



Crop irrigation with treated wastewater: Uptake of pharmaceuticals by crops, fate and processes in arable soils

**Benny Chefetz, Myah Goldstein, Tomer Malchi,
Ran Yakir, Evelyn Colon de Mello, Amnon
Grossberger, Galit Tadmor, Moshe Shenker and
Yitzhak Hadar**

**Department of Soil and Water Sciences,
The Hebrew University of Jerusalem, ISRAEL**



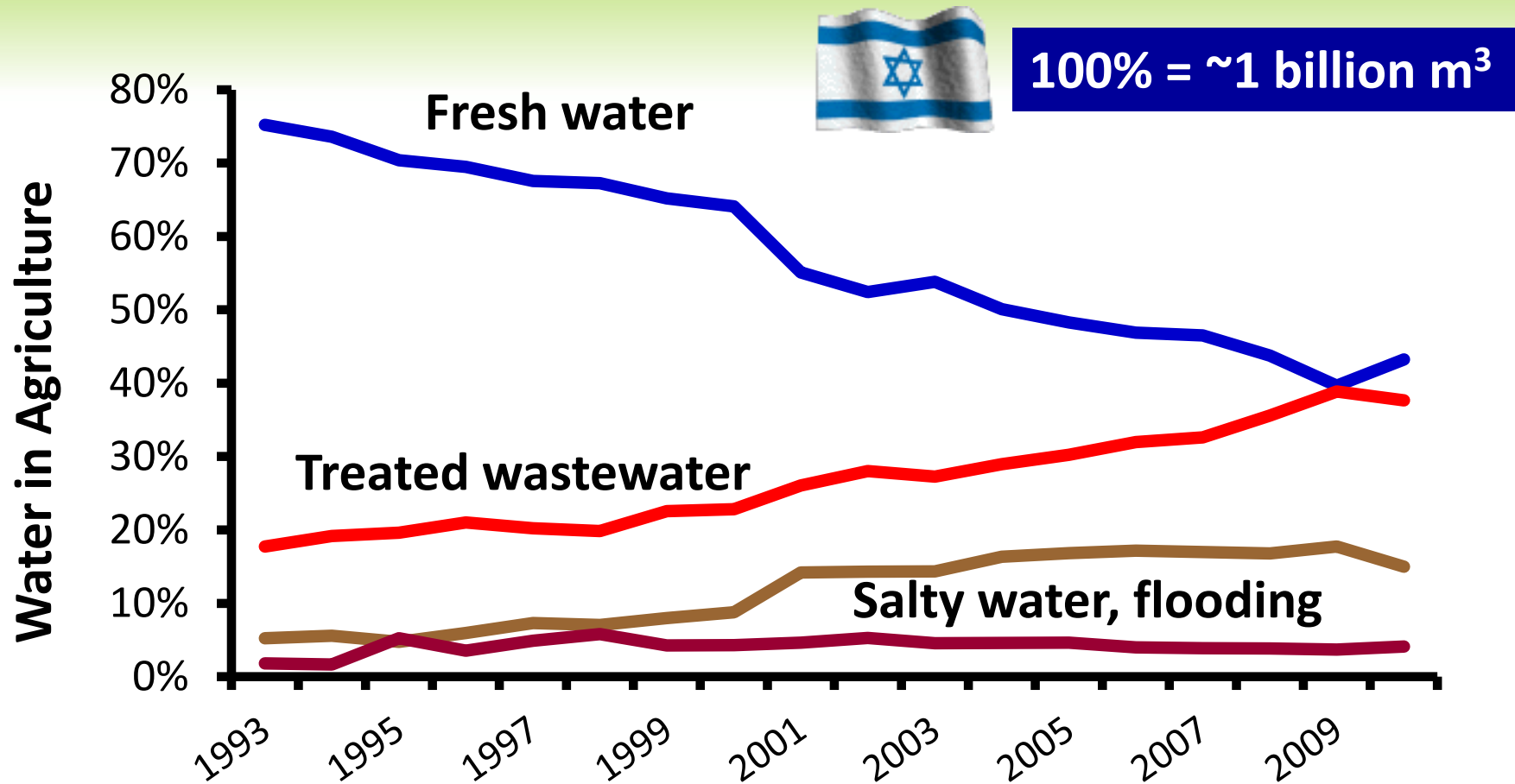
Outline

- **Motivation for the study**
 - Irrigation with treated wastewater (TWW)
 - Pharmaceutical and Personal Care Products (PPCPs) in irrigation water (TWW)
- **Fate of PPCPs in soils irrigated with TWW**
- **Uptake and translocation of PPCPs to plants**
 - Hydroponic, greenhouse, lysimeter experiments
- **Conclusion**



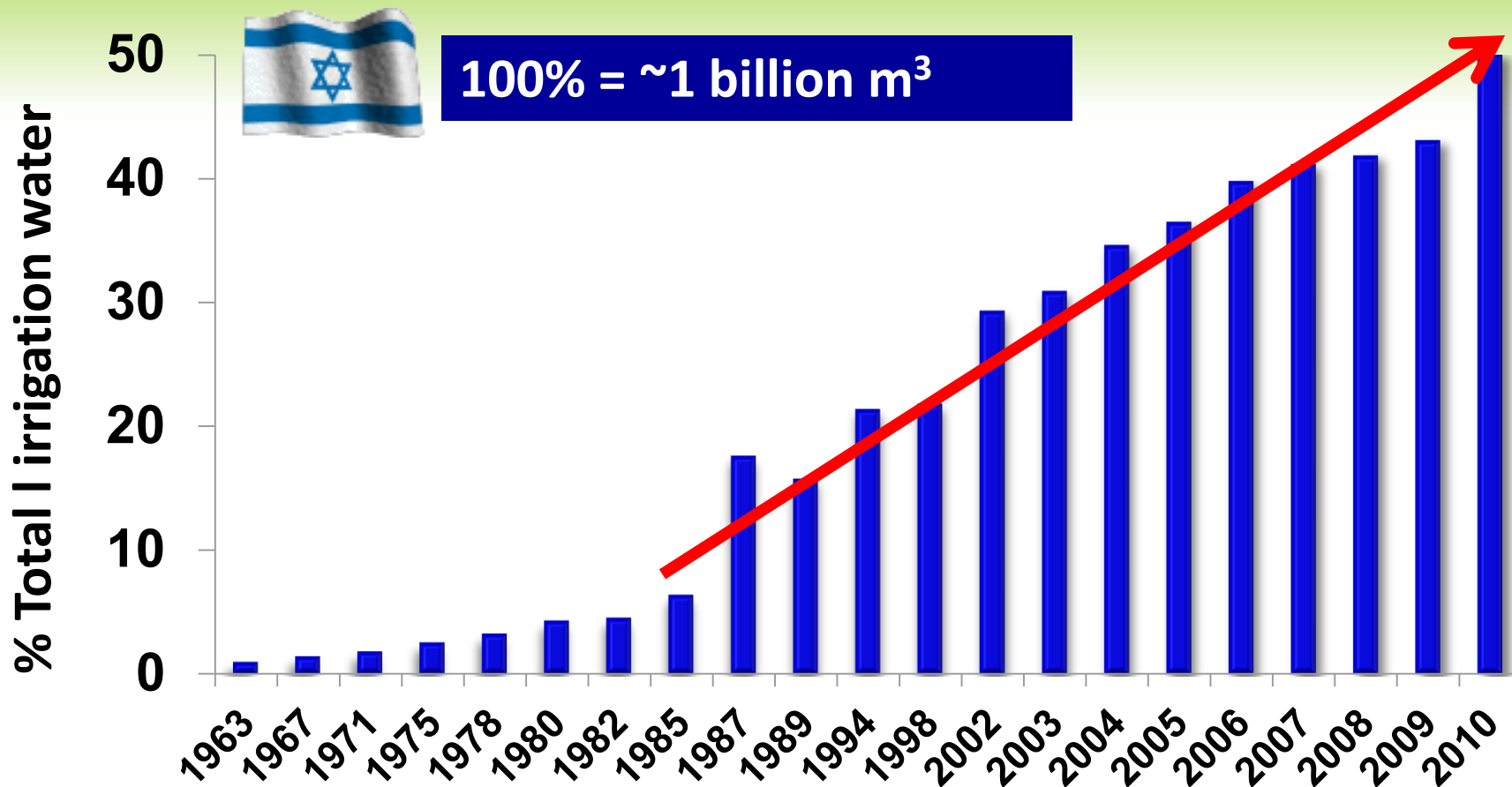


Water use by the Israeli agric. sector (1993-2012)





Irrigation with Reclaimed Wastewater (% of total)



The Use of TWW for Irrigation

High quality of TWW (10/10, BOD/TSS)

Disinfection + filtration + fecal coliforms 10
MPN/100 mL → unlimited irrigation

Medium quality of reclaimed WW (20/30 to 60/90, BOD/TSS)

Must have 3 barriers for irrigation

Low quality of reclaimed WW (>60/90, BOD/TSS)

Cannot be used for irrigation



Effluent – Quality

(Israel, new guidelines 2010)

		<u>Irrigation</u>	<u>Stream</u>
BOD	<i>mg/L</i>	10	10
TSS	<i>mg/L</i>	10	10
COD	<i>mg/L</i>	100	70
Fecal <i>coliforms</i>	<i>MPN/100 mL</i>	10	200
Dissolved oxygen	<i>mg/L</i>	>0.5	>3
Residual chlorine	<i>mg/L</i>	1	0.01
Total oil /hydrocarbons	<i>mg/L</i>		1.0
pH		6.5-8.5	7.0-8.5
Total nitrogen	<i>mg/L</i>	25	10
Ammonia	<i>mg/L</i>	20	1.5
Total phosphorus	<i>mg/L</i>	5	0.2



Effluent – Quality

(Israel, new guidelines 2010)

		Irrigation	Stream
Electrical conductivity	dS/m	1.4	
SAR	$(meq/L)^{0.5}$	5	
Chloride	ppm	250	400
Sodium	ppm	150	200
Boron	ppm	0.4	
Fluoride	ppm	2	



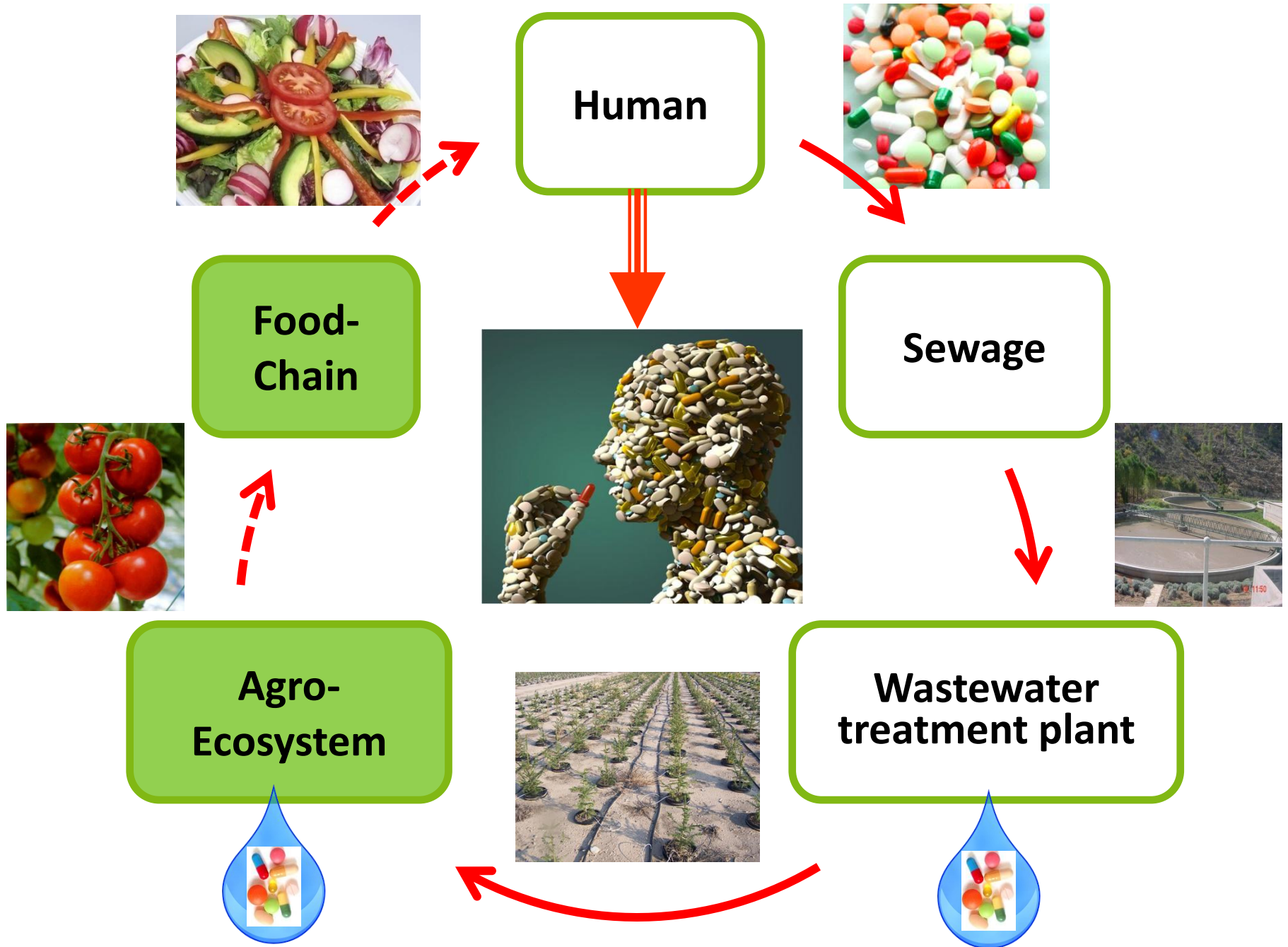
PPCPs in secondary treated wastewater (Shafdan, 2011)

	2/06	20/06	27/06	5/07	11/07
Caffeine	0.33	0.04	0.35	0.27	ND
Lamotrigine	1.64	1.82	1.58	2.11	1.66
Metoprolol	ND	ND	ND	ND	ND
Sulfapyridine	0.16	0.16	0.23	0.16	0.26
Erythromycin	ND	ND	ND	ND	ND
Sildenafil	ND	ND	ND	ND	ND
Sulfamethoxazole	0.34	0.27	0.30	0.35	0.43
Carbamazepine	1.02	1.03	1.06	1.32	1.05
Ketoprofen	ND	ND	ND	ND	ND
Bezafibrate	0.35	0.34	0.51	0.26	0.23
Clofibric acid	ND	ND	ND	ND	ND
Naproxen	ND	ND	ND	ND	ND
Diclofenac	0.54	0.64	0.47	1.01	0.85
Ibuprofen	ND	ND	ND	ND	ND
Gemfibrosil	ND	ND	ND	ND	ND
Triclosan	ND	ND	ND	ND	ND

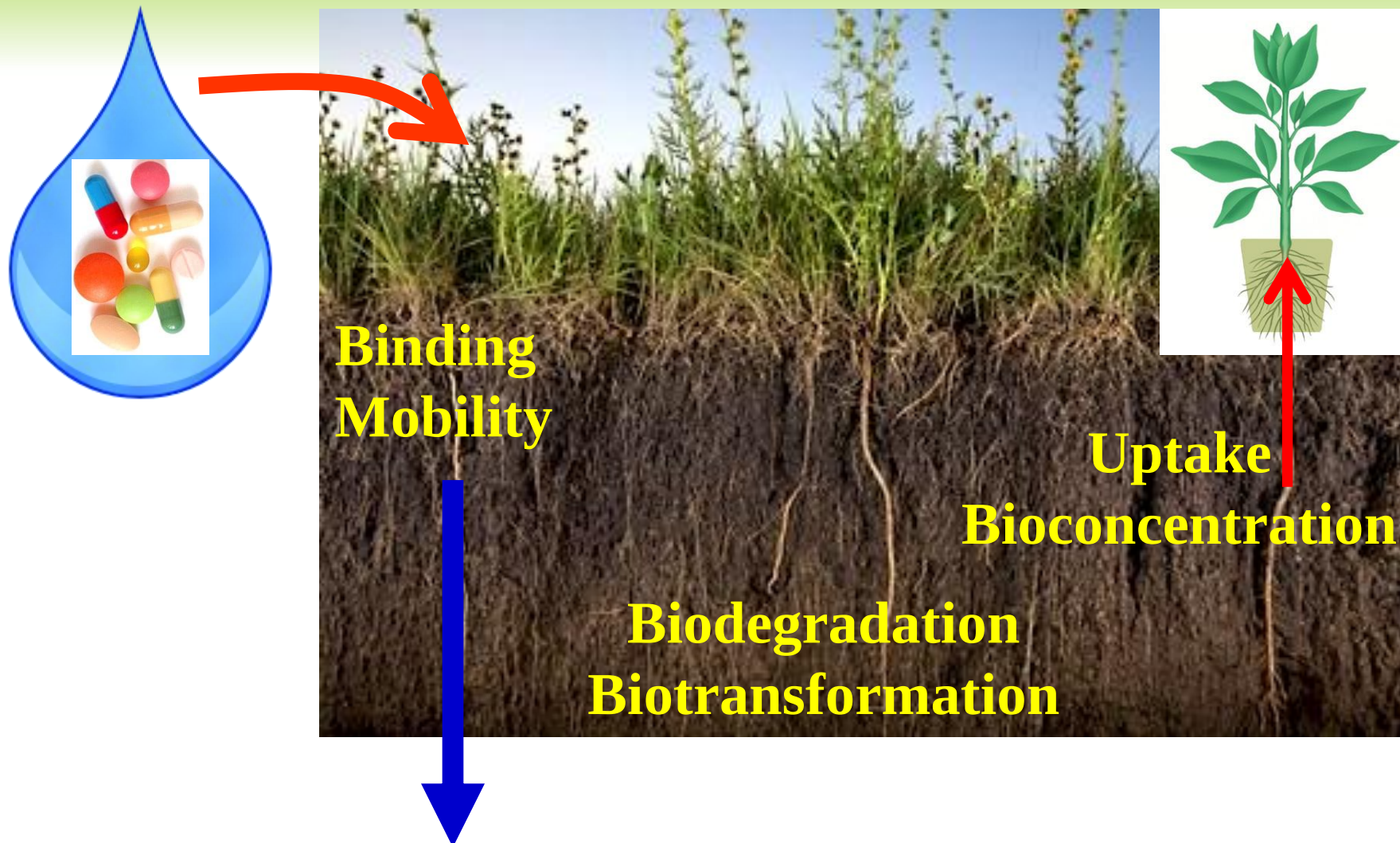


PPCPs in secondary treated wastewater (Kiryat Gat, 2011)

	30.6.11	7.7.11	7.18.11	25.7.11	16.8.11	24.8.11	30.8.11
	µg/L (ppb)						
Caffeine	0.7-1	0.75-75	0.19-34	0.14-0.57	0.67	0.45	0.8-0.66
Lamotrigine	1.87-1.91	0.1-1.42	0.31-0.32	0.06-1.27	0.08	0.14-0.73	0.1-0.19
Metoprolol	ND	ND	ND	0.06	ND	ND	ND
Sulfapyridine	ND	ND	ND	ND	ND	ND	ND
Erythromycin	0.14-0.16	0.14-0.17	0.17-0.19	0.14-0.22	0.14	0.11-0.18	0.17-0.26
Sildenafil	0.01	0.04-0.05	0.02-0.05	ND	ND	ND	ND
Sulfamethoxazole	0.05-0.08	0.06-0.07	0.02	0.01	0.01	0.01-0.02	0.02-0.06
Carbamazepine	0.45-0.47	0.41-0.43	0.31-0.33	0.43-0.67	0.24	0.77-0.79	0.68-0.89
Bezafibrate	1.01-1.20	0.79-0.8	0.34-0.35	0.45-0.79	0.06	0.11-0.12	0.06-0.14
Clofibric acid	ND	ND	ND	ND	ND	ND	ND
Ketoprofen	0.04-0.1	ND	0.03	0.02-0.03	0.04	0.01	0.01-0.04
Naproxen	ND	ND	ND	ND	ND	ND	ND
Diclofenac	0.02	ND	0.01-0.07	ND	0.01-0.07	0.01-0.13	0.03-0.25
Ibuprofen	ND	ND	ND	0.11	0.05	ND	ND
Gemfibrozil	0.03	0.79	0.04	0.02-0.03	0.02	ND	0.01
Triclosan	0.10	ND	ND	0.22-0.41	0.1-0.11	0.25-0.3	ND



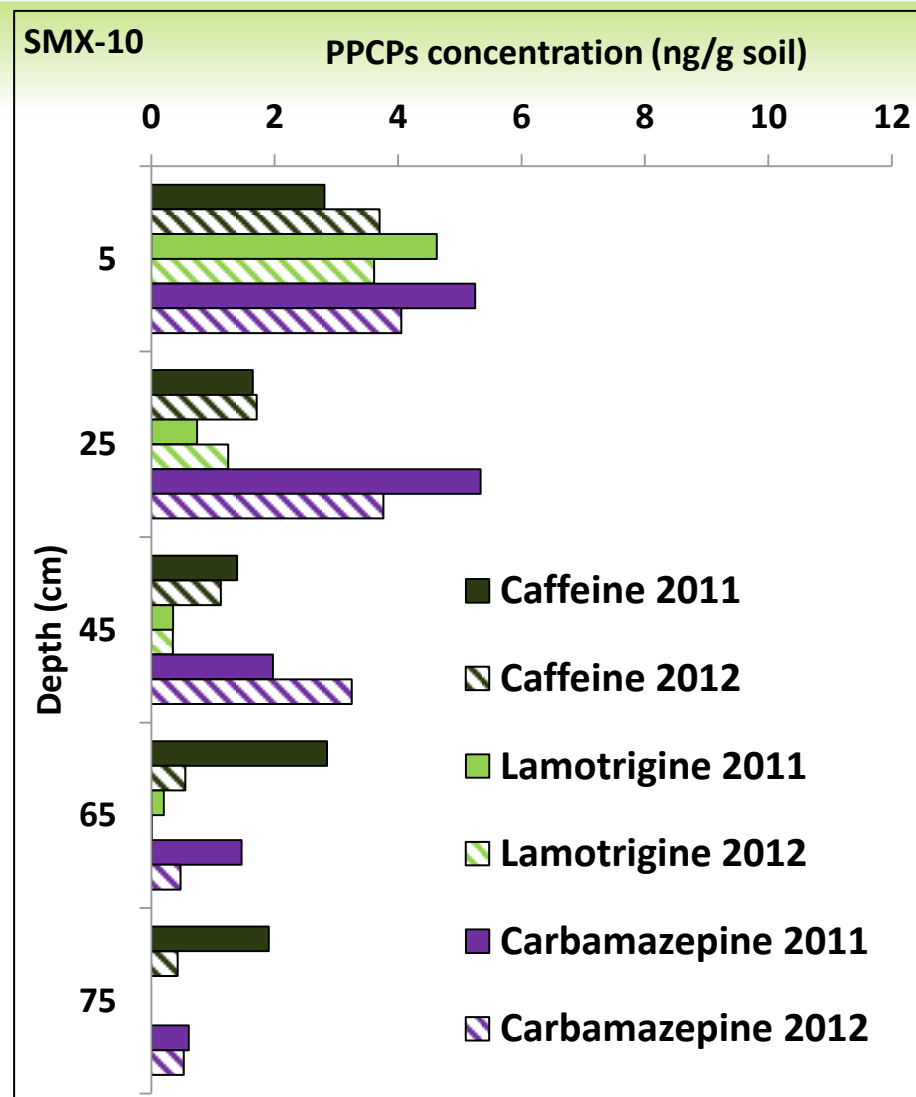
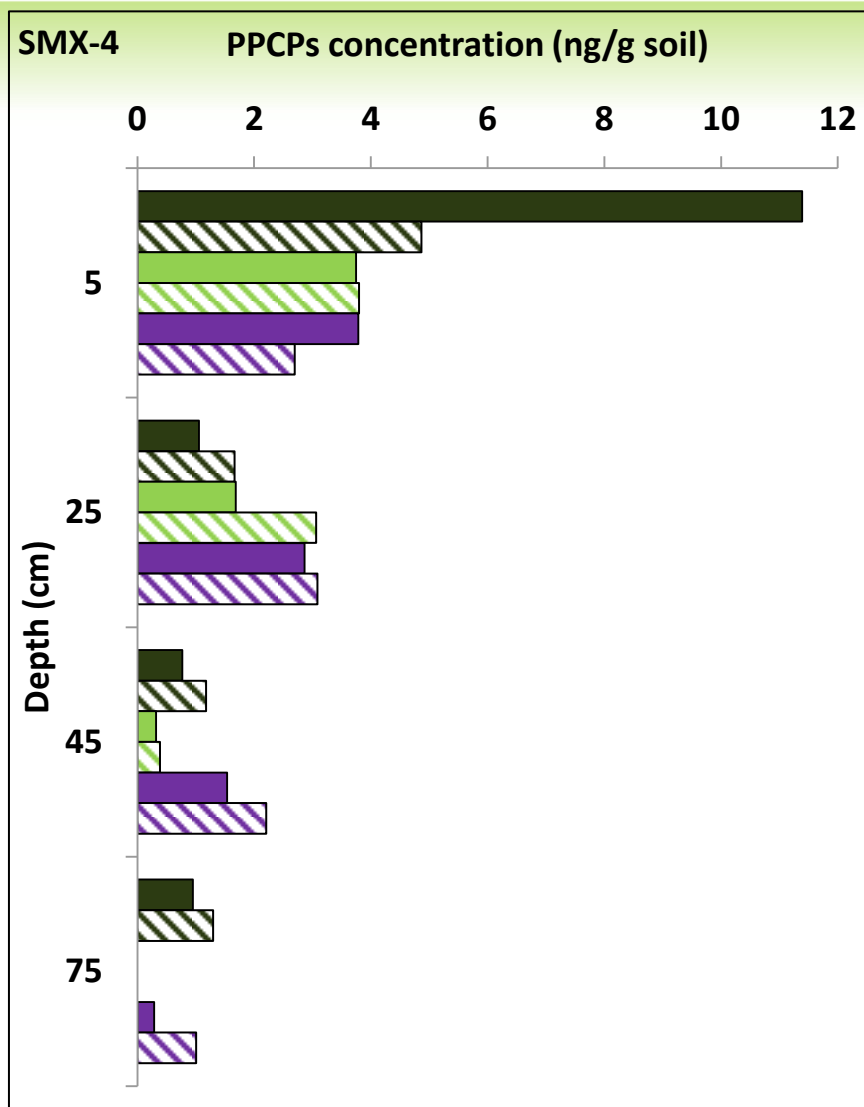
PPCPs: Fate in the Soil

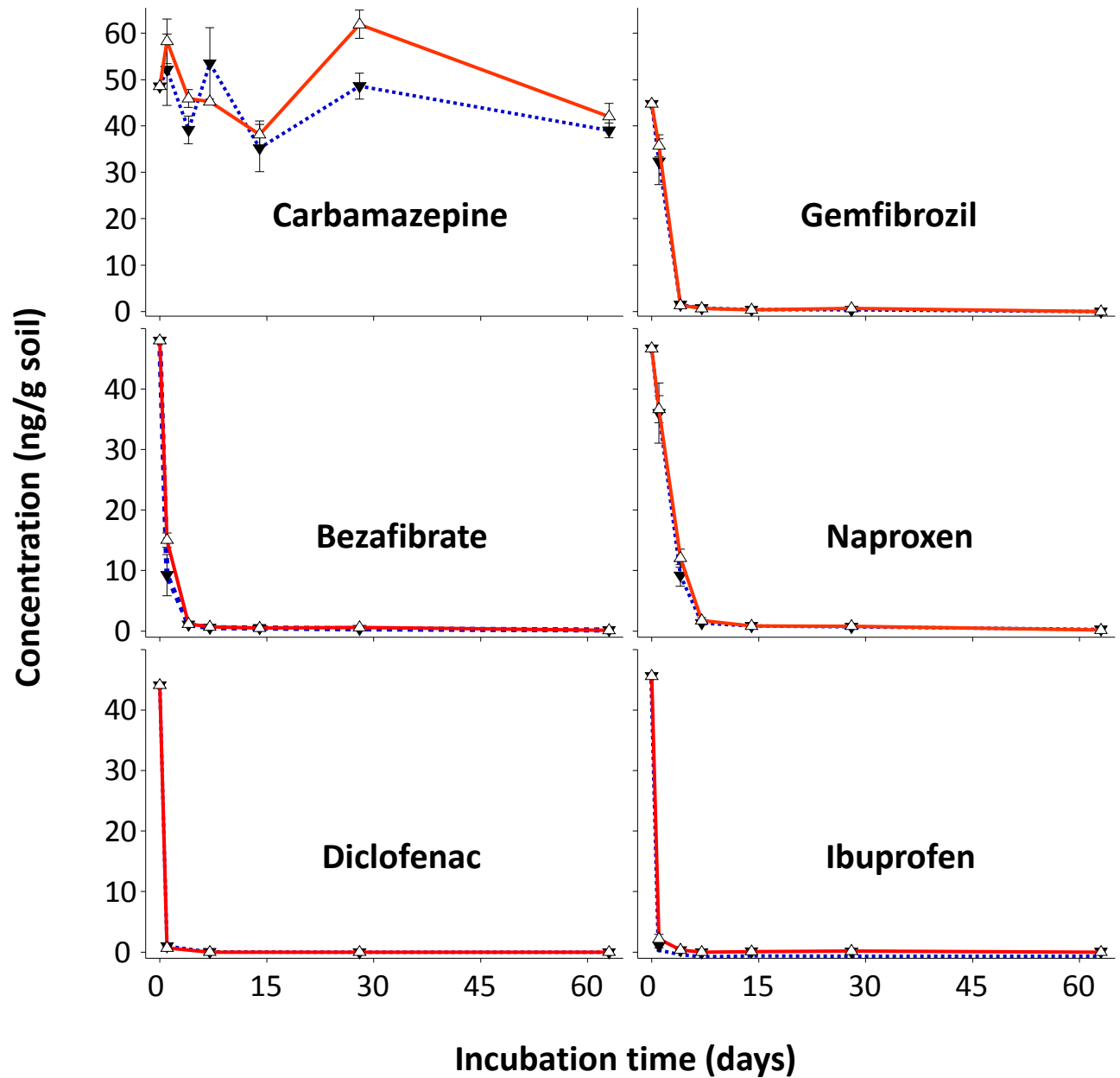


PPCPs: Fate in the Soil



PPCPs in Loess soil irrigated with STWW







PPCPs in the agro- environment: Uptake by crops



Hydroponic Experiments



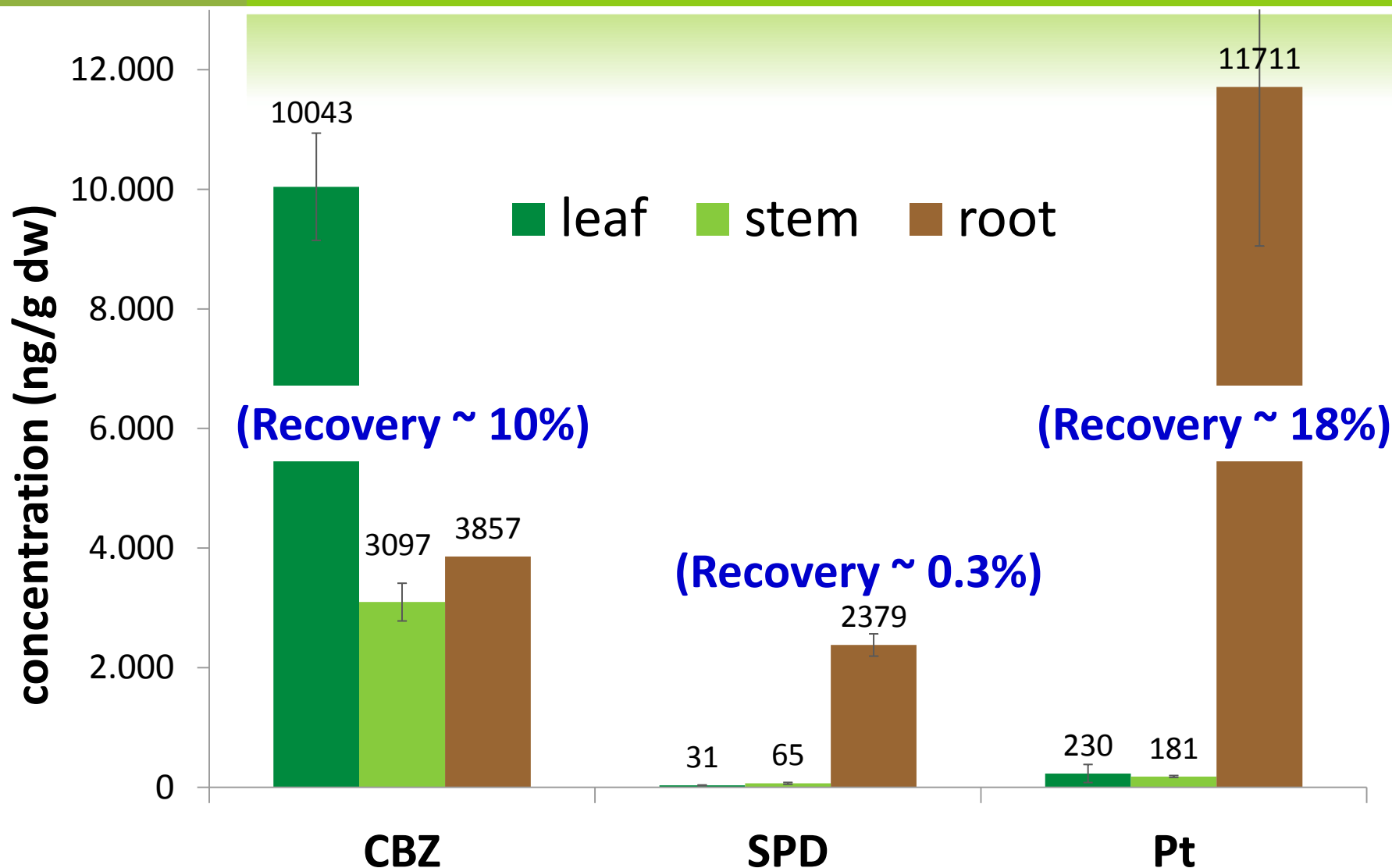


Selected physico-chemical properties of the studied PPCPs

Name	Formula	Uses	MW (g mol ⁻¹)	Aqueous solubility (mg L ⁻¹)	log <i>k</i> _{ow}	<i>pK</i> _a
Carbamazepine	C ₁₅ H ₁₂ N ₂ O	Anticonvulsant	236.27	125	2.45	
Carboplatin	C ₆ H ₁₂ N ₂ O ₄ Pt	Antineoplastic	371.25	19	-0.46	
Sulfapyridine	C ₁₁ H ₁₁ N ₃ O ₂ S	Antibacterial	249.3	268	0.35	8.43



Carbamazepine, Sulfapyridine and Carboplatin in cucumber organs





Concentrations of carbamazepine metabolites in cucumber plant parts

- Qualitative analysis of cucumber plants:

- ✓ LEAVES

- ✓ STEMS

- ✓ ROOTS

10,11-epoxy and/or 10,11-dihydroxyl-CBZ

- Quantitative analysis of 3 samples of cucumber leaves:

	[CBZ] ng/g	[OH-CBZ] ng/g	[OH-CBZ] %	[EP-CBZ] ng/g	[EP-CBZ] %
leaf 1	13872	76	0.6	3448	25
leaf 4	9198	83	0.9	2046	22
leaf 5	13107	66	0.5	2137	16

Greenhouse experiments

◎ **Test plant:** cucumber & tomato

◎ **Three types of soil:**

1. Alluvial Soil, Beit Oren, Israel
2. Sandy Soil, Rehovot, Israel
3. Aeolian Sand, Besor, Israel

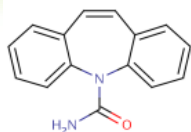
◎ **Irrigation treatments:**

1. Fresh water
2. Spiked Fresh water (1ppb)
3. TWW (Shafdan – secondary treatment)
4. Spiked TWW (Shafdan) (1ppb)

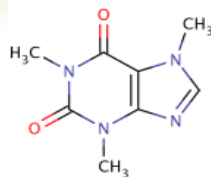


PPCPs

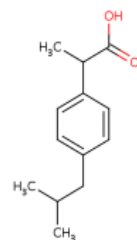
Carbamazepine



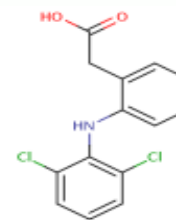
Caffeine



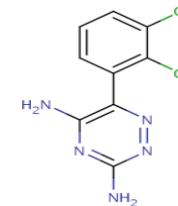
Ibuprofe



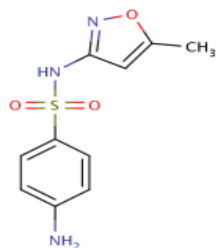
Diclofenac



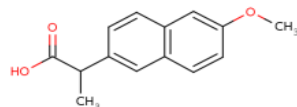
Lamotrigine



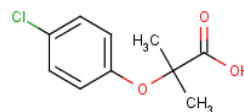
Sulfamethoxazole



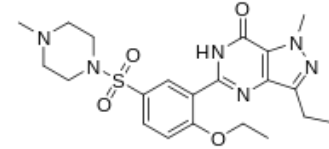
Naproxen



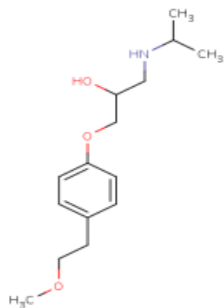
Clofibric acid



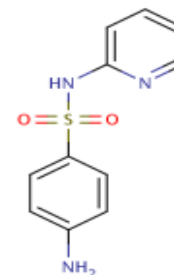
Sildenafil



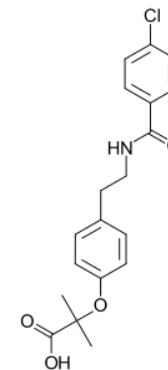
Metoprolol



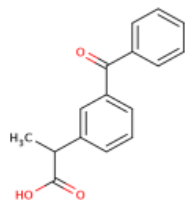
Sulfapyridine



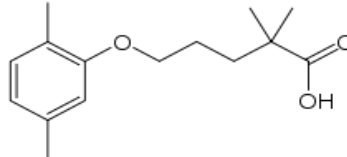
Bezafibrate



Ketoprofen

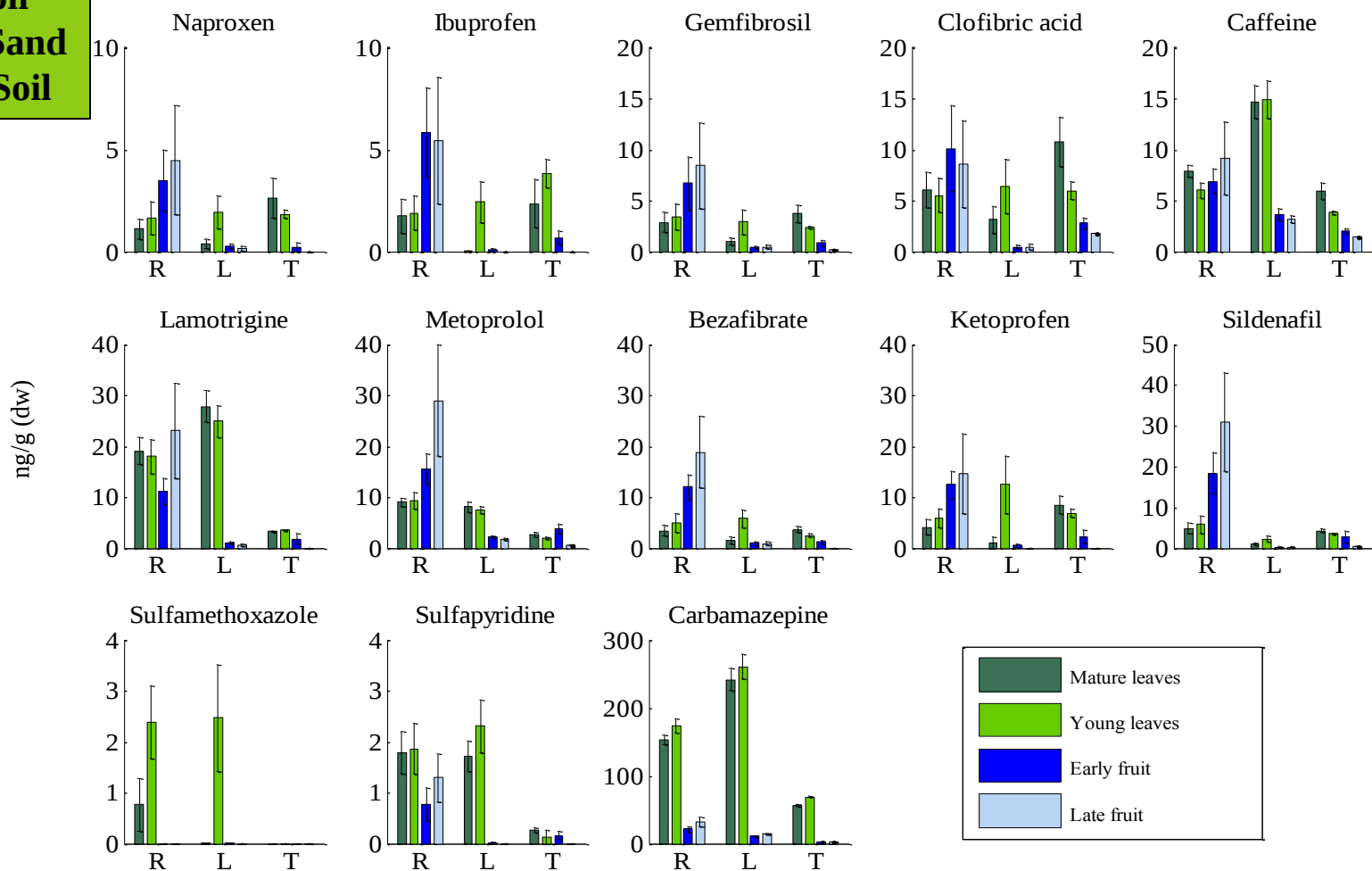


Gemfibrozil



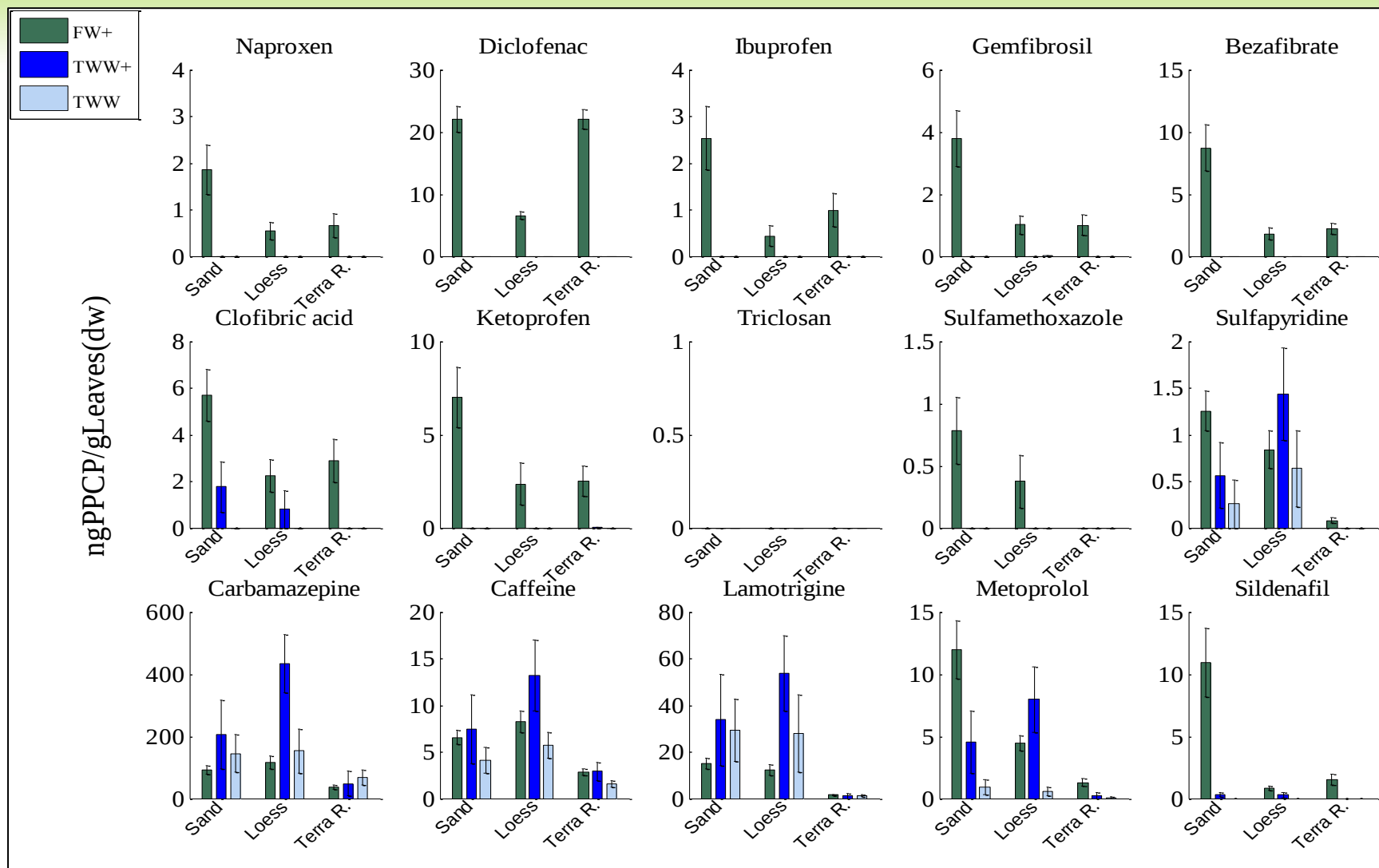
PPCPs concentrations in the cucumber plant parts

R – Sandy Soil
L – Aeolian Sand
T – Alluvial Soil

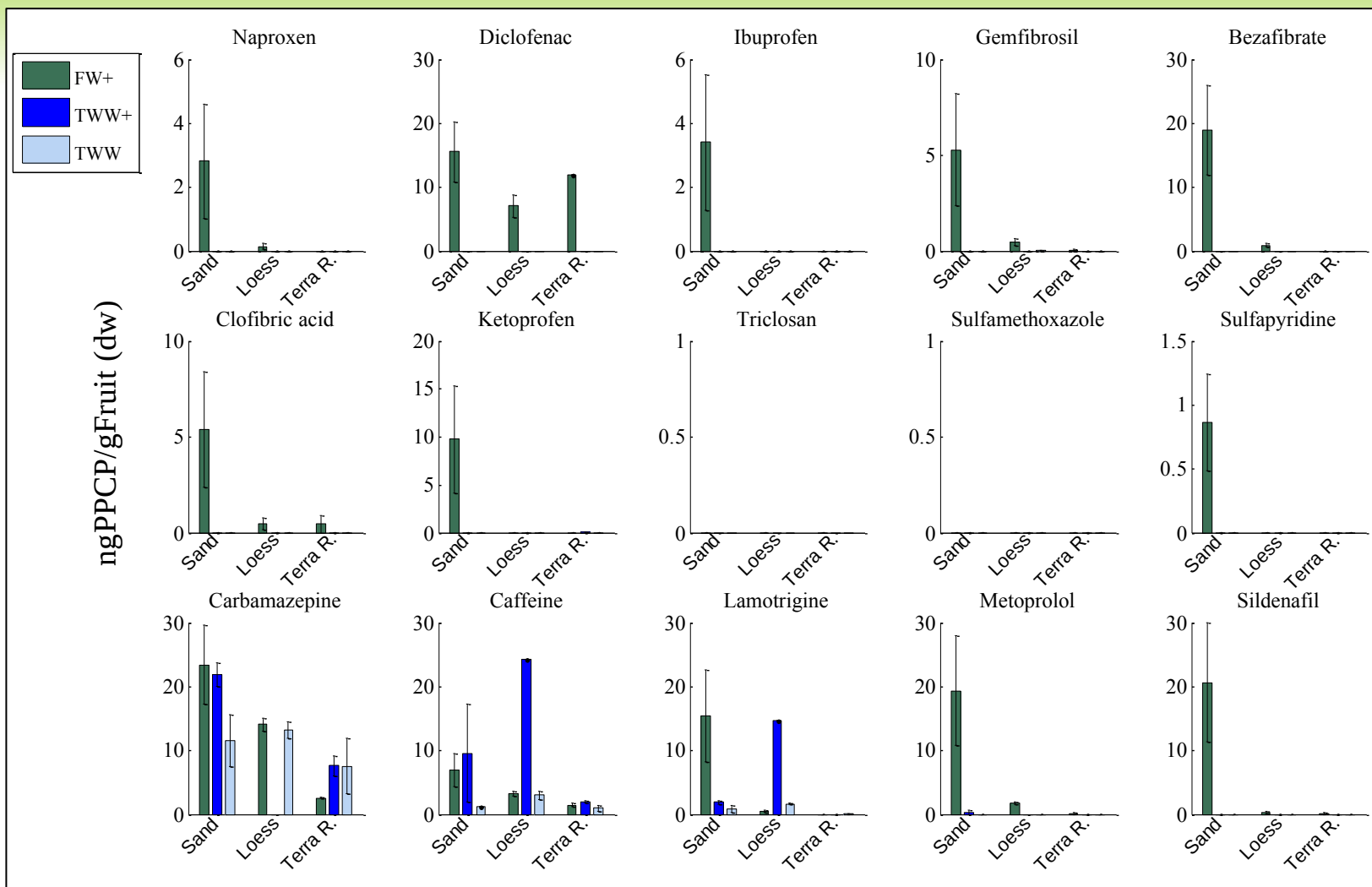


Spiked Fresh water (1ppb)

Cucumber PPCPs in Leaves



Cucumber PPCPs in Fruits



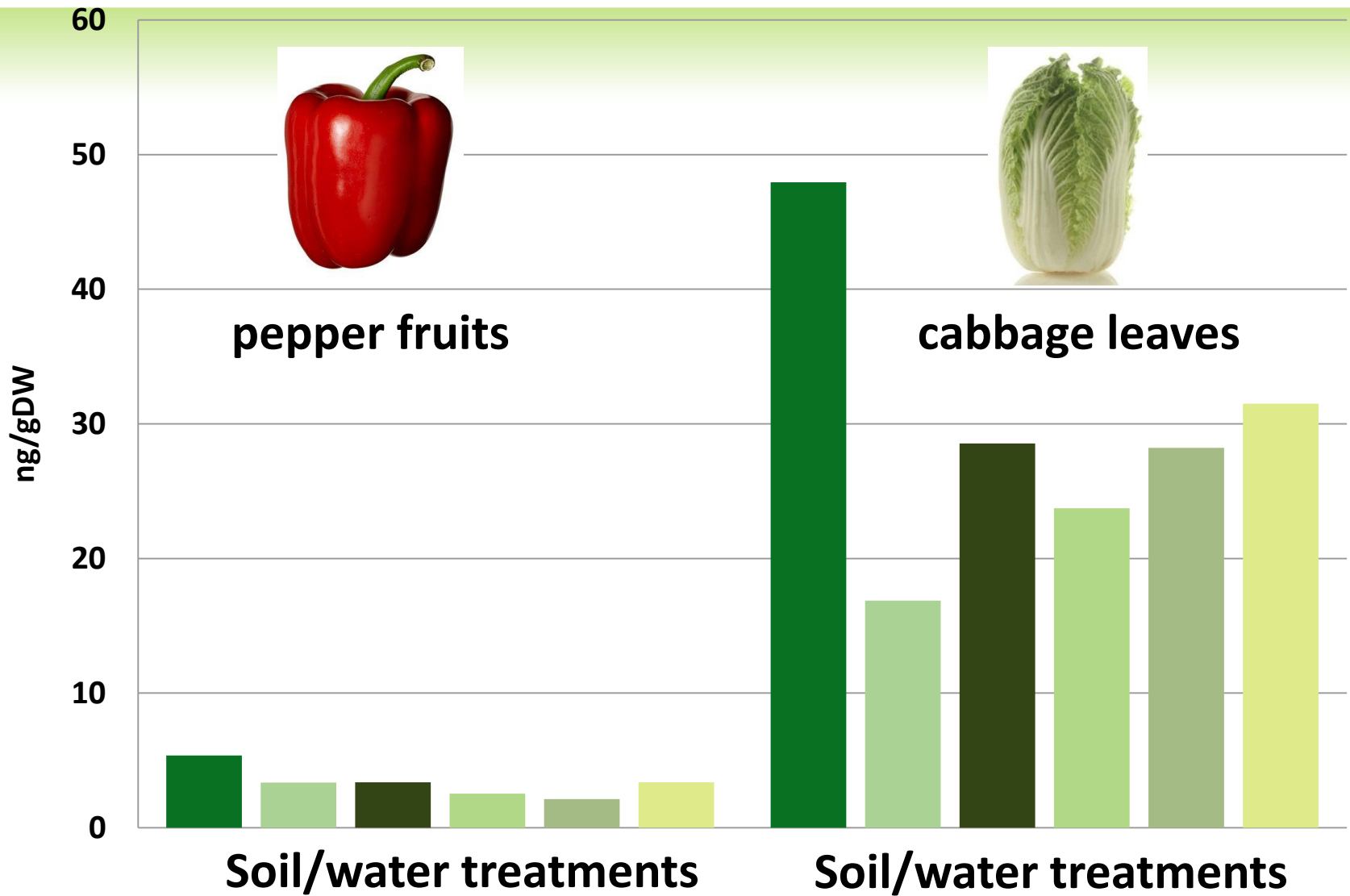


pepper fruits



cabbage leaves

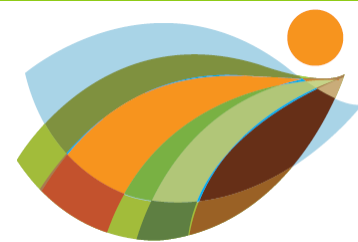
Carbamazepine level: pepper fruits vs. cabbage leaves



Consumption of crops contaminated with carbamazepine: Risks

	Adult		Boy	
	Minimal Therapeutic level (kg/day)	Carcinogenic level (kg/day)	Minimal Therapeutic level (kg/day)	Carcinogenic level (kg/day)
Pepper Fruit 	152	38,043	 36	9,076
Chinese Cabbage 	29	7,292	 7	1,740

Conclusions



- 👍 PPCPs are present in reclaimed wastewater used as irrigation water → PPCPs are introduced into agricultural soils → some PPCPs tend to retain in the top soil layer → some PPCPs can be taken up by crops.
- 💣 Can PPCPs enter the food-chain!?!; What are the risks (health) associated with that?
- 💣 Risk assessment for mixture of chemicals!
- 💣 Is there a need for new regulations for water quality (irrigation water)?

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