Seasonal drivers and risks of aquatic pesticide pollution in drought and post-drought conditions in three Mediterranean watersheds

R. Chow, L. Curchod, E. Davies, A.F. Veludo, C. Oltramare, M.A. Dalvie, C. Stamm, M. Röösli, S. Fuhrimann

HIGHLIGHTS

- Most samples (83%) across three catchments contained five or more pesticides.
- High total concentrations consist of a single/few pesticide(s) per catchment.
- Pesticide detections in water generally correlated with their application and rainfall events.
- About half the number of pesticides were detected after the drought ended in 2018.
- Pesticide application data and identification of transport pathways is required.

ABSTRACT

The Western Cape in South Africa has a Mediterranean climate, which has in part led to an abundance of agriculturally productive land supporting the wheat, deciduous fruit, wine, and citrus industries. South Africa is the leading pesticide user in Sub-Saharan Africa. There is limited data on the pesticide pollution of surface water over different seasons in low- and middle-income countries. We evaluated the seasonal drivers of aquatic pesticide pollution in three river catchments (Berg, Krom, and Hex Rivers) from July 2017 to June 2018 and April to July 2019, using 48 passive samplers. Our sampling followed the most severe drought (2015–2018) since recordings in 1960. Thus, our analyses focus on how drought and post-drought conditions may affect in-stream pesticide concentrations and loads. Samples were analyzed for 101 pesticide compounds using liquid chromatography–high-resolution mass spectrometry. Environmental Quality Standards (EQS) were used to assess the risks. We detected 60 pesticide compounds across the sampling periods. Our results indicate that all samples across all three catchments contained at least three pesticides and that the majority (83%) contained five or more pesticides. Approximately half the number of pesticides were detected after the drought ended in 2018. High concentration sums of pesticides (>1 µg/L) were detected over long time periods in the Hex River Valley (22 weeks) and in Piketberg (four weeks). Terbuthylazine, imidacloprid, and metsulfuron-methyl were detected in the highest concentrations, making up most of the detected mass, and were frequently above EQS. The occurrence of some pesticides in water generally correlated with their application and rainfall events. However, those of imidacloprid and terbuthylazine did not, suggesting that non-rainfall-driven transport processes are important drivers.

http://dx.doi.org/10.1016/j.scitotenv.2022.159784
Received 13 July 2022; Received in revised form 5 October 2022; Accepted 24 October 2022
Available online 31 October 2022

© 2022 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
1. Introduction

Mediterranean regions can be found worldwide and are well-known for their critical roles in securing global food supplies (Grigg, 1974; Joffre and Rambal, 2001). However, the industrial agricultural practices linked to Mediterranean regions can lead to unintended consequences, such as environmental pesticide pollution (Triassi et al., 2019; Barbieri et al., 2021; Haddaoui and Mateo-Sagasta, 2021). The Western Cape in South Africa is the only region in Sub-Saharan Africa with a Mediterranean climate, which has in part led to an abundance of agriculturally productive land that supports the wheat, deciduous fruit, wine, and citrus industries (Zwane, 2019). South Africa is the leading pesticide user in Sub-Saharan Africa, with >3000 pesticide products approved for use (Dabrowski, 2015). The active ingredients within these products can enter non-target environments (e.g., surface water, groundwater) where they can potentially persist and become a risk to the environment and human health (Sorensen et al., 2015; Stehle and Schulz, 2015; Chetty-Mhlanga et al., 2018; Spycher et al., 2018; Chetty-Mhlanga et al., 2021; Fuhrimann et al., 2022a). A systematic literature review on the environmental and human exposure risk of pesticides in Sub-Saharan Africa found few studies on aquatic pesticide pollution in South Africa; the studies that collected water samples were typically limited by short duration monitoring and analyzed for only a few pesticides (Fuhrimann et al., 2022b). Dabrowski (2015) found that agricultural pesticide application is common in the Western Cape; however, the extent to which these pesticides are polluting the local surface waters over different seasons and extreme hydrologic conditions (e.g., droughts) is largely unknown. For aquatic pesticide pollution to occur, areas within a catchment typically have to fulfill three criteria: 1) pesticide application has occurred; 2) they are hydrologically active; and 3) they are connected to streams allowing for fast flows with minimal retention processes (Frey et al., 2009; Doppler et al., 2014).

Recently, pesticides have been detected in biological specimens of rural populations in the Western Cape and there is some epidemiological evidence of health effects (English et al., 2012; Mwanga et al., 2016; Chetty-Mhlanga et al., 2021; Molomo et al., 2021). Concurrently, a cohort study, soil sampling, and passive air sampling is taking place within the same three watersheds. The cohort study investigated the potential effects of environmental pesticide exposure on the neurodevelopment and reproductive health of school-children (Chetty-Mhlanga et al., 2018; Chetty-Mhlanga et al., 2021) and so far found that urinary concentrations of organophosphate pesticide metabolites were associated with pesticide exposure (Molomo et al., 2021) and that self-reported pesticide exposures were associated with neurobehavioural outcomes (Chetty-Mhlanga et al., 2021). The soil sampling found that chlorpyrifos, carbaryl, and tebuconazole were detected with the highest concentrations (Degrendele et al., 2022), while the passive air sampling conducted in 2017 and 2018 consistently detected the insecticides carbaryl and chlorpyrifos (Veludo et al., 2022).

Aquatic pesticide pollution via drinking water could serve as a potential pathway for human exposure (Syafrudin et al., 2021). Furthermore, there are environmental risks to aquatic biota based on the persistence and mobility of certain pesticides (Dabrowski et al., 2014). For instance, Ojemaye et al. (2020a, 2020b) found herbicides in marine biota in Camps Bay and fish in Kalk Bay, both in the Western Cape. Therefore, there is a need to understand the processes that drive aquatic pesticide pollution in the Western Cape and potential strategies that could be employed to reduce it.

From June 2017 to January 2018, 53 pesticides and transformation products were detected under severe drought conditions (2015–2018) in the rivers of three agricultural catchments (i.e., Grabouw, Hex River Valley, Piketberg) in the Western Cape (Curchod et al., 2020). During this drought, high evaporation and low precipitation rates could have potentially concentrated pesticides in surface waters. Furthermore, agricultural activities, pest pressure, and related spraying may have differed due to the drought (Rosenzweig et al., 2001; Bloomfield et al., 2006; Delcour et al., 2015). The insecticides imidacloprid, thiacloprid, chlorpyrifos, acetamiprid, and herbicide terbuthylazine were found to have exceeded the environmental quality standards (EQS) values at least once between June 2017 and January 2018 (Curchod et al., 2020). All EQS values originated from Switzerland or the European Union (Swiss Center for Applied Ecotoxicology Eawag/EPFL, 2013; Moschet et al., 2014; Curchod et al., 2020), except for atrazine (Department of Water Affairs and Forestry, 1996). Whether the observed concentration levels in the year 2017 were exceptional due to the lowest ever recorded rainfall and river discharge needs to be compared with additional data. Since then, precipitation rates after the winter (i.e., June to August) of 2018 have largely recovered to historical averages (Ndebele et al., 2020). The results from Curchod et al. (2020) are included in this study (i.e., July 2017 to January 2018) as a basis for comparison to an additional nine sampling rounds that took place between February to June 2018 and April to July 2019.

The primary aim of our study is to evaluate the effects of seasonal drivers (i.e., application and rainfall) on aquatic pesticide pollution by expanding on the previous analysis of temporal variation of pesticide mixtures in rivers by Curchod et al. (2020) with nine additional sampling rounds and additional pesticide application data in the form of spray guidelines from agricultural co-operatives and an expert interview. Thus, our main objective is to compare the seasonal fluctuations of aquatic pesticide concentrations and total transport load during the drought with those during the rainier seasons (Section 3.1: Overview). We also compiled additional pesticide application data, in the form of spray guidelines from agricultural co-operatives and an expert interview, to evaluate the temporal patterns of pesticide application and their detection in rivers (Section 3.2: Temporal patterns of pesticide application and exceedances). Finally, we include a detailed assessment of the insecticide imidacloprid and herbicide terbuthylazine, which were found to be of particular concern due to their relatively high concentrations and loads (Section 3.3: Transport of imidacloprid and terbuthylazine).

Our study addresses the following four research questions: (i) Does increased rainfall after the drought generate more runoff and thus higher levels of pesticides in the river? (ii) Is there a correlation between pesticide application and observed pesticide concentrations in surface water? (iii) Are there pesticides that pose a risk to the aquatic ecosystem during periods without (or low) agricultural pesticide application (i.e., off-season)? (iv) Are the highest number of detected pesticides and concentrations in surface waters usually associated with the rainy season (i.e., May to August)?

2. Material and methods

2.1. Water sampling

Aquatic pesticide pollution was monitored in three rivers of agricultural watersheds in the Western Cape, South Africa, from July 2017 to January 2018 by Curchod et al. (2020). The results presented here extend the sampling by Curchod et al. (2020), with nine additional sampling rounds conducted in the autumn and winter months of 2018 and 2019. Overall our study presents sampling results from July 2017 to June 2018 and April to July 2019.

Water sampling was conducted at three locations (Curchod et al., 2020): Krom River (Grabouw; 34°15′8″S, 19°3′14″E), Hex River (Hex River Valley; 33°31′48″S, 19°32′25″E), and Berg River (Piketberg;
Fig. 1 shows a map of the three study areas and the water sampling locations. Each watershed was chosen due to its high percentage of crop-specific agricultural land use. By area: Grabouw has ~81% pome fruits, Hex River Valley has ~98% table grapes, and Piketberg has ~56% cereals (WCG, 2018). Additional catchment characteristics have been summarized in Table S1 of the Supporting Information. Curchod et al. (2020) depicts the agricultural land use within each of the three study catchments. At each location, two pre-conditioned Chemcatchers® SDB-RDP (polyStyreneDivinylBenzene-Reverse Phase Sulfonated) covered by polyether sulfone (PES) membranes were deployed in the river for two weeks per month (Moschet et al., 2015).

Five sampling rounds were conducted in 2018 between February 8th and June 15th (sampling periods: (i) 08.02–23.02, (ii) 07.03–21.03, (iii) 06.04–20.04, (iv) 02.05–16.05, (v) 31.05–15.06); and four sampling rounds were conducted in 2019 between April 18th and July 24th (sampling periods: (i) 18.04–02.05, (ii) 02.05–16.05, (iii) 31.05–14.06, (iv) 10.07–24.07). Over the nine sampling rounds a total of 27 samples were collected (i.e., one per catchment).

After collection, the SDB disks were put in single 7 mL amber vials and transported in a cooled box at 4 °C to the Chemical Engineering Laboratory at the University of Cape Town (UCT) and stored at −18 °C. At each sampling round, one field blank SDB disk was taken along for quality control. Samples were then transported at 4 °C to the Swiss Federal Institute of Aquatic Science and Technology (Eawag) in Switzerland for analysis.

2.2. Preparation and extraction of passive sampler

Before deployment, the SDB disks and the PES membrane were conditioned in MeOH and then in nanopure water (30 min each; Vermeirssen et al., 2009). The SDB disks were then covered by a PES membrane, assembled on the holders, and stored in nanopure water until deployment. Only one SDB disk in each pair was analyzed, the second was stored for quality control.

Moschet et al. (2015) describes in detail the extraction process used in this study. An abbreviated version is described here and by Curchod et al. (2020). Firstly, 6 mL of acetone was added to the vials containing the SDB disks, which were then shaken for 30 min on a rotary shaker. Secondly, the acetone was transferred into a new glass tube with the addition of an internal standard (purchased from Sigma-Aldrich), then 5 mL of methanol was added to the SDB disks for a second extraction. The internal standard used and percent recoveries for detected compounds are provided in Table S3 in the Supporting Information. Thirdly, the extract of acetone was concentrated to a volume of 1 mL and then mixed with the extract of methanol. Finally, the 6 mL extract was filtrated with a polytetrafluoroethylene (PTFE) filter (0.45 μm) and then evaporated to a volume of 0.1 mL. The final extract was adjusted to 1 mL by adding nanopure water, centrifuged at 4000 rpm for 30 min, then transferred into a vial for analysis.

2.3. Chemical analysis of passive samplers

Chromatographic separation of the sample was achieved by using a reversed phase XBridge C18 column (Waters™). For detection, a QExactive Orbitrap mass spectrometer (MS) with electrospray ionization (Thermo Fisher Scientific) was used, which was operated in full scan mode. Each sample was analyzed in positive and negative mode separately. Eluents for the chromatographic gradient used were methanol and nanopure water, both acidified with 0.1% formic acid. Chromatographic peaks of target analytes were automatically detected (mass accuracy <5 ppm, peaks with a minimum of 5 data points) by using retention times (RT) of the target analytes, confirmed with product ion MS/MS fragments. These were compared to RT and fragments from identical reference standards (purchased from Sigma-Aldrich). Also, the peak of each target compound was reviewed manually in all samples for further quality control. In total, 101 compounds were analyzed (72 pesticide compounds and 29 of their transformation products), which was a refined list of analytes based on previous detections by Curchod et al. (2020). Curchod et al. (2020) initially targeted 248 analytes adapted to compounds registered for use in South Africa (AVCASA, 2017) and were previously detected in South African rivers (Dalvie et al., 2011). More details regarding the instrumental setup used for the high-resolution mass spectrometry coupled to liquid chromatography can be found in Table S2 in the Supporting Information. The specific limits of quantifications (LOQ), retention time, precursor mass, internal standard used, R² from linear calibration, and relative recovery for each detected compound from February 2018 to July 2019 can be found in Table S3 in the Supporting Information.

Time-weighted average concentrations \(c_{w,t} \) (ng/L) were calculated (Eq. 1) by dividing the cumulative pesticide mass captured via the passive samplers \(m_{SDS} \) (ng/disk) by their deployment time \(t \) (days) and compound-specific limits of quantification. The detection of compounds is described in detail in Table S3.
sampling rates $R_s$ (L/day) from the literature where available (Moschet et al., 2015; Ahrens et al., 2015; Charriau et al., 2016; Curchod et al., 2020).

$$c_u = \frac{m_{OCB}}{I \cdot R_s}$$ (1)

For pesticides without $R_s$, literature values (8 out of 33), we chose a modal $R_s$ value of 0.095 L/day (based on all available $R_s$ values) because others have found that compound properties are unreliable predictors of sampling rates (Moschet et al., 2015; Schreiner et al., 2020). $R_s$ values were summarized in Table S6 in the Supporting Information. Concentrations were then converted to mass transport rates or loads (g/d) by calculating the product of the time-weighted concentration and the average daily river discharge rate over each sampling period.

2.5. Pesticide application data

Daily rainfall and river discharge data covering the sampling periods was retrieved from the South African Environmental Affairs Department (EAD, 2020) and the Department of Water & Sanitation (DWA, 2020), respectively. Curchod et al. (2020) present the locations of the rain gauges (EAD, 2020) and the Department of Water Affairs (DWA, 2020). Curchod et al. (2020) present the locations of the rain gauges (EAD, 2020) and the Department of Water Affairs (DWA, 2020).

2.4. Data collection to assess catchment hydrology

Three closest rain gauges to the study areas were 12, 13 and 8 km away from the sampling points in Grabouw, Hex River Valley and Piketberg, respectively. The closest stations recording daily river discharge were 3, 6, and 21 km away from the sampling points in Grabouw (station G4H030 on Palmiet River), Hex River Valley (station H2H006 on Hex River) and Piketberg (station G1H013 on Berg River).

2.5. Pesticide application data

Obtaining up-to-date lists of all the active ingredients within the pesticide products registered (and banned) for use in South Africa is challenging because no public register exists, and the lack of transparency in the South African pesticide market (Clausing et al., 2021). Nonetheless, farming activities were assessed from November 2017 to July 2019 by conducting structured interviews with farmers from 57 farms within the study areas. All farms were located upstream of the water sampling points. The farmer interviews included a questionnaire regarding agricultural activities (e.g., seasonality of crop planting and harvesting). Furthermore, pesticide spray records were obtained from 38 out of the 57 farms (see Table S3 from Curchod et al., 2020).

Additional application data was obtained from spraying guidelines used by the three Agricultural Co-operatives in the study areas (two for pome fruits and one for table grapes) and from an interview with an agricultural expert (S7 of the Supporting Information contains the consent form and questionnaire). Independence between the detection of pesticides in surface water with their application was determined by creating a contingency table (Table 2) and performing a chi-square test (Howell, 2011).

3. Results and discussion

3.1. Overview

Table 1 provides a general overview of the monthly distribution of crop-specific harvest (and planting for wheat) and pesticide application based on the farmers’ interviews and spray records. We can better understand the timing of pesticide application from the timing of harvesting because harvesting typically occurs after a waiting period following pesticide application to allow the pesticides to naturally dissipate, thus minimizing residues on crops (Bajwa and Sandhu, 2014). For wheat crops, pesticides are usually applied in the winter (i.e., June and July), whereas for apple, pear, citrus, table and wine grape crops, pesticide application occurs throughout the spring and early summer (i.e., September to December). We define the spray-season as the period from August to January, when the most pesticides are applied for a majority of the crop types; and the off-season as the period from March to July, when there is minimal or no pesticide application. There is an exception to our definition of off-season for wheat, which is mostly found in Piketberg. The potential effects of this exception are discussed in this section.

Fig. 2 provides a general overview of the total number of pesticides and transformation products detected by catchment and sampling period. On average, the number of detections is approximately halved (i.e., from 35 to 19) when going from the spray-season (i.e., August 2017 to January 2018) to the off-season (i.e., March to June 2018 and April to July 2019). Grabouw and the Hex River Valley have 81.5% pome fruits (i.e., apples and pears) and 97.6% table grapes by land area, respectively. Both crop types have their peak pesticide applications in October (Table 1), which corresponds well with the relatively high number of pesticides detected in 2017 (Fig. 2). As expected, we observed a lower number of detections in the off-season sampling in 2018 and 2019 in both Grabouw and the Hex River Valley. Piketberg has a more mixed land use, with most of the land (56.0%) being used for cereals (e.g., wheat, rice, maize, oat, barley, rye). Peak pesticide application for wheat is typically in June and July (Table 1), which was sampled in the off-season and could explain the smaller decrease in the number of detections in Piketberg compared to Grabouw and the Hex River Valley.

Our results indicate a general decrease in the pesticide mass captured (ng/disk) by passive samplers, concentrations, and the number of pesticides being detected in the 2018 and 2019 off-season when compared to the

| Crop      | Activity | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | N  |
|-----------|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| Apples    | Harvest  |     |     |     |     |     |     |     |     |     |     |     | 8  |    |
|           | Spraying |     |     |     |     |     |     |     |     |     |     |     | 5  |    |
| Pears     | Harvest  |     |     |     |     |     |     |     |     |     |     |     |    | 7  |
|           | Spraying |     |     |     |     |     |     |     |     |     |     |     | 2  |    |
| Citrus    | Harvest  |     |     |     |     |     |     |     |     |     |     |     |    | 5  |
|           | Spraying |     |     |     |     |     |     |     |     |     |     |     | 3  |    |
| Table     | Harvest  |     |     |     |     |     |     |     |     |     |     |     |    | 25 |
| Grapes    | Spraying |     |     |     |     |     |     |     |     |     |     |     | 18 |    |
| Wine      | Harvest  |     |     |     |     |     |     |     |     |     |     |     |    | 1  |
| Grapes    | Spraying |     |     |     |     |     |     |     |     |     |     |     | 5  |    |
| Wheat     | Harvest  |     |     |     |     |     |     |     |     |     |     |     |    | 3  |
|           | planting |     |     |     |     |     |     |     |     |     |     |     | 7  |    |
|           | Spraying |     |     |     |     |     |     |     |     |     |     |     |    |    |
spray-season (i.e., months of peak pesticide application) in 2017. This may be attributed to two main factors: 1) higher rainfall in non-critical source areas could be leading to a dilution of aquatic pesticide mass captured; and 2) less pesticides are typically applied in the off-season (i.e., winter) months, which were the focus of the 2018 and 2019 sampling.

Fig. 3 shows a detailed summary of the spray records, hydrological activities, and passive sampling data in the three study areas by month and year. Tables S4a, S4b, and S4c in the Supporting Information lists concentrations (ng/disk) for all detected pesticide compounds in Grabouw, Hex River Valley, and Piketberg, respectively. According to the interviews with farmers (Table 1) the highest pesticide application rates for most crop types occur from September to December, which coincides with peaks in cumulative pesticide mass within the rivers of all catchments (Fig. 3C). The correlation between pesticide application and their detection in surface water is analyzed further in Section 3.2. When comparing the pesticide levels with farmers’ spray records (Fig. 3A), which included the quantity and type of pesticides applied, there was very little agreement. This may be because the 38 spray records represents only 2.8% of the 1356 known farms within the three catchments. According to the spray records (Fig. 3A), fungicides were applied in the highest quantity, yet they were detected the least. This could be partially explained by the chemical properties of the fungicides applied (Table S5). The fungicides applied but not detected in the rivers had a median half-life (DT_{50}) of 3 days and a median organic carbon-water partitioning coefficient (K_{foc}) of 2287, while the fungicides that were applied and detected had a median DT_{50} of 8.5 days and median K_{foc} of 772 (Lewis et al., 2016). In Section 3.2, we provide a comparison between the pesticides detected in the rivers and all the pesticide application data described in Section 2.5.

Our results indicate that all samples across all three catchments contained at least three pesticides and that a majority (83%) of the samples contained five or more pesticides. Two catchments in particular had very high concentrations (>1 µg/L) over long time periods (22 weeks in the Hex River Valley and four weeks in Piketberg). High concentrations are typically caused by only a single/few pesticide(s) per catchment (i.e., terbuthylazine in Grabouw, imidacloprid in Hex River Valley and terbutylazine and metsulfuron-methyl in Piketberg).

Drought vs. Post-Drought: July was the only month sampled in both drought and post-drought conditions (i.e., 2017 and 2019). Comparing July 2017 and 2019 in Grabouw and the Hex River Valley we can see that 38% and 77% less pesticide mass was captured, respectively (Fig. 3C). Our results suggest that the severe drought may have led to less degradation and/or dilution of aquatic pesticide pollution in July 2017 when compared to July 2019. This is consistent with Franco-Andre et al. (2016), who found that pesticide degradation in non-irrigated soil was lower than for watered soils, suggesting that drought conditions may lead to greater persistence of pesticides in the environment. However, in Piketberg, pesticide mass captured increased by 24% from July 2017 and 2019 (Fig. 3C). This post-drought increase in pesticide mass may be due to a greater coincidence of rainfall following pesticide application, which may be the result of the relatively larger catchment size and mixture of crop types in Piketberg compared to Grabouw and the Hex River Valley. The following sub-sections discuss the results for each study area.

Grabouw: In general, less pesticide mass was detected in the off-season when compared to the peak spraying season (Fig. 3C). Peaks in captured mass occur in October and November 2017, which coincides with the peak spraying for apples and pears (Table 1). In both off-seasons (i.e., Mar–Jun 2018 and Apr–Jul 2019) we observed a similar increasing trend in pesticide mass, which suggests that increasing rainfall when transitioning from autumn to winter is associated with an increase in pesticide losses (i.e., the percent of applied pesticides removed from their site of application). Singer (2005) observed a similar positive relationship between pesticide losses and river discharge into Lake Greifensee, Switzerland.

Hex River Valley: Pesticide mass exceeded about 200 ng/disk in most sampling periods (Fig. 3C). Most of the pesticide mass captured were insecticides, virtually all of which was imidacloprid (94% on average of detected insecticides). Periods with lower mass captured generally coincide with greater rainfall in the off-season. A large peak in pesticide mass was captured in October 2017, which coincides with the peak pesticide application for table grapes (Table 1). In both off-seasons (i.e., Mar–Jun 2018 and Apr–Jul 2019) we observed a similar increasing trend in pesticide mass, which suggests that increasing rainfall when transitioning from autumn to winter is associated with an increase in pesticide losses (i.e., the percent of applied pesticides removed from their site of application). Singer (2005) observed a similar positive relationship between pesticide losses and river discharge into Lake Greifensee, Switzerland.

Piketberg: The majority of the detected mass were the herbicides terbutylazine, simazine, metolachlor, and metsulfuron-methyl (Fig. 3C). The peaks in detected mass usually coincide with lower rainfall and river flow, as well as the spraying of crop types other than cereals (Table 1). The high variety of crop types in Piketberg could explain the high concentrations in October and November 2017. The hydrological conditions (i.e., rainfall and river flows) appear to be about the same in both 2018 and 2019, which suggests the differences between the years could be due to differences in agricultural activity (e.g., crops planted, pesticide application rates, pest pressure) or the coincidence of rainfall with pesticide application (i.e., pesticide application followed by rainfall events in May 2018). The number of detected pesticides appears to decrease in the 2018 off-season (Fig. 3E); however, there is an increasing number of detected pesticides in the 2019 off-season and two large concentration peaks in Apr and May 2019 that is mainly comprised of the herbicide metsulfuron-methyl (Fig. 3D). Prior to 2019 metsulfuron-methyl was not detected,
which suggests that a change in pesticide application is the main driver of the exceptional off-season number of pesticides being detected and concentrations.

3.2. Temporal patterns of pesticide application and exceedances

Fig. 4 shows the annual distribution of the pesticide application data and all pesticides that exceeded their EQS value at least once (or were detected) from 2017 to 2019. Fig. 4 aims to show whether there is a correlation between the detection of pesticides in surface water with their application. By analyzing the monthly occurrence of the two, we can answer the question what is the probability that 3 or less applications cause no detection of pesticides in the rivers? First, we classify all sampling events in Fig. 4 (8 pesticides × 12 months = 96 sampling events) into two categories: detects (N = 61) and non-detects (N = 35). Second, if we assume the 18 known agricultural applications are randomly distributed across all 96 sampling events, the respective binomial distribution would yield a probability of 6.2% that application and no detection is caused by a random process. Thus, the data suggests that a known agricultural application of certain pesticides (i.e., pesticides that have exceeded their EQS value at least once from 2017 to 2019) is likely the cause of its detection in surface water.

The coincidence of pesticide application and the observed pesticide levels in surface water indicate that acetamiprid, chlorpyrifos, and thiacloprid in Grabouw, and metsulfuron-methyl in Piketberg are most likely driven by application followed by rainfall-runoff events (Table 2). A chi-squared test for the null hypothesis that agricultural application of pesticides and their detection in rivers are independent for acetamiprid, chlorpyrifos, metsulfuron-methyl, and thiacloprid produced a test statistic of 1.84, which was less than the chi-squared value of 7.82 (df = 3, α = 0.05). Therefore, we can reject the null hypothesis that agricultural application and the detection are independent for acetamiprid, chlorpyrifos, metsulfuron-methyl, and thiacloprid in the three monitored catchments. While the occurrence of some pesticides coincides with their application, others detected at relatively high concentrations are not limited to their application periods (i.e., imidacloprid and terbuthylazine).

Imidacloprid was found to exceed EQS values in all three catchments consistently throughout the year, especially in the Hex River Valley, despite having only a single annual application (Table 2). Our results suggest that imidacloprid is particularly persistent in the environment, where it may be stored in the shallow subsurface where it is gradually transported to surface water via interflow and groundwater. If imidacloprid is present in groundwater, there could be potential human health risks because most rural communities in South Africa rely on groundwater as their main source of drinking water (Department of Water and Sanitation, 2016). Like imidacloprid, terbuthylazine was also found consistently throughout the year in Piketberg; however, more perplexing is the absence of terbuthylazine application from the spray records (Table 2). A chi-squared test for the null hypothesis that detecting pesticides in rivers is related to their agricultural application for terbuthylazine and imidacloprid produced a test statistic of 1.07, which was less than the chi-square value of 7.82 (df = 3, α = 0.05). Therefore, we can reject the null hypothesis that detection of terbuthylazine and imidacloprid is related to agricultural application in the three monitored catchments. Our results suggest that either terbuthylazine application is underreported/incomplete or is being transported from neighbouring catchments.

Grabouw: An exceedance of acetamiprid in Nov 2017 corresponds to the spray records and guidelines, while a detection in Dec 2017 only corresponds to the spray records. An exceedance of chlorpyrifos concentrations in Aug and Sep 2017 coincides with the spray records. The expert indicated that chlorpyrifos is typically sprayed in Nov; however, it was not detected in the surface water. Nov 2017 had higher rainfall than in Sep and Oct 2017, which suggests that the rainfall did not occur in critical chlorpyrifos source areas (Doppler et al., 2014), thus leading to a non-detect in Nov 2017. Imidacloprid was detected throughout the year, with exceedances from Oct to Jul. However, the expert and spray guidelines indicate that imidacloprid is typically applied once in the month of Oct for pome fruits. Spray records indicated that thiacloprid is usually applied from Oct to Mar, which closely aligns with its exceedances and detections in surface water.

Hex River Valley: Imidacloprid was the only pesticide exceeding EQS values in the Hex River Valley. It exceeded throughout the year in every sampling interval; however, spray records and guidelines indicate that imidacloprid is applied only once a year in Sep to target mealy bugs (Fig. 5). Therefore, its application alone cannot explain the magnitude and frequency of imidacloprid exceedances. Another interesting note is that the Hex River Valley has the most-fold exceedances in imidacloprid concentrations, yet has the lowest rainfall and streamflows compared to the other catchments (Figs. 3 and 4). These findings are consistent with Masiá et al. (2013), who found that lower streamflows were associated with higher pesticide concentrations. High imidacloprid concentrations associated with low rainfall may be due to less dilution from less rainfall occurring in non-critical imidacloprid source areas, as well as continuous leaching and transport of imidacloprid to surface water via groundwater.

Piketberg: According to spray records, metsulfuron-methyl had applications in Apr, May, and Jul, which closely corresponds to exceedances in Apr, May, and Jun 2019 (Fig. 5). Terbuthylazine was detected every month and exceeded in Oct and Nov 2017. However, no terbuthylazine application was mentioned in any of the application data. Curchod et al. (2020) suggested that herbicide application may be underreported or unrepresentative in the spray records, which could explain the lack of known terbuthylazine use in Piketberg despite the prevalence of corns and cereals (typically treated with terbuthylazine; Du Preez et al., 2005). Imidacloprid had a recorded spray in Aug, which corresponds to an exceedance in Aug. However, similar to Grabouw and Hex River Valley, there are numerous other detections and exceedances of imidacloprid that do not correspond to the spray records.

3.3. Transport of imidacloprid and terbuthylazine

According to Dabrowski et al. (2014), both terbuthylazine and imidacloprid have a weighted hazard rank of 5th and 9th out of 48 active ingredients, respectively. The 48 active ingredients represent the majority (~92%) of the pesticides applied in South Africa. The weighted hazard ranking of agricultural pesticides was based on the quantity used, environmental mobility, and potential human health effects.

Furthermore, both terbuthylazine and imidacloprid have relatively high Groundwater Ubiquity Scores of 2.19 and 3.69, respectively (Lewis et al., 2016), which supports the possibility that terbuthylazine and imidacloprid are being leached to the groundwater where they are stored and later transported to surface water. Terbuthylazine has been detected in South African groundwater (Rimayi et al., 2018), while imidacloprid has been detected in Spanish and French groundwater (Pitarch et al., 2016; Pinasseau et al., 2019). Their presence in groundwater could be a potential human health risk because most rural communities in South Africa rely on groundwater as their main source of drinking water (Department of Water and Sanitation, 2016).
types of application data (i.e., spray guidelines from Agricultural Co-ops, spray records (Curchod et al., 2020), and an expert interview). (I) = Insecticide, (H) = Herbicide.

values. There are no records of terbuthylazine application in any of the three catchments. Spray records indicate three imidacloprid applications in 2017, two in the Hex River Valley in September, and one in Piketberg in August (Fig. 5B).

Although our results indicate that increased rainfall and changes in pesticide application rates in the off-season led to lower pesticide mass captured (ng/disk) and concentrations (ng/L), we observed similar levels of pesticide transport in the off-season when compared to the late spring-early summer. For both imidacloprid and terbuthylazine, the peak in load during the spray-season is mainly the result of high concentrations while the peaks in the off-season are mainly the result of higher rainfall and river flows. Despite lower concentrations during the off-season, the transport load is comparable (or higher) to those during the spray-season due to greater rainfall-runoff and river flows. This suggests that winter rains can drive pesticide losses higher in the off-season, despite less pesticide application than the spray-season.

**Imidacloprid**: Results for imidacloprid concentrations (Fig. 5B) show 14, 16, and 7 out of 16 samples exceeded EQS values for Grabouw, Hex River Valley and Piketberg, respectively. In Grabouw, the maximum exceedance was ten times EQS in Feb 2018; in the Hex River Valley, every sample exceeded EQS, ranging from approximately 19 times EQS in Jul 2019 to 214 times EQS in Oct 2017; in Piketberg, the maximum exceedance was ten times EQS in Jun 2018. Transport loads peak in Grabouw and Hex River Valley during the spray-season (i.e., Oct 2017) and the off-season (i.e., Jun 2018 and Jul 2019), while in Piketberg, peaks in load were only observed in the off-season.

Of particular concern are imidacloprid concentrations in the Hex River Valley, where elevated levels were still being detected several months after pesticide application for table grapes, which generally ends in January. This suggests that imidacloprid is persistent in the environment or is continuously applied in the late summer and early autumn. However, there is no indication from any of the application data that imidacloprid is applied from February to May. Although there is the possibility that the source of imidacloprid could be from non-agricultural application, such as for forest plantations (Ndlovu et al., 2022). The absence of consistent imidacloprid application throughout the year (i.e., only once per year according to application data), but concentrations exceeding EQS values every month, suggests that there may be long-term subsurface storage of imidacloprid that is gradually transported to the surface via interflow and groundwater in the Hex River Valley (Vonberg et al., 2014; Wettstein et al., 2016; Chow et al., 2020). According to Lewis et al. (2016), imidacloprid is highly water-soluble (610 mg/L at 20 °C) and leachable (Groundwater Ubiquity Score Index of 3.69). Transport of imidacloprid through the atmosphere from neighbouring catchments is highly unlikely because it is non-volatile and is typically applied directly into the soil (Bonmatin et al., 2015; Lewis et al., 2016).

Another possible explanation for the consistently high levels of imidacloprid, despite its low frequency of application, could relate to the transport and release of systemic pesticides (Sánchez-Bayo, 2014). Kreutzweiser et al. (2009) found that the consumption of decomposing leaves of plants that were treated with imidacloprid caused sublethal effects, illustrating that imidacloprid can be taken up and distributed throughout the plant tissue, thus becoming a long-term source. Imidacloprid stored in plant materials could be gradually shed from the plant and continuously transported into the rivers by wind and runoff processes, where they can degrade and be released to the water. In addition to imidacloprid being prevalent in surface water of agriculturally intensive catchments, Mitchell et al. (2017) found imidacloprid frequently within honey in South Africa and around the world.

**Terbuthylazine**: Fig. 5C shows that terbuthylazine concentrations exceed EQS twice in Piketberg, both during the 2017 spray-season (i.e., Oct and Nov). EQS exceedances were not observed in Grabouw and the Hex River Valley (Fig. 5C). The peaks in load are generally an order of magnitude

---

**Table 2**

Summary of monthly agricultural pesticide application (App.) and detection of parent compounds exceeding EQS values. True-positives: The detection (or non-detection) of four active ingredients correspond well with known agricultural pesticide application (or no application). False-positives: Two active ingredients are consistently detected without any known agricultural application.

| Active Ingredient | Catchment       | True-Positive | False-Negative | % True-Positive | % False-Negative |
|-------------------|-----------------|---------------|----------------|----------------|-----------------|
|                   | App. & Detect   | No App. & No Detect | App. & No Detect | No App. & Detect |
| Acetamiprid       | Grabouw         | 2             | 1              | 92%            | 8%              |
| Chlorpyrifos      | Grabouw         | 2             | 1              | 92%            | 8%              |
| Metsulfuron-methyl| Piketberg       | 2             | 1              | 83%            | 17%             |
| Thiacloprid       | Grabouw         | 6             | 0              | 75%            | 25%             |
| Imidacloprid      | Grabouw         | 1             | 0              | 8%             | 92%             |
|                   | Hex River Valley| 1             | 0              | 8%             | 92%             |
|                   | Piketberg       | 1             | 0              | 8%             | 92%             |
| Terbuthylazine    | Piketberg       | 0             | 0              | 0%             | 100%            |
greater in Piketberg than those in Grabouw and the Hex River Valley, mainly because Piketberg is a much larger catchment and thus has higher stream flows. In Grabouw and Piketberg, we see a similar pattern in loads compared to imidacloprid whereby peaks occur both during the spray-season (i.e., Nov 2017) and the off-season (i.e., Jun 2018 and Jul 2019). Terbuthylazine pollution in South African surface waters appears to be ubiquitous and has been recently observed by several others at similar concentrations in agricultural catchments and in rivers after wastewater treatment (Wooding et al., 2017; Rimayi et al., 2018). Despite terbuthylazine’s presence in our study catchments, there is no indication of its use according to our application data. Improper storage, handling, and disposal of terbuthylazine could lead to its presence in surface waters (Dalvie et al., 2006); however, we do not have direct evidence of this in our study areas. Herbicides could originate from non-agricultural sectors such as commercial forestry; however, Roberts et al. (2021) found that glyphosate-based products account for most herbicides applied in commercial forestry in South Africa. An alternative source of herbicides could be the removal of alien vegetation (Andrade-Rivas and Rother, 2015) and weed control along roadsides, rivers, and in household yards (Skark et al., 2004; Pérez et al., 2011). Yet another source of terbuthylazine could be volatilization and transport through the atmosphere from neighbouring catchments. Fuhrimann et al. (2020) found that terbuthylazine had the highest detection frequencies from passive air

Fig. 5. Shows the 16 two-week sampling periods conducted in the Western Cape, South Africa from July 2017 to July 2019. (A) Daily average rainfall (mm/day) and daily average river flow volume (m$^3$/day) over the sampling period, ‘+’ indicates drought period, ‘*’ monthly total rainfall may be unreliable due to missing daily values; (B) 14-day average concentration (blue bars) and load [solid red line] of imidacloprid over the sampling period, ‘‡’ indicates the months of imidacloprid application according to spray records (Curchod et al., 2020); (C) 14-day average concentration [blue bars] and load [solid red line] of terbuthylazine over the sampling period. Environmental quality standard (EQS) [dashed red line]. Note: secondary y-axis for B and C varies in scale due to high differences in pesticide load between areas.
Our study indicates that all samples across all three catchments contained at least three pesticides and that a majority (83%) of the samples contained five or more pesticides. Two catchments in particular had very high concentrations (>1 μg/L) over long time periods (22 weeks in the Hex River Valley and four weeks in Piketberg). High concentrations are typically caused by only a single/few pesticide(s) per catchment (i.e., terbuthylazine in Grabouw, imidacloprid in Hex River Valley and terbutylazine and metasulfonyl-methyl in Piketberg). The total number of detected pesticides and total concentration in surface water is only partially explainable by their application data and rainfall patterns. While the occurrence of some pesticides coincides with their application, others detected at relatively high concentrations are not limited to their application periods. This suggests that non-rainfall-driven pesticide transport processes are important. Major sources of pesticides and transport processes dominating the total concentrations are still poorly understood. Given this lack of understanding, it is challenging to take targeted mitigation measures (other than banning specific pesticides). Finally, providing a sound scientific basis for implementing specific mitigation measures would require comprehensive pesticide application data and a targeted study identifying the dominant transport pathways (e.g., air and groundwater transport) for major pesticides (e.g., imidacloprid and terbutylazine).

Aquatic pesticide pollution is of continuous concern in agriculturally intense provinces of South Africa, such as the Western Cape. In order to better understand the potential environmental and human health risks, we must establish continuous and consistent monitoring programs for pesticide pollution in agriculturally intensive catchments, coupled with a recording system of pesticide use at the farm level. Equipped with a better understanding of the drivers of aquatic pesticide pollution will lead to more sustainable agricultural practices and the development of context-specific risk thresholds that will benefit both the South African environment and economy.

CRediT authorship contribution statement

R. Chow: Writing – original draft, Writing - review and editing, Formal Analysis, Resources, Visualization, Supervision, L. Curchod: Investigation, Data curation. E. Davies: Investigation, Data curation, Visualization. A.F. Veludo: Visualization. C. Oltramare: Investigation, Data curation. M.A. Dalvie: Conceptualization, Funding acquisition, Writing-Reviewing and Editing. C. Stamm: Conceptualization, Writing- Reviewing and Editing. M. Röösi: Conceptualization, Funding acquisition, Writing- Reviewing and Editing. S. Fuhrimann: Conceptualization, Funding acquisition, Writing- Reviewing and Editing.

Funding

Eawag – Academic Transition Grant for Reynold Chow. Stellenbosch University Earth Sciences Departmental Bursary for Emma Davies. The Swiss National Science Foundation Postdoctoral Mobility Grants (P400PM_180757 and P4P4PM_199228) for Samuel Fuhrimann. The South African National Research Foundation (NRF) SARChI Programme (Grant number 94883), the Swiss State Secretariat for Education, Research and Innovation, the University of Basel and the Swiss TPH to support the CapSA project team.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Acknowledgments

The corresponding author would like to thank EAWAG (Academic Transition Grant) for their support. We gratefully acknowledge the participating farms and the involved farm organizations. We further thank the South African Weather Service for the rainfall and discharge data and the Western Cape Government Department of Agriculture for agriculture land use data. We also thank the research staff who did the water sample collection and farm interviews, namely L. Masinyana, M. Dawson, M. Mugari and B. Michelsen. We would also like to thank P. Januarie, W. Basera, D. September for their support with the farm selection and F. Weiss for technical advice.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.159784.

References

Ahrens, L., Danschvab, A., Lau, A.E., Kreuger, J. 2015. Characterization of five passive sampling devices for monitoring of pesticides in water. J. Chromatogr. A 1405, 1-11.
Andrade-Rivas, F., Rother, H.A. 2015. Chemical exposure reduction: factors impacting on South African herbicide sprayers personal protective equipment compliance and high risk work practices. Environ. Res. 142, 34-45.
AVICAP, 2017. Crop protection and agricultural remedies database (WWW document). Archived by WebCite®. http://www.webcitation.org/73fdjO3W (accessed 9.26.18).
Bajwa, U., Sandhu, K.S. 2014. Effect of handling and processing on pesticide residues in food a review. J. Food Sci. Technol. 51 (2), 201-220.
Barbieri, M.V., Peris, A., Postigo, C., Moya-Garcés, A., Monllor-Alcaraz, L.S., Rambla-Alegre, B. Michelsen. We would also like to thank P. Januarie, W. Basera, D. September for their support with the farm selection and F. Weiss for technical advice.

Department of Water Affairs and Forestry, 1996. South African Water Quality Guidelines. vol. 5 (Aquatic Ecosystems).
Department of Water and Sanitation, 2016. National Groundwater Strategy, Pretoria, South Africa.
Doppler, T., Lück, A., Camenzuli, L., Kuxnis, M., Stamm, C. 2014. Critical source areas for herbi-

The corresponding author would like to thank EAWAG (Academic Transition Grant) for their support. We gratefully acknowledge the participating farms and the involved farm organizations. We further thank the South African Weather Service for the rainfall and discharge data and the Western Cape Government Department of Agriculture for agriculture land use data. We also thank the research staff who did the water sample collection and farm interviews, namely L. Masinyana, M. Dawson, M. Mugari and B. Michelsen. We would also like to thank P. Januarie, W. Basera, D. September for their support with the farm selection and F. Weiss for technical advice.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.159784.

References

Ahrens, L., Danschvab, A., Lau, A.E., Kreuger, J. 2015. Characterization of five passive sampling devices for monitoring of pesticides in water. J. Chromatogr. A 1405, 1-11.
Andrade-Rivas, F., Rother, H.A. 2015. Chemical exposure reduction: factors impacting on South African herbicide sprayers’ personal protective equipment compliance and high risk work practices. Environ. Res. 142, 34-45.
AVICAP, 2017. Crop protection and agricultural remedies database (WWW document). Archived by WebCite®. http://www.webcitation.org/73fdjO3W (accessed 9.26.18).
Bajwa, U., Sandhu, K.S. 2014. Effect of handling and processing on pesticide residues in food: a review. J. Food Sci. Technol. 51 (2), 201-220.
Barbieri, M.V., Peris, A., Postigo, C., Moya-Garcés, A., Monllor-Alcaraz, L.S., Rambla-Alegre, B. Michelsen. We would also like to thank P. Januarie, W. Basera, D. September for their support with the farm selection and F. Weiss for technical advice.

Department of Water Affairs and Forestry, 1996. South African Water Quality Guidelines. vol. 5 (Aquatic Ecosystems).
Department of Water and Sanitation, 2016. National Groundwater Strategy, Pretoria, South Africa.
R. Chow et al.

Science of the Total Environment 858 (2023) 159784

Pitaréch, E., Cervera, M.I., Portolés, T., Ibáñez, M., Barreda, M., Renaud-Prunetonosa, A., Morell, I., López, F., Albarrán, F., Hernández, F., 2016. Comprehensive monitoring of organic micro-pollutants in surface and groundwater in the surrounding of a solid-waste treatment plant of Castellón, Spain. Sci. Total Environ. 548, 211–220.

Rimayi, C., Oduosanya, D., Weiss, J.M., de Boer, J., Chimuka, L., 2018. Seasonal variation of chloro-s-triazines in the Hartbeespoort Dam catchment, South Africa. Sci. Total Environ. 613, 472–482.

Roberts, J.C., Little, K.M., Rolando, C., 2021. Estimated herbicide use in the commercial forest sector in South Africa. Aust. For. 84 (3), 108–121.

Rosenzweig, C., Iglesius, A., Yang, X.B., Epstein, P.R., Chivian, E., 2001. Climate Change and

Skark, C., Zullei-Seibert, N., Willme, U., Gatzemann, U., Schlett, C., 2004. Contribution of non-agricultural pesticides to pesticide load in surface water. Pest Manag. Sci. 60 (6), 525–530.

Sänger, H., 2005. Pestizidbelastung von Oberflächenwässer: auswirkungen der ökologischen Massnahmen in der Landwirtschaft. GWA 85 (11), 679–886.

Sánchez-Bayo, F., 2014. The trouble with neonicotinoids. Science 346 (6211), 806–807.

Schäfer, R.B., 2020. Sampling rates for passive samplers exposed to a peak of 42 organic pesticides. Sci. Total Environ. 740, 140376.

Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Gooddy, D.C., Bell, R.A., Wooding, M., Rohwer, E.R., Naudé, Y., 2017. Determination of endocrine disrupting chemicals and antiretroviral compounds in surface water: a disposable sorptive sampler. Water Res. 121, 460–465.

Spycher, S., Mangold, S., Doppler, T., Junghans, M., Wittmer, L., Stamm, C., Singer, H., 2018. Pesticide risks in small streams—how to get as close as possible to the stress imposed on aquatic organisms. Environ. Sci. Technol. 52 (8), 4526–4535.

Sytarudin, M., Kristanti, R.A., Yuriarto, A., Hadibratara, T., Rhee, J., Al-Onazi, W.A., Algarni, T.S., Almarri, A.H., Al-Mohaimed, A.M., 2021. Pesticides in drinking water—a review. Int. J. Environ. Res. Public Health 18 (2), 468.

Triasti, M., Nardone, A., Giovinetti, M.C., De Rosa, E., Canzanelia, S., Sarnacchiaro, P., Montuori, P., 2019. Ecological risk and estimates of organophosphate pesticides loads into the Central Mediterranean Sea from Volturno River, the river of the “Land of Fires” area, southern Italy. Sci. Total Environ. 678, 741–754.

Veludo, A.F., Figueiredo, D.M., Degreendele, C., Matinyana, L., Curchod, L., Kohoutek, J., Rukůčka, P., Martiník, J., Průhýlová, V., Klánová, J., Dalvie, M.A., 2022. Seasonal variations in air concentrations of 27 organochlorine pesticides (OCPs) and 25 current-use pesticides (CUps) across three agricultural areas of South Africa. Chemosphere 289, 133162.

Vermeirssen, E.L., Bramaz, N., Hollender, J., Singer, H., Escher, B.I., 2009. Passive sampling combined with eco-toxicological and chemical analysis of pharmaceuticals and biocides—evaluation of three ChemcatcherTM configurations. Water Res. 43 (4), 903–914.

Vonberg, D., Vanderborght, J., Cremer, N., Pütz, T., Herbst, M., Vereecken, H., 2014. 20 years of long-term atrazine monitoring in a shallow aquifer in western Germany. Water Res. 50, 294–306.

WGC, 2018. CapeFarmMapper [WWW Document]. West. Cape Gov. Crop Census 2013 (Arched by WebGite®. http://www.webcitation.org/73MY7gLgP. https://gis.elsenburg.com/apps/cfm/. accessed 10.22.18.

Wettstein, F.E., Kasteel, R., García Delgado, M.F., Hanke, I., Huntscha, S., Balmer, M.E., Poiger, T., Bucheli, T.D., 2016. Leaching of the neonicotinoids thiamethoxam and imidacloprid from sugar beet seed dressings to subsurface tile drains. J. Agric. Food Chem. 64 (33), 6407–6415.

Wooding, M., Rohwer, E.R., Naude, Y., 2017. Determination of endocrine disrupting chemicals and antiviral compounds in surface water: a disposable sorptive sampler with comprehensive gas chromatography–time-of-flight mass spectrometry and large volume injection with ultra-high performance liquid chromatography–tandem mass spectrometry. J. Chromatogr. A 1496, 122–132.

Zwan, E.M., 2019. Impact of climate change on primary agriculture, water sources and food security in Western Cape, South Africa. Jambá: J. Disaster Risk Stud. 11 (1), 1–7.