Fate of organic pollutants at the field scale: distribution in flowpaths

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Appended material

Appendix 1- Sampling locations and methods

A1. Sampling campaign

Table 1S: Storms sampling campaigns winter 2022

Storms	Sampling date+ Day in the week	Storm dates	Analysis
1st	16/1/2022, Sun	14-16/1/2022	Nutrients, pesticides, sediments
2nd	27/1/2022, Thu	23-30/1/2022	Nutrients, Pesticides, sediment

Table 2S: Sampling campaign location and date of collection. Compare locations to figure 1S-2S.

Location	Stream	Field	Drainage channels	Subsurface	Groundwater	Comments
			1st storm (16/1/2022)			
S	12/1					Stream
S1	16/1					Stream
SP2-1				12/1		West pipe*
WWM				16/1		West West Manhole 400 m from the stream
EF1		16/1				Surface runoff
EF3		16/1				Surface runoff
EF4		16/1				Surface runoff
EF2			16/1			Secondary channel
EF5			16/1			Secondary channel
EF6			16/1			Primary channels

EF7		16/1			Primary channels
WF8	16/1				Surface runoff
POWF14	16/1				Surface runoff, onion field
CWF15	16/1				Surface runoff, cotton field
WF10		16/1			Secondary channel
EEM			25/1		East East Manhole
WPzD, WPzSH				23/1	**West piezometers are deep and shallow
EPzD, EPzSh				23/1	East piezometer deep and shallow

2nd storm (27/1/2022)

S2	27/1				Stream
EF1	27/1				Surface runoff
EF4	27/1				Surface runoff
EF3	27/1				Surface runoff
EF2		27/1			Secondary channel
EF5		27/1			Secondary channel
EF6		27/1			*** Primary channels
PEF6		27/1			Additional water sample in EF6
EF7		27/1			Primary channels
WF8	27/1				Surface runoff
WF9	27/1				Surface runoff
WF10		27/1			Secondary channel
WF12		27/1			Secondary channel
POWF14	27/1				Surface runoff, onion field
WF15	27/1				Surface runoff
WF16		27/1			Secondary channel
WF17		27/1			Secondary channel
2WF18		27/1			Primary channel
WM			3/2		West Manhole
WPzD, WPzSH				27/1	****West piezometers deep and shallow
EPzD, EPzSh				27/1	

		East piezometer deep and shallow
SP2-2 -SP2-7	22-27/2	*****West pipe outlet (6 sequential samples)

. S-; SP2-West pipe; EF- East field; WF- West field OWF14-runoff from onion plot; CWF15-runoff from cotton plot; WF10, WF12- Secondary channels (wheat plot); WF16, WF17- Secondary channel draining both onion and cotton plots; WF18- Primary channel (common to onion and cotton); WWM- most western manhole; WM-western manhole; EEM- Most eastern manhole; WPzSh- West shallow piezometer; EPzSh-East shallow piezometer. P prefix- a substitute sample collected from nearby water after runoff stopped or if the sample was empty/lost. *Subsurface pipe outlet taken 4 days before it was submerged in storm **No groundwater was measured on the 1st storm. For comparison with the 1st storm data, the first day in groundwater campaign was taken to be representative 1st storm groundwater concentrations (taken four days after the end of the storm). ***Almost full of sediments, water was sufficient only for pesticide analysis (not enough for nutrients). **** The groundwater campaign overlapped the 2nd storm to investigate the storms' direct effect on groundwater quality. ***** before, during, and after the storm on 25-27/2 (total rain of 14 mm).

Figure 1S: East field locations

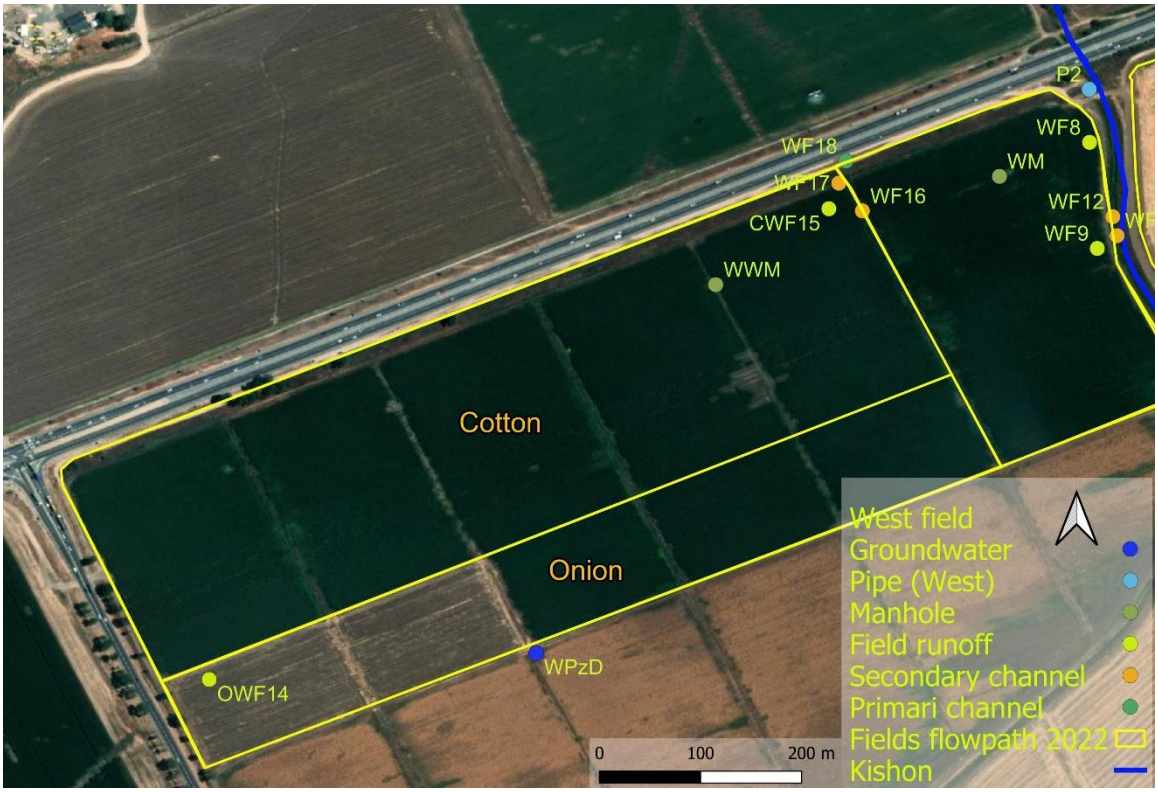


Figure 2S: West field locations

Figure 3S: *RCU (A) installed before rain; (B) RCU with flume open. The glass bottle is inserted into the designated cylindric space; (C) Ready for the storm, RCU with the roof protecting rain dilution; and (D) RCU after removing the roof to collect the full sample.*

Appendix B- Results

Table 3S: *This table defines the dominant flowpaths for each compound according to maximum detected concentrations (conc.). It also includes the highest concentration during the irrigation event on 28-29/4 in a separate category. The Farmers' application timing, including the last application date, is defined for 15*

relevant compounds. ES/ED- East shallow/deep piezometers; WS, WD- West shallow/deep piezometers. n.d. -not detected. Bromacil, naproxen, and ibuprofen were added only in winter 2022 to the analyzed compounds. Where no application dates are available, it is assumed that the compound has not been applied since 2/2020 in the East field and as of 11/2012 in the West field.

Name of organic compound	**Max conc. in winter 2022 (ng/L) + location**	**Max concentration in irrigation (ng/L)**	**Concentration (ng/L) in groundwater+location**	**Date of last application by the farmer (E-East field, W-west field)**	**Number of samples in winter 2022 (of total 64)**
Acetaminophen*	1308 West West manhole	n.d.	West piezometers only 17.34 WS		9
Acetamiprid	1.5 West Primary channel	n.d.	West deep piezometer 0.39	16.6.2016 W	11
Ametryn	1.27 West shallow piezometer	1.49	Deep and shallow East piezometers, Shallow West piezometer 1.37 WS	14.6.2015 W	18
Atrazine	31 West manhole	219.07	All piezometers 3.87 WD	9.12.2020 W	33
Atrazinen desethyl	127 West manhole	623.37	None		20
Atrazine desisopropyl	86 West manhole	312.16	None		17
Azoxystrobin	7.87 West field onion runoff	2.4	All piezometers 1.85 WD	7.7.2019 W	53
Bezafibrate*	21.6 East field runoff	n.d.	None		4
Boscalid	302 East filed, West field onion runoff	45.75	All piezometers 17.31 WS		50
Bromacil	46.5 West pipe outlet	n.d.	None		11
Caffeine	2799 West field runoff	1190	All piezometers 620 ED		35
Carbamazepine*	1421 West West manhole	884.11	All piezometers 119 ED		63
Carbamazepine 10,11n.d.epoxide	305 West manhole	175.91	Shallow East piezometer, West deep piezometer 8.87 ES		48
Carbamazepine 2 hydroxy	4.8 East field primary channel	173.08	None		3
Carbamazepine trans- 10,11-dihidroxy	68 West West Manhole	173.08	East shallow piezometer only 12.34		24
Carbendazim	14 West deep piezometer	0.23	All piezometers 13.95 WD		38
Carbofuran	0.51 West deep piezometer	n.d.	West deep piezometer 0.51		1
Chlorantraniliprole	1475.7 Onion plot runoff	539.01	West deep piezometer 8.94	19.7.2019 W	33

Cyproconazole	31.2 East field secondary channel	n.d.	None	8.6.2018 W	4
Diazinon	0.64 East deep piezometer	n.d.	East deep piezometer, West piezometers 0.64 ED		9
Diclofenac*	12.72 West field secondary channel	n.d.	East shallow and West deep piezometers 3.58 WS		5
Difenoconazole	17.12 West field runoff	n.d.	All piezometers 5.71 WS	14.3.2018 W	45
Diflufenican	6585 West field onion runoff	n.d.	All piezometers 0.65 ES, WS		25
Dimethomorph cis/trans	6.17 East field secondary channel & West field deep piezometer	n.d.	West deep piezometer 6.17		7
Diuron	98996# East field runoff	4.93	All piezometers 123 ED	17.2.19 W 30.12.21 E	62
Fenaminphos sulfoxide	636 West field secondary channel	1.43	None		25
Fenaminphos	28.2 West field primary channel	12.65	None		4
Fenhexamid	19.8 West West Manhole	n.d.	None		1
Fluometuron	12 Pipe outlet	12.65	Shallow East, deep West piezometers 3.16 ED		21
Flutriafol	0.45 West shallow piezometer	7.5 Ponding water	West deep piezometer 0.45		1
Hexazinone	1.2 West manhole	1.55	None		4
Ibuprofen*	571.7 West pipe outlet	n.d.	None		7
Imidacloprid	10621.2# West field onion runoff	66.97	All piezometers 15.28 ED, WD		44
Indaziflam	1.21 East primary channel	n.d.	None		2
Lamotrigine*	130 West manhole	79.23	East and West shallow piezometers 11.11 WS		42
Metalaxyl	36.98 East field secondary channel	7.2	All piezometers 1.44 WD		62
Metazachlor	7.65 West pipe outlet	n.d.	None		1
Methomyl	3.91 West field onion runoff	n.d.	None		1
Methoxyfenozide	971 West West manhole	1379.8	All piezometers 5.64 ES	30.6.2020 W	55
Metolachlor	92 West shallow piezometer	40.24	All piezometers 92 WS	11.3.2020 W	63
Metribuzin	8 Onion plot runoff	n.d.	2.48 WD	11.11.2019 W	2

Naproxen*	5 East deep piezometer	n.d.	East deep piezometer 4.97		1
Oxadiazon	10808.9[#] West field onion runoff	n.d.	None	10.1.2022 W	13
Penconazole	5.8 East field secondary channel	6.39	East shallow, West deep, and shallow piezometers 2.92 WD		16
Pendimethalin	11574[#] West field onion runoff	n.d.	All piezometer 1.15 WS	20.2.16 W	35
Pirimicarb	(Only in irrigation)	1.08	None		
Prochloraz	0.5 Subsurface West pipe outlet	n.d.	None		1
Prometon	0.4 West manhole	0.58	None		3
Prometryn	1.52 Subsurface west pipe outlet	n.d.	West shallow piezometer 0.92		7
Propachlor	0.06 East shallow piezometer	n.d.	East shallow piezometer 0.06		1
Propamocarb	57.91 West deep piezometer	n.d.	All piezometer 57 WD		63
Propazine	(Only in irrigation)	2.47	None		
Propiconazole	7.3 East field runoff	n.d.	West shallow piezometer 1.85		2
Propoxur	367.3 West West manhole	526.89	All piezometers 22.59 ED		43
Propyzamide	93.6 East field secondary channel	n.d.	West piezometers 15.24 WS	12.2.2018 W	17
Sildenafil*,**	139.96 West field primary channel	n.d.	East deep piezometer 21.16		3
Simazine	7.38 West deep piezometer	n.d.	West deep piezometers 7.38		
Sulfamethoxazole	1.87 West West manhole	17.34	None		1
Sulfapyridine*	(Only in irrigation)	0.59			
Tebuconazole	42.5 West field onion runoff/East file secondary channel	16.12	All piezometers 18.54 WD	11.5.2018 W	51
Tebuthiuron	1.6 West West Manhole	1.99	None		8
Terbutryn	79.15 West shallow piezometer	10.23	All piezometers 9.27 WS		50
Thiacloprid	0.82 West field onion runoff	n.d.	None		2
Triadimenol A	(Only in irrigation)	14.75, ponding water		16.6.16 W	0

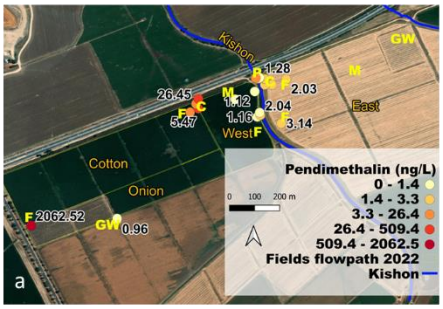
Measured concentrations were very high. Actual concentrations will be higher than reported; *- Pharmaceuticals (rather than pesticides); **- data contain significant errors for this compounds

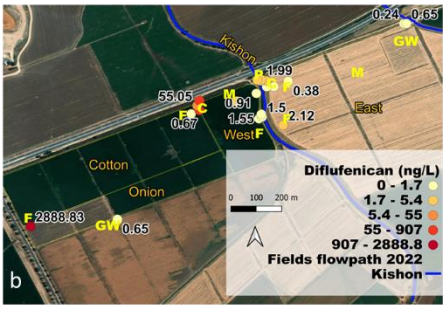
Table 4S: Application dates of analyzed compounds in the West field, ordered by first application date. Onion in parentheses states application in onion plot (contained carrot or tomatoes for some years)

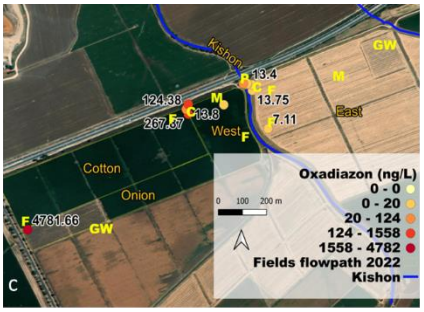
West field	dates
Diuron	21/09/2015, 29/09/2015, 1/10/2015, 17/02/2019
Ametryn	14/06/2015
Pendimethalin	20/02/2016 (onion), 10/1/2022 (onion)
Propyzamide	02/03/2016, 12/02/2018
Acetamiprid	22/05/2016, 16/06/2016
Triadimenol	16/06/2016
Metolachlor	12/02/2018, 11/03/2020
Terbutryn	15/01/2018
Difenoconazole	14/03/2018
Chlorantraniliprole	14/03/2018, 12/06/2019 (onion), 26/06/2019 (onion)
Tebuconazole	11/05/2018
Cyproconazole	14/06/2018
Methoxyfenozide	23/05/2019, 30/06/2020
Imidacloprid	30/06/2019 (onion), 22/11/2022 (onion)
Azoxystrobin	23/10/2019, 07/07/2019
Metribuzin	11/11/2019
Atrazine	09/12/2020
Oxadiazon	12/12/2021 (onion), 10/1/2022 (onion)
Diflufenican	10/01/2022 (onion)
East field	
Diuron	30/12/2021

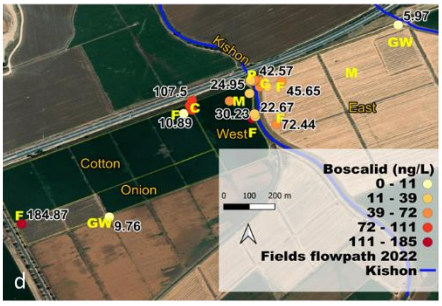
Table 5S: Compare of concentration sum in channels runoff and fields runoff. Sum did not include diuron, to avoid masking of the trends.

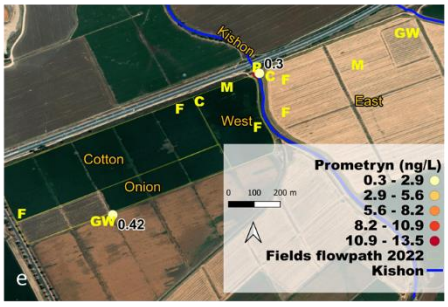
Storms	**West channel**	**West field**	**East Channel**	**East field**
1st	4996.35	351.29	439.68	281.81
2nd	2936.47	343.32	157.30	114.88
Sum	7932.82	694.61	596.98	396.69

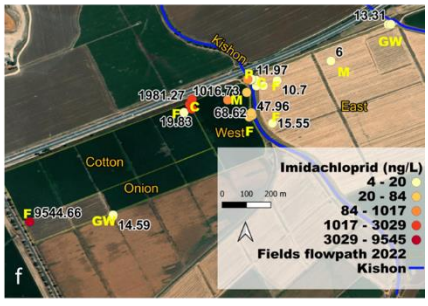

Kishon
GW
M
East
West
Cotton
Onion
F 2062.52
GW 0.96
26.45
5.47
1.28
2.03
1.12
2.04
1.16
3.14
Pendimethalin (ng/L)
0 - 1.4
1.4 - 3.3
3.3 - 26.4
26.4 - 509.4
509.4 - 2062.5
Fields flowpath 2022
Kishon
a

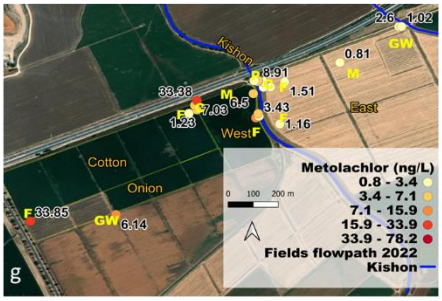

Kishon
GW
M
East
West
Cotton
Onion
F 2888.83
GW 0.65
55.05
0.87
0.91
1.55
1.99
0.38
1.5
2.12
0.24
0.65
Diflufenican (ng/L)
0 - 1.7
1.7 - 5.4
5.4 - 55
55 - 907
907 - 2888.8
Fields flowpath 2022
Kishon
b

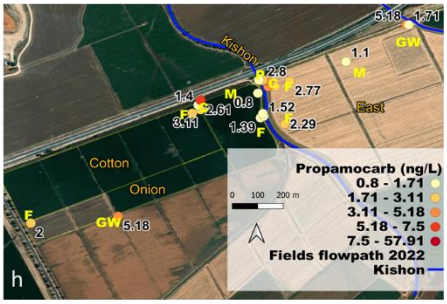

Kishon
GW
M
East
West
Cotton
Onion
F 4781.66
GW
124.38
267.37
13.8
13.4
13.75
7.11
Oxadiazon (ng/L)
0 - 0
0 - 20
20 - 124
124 - 1558
1558 - 4782
Fields flowpath 2022
Kishon
c

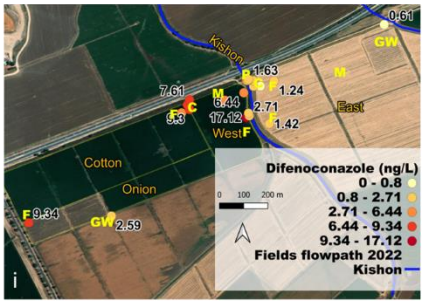

Kishon
GW
M
East
West
Cotton
Onion
F 184.87
GW 9.76
107.5
10.89
24.95
30.23
42.57
45.65
22.67
72.44
5.97
Boscalid (ng/L)
0 - 11
11 - 39
39 - 72
72 - 111
111 - 185
Fields flowpath 2022
Kishon
d

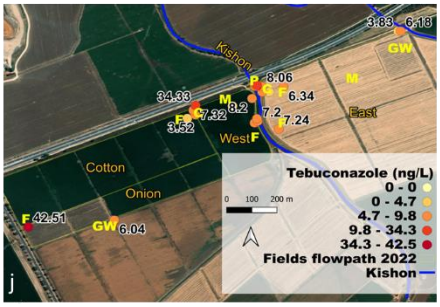

Kishon
GW
M
East
West
Cotton
Onion
F
GW 0.42
0.3
Prometryn (ng/L)
0.3 - 2.9
2.9 - 5.6
5.6 - 8.2
8.2 - 10.9
10.9 - 13.5
Fields flowpath 2022
Kishon
e

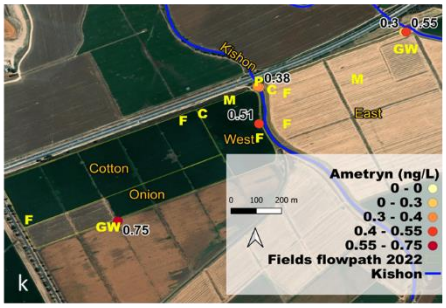

Kishon
GW
M
East
West
Cotton
Onion
F 9544.66
GW 14.59
1981.27
1016.73
19.83
68.62
11.97
10.7
47.96
15.55
6
13.31
Imidachloprid (ng/L)
4 - 20
20 - 84
84 - 1017
1017 - 3029
3029 - 9545
Fields flowpath 2022
Kishon
f

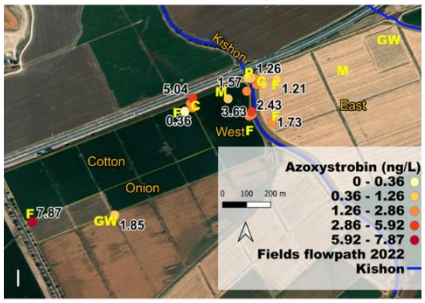

Kishon
GW
M
East
West
Cotton
Onion
F 33.85
GW 6.14
33.38
1.23
7.03
8.5
3.43
1.51
1.16
2.6
1.02
0.81
Metolachlor (ng/L)
0.8 - 3.4
3.4 - 7.1
7.1 - 15.9
15.9 - 33.9
33.9 - 78.2
Fields flowpath 2022
Kishon
g

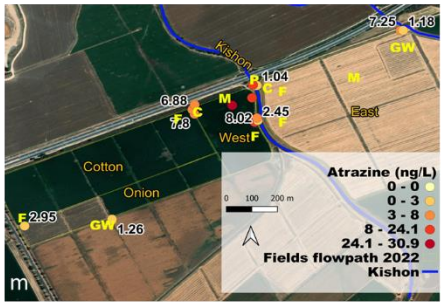

Kishon
GW
M
East
West
Cotton
Onion
F
2
GW 5.18
1.4
3.11
2.61
0.8
1.52
1.39
2.77
2.29
2.8
1.1
5.18
1.71
Propamocarb (ng/L)
0.8 - 1.71
1.71 - 3.11
3.11 - 5.18
5.18 - 7.5
7.5 - 57.91
Fields flowpath 2022
Kishon
h

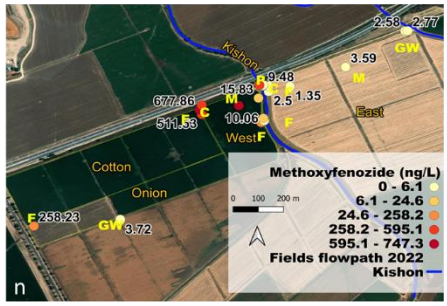

Kishon
GW
M
East
West
Cotton
Onion
F 9.34
GW 2.59
7.61
5.33
6.44
17.12
1.63
2.71
1.24
1.42
0.61
Difenoconazole (ng/L)
0 - 0.8
0.8 - 2.71
2.71 - 6.44
6.44 - 9.34
9.34 - 17.12
Fields flowpath 2022
Kishon
i

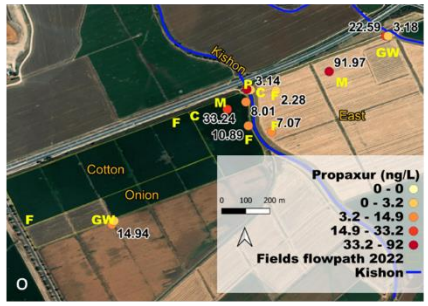

Kishon
GW
M
East
West
Cotton
Onion
F 42.51
GW 6.04
34.33
3.52
7.32
8.2
7.2
6.34
7.24
3.83
6.18
Tebuconazole (ng/L)
0 - 0
0 - 4.7
4.7 - 9.8
9.8 - 34.3
34.3 - 42.5
Fields flowpath 2022
Kishon
j

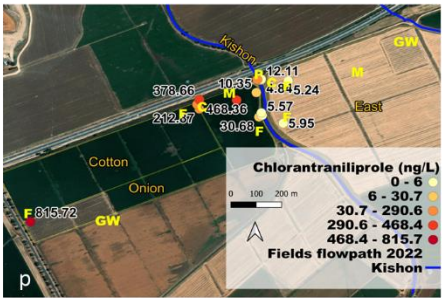

Kishon
GW
M
East
West
Cotton
Onion
F
GW 0.75
0.51
0.38
0.3
0.55
Ametryn (ng/L)
0 - 0
0 - 0.3
0.3 - 0.4
0.4 - 0.55
0.55 - 0.75
Fields flowpath 2022
Kishon
k

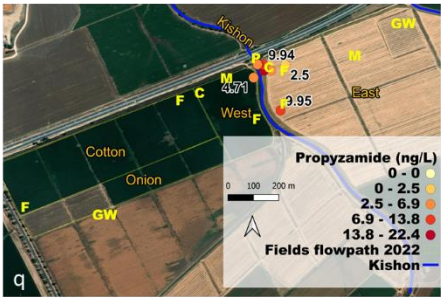

Kishon
GW
M
East
West
Cotton
Onion
F 7.87
GW 1.85
5.04
0.36
1.57
3.68
1.26
2.43
1.21
1.73
Azoxystrobin (ng/L)
0 - 0.36
0.36 - 1.26
1.26 - 2.86
2.86 - 5.92
5.92 - 7.87
Fields flowpath 2022
Kishon
l

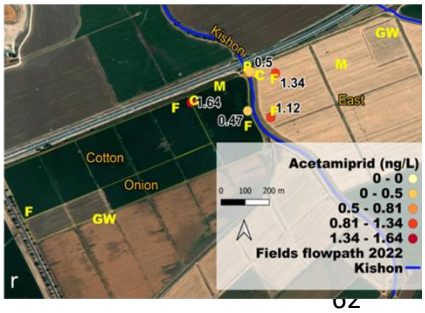

Kishon
GW
M
East
West
Cotton
Onion
F 2.95
GW 1.26
6.88
7.8
8.02
1.04
2.45
7.25
1.18
Atrazine (ng/L)
0 - 0
0 - 3
3 - 8
8 - 24.1
24.1 - 30.9
Fields flowpath 2022
Kishon
m


Kishon
GW
M
East
West
Cotton
Onion
F 258.23
GW 3.72
677.86
511.33
15.83
10.06
9.48
2.5
1.35
3.59
2.58
2.77
Methoxyfenozide (ng/L)
0 - 6.1
6.1 - 24.6
24.6 - 258.2
258.2 - 595.1
595.1 - 747.3
Fields flowpath 2022
Kishon
n


Kishon
GW
M
East
West
Cotton
Onion
F
GW
14.94
33.24
10.89
3.14
8.01
2.28
7.07
91.97
22.59
3.18
Propaxur (ng/L)
0 - 0
0 - 3.2
3.2 - 14.9
14.9 - 33.2
33.2 - 92
Fields flowpath 2022
Kishon
o


Kishon
GW
M
East
West
Cotton
Onion
F 815.72
GW
378.66
212.57
468.36
30.68
10.35
12.11
5.84
45.24
5.57
5.95
Chlorantraniliprole (ng/L)
0 - 6
6 - 30.7
30.7 - 290.6
290.6 - 468.4
468.4 - 815.7
Fields flowpath 2022
Kishon
p


Kishon
GW
M
East
West
Cotton
Onion
F
GW
4.71
9.94
2.5
9.95
Propyzamide (ng/L)
0 - 0
0 - 2.5
2.5 - 6.9
6.9 - 13.8
13.8 - 22.4
Fields flowpath 2022
Kishon
q


Kishon
GW
M
East
West
Cotton
Onion
F
GW
1.64
0.47
0.5
1.34
1.12
Acetamiprid (ng/L)
0 - 0
0 - 0.5
0.5 - 0.81
0.81 - 1.34
1.34 - 1.64
Fields flowpath 2022
Kishon
r

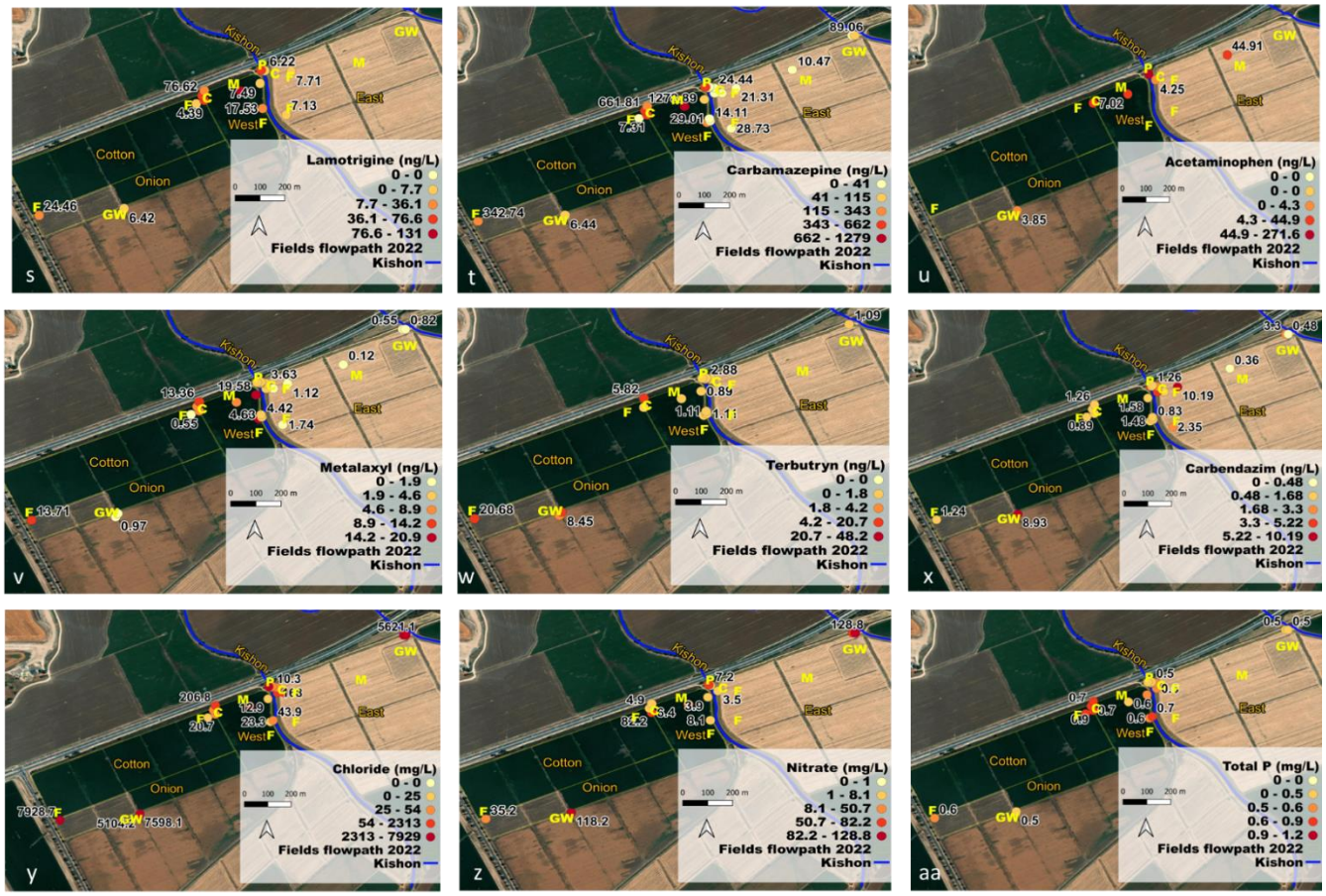


Figure 4S: *Field spatial distribution of concentration for pesticides, pharmaceuticals, and nutrients during the 2nd storm. Concentrations (organic compounds-ng/L, nutrients-mg/L) are given on a color scale from lowest (light yellow) to highest (red). The quantity is also labeled in black for a few locations. Flowpaths are labeled: M-manhole, GW-groundwater, F-field runoff, C-channels, and P-pipe outlet. Field sections due to different crops are sketched as well.*