Supporting Information

S1. Characterisation and results of Rhine data set

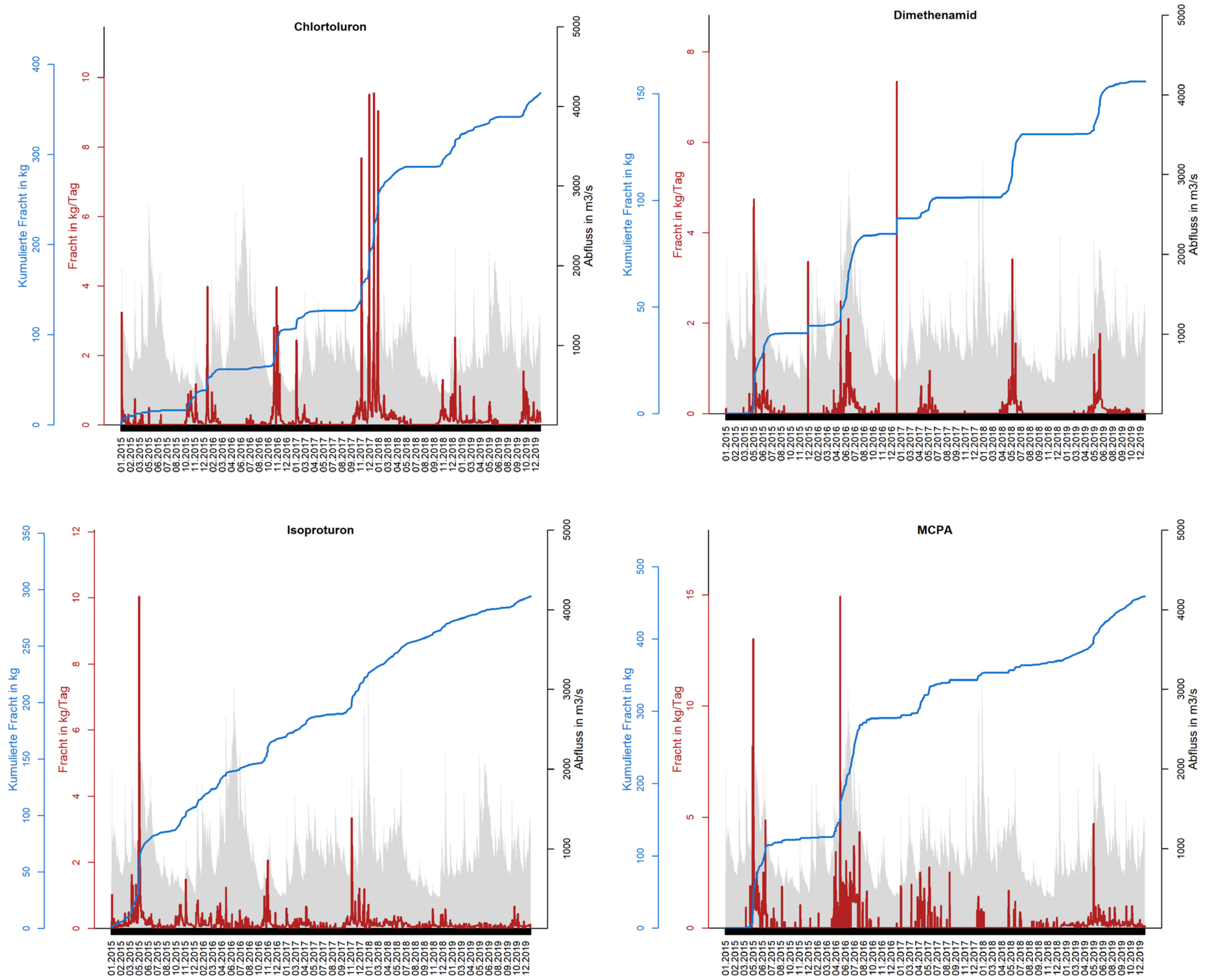


Figure S1: Time-series (2015-2019) of cumulative mass load, transport rate (primary y-axes), and discharge (secondary y-axis) at the Rhine River at Basel for chlortoluron and dimethenamid (top two panels), and isoproturon and MCPA (bottom two panels).

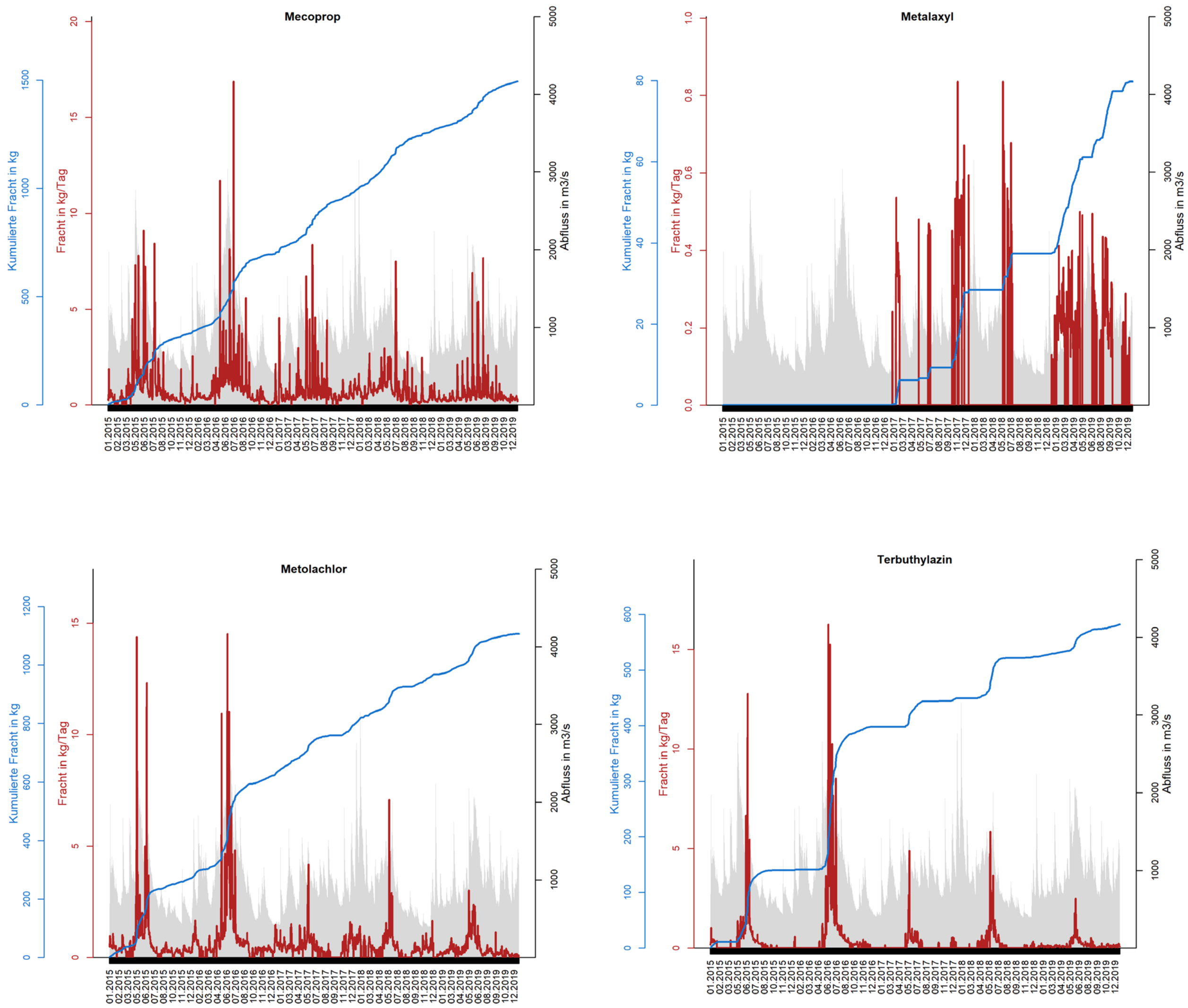


Figure S2: Time-series (2015-2019) of cumulative mass load, transport rate (primary y-axes), and discharge (secondary y-axis) at the Rhine River at Basel for mecoprop and metalaxyl (top two panels), and metolachlor and terbuthylazine (bottom two panels).

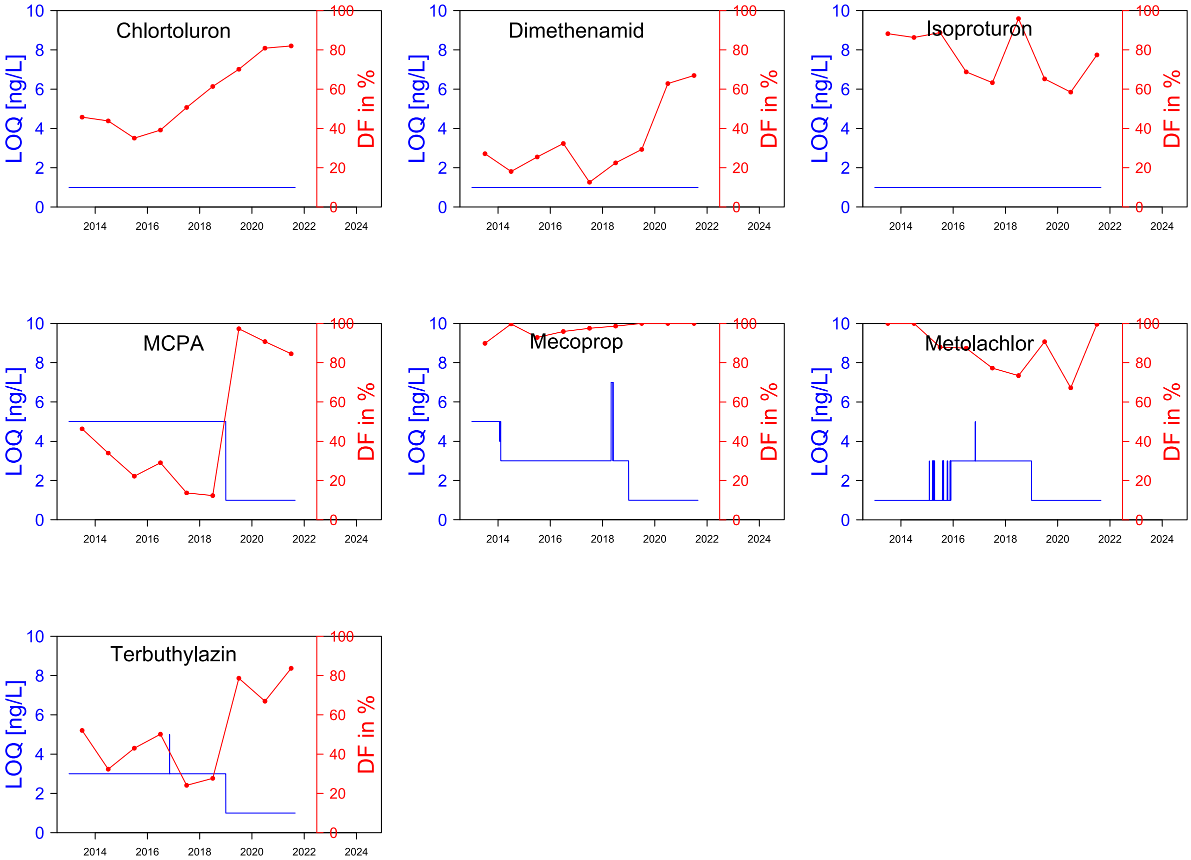


Figure S3. Temporal development of limit of quantification (LOQ) and of detection frequency (DF) of compounds fulfilling criteria 1 (data on usage). 2 (primarily used for plant protection) and 3 (sufficiently high DF). Values for DF are plotted in middle of corresponding calendar year.

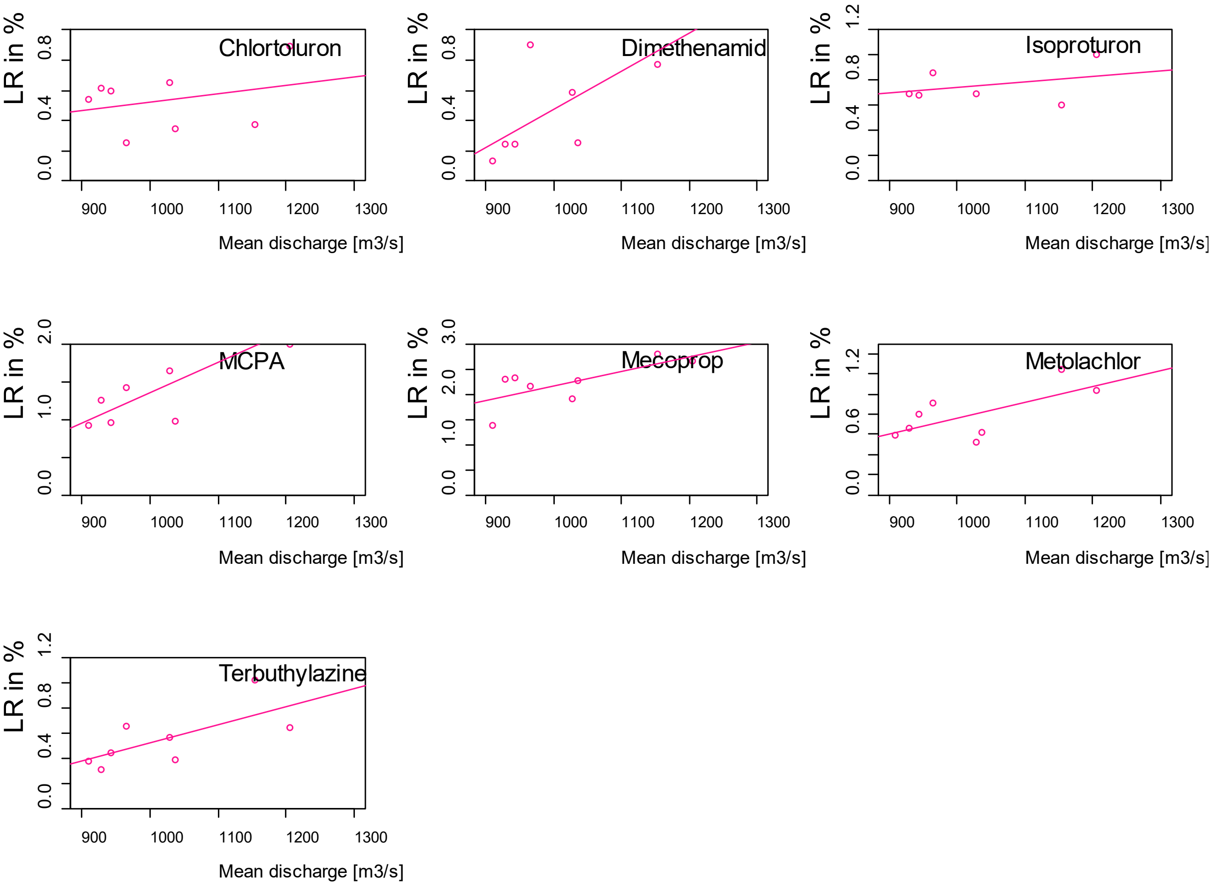


Fig. S4: Loss rates of selected pesticides as a function of average annual discharge at the Rhine River monitoring station at Basel.

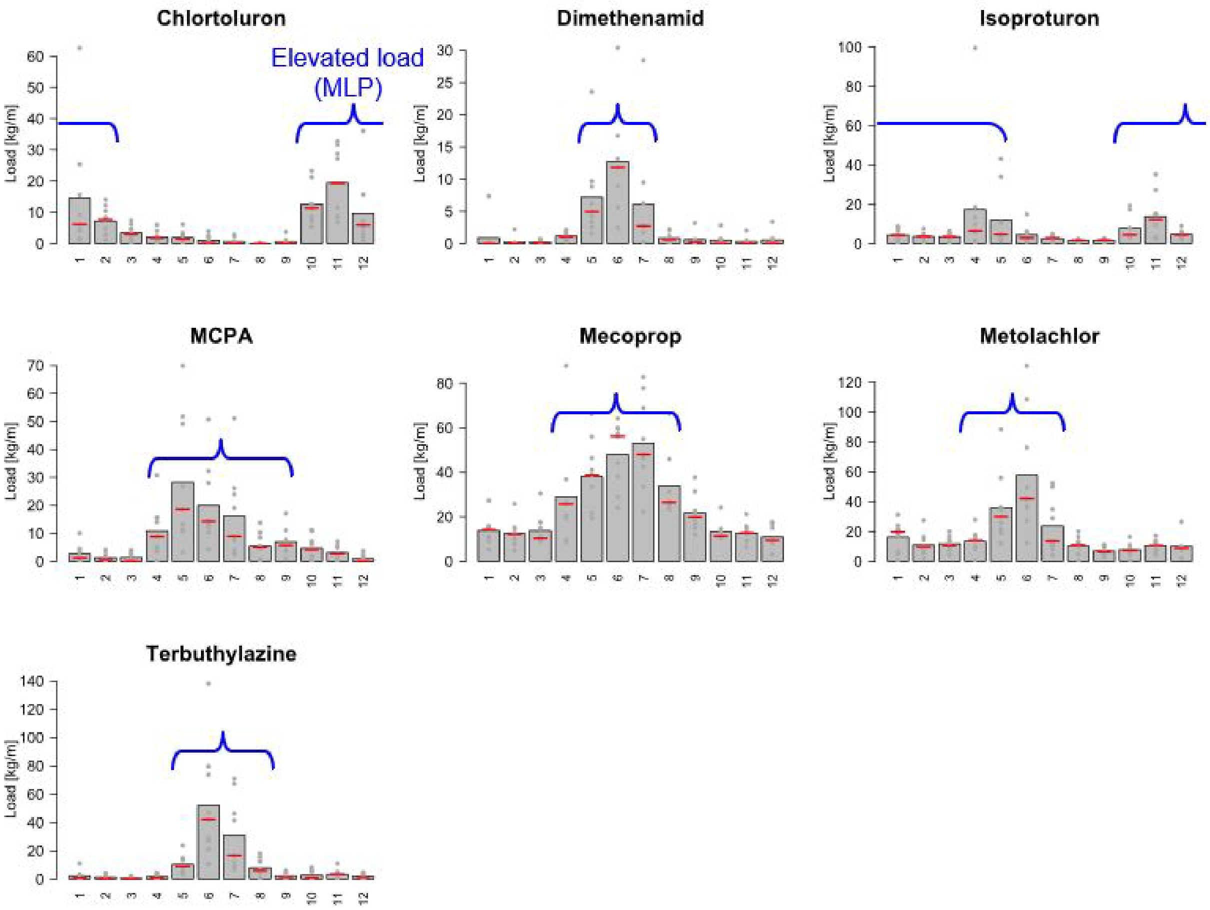


Fig. S5: Seasonal development of the monthly loads of selected pesticides at the Rhine monitoring station at Basel and the delineation of main loss periods (MLP; blue bracket). MLPs were selected on a visual basis of the seasonal loads with the months typically making up to 90% of the cumulative annual load. The grey bar is the mean load of all evaluated years, the grey dots are the loads of the evaluated years and the red line indicates the position of the median load.

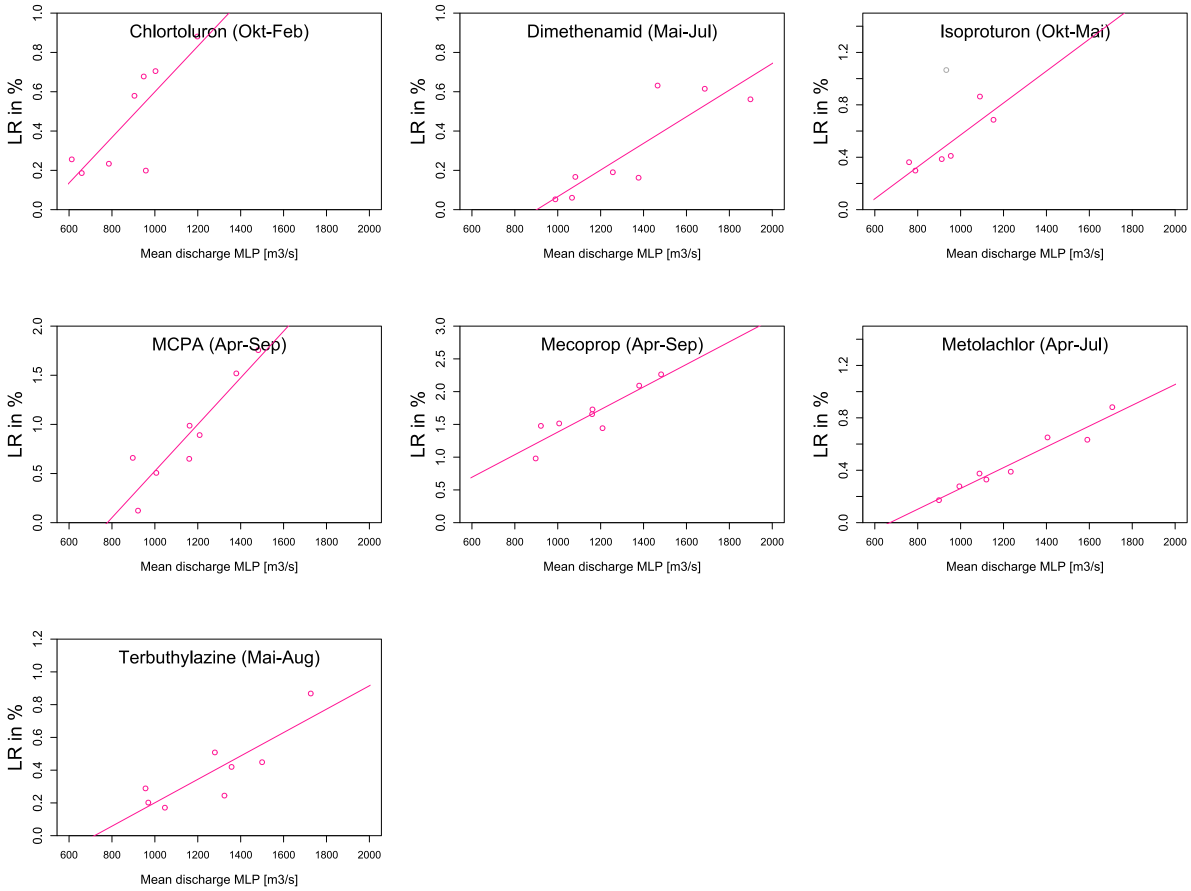


Fig. S6: Loss rates of selected pesticide as a function of average discharge during the main loss period at the Rhine monitoring station at Basel. In the case of isoproturon the value of the last year before the withdrawal from the market (grey circle) was not included in the calculation because the sale was stopped halfway through the year.

Compound Name	Legal status	LOQ 2013-2021 [ng/L]	DF 2020	DF 2013-2021 (min, max)	Suitable for Evaluation	Sale 2013-2020 [t] (min, max)	Main usages
Carbendazim	P, B	1	100%	99% (95,100)	No	0.7 (0.4, 1.0) [1]	Orchards, antifiungal biocide
Mecoprop	P, B	1	100%	97% (89, 100)	Yes	13.9 (9.6, 18.2)	Cerals, orchards, amenity use, building materials
MCPA	P	1 – 5	91%	48% (12, 97)	Yes	9.9 (7.5, 12.5)	Meadows, amenity use
Chlortoluron	P	1	81%	57% (35, 82)	Yes	15.7 (9.1, 21.5)	Cereals
Metolachlor	P	1 – 3	67%	87% (67, 100)	Yes	26.9 (16.8, 33.3)	Maize, sugar beet
Terbuthylazine	P, BX	1 – 3	67%	51% (24.1, 84)	Yes	23.4 (14.0, 31.1)	Maize
Dimethenamid	P, BX	1	63%	33% (13, 67)	Yes	10.6 (3.3, 22.2)	Maize, sugar beet
Isoproturon	P(X), B	1	59%	77% (58, 96)	Yes	11.3 (1.0, 22.5)	Cereals
Metalaxyl	P	2 – 5	51%	18% (0, 51)	Candidate	2.2 (1.7, 2.6)	Vegetables, Potatoes, Vineyards
Cyproconazole	P, B	3 – 5	5%	6% (0.2, 36)	No	1.3 (0.7, 1.7)	Cereals

Table S1: Substances fulfilling the three criteria described in Section 2.1 and sorted by detection frequency (DF) in 2020 including all compounds with DF > 5%. Abbreviations: P: authorized as plant protection product, B: authorized as biocide product, X. authorization revoked between 2013 and 2020, LOQ: Limit of Quantification. DF 2013-2021: Detection frequency of from 2013 to 2021 calculated as the mean of the 9 annual DFs with minimum and maximum value in brackets. Grey shading indicates that the substances are not suitable for evaluation because: carbendazim is predominantly used as a biocide and not as a plant protection product, cyproconazole has a mean DF far below 20%, and metalaxyl has a mean DF slightly below 20% but DF > 40% in the last two years. [1] Carbendazim sales data from 2013-2018 (no sale as PPP after 2018).

S2. Characterisation and results of Eschibach data set

Compound	DT_{50} (Days)	K_{foc}	GUS	P_v (mPa)
Atrazine	2.6*	174	2.57	0.039
Chlortoluron	44.4	147.22	2.01	0.008
Dimethenamid	16.4*	69	2.41	0.37
Isoproturon	40	122	2.61	5.5E-3
MCPA	13.5	73.88	3.13	0.4
Mecoprop	37	31	2.29	1.6
Metolachlor	88	163	2.36	1.7
Terbuthylazine	6	231	2.19	0.152

**Aqueous photolysis DT50 (days) at pH 7.*

Table S2: Summary of herbicides selected for analyses in this study and their physico-chemical properties. DT_{50} for water phase only. K_{foc} – organic carbon normalized Freundlich distribution coefficient. GUS – Groundwater Ubiquity Score, potential leaching index. P_v – vapour pressure at 20 ºC. Values from Lewis et al. (2016). Atrazine is included because of the analysis of water quality modelling from the Eschibach catchment.

S2.1 The challenge of hydrological conditions confounding the effects of mitigation measures

A significant confounding factor that contributes to the uncertainty of attributing water quality improvements to mitigation measures are the hydrological conditions, due to its high spatial and temporal variability. One of the main sources of aquatic pesticide pollutions is from fast transport pathways driven by hydrological activity (Leu et al., 2010). However, the exact quantities of hydrologically-driven pesticide transport will depend to a large extent on the intensity and timing of rainfall events relative to pesticide application patterns (Lerch et al., 2011).

For instance, the effectiveness of implemented mitigation measures could be obscured in years with less than average rainfall (i.e., drought conditions), because lower levels of hydrologically-driven pesticide transport would be expected (Figure S7a). Thus, to evaluate the "true" effectiveness of the mitigation measures it would be important to compare the annual pesticide levels in years with appreciable amounts of precipitation. We have termed this hypothetical quantity of precipitation, the critical amount of precipitation (P_{crit}). An important note is that we assume a homoscedastic relationship between annual aquatic pesticide levels and precipitation in our conceptual example (Figure S7a) for illustration purposes. Theoretically, effective mitigation should produce a significant change in the relationship between annual precipitation and aquatic pesticide pollution levels in years with appreciable amounts of precipitation (Figure S7a).

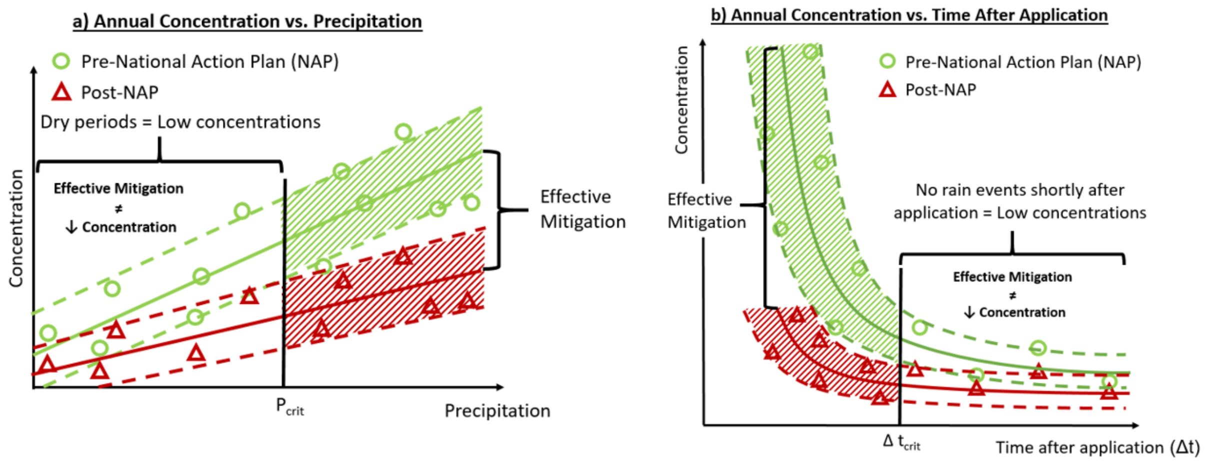


Figure S7. Conceptual diagram of the challenge to determine the effectiveness of mitigation measures with below average years of annual precipitation and rainfall events that occur long after pesticide application: a) relationship between pesticide concentrations and total annual precipitation, b) relationship between pesticide concentrations and the time elapsed between pesticide application and rainfall events.

Timing of rainfall events relative to pesticide application is another important hydrological factor that affects aquatic pesticide levels (Figure S7b). There is usually an inverse relationship between aquatic pesticide levels and the time elapsed between pesticide application and rainfall (Leu et al., 2004; Doppler et al., 2012). Therefore, a decrease in aquatic pesticide pollution could be caused by precipitation events occurring long after their application and not because of mitigation measures. Thus, to evaluate the "true" effectiveness of mitigation measures it would be important to compare annual aquatic pesticide levels below a certain duration of time between pesticide application and rainfall events (Δt). We call this threshold Δt_{crit} and hypothesize that it would be a function of the chemical properties of the pesticides, such as the degradation half-life (Table S2). We expect that effective mitigation would produce a significant difference in the relationship between aquatic pesticide pollution levels and years when rain events occur shortly after pesticide application (Figure S7b).

Using simulated annual atrazine concentrations from the Eschibach model we can define P_{crit} by plotting the maximum 14-day average concentrations vs. the cumulative precipitation over the same 14-day period (Figure S8). We can see that it generally agrees with the concept presented in Figure S7a, that concentration and precipitation are proportional. The data points for 2014 do not seem to agree with our concept, that the difference between control and mitigation above P_{crit} should be larger. However, when we look at Figure S8, we can see that the timing of 2014's rainfall events that cause the maximum concentration occur more than 50 days after pesticide application, which explains its low concentrations. Through visual inspection we set $P_{crit} = 46.6$ mm, which is the cut-off to include data points from 2016.

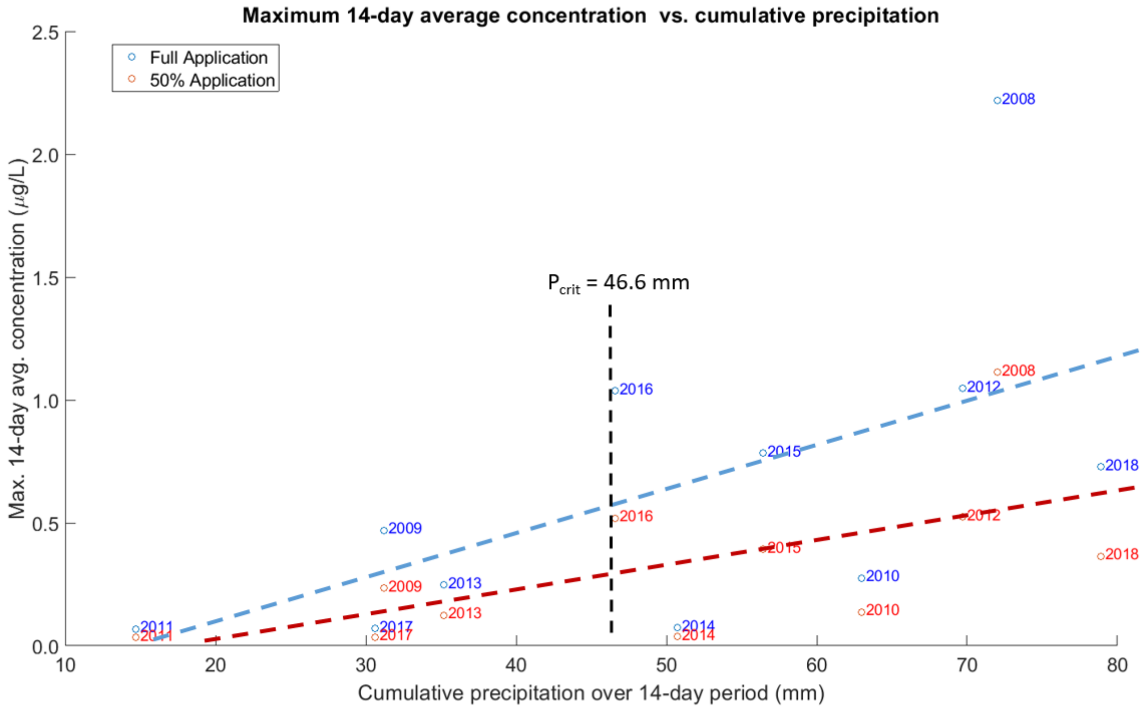


Figure S8. Maximum 14-day average concentration vs. cumulative precipitation. Dashed coloured lines represent linear best-fits. Dashed black line represents the cut-off for P_{crit}.

To define Δt_{crit} we plot the maximum 14-day average concentrations vs. Δt, the time elapsed between pesticide application and the rainfall event (Figure S9). Again, we see that it generally agrees with the concept presented in Figure S7b, that concentration and Δt are inversely proportional. However, there are several data points (when $\Delta t < 10$ days) that do not agree well with our concept. Some of those years are associated with low magnitudes of precipitation (i.e., 2009 and 2011 in Figure S8), which can explain part of the discrepancy. Through visual inspection we set $\Delta t_{crit} = 30$ days, which is when the data points between control and mitigation show small differences (i.e., 2014 and 2017).

We hypothesize that focusing the statistical analysis on annual herbicide concentrations with years where rainfall is above P_{crit} and when the time between herbicide application and rainfall events are below Δt_{crit} (as difficult as that would be to define) will lead to more confidence in attributing the effects of reduced pesticide losses to mitigation measures. However, it should be noted that all simulated data was used in the statistical analysis presented in this paper (i.e., no data points Δt_{crit} <10 days were omitted from the analysis).

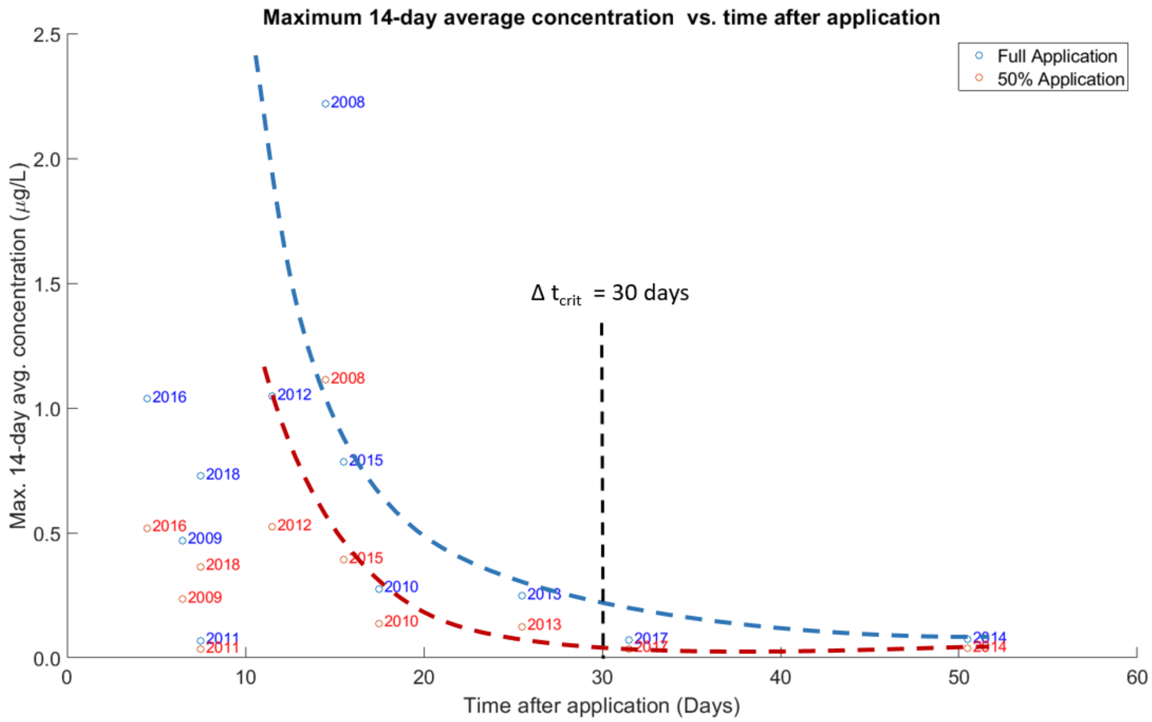


Figure S9. Maximum 14-day average concentration vs. time after application (Δt). Dashed coloured lines represent best-fits (omitting data points Δt <10). Dashed black line represents the cut-off for Δt_{crit}.

S2.2 Time-series of annual simulated discharge and atrazine concentrations for the Eschibach catchment from 2008 to 2018. Each year's time-series shows one day before and 100 days after (atrazine & terbuthylazine) pesticide application. X-axes are in units of the model time-steps (Δt = 10 minutes). The x-axes range changes from year to year because the simulated data is taken from one continuous 11-year model run.

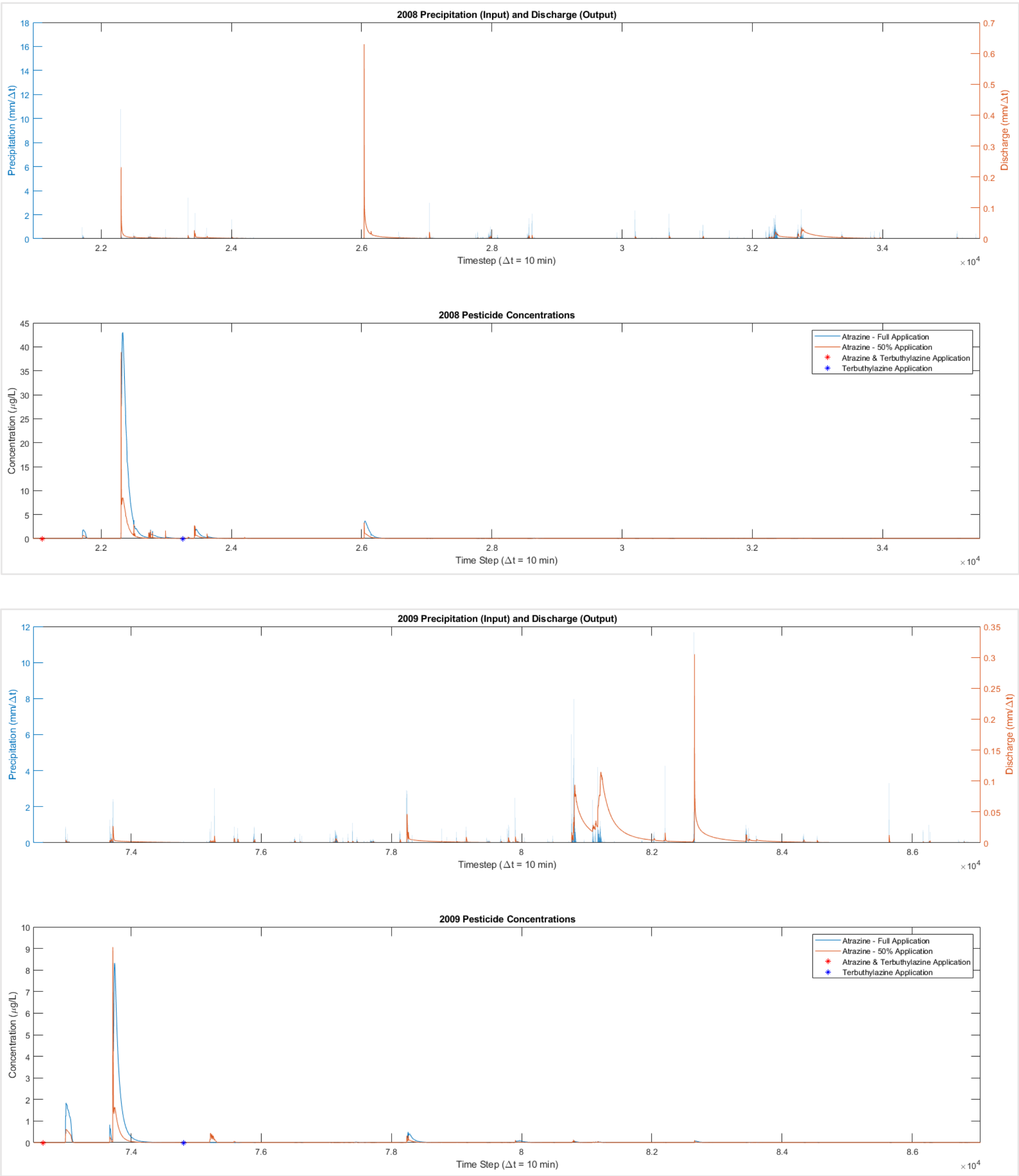


Fig. S10: 2008 (top two panels) and 2009 (bottom two panels) time-series of simulated discharge and atrazine concentrations (bottom panel) for the Eschibach catchment. Control scenario (full application - blue line in lower panel) and mitigation scenario (50% reduction in application - orange line in lower panel).

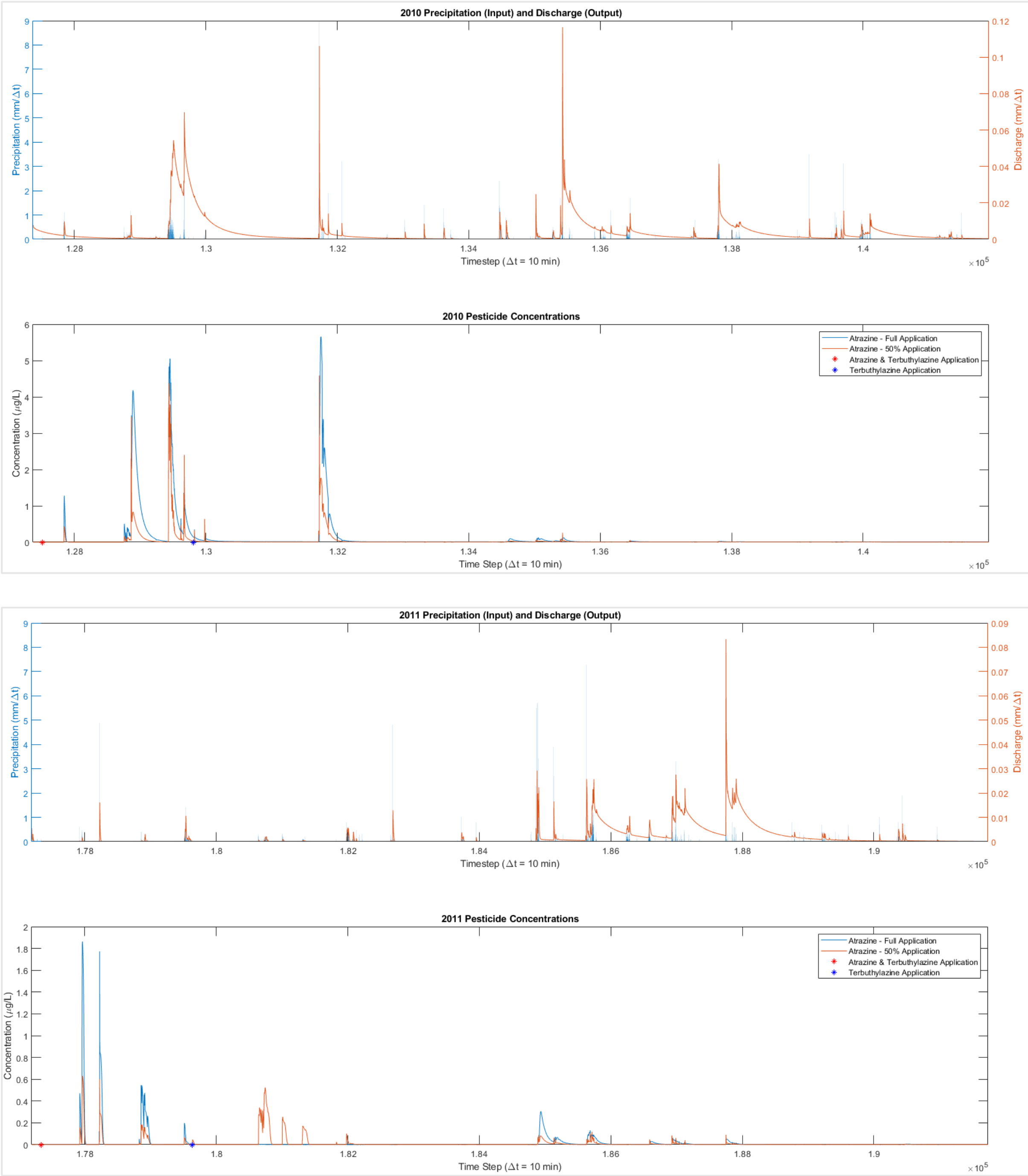


Fig. S11: 2010 (top two panels) and 2011 (bottom two panels) time-series of simulated discharge and atrazine concentrations for the Eschibach catchment. Control scenario (full application - blue line in lower panel) and mitigation scenario (50% reduction in application - orange line in lower panel).

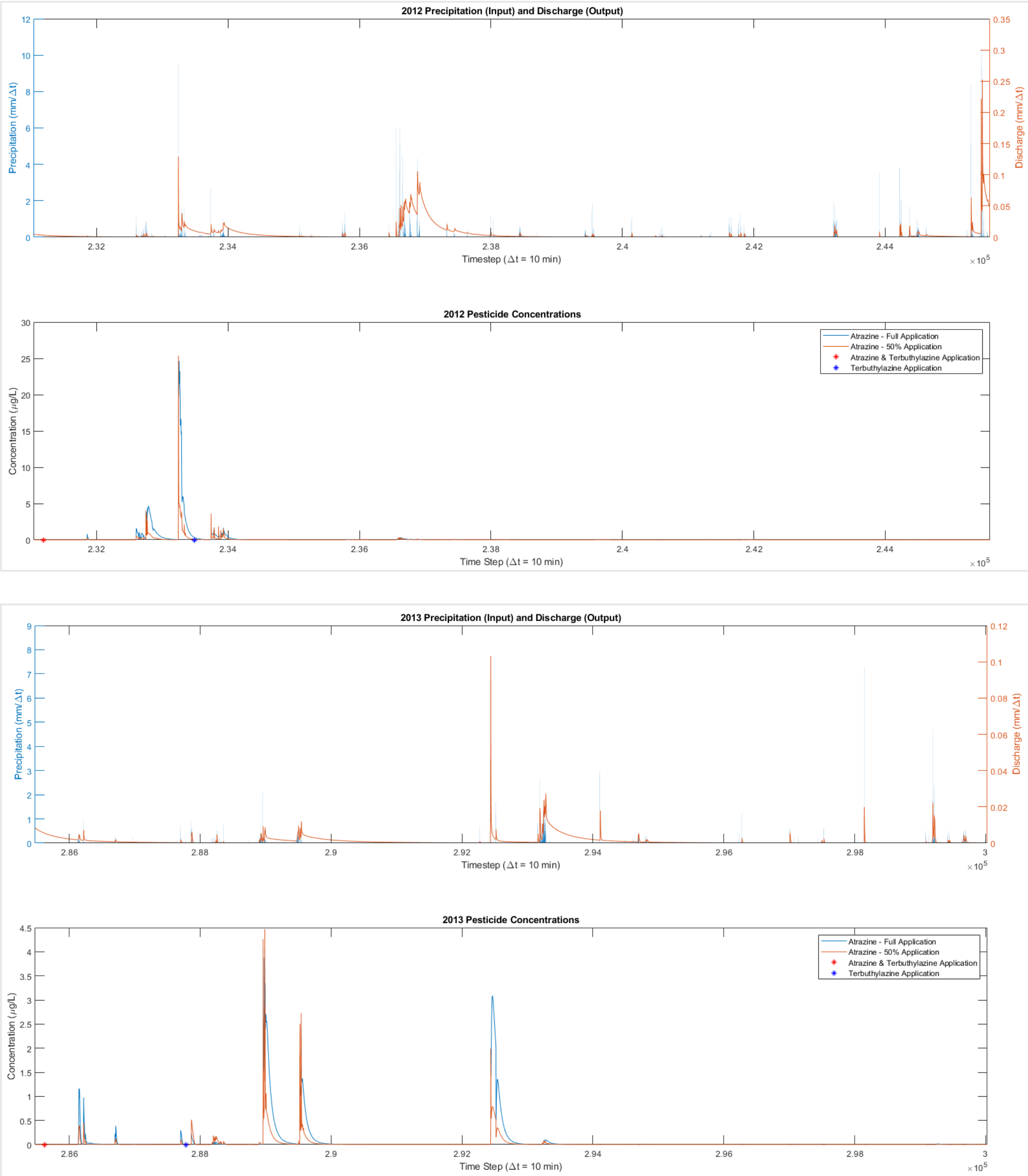


Fig. S12: 2012 (top two panels) and 2013 (bottom two panels) time-series of simulated discharge and atrazine concentrations for the Eschibach catchment. Control scenario (full application - blue line in lower panel) and mitigation scenario (50% reduction in application - orange line in lower panel).

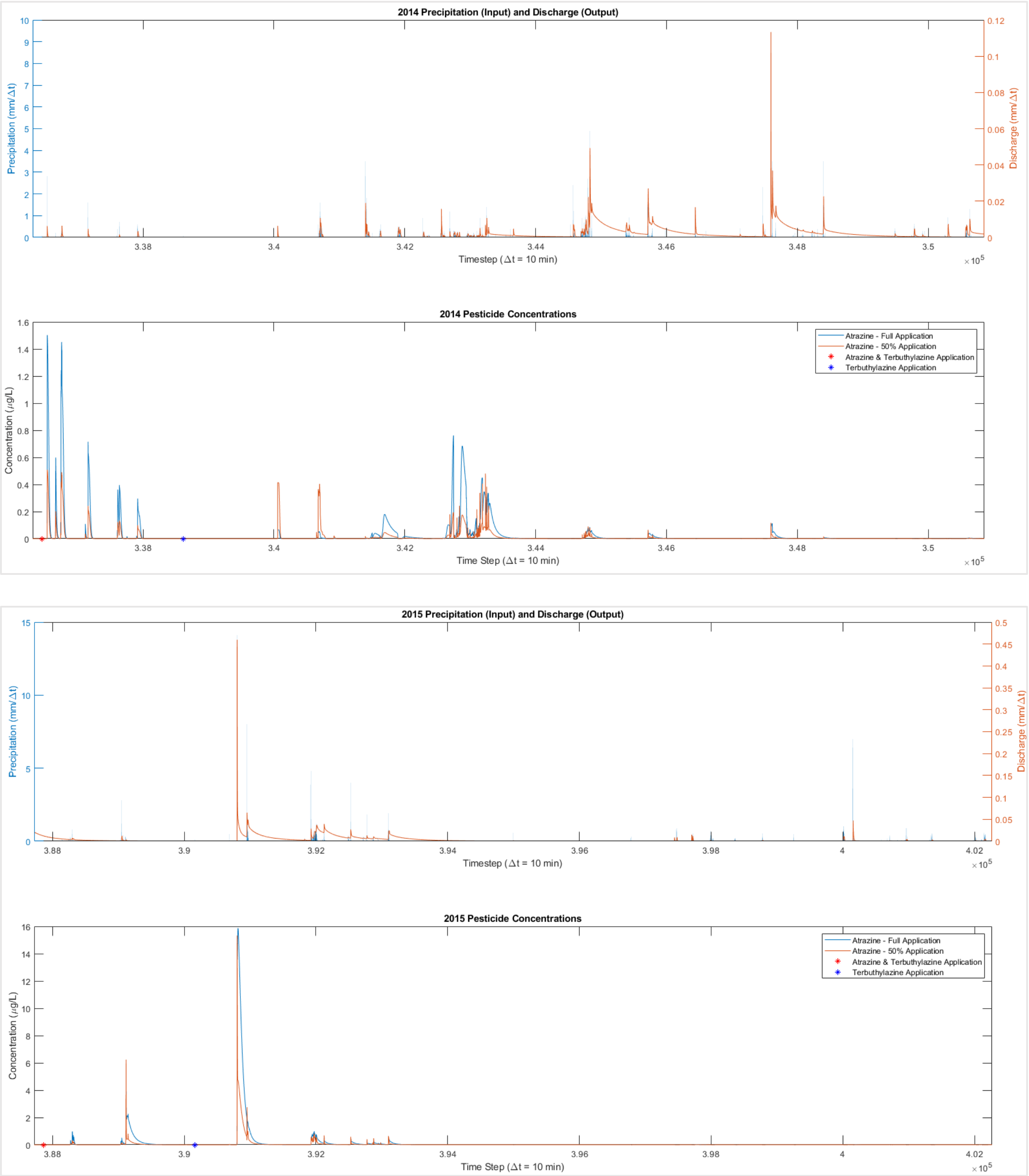
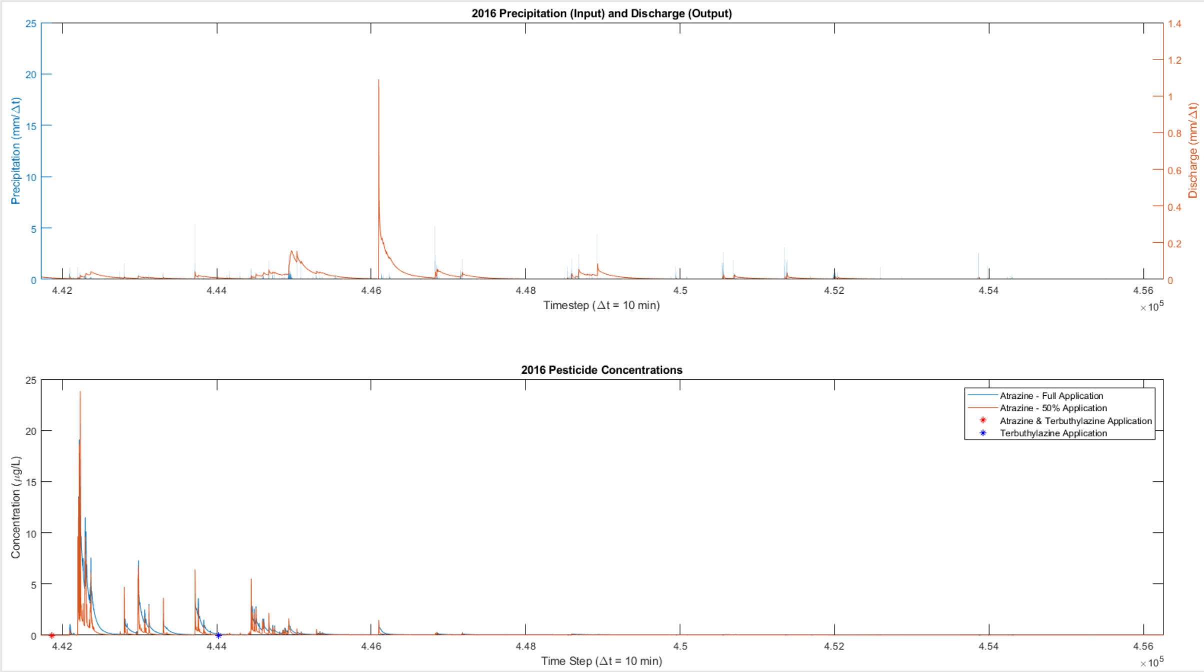


Fig. S13: 2014 (top two panels) and 2015 (bottom two panels) time-series of simulated discharge and atrazine concentrations for the Eschibach catchment. Control scenario (full application - blue line in lower panel) and mitigation scenario (50% reduction in application - orange line in lower panel).



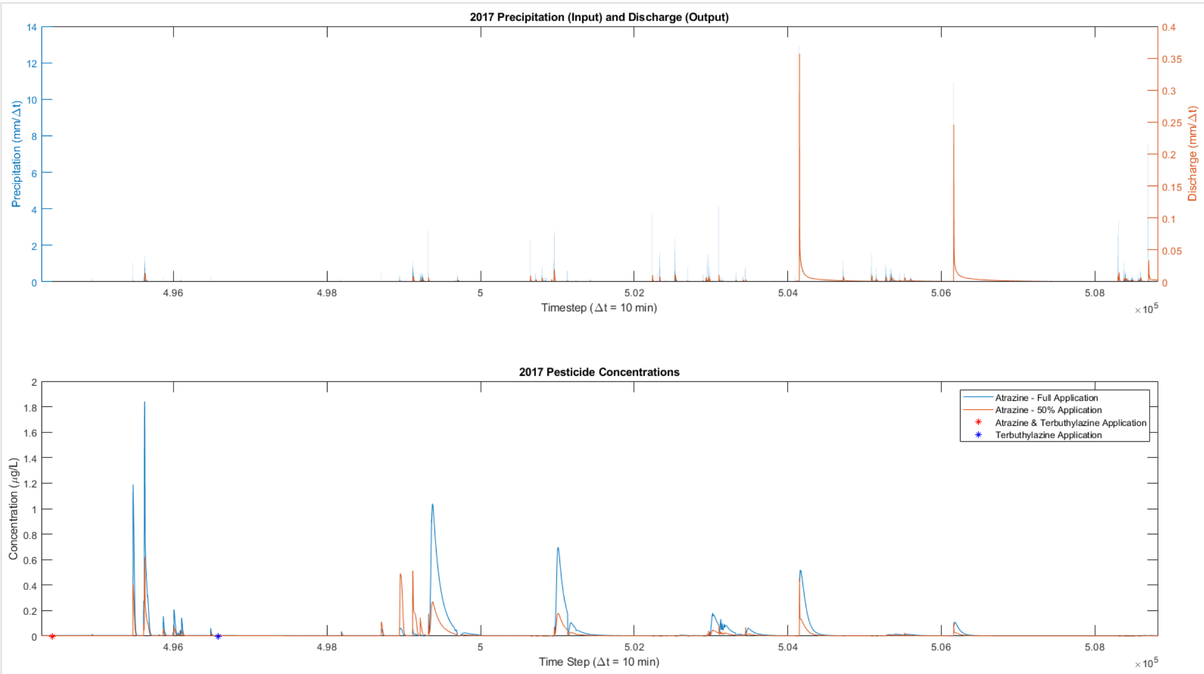


Fig. S14: 2016 (top two panels) and 2017 (bottom two panels) time-series of simulated discharge and atrazine concentrations for the Eschibach catchment. Control scenario (full application - blue line in lower panel) and mitigation scenario (50% reduction in application - orange line in lower panel).

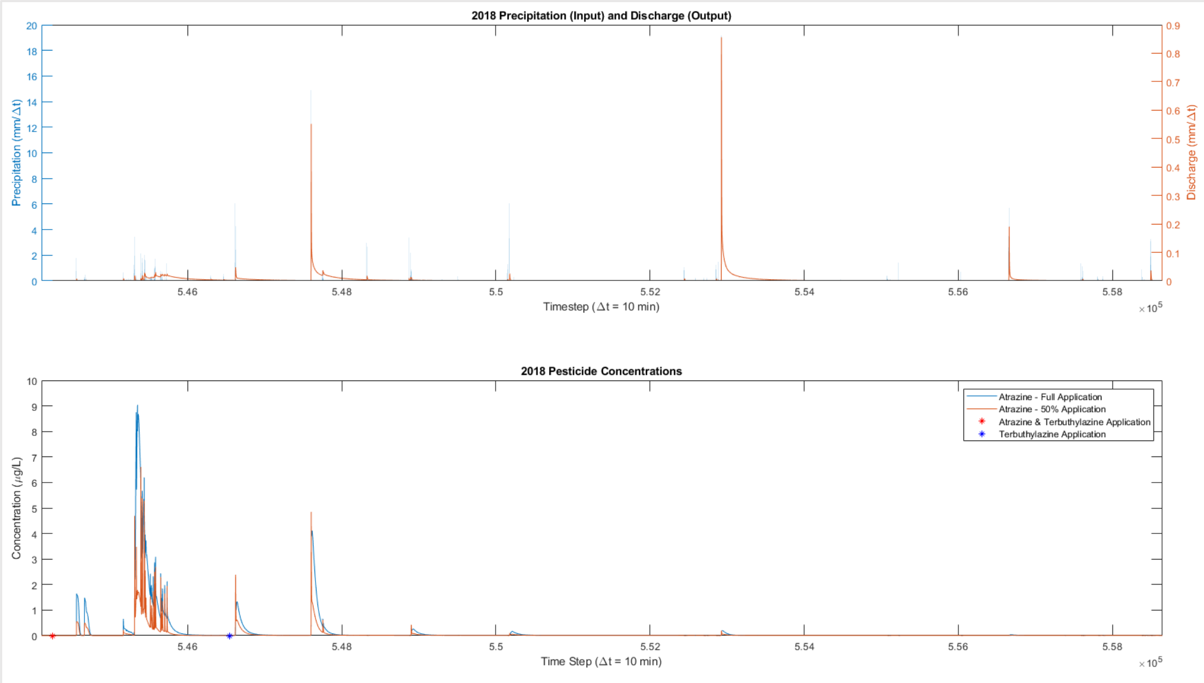


Fig. S15: 2018 time-series of simulated discharge and atrazine concentrations for the Eschibach catchment. Control scenario (full application - blue line in lower panel) and mitigation scenario (50% reduction in application - orange line in lower panel).

References

Leu, C., Singer, H., Stamm, C., Müller, S.R. and Schwarzenbach, R.P., 2004. Simultaneous assessment of sources, processes, and factors influencing herbicide losses to surface waters in a small agricultural catchment. Environmental Science & Technology, 38(14), pp.3827-3834.

Lewis, K.A., Tzilivakis, J., Warner, D.J. and Green, A., 2016. An international database for pesticide risk assessments and management. Human and Ecological Risk Assessment: An International Journal, 22(4), pp.1050-1064.