Development and field validation of an indicator to assess the relative mobility and risk of pesticides in the Lourens River catchment, South Africa.

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1   **Abstract**

2

3   A GIS based pesticide risk indicator that integrates exposure variables (i.e. pesticide application,

4   geographic, physicochemical and crop data) and toxicity endpoints (using species sensitivity

5   distributions) was developed to estimate the Predicted Relative Exposure (PREX) and Predicted

6   Relative Risk (PRRI) of applied pesticides to aquatic ecosystem health in the Lourens River

7   catchment, Western Cape, South Africa. Samples were collected weekly at five sites from the

8   beginning of the spraying season (October) till the beginning of the rainy season (April) and were

9   semi quantitatively analysed for relevant pesticides applied according to the local farmers spraying

10   programme. Monitoring data indicate that physicochemical data obtained from international databases

11   are reliable indicators of pesticide behaviour in the Western Cape of South Africa. Sensitivity analysis

12   identified K_{OC} as the most important parameter influencing predictions of pesticide loading derived

13   from runoff. A comparison to monitoring data showed that the PREX successfully identified hotspot

14   sites, gave a reasonable estimation of the relative contamination potential of different pesticides at a

15   site and identified important routes of exposure (i.e. runoff or spray drift) of different pesticides at

16   different sites. All pesticides detected during a monitored runoff event, were indicated as being more

17   associated with runoff than spray drift by the PREX. The PRRI identified azinphos-methyl and

18   chlorpyrifos as high risk pesticides towards the aquatic ecosystem. These results contribute to

19   providing increased confidence in the use of risk indicator applications and, in particular, could lead

20   to improved utilisation of limited resources for monitoring and management in resource constrained

21   countries.

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23   **Keywords:** pesticides; risk indicator; validation; Lourens River; South Africa

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29   **1. Introduction**

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31   Nonpoint source agricultural pollution is generally considered one of the major threats to surface

32   water quality in rural areas (Loague et al., 1998). Nutrients, sediments and pesticides potentially

33   enter aquatic environments via runoff, leaching and spray drift and pose a risk to the communities that

34   inhabit them. Of all nonpoint source pollutants, insecticides are among the most crucial chemical

35   stressors, simply because of their extremely high toxicity to many non-target aquatic organisms (fish

36   and macroinvertebrates). Only a few studies have investigated the occurrence and effects of current-

37   use pesticides in South Africa. The most extensive research has been performed in the Lourens River,

38   in the Western Cape of South Africa. Studies have shown that current-use insecticides frequently

39   enter the river via runoff and spray drift (Schulz, 2001a; Schulz, 2001b; Dabrowski and Schulz,

40   2003). Although contamination is transient, field, experimental microcosm (Schulz et al., 2002) and

41   in-situ bioassay studies (Schulz, 2003) have shown that measured pesticide levels pose significant

42   risks to aquatic macroinvertebrate communities in the Lourens River. Another study measured high

43   levels of chlorpyrifos and endosulfan in a number of agricultural catchments throughout the Western

44   Cape (London et al., 2000).

45

46   Despite these findings, the potential impact of pesticides in South African surface waters has

47   generally been a low priority and is generally not considered in aspects of water resource

48   management, especially with regards to routine monitoring. Even in developed countries, despite

49   strict regulatory procedures, pesticides are frequently detected in surface waters at concentrations that

50   exceed environmentally acceptable levels (Stehle et al., 2012). Although intensive monitoring and

51   sampling can identify pesticide impacts, the cost of analysis and logistics makes this a highly costly

52   exercise (particularly in the context of less developed countries). Thus there is a need to develop cost

53   effective methods of predicting the environmental risks of pesticide use on a catchment specific basis

54   which can be used to prioritize specific pesticides for monitoring purposes and identify spatial

55 patterns of contamination. Environmental pesticide risk indicators provide a relative indication of the

56 impact of pesticides (Levitan et al., 1995), with an emphasis on relatively few and simple data input

57 parameters (Kookana et al., 2005). Risk indicators vary greatly in terms of their purpose, and

58 methodology and are often very broad in scope covering, for example, the impact on aquatic

59 organisms, soil organisms, bees, occupational exposure and human health effects (Reus et al., 2002).

60 With respect to aquatic ecosystems, risk indicators are generally regarded as lower tier risk

61 assessment tools that provide a relative assessment of the environmental impact of pesticides through

62 integration of multiple catchment-scale factors that influence the fate, transport and toxicity of

63 pesticides. These include site specific geographical conditions (e.g. soil type, soil organic matter

64 content, water input, slope of land, soil loss, recharge rate, depth of water table etc), ecotoxicological

65 (e.g. LC_{50} data or species sensitivity distributions) and environmental fate (e.g. half-life and K_{OC}

66 values) properties and pesticide use data (Sánchez-Bayo et al., 2002; Sala and Vighi, 2008). On a

67 first level of assessment, risk indicators may be designed to prioritise pesticides in terms of their

68 anticipated risk towards the aquatic environment (Kookana et al., 2005). Integration of GIS may

69 enable the identification of potential trouble spots and vulnerable areas where risk reduction might be

70 requisite (Pollock et al., 2005). Furthermore, risk indicators can potentially highlight the most

71 important route of contamination of surface waters (i.e. via runoff during rainfall or spray drift during

72 pesticide application) and therefore provide valuable insight with respect to risk mitigation strategies

73 for certain pesticides (Huber et al., 2000;Verro et al., 2002). Risk indicators are therefore attractive

74 alternatives to expensive, intensive monitoring campaigns or more data intensive mechanistic models.

75 Given these attributes, risk indicators may be particularly beneficial to developing countries, where

76 the costs of monitoring are prohibitive and data requirements are lacking or difficult to obtain.

77

78 While a number of indicator methodologies have been developed, very few studies have attempted to

79 validate the outputs of the indicators. This is particularly relevant in more arid countries such as South

80 Africa which often make use of physicochemical data derived in northern temperate countries for

81 exposure assessment predictions (Dabrowski and Schulz, 2003). The paper describes the development

82 and validation of a risk indicator designed to assess the relative potential exposure and risk of

83 pesticides in agricultural surface waters. The objective of the indicator is to provide a relative,

84 qualitative measure of pesticide mobility and associated risk to aquatic organisms and not exact

85 quantitative measures of risk. The tool integrates ecotoxicological effect data and exposure indicators

86 using empirical modelling and GIS techniques to a.) identify high priority pesticides in a catchment in

87 terms of their mobility and potential toxicological effects b.) identify high risk areas (or hotspots)

88 within a catchment where pesticide inputs are unacceptably high and c.) characterise the most

89 important route of transport (i.e. runoff or spray drift). Results of the mobility indicator are compared

90 to field monitoring data in an attempt to validate predictions made by the indicator.

91

92 **2. Materials and Methods**

93

94 *2.1 Study Area*

95

96 The Lourens River rises at an altitude of 1080 m in a naturally vegetated fynbos (part of the Cape

97 floral kingdom, endemic to South Africa) area and flows in a south-westerly direction for 20 km

98 before discharging into False Bay at the Strand (S34°06´; E18°48´). The catchment region is

99 characterised by intensive farming, with orchards and vineyards in its middle reaches. The Lourens

100 River has a total catchment area of 92 km^2 and receives an annual mean rainfall of 915 mm, most of

101 which falls during the autumn, winter and early spring months between April and October, as is

102 characteristic of the region's Mediterranean climate. The main soil type is silty loam and the slopes in

103 the catchment vary between < 2 % in the area near the river and < 8 % in the upstream stretches of the

104 river and some of the tributaries. Apples, grapes (for wine production), pears and plums are grown in

105 the area, to which a number of insecticides and fungicides are applied on an annual basis, mainly

106 between August and February of the following year. Previous studies in this catchment have shown

107 runoff and spray drift to be important routes of entry into tributaries of the Lourens River (Schulz,

108 2001a; Dabrowski and Schulz, 2003).

109

110   Five sites were selected for monitoring and validation purposes. One site was located in the Lourens

111   River main stem (LR) and was representative of the entire catchment (Fig. 1). Four additional

112   sampling sites, (named after the orchard in closest proximity to the site - BB7, LG4, C and VW) were

113   located within four tributaries flowing into the Lourens River. Each of the four tributaries are

114   characterised by different crops, buffer zone distances and slope categories (Fig. 1). The catchment

115   area of each of the tributaries was delineated using GIS. This allowed for the characterisation of

116   geographical attributes and the quantification of crop coverage (and associated pesticide use) within

117   the sub-catchments.

118

119   *2.2 General Approach*

120

121   The indicator involves four distinct steps. First, pesticide application was estimated for each sub-

122   catchment based on crop area and crop specific pesticide application information. Secondly, Predicted

123   Environmental Loads (PEL; kg) of all applied pesticides moving into the tributaries via the

124   combination of runoff and spray drift were estimated for each sub-catchment. Thirdly, the PEL and

125   simple hydrological characteristics of the tributaries were used to estimate predicted environmental

126   concentrations (PECs; $\mu g\ L^{-1}$) for each pesticide in each sub-catchment. The PECs were expressed as

127   a ratio of the pesticide with the highest PEC across all sub-catchments, so as to provide a predicted

128   relative exposure (PREX) score of mobility of all pesticides across all sub-catchments included in the

129   analysis. Finally, the PECs and relevant aquatic toxicity data were used to derive toxicity to exposure

130   ratios (TERs) which provide an estimation of risk. The TERs were also expressed as a ratio of the

131   pesticide with the highest TER across all sub-catchments so as to provide a predicted relative risk

132   indicator score (PRRI) for all pesticides applied in all sub-catchments.

133

134   *2.3 Pesticide Use*

135

136   Pesticide application data were obtained from spray records provided by the farmers. For each sub-

137   catchment the total amount of pesticide (kg) applied to each orchard type was estimated based on

138   orchard area and the rate and frequency of application. This was done for each of the four tributaries

139   as well as for the entire catchment (Supplementary Data Table S1). Azinphos-methyl, chlorpyrifos,

140   carbendazim, prothifos and methyl parathion are all applied in relatively high quantities.

141   Flufenoxuron, propiconazole, beta-cyfluthrin and cypermethrin are all applied in low quantities.

142

143   *2.4 Spray Drift Loads*

144

145   Using GIS, distinct buffer zone distance categories (5, 7.5, 10, 15, 20, 30 and 40 m) were created for

146   each river stretch in the catchment (assuming 40 m is the maximum distance at which contamination

147   would occur). This process identified orchards that fell within each of the buffer distance categories.

148   The associated buffer zone width and total pesticide application for each of these orchards were used

149   as input to estimate the contribution of spray drift to total pesticide loads entering the adjacent

150   tributary. No vegetated hedges were located between orchards and the tributaries. For each orchard,

151   the total loss of active ingredient per crop type was calculated using a formula generated from drift

152   values derived by (Rautmann et al., 1999):

153

154   $$L_{\%spray} = 1/(a+bx^2)$$

155

156   where $a = 0.03597$ and $b = 0.00179$ and x is the buffer zone width. The $L_{\%spray}$ value and the total

157   pesticide application per orchard were used to estimate the total loss of the active ingredient from the

158   field during the spraying season. For each crop type, the total loss of each active ingredient was

159   multiplied by the water index (Supplementary Data Table S2) to obtain a final loss (kg) per crop type.

160   The water index is the probability of surface water lying adjacent to a field and is expressed as a ratio

161   of the length of the water body (L_{WB}) lying adjacent to the field to the perimeter (P_{Field}) of the field:

162

$$WI = \frac{L_{WB}}{P_{Field}}$$

163

164 The total loss of each active ingredient derived from spray drift was calculated by summing the total

165 loss of each active ingredient from each crop type.

166

167 *2.5 Runoff Loads*

168

169 Only orchards directly adjacent to river reaches were included for analysis in the calculation of the

170 proportion of pesticide loading attributed to runoff. A digital elevation model (DEM) for the

171 catchment area was transformed into slope categories using Spatial Analyst in ArcGIS 9.3 (Fig 1).

172 Each orchard area was over-layed with the slope profile, so as to generate a shapefile containing

173 polygons describing crop type and the associated slope category (percentage). As some orchards

174 covered more than one slope category, these fields were sub-divided into smaller polygons, each with

175 its own unique slope category. It was assumed that runoff will only take place during rainfall events in

176 excess of 10 mm (Huber et al., 2000).

177

178 Rainfall data from a weather station in the catchment was assessed over a ten year period. The

179 average rainfall for all events exceeding the 10 mm threshold was 20 mm. The total length of the

180 spraying season is approximately 210 days (i.e. from beginning of August to the end of February).

181 During this period an average of ten rainfall events in excess of 10 mm are expected to occur. The

182 rainfall interval was therefore assumed to be 20 days (i.e. one rainfall event every 20 days).

183 Considering the rainfall interval of 20 days, a rainfall event could occur at least 0 days after a spraying

184 event or at the most 20 days after the spraying event. Thus the median of this interval was chosen (i.e.

185 10 days) as the typical number of days for a rainfall event to occur after application.

186

187 For each orchard, the total loss of active ingredient per crop type was calculated using a formula by

188 Reus et al. (1999):

189

190
$$L\%_{runoff} = \left(\frac{Q}{P}\right) \times f \times \exp\left(-t \times \frac{\ln 2}{DT50_{soil}}\right) \times \frac{100}{(1 + Kd)}$$

191

192   where $L\%_{runoff}$ = percentage of application dose being available in runoff water as a dissolved

193   substance; Q = runoff amount (mm) calculated according to hydrological models (Lutz (1984) and

194   Maniak (1992)); P = precipitation amount (mm); $DT50_{soil}$ = half-life of active ingredient in soil (d); f

195   = $f1 \cdot f2 \cdot f3$, the correction factor reflecting the influence of slope ($f1$ = 0.02153·slope +

196   0.001423·slope^2), plant interception (PI), the percentage of applied pesticide intercepted by trees in

197   the orchards ($f2$ = 1 - PI/100), and buffer width ($f3$ = 0.83^{WBZ}, and WBZ is the width of buffer zone

198   [m]; if the buffer zone is not densely covered with plants, the width is set to zero); t = time (d)

199   between application and rainfall; Kd = (K_{OC}·OC%), a factor reflecting the tendency of the pesticide to

200   bind to organic carbon in the soil mL g^{-1}, where K_{OC} is the sorption coefficient of the active ingredient

201   to organic carbon (mL g^{-1}) and OC% is the organic carbon content of the soil. The tables developed

202   by Lutz (1984) and Maniak (1992) were used to obtain the Q value corresponding to the average

203   rainfall for events above 10 mm for this catchment (i.e. 4.93 for a rainfall event of 20 mm). The

204   organic carbon content of the soil was assumed to be 0.75 % (AGIS, 2012). The plant interception

205   factor was assumed to be 80 % (i.e. 80 % of the applied substance lands on the crop). A buffer width

206   of 0 m was used as input as throughout the catchment, deep erosion rills provide a direct pathway

207   between orchards and adjacent water bodies, thus making the effectiveness of any vegetated buffer

208   strip negligible. Pesticide physicochemical data was obtained from the EU-Footprint database

209   (Supplementary Data Table S3; FOOTPRINT, 2006).

210

211   The total loss of active ingredient per crop type was calculated for each orchard segment (i.e. polygon

212   with associated orchard type and slope category), using the $L\%_{runoff}$ value and the total amount of

213   pesticide applied to the orchard during the spraying season. The total loss of each pesticide per

214   orchard was calculated and multiplied by the water index to estimate the final load derived from

215   runoff. The total loss of each active ingredient was then calculated by summing the total loss across

216   each crop type (i.e. for those active ingredients applied to more than one crop type). For each sub-

217   catchment the total loss of active ingredient associated with spray drift and runoff was summed to

218   provide a final estimate of PEL.

219

220 *2.6 Predicted Relative Exposure (PREX)*

221

222 The PEC (μg L^{-1}) for each pesticide at each sub-catchment was calculated as follows:

223

$$PEC = \frac{PEL}{D}$$

224

225

226 where D is the discharge of the stream in m^3 s^{-1}. This calculation does not take temporal aspects of

227 contamination into consideration and assumes that the concentration is derived from all pesticide

228 losses occurring simultaneously and entering the water resource simultaneously over a 24 hour period.

229 However, the indicator is designed to provide an estimate of the relative concentrations of a number

230 of pesticides compared to one another and is not designed to give accurate pesticide concentrations as

231 would be detected in the field.

232

233 The PEC for each pesticide in each sub-catchment was expressed as a ratio of the highest PEC for all

234 pesticides included in the analysis (176.9 μg L^{-1} for dimethomorph at LG4), resulting in (PREX)

235 scores ranging from 1 downwards. This method of calculating the PREX scores ensures that the

236 transport and concentration of the different active ingredients is expressed relative to the active

237 ingredient with the highest PEC. The scores were used to assign an exposure category to each

238 pesticide, namely, Very Low (0 – 0.2), Low (0.2 – 0.4), Medium (0.4 – 0.6), High (0.6 – 0.8) and

239 Very High (0.8 - 1). This method of categorisation implies that results are specific to this study area.

240 However, the methodology can easily be applied to other catchments or to more than one catchment

241 simultaneously, using the highest PEC for all pesticides across all catchments as the benchmark

242 against which to determine PREX scores.

243

244 *2.7 Predicted Relative Risk (PRRI)*

245

246 The PEC for each pesticide in each sub-catchment was divided by the corresponding toxicity value to

247 obtain the TER. SSDs were derived using BurrliOz software (Campbell at al., 2000) and the

248 concentration at which 95 % of freshwater species (which included fish, invertebrates and algae)

249 would be protected was used as the toxicity value for each active ingredient. Only LC50 data were

250 used to derive the SSD. For some pesticides (dimethomorph, flufenoxuron, flusilazole, prothiofos,

251 thiacloprid and trifloxystrobin), insufficient data were available to construct a SSD. In these instances

252 the risk was calculated using LC50 value for *Daphnia magna*. Toxicity data were obtained from the

253 USEPA EcoTox database (USEPA, 1994). Chlorpyrifos at site C had the highest TER (190.4) and all

254 TERs for all pesticides in each sub-catchment were divided by this value to obtain the final PRRI

255 value. The scores were used to assign a risk category to each pesticide, namely, Very Low (0 – 0.2),

256 Low (0.2 – 0.4), Medium (0.4 – 0.6), High (0.6 – 0.8) and Very High (0.8 - 1).

257

258 *2.8 Sensitivity Analysis*

259

260 A sensitivity analysis was performed to determine the relative importance of input variables in the

261 runoff and spray drift models used to calculate the PREX. This was performed according to the

262 methodology presented in Dubus et al. (2003). The method of analysis is a simple approach and is

263 referred to as one-at-a-time sensitivity analysis. This involves varying input parameters

264 independently, one at a time, all other parameters being constant and observing the influence on

265 model predictions. For this analysis, runoff and spray drift model input parameters were varied in

266 increments within realistic minimum and maximum ranges (Supplementary Data Table S4).

267

268 The assessment of model sensitivity was based on the ratio of the relative variation in model output to

269 the relative variation in model input. For each variation increment, the relative variation in model

270 input and model output were calculated as follows:

271

$$Input\ Variation = \frac{I - I_{BC}}{I_{BC}} \times 100$$

272

$$Output\ Variation = \frac{O - O_{BC}}{O_{BC}} \times 100$$

273

274 where I is the value of the input parameter, I_{BC} is the value of the input parameter for the base-case

275 scenario, O is the value of the output variable, and O_{BC} is the value of the output variable for the base-

276 case scenario. The base-case scenario is the set of input variables that are representative of typical or

277 average conditions (i.e. the input variables that provide a general description of the application,

278 physicochemical and geographical characteristics – Supplementary Data Table S4). For runoff, the

279 base-case input parameters for physicochemical properties were the median values for those

280 properties for all pesticides applied in the Lourens River catchment. Area, slope and application rate

281 were all defined by the median values for those parameters. Only those input parameters that varied

282 amongst pesticides and sites were included in the sensitivity analysis. For spray drift average distance

283 of crops to streams and median pesticide application characteristics were used for the base-case

284 scenario (Supplementary Data Table S4).

285

286 The ratio of variation (ROV) can be defined as follows:

287

$$ROV = \frac{Output\ Variation}{Input\ Variation}$$

288

289 The ratio can be either positive or negative. It takes negative values if a decrease in an input parameter

290 results in an increase in the output value or if an increase in an input parameter results in a decrease in

291 the output value. The sign of the ratio is not critical when the aim is to classify input parameters

292 according to their influence on model output. An ROV of 1 means that a variation in the model input

293 will result at maximum in the same variation in the model output. An ROV of 10 will result in a

294 maximum variation of the output by 10 times.

295

296 *2.9 Sampling Design*

297

298   A field monitoring study was designed in order to attempt to validate the outcomes of the risk

299   indicator methodology. Due to the transient nature of pesticide contamination, it is often difficult to

300   detect pesticides using a routine sampling routine. Samples were therefore collected so as to coincide

301   with periods when pesticide contamination of the water bodies is expected to occur. Weekly sampling

302   was conducted during the main pesticide application period (beginning of October 2009 to end of

303   February 2010), which is characterised by and high winds, with spray drift being the most likely route

304   of entry for pesticides into surface waters. Occasional storm events during this period lead to high

305   input of pesticides (Schulz 2001b). Weekly sampling commended again from the beginning of August

306   2010 to end of September 2010 to coincide with a high rainfall period and the start of the spraying

307   season.

308

309   Water samples were collected in 1 L acetone-washed glass containers with a screw cap lined with

310   clean aluminium foil. Samples were immediately placed in a cool box containing ice and kept in dark

311   conditions. Sediment samples were collected at deposition zones at each of the sites. Sediment

312   samples were collected from approximately the top 1 cm of deposition zones at each site using a metal

313   scoop and were stored in 250 mL glass containers. All samples were stored at 4 degrees or below

314   from time of collection until extraction. In addition, a runoff event (18 mm of rainfall during a one

315   hour period) was monitored during November 2010. Samples were collected by auto-runoff samplers

316   designed to collect samples during increased discharge according to methods described in Dabrowski

317   et al. (2002a) and are representative of peak concentrations during runoff conditions. Water (filtered

318   prior to analysis) and sediment samples were extracted and prepared for analysis according to

319   methods described in Dabrowski et al. (2002a). The detection of target pesticides was performed by

320   Hearshaw and Kinnes Analytical Laboratory using a semi-quantitative multi-residue screening

321   analysis analysed by using liquid chromatography-mass spectrometry. All active ingredients apart

322   from flufenoxuron were included in the screening analysis. For water samples, the limits of detection

323   were 0.05 µg L^{-1} for carbendazim and flusilazole; 0.1 µg L^{-1} for alpha-cypermethrin, beta-cyfluthrin,

324   chlorpyrifos, cypermethrin, endosulfan, methyl-parathion, prothiofos and trifloxystrobin; 0.5 µg L^{-1}

325   for carbaryl, dimethomorph and thiacloprid and 1 µg L^{-1} for azinphos-methyl and propiconazole. For

326   sediment samples, limits of detection were 10 µg kg^{-1} for all active ingredients.

327

328   **3. Results and Discussion**

329

330   *3.1 Measured Pesticide Exposure*

331

332   Monitoring data clearly indicate that site LG4 and C are more contaminated than sites BB7 and VW

333   (Table 1). In general the frequency of detection of pesticides for all sites was relatively low

334   (particularly in the water phase), and only nine of the fifteen pesticides analysed for were detected.

335   Azinphos-methyl, carbaryl, carbendazim, chlorpyrifos, dimethomorph, methyl parathion and

336   prothiofos were most commonly detected and were also the most heavily applied pesticides in the

337   catchment (Supplementary Data Table S1). Contamination would therefore seem to be closely linked

338   to the overall quantity of pesticides applied in the catchment. Similarly, of the six pesticides not

339   detected, the majority were applied in comparatively low quantities, particularly propiconazole,

340   cyfluthrin, alpha-cypermethrin and cypermethrin. However, the fact that azinphos-methyl,

341   carbendazim and methyl parathion were applied in similar quantities in LG4 and VW, yet were

342   detected more commonly in the LG4 tributary, indicates that additional geographical factors influence

343   the mobility of pesticides in the respective catchments. In this example the steeper slopes in the LG4

344   catchment (Fig. 1) most likely result in higher frequencies of contamination (Dabrowski et al.,

345   2002b). The low frequency of detection and concentrations of all pesticides in the catchment is not

346   surprising. As pesticide transport is event driven (i.e. as a result of spraying or rainfall in the

347   catchment), environmental pesticide concentrations are often transient and generally occur in peaks

348   for a relatively short period of time after the event (Holvoet et al., 2007). Although designing

349   monitoring programmes to take samples during expected peak transport periods (i.e. during the

350   spraying and runoff seasons) is likely to improve the ability to detect pesticide levels, weekly routine

351   sampling may often miss these peaks and result in non-detectable concentrations, particularly in small

352   catchments (Crawford, 2004; Holvoet et al., 2007). In this respect event-based runoff and spray-drift

353   sampling could provide a better assessment of pesticide exposure in streams and rivers (Stehle et al.,

354   2012). This was demonstrated by the fact that the runoff event monitored on the 15th of November

355   showed a relatively high number of detections within the context of this study (Table 2).

356

357   Pesticides were more frequently detected in the sediment phase (75 detections across all sites), the

358   most commonly detected being, azinphos-methyl, chlorpyrifos, prothifos and methyl parathion.

359   Partitioning between the sediment and water phase could largely be explained by the physicochemical

360   properties of the pesticides, particularly the K_{OC} values (Supplementary Data Table S3). Pesticides

361   with K_{OC} values higher than 1000 were found almost exclusively in the sediment phase (i.e. azinphos-

362   methyl, chlropyrifos, flusilazole, methyl parathion and prothiofos), while those below 1000 were

363   found almost exclusively in the water phase (i.e. carbaryl and dimethomorph). Carbendazim was

364   detected on a number of occasions in both the sediment and water phase. Data on physicochemical

365   properties of pesticides in South Africa is not locally available and values used in this study were

366   obtained from a European database. There is often a degree of reservation about using

367   physicochemical data from more temperate climates as combinations of the chemical properties as

368   well as site-specific conditions determine the fate and behaviour of pesticides (Daam and Van den

369   Brink, 2010). These conditions vary greatly among different agro-ecological zones making the direct

370   extrapolation of data between geographical regions very challenging (Ahmad and Kookana, 2007).

371   However, Wauchope et al. (2002) found that while there is often variation in the K_{OC} value of a

372   specific pesticide, the values are adequate for discriminating between the relative mobility of a

373   number of different pesticides. A study on the behaviour of three pesticides in South African soils

374   reported similar K_{OC} values to those reported in the international literature, while half-lives were

375   generally longer in South African soils (Meinhardt, 2009). Other studies performed in South Africa

376   have also shown good correspondence between K_{OC} values and partitioning of pesticides between the

377   sediment and water phase (Dabrowski et al., 2002b; Sereda and Meinhardt, 2005). These studies, as

378   well as data from this study indicate that the European values provide a relatively good indication of

379   pesticide behaviour in soils of South Africa and can be reliably used in environmental fate modeling

380   for South African conditions.

381

382   This observation is relevant considering that the sensitivity analysis showed the K_{OC} value plays an

383   important role in estimating runoff related loads in the calculation of the PREX score (Fig. 2a). The

384   closer the curve to the Y axis (i.e. the larger the slope of the line linking the origin and a particular

385   point), the more sensitive the model is to this parameter. Similarly, the closer the curve to the X axis

386   (i.e the smaller the slope of the line linking the origin and a particular point), the less sensitive the

387   model is to this parameter. Curves corresponding to positive influences (an increase in model output

388   resulting from an increase in model input or a decrease in model output resulting from a decrease in

389   model input) are located in the top right and bottom left quadrants while those corresponding to

390   negative influences (an increase in model output resulting from a decrease in model input or a

391   decrease in model output resulting from an increase in model input) are situated in the top left and

392   bottom right quadrants. Thus, for runoff, the model is most sensitive to the input of K_{OC} with lower

393   values resulting in large changes in output variation. For half-life runoff output is sensitive to shorter

394   half-lives, resulting in decreased model output (i.e. lower transport in runoff). As half-life increases it

395   results in an increase in the model output (i.e. higher pesticide transport in runoff), however the model

396   becomes less sensitive to this parameter at higher half-lives. For slope, variation just about or below

397   the base-case scenario (i.e. the origin) results in almost linear response with respect to model output.

398   However as slope increases further, the model becomes more sensitive to this particular input

399   parameter. Application rate, frequency of application and the area of the treated crop all display a

400   linear relationship in terms of the effect of input variation on the model output. It is also important to

401   note that the 10 day input parameter was applied for all pesticides in all sub-catchments. In reality the

402   time will therefore not influence the relative mobility of the different pesticides within a single

403   catchment as this will be determined by half-life. However if two different catchments from two

404   geographical areas were compared, then timing of the rainfall event in relation to application would

405   be important.

406

407   For spray drift, the model is most sensitive to a decrease in distance between the point of application

408   and the water body (Fig. 2b). As buffer zone width increases, the model becomes less sensitive and

409 also results in a decrease in the model output. As for runoff, application rate, frequency of application

410 and the area of the treated crop all display a linear relationship in terms of the effect of input variation

411 on model output. In summary, these results show that for a given pesticide K_{OC} and buffer zone width

412 have the highest influence on model predictions for runoff and spray drift, respectively.

413

414 *3.2 Predicted Pesticide Exposure*

415

416 Field validation of predictive indicators and models is very challenging, particularly with respect to

417 pesticides, where a number of factors influence their transport into and fate within an aquatic

418 resource. Detections of pesticides in water and sediment at each site were used to assess the accuracy

419 of the indicator in predicting pesticide exposure. Dissolved pesticides can easily be incorporated into

420 the sediment during runoff or spray drift events after entering the stream (Erstfeld, 1999; Rand, 2004).

421 In this respect, sediment results are important in terms of validating the indicator. However,

422 depending on the hydrology of the stream and physicochemical properties of the pesticide, repeated

423 monitoring of sediment at a site may be representative of a single contamination event. For example

424 prothiofos with a relatively high half-life (45 days), was detected frequently in the sediment at C and

425 LG4. These two streams also had the lowest discharge of all streams monitored, potentially reducing

426 the potential for contaminated sediment to be washed away. Thus, the combination of high half-life

427 and low stream discharge could potentially result in this specific pesticide being repeatedly detected

428 over a comparatively long period of time, resulting in a high observed frequency of detection. Finally

429 sediment and adsorbed pesticides are physically washed into streams during heavy rainfall events, a

430 process not covered by the indicator published here. Of the commonly applied pesticides, prothiofos

431 had the highest K_{OC} and sediment bound input is therefore a likely means of contamination.

432

433 Apart from prothifos, the mobility and occurrence of pesticides in water and sediment samples

434 collected in the Lourens River catchment was relatively well predicted by the runoff and spray drift

435 transport models applied in estimation of PREX scores (Fig. 3). An overview of the PREX scores per

436 sub-catchment clearly identified sites C and LG4 as the most contaminated sites, with a comparatively

437 higher number of pesticides falling in the medium to very high categories. In contrast, PREX scores

438 for all pesticides at BB7 and VW were predominantly classified as having medium to very low

439 exposure potential. These broad patterns correspond well with the monitoring data observed in Table

440 1. Furthermore the indicator identified carbendazim, carbaryl, azinphos-methyl, dimethomorph and

441 methyl-parathion as the pesticides most likely to enter water resources across the catchment. These

442 were the most commonly detected pesticides across all sites.

443

444 At BB7 only carbaryl fell into the medium category and was the only pesticide detected in the water

445 phase. Azinphos-methyl and methyl-parathion fell in the low category and were detected a relatively

446 fewer occasions than at C and LG4. While flusilazole fell in the very low category, in comparison to

447 other sites, it had the highest PREX score at BB7 and was detected in the sediment on one occasion.

448 Carbendazim and azinphos-methyl had the highest PREX scores at site C, and, in comparison to other

449 active ingredients for this site, were detected relatively frequently, in water and sediment samples.

450 Methyl parathion, chlorpyrifos and prothiofos had comparatively lower PREX scores, falling in the

451 low to medium categories. Of these active ingredients chlorpyrifos and prothiofos were detected on

452 two and thirteen occasions in the sediment, respectively. Methyl parathion was not detected at this

453 site. Dimethomorph had the lowest PREX score of those active ingredients in the high category and

454 was detected on one occasion in the water phase. Dimethomorph applied in the LG4 sub-catchment

455 scored the highest PREX score for all pesticides included in the index. However, this pesticide was

456 detected on only one occasion in the water phase. Carbendazim also fell in the very high category and

457 was detected on three occasions in water and sediment samples. Carbaryl, methyl parathion and

458 azinphos-methyl also had relatively high PREX scores. Carbendazim and carbaryl were both detected

459 on two occasions at comparatively high maximum concentrations in the water phase, whilst azinphos-

460 methyl (six detections) and methyl-parathion (seven detections) were detected frequently in the

461 sediment phase (methyl parathion was also detected on one occasion in the water phase at a

462 concentration of <0.1 μg L^{-1}). Other active ingredients that were detected in the water phase at this

463 site were chlorpyrifos, prothiofos and trifloxystrobin. These pesticides had comparatively lower

464 PREX scores, falling in the medium and low categories. Prothiofos was however detected more

465 frequently in the sediment, even more so than azinphos-methyl and methyl-parathion, which scored

466 much higher PREX scores. VW also showed relatively low contamination, with only two detections

467 in the water phase (carbendazim and chlorpyrifos) and a relatively low number of detections in the

468 sediment. All pesticides in this sub-catchment had relatively low PREX scores. Of all the pesticides

469 included in the analysis for site VW, carbendazim and chlorpyrifos had the highest and third highest

470 PREX scores. These pesticides were detected more frequently in the water and sediment phase than

471 any other pesticide applied in this sub-catchment. Azinphos-methyl, with the second highest PREX

472 score was detected on one occasion in the sediment. Site LR had only one pesticide with a PREX

473 score falling in the high category (carbendazim). This pesticide, together with methyl parathion

474 (which was only detected in the sediment phase) was detected most frequently, with three detections

475 in each of the water and sediment phases. Apart from methyl parathion all other pesticides detected at

476 this site were detected less frequently.

477

478 *3.3 Relative Contribution of Runoff and Spray Drift*

479

480 Assessment of a runoff event in particular is a good measure of the reliability of the model used to

481 predict PELs and subsequent PECs, as runoff events result in the mobilisation of a number of

482 pesticides simultaneously and the level of contamination is dependent on a number of

483 physicochemical and geographical properties. In contrast the variables resulting in contamination

484 from a spray drift event are far less complex and much easier to predict. Assuming that the relative

485 contributions of runoff and spray drift to the PEL from each sub-catchment are accurate (Fig. 4), one

486 would expect pesticides associated with high runoff loss to be present in samples collected from the

487 field during the runoff event on the 15th of November (Table 2).

488

489 For site BB7, carbaryl and methyl parathion are both highly associated with runoff activity,

490 accounting for an estimated 84 and 75 %, respectively, of the total PEL when compared to spray drift.

491 Both of these pesticides were detected in samples collected during the runoff event. No pesticides that

492 were predominantly associated with spray drift were detected in collected samples. For site C, of the

493   pesticides with PREX scores falling in the high category, dimethomorph and carbendazim have the

494   highest association with runoff activity (94 and 38 %, respectively). Both of these pesticides were

495   detected in the water phase during the runoff event. Azinphos-methyl and prothifos were also detected

496   and could be present as a result of sediment mobilised by the runoff event. For Site LG, runoff plays a

497   major role in the transport of pesticides with high PREX scores. Carbaryl, carbendazim,

498   dimethomorph and methyl parathion all have high relative runoff contributions to total loss (91, 99, 87

499   and 96 %, respectively). All four of these pesticides were detected in the water phase during the

500   runoff event. For Site VW, the overall contribution of runoff to total pesticide losses is relatively low,

501   with spray drift clearly being estimated as the most important route of pesticide loss. No pesticides

502   were detected in water or sediment samples during the runoff event. For Site LR, carbaryl and

503   dimethomorph (88 and 86 %, respectively) and to a lesser extent carbendazim (55 %) all showed

504   relatively high proportions of runoff contributing to total pesticide loss. All three pesticides were

505   detected in the water phase during the runoff event.

506

507   The ability of the indicator to distinguish between relative runoff and spray drift contributions is

508   particularly useful with regards to identifying appropriate mitigation measures aimed at minimising

509   the transport of pesticides into surface waters. For example at site VW, where spray drift is the most

510   important route of entry, increasing buffer zone width (de Snoo and de Wit, 1998) or the

511   establishment of vegetative barriers in between the crops and adjacent water body (Reichenberger et

512   al., 2007) would effectively minimise transport of pesticides into this particular tributary. In contrast,

513   at site LG4, where runoff is clearly the predominant route of transport, establishment of vegetative

514   filter strips (Syversen and Bechmann, 2004) or effective drainage of runoff water into a constructed

515   wetland prior to entry into the tributary (Schulz et al., 2003) could potentially reduce pesticide

516   concentrations in this particular tributary.

517

518   *3.4 Pesticide Risk*

519

520   From a risk perspective, azinphos-methyl and chlorpyrifos posed the highest risk to the aquatic

521   ecosystem (Fig. 5). Sites LG4 and LR have the highest risk associated with pesticide contamination

522   with chlorpyrifos falling in the 'Very High and 'High' categories, respectively and azinphos-methyl

523   falling in the 'High' and 'Medium' categories, respectively. Site BB7 in particular, appears to have

524   the lowest risk associated with pesticide contamination with all pesticides falling in the 'Low'

525   category. VW and LG4 have similar risk profiles with chlorpyrifos falling in the 'Medium' category

526   and all other pesticides falling in the 'Low' category. The high risk of these pesticides is as a result of

527   their comparatively high toxicity values (Supplementary Data Table S1). Beta-cyfluthrin and

528   cypermethrin both have even higher toxicity (as indicated by their low toxicity concentrations).

529   However both of these pesticides had low transport potential as reflected by their PREX scores. In

530   contrast the majority of other pesticides with very low risk had very low toxicity. Previous research

531   has linked water and sediment associated azinphos-methyl concentrations to negative effects on

532   macroinvertebrate assemblages in the Lourens River catchment (Schulz et al., 2002; Thiere and

533   Schulz, 2004a; Thiere and Schulz, 2004b). Validation of the risk component of the indicator could

534   include a community assessment analysis although it is difficult to distinguish between effects

535   resulting from pesticide contamination and other factors such as sedimentation and habitat

536   modification (Bollmohr and Schulz, 2009).

537

538   **4. Conclusion**

539

540   The objective of this paper was to produce an indicator that provides a reliable assessment of the

541   relative exposure and risk of commonly applied pesticides in an agricultural catchment. The outputs

542   of the PREX and PRRI do not represent the absolute exposure and risk but a relative exposure and

543   risk rating among pesticides or land uses in a catchment. It does not take any pesticide interactions or

544   degradation beyond the point of its entry in waterways, (i.e. it provides the "edge of field" scenario).

545   Furthermore the method does not address the mobility and risks of pesticides bound to eroded

546   sediment. Further development of the indicator could focus on incorporating pesticide degradation

547   and sorption dynamics with a simple sediment loss model to estimate pesticide loss via this pathway,

548   such as in Kookana et al. (2005). It is also important to note that the detection limits of many of the

549   pesticides that were monitored in this study were comparable to the toxicity endpoint derived for the

550   pesticides. In these cases, the absence of detection would not necessarily imply the absence of risk

551   and detailed monitoring campaigns would need to ensure detections limits do not exceed toxicity

552   endpoints for a realistic assessment of risk. Improved detection limits would also significantly

553   enhance the ability to validate the risk indicator more accurately. Finally in cases where SSDs cannot

554   be derived for a pesticide, consideration should be given to applying a safety factor to single species

555   toxicity data (Raimondo et al., 2008).

556

557   However, with respect to the Lourens River, the indicator was successful in differentiating between

558   highly contaminated and less contaminated sites, and outputs of the PREX compared relatively well

559   with field based data. A limitation of the validation procedure is that pesticide analysis revealed only

560   the absence or presence of a target pesticide as opposed to a quantitative concentration, which would

561   have been more useful in terms of providing further resolution in differences in contamination

562   between sites. However the methodology adopted here is useful, in that the screening analysis

563   together with the PREX and PPRI indicator allowed for a relatively low cost identification of specific

564   pesticides for more detailed quantitative monitoring in the future. A further advantage of the indicator

565   method described here is that it relies on data input that is easily acquired through freely available

566   databases and GIS tools. In practice the most challenging information to acquire is reliable pesticide

567   application information. These results are important in demonstrating the potential effectiveness of

568   risk indicators, as while many such methodologies have been developed, very few have been

569   validated through field based monitoring. Previous studies in the Lourens River catchment have

570   shown the runoff and spray drift models used in this indicator to be very effective in predicting

571   environmental concentrations of pesticides (Schulz et al., 2001; Dabrowski and Schulz, 2003) and

572   these equations have been used in many indicator methodologies in other southern hemisphere

573   (Kookana et al., 2005) and European (Berenzen et al., 2005) countries in particular. These results

574   therefore contribute to providing increased confidence in the use of these models in this and other risk

575　　indicator applications and, in particular, could therefore lead to improved utilisation of limited

576　　resources for monitoring and management in resource constrained countries.

577

578　　**5. Acknowledgements**

579

582

583　　**6. References**

584

585　　AGIS (Agricultural Geo-Referenced Information System). 2012. Natural Resources Atlas.

586　　　　Agricultural Research Council [http:www.agis.agric.za/agisweb/nr-atlas]. Last accessed

587　　　　[November 2012].

588　　Ahmad, R. and Kookana, R.S. 2007. Geographical Extrapolation of Pesticide Environmental Fate

589　　　　Data: Challenges, Risks, and Opportunities. In: Kennedy, I.R. Solomon, K.R., Gee, S.J.,

590　　　　Crossan, A.N., Wang, S. and Sanchez-Bayo, F. (Eds). Rational Environmental Management

591　　　　of Agrochemicals: Risk Assessment, Monitoring and Remedial Action.

592　　Berenzen, N., Lentzen-Godding, A., Probst, M., Schulz, H., Schulz, R. and Liess, M. 2005. A

593　　　　comparison of predicted and measured levels of runoff-related pesticide concentrations in

594　　　　small lowland streams on a landscape level. Chemosphere. 58, 683-691.

595　　Bollmohr, S. and Schulz, R., 2009. Seasonal changes of macroinvertebrate communities in a Western

596　　　　Cape river, South Africa, receiving nonpoint-source insecticide pollution. Environ. Toxicol.

597　　　　Chem. 28, 809-817.

598　　Campbell, E., Palmer, M.J., Shao, Q. and Wilson D. 2000. BurrliOZ: A Computer Program for the

599　　　　Estimation of the Trigger Values for the ANZECC & ARMCANZ Water Quality Guidelines.

600　　　　In: National water quality management strategy, Australian and New Zealand guidelines for

601　　　　fresh and marine water quality. ANZEC & ARMCANZ, Canberra, Australia.

602 Crawford, C.G., 2004. Sampling strategies for estimating acute and chronic exposures of pesticides in
603   streams. J. Am. Wat. Res. Ass. 40, 485-502.

604 Daam, M. and Van den Brink, P., 2010. Implications of differences between temperate and tropical
605   freshwater ecosystems for the ecological risk assessment of pesticides. Ecotoxicology. 19, 24-
606   37.

607 Dabrowski, J.M., Peall, S K.C., Reinecke, A.J., Liess, M. and Schulz, R., 2002a. Runoff-related
608   pesticide input into the Lourens River, South Africa: basic data for exposure assessment and
609   risk mitigation at the catchment scale. Water Air Soil Poll. 135, 265-283.

610 Dabrowski, J.M., Peall, S.K.C., Van Niekerk, A., Reinecke, A.J., Day, J.A. and Schulz, R., 2002b.
611   Predicting runoff-induced pesticide input in agricultural sub-catchment surface waters:
612   linking catchment variables and contamination. Water Res. 36, 4975-4984.

613 Dabrowski, J.M. and Schulz, R., 2003. Predicted and measured levels of azinphos-methyl in the
614   Lourens River, South Africa: comparison of runoff and spray drift. Environ Toxicol. Chem.
615   22, 494-500.

616 Dubus, I.G., Brown, C.D. and Beulke, S. 2003. Sensitivity analysis of four pesticide leaching models.
617   Pest Manage. Sci. 59, 962-982.

618 de Snoo, G.R. and de Wit, P.J., 1998. Buffer zones for reducing pesticide drift to ditches and risk to
619   aquatic organisms. Ecotox. Environ. Safe. 41, 112-118.

620 Erstfeld, K. 1999. Environmental fate of synthetic pyrethroids during spray drift and field runoff
621   treatments in aquatic microcosms. Chemosphere. 39, 1737-1769.

622 FOOTPRINT, 2006. The FOOTPRINT Pesticide Properties DataBase. Database collated by the
623   University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704.
624   Last Accessed: November 2012.

625 Holvoet, K.M.A., Seuntjens, P. and Vanrolleghem, P.A., 2007. Monitoring and modeling pesticide
626   fate in surface waters at the catchment scale. Ecol. Model. 209, 53-64.

627 Huber, A., Bach, M. and Frede, H.G., 2000. Pollution of surface waters with pesticides in Germany:
628   modeling nonpoint source inputs. Agric. Ecosyst. Environ. 80, 191-204.

629 Kookana, R.S., Correll, R.L. and Miller, R.B., 2005. Pesticide Impact Rating Index - A pesticide risk
630   indicator for water quality. Water Air Soil Poll. 5, 45-65.

631 Levitan, L., Merwin, I. and Kovach, J., 1995. Assessing the relative environmental impacts of
632   agricultural pesticides: the quest for a holistic method. Agric., Ecosyst. Environ. 55, 153-168.

633 Loague, K.L., Corwin, D.L. and Ellsworth, T.L., 1998. The challenge of predicting nonpoint source
634   pollution. Environ. Sci. Technol. 32, 130-133.

635 London, L., Dalvie, M.A., Cairncross, E. and Solomons, A., 2000. The Quality Of Surface And
636   Groundwater In The Rural Western Cape With Regards To Pesticides. WRC Report No.
637   795/1/00, Water Research Commission, Pretoria.

638 Lutz ,W., 1984. Berechnung von Hochwasserabflu¨ssen unter Anwendung von Gebietskenngro¨ßen.
639   24. Technical Report. Institute of Hydrology and Water Research, University Karlsruhe,
640   Karlsruhe, Germany.

641 Maniak, U., 1992. Regionalisierung von Parametern fu¨ r Hochwasserabflussganglinien. In Kleeberg
642   HB, ed, Regionalisierung von Hydrologie, Vol 11. Commission for Water, German Society
643   for the Advancement of Sciences, Bonn, Germany, pp 325–332.

644 Meinhardt, H.R., 2009. Evaluation Of Predictive Models For Pesticide Behaviour In South African
645   Soils. PhD Thesis. North-West University.

646 Pollock, D.W., Kookana, R.S. and Correll, R.L., 2005. Integration of the Pesticide Impact Rating
647   Index with a geographical information system for the assessment of pesticide impact on water
648   quality. Water Air Soil Poll. 5, 67-88.

649 Raimondo, S., Vivian, D.H., Delos, C. and Barron, M.G., 2008. Protectiveness of species sensitivity
650   distribution hazard concentrations for acute toxicity used in endangered species risk
651   assessment. Environ. Toxicol. Chem. 27: 2599-2607.

652 Rand, G.M., 2004. Fate and effects of the insecticide-miticide chlorfenapyr in outdoor aquatic
653   microcosms. Ecotox. Environ. Safe. 58, 50-60.

654 Rautmann, D., Streloke, M. and Winkler, R., 1999. New basic drift values in the authorization
655   procedure for plant protection products. 133-141.

656 Reichenberger, S., Bach, M., Skitschak, A. and Frede, H-G., 2007. Mitigation strategies to reduce

657   pesticide input into ground- and surface water and their effectiveness: A review. Sci. Total

658   Environ. 384, 1-35.

659 Reus, J., Lenndertse, C., Bockstaller, C., Fomsgaard, I., Gutsche, V., Lewis, K., Nilsson, C.,

660   Pussemier, L., Trevisan, M., Van der Werf, H., Alfarroba, F., Blümel, S., Isart, J., Mc Grath,

661   D., Seppälä, T., 1999. Annex I: Run-off submodel. In: Comparing Environmental Risk

662   Indicators for Pesticides. Results of the European CAPER Project. Centre for Agriculture and

663   Environment Utrecht, CLM 426, pp. 80–82.

664 Reus, J., Leendertse, P., Bockstaller, C., Fomsgaard, I., Gutsche, V., Lewis, K., Nilsson, C.,

665   Pussemier, L., Trevisan, M., van der Werf, H., Alfarroba, F., Blümel, S., Isart, J., McGrath,

666   D. and Seppälä, T., 2002. Comparison and evaluation of eight pesticide environmental risk

667   indicators developed in Europe and recommendations for future use. Agric, Ecosyst. Environ.

668   90, 177-187.

669 Sala, S. and Vighi, M., 2008. GIS-based procedure for site-specific risk assessment of pesticides for

670   aquatic ecosystems. Ecotox. Environ. Safe. 69, 1-12.

671 Sánchez-Bayo, F., Baskaran, S. and Kennedy, I.R., 2002. Ecological relative risk (EcoRR): another

672   approach for risk assessment of pesticides in agriculture. Agric, Ecosyst. Environ. 91, 37-57.

673 Schulz, R., 2001a. Comparison of spray drift- and runoff-related input of azinphos-methyl and

674   endosulfan from fruit orchards into the Lourens River, South Africa. Chemosphere. 45, 543-

675   551.

676 Schulz, R., 2001b. Rainfall-induced sediment and pesticide input from orchards into the Lourens

677   River, Western Cape, South Africa: importance of a single event. Water Res. 35, 1869-1876.

678 Schulz, R., 2003. Using a freshwater amphipod in situ bioassay as a sensitive tool to detect pesticide

679   effects in the field. Environ Toxicol. Chem. 22, 1172-1176.

680 Schulz, R., Hahn, C., Bennett, E.R., Dabrowski, J.M., Thiere, G. and Peall, S.K.C., 2003. Fate and

681   effects of azinphos-methyl in a flow-through wetland in South Africa. Environ. Sci. Technol.

682   37, 2139-2144.

683   Schulz, R., Peall, S.K.C., Dabrowski, J.M. and Reinecke, A.J., 2001. Spray deposition of two
684   insecticides into surface waters in a South African orchard area. J. Environ. Qual. 30, 814-
685   822.

686   Schulz, R., Thiere, G. and Dabrowski, J.M., 2002. A combined microcosm and field approach to
687   evaluate the aquatic toxicity of azinphos-methyl to stream communities. Environ Toxicol.
688   Chem. 21, 2172-2178.

689   Sereda, B.L. and Meinhardt, H.R., 2005. Contamination of the water environment in malaria endemic
690   areas of KwaZulu-Natal, South Africa, by agricultural insecticides. B. Environ. Contam.
691   Toxicol. 75, 530-537.

692   Stehle, S., Knäbel, A. and Schulz, R., 2012. Probabilistic risk assessment of insecticide concentrations
693   in agricultural surface waters: a critical appraisal. Environ. Monit. Assess. 185, 6295-6310.

694   Syversen, N. and Bechmann, M., 2004. Vegetative buffer zones as pesticide filters for simulated
695   surface runoff. Ecol. Eng. 22, 175-184.

696   Thiere, G. and Schulz, R., 2004a. Runoff-related agricultural impact in relation to macroinvertebrate
697   communities of the Lourens River, South Africa. Water Res. 38, 3092-3102.

698   Thiere, G. and Schulz, R., 2004b. Runoff simulation with particle-associated azinphos-methyl in
699   multispecies stream microcosms: implications for the field. Environ Toxicol. Chem. 23, 1984-
700   1990.

701   USEPA (US Environmental Protection Agency), 1994. Aquatic Toxicity Information Retrieval
702   (AQUIRE). Office of Research and Development. National Health and Environmental Effects
703   Research Laboratory, Mid-Continental Ecology Division, Duluth, MN.

704   Verro, R., Calliera, M., Maffioloi, G., Auteri, D., Sala, S., Finizio, A. and Vighi, M., 2002. GIS-based
705   system for surface water risk assessment of agricultural chemicals. 1. Methodological
706   approach. Environ. Sci. Technol. 36, 1532-1538.

707   Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A.,
708   Kordel, W., Gerstl, Z., Lane, M. and Unsworth, J.B., 2002. Pesticide soil sorption parameters:
709   theory, measurement, uses, limitations and reliability. Pest Manag. Sci. 58, 419-445.