

Mitigation of Pesticides and Copper in a Stormwater Wetland



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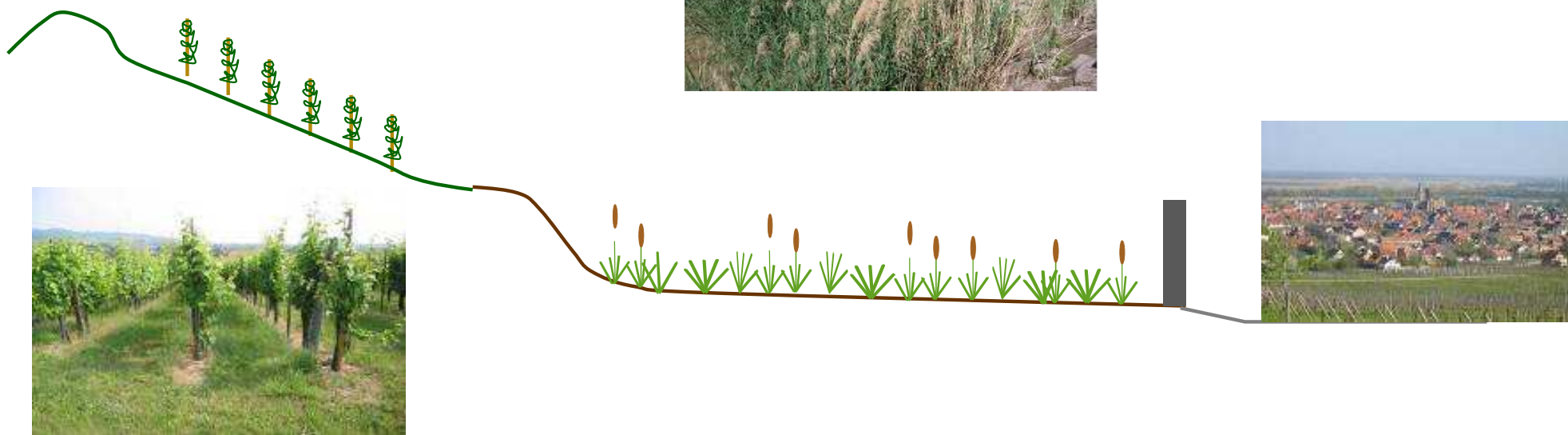
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University of Strasbourg/ENGEEES, CNRS, Strasbourg, France

Stormwater wetlands connected to an agricultural catchment

**Agricultural/urban
catchment**

Stormwater wetland

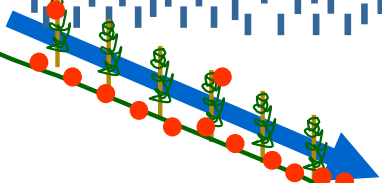
Town



Stormwater wetlands connected to an agricultural catchment

**Agricultural/urban
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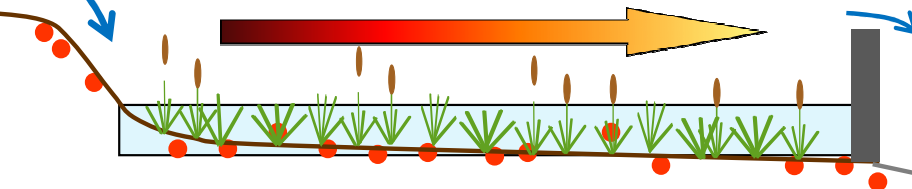
Pesticides



Stormwater wetland



Town

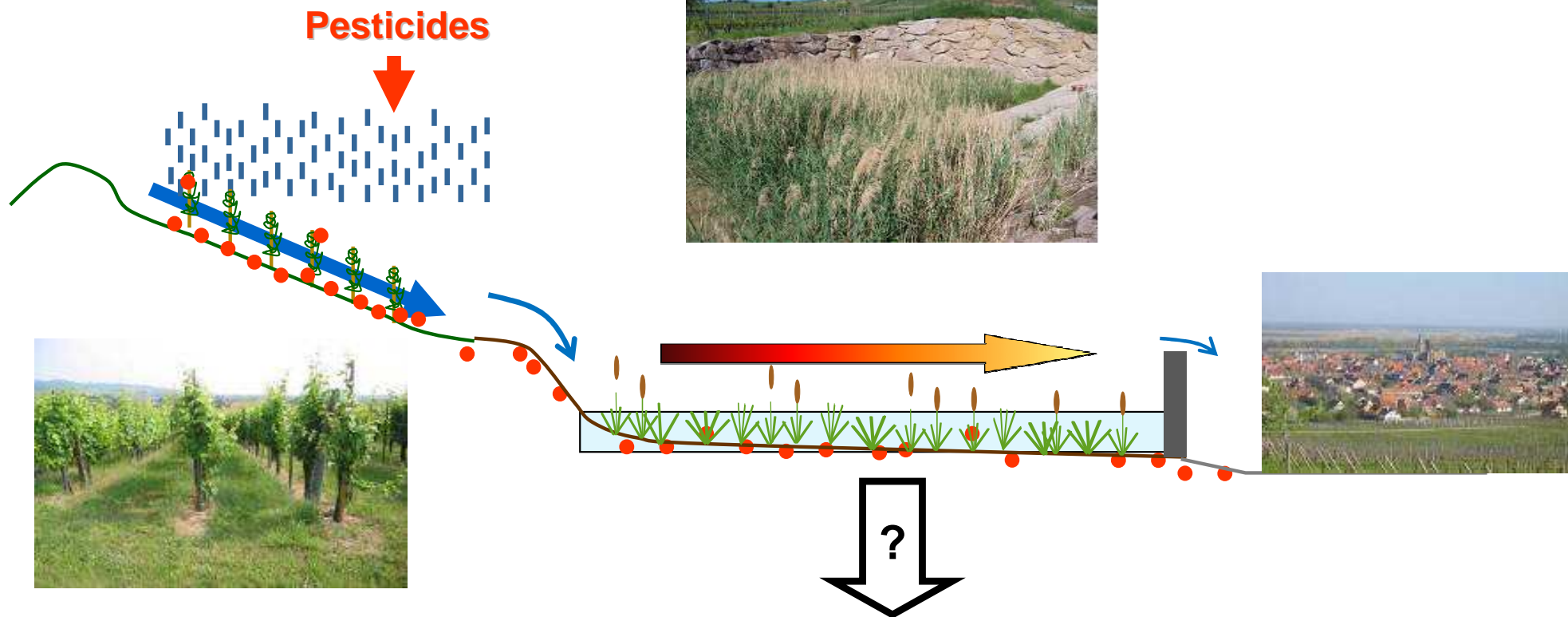


Stormwater wetlands connected to an agricultural catchment

**Agricultural/urban
catchment**

Stormwater wetland

Town



1. What is the capacity of stormwater wetlands to remove pesticide mixtures?
2. How is glyphosate and AMPA transported in stormwater wetlands?
3. How stormwater wetlands retain copper?

Stormwater wetlands collecting runoff: vineyard catchment

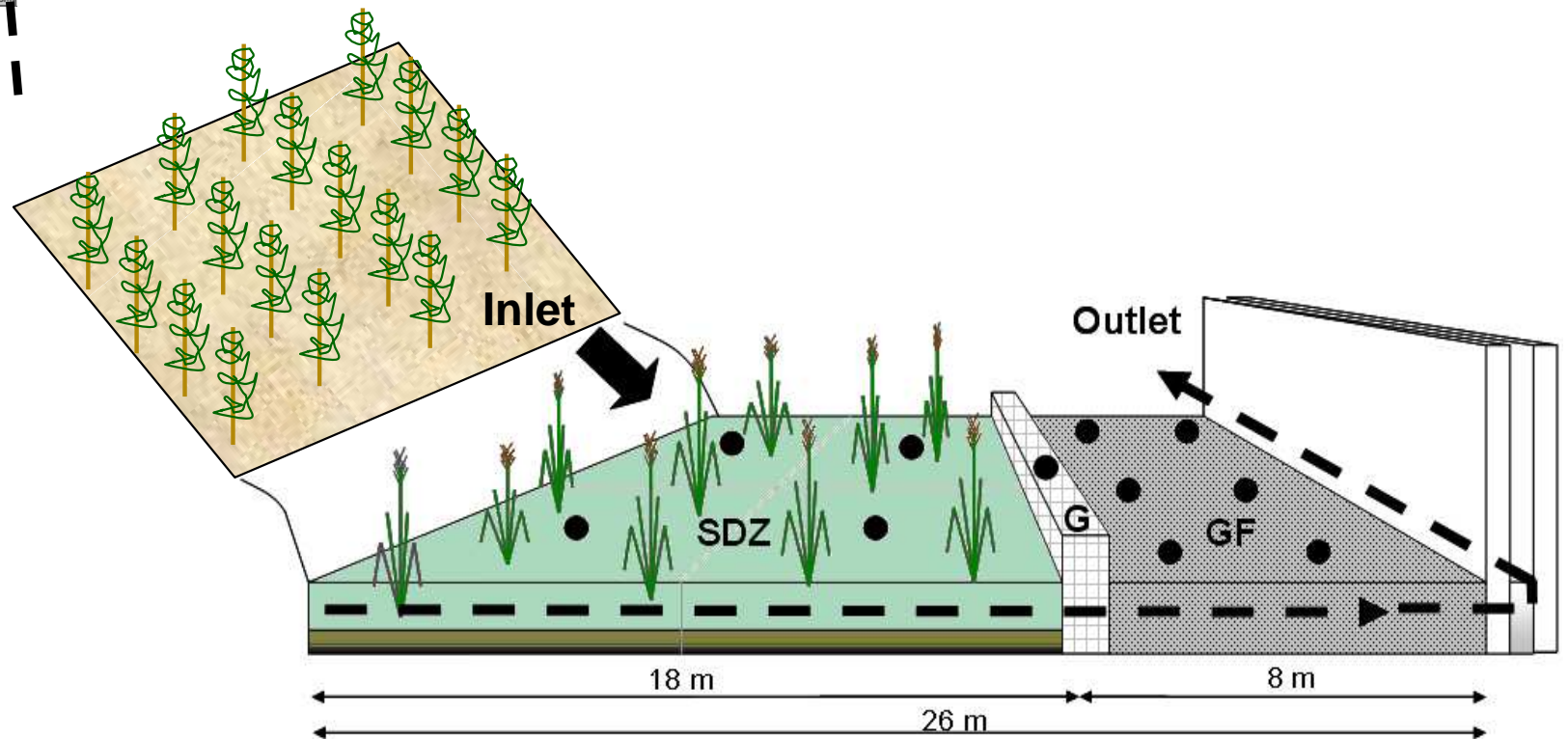
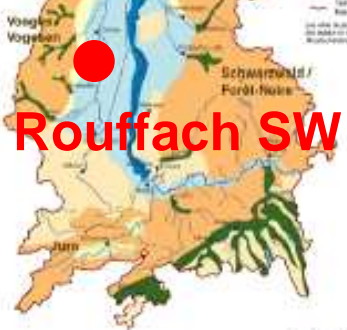
France



Alsace

Upper Rhine Region

France → 112 SW
Germany → 148 SW



Stormwater wetlands collecting runoff: vineyard catchment

France

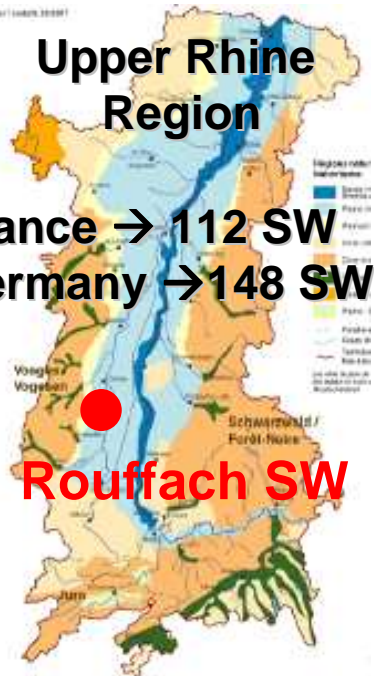


Alsace

Upper Rhine
Region

France → 112 SW
Germany → 148 SW

Rouffach SW



Catchment:

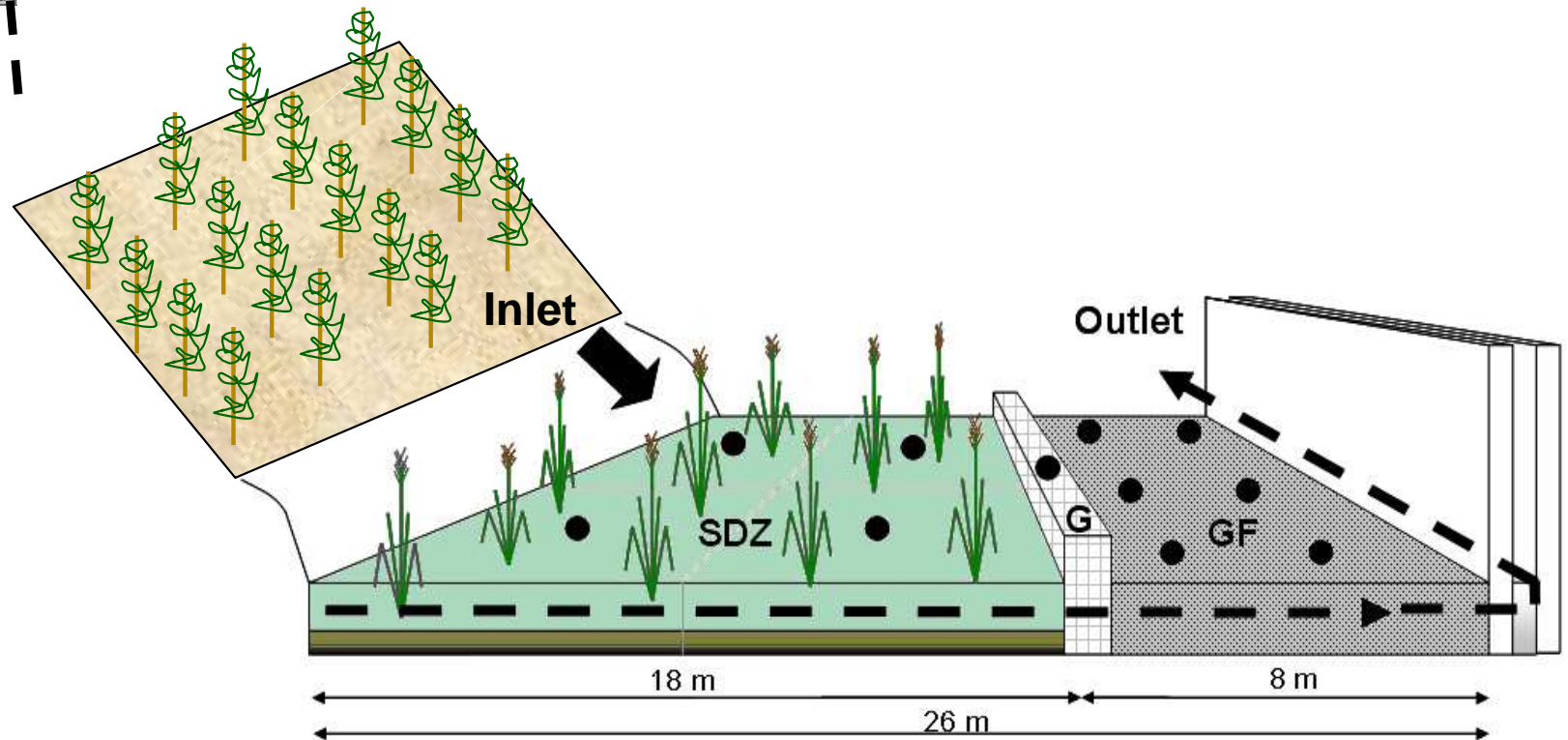
- Area : 42.7 ha
- 67 % vineyard
- Mean slope: 15 %
- P_{yearly} : 600 mm
- Runoff coeff.: 0.2 – 1.2%

• Pesticide application $\approx 50 \text{ kg y}^{-1}$

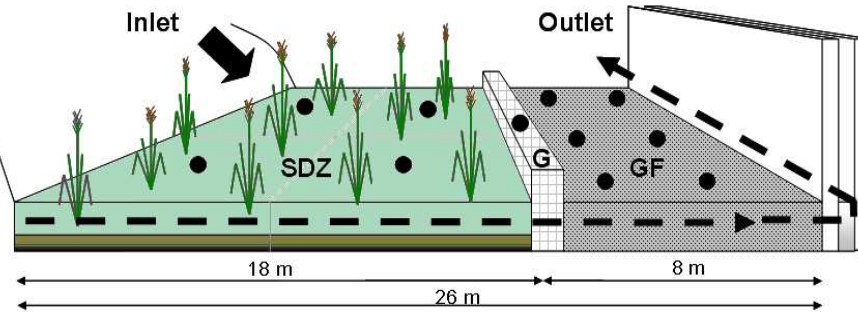
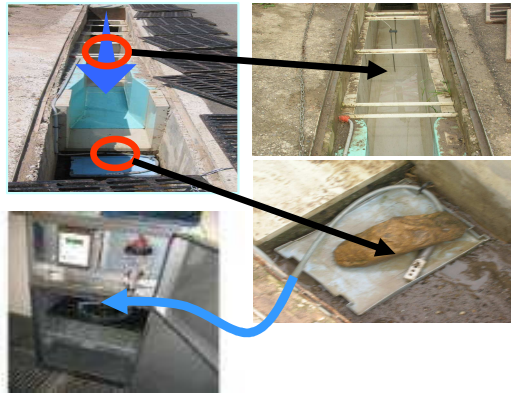
Wetland:

- Surface: 320 m²
- Volume: 1500 m³
- HRT: 8-12 hs
- Quiescent period: 10 d
- Vegetation: *Phragmites australis*

• Pesticide in runoff $\approx 10 \text{ g y}^{-1}$



Sampling scheme and analyses

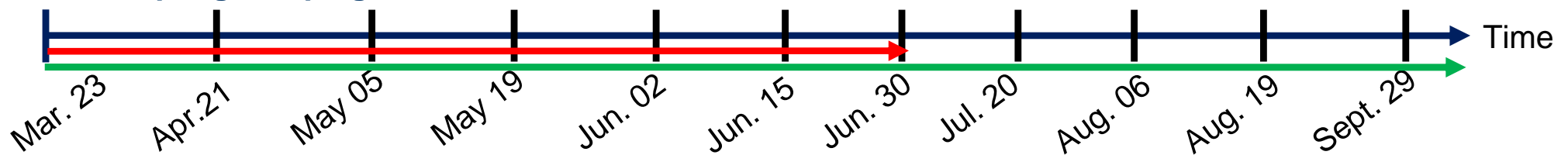


- Discharge measurements
- Hydrochemical parameters
- Pesticide analysis: (+Copper)
 - *Runoff water*
 - *Wetland water column*
 - *Suspended solids*
 - *Wetland sediments*

8 Fungicides
7 Herbicides
1 Insecticide
4 Degradation products

Mass balances ←

⇒ Sampling campaigns in 2009, 2010 and 2011



Selection of pesticides

Molecule	Log K_{ow}	Aqueous photolysis DT ₅₀ (pH = 7)	Aqueous hydrolysis DT ₅₀ (20°C, pH = 7)
	[-]	[day]	[day]
Azoxystrobine	2.50	8.7	stable
Cymoxanil	0.67	1.7	1.1
Cyprodinil	4.00	13.5	stable
Carbendazim	1.48	stable	350
Dimethomorphe	2.68	97	70
Diuron	2.87	43	Stable
<i>DCPU</i>	n.a.	n.a.	n.a.
<i>DCPMU</i>	n.a.	n.a.	n.a.
<i>3.4-dichloroaniline</i>	2.69	0.25	n.a.
Flufenoxuron	4.01	6	267
Gluphosinate	-3.96	n.a.	n.a.
Glyphosate	-3.2	69	Stable
<i>AMPA</i>	-1.63	n.a.	n.a.
Isoxaben	3.94	6	Stable
Kresoxim methyl	3.40	28	34
Metalaxyl	1.65	Stable	106
Pyrimethanile	2.84	Stable	Stable
Simazine	2.30	1.9	96
Terbuthylazine	3.40	Stable	Stable
Tetraconazole	3.56	217	Stable

Fungicides

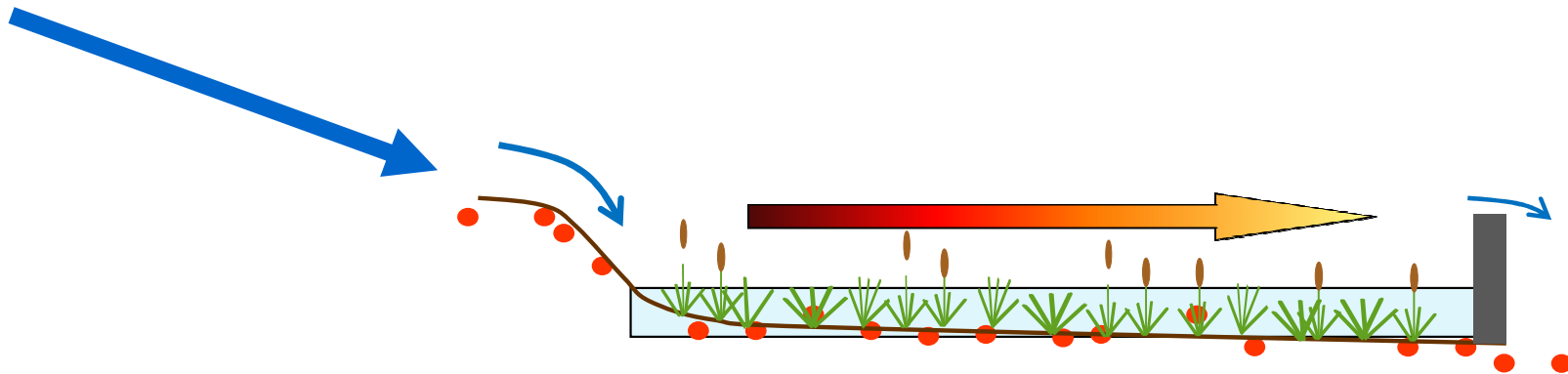
Herbicides

Insecticides

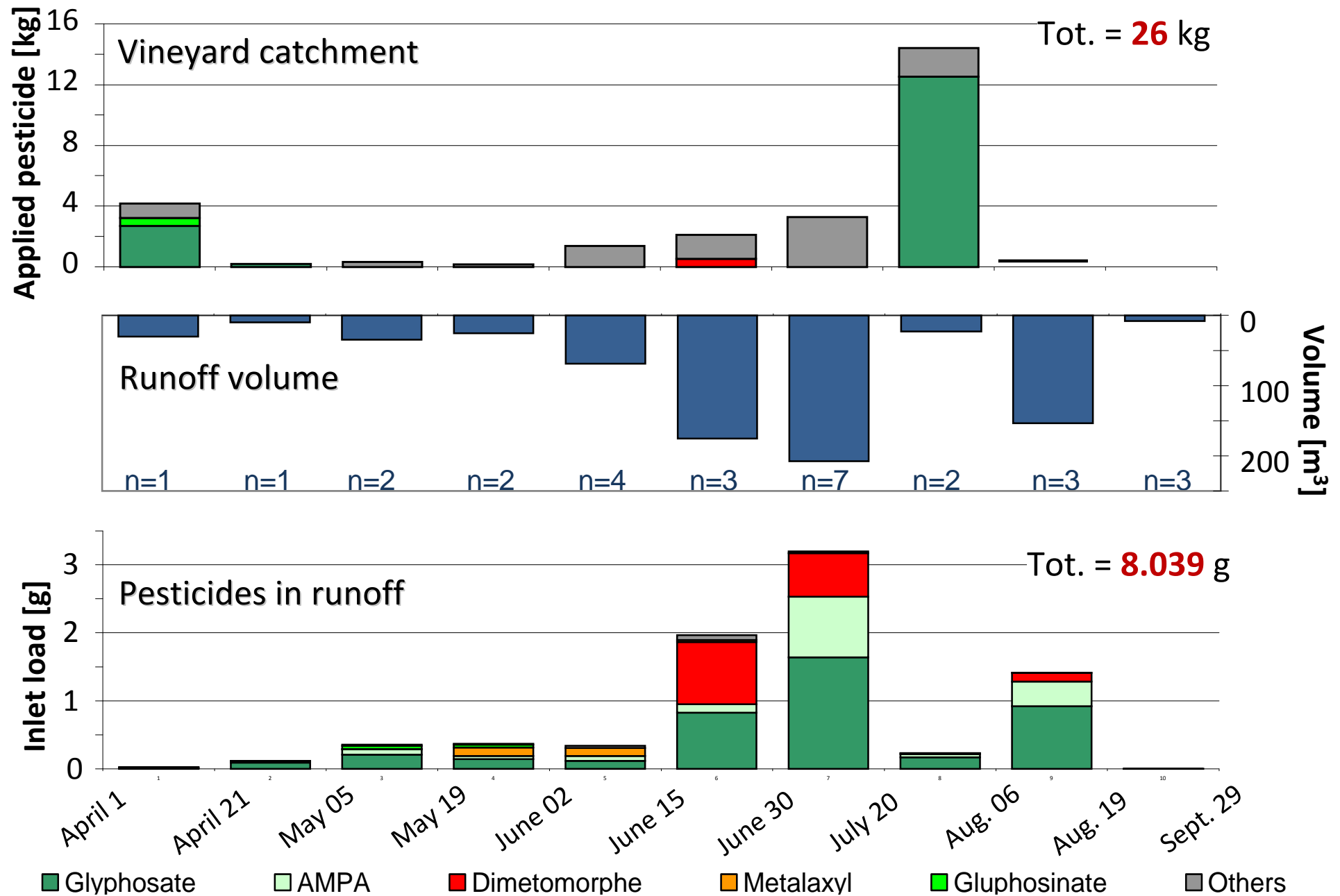
Degradation products

n.a.: not assessed

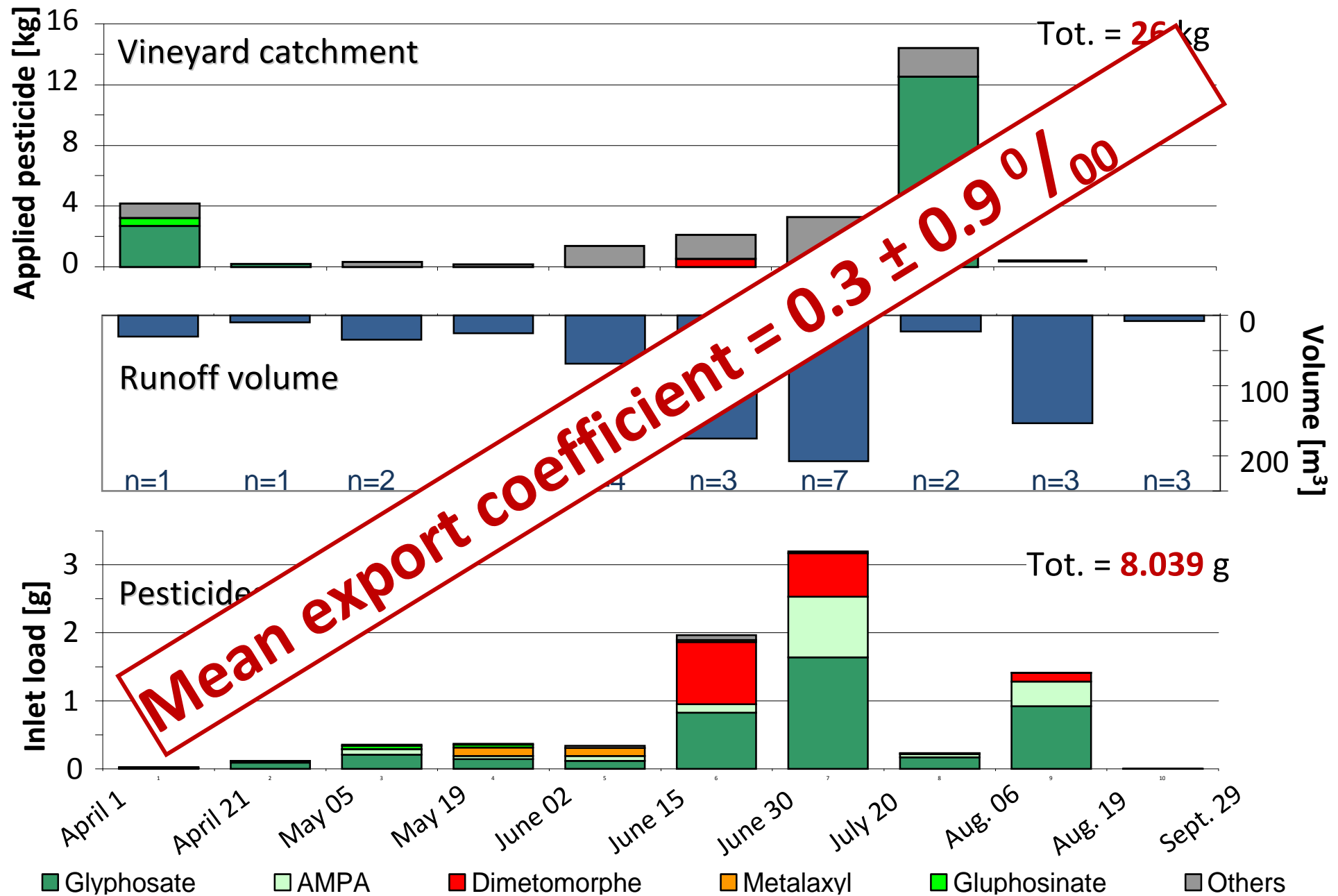
1. What is the capacity of stormwater wetlands to remove pesticide mixtures?



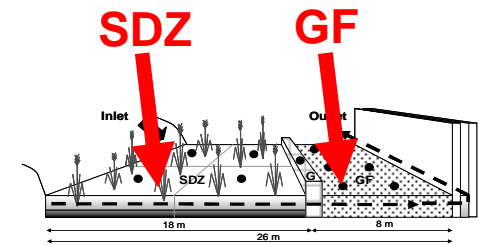
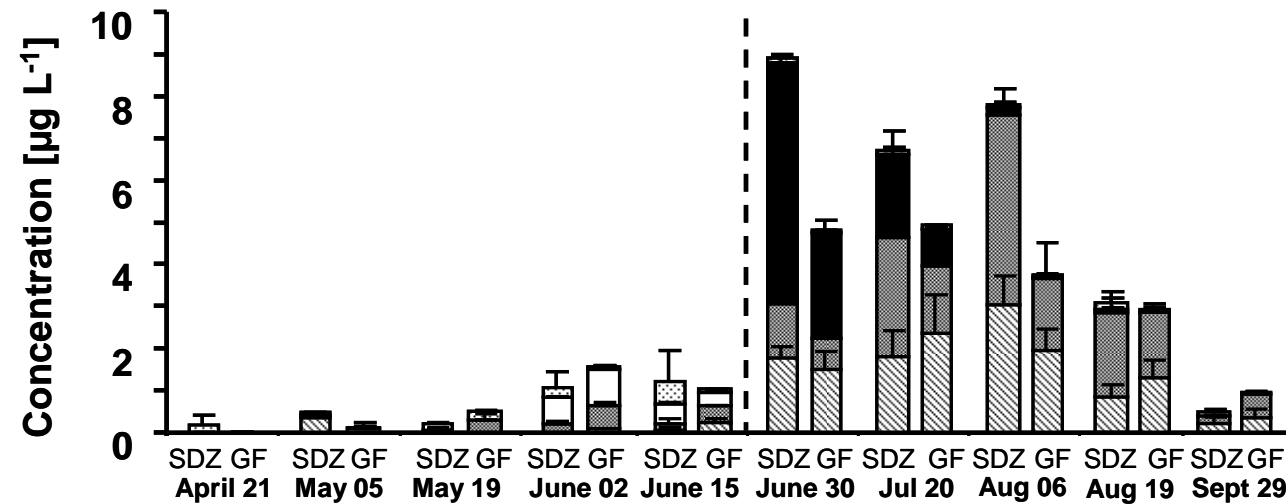
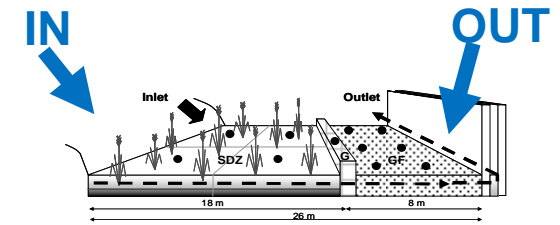
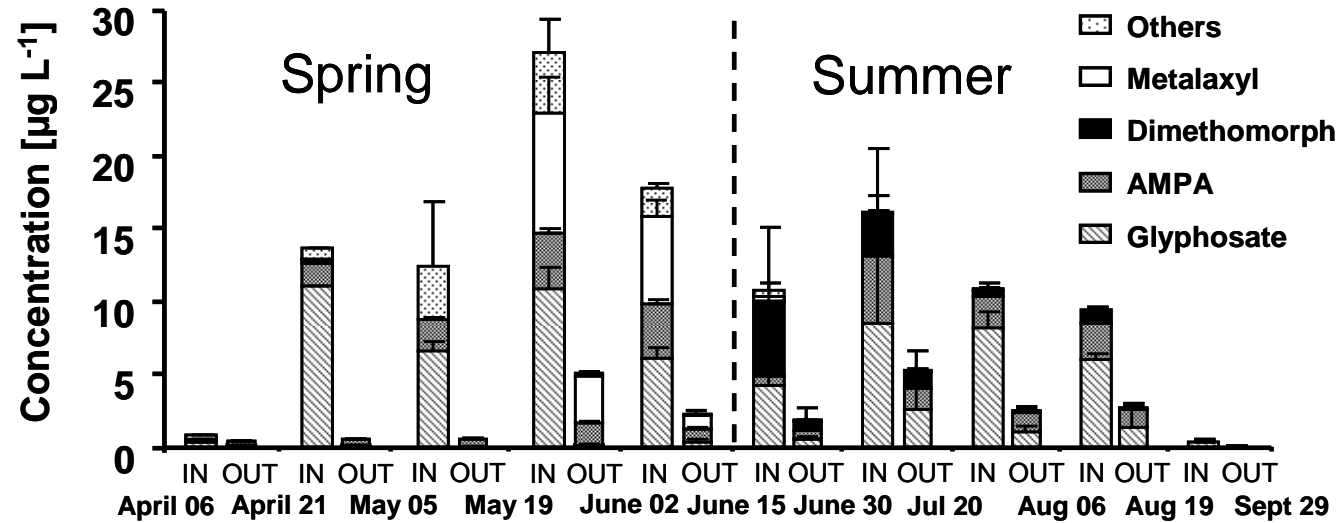
Pesticide mass transfer: vineyard catchment to wetland



Pesticide mass transfer: vineyard catchment to wetland



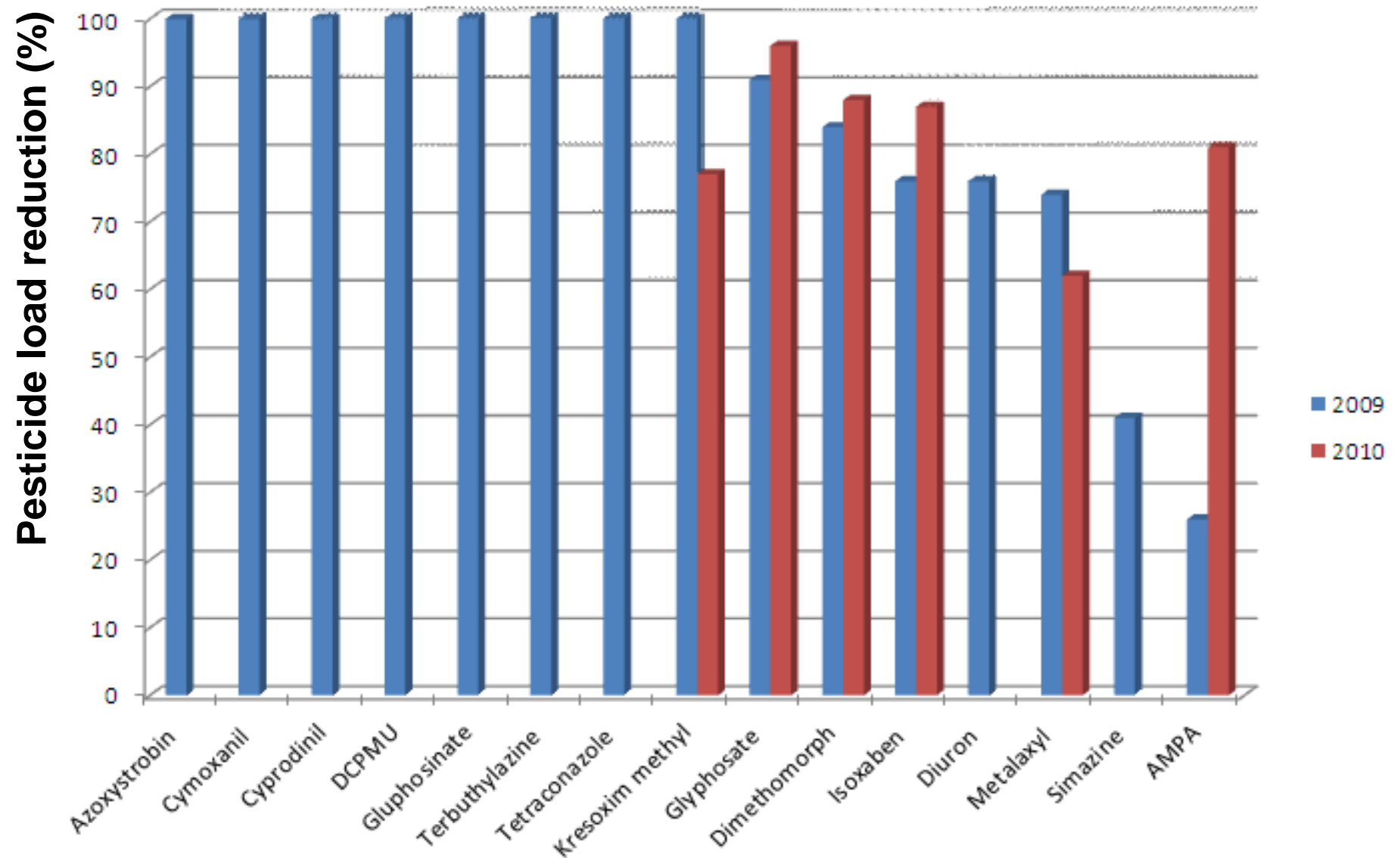
Reduction of pesticide concentration



=> [IN] > [SDZ] > [GF] > [OUT]

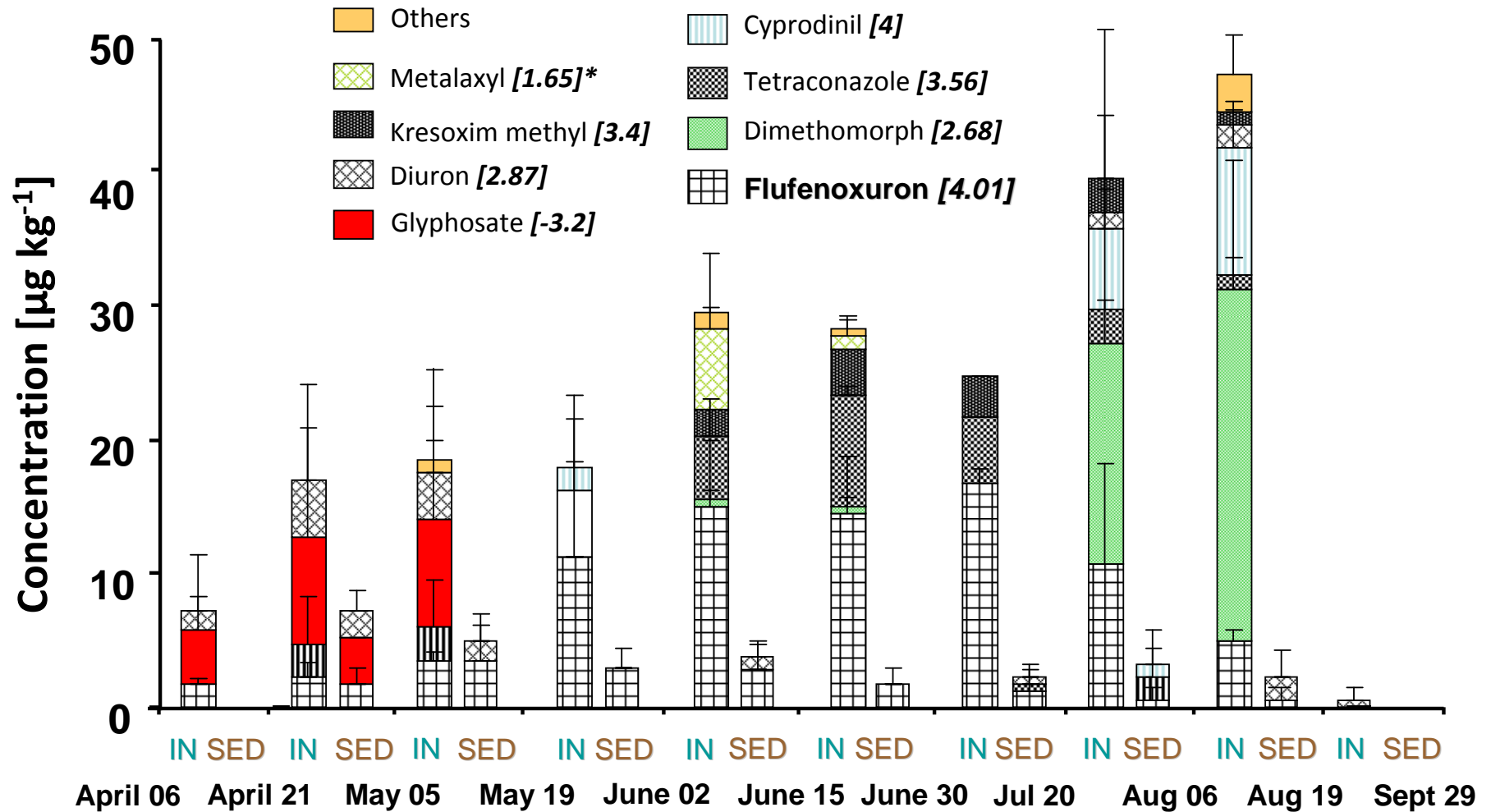
=> High temporal variability: lower efficacy in summer

Annual variation of pesticide removal



Pesticide concentrations in wetland sediments

*Log K_{ow} (PPDB)



=> No temporal accumulation or persistence of pesticides in the wetland sediments

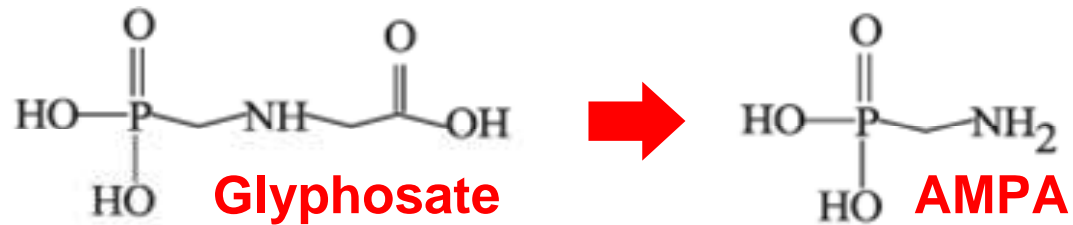
Seasonal variation of pesticides removal

		Spring			Summer		
		Apr. 06 – June 15			June 15 – Sept. 29		
		Inlet	Outlet	R [%]*	Inlet	Outlet	R [%]*
Dissolved pesticides	[mg]	1291	339	72	6819	2181	73
Suspended-solids associated pesticides	[mg]	2.07	n.d.	n.d.	196	n.d.	n.d.
Suspended solids	[kg]	207	3	99	739	99	88
Dissolved organic carbon	[kg]	3.6	5.8	-34	6.1	7.1	-18

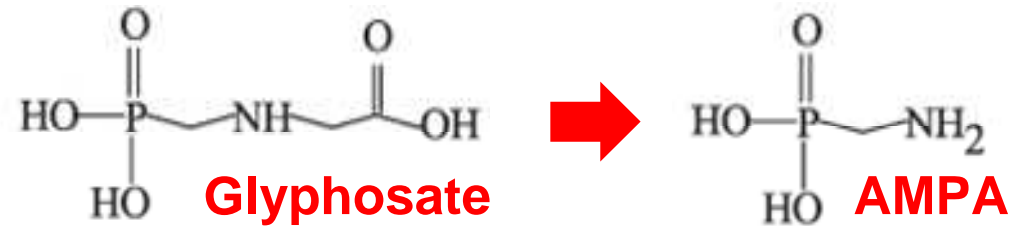
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		Inlet	Outlet	R [%]*	Inlet	Outlet	R [%]*	
Dissolved pesticides	[mg]	1291	339	72	6819	2181	73	➔ No seasonal Changes
Suspended-solids associated pesticides	[mg]	2.07	n.d.	n.d.	196	n.d.	n.d.	➔ Low Kd values
Suspended solids	[kg]	207	3	99	739	99	88	➔ High trapping efficiency
Dissolved organic carbon	[kg]	3.6	5.8	-34	6.1	7.1	-18	➔ Possible transfer as DOC-associated pesticides

2. How is glyphosate and AMPA transported in stormwater wetlands?



Transport of glyphosate and AMPA



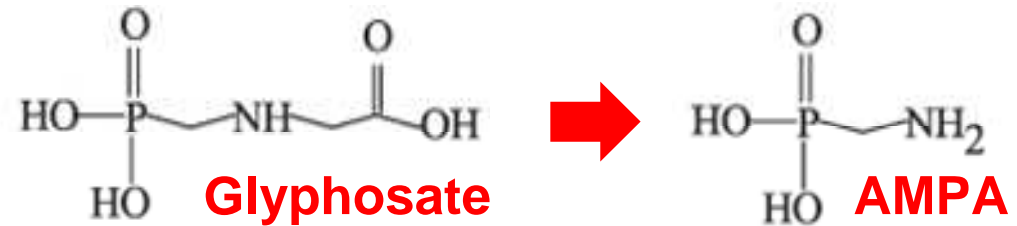
$$MEL_{gly} = \text{Load}(\text{Glyphosate}) + \left\{ \text{Load}(\text{AMPA}) \left[\frac{MW_{gly}}{MW_{AMPA}} \right] \right\}$$

Where

MW_{gly} = molecular weight of glyphosate ($0.16907 \text{ kg mol}^{-1}$)

MW_{AMPA} = molecular weight of AMPA ($0.11104 \text{ kg mol}^{-1}$)

Transport of glyphosate and AMPA



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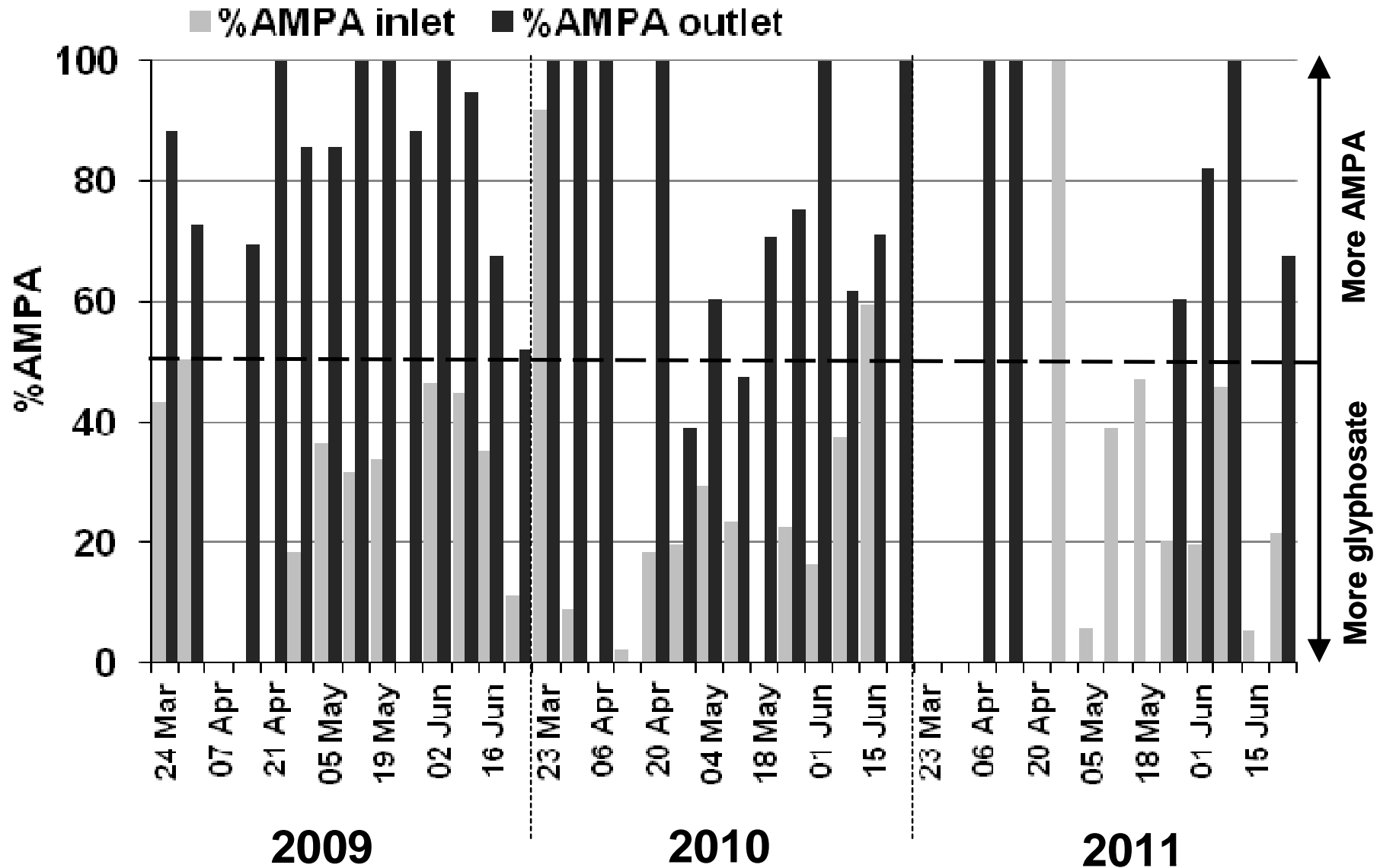
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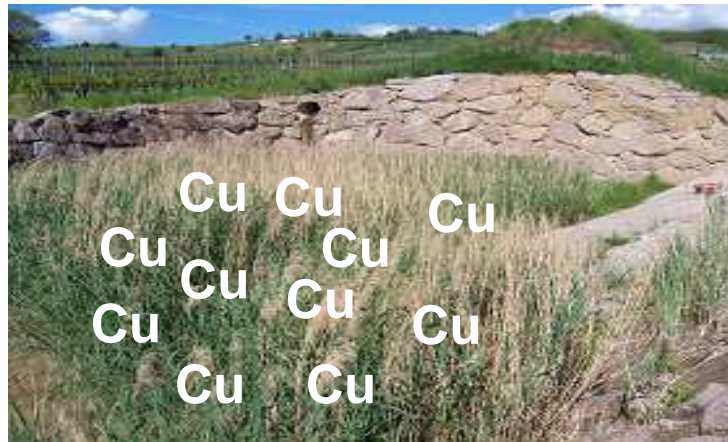
MW_{AMPA} = molecular weight of AMPA ($0.11104 \text{ kg mol}^{-1}$)

	MEL_{gly} (inflow) [mg]	MEL_{gly} (outflow) [mg]	Removal efficiency [%]	% covered by vegetation
2009	2.38	1.78	75%	<1% - 25%
2010	14.10	12.61	90%	100%
2011	20.79	20.52	99%	100%

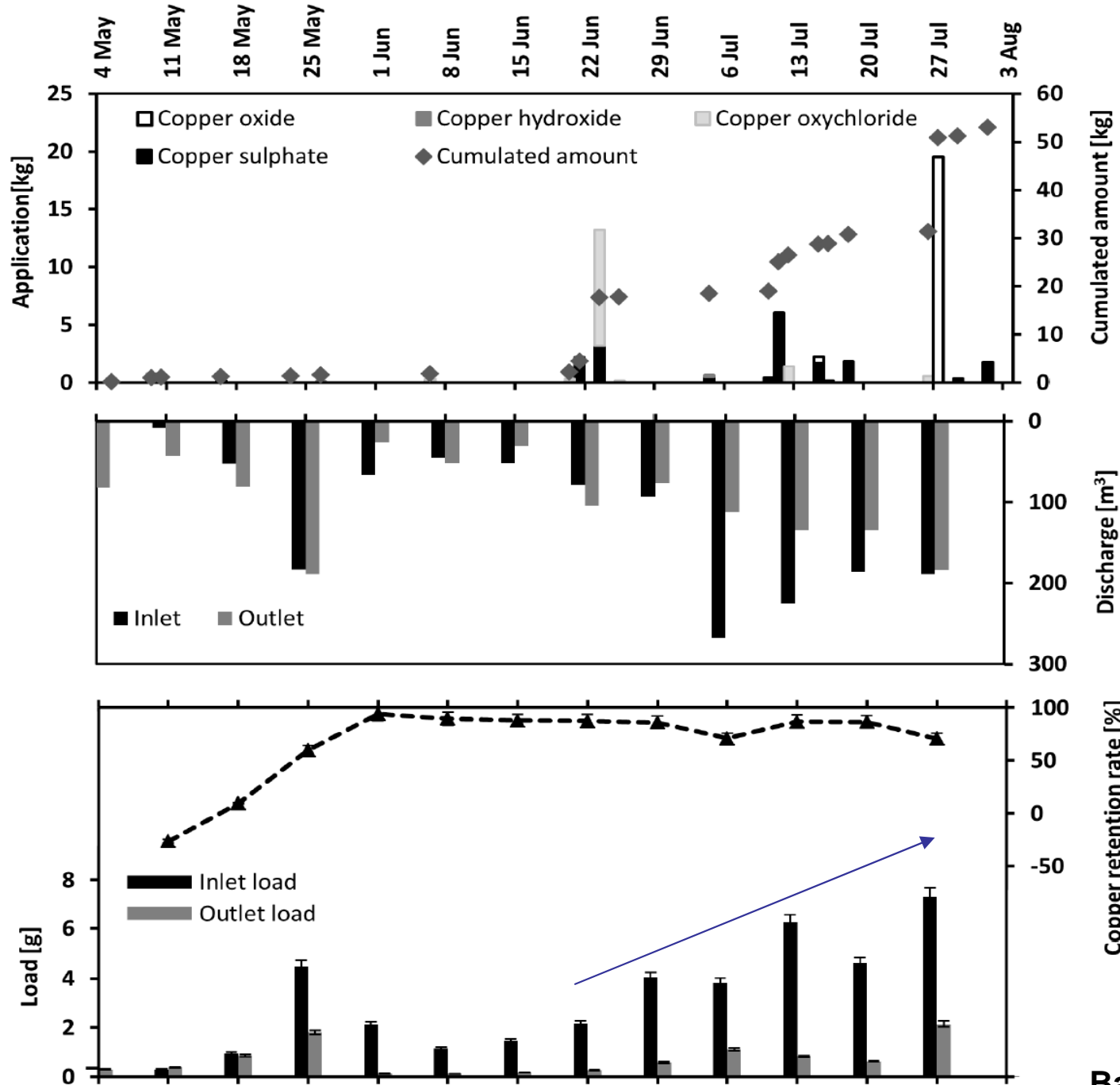
Temporal change of the %AMPA



2. How stormwater wetlands retain copper?



Transport of copper in the wetland

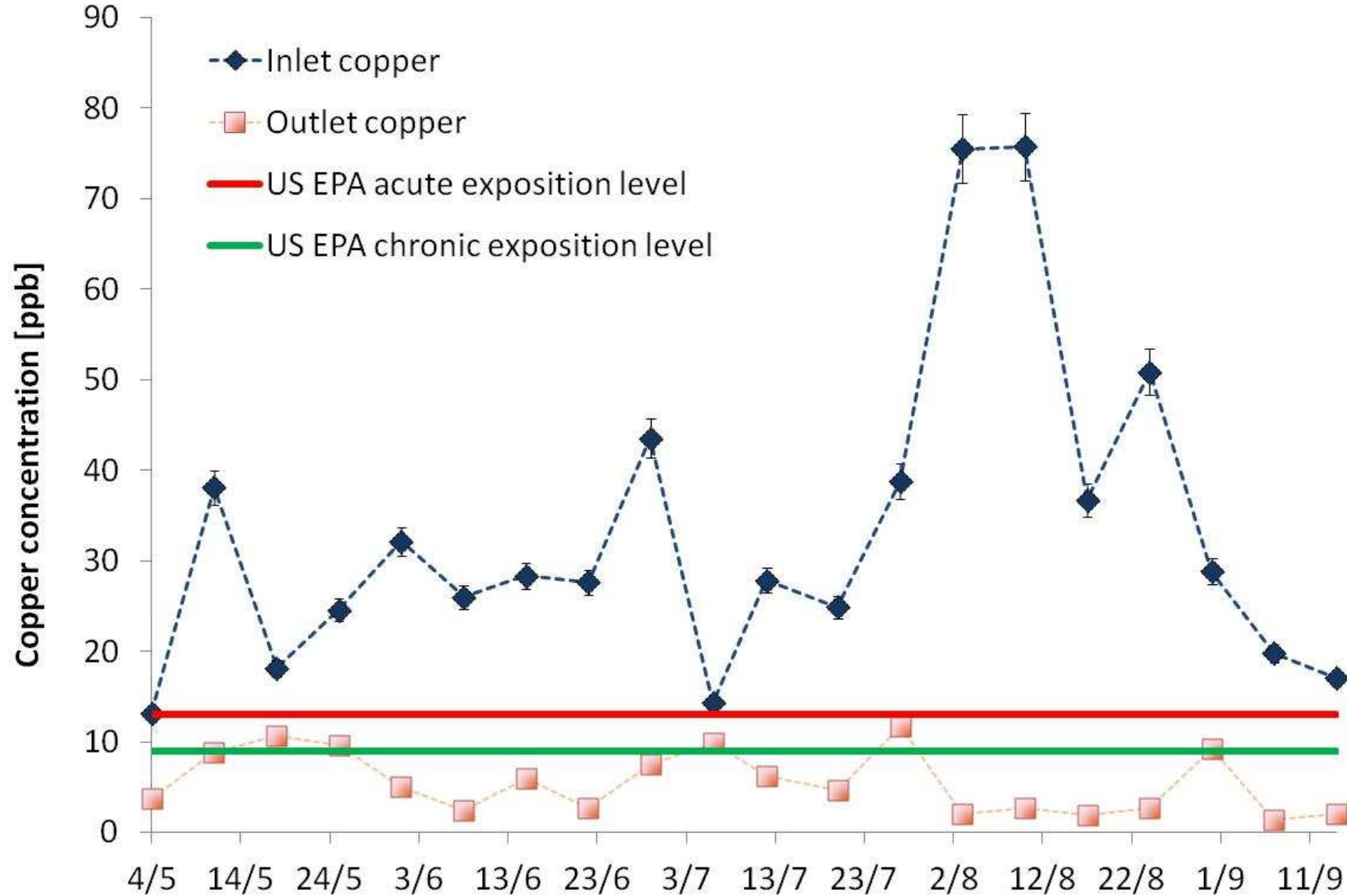


Copper use

Runoff discharge

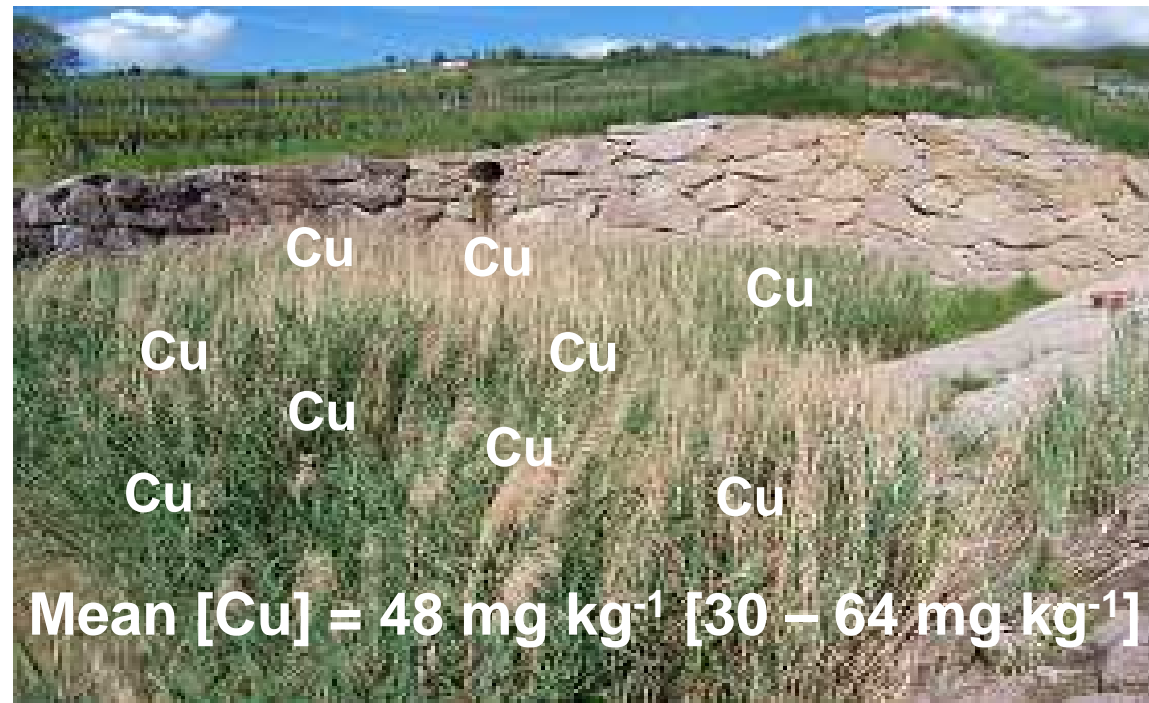
Copper loads and retention

Copper concentrations



=> Decrease of copper concentration from wetland inlet to outlet

Copper concentrations in wetland sediments (2011)



- ⇒ Accumulation of copper in the wetland sediments
- ⇒ How to manage contaminated sediments?

Conclusions

1. What is the capacity of stormwater wetlands to remove pesticide mixtures?

- Load removal: **between 39%** (simazine) **and 100%** (cymoxanil, gluphosinate, kresoxim methyl and terbuthylazine)
- Low transfer from the water column to the sediments (or fast degradation in sediment)
- Trapping of solids (> 90%) and hydrophobic pesticides ($\text{Log}K_{ow} > 3$)

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3. How stormwater wetlands retain copper?

- Copper concentration **decreased below the toxicity exposition levels**
- **82% of inlet copper load trapped** in the wetland
- Copper isotope composition analysis: sorption to Al- and Fe(hydro)oxides is critical

Stormwater wetlands:

=> Complementary tools for managing contaminated runoff from agricultural catchments?

=> Dynamic system for studying the transfer of pesticides



Thank you!

**Research group: « Wetland biogeochemistry and contaminant transfert »
(UMR 7517 UdS-CNRS)** <http://lhyges.u-strasbg.fr/>

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RITTMO-Environment



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CYTRIX

