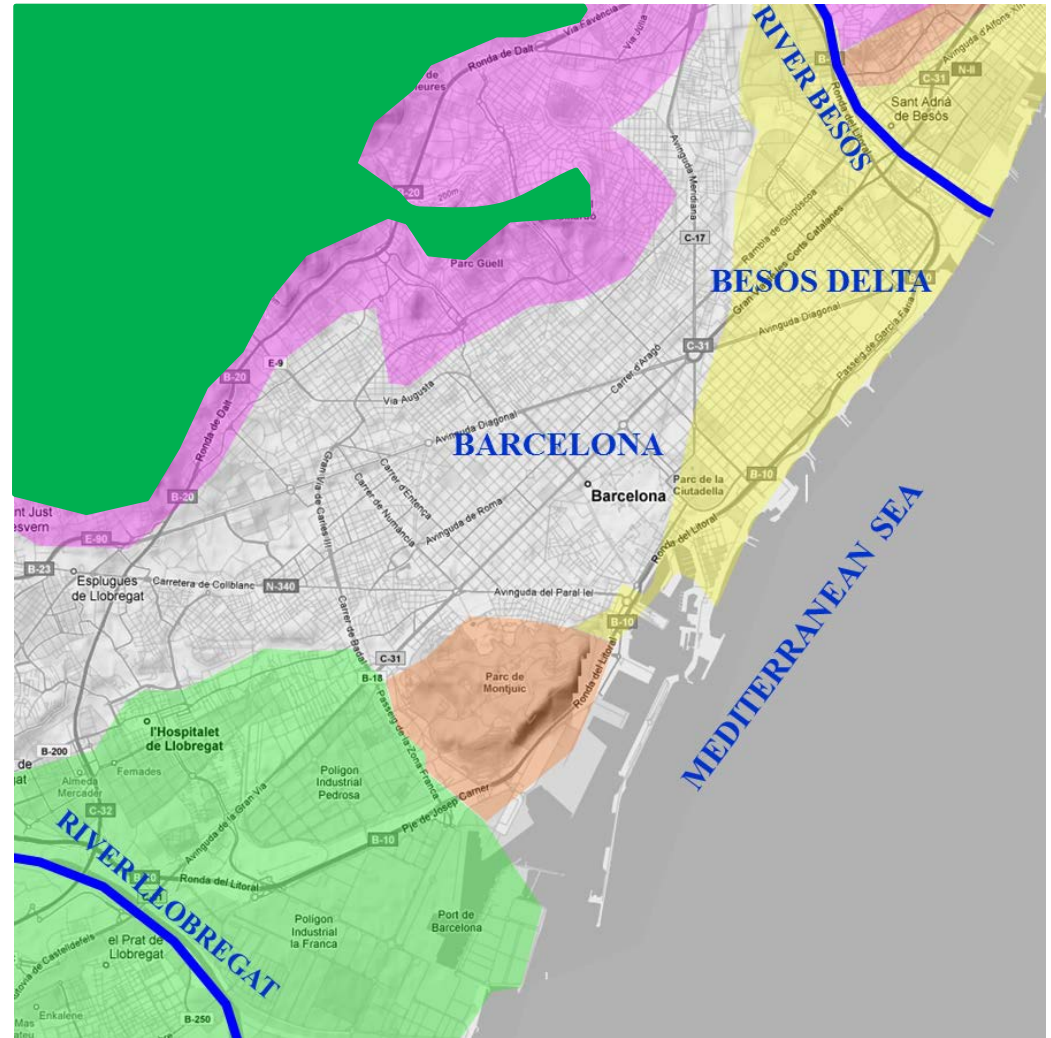
Information needed to apply this method:

1. **Concentrations** of **DAs** in the recharge sources

2. **Quantify** the **mixing ratios** of recharge sources in GW

DRUGS OF ABUSE (DAs)

Fate of the DAs in groundwater

Potential recharge sources

- ■ "Natural" Recharge
- ■ Runoff
- ■ Ter water supply
- ■ Llobregat water supply
- ■ Ter sewage water
- ■ Llobregat sewage water
- ■ River Besòs
- ■ Sea Water

(Vázquez-Suñé et al., 2010)

Fate of the DAs in groundwater

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(Vázquez-Suñé et al., 2010)

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Fate of the DAs in groundwater

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Fate of the DAs in groundwater

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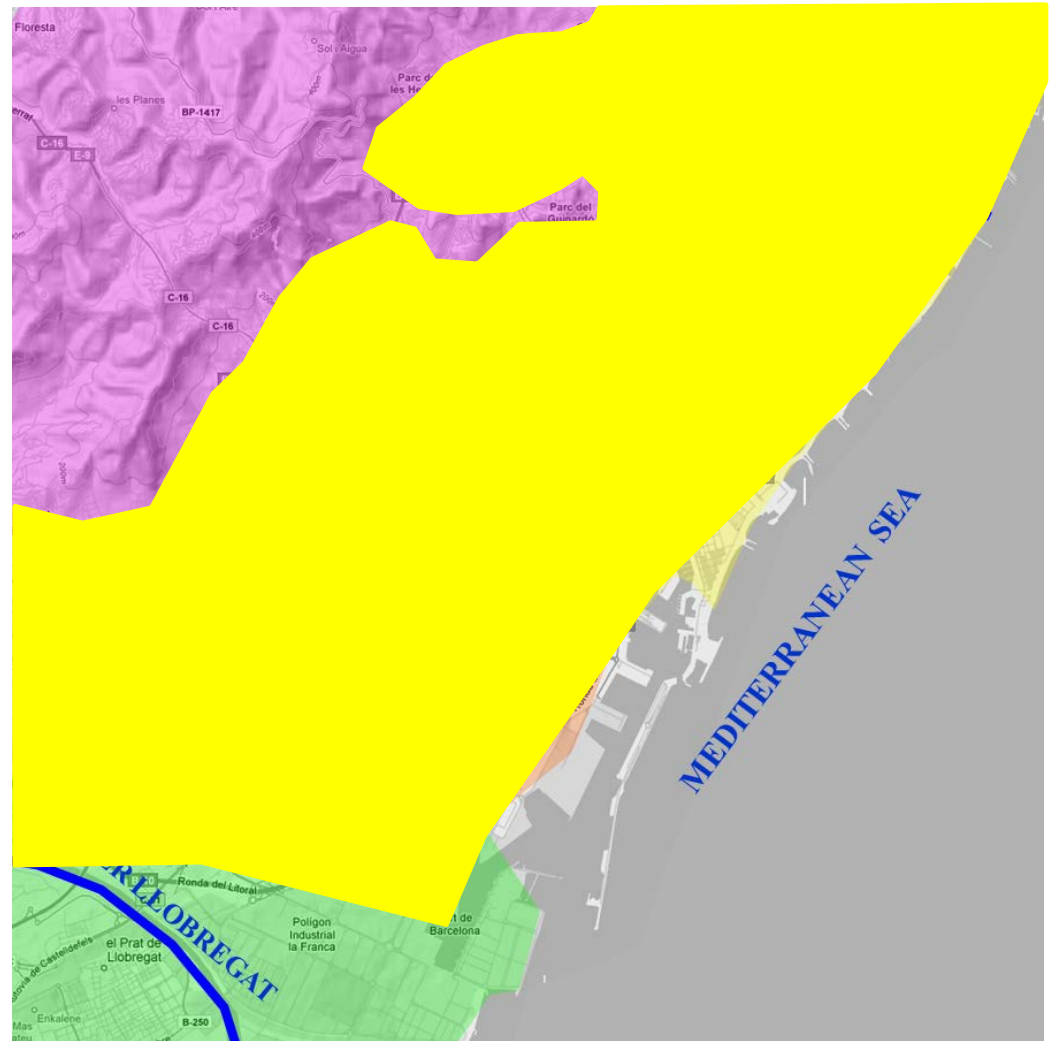- River Besòs
- Sea Water

(Vázquez-Suñé et al., 2010)

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DRUGS OF ABUSE (DAs)

Fate of the DAs in groundwater

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(Vázquez-Suñé et al., 2010)

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(Vázquez-Suñé et al., 2010)

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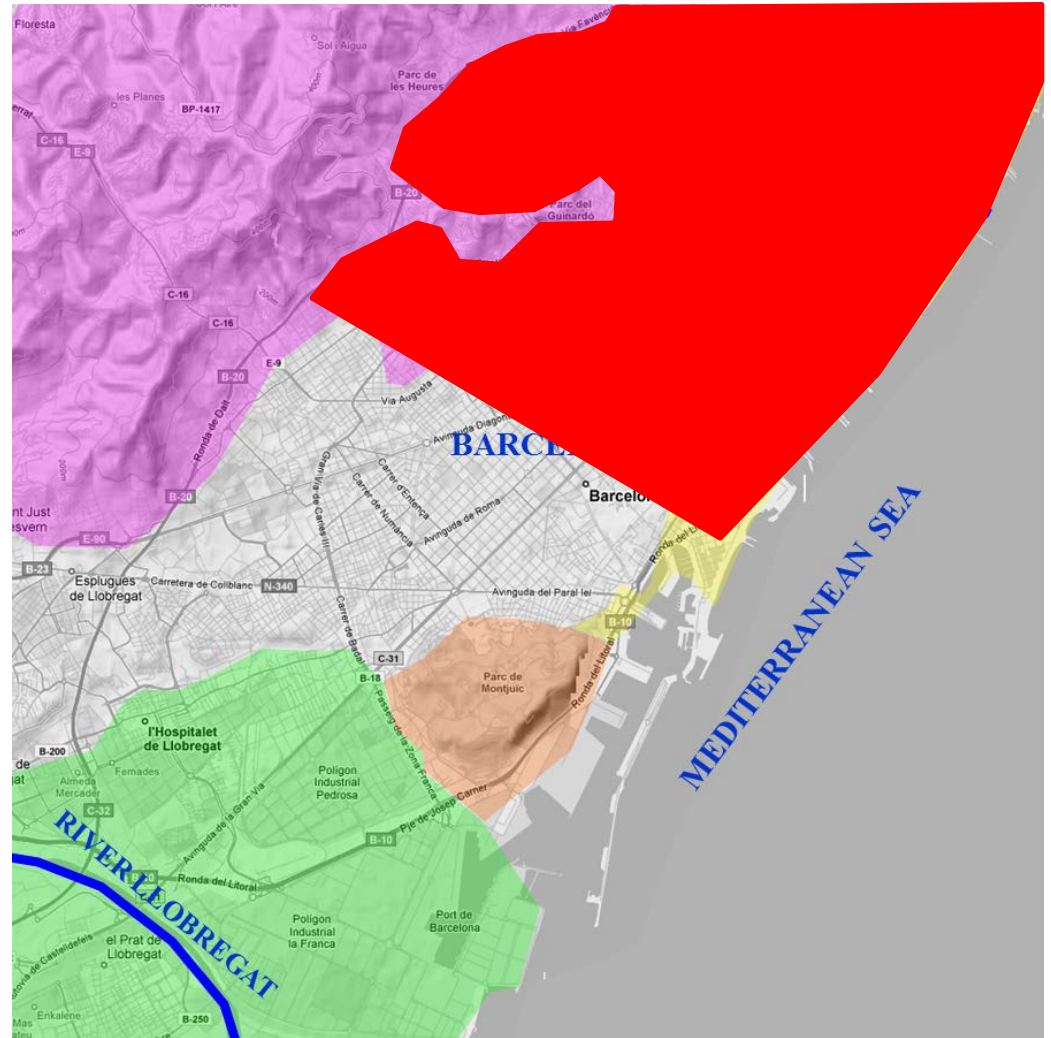- 🟦 River Besòs
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(Vázquez-Suñé et al., 2010)

DRUGS OF ABUSE (DAs)

Fate of the DAs in groundwater

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(Vázquez-Suñé et al., 2010)

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Fate of the DAs in groundwater

We have proposed a methodology that uses the mixing proportions (MIX, Carrera et al., 2004)

Information needed to apply this method:

1. **Concentrations** of **DAs** in the recharge sources

DAs concentration in the recharge sources

End-members		CO	BE	MOP	MET	EDDP	MDMA	EPH	DIA	LOR
Besòs River(RIV)	W1	-	21.4	2.6	6.4	11.8	3.0	40.2	2.1	13.0
	D1	-	131.9	15.8	39.4	72.9	18.3	225.0	12.9	80.1
	D2	-	172.1	20.6	51.5	95.1	23.8	300.0	16.8	104.6
Water Supply	TER LLOB	0.4	0.4	-	0.4	2.5	0	-	-	-
Sewage water	SW_TER SW_LLOB	50	500	-	7.5	12	50	-	-	-
Rainfall recharge non-urban	R_R	0	0	0	0	0	0	0	0	0

"-" : non included in the analysis

Fate of the DAs in groundwater
Mixing ratios of recharge sources in GW
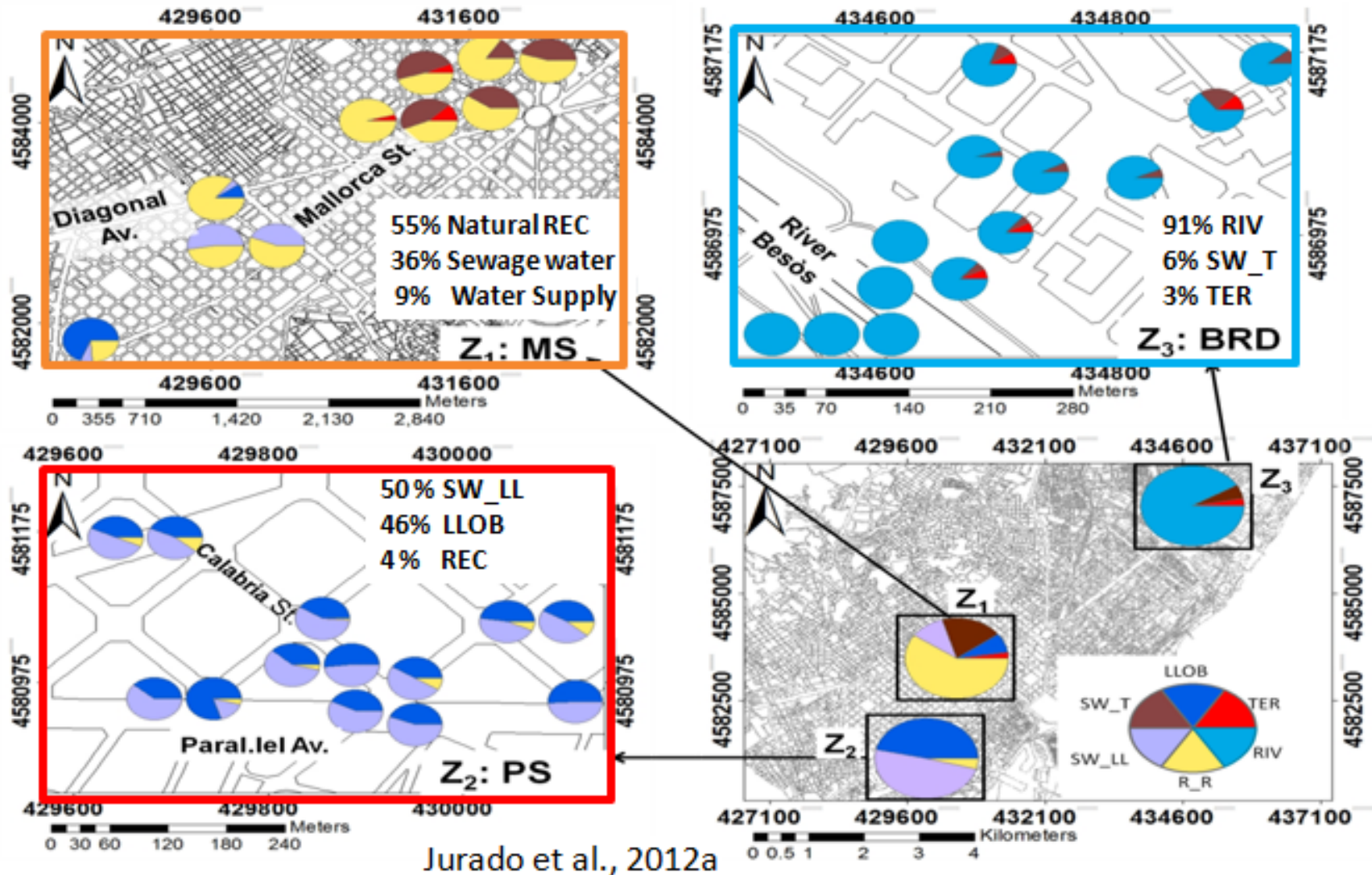
Jurado et al., 2012a

DRUGS OF ABUSE (DAs)

Fate of the DAs in groundwater

Natural attenuation of DAs in the aquifer
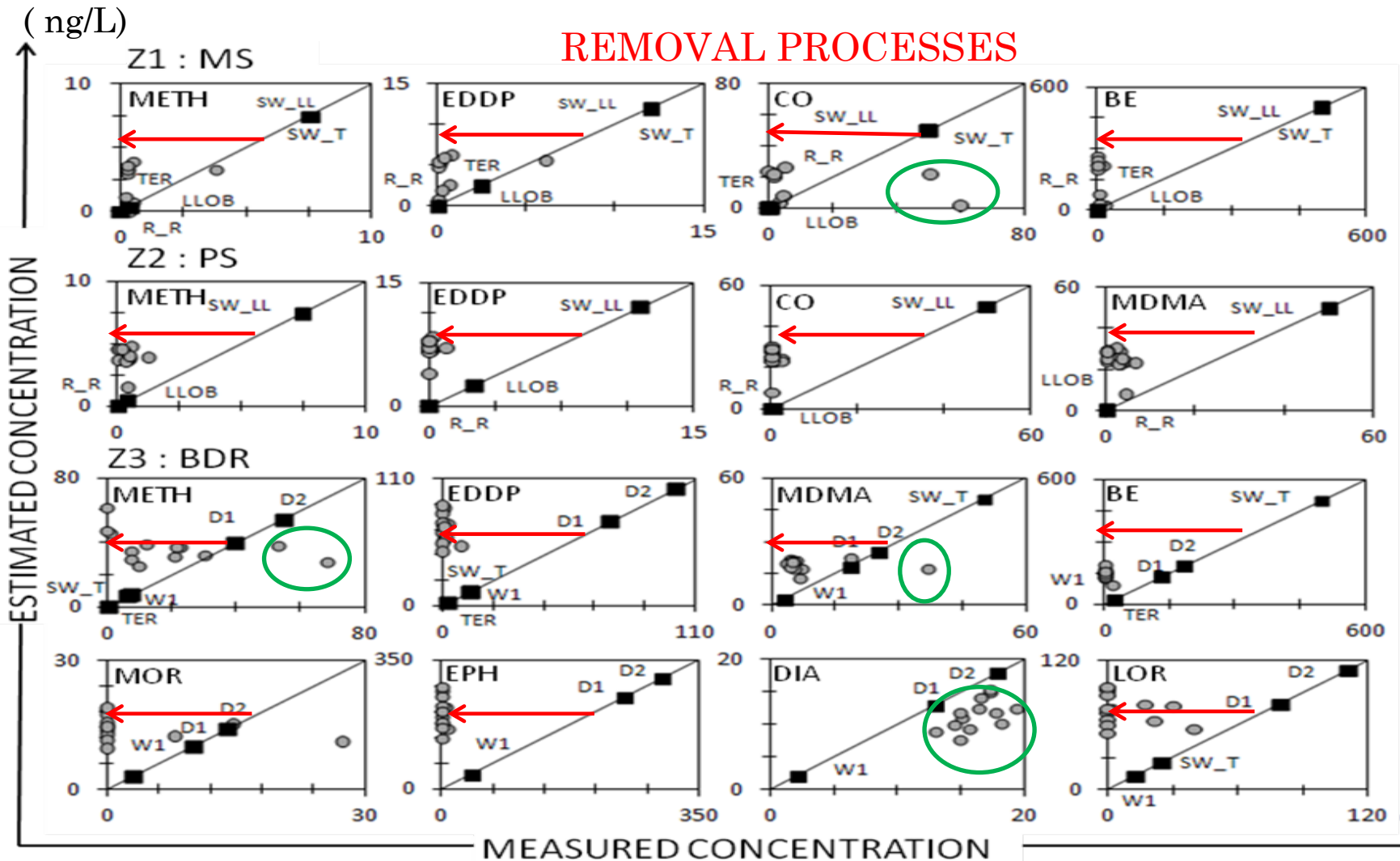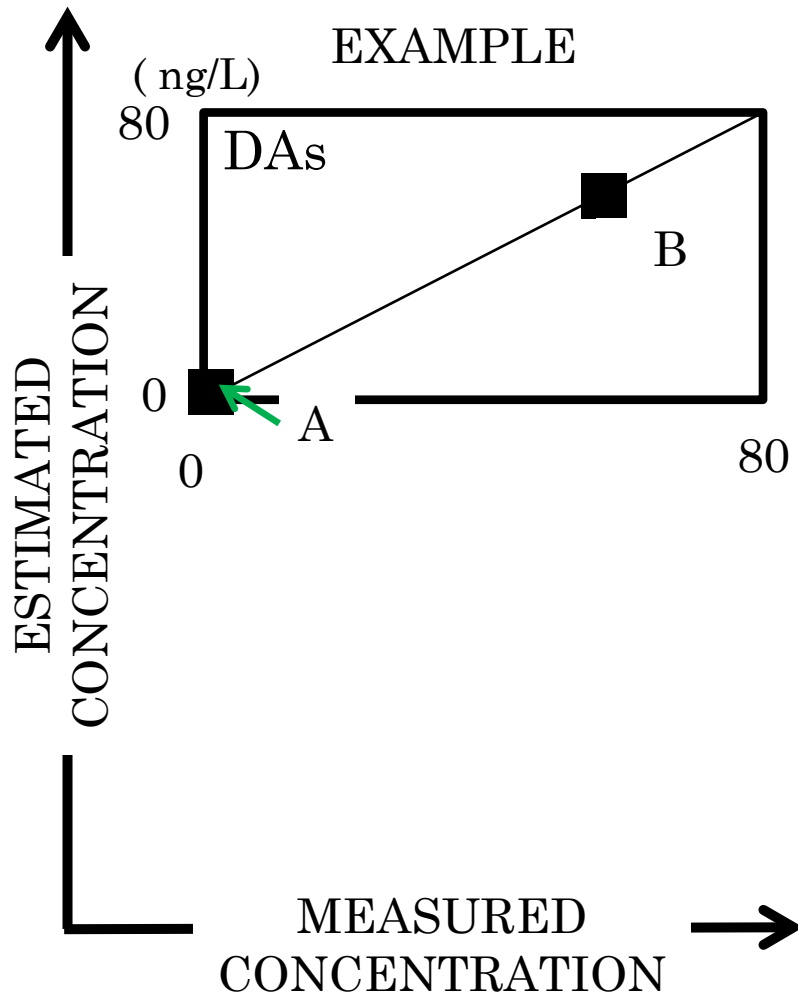
Fate of the DAs in groundwater

Fate of the DAs in groundwater

DRUGS OF ABUSE (DAs)

Fate of the DAs in groundwater

EXAMPLE

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DRUGS OF ABUSE (DAs)
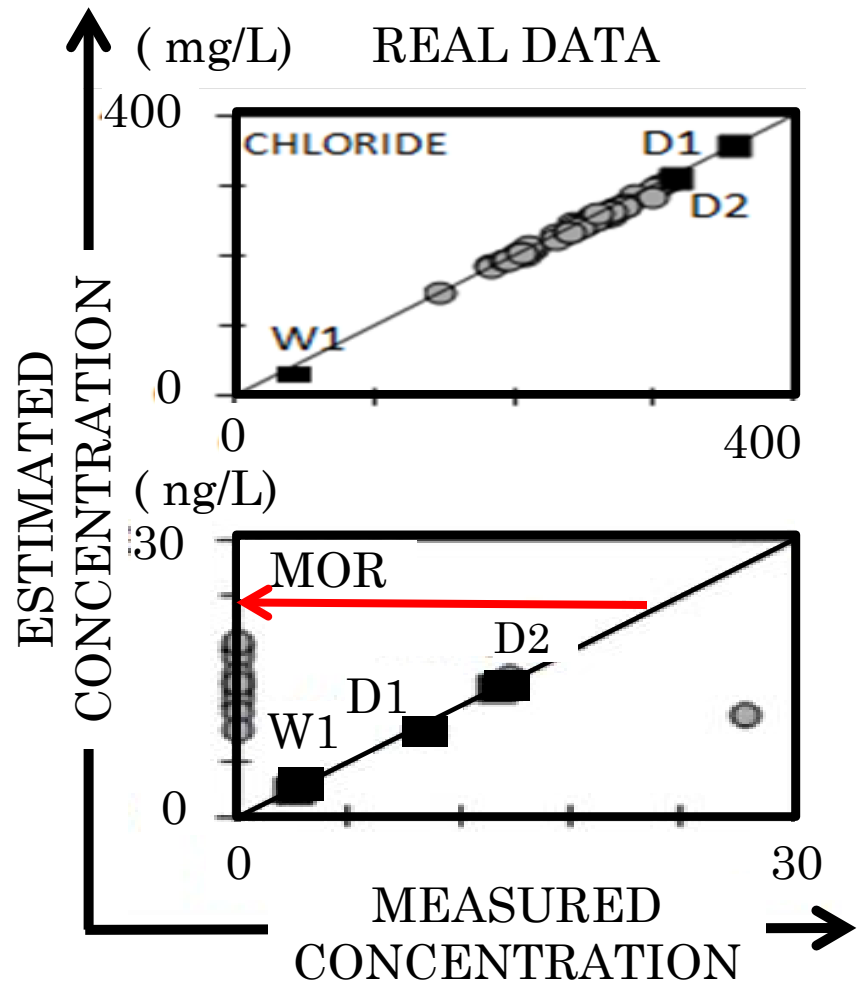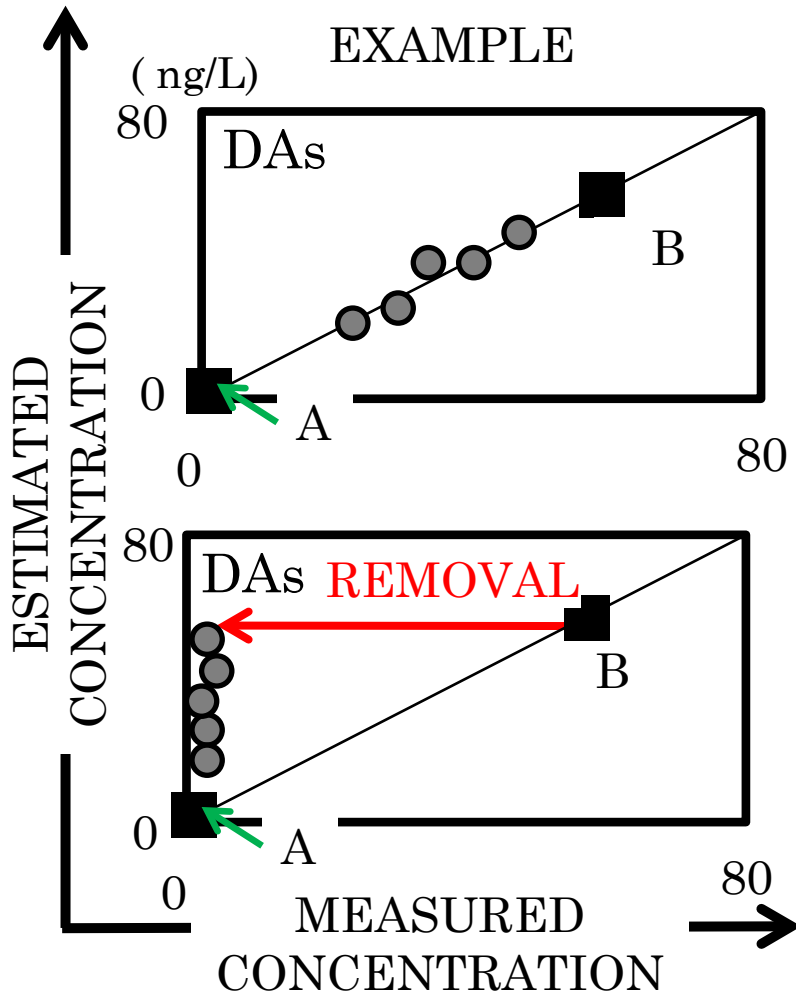
Fate of the DAs in groundwater

Fate of the DAs in groundwater

Natural attenuation of DAs in the aquifer

REMOVAL PROCESSES
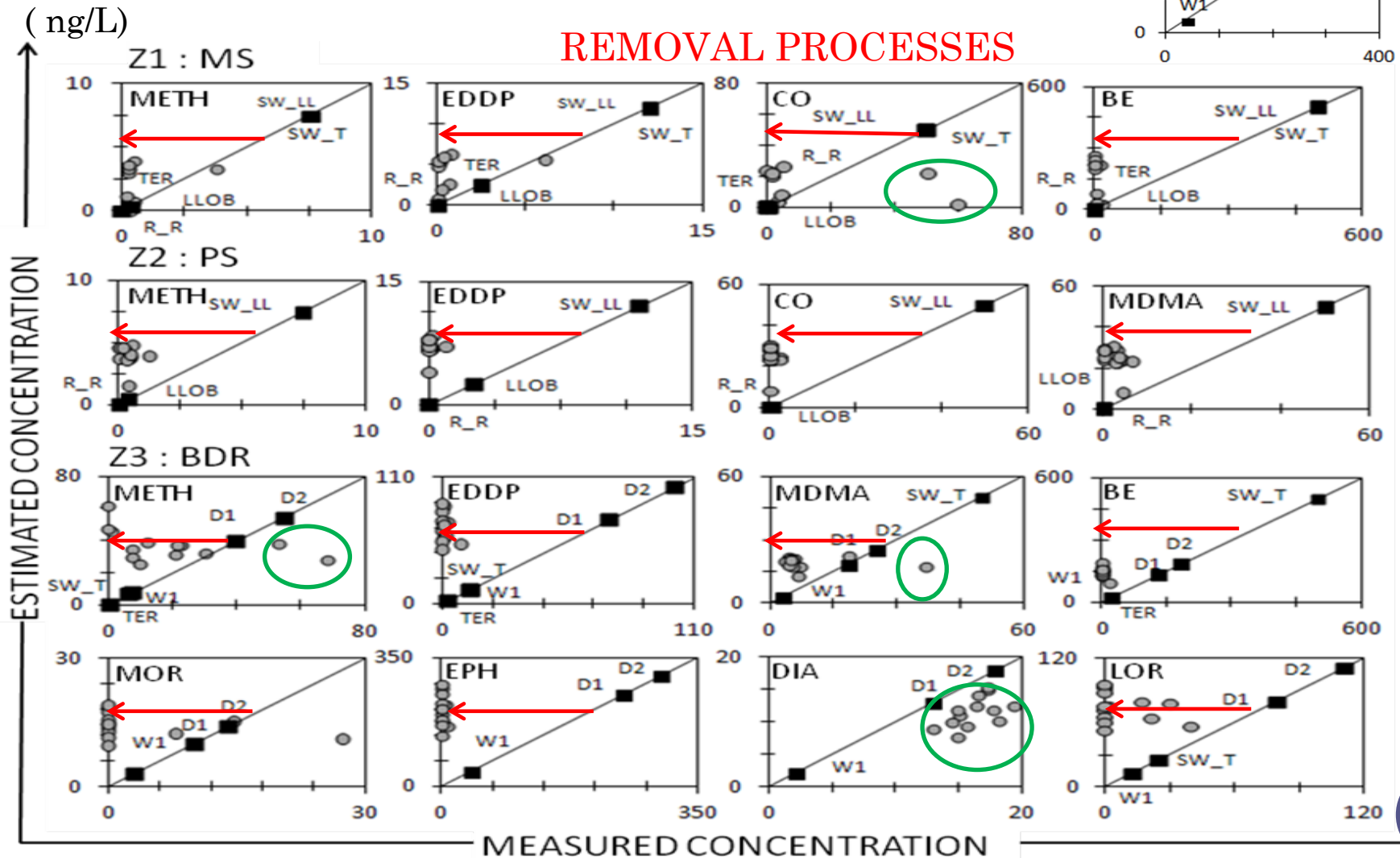
Fate of the DAs in groundwater

Attenuation of DAs in the urban GW of Barcelona

GW of MS and PS
- ❖ NO3 + O2 ➔ oxidizing environment

GW of BDR
- ❖ Reducing environment (NH4)

> Natural attenuation of DAs in GW under oxidizing and reducing conditions.

> Adsorption, biodegradation and transformation processes.

Occurrence, fate and risk assessment of personal care products in river-groundwater interface.

Serra-Roig, M.P, **Jurado. A.**, Díaz-Cruz, M.S., Vázquez-Suñé, E., Pujades, E., Barceló, D. (2016). Occurrence, fate and risk assessment of personal care products in river-groundwater interface. Sci. Total Environ., 568, 829-837.
DOI: http://dx.doi.org/10.1016/j.scitotenv.2016.06.006

PERSONAL CARE PRODUCTS

What are Personal Care Products (PCPs)?

PCPs are a group of organic chemicals added at different products widely used in daily human life (lotions, toothpaste, cosmetics and even food).

PERSONAL CARE PRODUCTS

How many PCPs do you use on a typical day?

(Modified from http://www.ingeniouspress.com/)

PERSONAL CARE PRODUCTS

How many PCPs do you use on a typical day?

I can use between 5 and 17 PCPs of this list

Hair Care	Y/N	Body Care	Y/N	Makeup	Y/N
Shampoo	✖	Bar Soap/Body Wash	✖	Eye base	✖
Conditioner	✖	Hand Soup	✖	BB/CC Cream	
Hair Spray		Body Scrub/Exfoliant		Foundation	
Hair Mousse		Bath SaltsBomb		Concealer	
Hair Mask/Mud	✖	Body Butter		Eyeliner	
Styling Gel/Wax		Deodorant	✖	Eyebrow Liner	
Total		Lotion	✖	Mascara	✖
Facial Care		Body Oil	✖	Eye Shadow	✖
Makeup Remover	✖	After Wax Cream		Lip liner	
Cleanser		Sunscreen	✖	Lipstick	✖
Exfoliant		Bug Spray		Loose Powder	
Toner		Perfume	✖	**Total**	
Facial Serum/Oil		**Total**			
Day Cream	✖	**Hands & Feet**			
Night Cream	✖	Hand Cream			
Eye Cream		Foot Cream			
Mask/Peel		Foot Exfoliant			
Lip Balm		Cuticle Oil			
Shaving Cream		Nail Polish			
Aftershave		Nail Polish Remover			

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PERSONAL CARE PRODUCTS

THE AIMS OF THE STUDY:

❖ Investigate the occurrence and to asses the fate of selected PCPs in the urban river-groundwater interface using mixing analysis.

❖ Assess the environmental risk of PCPs

UV filters
Parabens
Triazoles

Study area: Besòs River Delta catchment (NE Spain)
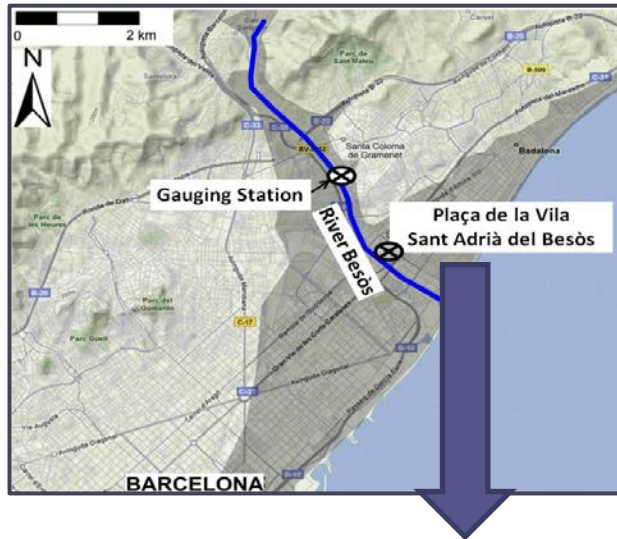
- ❖ Urban aquifer
- ❖ Reducing environment
- ❖ Besòs River is the main aquifer recharge source.
- ❖ Underground car park pumping 150 l/s
- ❖ Monitoring system (6 observation points)

Plaça de la Vila observation points
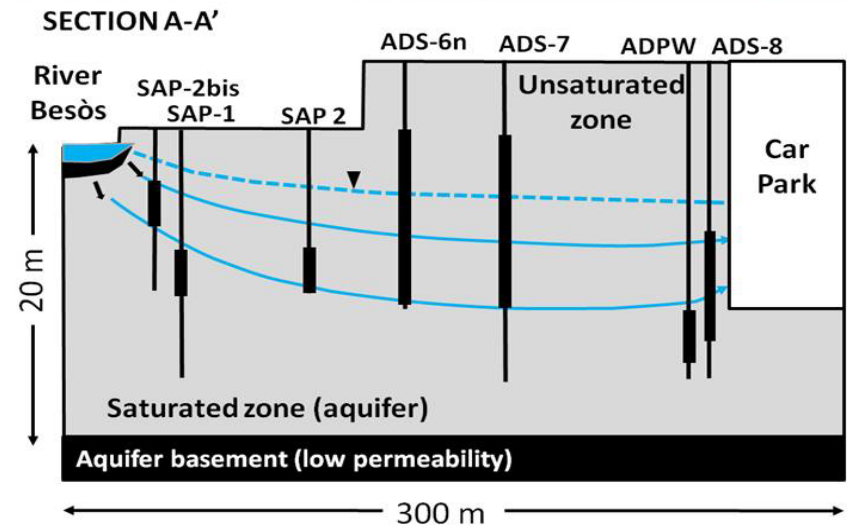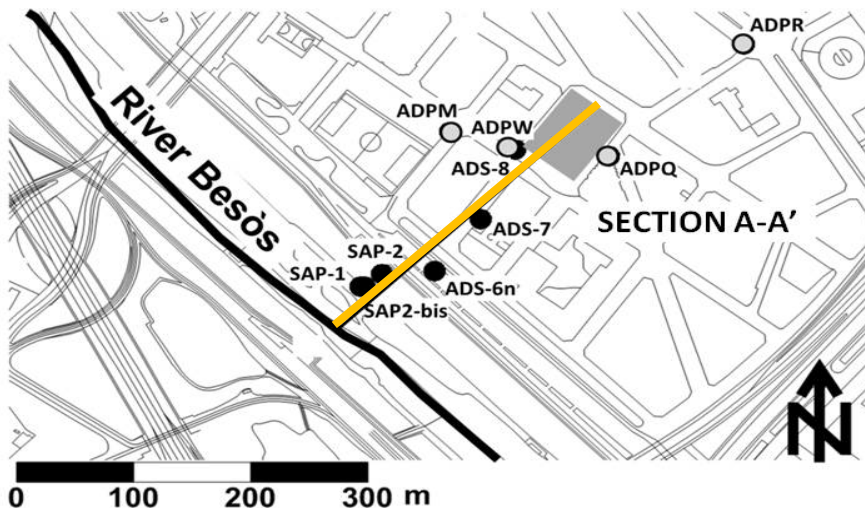
PERSONAL CARE PRODUCTS

Sampling campaigns

General analysis

PCPs (13, C1-C3)
- ❖ UV Filters (6, C1-C3)
- ❖ Triazoles (3, C2-C3)
- ❖ Parabens (4, C2-C3)

PCPs	Target compounds	Acronym	Sampling Campaign		
			C1	C2	C3
UV-Filters	Benzophenone 1	BP1	X	X	X
	Benzophenone 3	BP3	X	X	X
	Benzophenone 4	BP4	X	X	X
	4,4'-Dihydroxybenzophenone	4DHB	X	X	X
	Ethyl-PABA	Et-PABA	X	X	X
	4-Methylbenzylidene camphor	4MBC	X	X	X
Triazoles	Benzotriazole	BZT		X	X
	Methyl Benzotriazole	MeBZT		X	X
	Dimethyl Benzotriazole	DMBZT		X	X
Parabens	Benzylparaben	BePB		X	X
	Butylparaben	BuPB		X	X
	Propylparaben	PrPB		X	X
	Methylparaben	MePB		X	X

PERSONAL CARE PRODUCTS

General results

PCPs	Analyte	Frequency of detection (%)	Concentrations (ng/L)	
			Range	Max.
UV-Filters	BP1	17	nd-10	10
	BP3	42	nd-10.5	10.5
	BP4	8	nd-34.4	34.4
	4DHB	8	nd-10.5	10.5
	4MBC	73	nd-73.1	73.1
	Et-PABA	8	nd-19	19
Triazoles	BZT	100	626-1500	1500
	MeBZT	100	358-1980	1980
	DMBZT	8	nd-59.7	59.7
Parabens	MePB	25	nd-194	194
	PrPB	8	nd-61.9	61.9
	BuPb	0	nd	-
	BePb	0	nd	-

PERSONAL CARE PRODUCTS

General results

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			Range	Max.
UV-Filters	BP1	17	nd-10	10
	BP3	42	nd-10.5	10.5
	BP4	8	nd-34.4	34.4
	4DHB	8	nd-10.5	10.5
	4MBC	73	nd-73.1	73.1
	Et-PABA	8	nd-19	19
Triazoles	BZT	100	626-1500	1500
	MeBZT	100	358-1980	1980
	DMBZT	8	nd-59.7	59.7
Parabens	MePB	25	nd-194	194
	PrPB	8	nd-61.9	61.9
	BuPb	0	nd	-
	BePb	0	nd	-

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PERSONAL CARE PRODUCTS

General results

PCPs	Analyte	Frequency of detection (%)	Concentrations (ng/L)	
			Range	Max.
UV-Filters	BP1	17	nd-10	10
	BP3	42	nd-10.5	10.5
	BP4	8	nd-34.4	34.4
	4DHB	8	nd-10.5	10.5
	4MBC	73	nd-73.1	73.1
	Et-PABA	8	nd-19	19
Triazoles	BZT	100	626-1500	1500
	MeBZT	100	358-1980	1980
	DMBZT	8	nd-59.7	59.7
Parabens	MePB	25	nd-194	194
	PrPB	8	nd-61.9	61.9
	BuPb	0	nd	-
	DePb	0	nd	-

PERSONAL CARE PRODUCTS

General results

PCPs	Analyte	Frequency of detection (%)	Concentrations (ng/L)	
			Range	Max.
UV-Filters	BP1	17	nd-10	10
	BP3	42	nd-10.5	10.5
	BP4	8	nd-34.4	34.4
	4DHB	8	nd-10.5	10.5
	4MBC	73	nd-73.1	73.1
	Et-PABA	8	nd-19	19
Triazoles	BZT	100	626-1500	1500
	MeBZT	100	358-1980	1980
	DMBZT	8	nd-59.7	59.7
Parabens	MePB	25	nd-194	194
	PrPB	8	nd-61.9	61.9
	BuPb	0	nd	-
	BePb	0	nd	-

Detailed results

PCPs	Analyte	Frequency of detection (%)			Max. Concentrations (ng/L)		
		C1 (n=5)	C2 (n=5)	C3 (n=6)	C1	C2	C3
UV-Filters	BP1	20	0	33	10	-	10
	BP3	40	0	83	10.5	-	10.5
	BP4	20	0	17	10	-	34.4
	4DHB	0	0	17	-	-	10.5
	Et-PABA	0	0	17	-	-	19
	4MBC	60	80	83	12	30	73.1
Triazoles	BZT		100	100		1500	1350
	MeBZT		100	100		1980	918
	DMBZT		0	17		-	59.7
Parabens	MePB		0	67		-	194
	PrPB		0	17		-	61.9
	BuPB		0	0		-	-
	BePB		0	0		-	-

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PERSONAL CARE PRODUCTS

Detailed results

PCPs	Analyte	Frequency of detection (%)			Max. Concentrations (ng/L)		
		C1 (n=5)	C2 (n=5)	C3 (n=6)	C1	C2	C3
UV-Filters	BP1	20	0	33	10	-	10
	BP3	40	0	83	10.5	-	10.5
	BP4	20	0	17	10	-	34.4
	4DHB	0	0	17	-	-	10.5
	Et-PABA	0	0	17	-	-	19
	4MBC	60	80	83	12	30	73.1
Triazoles	BZT		100	100		1500	1350
	MeBZT		100	100		1980	918
	DMBZT		0	17		-	59.7
Parabens	MePB		0	67		-	194
	PrPB		0	17		-	61.9
	BuPB		0	0		-	-
	BePB		0	0		-	-

PERSONAL CARE PRODUCTS

Detailed results

PCPs	Analyte	Frequency of detection (%)			Max. Concentrations (ng/L)		
		C1 (n=5)	C2 (n=5)	C3 (n=6)	C1	C2	C3
UV-Filters	BP1	20	0	33	10	-	10
	BP3	40	0	83	10.5	-	10.5
	BP4	20	0	17	10	-	34.4
	4DHB	0	0	17	-	-	10.5
	Et-PABA	0	0	17	-	-	19
	4MBC	60	80	83	12	30	73.1
Triazoles	BZT		100	100		1500	1350
	MeBZT		100	100		1980	918
	DMBZT		0	17		-	59.7
Parabens	MePB		0	67		-	194
	PrPB		0	17		-	61.9
	BuPB		0	0		-	-
	BePB		0	0		-	-

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Fate of the PCPs in groundwater
Main recharge source is the River Besòs
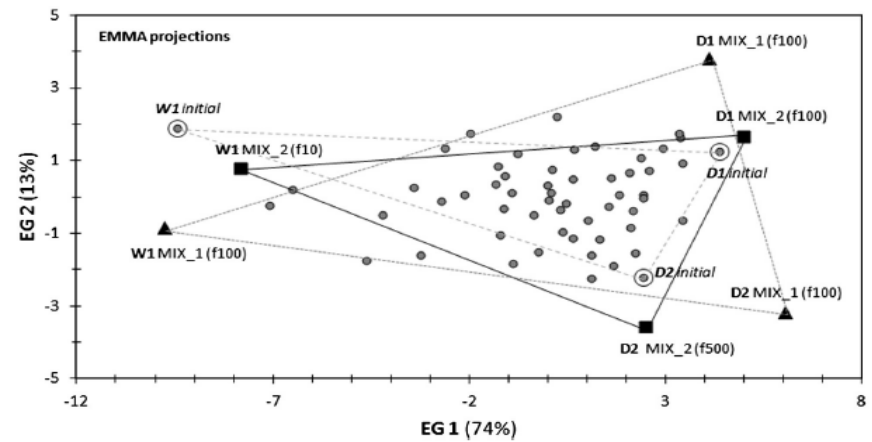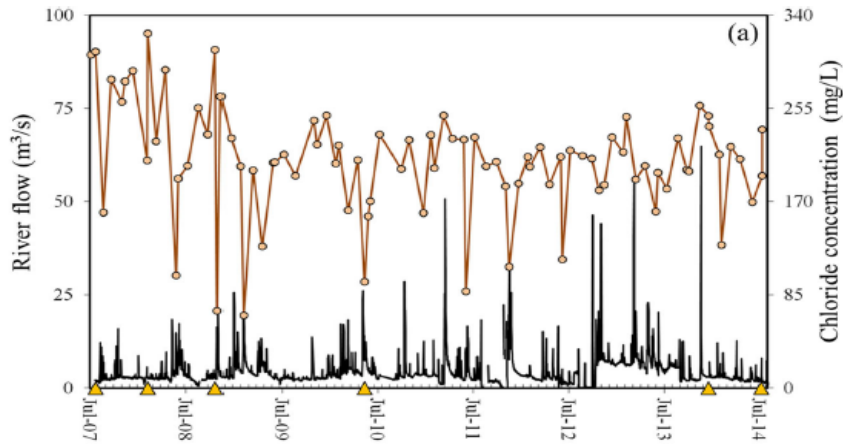
EMMA→ River Besòs seasonal variability

Fate of the PCPs in groundwater

Main recharge source is the River Besòs

EMMA→ River Besòs seasonal variability
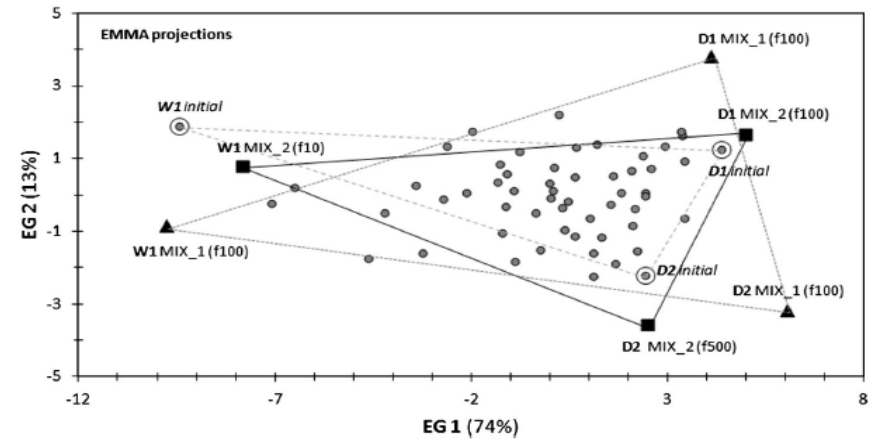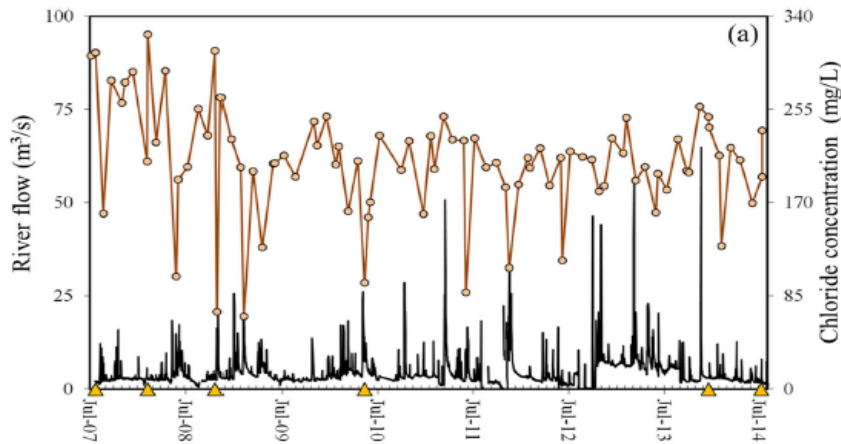
Besòs River ➡ **3** river **end-members** are necessary **to characterize** the chemical **variability** of the river

River Besòs end-member (mg/L) (Tubau et al., 2014)

Recharge sources		Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	EC	NO_3^-	NH_4^+	Mg^{2+}	TOC	O_2	Na^+	K^+
Wet river end-member	(W1)	43.7	52.8	222.7	62.2	586	13.4	4.1	13.3	6.3	8.7	29.0	7.2
Dry river end-member 1	(D1)	356.2	205.9	500.5	139.9	1977	7.4	31.5	24.2	12.4	8.3	280.9	51.1
Dry river end-member 2	(D2)	315.8	198.6	470.3	151.3	1891	13.2	3.6	30.1	8.7	10.6	246.6	36.4

PERSONAL CARE PRODUCTS

Fate of the PCPs in groundwater

Evaluation of the **proportions** in which river **end-members** **contribute** to the **resident water** of the aquifer for the 3 sampling campaigns
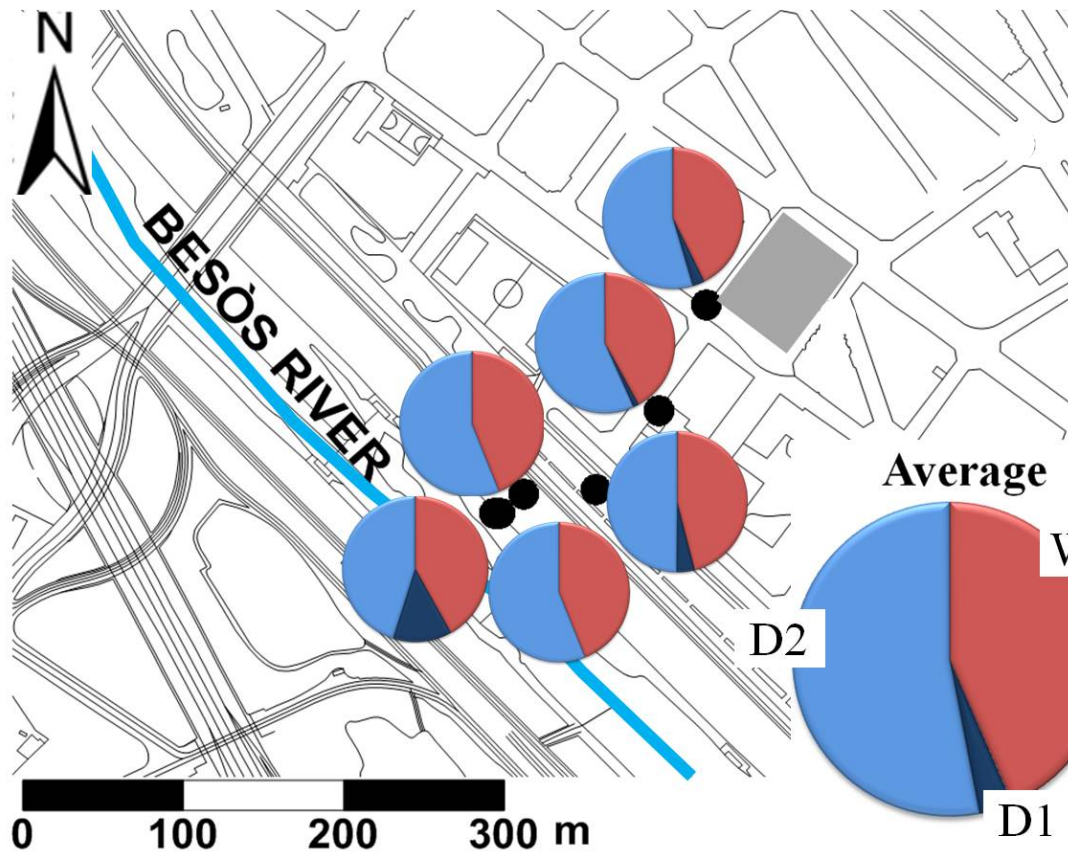
Average mixing ratios

Campaign	W1	D1	D2
C1	40.6	7.1	52.3
C2	44.1	3.5	52.5
C3	44.4	3.3	52.3
Cm	43.1	4.6	52.3

PERSONAL CARE PRODUCTS

Fate of the PCPs in groundwater

PCP concentrations in the recharge sources

Analyte	Besòs River concentrations (ng/L)	
	Measured	Bibliography
UV-Filters		
BP1	nd-10	31.2-48.2
BP3	24.9-58	20.9-52.2
4MBC	nd-12	<LOQ-13.1
Triazoles		
BZT	744-965	1080-2855.6
MeBZT	622-1340	925-5004
Parabens		
MePB	nd-102	-

Concentration of the PCPs in the River Besòs end-members

River end-members	BP1	BP3	4MBC	BZT	MeBZT	MePb
D1	20	40	37	1716	2018	121
D2	26	53	45	2241	2637	158
W1	3	7	5	279	328	20
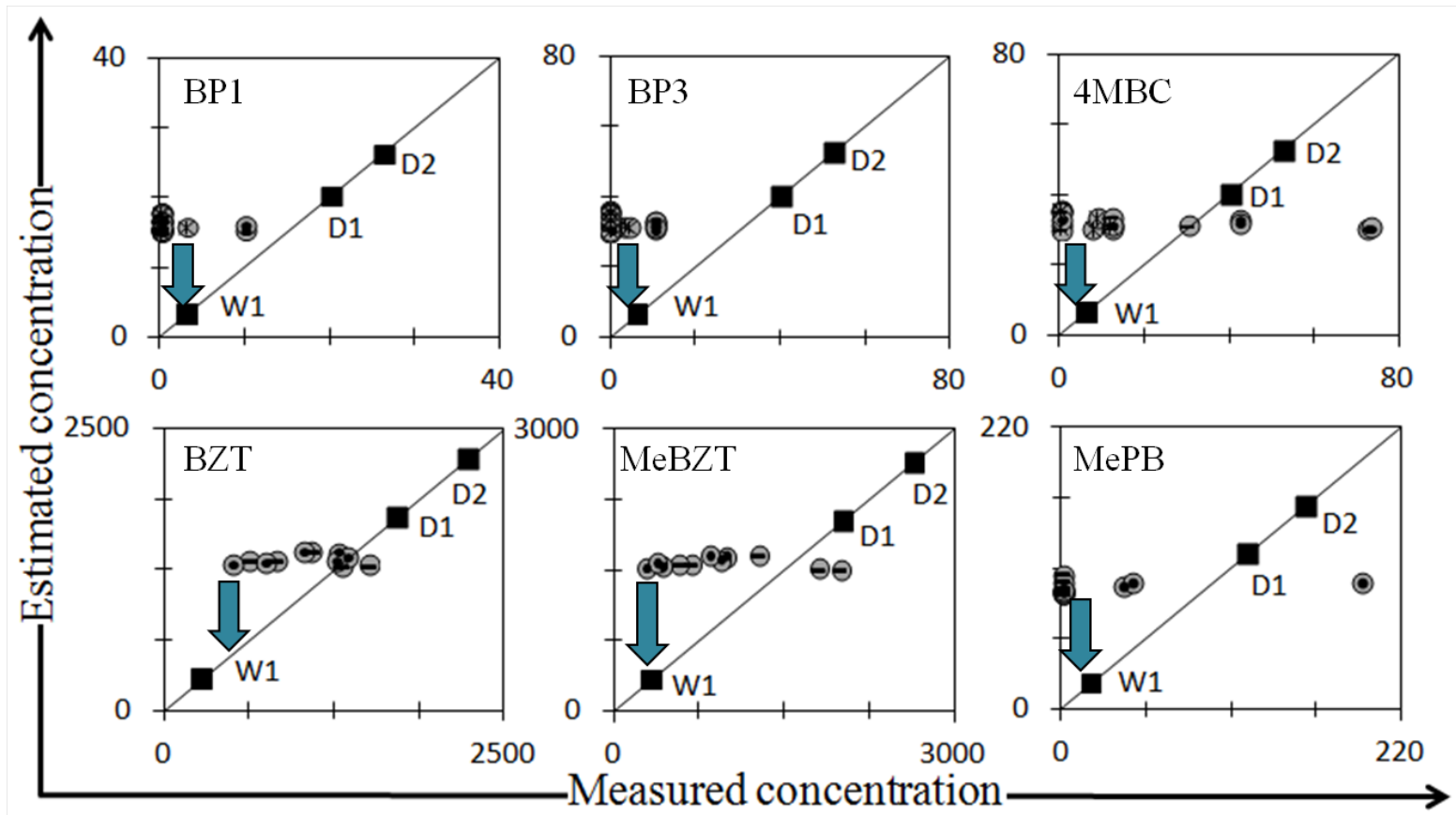
Fate of the PCPs in groundwater

Fate of the PCPs in groundwater

Which are the most persistent PCPs?

$$RR\ (\%) = 100\ x\ \frac{Ce - Cm}{Ce}$$

Ce = estimated concentration (Mix Code)
Cm = measured concentration

BZT>MeBZT>4MBC>MePb>BP3>BP1

	RR (%)		
	C1	**C2**	**C3**
BP1	87	100	83
BP3	87	100	77
MePb	-	94	76
4MBC	78	58	62
MeBZT	-	49	64
BZT	-	38	24

PERSONAL CARE PRODUCTS

Fate of the PCPs in groundwater

PCPs	Analyte	Frequency of detection (%)	Concentrations (ng/L)	
			Range	Max.
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	BuPb	0	nd	-
	BePb	0	nd	-

PERSONAL CARE PRODUCTS

Environmental risk assessment

❖A risk assessment was conducted for the PCPs using hazard quotients (HQ)

$$HQ = \frac{\text{Exposure concentration}}{\text{Toxicological benchmark concentration}}$$

❖ The estimated HQ corresponded to the aquatic species *Vibrio fischeri*, *Daphnia magna*, *Raphidocelis subcapitata*, *Ceriodaphnia dubia* and *Pimephales promelas*.

❖Individual HQs are very low: of 10^{-4} to 10^{-2} →PCPs do not present any environmental in the range of concentrations found in river and ground samples for all the species assayed.

GENERAL CONCLUSIONS

❖ Urban **groundwater** of Barcelona contains DAs and PCPs in **low** but **measurable concentrations.** Only **two** triazoles were found at **significant concentrations**: MeBZT (1980 ng/L) and BZT (1500 ng/L).

❖DAs have been **more** widely **detected** in **Besòs River Delta** than in Poble Sec and Mallorca Street. This is due to the fact that River Besòs receives large amounts of WWTPs effluents.

❖**Concentrations** in the **aquifer** are generally much **lower** than those expected due to mixing, as calculated by mixing ratios. This might suggest **significant removal** of **DAs** (PS, MS, SAD) and **PCPs** in the **aquifers.** However, **triazoles** are **barely removed** under the reducing conditions of Besòs River Delta aquifer.

GENERAL CONCLUSIONS

❖**Redox conditions** of the aquifer play a **major role** in the **removal** of EOCs in the aquifer.

❖ The **potential environmental risk** posed by PCPs has been evaluated in the river-groundwater interface **resulting in no hazard** for the species assayed.

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