# Temporal variation of pesticide mixtures in rivers of three agricultural watersheds during a major drought in the Western Cape, South Africa

Lou Curchod [a, b, c, d], Christelle Oltramare [c], Marion Junghans [d], Christian Stamm [c], Mohamed Aqiel Dalvie [e], Martin Röösli [a, b], Samuel Fuhrimann [e, f, *]

[a] Swiss Tropical and Public Health Institute (Swiss TPH), 4002, Basel, Switzerland
[b] University of Basel, 4002, Basel, Switzerland
[c] Swiss Federal Institute of Aquatic Science and Technology (eawag), 8600, Dübendorf, Switzerland
[d] Swiss Centre for Applied Ecotoxicology, 8600, Dübendorf, Switzerland
[e] Centre for Environmental and Occupational Health Research, School of Public Health and Family Medicine, University of Cape Town, 7925, Cape Town, South Africa
[f] Institute for Risk Assessment Sciences (IRAS), Utrecht University, 3584, Utrecht, the Netherlands

## ARTICLE INFO

## ABSTRACT

South Africa is the leading pesticide user in Sub-Saharan Africa. However, little is known about the occurrence of pesticide mixtures in surface water and potential environmental risks in Africa.

This study investigated the occurrence of pesticides mixtures in three watersheds during a drought year in South Africa. The study was conducted in the Krom River, Berg River and Hex River watersheds within larger agriculture systems in the Western Cape. Pesticide spray records were collected from 38 farms. A total of 21 passive water samplers (styrenedivinylbenzene disks (SDB)) were deployed, each for two weeks per month, over seven sampling rounds during the main pesticide application period between July 2017 and January 2018. Samples were analyzed for 248 pesticide compounds using LC-HR-MS/MS. Pesticide occurrence was analyzed for temporal agreement with pesticide spraying events (Cohen's κ) and correlation with rainfall patterns and river discharge (Pearson correlation ($r_p$)). Pesticide time-weighted average concentrations were estimated and compared to environmental quality standards (EQS). According to the farm spray records, 96 different pesticides were sprayed during the sampling period and differed considerably between the three study areas, seasons and crops grown. In total, 53 compounds were detected in river water. We detected 39% of compounds from the spraying records and demonstrated close temporal correlations of seasonal patterns for 11 pesticide compounds between reported on spraying records and observations in the streams (κ = 0.90). However, 23 detected pesticides were not found on spray records, many of them being herbicides. Most of the estimated two-week average pesticide concentrations were below 40 ng/L. The insecticides imidacloprid, thiacloprid, chlorpyrifos and acetamiprid and the herbicide terbuthylazine exceeded at least once their EQS 58-fold (EQS 13 ng/L), 12-fold (EQS 10 ng/L), 9-fold (EQS 0.46 ng/L), 5-fold (EQS 24 ng/L) and 3-fold (EQS 220 ng/L), respectively. Our study substantially widens the view on pesticide pollution in surface water compared to previous studies in Sub-Saharan Africa by targeting more than 200 pesticides using passive sampling systems. This broad assessment revealed the presence of 53 compounds, some of them in high concentrations, indicating possible adverse effects on biota and the quality of the ecosystem. Whether the observed concentration levels in the year 2017 were exceptional due to the lowest ever recorded rainfall and river discharge needs to be tested with additional data to better understand how pesticide pollution levels manifest under average rainfall and river discharge conditions.

© 2019 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

## 1. Introduction

South Africa is the leading pesticide user in Sub-Saharan Africa (Dabrowski, 2015; Dalvie et al., 2009) with more than 3'000

* Corresponding author. Yalelaan 2, 3584, CM Utrecht, the Netherlands.
E-mail address: s.fuhrimann@uu.nl (S. Fuhrimann).

pesticide products containing 700 different pesticide compounds legally registered for agricultural use (AVCASA, 2017). Pesticide compounds (also referred to as parent compounds or active ingredient) can enter non-target environments, such as surface and groundwater where they persist or metabolize to transformation products (TPs) and may present a risk for environmental and human health (Moschet et al., 2015; Sorensen et al., 2015; Stehle and Schulz, 2015). A thorough understanding of pesticide occurrence in surface water is of increasing importance as changing environmental conditions due to climate change, such as an increase in temperature or more frequent extreme events, may considerably impact on the use of pesticides and their environmental fate (Bloomfield et al., 2006; Delcour et al., 2015; Rosenzweig et al., 2001). For example, pest infestations often coincide with changes in climatic conditions (Delcour et al., 2015; Rosenzweig et al., 2001), implying a potential increase in pesticide use during extreme events such as droughts or heavy rains (Bloomfield et al., 2006; Rosenzweig et al., 2001). Contrary, a decrease in rainfall may reduce pesticide transport processes such as run-off and lower pesticide concentration in surface water (Bloomfield et al., 2006; Otieno et al., 2013).

In the past, monitoring programs have been developed mainly in high-income countries to better understand seasonal occurrence and cumulative risks of pesticide mixtures (Spycher et al., 2018; Finizio et al., 2011; Gilliom et al., 2006; Gustavsson et al., 2017; Herrero-Hernández et al., 2017; Kapsi et al., 2019; Moschet et al., 2014; Stenrød, 2015). Such investigations are costly and therefore studies analyzing a broad range of pesticide mixtures used in agriculture and covering seasonal trends are rare in low- and middle-income countries (LMICs) in general and Sub-Saharan Africa in specific (Chepchirchir et al., 2017; Unyimadu et al., 2018; Yahaya et al., 2017).

In Sub-Saharan Africa, most of the studies focused on persistent pesticides such as organochlorines which are in many cases banned for agriculture use (Amdany et al., 2014; Chepchirchir et al., 2017; Teklu et al., 2016; Unyimadu et al., 2018; Yahaya et al., 2017). Only a few studies conducted in the past 10 years investigated currently used pesticides in agriculture and are found to be restricted in the following dimensions due to limited resources (Aneck-Hahn et al., 2018; Houbraken et al., 2017; Lehmann et al., 2018, 2017; Mekonen et al., 2016; Nesser et al., 2016; Otieno et al., 2010; Wooding et al., 2017): (i) temporal coverage (relying mostly on grab sampling); (ii) number of compounds studied (up to a maximum of 33 target compounds analyzed); and (iii) seasonality (sampling schemes fail to consider seasonal patterns). Passive sampling methods are one practical possibility to overcome some of these limitations (Moschet et al., 2015). Passive samplers, such as the Chemcatchers® (styrenedivinylbenzene (SDB) disks), allowed relatively easy deployment in the field and proofed to be a cost-effective and robust monitoring tool even in remote areas with little infrastructure available (Chepchirchir et al., 2017; Moschet et al., 2015). Using Chemcatchers® screening can increase the temporal coverage and the probability of detecting a broad range of polar and semi-polar compounds (Moschet et al., 2014). Passive samplers reflect time-averaged concentrations. Hence, they do not reflect possible peak concentrations and may substantially underestimate the acute exposure to toxic compounds (Spycher et al., 2018). Such short-term, episodic concentration peaks are known to negatively impact aquatic invertebrates (Beketov et al., 2013).

In addition to the lack of knowledge of pesticide mixtures in water, there is little understanding of pesticide use on farms in LMICs (Dabrowski, 2015; Dalvie et al., 2009). Currently, there is a growing number of farms which record their pesticide use on spray records to adhere to good agriculture practice (GAP) or to obtain export certifications (GLOBALG.A.P., 2019). However, the few efforts

which generated an overview of used pesticides relied on country-wide annual pesticide sales data. The sales data lack temporal and spatial information and reported a mismatch between pesticide use and detects in the environment (Dabrowski, 2015; Dalvie et al., 2009). Hence, there is a need to measure the temporal and spatial variation of pesticide mixtures and compare it with actual pesticide use data in LMICs.

The present study was conducted in the Western Cape, South Africa, which is experiencing acute pressure from climate change. The Western Cape hit by an extreme drought between 2016 and 2018 that impacted profoundly on the water availability for domestic and agricultural use while reducing crop yields and changing pest patterns (Godsmark et al., 2018; Zwane, 2019). Therefore, this study aim was to investigating the occurrence of pesticide mixtures using passive water sampling systems in three watersheds during the drought year in 2017 and 2018 in South Africa. We addressed three research questions: (i) what is the seasonal variation and potential risks for the environment of the measured pesticides?; (ii) can pesticide spray records be used to predict the occurrence of pesticide mixtures in surface water?; and (iii) to what extent are measured pesticide levels driven by weather conditions and hydrology? For all questions, it is discussed how the prevailing major drought during the study period may have affected the results.

## 2. Materials and methods

### 2.1. Study area and pesticide spraying records

The study was conducted in the Western Cape, South Africa. The Western Cape includes 1.9 million ha agriculture land (14.5% of its total surface area), while 70′000 households depend on agriculture (3.6% of the total households; STATS SA 2016; WCG 2018). This study focused on three river watersheds within different large-scale agricultural systems (Fig. 1; Fig. S1 and Table S1 of the Supplementary Information (SI)). The different crops grown in the study areas allow for comparison of crop-specific pesticide mixtures (Grabouw (pome fruits, 81% of the area), Hex River Valley (table grapes, 98% of the area) and Piketberg (cereals, 56% of the area; WCG, 2018)). The study is linked to the Child health Agriculture Pesticide study in South Africa (CapSA), which prospectively investigates reproductive and neurobehavioral health effects of environmental pesticide exposure in children (Chetty-Mhlanga et al., 2018).

Pesticide spray records were collected from 38 farms covering the period between November 2017 and April 2018. The farms were located upstream of the water sampling points (between 2373 and 12 853 m in Grabouw; 3012 and 13 806 m in Hex River Valley and 958 and 35 029 m in Piketberg) (Table S1 of the SI). Time, location and total amounts of applied pesticide compounds (in kg/ha) were extracted from the spraying records. The spray records summarize all reported insecticide and fungicide applications on the crops. However, herbicide applications are often not recorded as they are not directly applied to the plants themselves but only to the soils (personal communication with farmers). Informed consents have been obtained from each participating member of the farm management and stakeholder. The study received ethical clearance from the University of Cape Town's Research Ethics Committee (HREC 234/2009).

### 2.2. Water sampling

Water sampling was undertaken downstream of the enrolled farms in each valley (Fig. 1 and Fig. S1 of the SI). Sampling locations were placed in the Krom River (Grabouw; 34°15′8″S, 19°3′14″E),
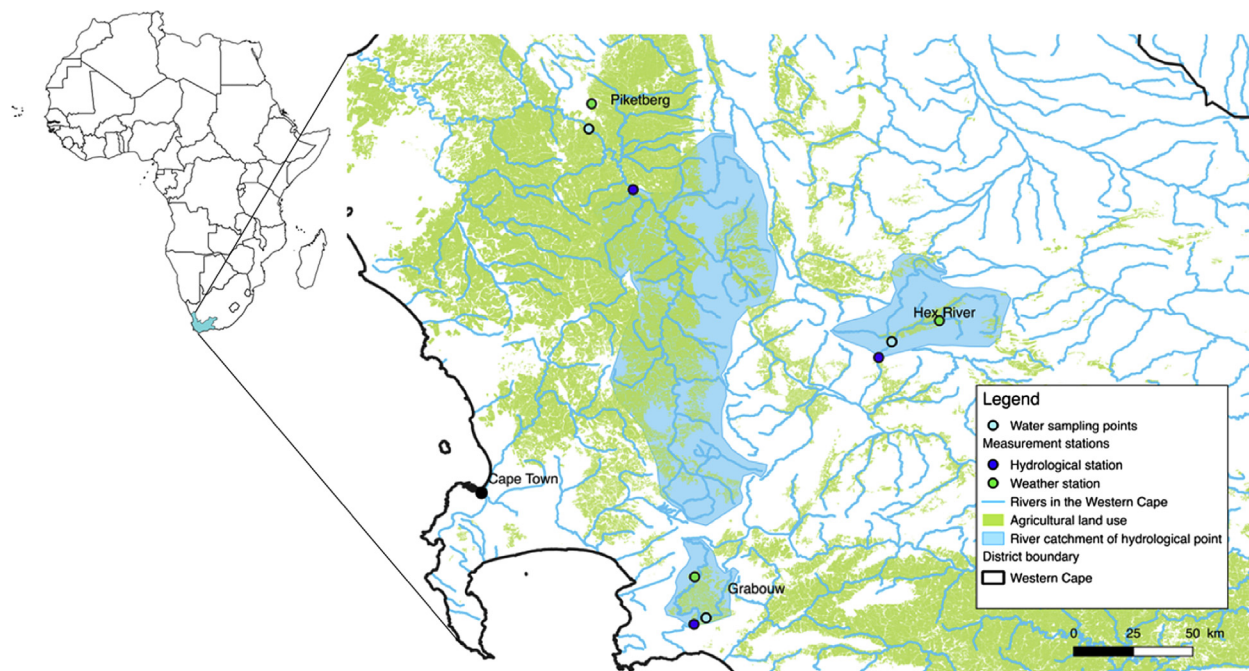
**Fig. 1.** Map showing the three watersheds where the study was conducted in the Western Cape, South Africa, between July 2017 and January 2018 (see Supplementary Information Fig. S1 for detailed maps including land use and river systems).

Hex River (Hex River Valley; 33°31′48″S, 19°32′25″E) and Berg River (Piketberg; 32°58′19″S, 18°44′48″E). At each of the three sampling points, two pre-conditioned Chemcatchers® (SDB-RDP (polyStyreneDivinylBenzene-Reverse Phase Sulfonated) covered by polyether sulfone (PES) membranes) were deployed for two weeks per month (Moschet et al., 2015). Over seven sampling rounds a total of 21 duplicate samples were collected between the 23rd July 2017 and the 31rd January 2018 (sampling periods: (i) 23.07.2017−06.08.2017, (ii) 22.08.2017−05.09.2017, (iii) 19.09.2017−03.10.2017, (iv) 17.10.2017−02.11.2017, (v) 14.11.2017−28.11.2017, (vi) 14.12.2017−29.12.2017 and (vii) 17.01.2018−31.01.2018). 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. Finally, samples were transported at 4 °C to the Swiss Federal Institute of Aquatic Science and Technology (Eawag) in Switzerland for analysis.

### 2.3. Preparation and extraction of passive sampler

The passive samplers were prepared according to Vermeirssen et al. (2009). Briefly, before the deployment, the SDB disks and the PES membrane were conditioned in MeOH and then in nanopure water (30 min each). The SDB disks covered by a PES membrane were assembled on the holders. The passive samplers were stored in nanopure water until deployment. Only one replicate of the SDB disks was analyzed. The second one was kept for quality control. The extraction was done according to Moschet et al. (2013). The vials containing the SDB disks were filled with 6 mL of acetone and shaken for 30 min on a rotary shaker. After transferring the total volume of acetone into a new centrifuge glass tube, 5 mL of methanol was added to the SDB disks for a second extraction and shaken for another 30 min. The extract of acetone was concentrated to a volume of 1 mL and then mixed with the methanol from the second extraction. The 6 mL extract was further filtrated with a polytetrafluoroethylene (PTFE) filter (0.45 um pore size) and then evaporated to a volume of 0.1 mL. The final extract was adjusted to 1 mL by adding nanopure water. The samples were centrifuged at 4000 rpm at 21 °C for 30 min. The supernatant was transferred into an offline vial for the analysis.

### 2.4. Water analysis

The samples were measured by liquid chromatography − high-resolution mass spectrometry (LC-HR-MS/MS) using an XBridge C18 column for chromatography separation. The detection was performed on a QExactive MS with electrospray ionization (ESI). Eluents for the chromatographic gradient used were methanol and nanopure water, both acidified with 0.1% formic acid. In total, 248 compounds were analyzed (187 pesticide compounds and 61 of their TPs; Table S2 of the SI). The lists of targeted analytes were taken from a similar study in Switzerland (Moschet et al., 2015) and adapted according to the registration status of the compounds in South Africa (AVCASA, 2017) and previous detection in rivers in South Africa (Dalvie et al., 2011). The specific limits of detection (LOD) and limits of quantifications (LOQ) for each compound are provided in Table S2 of the SI.

### 2.5. Data collection to assess catchment hydrology

Daily rainfall data between 1960 and 2018 were accessed from the three closest rain gauging stations to the study areas at 12, 13 and 8 km away from the sampling points in Grabouw (34°8′42″S, 19°1′26″E), Hex River Valley (33°28′26″S, 19°39′54″E) and Piketberg (32°54′22″S, 18°45′14″E), respectively (Fig. 1 and Fig. S1 of the SI; EAD, 2018). Daily river discharge data since 1980 have been obtained from the closest recording stations from the sampling points. The distance between these points is 3 km for Grabouw (station G4H030 on Palmiet River), 6 km for Hex River (station H2H006 on Hex River) and 21 km for Piketberg (station G1H013 on Berg River; Fig. 1 and Fig. S1 of the SI; DWA 2019).

## 2.6. Data analysis

For a comparison between the crops the mean amount of pesticides sprayed per crop (kg/ha) was calculated over all farms producing the same crop. To investigate the correlation between measured amounts of pesticide compounds, rainfall and water discharge of each river watershed Pearson regression analysis ($r_p$) was used. To analyze the agreement between pesticides reported on the spraying records with pesticides measured on the passive samplers, Cohen's κ coefficient was used.

The time-weighted average concentrations of the different compounds in the water phase were calculated using compound-specific sampling rate $R_s$ from the literature where available (Charriau et al., 2016; Ahrens et al., 2015; Moschet et al., 2014). If several values were available from these references, we used the average as the expected value $R_s$. Because sampling rates may vary with flow conditions or biofilm and sedimentation on the disks, we considered those sampling rates as uncertain and considered a one-order of magnitude range ($R_s$ multiplied/divided by 3.16, see Table S7 of the SI). Such a range covers 90% of the empirical variance observed among compounds in a previous field study (Moschet et al., 2014).

To assess the ecotoxicological relevance of time-weighted average pesticides concentrations the values were compared to existing environmental quality standards (EQS). Since such standards for surface waters are only available for two pesticides in South Africa (atrazine, endosulfan (Department of Water Affairs and Forestry, 1996)), a consistent set of EQS from the Switzerland or the EU were used (Moschet et al., 2014; Swiss Center for Applied Ecotoxicology Eawag/EPFL, 2013). Acute and chronic EQS values are derived according to a standardized procedure (European Commission, 2011). EQS indicate compound-specific concentrations which may adversely affect aquatic biota. Because the EQS approach is conceptually similar to the procedure outlined by South African authorities (Department of Water Affairs and Forestry, 1996) and it considers data across the entire spectrum of aquatic organisms, we have chosen this approach acknowledging that the choice of other reference values (such as Regulatory Acceptable Concentrations RACs, or toxic units) may also be a valid option when assessing the risk of pesticides in surface waters. When no EQS was available, a limit of 100 ng/L was assumed (ISPRA, 2018). An assessment of the risk of the pesticide mixtures was not done because it was beyond the scope of this study. In general, the risk of a pesticide mixture is similar to or higher than the risk of the highest risk for the single mixture components (Price et al., 2012). The analysis was done in R (R Foundation for Statistical Computing — R version 3.5.3, RStudio Version 1.1.456).

## 3. Results and discussion

### 3.1. Pesticide spraying records

Between July 2017 and January 2018, 96 different pesticide compounds (47 fungicides, 31 insecticides and 18 herbicides) were recorded to be sprayed over 341 spraying applications on the 38 farms (Table S3 of the SI). The sprayed pesticide compounds reflect 15% of the currently registered pesticides in South Africa (AVCASA, 2017). There were considerable differences in the numbers of pesticides used between Piketberg, Hex River Valley and Grabouw (n = 36, 48 and 71, respectively; Fig. 2C). The mixtures differed also considerably between seasons and crops. Mean amounts of all applied pesticides per ha over the seven months was highest in table grapes (34 kg/ha), followed by pome fruits (29 kg/ha), wine grapes (21 kg/ha), citrus (5 kg/ha) and wheat (3 kg/ha). The most used crop-specific pesticides (>80% of total amounts applied) were:

penconazole (56%), mancozeb (27%) and spiroxamine (4%) for table grapes in Hex River Valley; mancozeb (76%), glyphosate (4%) and chlorpyrifos (4%) for pome fruits in Grabouw; and 2,4-d (40%), bromoxynil (23%) and MCPA (18%) for wheat in Piketberg.

Fungicides were applied in highest amounts on table grapes (97% of all pesticides applied) and pome fruits (88%) while on wheat herbicides were sprayed mostly (82%, respectively; Fig. 2C, Table S3 of the SI). However, our collected spray records have a bias in underreporting herbicides as in many cases only fungicides and insecticides are recorded due to their direct applications on crops (personal communication with farmers, 2019). High use of herbicides is however expected according to the South Africa pesticide sales statistic from 2009 (Dabrowski et al., 2014). There, herbicides are reported to be the most used pesticides over all crops followed by fungicides and insecticides (50%, 41%, and 8% of the total use, respectively).

### 3.2. Pesticide occurrence in the streams during drought conditions

#### 3.2.1. Catchment hydrology and the effect of the drought

All three watersheds were under extreme water shortage due to the drought condition which was reported for the whole Western Cape between 2016 and 2018 (WCG, 2017; Zwane, 2019). During the sampling in 2017, water discharge rates were the lowest on record (since 1980) while total rainfall over the year was within the three lowest measurements for all three study areas (since 1960; Fig. S2; EAD, 2018). Nevertheless, there were slight differences in the severity of the drought between the study areas. During the seven-months sampling period Grabouw was the wettest area and received 179 mm of rain (range 2−60 mm/two-week). Piketberg and Hex River Valley received three times less rain (56 mm (range 0−26 mm/two-week) and 51 mm (range 0−37 mm/two-week)), respectively (Fig. 2A; EAD, 2018). Water flow was highest in the Grabouw area with 125 mm ranging between 0.5 and 15.9 mm/two-week (0.04−1.40 m³/s), while both Hex River and Berg River had a flow of 12 mm (range 0.4−1.3 mm/two-week (0.21−0.75 m³/s) and 0.2−1.8 mm/two-week (0.58−4.67 m³/s), respectively; Fig. 2B). In the following sections we describe to which degree the spatio-temporal patterns of pesticide compounds detected reflect the reported pesticide applications during the study.

#### 3.2.2. Pesticide compounds detected

Out of the 248 analyzed compounds (187 pesticide compounds and 61 TPs), 34 parent compounds (18% of the analyzed active ingredients) and 19 TPs (31% of the analyzed TP) were detected (Table S4 of the SI). The 34 pesticide compounds detected above LOD consisted of 13 fungicides, 12 herbicides and nine insecticides (Fig. 3). Out of the 96 pesticide compounds that have been reported on the spray records, 35 compounds were covered by the analytical method. These included six out of the eight dominating compounds in the spraying records (Tables S3 and S4 of the SI). Only the fungicide mancozeb and the herbicide glyphosate, which are hardly stable in the environment or require particular analytical methods, were not covered. Besides, 18 of the 96 pesticide compounds were metals or organic compounds (e.g., zinc, copper, manganese), which require different analytics. Out of the three major crops in the study areas (wheat, pome fruits and table grapes) this study covers over 50% of the applied pesticide compounds (Table S5 of the SI).

Out of 34 compounds from the spraying records, which we analyzed, 13 compounds (39%) could be detected. Out of these compounds three (chlorpyrifos, penconazole, spiroxamine) belong to compounds sprayed in the highest quantities according to the spray records. Another 10 compounds, which were reported in the spray records, were found as well in the rivers (Fig. 4). Also, 23
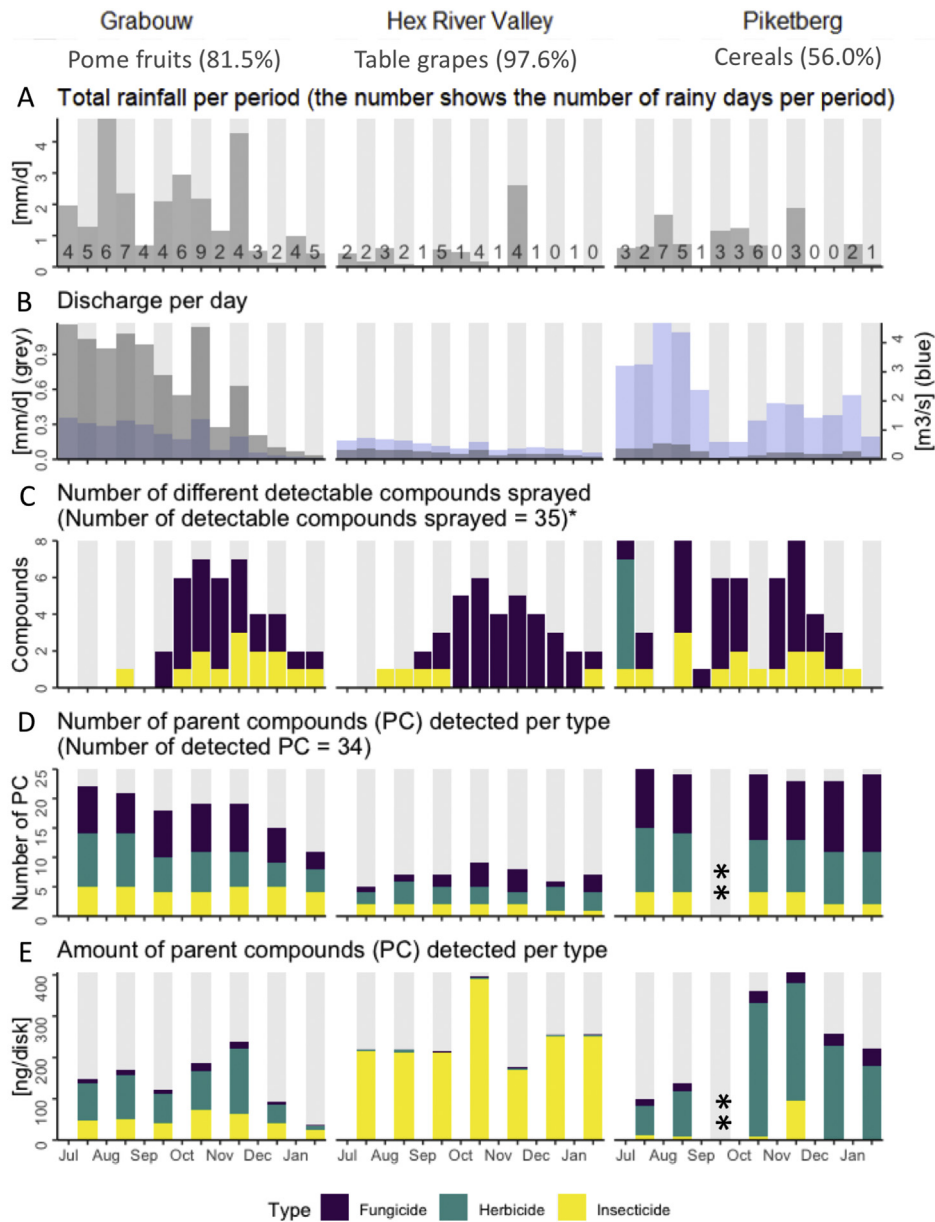
**Fig. 2.** Bar chart showing the seven two-week sampling periods (grey background) in the study conducted in the Western Cape, South Africa, between July 2017 and January 2018. (A) Total rainfall [mm/day]***; (B) total water discharge [mm/day] and [m3/s]****; C) number of compounds reportedly sprayed per study area (spray records); (D) number and (E) amount of parent compounds detected. All numbers are reported per two-week periods.
* 19 fungicides, 8 insecticides and 7 herbicides ** The sample of September in Piketberg was found out of the water. It has been taken out of the further analysis; *** (EAD, 2018); **** (DWA, 2019).

pesticide compounds were detected that were not reported on the spraying records (11 out of 12 detected herbicides, five out of 13 fungicides and five out of nine insecticides; Table S5 of the SI). The low ratio between reports and detects of herbicides could originate from a reporting bias (see section 3.2), earlier applications or non-agriculture use for alien vegetation removal (Andrade-Rivas and Rother, 2015) and weed control alongside roads. For example, non-reported triazine herbicides (atrazine, simazine, terbuthylazine, prometon and prometryn) were frequently observed in the rivers but not recorded on any spray records. The occurrence of these compounds was also shown in previous studies in other areas of South Africa (Rimayi et al., 2018; Wooding et al., 2017). Atrazine was reported to be one of the pesticides sold in the highest quantities in South Africa in 2009 (Dabrowski, 2015).

The ratio between parent compounds and TPs can yield insight into the residence time of the pesticide compounds in the soil-groundwater system, where high values point to a recent application (Leu et al., 2004). Seven pesticide compound-TP pairs could be observed in this study (for the pesticide compounds atrazine, azoxystrobin, imidacloprid, metolachlor, simazine, terbuthylazine and thiacloprid) at least in one study area. Except for metolachlor, the pesticide compound/TP ratios reveal clear trends with the concentration of the parent compounds (Fig. S3 of the SI). This indicates on the one hand, that these pesticides stem from recent applications in the watersheds because we observed in samples with large parent concentrations high parent to TP ratios (except for simazine in Piketberg). On the other hand, in samples with low parent levels, the small ratios indicate long residence times. This
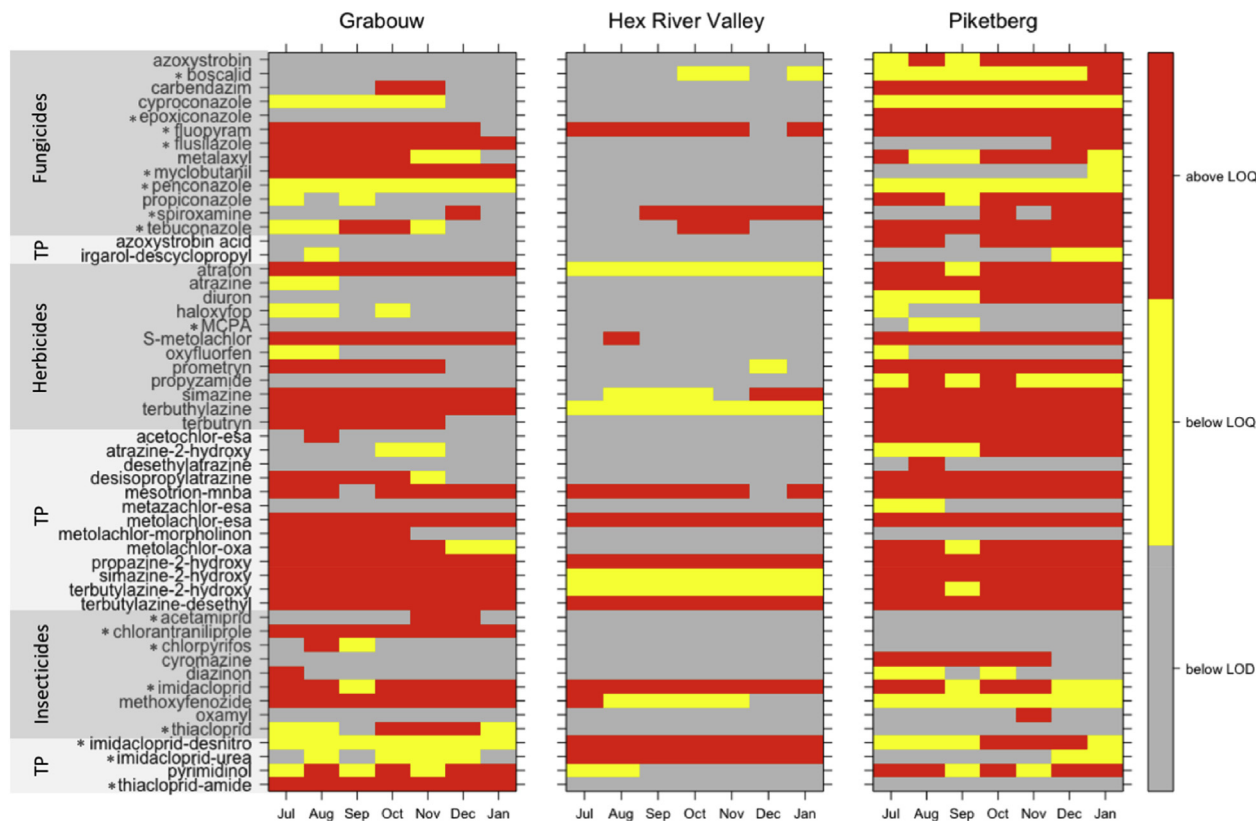
**Fig. 3.** Heat map showing the 53 compounds detected above the limit of detection (LOD) and above limit of quantification (LOQ) stratified by area, type of pesticide compound (n = 34) and transformation products (TPs; n = 19) in the study conducted in the Western Cape, South Africa between July 2017 and January 2018.
*reported to be sprayed according to the spraying records collected.

implies that we also observed background concentrations from previous applications. This is not surprising given the persistence of compounds such as triazine herbicides (water-sediment $DT_{50}$ between 33 and 228 days; Table S7 of the SI; University of Hertfordshire, 2018) and is a well-known phenomenon (Gomides Freiatas et al., 2008).

Several (n = 20) compounds on our target list were reported to be sprayed but not detected. Out of them, one was not sprayed during the months of our sampling period (prosulfocarb). A possible explanation could be that the mean LOD of the 20 non-detected compounds is almost 8-times higher than the mean LOQ of the 11 compounds that were sprayed and detected (9.8 and 1.3 ng/disk, respectively).

### 3.2.3. Spatial patterns

Generally, it is observed that pesticides found in surface waters reflect the cropping patterns (Gilliom, 2007). Accordingly, it was not surprising to detect differences in individual pesticide compounds occurrence in the three rivers (Fig. 3). Most pesticide compounds were detected in Piketberg (28 pesticide compounds, 13 fungicides, 12 herbicides and five insecticides), followed by Grabouw (26 pesticide compounds, 10 fungicides, nine herbicides and seven insecticides) and Hex River Valley (11 pesticide compounds, five herbicides, four insecticides). Specific differences between study areas were apparent for thiacloprid (insecticide; only detected in Grabouw) and propyzamide (herbicide; only detected in Piketberg; Fig. 5). In Hex River Valley, mainly insecticides were detected while primarily fungicides were reported to be sprayed (Fig. 2C–E). In Grabouw and Piketberg, herbicides were detected in the largest amounts throughout the

seven sampling rounds, while only reported to be sprayed during July in Piketberg.

### 3.2.4. Temporal patterns

We found strong temporal agreement (κ = 0.90) between spraying events and occurrence in river water for 11 compounds (five insecticides and six fungicides) over the 220 possible observations over the three study areas and the seven sampling rounds, respectively six in Piketberg (Table 1, Fig. 4). The agreement was only moderate (κ = 0.42) for the compounds detected and applied when considering the whole sampling period and the three areas (33 possible observations). Moreover, three TPs of sprayed compounds were detected (imidacloprid-desnitro, imidacloprid-urea and thiacloprid-amide; Fig. 4B), which correlated in each case with the spraying of the pesticide compounds (n = 4) or the absence of spraying activity led to no quantification (n = 5). This suggests, first, that the spraying records collected provided a good representation of these specific insecticides and the fungicides applied, and second, that pesticide compounds entered surface water within a short time after application.

In addition, to the pesticide application patterns one might also expect temporal relationships between pesticide occurrence in river water with rainfall events and discharge quantity (Doppler et al., 2012; Leu et al., 2005; Schulz, 2004; Thurman et al., 1991) leading to sometimes pronounced seasonality (Leu et al., 2010). Indeed, Grabouw, which had received the most rainfall, both bi-weekly discharge and rainfall quantities were positively correlated to the total measured amount of all pesticide compounds on the passive samplers (ng/disk) ($r_p$ 0.84 and 0.73, respectively). For the two other rivers we could only find weak non-significant
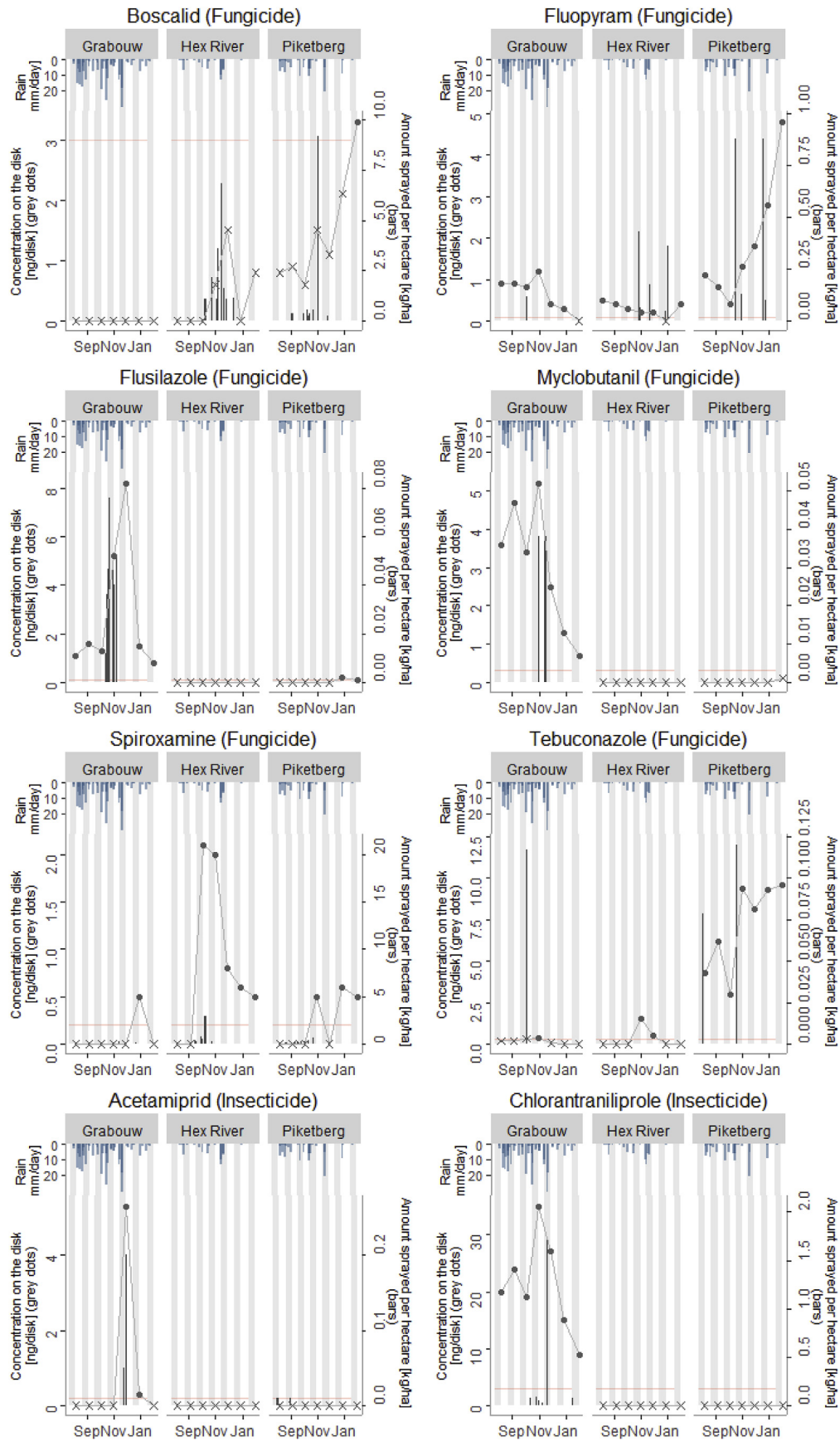
**Fig. 4.** Bar chart showing the 11 parent compounds and three transformation products (TPs) detected in water and sprayed according to spraying records in the Western Cape, South Africa between July 2017 and January 2018. Grey background: two-week sampling periods; red line: limit of quantification (LOQ); grey dots: time weighted average concentration measured above LOQ; grey crosses: time weighted average concentration measured between LOQ and limit of detection (LOD); black vertical lines: daily spraying events; blue vertical lines: daily rainfall events [mm/d]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
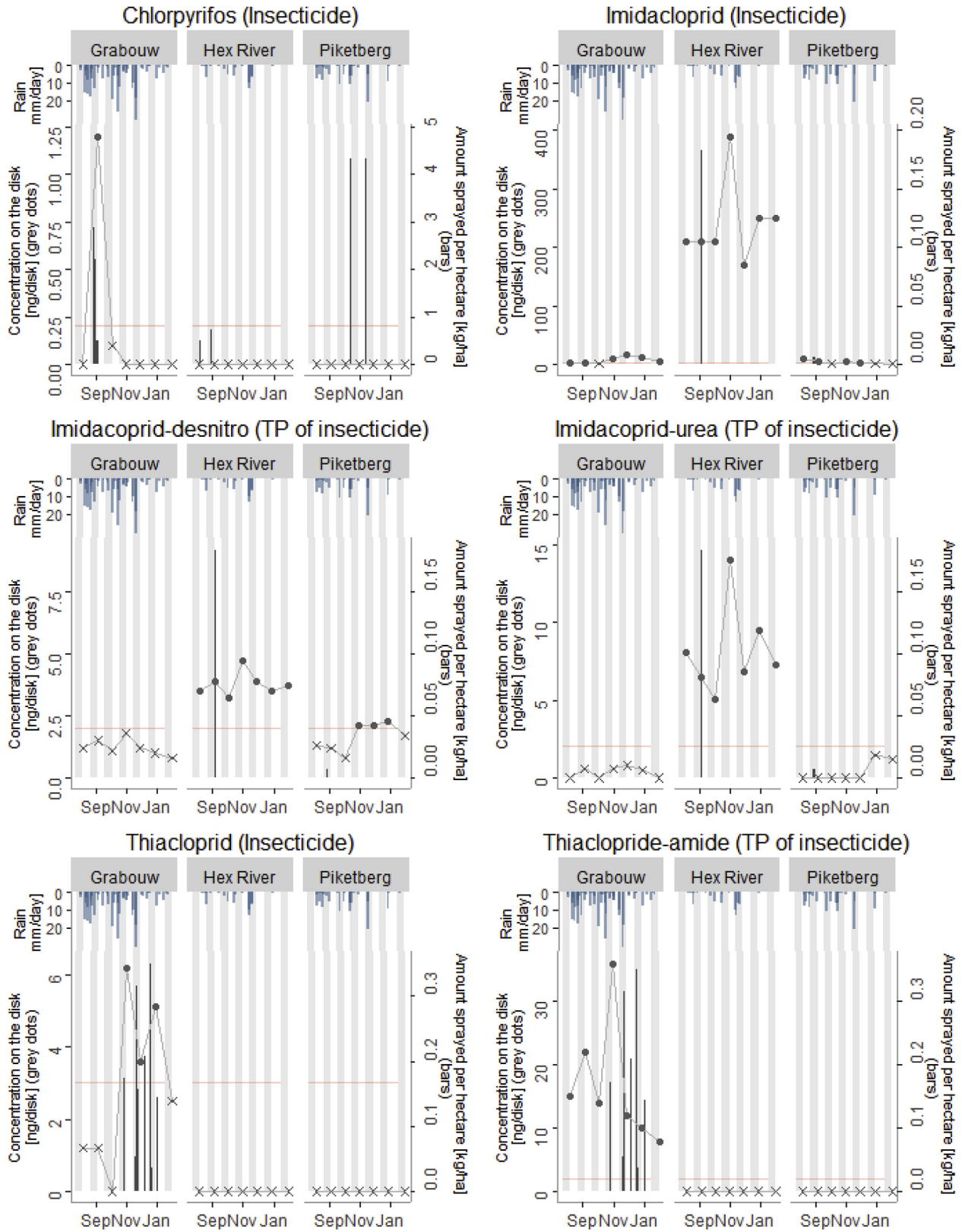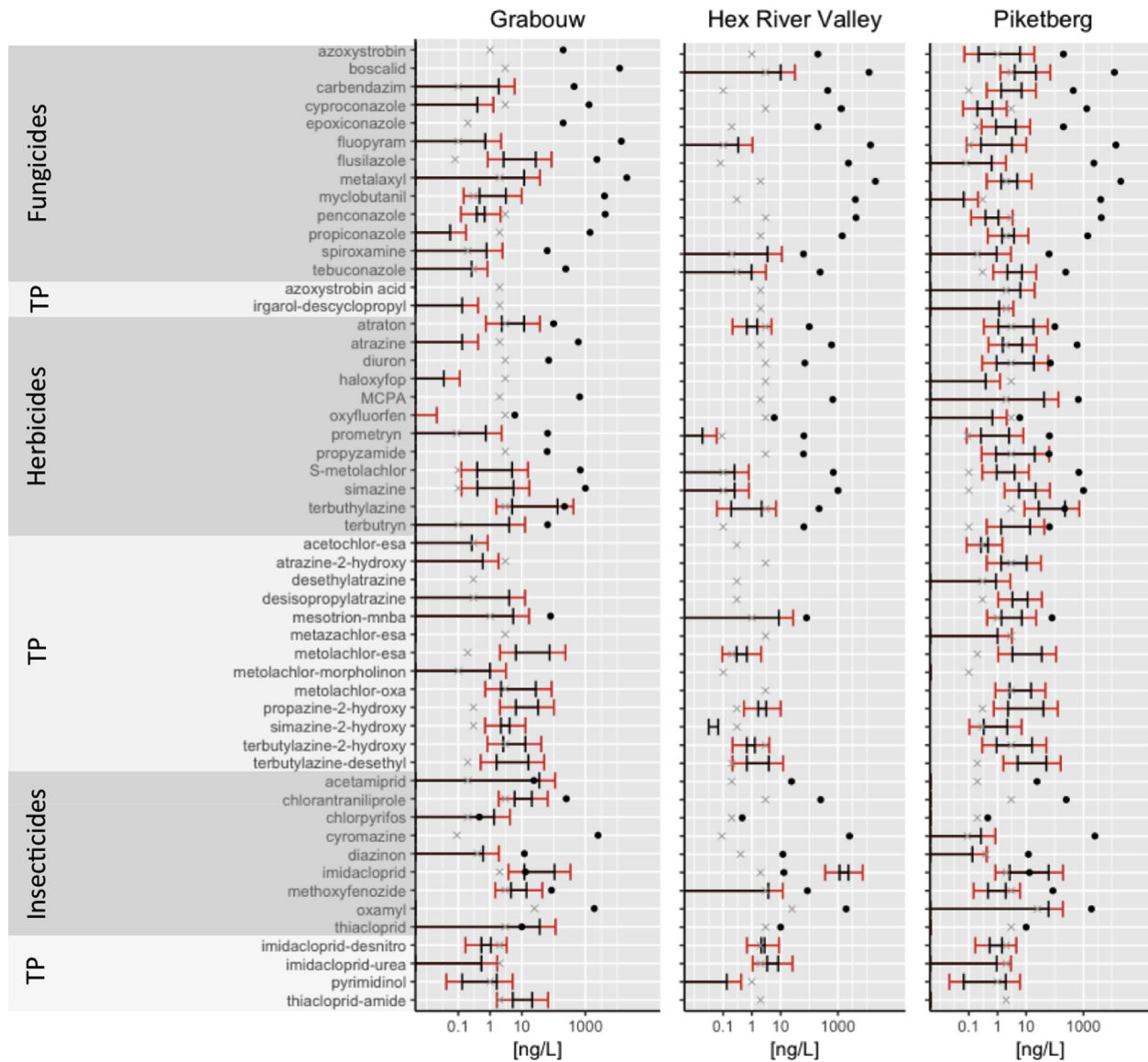
**Fig. 4.** (*continued*).

**Fig. 5.** Bar chart showing the range of estimated time-weighted average concentrations for the 53 detected pesticide compounds [ng/L]. Black line: range assuming sampling rate given in Table S7 [L/d]; red error bars: uncertainty range considering a factor of 10; grey crosses: limit of quantification (LOQ); black dots: environmental quality standards (EQS see Table S6). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 1**
Contingency table and level of agreement (Cohen's κ coefficient) for the 11 pesticide compounds applied according to spray records and measured in water above limit of detection (LOD) (A) overall seven sampling periods and three sites (n = 33) and (B) for each of the seven sampling periods individually (n = 220)* in the study conducted in the Western Cape, South Africa between July 2017 and January 2018.

| Measured any of the 11 pesticides compound above LOD in the water sample | (A) Applied according to spray records over the seven months, (3 sampling areas x 11 pesticides), κ** = 0.43 | | | (B) Applied according to spray record at a specific month (20 sampling rounds x 11 pesticides)*, κ** = 0.90 | | |
|---|---|---|---|---|---|---|
| | Yes | No | Total | Yes | No | Total |
| Yes | 18 (55%) | 4 (12%) | 22 (57%) | 37 (17%) | 63 (29%) | 100 (45%) |
| No | 3 (9%) | 8 (24%) | 11 (33%) | 7 (3%) | 113 (51%) | 120 (55%) |
| TOTAL | 21 (64%) | 12 (36%) | 33 (100%) | 44 (20%) | 176 (80%) | 220 (100%) |

*for Piketberg there were only 6 sampling periods considered, ** Cohen's κ coefficient.

correlations.

### 3.3. Pesticide concentrations ecotoxicological relevance

The time-weighted average concentrations for all bi-weekly samples (Fig. 5 and Table S5 of the SI) were in the low ng/L range. This has also been observed for similar time-averaged samples under much wetter conditions in Europe (Moschet et al., 2014; Spycher et al., 2018). Four pesticide compounds and three TPs have been quantified with a maximum concentration between 40 and

2300 ng/L based on the expected sampling rates ($R_s$) (two herbicides: terbuthylazine and MCPA, two insecticides: imidacloprid and oxamyl and three TPs of herbicides: propaxine-2-hydroxy, terbuthylazine-desethyl and metolachlor-esa). If the sampling rates were lower (e.g., due to low flow velocities under the drought conditions), the real concentrations might even have been higher.

Taking composite samples over two weeks can have several effects on the detected concentration patterns. On the one hand, the maximum concentration levels will be dampened. A comparison of pesticide patterns in Swiss streams (Spycher et al., 2018) between 0.5-day samples and two-week composite samples as used here, indicates that peak concentrations may be 10-fold underestimated. On the other hand, the duration of exceedance of a critical concentration may be overestimated. The same Swiss study showed in one study area that acute water quality criteria were exceeded 36% of the time with sampling intervals down to 0.5 days, while with the two-week composite samples criteria were exceeded 61% of the time.

When considering the time-weighted average concentrations, Fig. 5 shows that for most compounds (47 out of 53), the observed pesticide levels were below the EQS values. However, the three insecticides chlorpyrifos, thiacloprid and imidacloprid exceeded EQS between nine, 12 and 558-fold (with possible maximum concentrations of 4.2 ng/L, 115.2 ng/L and 7249.4 ng/L, respectively; Table S5 of the SI). Specifically, the concentration of imidacloprid exceeded its EQS in all samples. Both chlorpyrifos and imidacloprid have been repeatedly detected in different environments at concentration levels raising concerns in South Africa and other parts of the world (Dalvie et al., 2003; Manrakhan et al., 2013; McGregor, 1999; Mitchell et al., 2017; Motsoeneng and Dalvie, 2015). Concentrations of the two compounds acetamiprid and terbuthylazine were also detected at least once 5 and 3-fold above the EQS when assuming a fast sampling rate. Exceedances of EQS to that degree reported here suggest that sensitive species in the aquatic communities are at risk.

### 3.4. Limitations

Our study has three main limitations that need to be considered. First, spraying records have been obtained from a small subsample of farms in the study areas. The 38 chosen farms cover 7% of the total agricultural land and grow 8 from 40 different crops in the three study areas. Further investigations would need to include a larger subsample of farms and establish an additional reporting strategy for herbicide use. Second, despite a broad analytic coverage, we were not able to analyze some pesticides that were used in high quantity (e.g., the fungicides mancozeb, ametoctradin and dimethomorph; the herbicides glyphosate, trifluralin and paraquat and the insecticides prothiofos, omethoate and indoxacarb). For some of them (e.g., mancozeb or glyphosate) very specific analytical methods are required, which was beyond the means of our study (Mujawar et al., 2014; Poiger et al., 2017). Third, as passive water samples were collected over two-week periods, evaluation of peak concentrations due to spraying or rain events was not possible. The sampling duration may also cause nondetects of compounds if their occurrence was limited to episodes only. Finally, due to limited resources, not the full spraying period is covered in this study. However, this study showed that it is possible to detect a broad range of compounds with large differences in physico-chemical properties in different remote watersheds with little infrastructure available on-site.

### 4. Conclusion

Our study substantially widened the view on pesticide pollution in surface water compared to previous studies in Sub-Saharan Africa, by including more than 200 pesticide compounds using passive sampling systems in surface water while systematically comparing it with agriculture use. The presented results demonstrate that a wide variety of pesticide compounds is present in streams draining agricultural watersheds. Strong agreement for a spatio-temporal relationship between applications and occurrence in river water can be expected for specific insecticides and fungicides. We analytically covered about 27% of all registered pesticides in South Africa, and thus, real pesticide occurrence is expected to be higher in the water bodies. Also, we detected several herbicides in the water that were not reported on the spraying record of the farms.

The most severe drought since recordings in 1960 was encountered during the main spraying season in the Western Cape during the study period. These meteorological conditions have likely affected the use and subsequent fate of the measured pesticide compounds in the watershed. Hence, our results shed light on pesticide pollution from agricultural areas during extreme drought conditions, which are expected to increase in future driven by climate change. Given the extreme weather conditions during the study, more data are needed to better understand how pesticide pollution levels manifest under average rainfall and river discharge conditions.

Further, the insecticide imidacloprid exceeded the EQS when assuming the highest sampling rate in all samples and up to 558-fold (EQS 13 ng/L). Additionally, thiacloprid, chlorpyrifos, acetamiprid and terbuthylazine were detected at least once 12, 9, 5 and 3-fold above the EQS, respectively. These pesticide compounds have also been reported elsewhere in Africa and around the world to cause environmental and public health issues. To adequately address the ecological relevance of pesticide pollution it would be useful to complement the study approach in the future with samples taken at higher temporal resolution and to develop ecotoxicological quality criteria which are specific for the ecological context of southern Africa.

### 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.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wroa.2019.100039.

## References

Ahrens, L., Daneshvar, 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.

Amdany, R., Chimuka, L., Cukrowska, E., Kukučka, P., Kohoutek, J., Vrana, B., 2014. Investigating the temporal trends in PAH, PCB and OCP concentrations in Hartbeespoort Dam, South Africa, using semipermeable membrane devices (SPMDs). WATER SA 40, 425–436.

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. https://doi.org/10.1016/j.envres.2015.05.028.

Aneck-Hahn, N.H., Leusch, F.D.L., Bruchet, A., Schriks, M., Scheurer, M., Balaguer, P., Grimaldi, M., Neale, P.A., Arnal, C., Schlichting, R., Hebert, A., Leroy, G., Escher, B.I., Esperanza, M., 2018. Analysis of endocrine activity in drinking water, surface water and treated wastewater from six countries. Water Res. 139, 10–18. https://doi.org/10.1016/j.watres.2018.03.056.

AVCASA, 2017. CROPLIFE South Africa AGRICULTURAL REMEDIES DATABASE [WWW document]. Archived by WebCite®. https://www.webcitation.org/73FsUOd3W. http://www.avcasa.co.za/index.php/component/content/article?layout=edit&id=3. accessed 9.26.18.

Beketov, M.A., Kefford, B.J., Schäfer, R.B., Liess, M., 2013. Pesticides reduce regional biodiversity of stream invertebrates. Proc. Natl. Acad. Sci. 110 (27), 11039–11043. https://doi.org/10.1073/pnas.1305618110.

Bloomfield, J.P., Williams, R.J., Gooddy, D.C., Cape, J.N., Guha, P., 2006. Impacts of Climate Change on the Fate and Behaviour of Pesticides in Surface and Groundwater — a UK Perspective, vol. 369, pp. 163–177. https://doi.org/10.1016/j.scitotenv.2006.05.019.

Charriau, A., Lissalde, S., Poulier, G., Mazzella, N., Buzier, R., Guibaud, G., 2016. Overview of the Chemcatcher® for the passive sampling of various pollutants in aquatic environments Part A: principles, calibration, preparation and analysis of the sampler. Talanta 148, 556–571. https://doi.org/10.1016/j.talanta.2015.06.064.

Chepchirchir, B.S., Paschke, A., Schüürmann, G., 2017. Passive sampling for spatial and temporal monitoring of organic pollutants in surface water of a rural-urban river in Kenya. Sci. Total Environ. 601– 602, 453–460. https://doi.org/10.1016/j.scitotenv.2017.05.143.

Chetty-Mhlanga, S., Basera, W., Fuhrimann, S., Mufaro, M., Wyk, J. Van, Probst-Hensch, N., Delport, S., Lee, M.M., Roosli, M., Dalvie, M.A., 2018. A prospective cohort study of school-going children investigating reproductive and neuro-behavioral health effects due to environmental pesticide exposure in the Western Cape, South Africa: study protocol. BMC Public Health 18, 857, 13.

Dabrowski, J.M., 2015. Development of pesticide use maps for South Africa. South Afr. J. Sci. 111, 1–7. https://doi.org/10.17159/sajs.2015/20140091.

Dabrowski, J.M., Shadung, J.M., Wepener, V., 2014. Prioritizing agricultural pesticides used in South Africa based on their environmental mobility and potential human health effects. Environ. Int. 62, 31–40. https://doi.org/10.1016/j.envint.2013.10.001.

Dalvie, M.A., Cairncross, E., Solomon, A., London, L., 2003. Contamination of rural surface and ground water by endosulfan in farming areas of the Western Cape, South Africa. Environ. Health 2, 1. https://doi.org/10.1186/1476-069X-2-1.

Dalvie, M.A., Africa, A., London, L., 2009. Change in the quantity and acute toxicity of pesticides sold in South African crop sectors, 1994-1999. Environ. Int. 35, 683–687. https://doi.org/10.1016/j.envint.2008.12.004.

Dalvie, M.A., Naik, I., Channa, K., London, L., 2011. Urinary dialkyl phosphate levels before and after first season chlorpyrifos spraying amongst farm workers in the Western Cape, South Africa. J. Environ. Sci. Health. B. 46, 163–172. https://doi.org/10.1080/03601234.2011.535384.

Delcour, I., Spanoghe, P., Uyttendaele, M., 2015. Literature review: impact of climate change on pesticide use. FRIN 68, 7–15. https://doi.org/10.1016/j.foodres.2014.09.030.

Department of Water Affairs and Forestry, 1996. South African Water Quality Guidelines, vol. 7. Aquatic Ecosystems.

Doppler, T., Camenzuli, L., Hirzel, G., Krauss, M., Lück, A., Stamm, C., 2012. The spatial variability of herbicide mobilization and transport at catchment scale: a field experiment. Hydrological and Earth System Sciences 16, 1947–1967.

DWA, 2019. Department water & sanitation: hydrological services [WWW document]. Archived by WebCite®. http://www.webcitation.org/75gcdZIno. http://www.dwa.gov.za/Hydrology/. accessed 1.25.19.

EAD, 2018. South African weather service [WWW document]. Environ. Aff. Dep. Repub. South Africa (Archived by WebCite®. http://www.webcitation.org/73MYCXg76. http://www.weathersa.co.za/climate. accessed 10.22.18.

European Commission, 2011. Common Implementation Strategy for the Water Framework Directive. Technical Guidance for Deriving Environmental Quality Standards.

Finizio, A., Azimonti, G., Villa, S., 2011. Occurrence of pesticides in surface water bodies: a critical analysis of the Italian national pesticide survey programs.

J. Environ. Monit. 13, 49–57. https://doi.org/10.1039/c0em00192a.

Gilliom, R.J., 2007. Pesticides in US streams and groundwater. Environ. Sci. Technol. 41, 3408–3414. https://doi.org/10.1021/es072531u.

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.a., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., Wolock, D.M., 2006. The quality of our nation's waters-pesticides in the nation's streams and groundwater, 1992–2001, 1291. U.S. Geological Survey Circular.

Godsmark, C.N., Irlam, J., van der Merwe, F., New, M., Rother, H.A., 2018. Priority focus areas for a sub-national response to climate change and health: a South African provincial case study. Environ. Int. 122, 31–51. https://doi.org/10.1016/j.envint.2018.11.035.

Gomides Freitas, L., Singer, H., Müller, S.R., Schwarzenbach, R.P., Stamm, C., 2008. Source area effects on herbicide losses to surface waters - a case study in the Swiss Plateau. Agric. Ecosyst. Environ. 128 (3), 177–184. https://doi.org/10.1016/j.agee.2008.06.014.

Gustavsson, M., Kreuger, J., Bundschuh, M., Backhaus, T., 2017. Pesticide mixtures in the Swedish streams: environmental risks, contributions of individual compounds and consequences of single-substance oriented risk mitigation. Sci. Total Environ. 598, 973–983. https://doi.org/10.1016/j.scitotenv.2017.04.122.

Herrero-Hernández, E., Rodríguez-Cruz, M.S., Pose-Juan, E., Sánchez-González, S., Andrades, M.S., Sánchez-Martín, M.J., 2017. Seasonal distribution of herbicide and insecticide residues in the water resources of the vineyard region of La Rioja (Spain). Sci. Total Environ. 609, 161–171. https://doi.org/10.1016/j.scitotenv.2017.07.113.

Houbraken, M., Habimana, V., Senaeve, D., López-Dávila, E., Spanoghe, P., 2017. Multi-residue determination and ecological risk assessment of pesticides in the lakes of Rwanda. Sci. Total Environ. 576, 888–894. https://doi.org/10.1016/j.scitotenv.2016.10.127.

ISPRA, 2018. Pesticides in Water Italian Monitoring 2016 Synthesis Report. Rome.

Kapsi, M., Tsoutsi, C., Paschalidou, A., Albanis, T., 2019. Environmental monitoring and risk assessment of pesticide residues in surface waters of the Louros River (N.W. Greece). Sci. Total Environ. 650, 2188–2198. https://doi.org/10.1016/j.scitotenv.2018.09.185.

Lehmann, E., Turrero, N., Kolia, M., Konaté, Y., de Alencastro, L.F., 2017. Dietary risk assessment of pesticides from vegetables and drinking water in gardening areas in Burkina Faso. Sci. Total Environ. 601–602, 1208–1216. https://doi.org/10.1016/j.scitotenv.2017.05.285.

Lehmann, E., Fargues, M., Nfon Dibié, J.J., Konaté, Y., de Alencastro, L.F., 2018. Assessment of water resource contamination by pesticides in vegetable-producing areas in Burkina Faso. Environ. Sci. Pollut. Res. 25, 3681–3694. https://doi.org/10.1007/s11356-017-0665-z.

Leu, C., Singer, H., Stamm, C., Müller, S.R., Schwarzenbach, R.P., 2004. Simultaneous assessment of sources, processes, and factors influeincing herbicide losses to surface waters in a small agricultural catchment. Environ. Sci. Technol. 38, 3827–3834. https://doi.org/10.1021/es0499602.

Leu, C., Singer, H., Müller, S.R., Schwarzenbach, R., Stamm, C., 2005. Comparison of atrazine losses in three small headwater catchments. J. Environ. Qual. 34, 1873–1882.

Leu, C., Schneider, M.K., Stamm, C., 2010. Estimating catchment vulnerability to diffuse herbicide losses from hydrograph statistics. J. Environ. Qual. 39, 1441–1450. https://doi.org/10.2134/jeq2009.0323.

Manrakhan, A., Kotze, C., Daneel, J.H., Stephen, P.R., Beck, R.R., 2013. Investigating a replacement for malathion in bait sprays for fruit fly control in South African citrus orchards. Crop Protect. 43, 45–53. https://doi.org/10.1016/j.cropro.2012.09.010.

McGregor, F.J., 1999. The Mobility of Endosulfan and Chlorpyrifos in the Soils of the Hex River Valley.

Mekonen, S., Argaw, R., Simanesew, A., Houbraken, M., Senaeve, D., Ambelu, A., Spanoghe, P., 2016. Pesticide residues in drinking water and associated risk to consumers in Ethiopia. Chemosphere 162, 252–260. https://doi.org/10.1016/j.chemosphere.2016.07.096.

Mitchell, E.A.D., Mulhauser, B., Mulot, M., Mutabazi, A., Glauser, G., Aebi, A., 2017. A worldwide survey of neonicotinoids in honey. Science 84 358, 109–111. https://doi.org/10.1126/science.aan3684.

Moschet, C., Wittmer, I., Simovic, J., Junghans, M., Piazzoli, A., Singer, H., Stamm, C., Leu, C., Hollender, J., 2014. How a complete pesticide screening changes the assessment of surface water quality. Environ. Sci. Technol. 48, 5423–5432. https://doi.org/10.1021/es500371t.

Moschet, C., Piazzoli, A., Singer, H., Hollender, J., 2013. Alleviating the Reference Standard Dilemma Using a Systematic Exact Mass Suspect Screening Approach with Liquid Chromatography-High Resolution Mass Spectrometry. Anal. Chem. 85, 10312–10320. https://doi.org/10.1021/ac4021598.

Moschet, C., Vermeirssen, E.L.M., Singer, H., Stamm, C., Hollender, J., 2015. Evaluation of in-situ calibration of chemcatcher passive samplers for 322 micropollutants in agricultural and urban affected rivers. Water Res. 71, 306–317. https://doi.org/10.1016/j.watres.2014.12.043.

Motsoeneng, P.M., Dalvie, M.A., 2015. Relationship between urinary pesticide residue levels and neurotoxic symptoms among women on farms in the Western Cape, South Africa. Int. J. Environ. Res. Public Health 12, 6281–6299. https://doi.org/10.3390/ijerph120606281.

Mujawar, S., Utture, S.C., Fonseca, E., Matarrita, J., Banerjee, K., 2014. Validation of a GC-MS method for the estimation of dithiocarbamate fungicide residues and safety evaluation of mancozeb in fruits and vegetables. Food Chem. 150, 175–181. https://doi.org/10.1016/j.foodchem.2013.10.148.

Nesser, G.A.A., Abdelbagi, A.O., Hammad, A.M.A., Tagelseed, M., Laing, M.D., 2016.

Levels of pesticides residues in the White Nile water in the Sudan. Environ. Monit. Assess. 188 https://doi.org/10.1007/s10661-016-5367-3.

Otieno, P.O., Lalah, J.O., Virani, M., Jondiko, I.O., Schramm, K.W., 2010. Soil and water contamination with carbofuran residues in agricultural farmlands in Kenya following the application of the technical formulation Furadan. J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes 45, 137–144. https://doi.org/10.1080/03601230903472058.

Otieno, P.O., Owuor, P.O., Lalah, J.O., Pfister, G., Schramm, K., 2013. Impacts of climate-induced changes on the distribution of pesticides residues in water and sediment of Lake. Springer Netherlands, pp. 2723–2733.

Poiger, T., Buerge, I.J., Bächli, A., Müller, M.D., Balmer, M.E., 2017. Occurrence of the herbicide glyphosate and its metabolite AMPA in surface waters in Switzerland determined with on-line solid phase extraction LC-MS/MS. Environ. Sci. Pollut. Res. 24, 1588–1596. https://doi.org/10.1007/s11356-016-7835-2.

Price, P., Han, X., Junghans, M., Kunz, P., Watts, C., Leverett, D., 2012. An application of a decision tree for assessing effects from exposures to multiple substances to the assessment of human and ecological effects from combined exposures to chemicals observed in surface waters and waste water effluents. Environ. Sci. Eur. 24, 34. https://doi.org/10.1186/2190-4715-24-34.

Rimayi, C., Odusanya, 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. 613–614, 472–482. https://doi.org/10.1016/j.scitotenv.2017.09.119.

Rosenzweig, C., Iglesias, A., Yang, X.B., Epstein, P.R., Chivian, E., 2001. Climate change and extreme weather events: implications for food production, plant diseases, and pests. Glob. Chang. Hum. Health 2, 90–104. https://doi.org/10.1023/A:1015086831467.

Schulz, R., 2004. Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: a review. J. Environ. Qual. 33, 419–448.

Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Gooddy, D.C., Bell, R.A., Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S., 2015. Emerging contaminants in urban groundwater sources in Africa. Water Res. 72, 51–63. https://doi.org/10.1016/j.watres.2014.08.002.

Spycher, S., Mangold, S., Doppler, T., Junghans, M., Wittmer, I., 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, 4526–4535.

STATS SA, 2016. Community Survey 2016 Agricultural Households. Community Survey Pretoria: Statistics South Africa.

Stehle, S., Schulz, R., 2015. Agricultural insecticides threaten surface waters at the global scale. Proc. Natl. Acad. Sci. 112 https://doi.org/10.1073/pnas.1500232112, 5750 LP-5755.

Stenrød, M., 2015. Long-term trends of pesticides in Norwegian agricultural streams and potential future challenges in northern climate. Acta Agric. Scand. Sect. B Soil Plant Sci 65, 199–216. https://doi.org/10.1080/09064710.2014.977339.

Swiss Center for Applied Ecotoxicology Eawag/EPFL, 2013. Proposals for acute and chronic quality standards [WWW document]. https://www.ecotoxcentre.ch/expert-service/quality-standards/proposals-for-acute-and-chronic-quality-standards/ accessed 7.11.19.

Teklu, B.M., Adriaanse, P.I., Van den Brink, P.J., 2016. Monitoring and risk assessment of pesticides in irrigation systems in Debra Zeit, Ethiopia. Chemosphere 161, 280–291. https://doi.org/10.1016/j.chemosphere.2016.07.031.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Kolpin, D.W., 1991. Herbicides in surface waters of the Midwestern United-States - the effect of spring flush. Environ. Sci. Technol. 25, 1794–1796.

University of Hertfordshire, 2018. PPDB : pesticide properties database [WWW document]. Archived by WebCite®. http://www.webcitation.org/73FtNajXx. https://sitem.herts.ac.uk/aeru/ppdb/en/. accessed 9.21.18.

Unyimadu, J.P., Osibanjo, O., Babayemi, J.O., 2018. Selected persistent organic pollutants (POPs) in water of River Niger: occurrence and distribution. Environ. Monit. Assess. 190 https://doi.org/10.1007/s10661-017-6378-4.

Vermeirssen, E.L.M., Bramaz, N., Hollender, J., Singer, H., Escher, B.I., 2009. Passive sampling combined with ecotoxicological and chemical analysis of pharmaceuticals and biocides — evaluation of three ChemcatcherTM configurations. Water Res 43, 903–914. https://doi.org/10.1016/j.watres.2008.11.026.

WCG, 2017. Informing the Western Cape Agricultural Sector on the 2015-2017 Drought. Cape Gov, West. Drought Fact Sheet 1–44.

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

Wooding, M., Rohwer, E.R., Naudé, Y., 2017. Determination of endocrine disrupting chemicals and antiretroviral 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. https://doi.org/10.1016/j.chroma.2017.03.057.

Yahaya, A., Okoh, O.O., Okoh, A.I., Adeniji, A.O., 2017. Occurrences of organochlorine pesticides along the course of the Buffalo river in the eastern cape of South Africa and its health implications. Int. J. Environ. Res. Public Health 14. https://doi.org/10.3390/ijerph14111372.

Zwane, E.M., 2019. Impact of climate change on primary agriculture, water sources and food security in Western Cape, South Africa. Jàmbá J. Disaster Risk Stud 11, 1–7. https://doi.org/10.4102/jamba.v11i1.562.