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

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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**

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

100% = ~1 billion m^3

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Irrigation with Reclaimed Wastewater (% of total)

100% = ~1 billion m^3

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)

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

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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

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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

Human

Food-Chain

Sewage

Agro-Ecosystem

Wastewater treatment plant

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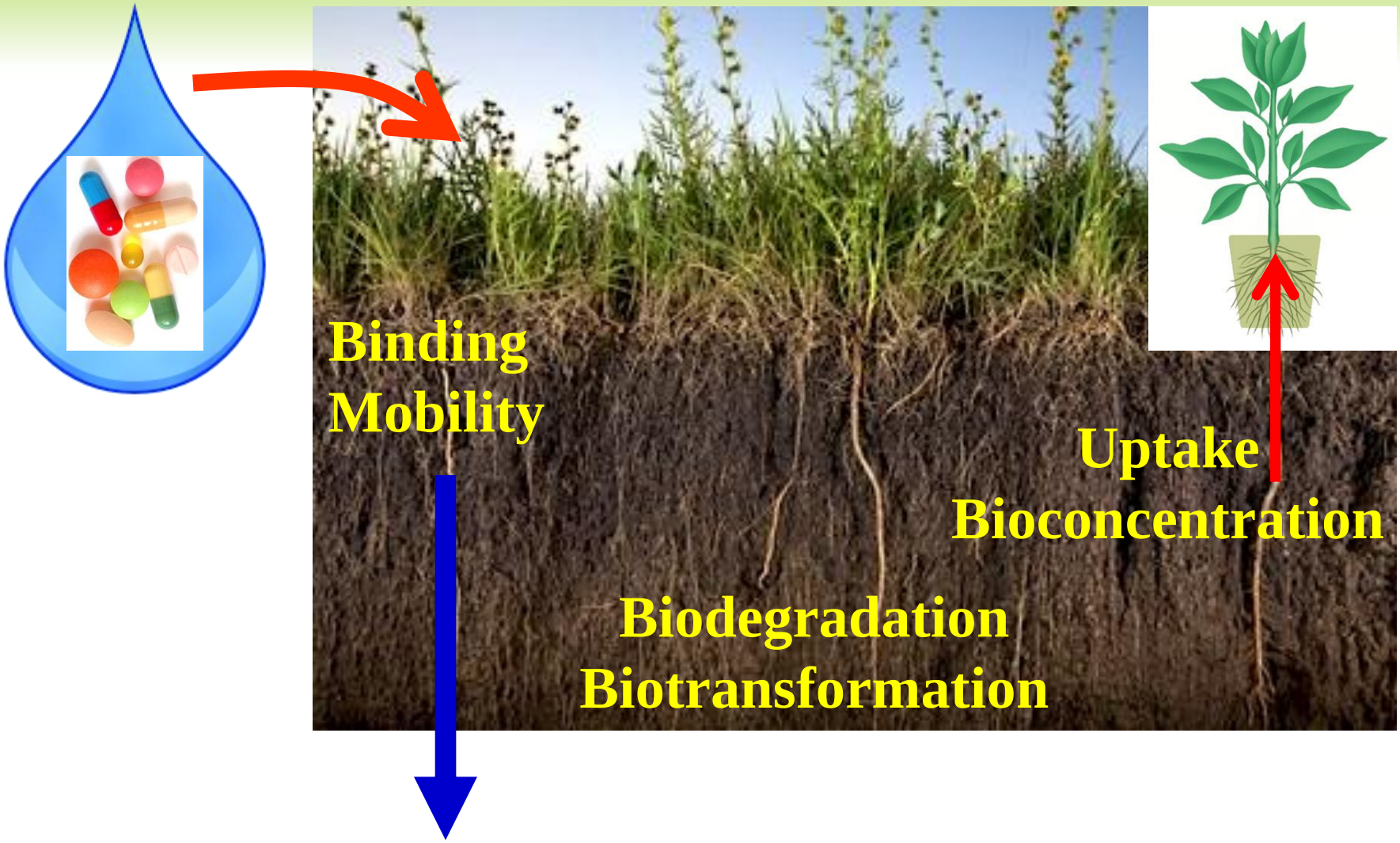
PPCPs: Fate in the Soil



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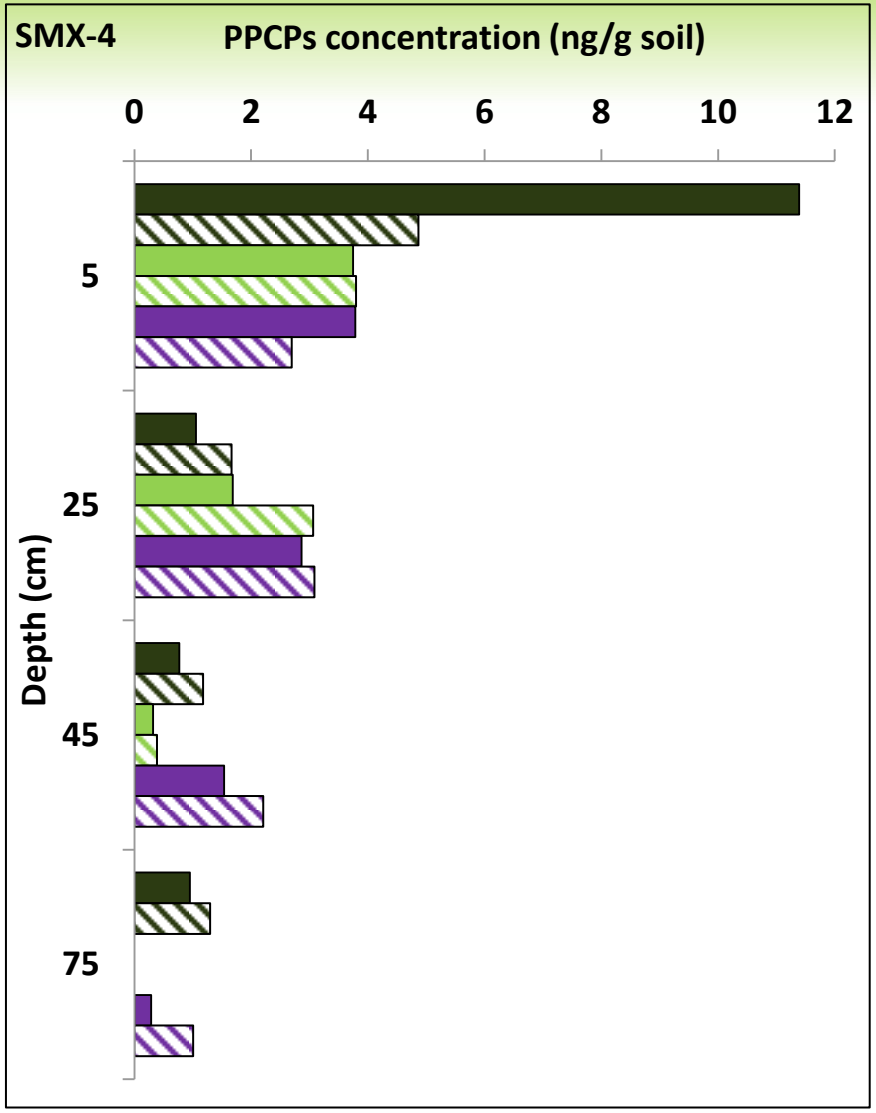
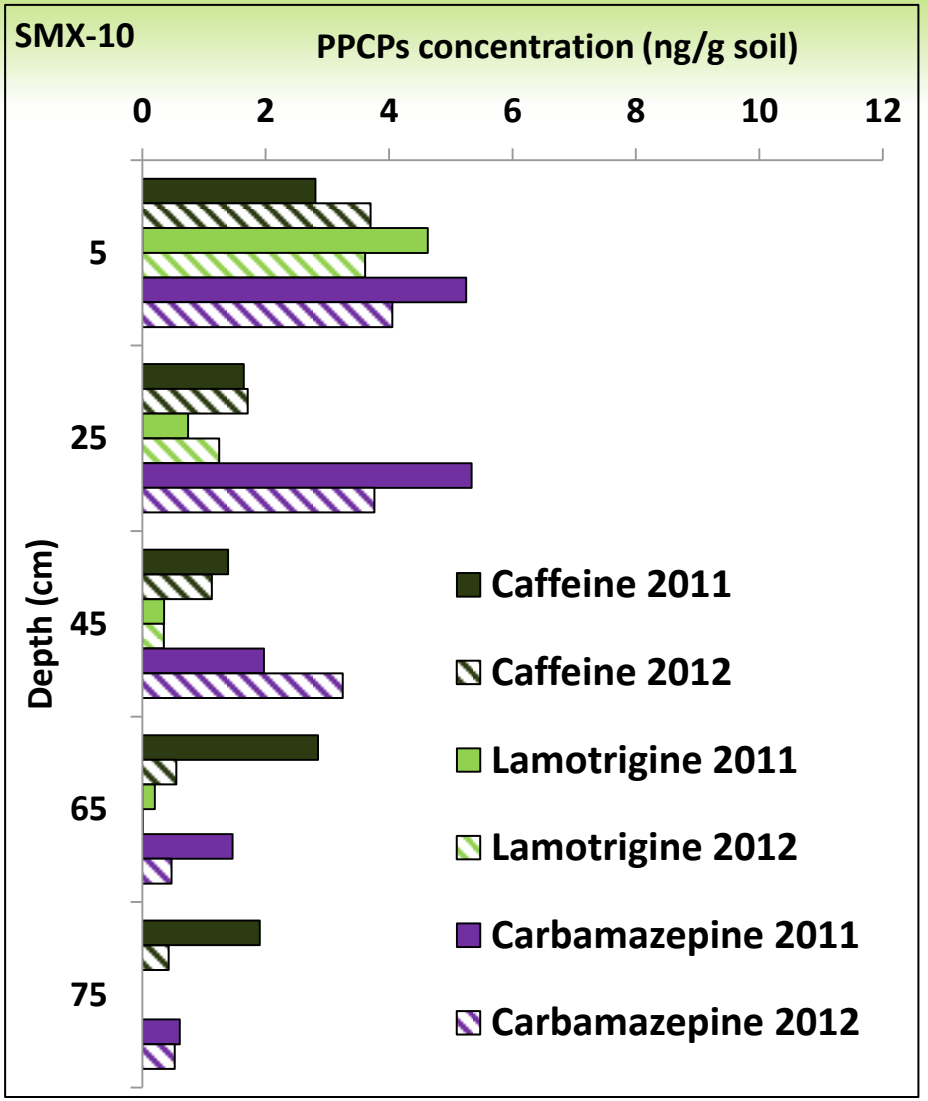
PPCPs: Fate in the Soil

PPCPs in Loess soil irrigated with STWW





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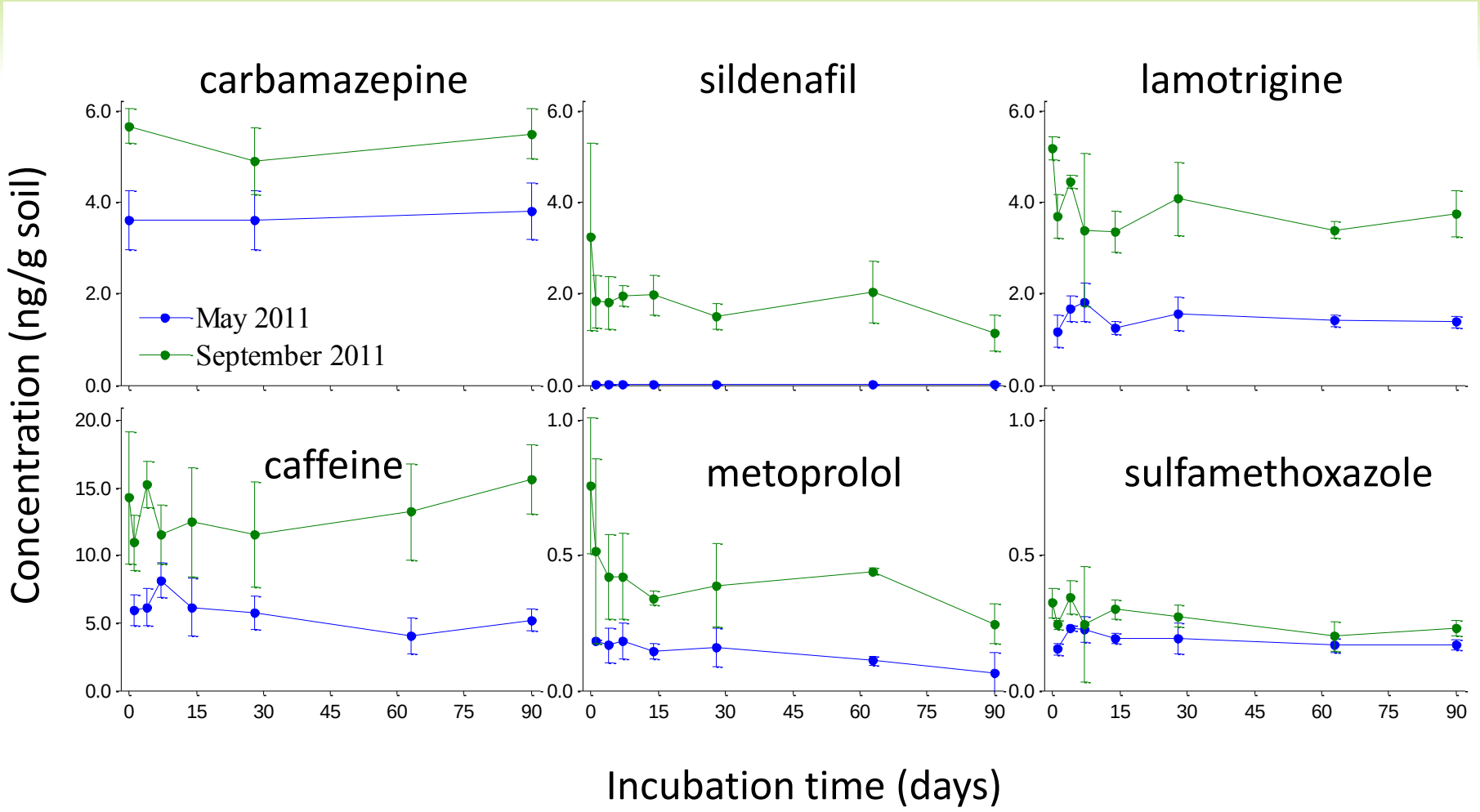
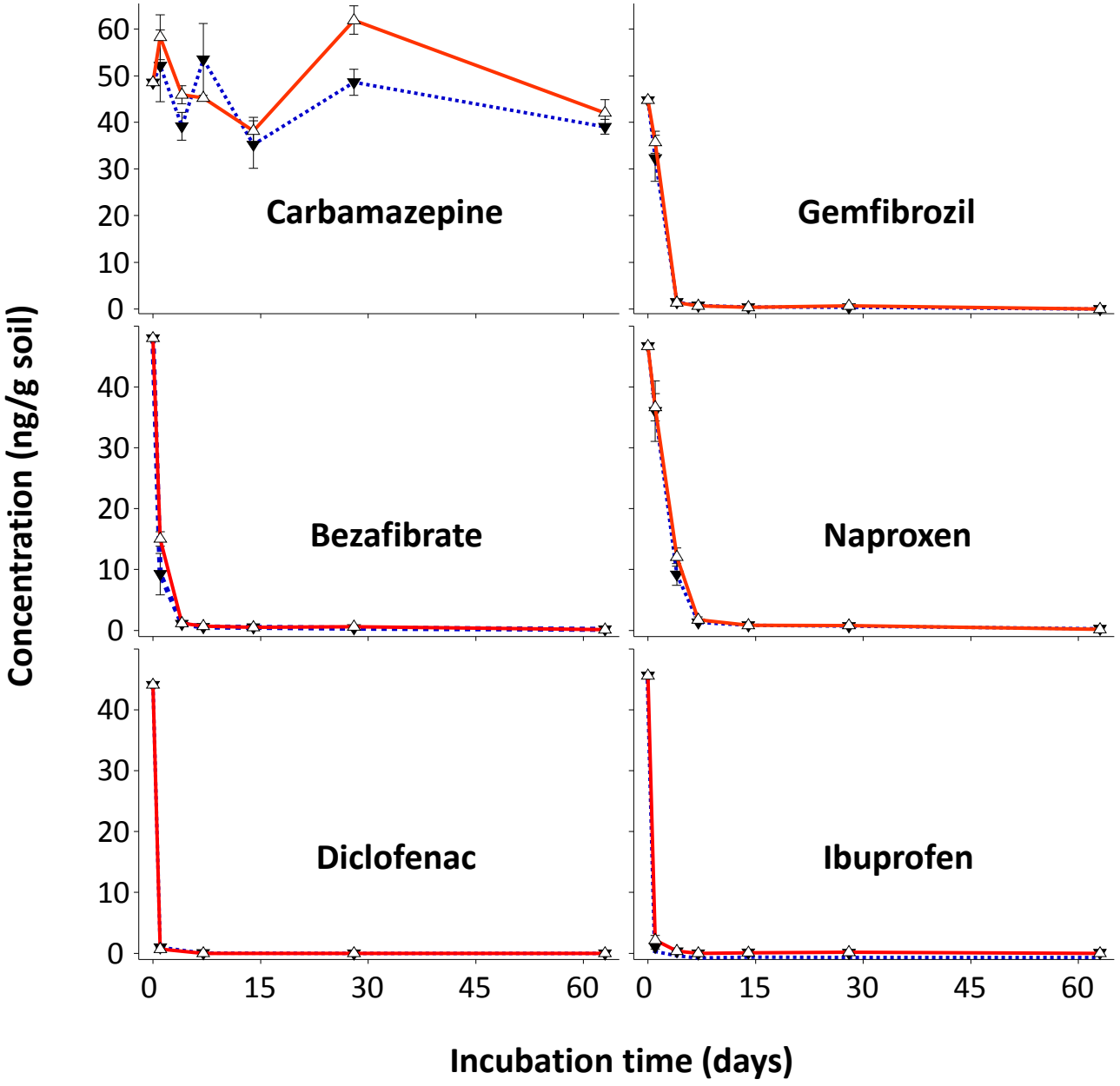
PPCPs in soil: 90 days of incubation




Carbamazepine
Gemfibrozil
Bezafibrate
Naproxen
Diclofenac
Ibuprofen
Concentration (ng/g soil)
Incubation time (days)
0
10
20
30
40
50
60
0
15
30
45
60

PPCPs in the agro- environment: Uptake by crops

Hydroponic Experiments

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Selected physico-chemical properties of the studied PPCPs

Name	Formula	Uses	MW (g mol^{-1})	Aqueous solubility (mg L^{-1})	log k_{ow}	pk_a
Carbamazepine	$C_{15}H_{12}N_2O$	Anticonvulsant	236.27	125	2.45	
Carboplatin	$C_6H_{12}N_2O_4Pt$	Antineoplastic	371.25	19	-0.46	
Sulfapyridine	$C_{11}H_{11}N_3O_2S$	Antibacterial	249.3	268	0.35	8.43

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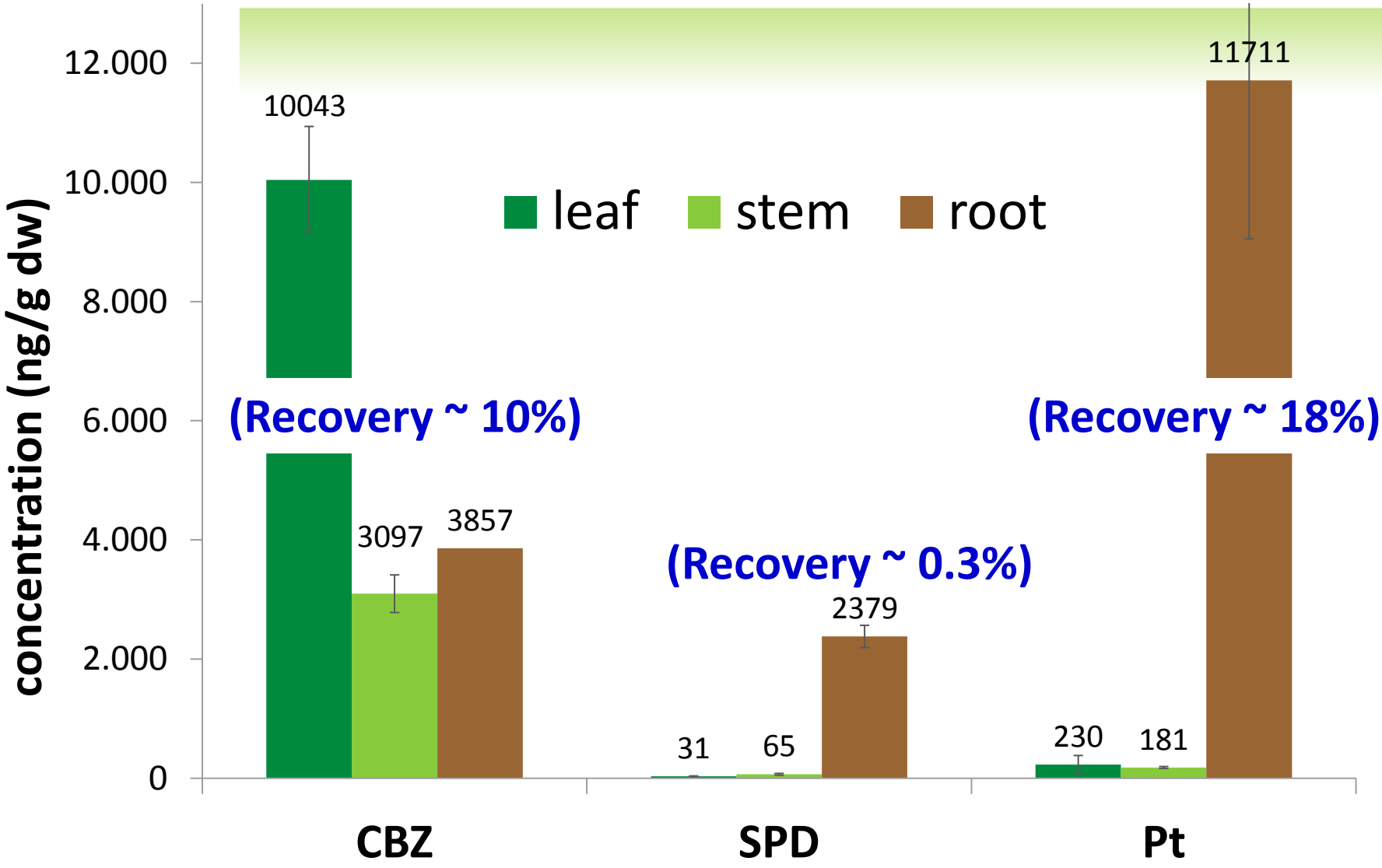
Carbamazepine, Sulfapyridine and Carboplatin in cucumber organs



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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**

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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)

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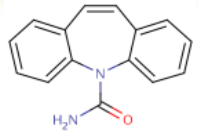
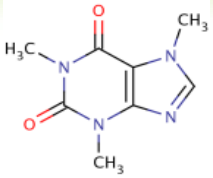
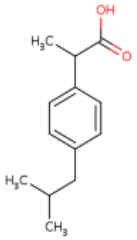
Carbamazepine



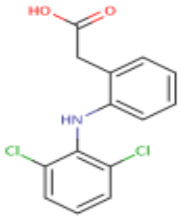
Caffeine



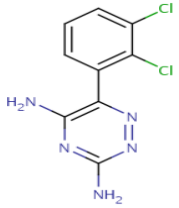
Ibuprofe



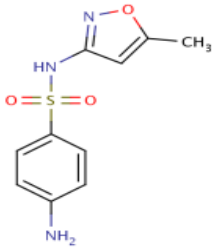
Diclofenac



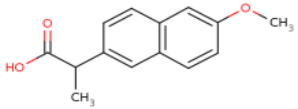
Lamotrigine



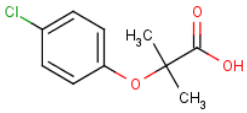
Sulfamethoxazole



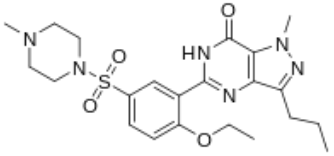
Naproxen



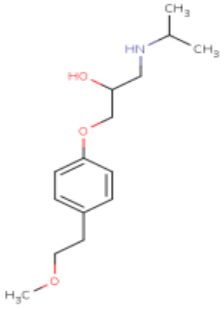
Clofibric acid



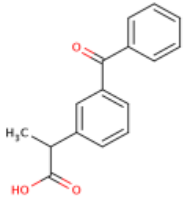
Sildenafil



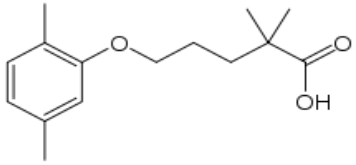
Metoprolol



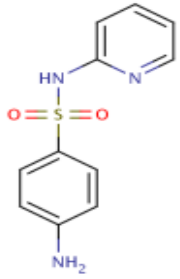
Ketoprofen



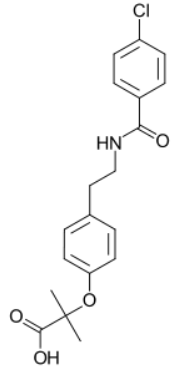
Gemfibrozil



Sulfapyridine



Bezafibrate



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PPCPs concentrations in the cucumber plant parts

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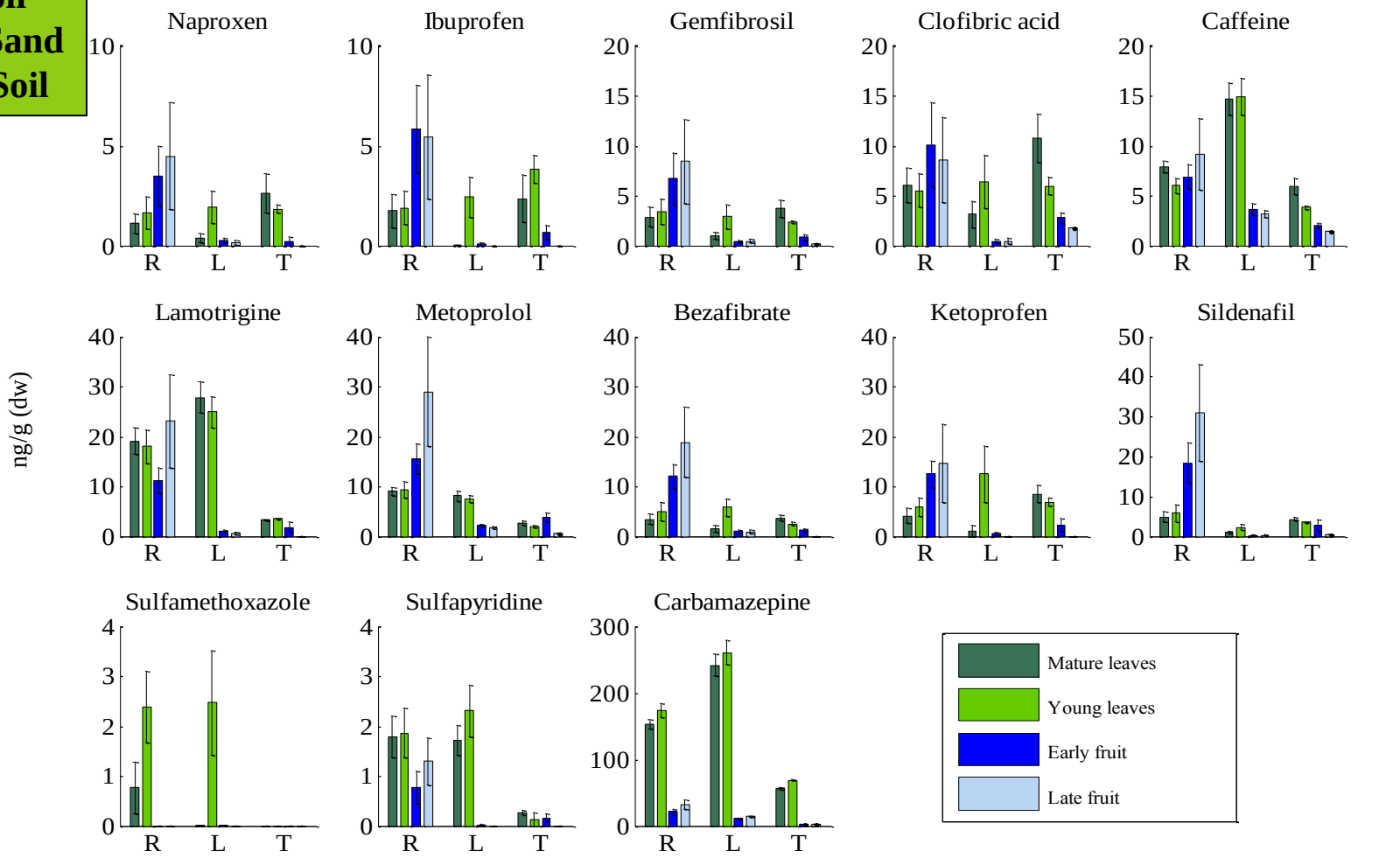
R – Sandy Soil
L – Aeolian Sand
T – Alluvial Soil



Spiked Fresh water (1ppb)

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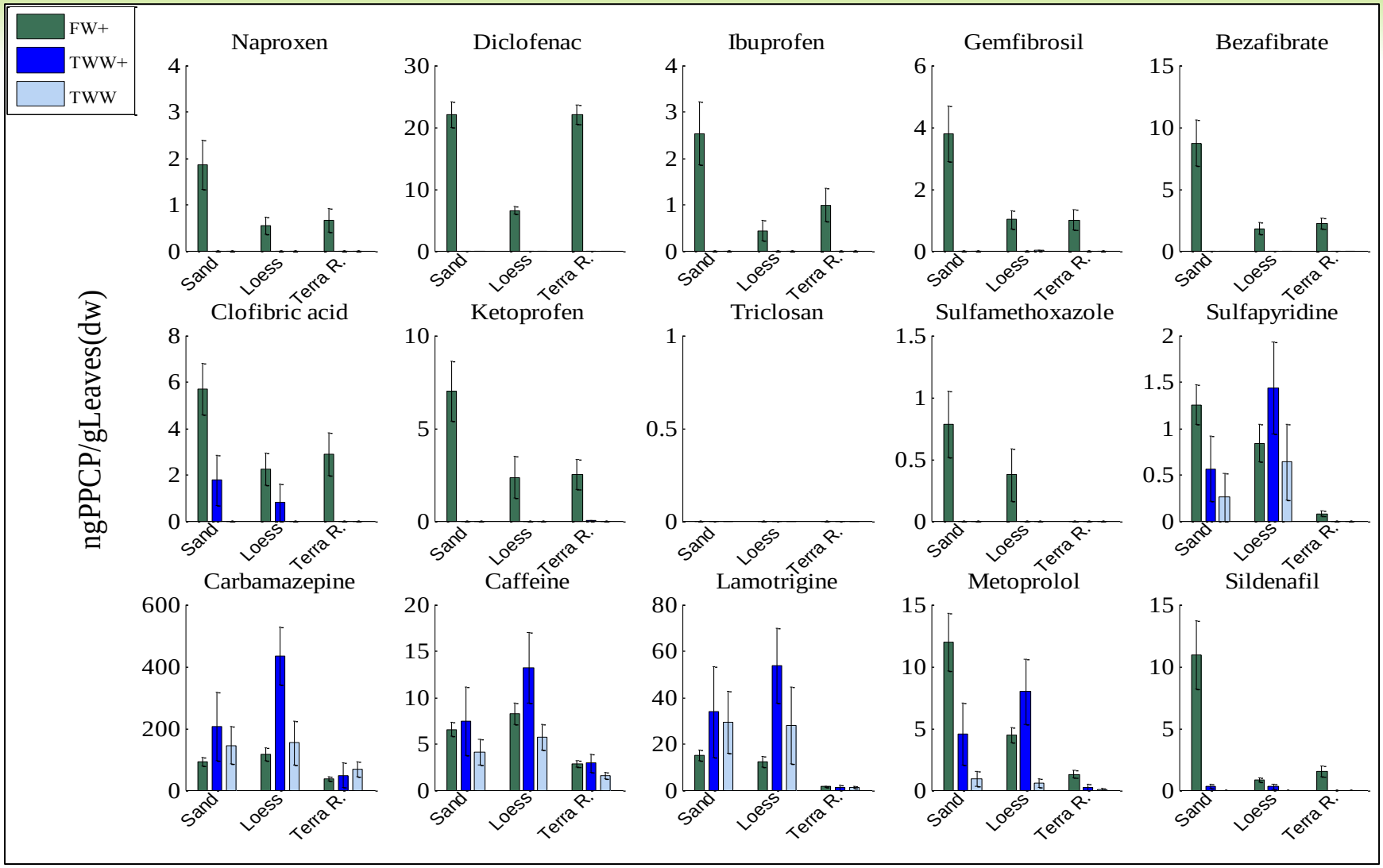
Cucumber
PPCPs in Leaves



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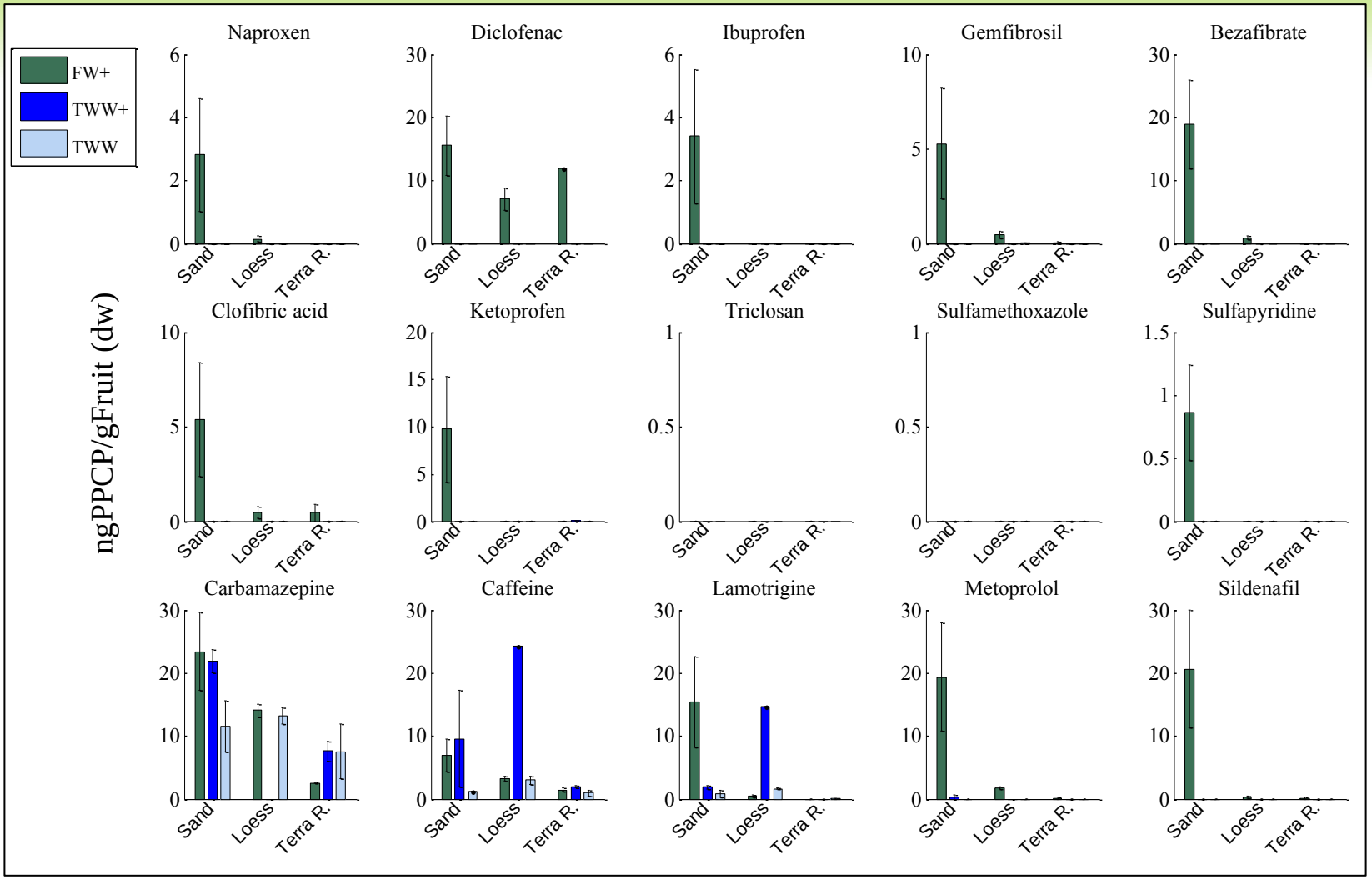
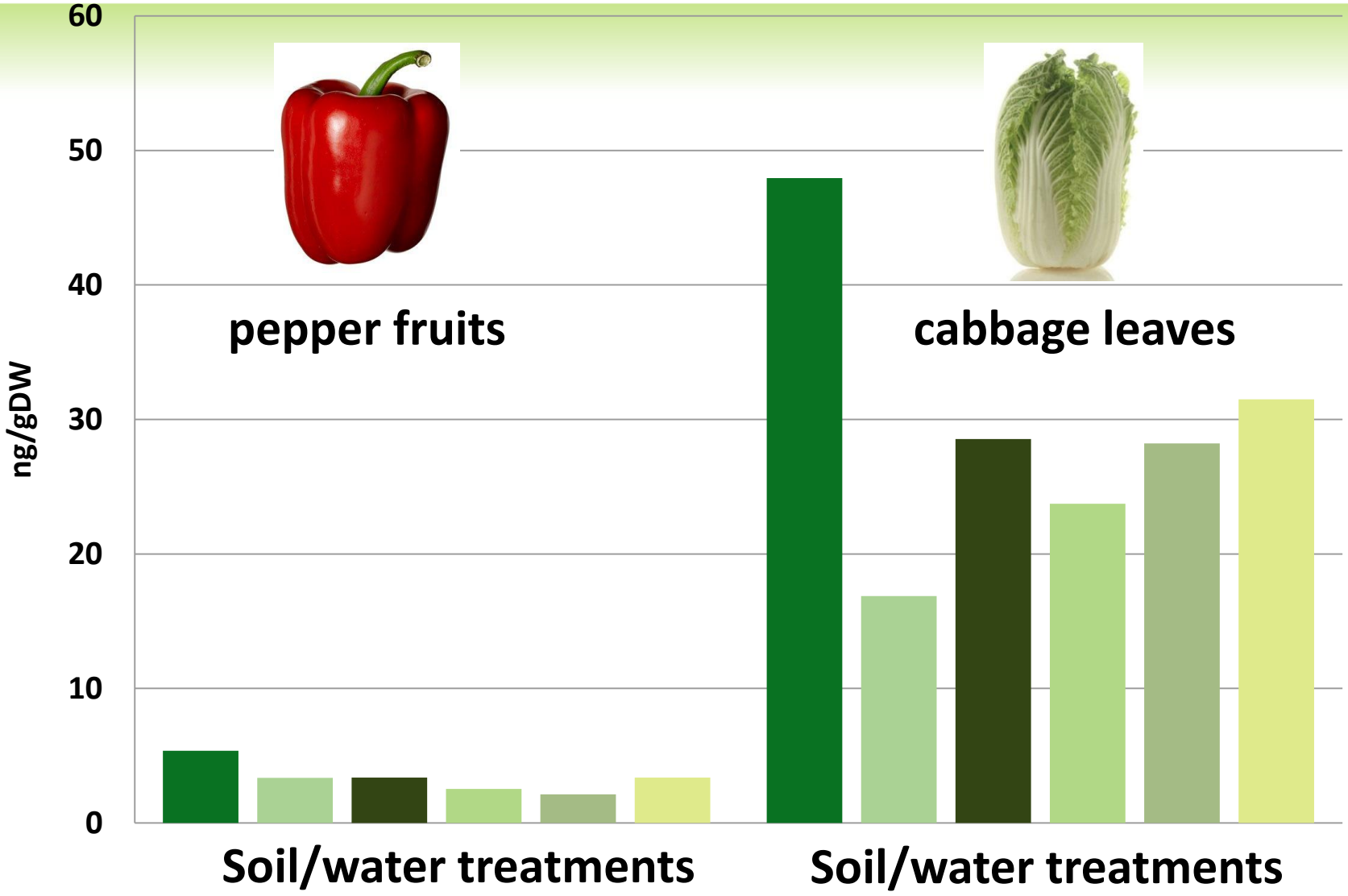
Cucumber PPCPs in Fruits



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

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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)?

Acknowledgments

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- **Ministry of Agriculture**, Israel