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An indicator to assess risks on water and air of pesticide spraying in crop fields

<u>Frédéric Pierlot ^{1,2}</u>; Jonathan Marks-Perreau ³; Emma Soulé ⁴; Olivier Keichinger ⁵; Carole
 Bedos ⁶; Laetitia Prevost ²; Paul Van Dijk²; Christian Bockstaller ⁴

- 6
- ¹ LAE, Université de Lorraine, INRAE, F54000 NANCY, France frederic.pierlot@univ lorraine.fr
- 9 ² Chambre Régionale d'Agriculture Grand Est, Laxou, France
- 10 ³ Arvalis, Institut du végétal, France
- ⁴ LAE, Université de Lorraine, INRAE, F68000 COLMAR France
- ⁵ Chercheur indépendant, France
- ⁶ Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 91120 Palaiseau, France
- 14
- 15 Highlights:
- 16 Stakeholders need tools to assess environmental risks of pesticide
- I-Phy3 assesses the risk on 3 environmental compartments (air / surface water / ground water)
- 19 Knowledge of recent studies and expertise on pesticides are combined in I-Phy3
- 20 I-Phy3 yielded better validation results than previous versions of the indicator
- A good compromise between ease of use and predictive capability is offered by I-Phy3
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- 23

24 Abstract

25 Stakeholders involved in actions to reduce the use and the impacts on the environment or human health of pesticides need operational tools to assess crop protection strategies in 26 regard to these impacts. I-Phy3 brings together all improvements introduced since the first 27 version of the indicator to better meet user's needs and requirements of integrating processes. 28 I-Phy3 was deeply modified to ensure its predictive quality. I-Phy3 is structured in three levels 29 of aggregation in form of hierarchical fuzzy decision trees designed with the CONTRA method. 30 At the 1st level, five basic subindicators assess the risk of contamination (RC) for the different 31 transfer pathways involved in surface water, ground water and atmosphere contamination: 32 leaching, runoff, drainage, drift, volatilization. At the 2nd level, RC subindicators are aggregated 33 with a toxicity variable (human or aquatic) in a risk indicator. At the 3rd level, the global indicator 34 I-Phy3 results from the aggregation of three risk indicators for groundwater, surface waters 35 and air. I-Phy3 yielded better validation results than its previous versions. This effort to assess 36 the predictive quality of the indicator should be pursued and completed by a feasibility and 37 utility test by end-users. A subindicator on risk of soil contamination is a gap which remains to 38 39 fill.

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Keywords: Indigo method; risk assessment; I-Phy3; pesticide transfer pathways; water
 quality; air quality

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46 **1. Introduction**

47 The incredible and securing rise of agriculture production since the end of the Second World 48 War, was favored partially by the widespread use of pesticides. Nevertheless, side effects on 49 the environment (Richardson, 1998) and in particular on water quality (Flury et al., 1995; Grung et al., 2015; Lopez et al., 2015; Real et al., 2005), air (Hulin et al., 2021; Lichiheb et al., 2015) 50 51 and accumulation in soil (Silva et al., 2019; Tang and Maggi, 2021) have been observed. These contaminations lead to exposure of non-target ecosystems as well as populations that may 52 have ecotoxicological and/or toxicological impacts. Consequently, regulations on pesticide use 53 have been continuously reinforced since the Council Directive 79/117/EEC with the Council 54 Directive EC 1107/2009 es and the Pesticide Package 2009/128/CE on sustainable use of 55 pesticides. This was amended by the Commission Directive (EU) 2019/782 introducing a 56 monitoring of risk by the HRI indicator (Methodology for calculating harmonized risk indicators 57 for pesticides under Directive 2009/128/EC, 2021) (European Commission. Statistical Office 58 of the European Union., 2021; (Lykogianni et al., 2021). In all cases, stakeholders involved in 59 actions to reduce the use and impacts of pesticides need operational tools to assess crop 60 protection strategies. The aim of such assessment may be to monitor and to report on the 61 62 current status of environmental compartments quality, to produce references for the good management of crop protection and to work on innovative systems (Bockstaller et al., 2015). 63

The need for assessment tools dealing with pesticide issues has led to the development of 64 65 numerous indicators. The simplest ones rely on the supplied quantities, the Quantity of Active Ingredients (QAI) or the Treatment Frequency Index (TFI) calculating the ratio of applied 66 pesticide to the registered rate (Hossard et al., 2017; Uthes et al., 2019). Although those 67 68 indicators have been developed to describe the evolution of pesticide use intensity, they are 69 often used as main indicators to address the environmental effects due to pesticide spraying in environmental assessment method (Eckert et al., 2000; Vilain et al., 2008). Pesticide risk 70 indicators (Levitan, 2000) requiring complementary variables such as active ingredient 71 properties, crop management data and pedoclimatic variables are more elaborate and were 72 73 reviewed by several authors (Feola et al., 2011; Keichinger et al., 2013; Maud et al., 2001; 74 Reus et al., 2002). Some deserve more attention. While the Danish Pestice Load (Kudsk et al., 75 2018) is based on a quite simple scoring approach of pesticide properties,, other EPRIP2 (Trevisan et al., 2009),, POCER (Vercruysse and Steurbaut, 2002) or SYNOPS (Strassemeyer 76 77 and Gutsche, 2010), the indicators of the HAIR project (Kruijne et al., 2011)) rest on 78 quantitative equations addressing several factors (pesticide properties, soil climate, etc.). This 79 array of indicators may be explained by the context of use (purpose, environmental covered addressed, scales, means, etc.) and the research of compromise between integration of 80 process and feasibility (Bockstaller et al., 2015) Among those indicators, the I-Phy indicator, in 81 its two versions, assessing risk for ground water, surface water and air, distinguished by its 82 original construction of a fuzzy decision tree combining qualitative and quantitative data. It was 83 developed for an assessment at the field level, first for arable cropping systems and later its 84 was adapted to viticulture (Thiollet-Scholtus and Bockstaller, 2015). Its aim was to help 85 advisers guide farmers in their choice of active ingredients and application methods at limit 86 pressure on the environment. In the validation study of Pierlot et al. (2017), I-Phy1 (first version, 87 van der Werf et Zimmer 1998) came out as one of the "best" indicators for transfer by leaching. 88 89 Lindahl et Bockstaller (2012) proposed an upgraded version assessing the pesticide transfer 90 by leaching to better take into account preferential transfer (I-Phy2), that was overlooked by I-91 Phy1. However, its predictive quality was not improved.

Furthermore, assessments of transfer and toxicity of pesticides in I-Phy1 were combined in a 92 93 calculation of pesticide risk. Yet, stakeholders and advisers working directly with farmers require a separate assessment of transfer to gain insight of water bodies contamination with 94 respect to the European rules for water bodies quality (DCE). This demand was motivated by 95 their need to gain knowledge on water quality in terms of pesticide contamination. 96 Ecotoxicological risk integrating transfer and toxicity remains a matter of interest when 97 stakeholders consider the impact of pesticide use on biocenosis. In both cases, the 98 99 implementation of assessment tools is aimed at helping them prioritize their actions.

Here is presented I-Phy3 which brings together all improvements introduced since the first 100 version of the indicator to better meet users' needs and requirements of integrating processes 101 to ensure its predictive quality. Based on the knowledge gained on pesticide transfers and risks 102 103 for the last 20 years, the indicator was restructured to separate transfer assessment from risks on living organisms assessment, new input variables were introduced and most algorithms 104 deeply revised. This article presents the new calculation algorithms for arable crops as well as 105 results of the indicator evaluation for its predictive quality. Besides the design of the indicator 106 and validation results, possibilities for implementing the indicator are discussed. 107

108

109 2. Material and methods

The design of I-Phy3 started with the selection of input variables (section 2.1). Those variables 110 were aggregated into several subindicators and then in a global indicator I-Phy3. The 111 methodology is described in section 2.2 and the structure of the indicator in section 2.3. The 112 113 predictive quality of the indicator was then assessed by comparison of indicator outputs calculated on sites with measured values of water or air contamination. Section 2.4 presents 114 the study sites used to collect measurements of water (EQUIPE project) or air (Repp'Air 115 project) contaminations while section 2.5 presents the methodology to assess predictive 116 quality of the indicator. 117

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119 **2.1. Selection of input variables**

120 Input variables were selected from a literature review, starting from the work of van der Werf 121 (1996) and on expertise based on experimental data (e.g. see section 2.3.2 for contamination 122 of groundwater).

For pesticides properties, we used the revised Pesticide Properties Database PPDB which is 123 updated since more than 20 years with more reliable value available for each active ingredient 124 (a.i.) and used in many risk assessment studies (Lewis et al., 2016). PPDB can be browsed 125 on a website (PPDB : Pesticide Properties Database, 2020) or purchased in form of an Access 126 database. Values of pesticide properties were extracted from the latter (version 127 20/05/11).(Tomlin et al., 1995) For the DT50, the value proposed for laboratory rather than the 128 "typical value" proposed by the database resulting from an expert work was selected. This 129 choice resulted also from the calibration work with monitoring data in the Rhine plain (ERMES 130 2017, Koller et al. 2015) for four active ingredients (see section 2.3.3). For some few active 131 ingredients, values as listed in Supplementary Materials S1 were modified. For some few other 132 a.i., values were taken from other sources because of missing value in PPDB. Overall, 498 133 active ingredients were integrated in the database. 134

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2.2. Design of indicators

The indicator I-Phy3 as well as all subindicators are calculated for a single active ingredient and then aggregated for a spraying program. They are expressed on a continuous performance scale between 0 (highest risk) and 10 (lowest risk), which allows an operational user of the indicators by non-scientific users. (Bockstaller et al., 2008). (Craheix et al., This scale can be easily inverted between 0 (lowest risk) and 10 (highest risk) for a use of I-Phy3 for specific risk assessment for which high values of indicators are usually associated to high risk".

Fuzzy decision trees were implemented to design the indicator I-Phy and its different 144 subindicators like in the first version of the indicator (Roussel et al., 2000; van der Werf and 145 Zimmer, 1998). Fuzzy decision trees present several advantages (Bockstaller et al., 2017): 146 they rely on linguistic "if then" rules with a transparency, at least semantic through linguistic 147 148 rules that are easy to understand for non-specialists. They cope with qualitative as well as quantitative heterogeneous information. Furthermore, combining decision trees with fuzzy 149 logic makes it possible to mitigate threshold effects linked to the linguistic "if then" rules when 150 they are Boolean, i.e., consisting of two alternatives yes/no. Fuzzy logic introduces fuzzy 151 152 subsets to deal with the whole set of intermediate cases.

153 As shown in the simplified example, (Supplementary Materials S2), I-Phy3 and each subindicator require i) fuzzy subsets for each input variable with threshold values, ii) 154 membership functions to calculate membership degree of each variable to the favourable (low 155 risk) or unfavourable (high risk) subset, iii) decision trees. More details for fuzzy subsets and 156 membership functions are given in Supplementary Materials S3, while decision trees are 157 presented in section 2.3. Most decision trees were designed with the CONTRA method which 158 supports the design of fuzzy decision tree in a transparent way (Bockstaller et al., 2017) were 159 calibrated with a model (see section 2.3.3) or based on one variable (see sections 2.3.5 and 160 161 2.3.6). In this latter case, the membership degree to the favourable subset (expressed between 0 and 1) is transformed into an indicator score by multiplying the former by 10. 162

163

2.3. Description of the indicator

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2.3.1. Overview of the indicator structure and calculation

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As shown on Figure 1, I-Phy3 is structured in three levels of aggregation. At the 3^e level, the 167 global indicator I-Phy3 results from the aggregation of three risk indicators tackling three 168 environmental compartments like in version 1 (van der Werf and Zimmer, 1998): 1) 169 groundwater, 2) surface water and 3) air. At the 2nd level, each of this indicator of risk consists 170 in the aggregation of one or two sub indicators assessing the risk of contamination (RC) via 171 specific transfer pathways, with a toxicity variable, Admissible Daily Intake (ADI) or Aquatox 172 (highest toxicity level between fish, daphnia or alqua, for the human health and ecotoxicological 173 impacts respectively, see van der Werf and Zimmer (1998)). At the 1st level, five basic 174 175 subindicators assess the risk of contamination (RC) namely, a) the groundwater contamination by pesticide leaching (RCgw_{in}), b) surface water contamination by pesticide runoff or drainage 176 transfer (RCsw_w). Drainage transfer is characterized by an initial vertical transfer, *i.e.* leaching, 177 to an impermeable layer where till drains have been set to evacuate rapidly water excess. This 178 requires a specific calculation (see 3.1.4). c) surface water contamination by pesticide drift 179 180 (RCsw_{at}); d) air contamination by pesticide volatilization (RCair_{ad}) and e)) air contamination by pesticide drift (RCair₄). 181

The five risks of contamination are calculated for 1 kg of active ingredient (a.i.) and modulated 182 by the actual application rate which results from the calculation of a non-intercepted rate of a.i. 183 by the treated crop (see section 2.3.8): each of these five subindicators is transformed in a risk 184 between 0 (no) and 1 (high) and weighted by the percentage of sprayed area within the field. 185 It is then retransformed in a value of performance according to Equation 1. It was assumed 186 187 that there is a proportional relation between sprayed area and level of contamination (Melland et al., 2016): 188

189

 $= 10 \left(1 - \left(1 - \frac{RC_{100\%}}{10} \right) \right) \frac{\% Area}{100}$

(Equation 1)

- Where: 191
- RC_{final}: final result for a risk of contamination (see Figure 1) 192
- RC_{100%}: result for a risk of contamination calculated for 100% of sprayed area 193
- 194 %area: percentage of sprayed area within a field.
- I-Phy and each subindicator result from the aggregation based on a fuzzy decision tree. 195
- 196
- 197

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2.3.2. Groundwater contamination (RCgwlea)

Two variables of previous versions were kept: the GUS and the leaching potential for which a 199 new calculation method was proposed (Supplementary Materials S4.1.). A variable identified 200 201 as playing an important role was added: the water status of the soil when pesticides are applied (Pierlot et al., 2017) depending on climate and soil conditions. This variable was assessed 202 through the application period (Supplementary Materials S4.2). Finally, solubility as a fourth 203 variable was added. This property was identified as explaining of the discrepancy between the 204 205 low transfer risk calculated by previous indicator version and the alarming contamination level 206 of groundwater in Rhine Plain for the nicosulfuron active ingredient (ERMES, 2017). Nicosulfuron is characterized by a very high solubility in water (7500 mg.L-1). The role of 207 solubility in pesticide leaching is confirmed by literature (Elliott et al., 2000). While pesticide 208 209 properties are directly retrieved from data bases, the two other variables have to be calculated (Supplementary Materials 4.1 and 4.2). 210

No prominent weight was assigned to the GUS, like the version 1, regarding the aggregation 211 of the four input variables in a fuzzy decision tree (Table 1). This is justified by the fact that in 212 situations of preferential transfer, even active ingredient with favourable GUS like glyphosate 213 can be leached (Vereecken, 2005). We selected weights and modified some decision rules 214 proposed automatically by CONTRA as made possible by this method, to adjust indicators 215 outputs to results of groundwater monitoring of the Rhine Plain for four active ingredients 216 among the most used pesticides for the main crop of the region, maize' (dmat-p, mesotrion, 217 218 nicolsulfuron, s-metolachlor), (ERMES, 2017; Koller et al., 2015). Table 1 depicts the structure of the indicator. 219

220

2.3.3. Surface water contamination by drainage/runoff 221 (RCsw_{d/r}) 222

The calculation of this subindicator, coming from the work of Wohlfart (2008) is based on the runoff potential and a availability variable that is more elaborated than the use of the single DT50 in the first version (van der Werf and Zimmer 1998). The runoff potential depends on slope, on soil properties, texture, crusting sensitivity, hydromorphy, and also on management, tillage and implantation of buffers strip (Supplementary Materials S5). The availability variable is inspired from quantitative indicators like Synops (Strassemeyer and Gutsche, 2010) and Eprip2 (Trevisan et al., 2009). Equation 2 shows the calculation of the availability variable:

230 **Avai = r . e**^{-Ln(2)/(DT50.t)} (Equation 2)

231 Where:

Avai : availability of active ingredient

233 DT50 : soil half-life of active ingredient (days)

t: time in days between date of spraying and date of next runoff event with a default value of3 for a worst-case situation

r: A reduction coefficient assessing the reduction pesticide amount for runoff when the active
ingredient is incorporated (Mickelson et al., 2001). Considering the results of these authors,
we proposed a default value of 0.5 when incorporation and 1 when no incorporation.

239

Table 2 depicts the fuzzy decision tree aggregating those two variables. Outputs of the decision trees were calibrated with help of the PRZMv3.12 model (Carsel et al., 1986) for two rates (Wohlfahrt, 2008) and interpolated for 1 kg. Input variables belong either to the favourable set (F) or to unfavourable set (U).

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246 **2.3.4. Particular case of drained plot**

It has been clearly demonstrated that drained fields show a high risk of rapid transfer of 247 248 pesticide to adjacent surface water bodies through subsurface pipes (Brown and van Beinum, 2009). Although the initial transfer process consists in a preferential vertical transfer, final 249 impacted compartment is surface water and not groundwater. This is supported by the 250 251 variables playing a role in the determinism of pesticide loss in drained field (Brown and van Beinum, 2009), Kd (non-normalized KOC) and DT50 which are both aggregated in the GUS 252 variable main variable for the groundwater subindicator (see section 2.3.1.). To cope with this 253 254 specificity, was assumed that in drained field, pesticides are mainly transferable to surface 255 water and not groundwater although the transfer process is based initially on vertical leaching 256 like for RCgw_{ie} (see section 2.3.1.) when there is no higher risk by runoff.

257 Therefore, the following specific decision rules was introduced:

258

259 If the field is drained then RCsw_{dr} = MIN(RCsw_{dr} , RCgw_{lea})

260 If the field is drained and $RCsw_{dr} = RCgw_{les}$ then $RCgw_{les} = 10$ 261 (to avoid double counting of risk)

262 Where:

263 RCsw_{at}: contamination risk for surface water through drainage or runoff (see section 2.3.3)

- 264 RCgw_{iea}: contamination risk for groundwater through leaching (see section 2.3.2)
- 265

266 **2.3.5. Surface water contamination by drift (RCsw**dr)

While in the previous version of the indicator, coefficients were taken from a table resulting from a collection of expert judgment and measured values, the equations of Trevisan et al. (2009) were used here to calculate spray drift. This spray drift potential is divided by 5 when anti-drift nozzles are used. These spray drift values are transformed in a score between 0 and 10 as described in Supplementary Materials S6.

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2.3.6. Air contamination by volatilization (RCairvol)

274 Like for the subindicator spray drift to surface water (see previous section), the decision tree used in previous version of the indicator was replaced by quantitative equations calculating 275 pesticide volatilization (expressed in µg/m²/hr) in function of pesticide properties (Woodrow et 276 al., 1997). We added some abatement factors taking into account effect of soil components 277 (mulch, etc.), pesticide properties (penetration ability), and field edge (presence of hedges or 278 trees reducing transfer to outside of field) which is expected to contribute to decrease the 279 transfer risk. The calculation is given by Equation 3 and more details are given in 280 Supplementary Materials S7. 281

282

284 Voltot = (1 - Cedge). ((1 - Cform). (1 - ic). Volsol + (1 - Cprod). ic. Volplant)

283 (Equation 3)

285

- 286 Where:
- 287 Vol_{tot}: total volatilization (expressed in μ g/m²/hr)

Vol_{sol}: volatilization from soil (expressed in $\mu g/m_i/hr$), calculated according to Woodrow et al. (1997): LnVol_{sol}= 28.335+1.6158.Ln(Pv/(KOC.Sol) with: Pv: pressure vapor (Pa), KOC: soil adsorption coefficient (mg.L⁻¹), Sol: water solubility (mg.L⁻¹)

- Vol_{plant}: volatilization from plant (expressed in µg/m²/hr), calculated according to (Woodrow et al., 1997): LnVol_{plant}= 11.779+0.85543.Ln(Pv) with: Pv; pressure vapor (Pa)
- ic: interception of pesticide by crop (see 3.1.8 and Supplementary Materials S8.1)

c_{edge}: abatement coefficient (between 0 and 1) due to field edge, more precisely to the presence
 of a hedge reducing pesticide transfer to outside of field. Four variables are used to assess it:
 type of plant (persistent or deciduous), hedge density (number of field sides with a hedge and
 porosity of hedge), hedge height, spraying month (to assess the presence of leaves or not)

298 C_{torm}: abatement coefficient (between 0 and 1) due to the product formulation

 c_{prod} : abatement coefficient (between 0 and 1) due to penetration ability of the product in plant which limits pesticide volatilization and is assessed with pesticide mechanism of action, the octanol water coefficient (LogKow) and the use of an adjuvant to facilitate penetration.

303

2.3.7. Air contamination by drift (RCair_{dr})

This risk of air contamination by spray drift was not covered by the original version of I-Phy 304 (van der Werf and Zimmer, 1998) but was added to the version for wine growing activity (with 305 a simplified assessment including only the type of sprayer. A more elaborated decision tree 306 taking into account additional relevant variables like speed sprayer, the sprayer height, the use 307 308 of antidrift nozzle and the air pressure (Pressure) were included in this new version of the indicator according to the study of Bahrouni, Sinfort, et Hamza (2010) (Table 3). The CONTRA 309 method (was used to aggregate the five input variables in a fuzzy decision tree. This indicator 310 is weighted by an abatement coefficient, cede like for RCairvel (see Equation 3 and 311 Supplementary Materials 7.2). 312

313

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2.3.8. Integration of the a.i. application rate effect

In I-Phy3, the method proposed by Lindahl and Bockstaller (2012) was used to integrate the effect of the a.i. application rate in the calculation of each contamination subindicator. They proposed to calculate an effective dose of a.i. available for transfer by weighting the initial dose by an interception rate as shown in equation 4:

320 $Dose_{eff} = (1-ic).Dose_{ini}$ (Equation 4)

321

322 Dose_{eff}: effective rate of pesticide

ic: interception coefficient (see Supplementary Materials S98.1)

324 Dose_{ini}: initial rate of pesticide

They designed an algorithm which makes possible to reduce (if the dose is higher than 1 kg.ha) or increase (if the rate is lower than 1 kg.ha) the indicator value obtained for 1 kg/ha function of this effective dose. More details on the determination of the interception rate and the calculation of the indicator in function of the effective dose are given in Supplementary Materials S 8.

330

2.3.9 . Risk by compartment

332 Three subindicators of environmental risk, for ground water (I-Phy_w), surface water (I-Phy_w), and air (I-Phy_a) result from the aggregation of the five subindicators of contamination risk (RC) 333 with toxicity variables (see Figure 1). For groundwater, RCgw_{in} is aggregated with the daily 334 admissible intake (ADI) because this source is for human water supply. For surface water, two 335 subindicators, RCsw_a and RCsw_a are aggregated with a toxicity variable based on the highest 336 337 toxicity between Aquatox tackling toxicity for aquatic organisms and ADI for human toxicity (Roussel et al., 2000). Aquatox results from the highest toxicity for fish, daphnia and algae 338 (van der Werf and Zimmer, 1998). For air, two subindicators, RCair, and RCair, are aggregated 339 340 with ADI for human toxicity.

Regarding aggregation rules, a weight of 60 % is given to the contamination risk and 40 % to 342 toxicity for groundwater (Supplementary Materials S9). For surface water and air, 30 % is given 343 to each contamination risk and again 40 % to the toxicity with a small modification in the second 344 case (Table 4). We considered that a situation with a high risk of contamination is more 345 undesirable than a situation of toxic a.i. without any risk of contamination. This may be justified 346 by water potability threshold of 0.1 µg⁻¹ applied to all a.i. which leads water manager to focus 347 on water contamination. Furthermore, uncertainty exists on actual toxicity of a.i. which is not 348 well assessed by regulation tests (Centner, 2021) so that a situation with apparently no toxicity 349 may present a risk for human health. Similar decision rules to those for I-Phy_s are set to I-Phy_s. 350

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2.3.10. Final aggregated indicator (I-Phy)

The three subindicators of pesticide risk per compartment, ground (I-Phy_{aw})- and surface water 353 (I-Phy_s), air (I-Phy_s) are aggregated with the same weight of 33% given to each compartment 354 . However, to limit compensation, the score was reduced to 6 when there was a risk totally 355 unfavourable for one compartment (I-Phy_s or I-Phy_s or I-Phy_s or I-Phy_s or I-Phy_s or I-Phy_s 356 compartments were concerned by a totally unfavourable risk (Table 5). We consider that if 357 there is a risk maximal for one compartment, the value should be clearly under 7. This value 7 358 is a reference value expressing an acceptable risk for the environment used for the set of 359 360 indicators of the INDIGO method to which belongs I-Phy (Bockstaller et al., 1997).

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- 362

2.3.11. Implementation of the indicator

Calculations of the indicator are run on an Excel Sheet with one sheet in which all data on input variables are entered. Each line corresponds to a calculation for one active ingredient. Stable data (e.g. field characteristics) have to be copied from line to line. Users have access to all the detail of calculations with results expressed with a color code (see Figure 3).

368 **2.4.** Study sites

369

Measured data of environmental compartment contamination (groundwater, surface water, air) from several study sites (Figure 2) were used and compared with outputs of I-Phy3 for validation. The sites of the EQUIPE project (see 2.3.1) provided data on the transfer by drainage or runoff to surface water and vertical transfer by leaching. For the transfer to air, the data of the project Repp'Air was used. For each treatment, the I-Phy3 indicator was calculated with the help of an Excel sheet calculator with the aim of comparing the results with measurement data.

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378 2.4.1. Sites of the Equipe project

The EQUIPE (2014-2017) project aimed to assess the predictive quality of pesticide indicators addressing transfers to surface and ground water. To do so, outputs of 26 indicators (among them Synops, Eprip, I-Phy1, I-Phy2...) and a mechanistic model (MACRO) were compared to measure pesticide transfers at plot levels at four sites with different climate and soil conditions, and transfer pathways (Pierlot et al., 2017). The complete description of the 3 sites and the indicators and model tested is detailed in Supplementary Materials S10) The Jaillière

experimental station, located in the Pays de la Loire region (France), is under the influence of 385 386 an oceanic climate, with a brown hydromorphic clay-textured soil, resulting from alterite shale. This experimentation site consists of 10 agricultural plots of 0.5 to 1 ha each, where water from 387 drainage and runoff (saturation overland flow) are collected separately; ii) The experimental 388 389 station of the Magneraud, located in the Nouvelle-Aquitaine region (France), is also under the 390 influence of oceanic climate and is composed mainly of clayed and silty limestone soils developed on sand-stone strata characterized by alternating layers of hard limestone and marl. 391 392 This site is made up of 14 lysimetric plots of 1 m2 surface, with no vertical walls and no soil shuffle; and iii) the Geispitzen experimental station is located in the hills of the lower Sundgau 393 394 district (Alsace region, France) and has an attenuated oceanic climate. The hills are covered with loess-derived soils of silt loam texture overlying Oligocene molasses and marls. A sloping 395 field (5%) of about 9 ha was divided into 3 bordered fields with measuring flumes and automatic 396 397 water samplers at the down slope borders just upslope of a ditch drainage catchment runoff.

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399 2.342. Sites of the Repp'Air project

The 7 measurement sites selected for the Repp'Air project came from historical sites monitored 400 401 by regional Association of Air Quality Survey in association with Chambers of Agriculture in 402 order to have different agricultural systems: arable crops, vineyards, arboriculture, mixed 403 cropping-livestock, and "mixed" sites with different types of crops. Farm practice surveys were conducted during the 3 monitoring campaigns (2017, 2018, 2019) and for each site, to help in 404 405 the interpretation of local air contamination data. These investigations were conducted over a radius of 1 km around the air sampler installed at each site. The choice of the 1 km radius 406 407 was a compromise between technical feasibility (particularly in the wine-growing zone, where 408 the number of plots, often smaller than in field crops, is greater in a given area, implying a 409 greater number of farmers) and a surface area in agreement with atmospheric dispersion patterns at the local scale . Such radius value was sufficient to find a correlation between 410 pesticide in precipitation and land use (Grynkiewicz et al., 2001)). Atmospheric samples were 411 collected for a whole week during the spraying period (in average 27 weeks), this for 3 years 412 413 on the 7 sites concerned by the project, I.e. a total of 567 samples. Pesticide contents of each sample were analyzed in an external accredited laboratory and allowed to quantify a.i. 414 concentration in the atmosphere. 415

416

417**2.5.** Evaluation of the predictive quality of I-Phy3

Following Pierlot et al. (2017), two tests were carried out to compare outputs of I-Phy3 418 subindicators assessing the pesticide transfer to environmental compartments with 419 measured data (RC_{sw}; RC_{sw}, RC_{air}, see section 2.3.). First, a classical correlation test 420 between indicator outputs and measurements was carried out to calculate a correlation 421 coefficient r, and not the determination coefficient r^2 . The significance of the results by 422 calculating the p-value was also tested. Then, we ran a probability test consisting in comparing 423 the rank of indicator outputs and measurements through a contingency table. A similar ranking 424 means that the result of the indicator' calculation appears to be correct while when the indicator 425 426 rank is lower than the rank of the measured value, it is considered as an underestimation and 427 when it is higher than the rank of the measured value, it is considered as an overestimation. 428 The probability considered in the test is the sum of correct and overestimation. Indeed, I-Phy 429 assesses a potential risk (which can occur or not depending on climate events for example), so the positive result considered in this test are the sum of well-predicted events of transfer 430 and overestimation. (see a theoretical example in Table 6). Pierlot et al. (2017) set the rule that 431 an indicator is considered as acceptable when the probability is higher than 60% and the 432

correct estimation is higher than 40% to avoid considering an indicator whose results would systematically predict a high risk regardless of the context. This general analysis was completed by detailing the proportion of values in each class to assess the distribution of values and to check that results are not only due to one class (*e.g.* the class no risk, no pesticide in water).

- 438 For these analyses, regarding water contamination, the following measured variables available 439 in the EQUIPE project were used:
- 440 frequency of exceedance of the threshold of the water quality standard of drinking 441 water: $0.1 \ \mu g.L^{-1}$ (fd0.1)
- 442 fd0.1= $\frac{n_{1ijk}}{n_{ijk}}$ (Equation 5)

with n1_{*}: number of measurements with concentration > $0.1\mu g.L^{-1}$ for active ingredient i on plot j at sampling time k; n_{*}: total number of measurements for active ingredient i on plot j and sampling time k. The sampling was stopped when no a.i. was detected 3 consecutive weeks and lasted one year maximum after the spraying date (Pierlot et al., 2017)

- 447
- 448
- cumulated flux of active ingredient in mg/ha (ftotal) during the measurement period
- 450 ftotal = $\Sigma(f_{ijk})$

(Equation 6)

- 451 with f_{k} : flux of active ingredient i on plot j and sampling time k; $f_{k} = c_{k}$. w_{k} with c_{k} : concentration 452 of active ingredient i on plot j and sampling time k (μ g.L⁻¹) w_{k} : water flux (drainage or runoff) 453 from plot j during sampling time k (L)
- 454
- 455
- 456

• weighted average concentration on the period in μ g/L (CMP)

- 458 $CMP = \frac{\Sigma c_{ijk} \times w_{jk}}{\Sigma w_{jk}}$ (Equation 7)
- 459 with c_{k} : concentration of active ingredient i on plot j and sampling time k (µg.L-¹)
- 460 with c_{k} : concentration of active ingredient i on plot j and sampling time k (µg.L-¹)
- 461 with w_k : water flux (drainage or runoff) from plot j during sampling time k (L)
- 462

Regarding the assessment of predictive quality for the atmospheric compartment, the 463 correlation between indicator outputs and a value calculated from measurements was 464 analyzed. Those from the REPP'AIR project were atmospheric concentrations in each site. 465 466 For a given site and year, the pesticide concentration in the sample was considered as resulting from the volatilization and drift after spraying on fields from a buffer of 1km radius 467 around the sampler. Since temporal scales differed between spraying date (day), pesticide 468 469 concentration (week) and the indicator (year), it was not possible to compare the assessment of volatilization of transfer by I-Phy calculated at field level and raw weekly concentrations. For 470 each a.i. of one site and one year, the weekly concentrations were plotted against the area 471 sprayed with a.i. during the week. The slope of the linear regression ion between concentration 472 and area was derived as a proxy of the measured volatilization risk. This means that for a given 473 474 sprayed area, the higher the slope, the higher the concentration expressing a higher volatilization. This slope was compared to the mean of the indicator weighted by sprayed area 475

476 for each a.i. and for the sampling period. In this case, we worked on a limited number of points,477 so that it was not possible to run a probability test.

478

479 **3. Results**

(Elliott et al., 2000; ERMES, 2017; Lindahl and Bockstaller, 2012; Melland et al., 2016; Roussel et al., 2000; Vereecken, 2005; van der Werf and Zimmer, 1998)⁽¹⁾(ERMES, 2017; Koller et al., 2015)⁽²⁾(Brown and van Beinum, 2009; Buczko and Kuchenbuch, 2007; Carsel et al., 1986; Mickelson et al., 2001; Pierlot et al., 2017; Strassemeyer and Gutsche, 2010; Trevisan et al., 2009; Wohlfart, 2008)
(Babroupi et al., 2010; Bockstaller et al., 2017; Poussel et al., 2000; Thiollet-Scholtus and

(Bahrouni et al., 2010; Bockstaller et al., 2017; Roussel et al., 2000; Thiollet-Scholtus and
Bockstaller, 2015; van der Werf and Zimmer, 1998; Woodrow et al., 1997)

488 (Centner, 2021; van der Werf and Zimmer, 1998) 489

3.1. Examples of calculation

I-Phy3 was calculated for 4 to 7 fields of 33 arable farms from the Champagne Crayeuse (East 491 of France) presenting diversified rotations with winter wheat, winter and spring barley, sugar 492 493 beet, potatoes, winter rapeseed, etc. for the harvest year of 2020. Figure 3 presents three 494 levels of results. From the top, at a first level, results for different level of intensity are shown 495 in for winter barley. They vary between 10and 2.5 for an intensive program with the herbicide chlortoluron. This active ingredient presents a high risk for groundwater as shown at the 496 497 second level. Finally, explanation can be found at the third level. Chortoluron has very unfavorable property regarding the GUS, the soil is sensitive to leaching and spraying period 498 in autumn are unfavourable because the soil becomes wet. 499

500

501 Tables at second and third levels on Figure 3 were directly taken from the Excel calculator presenting the results of the final indicator and its sub indicators (see Figure 1). A continuous 502 503 colour code is used to provide information on the level of risk. Results of the sub indicators (e.g. RCeso,) are completed with the membership degree of each variable to the favourable 504 505 set (F), (see Supplementary 2). When this value was equal to 1, the variable is totally favourable, i.e. it does not present a risk for the environment. This helps identify the ones which 506 507 influence the calculated risk and by this way can help users to identify levers to improve the indicator and to reduce risk on the environment. 508

509 The example shows the ability of the indicator to differentiate crop management with different 510 level of intensity as well as risk level between active ingredients, and the possibility to explain 511 the results.

512

3.2. Predictive quality of contamination risk subindicators

514

3.2.1. Predictive quality assessment for the water compartment

Table 7 shows that the highest correlation between measured data in the fourth studied sites (one for each transfer pathway) and the outputs of the risk of contamination indicator for ground or surface water were obtained for the frequency of exceeding the threshold of the water quality

standard of drinking water (fd0.1), with value of correlation coefficient close to 0.50 (see 519 Supplementary Materials S12) and even more for RC_{surf}at Geispitzen. (r=0.66). Such values of 520 r are close to those found by Pierlot et al; (2017) for indicator with the same degree of 521 complexity. These results are better for three sites or equal for one site (Jaillière runoff) than 522 523 those of the previous versions of I-Phy. The comparison between either the cumulated flux of 524 active ingredient in mg.ha, (ftotal) during the measurement period or the weighted average concentration on the period in µg.L⁴ (CMP), and outputs of the indicator yielded lower value of 525 526 coefficient between 0.08 and 0.35. For the site of Magneraud (leaching) and Geispitzen (hortonian runoff), the new version yielded better value of correlation coefficients than the 527 528 previous one, which however remain at a lower level than for fd0.1, and much lower than 0.50.

The probability test reveals that the risk of contamination indicator for ground or surface water 529 530 yielded results meeting the criteria set for the test for fd0.1 and CMP for the fourth studied sites (except for the site of Geispitzen for fd0.1). (Table 8). For ftotal, the only test meeting the 531 criteria set was for the site of Le Magneraud with a probability of 68% and correct estimation 532 of 49%. In comparison with the previous version of I-Phy, the new one obtains better results 533 534 than I-Phy2 for the three sites of La Jailliere runoff, Le Magneraud and Geispitzen for all the tests, especially for the correct estimations. Compared to I-Phy1, I-Phy3 obtained better results 535 for the sites of Le Magneraud and Geispitzen for all the measured data whereas it surpassed 536 only for CMP for the site of La Jailliere runoff. From the analysis of the cases showing the 537 538 highest discrepancy (Table 9), it came out that 3 a.i. play a major role: epoxiconazole, diflufenican and isoproturon explain 35 cases out of 50. 539

540

541 **3.2.2. Predictive quality assessment for the air compartment**

Figure 4 shows a relatively clear correlation with a r of 0.73 between the slope coefficient of 542 the cumulative fluxes of a.i. and the means of risk of air contamination by volatilization (RCair_w). 543 544 this for only 12 a.i. for which there was enough data on the studied sites. Such a value is 545 satisfying regarding the elaboration degree of the indicator and when they are compared to the 546 coefficient for transfer to water. Nevertheless, unlike the risk of ground or surface water contamination, the outputs of risk of air contamination were not compared directly to 547 548 contamination measurements at plot scale but to a calculated value derived from measurements at a larger scale. 549

550

551

552 **4. Discussion**

553

4.1 Originality of the I-Phy3 indicator

I-Phv3 can be classified in the same class as I-Phv1 and I-Phv2 in the typology proposed by 554 Pierlot et al. (2017) classifying pesticide indicators assessing transfer risk to water in function 555 of their design. They are calculated with pesticide properties and use data, crop management 556 557 and field data (soil, slope, etc.). It does not only consist in a simple scoring of variables according to expert opinion or an aggregation separating risk linked to pesticide properties, 558 and risk linked to soil and climate. Variables are integrated according to knowledge on 559 processes, with some calibration procedure for some subindicators. Furthermore, through the 560 561 decision rules, calculations seem to be more easy to grasp than indicators based on quantitative equations like EPRIP2 (Trevisan et al., 2009), POCER (Vercruysse and Steurbaut, 562 2002) or SYNOPS (Strassemeyer and Gutsche, 2010). Regarding integration of toxicity 563 variables, those are aggregated in a qualitative way with transparent assumption in I-Phy3, 564

while in EPRIP2, SYNOPS or POCER, a risk ratio (concentration in the environment 565 566 compartment/concentration threshold for toxicological effect in this compartment) is used resulting in a quantitative assessment. Exposure of living beings to pesticide is assessed with 567 more precision in POCER or in models used in Life Cycle Analysis (Gentil et al., 2020) taking 568 into account behavior of target living beings (e.g. for the ingestion exposure pathway) than in 569 570 the other indicators. Regarding I-Phy3, a sub indicator assessing exposure and effect may be developed in the future by a separated decision tree and aggregated at the second level with 571 572 risk of contamination (RC) replacing the aggregation of RC with a toxicity variable (Figure 1). A work is ongoing on pesticide effects on human health taking into account variables and 573 knowledge inputs from the POCER indicator (Vercruysse and Steurbaut, 2002) and the more 574 elaborated Browse model (Butler Ellis et al., 2017). 575

576

Aggregation procedure using fuzzy decision tree is also very original in comparison with other 577 indicators as pointed out by several authors (Feola et al., 2011; Keichinger et al., 2013; Maud 578 579 et al., 2001; Reus et al., 2002). This aggregation method presents different advantages like the readability through linguistic rules, the possibility to cope with qualitative and quantitative 580 variables. the mitigation of threshold effect, section 2.2. For I-Phy3, the CONTRA method 581 (Bockstaller et al., 2017) was implemented to design fuzzy decision tree in order to enhance 582 583 transparency of the aggregation procedure. This confers a supplementary advantage to the 584 aggregation method. while aggregation is often criticized for а lack of transparency. However, calculation of final result for a given decision tree may remain a "black 585 box" without additional information of intermediate calculation (Bockstaller et al., 2017). This 586 587 problem was partially solved as discussed further in section 4.4. 588

589 **4.2. Novelties of I-Phy3 compared to the previous versions**

590

The structure of I-Phy3 was totally changed compared to the initial version (van der Werf and Zimmer, 1998) with the addition of a third level making it possible to deliver an assessment of the contamination risk disconnected from the toxicity of the pesticide. Contamination of environmental compartments is of major concern for many stakeholders working on water quality management due to the current drinking water standards based on a concentration threshold of 0.1 μ g.L⁻¹ independently from toxicity. This supplementary level may confer more complexity to the indicator but this might not be a problem (see section 4.4.).

598

599 We tried to integrate more processes into the design of I-Phy3 to consolidate the scientific basis. Nevertheless, the metamodelization approach derived from the mechanistic MACRO 600 601 model and implemented for the groundwater sub indicator in I-Phy2 was left. I-Phy2 version did not yield satisfying results regarding its predictive quality for pesticide leaching (see Table 602 603 7). This discrepancy may be due to a parametrization of MACRO which did not deliver better results for 6 out 7 parameter sets in the study of Pierlot et al. (2017). The new ground water 604 605 subindicator based on a simpler structure than this of I-Phy2 yielded better validation results 606 than I-Phy2 and slightly better results than I-Phy1.

The runoff surface water subindicator had already been improved in the second version 607 (Wohlfahrt, 2008). Besides the interception coefficient used for all indicators (ic, see Equation 608 4), it is the only subindicator that entails the temporal dimension in an explicit way in the 609 610 availability variable (see Equation 2). Nevertheless, for most usage, this temporal variable 611 giving the time between spraying and variable is set to 3 days, which is a worst-case value like 612 in other indicators like Synops (Strassemeyer et al., 2017) and Eprip2 (Trevisan et al., 2009). After all, it is still possible in the calculator to change the value and to make the indicator more 613 sensitive to the spraying date and the delay with the transfer event (*i.e.* significant rain). The 614 other subindicators were totally changed with additional information required, especially on 615 spraying conditions for spray drift to air and physical conditions of field margins. It was 616

assumed that information on spraying conditions and field margins characteristics are easily

- 618 accessible too.
- 619

Effect of tillage and pesticide incorporation were better integrated in the new version of I-Phy by means of a much broader knowledge basis than for the previous version of I-Phy. Now the effect was quantified more precisely than with a rough "expert value", especially for effect of tillage on runoff (meta-analysis of Elias, Wang, et Jacinthe (2018)). Such meta-analyses would be useful to parametrize the effect of tillage on vertical transfer and the effect of pesticide incorporation, for which some experimental results exist but remain fragmentary.

626

In I-Phy1, the effect of pesticide dose was assessed separately from the risk on environmental 627 compartment, the latter including the effect of crop interception. Like in I-Phy2, pesticide dose 628 and crop interception were combined since the amount that can be transferred from soil 629 surface to water is not the sprayed dose but depends on the interception by crop canopy. 630 631 Although a part of this amount intercepted by crop canopy can be washed off, we considered 632 like Rosenbaum et al. (2015) that in good practices conditions, pesticides are not sprayed just before an important rainfall so that this fraction can be neglected in this approach. This 633 integration makes it possible to avoid giving systematically a favorable value to pesticide rate 634 with low application rate like it was the case in I-Phy1. As shown in Lopez et al. (2015) for 635 metsulfuron-methyl as well as in the ERMES monitoring program for nicosulfuron, sulfonyl-636 637 urea herbicide sprayed at low rate (less 50 g/ha) are detected in groundwater and sometimes 638 at concentration exceeding quality water standards (Koller et al., 2015). With the new calculation method, even for low a.i. application rates, unfavorable values for risk of 639 640 contamination subindicators may be found.

641

642 **4.3 Design of the indicator**

643

The indicator relies on an approach combining a qualitative (decision tree) with a quantitative 644 645 approach (fuzzy subsets) which present several advantages as pointed out previously. But the 646 outputs of the indicators are not expressed in quantitative physical or ecotoxicological values. 647 In particular, the indicator does not deliver quantitative information on contamination levels in the environmental compartment, so that stakeholders have no information on the exceeding 648 of given standards like this for drinking water. This would require quantitative models which 649 are in most cases complicated to implement due to the type and amount of data required a 650 calibration procedure to carry out carefully to avoid false prediction as pointed out by Pierlot et 651 al. 2017 for MACRO. Another drawback of quantitative models is their reduced scope to one 652 653 or two environmental compartments. PestLCI 2.0 is an exception by covering the same compartments as I-Phy3 (Dijkman et al., 2012) and providing percentages of emissions from 654 655 the initial rate in each compartment. However, it does not calculate concentration in the 656 environment and is only for about 100 active ingredients in comparison with about 500 for I-657 Phy3.

658

659 In the assessment of the pesticide transfer pathways by many indicators, climate variables are 660 not directly included although variables like especially rainfall amount plays a significant role in pesticide transfer (Baran et al., 2021). This would require additional data and may complexify 661 662 calculations. One way would be to integrate them in the leaching and runoff potential variable 663 in function of location and even of the year. This is possible manually in the calculator for dry year; for example, it is easy to change the value into 0 (low potential). But adding an actual 664 value of the year may hide the effect of change of practice which is not the objective of the 665 indicator. Furthermore, intra annual effects of climate are taken into account by the period of 666 application according to the recommendation of Pierlot et al. (2017) for the groundwater 667 subindicator or by the availability variable (see Equation 5 for the surface subindicator). But in 668 case of transfer to air, climate is not included at all, neither for spray drift or volatilization. Wind 669

speed, a major driver for transfer to air (Lavin and Hageman, 2013), remains too difficult to getfor each treatment. Introducing such a variable would be an avenue for progress.

672

673 I-Phy3 like PestLCI 2.0 did not address contamination of soil by pesticides although several recent studies revealed a "hidden reality" of pesticide in soils (Riedo et al., 2021; Silva et al., 674 2019), especially for glyphosate (Silva et al., 2018), even in organic farming (Riedo et al., 675 676 2021). Furthermore, these last authors found a negative relation between the amount of pesticide residue in soil and microbial biomass and specifically the abundance of arbuscular 677 678 mycorrhizal fungi, a widespread group of beneficial plant symbionts likewise other parameters of soil biological activities (Wołejko et al., 2020). The lack of a soil subindicator was due to 679 680 knowledge gaps which these recent studies tend to bridge. Besides the issue of soil pesticide 681 residues in terms of amount and concentration, another aspect concerns the temporal dimension which should be included in future. Although a part of an active ingredient is 682 adsorbed in an irreversible way in the form of non-extractable bound residues (bounsten) 683 684 another non-negligible part may be released after several months (Suddaby et al., 2016). Furthermore, the cumulative effect of repeated treatments should also be addressed. 685 686

687 Last, the contamination by metabolites released by the degradation of active ingredients 688 should also be assessed (Baran et al., 2021) as it has been pointed out by pioneer studies (Dana W. Kolpin et al., 2000; D.W. Kolpin et al., 2000). But the integration of such an 689 690 assessment would probably complexify the indicator, exceeding an acceptable level. This 691 would require guantitative knowledge on the nature of the metabolite formed, the percentage of a.i. transformed in this product, properties (KOC, DT50, etc.), etc., data that does not 692 693 currently exist in databases. except for recently marketed a.i. (Lopez et al., 2015). In any case, some available information on metabolites was added indirectly in the database. For example, 694 695 in case when an active ingredient is rapidly degraded in its metabolites, (e.g. different form in 696 glyphosate acid, iodosulfuron-methyl in metsulfuron-metyl), properties of the metabolite are 697 attributed to a.i. For few pesticides like metazachlore, dimetolachlor (see Supplementary Materials S1), selected values for DT50 appear to be too favourable while they present 698 699 metabolites susceptible to be transferred to water bodies (Reemtsma et al., 2013). In this case 700 we decided to attribute a more unfavorable value to the DT50 of this active ingredient.

701 **4.4 Predictive quality**

Datasets used to assess the predictive quality of the water contamination risk were consequent. This was also the case for the air component in this study with several sites over the country and a 3 years campaign. Nevertheless, as pointed out by Pierlot et al. (2017), the effort should be pursued. Ideally, this work would require a broader combination of soil type, slopes and climatic conditions, and much more new active ingredients.

708

The simplification performed in the design of I-Phy3 may explain the mixed results in the validation test. Indeed, the compromise between accessibility of data and explanation of mechanical processes leads us to ignore some variables like soil moisture, which is important to explain transfers in pathway like agricultural drainage (Guimont et al., 2005) or wind speed as explained above. It was considered that the additional cost for collecting usable data does not compensate by loss of information for I-Phy3. Furthermore, these data are useful on a time step of a few days when I-Phy3 estimates transfer risk at the scale of the growing season.

716

The results obtained for I-Phy3 were overall better than those obtained with the previous versions. If the values of correlation coefficient are not always good, the results in the probability test are satisfying, particularly for the frequency of exceeding the threshold of the drinking water quality (fd0.1), particularly important for the stakeholders. The result of the test combines acceptable and overestimation of risk. Thus, it shows the ability of the indicator to assess a potential contamination which could or not be observed, depending on other factors like climate. Unacceptable underestimations were observed for one site at la Jaillière runoff dataset. It was showed that 3 a.i. (isoproturon, diflufenican and epoxiconazole) play a major
role in this underestimation. On this site, runoff was mostly to overland flow due to saturation
of the soil profile, a process which may be poorly covered by the indicator.

727 728

729 **4.5 Utilization**

730

The design of the I-Phy 3 indicator was not intended to be used directly by farmers themselves, 731 732 although this may be possible if farmers have time and support to interpret the results. It rather targets advisers trained by scientists who may deliver interpreted results to feed the 733 734 recommendations to farmers in addition to technical advice. The statement of Box (1976): "all models are wrong but some are useful", may be applied to I-Phy3. In spite of its mixed results 735 regarding its predictive quality, it may be used beyond the simple results obtained by the 736 737 indicator. Indeed, it makes possible initiation of discussion on pesticide use strategies with farmers integrating environmental aspects provided by the indicator and other aspects 738 (economic, management of weed and pest resistance, ...) not considered by the indicators. 739 Furthermore, if it does not give a precise value, it provides a positioning to some threshold, 740 like for instance to classify results in three classes (acceptable/mixed/unacceptable). But in 741 742 this case, we reintroduce a threshold effect that was avoided by the design method (see section 2.2.). This is also the case with quantitative mechanistic models as PEARL (Tiktak et 743 744 al., 2012) which deliver continuous values but can be presented in class when they are mapped 745 for stakeholders.

746

747 For the council advice, as stated by Bockstaller et al. (2008), both aggregated indicators and 748 non-aggregated sub-indicators have to be used in parallel. The aggregated I-Phy indicator may be associated with other sustainability indicators in a global assessment when there is a need 749 to reduce the number of indicators. In this case, non-aggregated subindicators should 750 complete and explain the global value in the analysis. The aggregated I-Phy indicator may also 751 752 serve to rank pesticides when all the environmental issues are considered by stakeholders while a non-aggregated subindicators, especially risk of contamination indicators may be 753 754 implemented by stakeholders dealing with one environmental compartment (e.g. 755 groundwater).

756

757 Currently the indicator is calculated with the help of an Excel sheet calculator, which facilitates its implementation because the software is a basic software on most of the users' offices. The 758 759 tool is transparent for the user, who can see all the decision rules. The problem is that it may also lead to misuse because the user can potentially and accidentally change the decisions 760 rules. This can be solved by protection of some cells. However, misuse also occurs in copying 761 762 and pasting lines, deleting formulas in the cell. To mitigate the problem, we can imagine a further online-version of the tool with data fields to be completed and calculations of the 763 764 different sub-indicators provided. In any case, the tool should remain transparent and not only provide calculation results but also the intermediate values to interpret them and identify the 765 766 variable(s) which plays the major role in the determination of the risk.

767

Last but not least, the I-Phy indicator is designed to predict the risk of pesticide transfer at field 768 769 level. Some of the stakeholders need to assess the risk of transfer at a higher level like a watershed or an administrative region (i.e. the managers of the Water Agencies in France or 770 the advisers in charge of water catchments). Some previous research work ((Wohlfahrt et al., 771 772 2010) shows that the contribution of the different plots to the watershed depends on the size of the plot in comparison to the size of the watershed and the distance and the connectivity 773 774 between the plot and the hydrological network. To simplify the use of the indicator at watershed scale and because they have no precise information about the real water flows in the 775 watershed, advisers consider only the size of the plot in comparison to the size of the 776 777 watershed. Another approach is to map the distribution of the indicator values set in small

classes like a 3 levels scale as traffic lights without any spatial aggregation, as discussed atthe beginning of this section.

780

781 **5.** Conclusion

This new version of the I-Phy indicator and its subindicators provides major changes in 782 comparison with previous versions, to better integrate processes of transfer of the pesticides 783 to the environmental compartment. The separation between contamination and toxicity, as well 784 as the transfer pathways are some examples to meet requirements of potential users like 785 786 adviser or stakeholders. For the air compartment, a spray drift subindicator was added but like previous versions, whereas soil is still not addressed by this indicator, partially due to 787 788 knowledge gaps. With the increasing focus on this compartment in publications, this gap is about to be filled and an addition of a new subindicator will be possible. While the effect of 789 degradation products of the a.i. is covered by I-Phy3 in an indirect way, their risks should be 790 791 covered in an explicit way to meet social concern for this issue. Last, the effort to assess the 792 predictive quality of the indicator should be pursued and should be completed by a feasibility 793 and utility test among end-users. This new version should still be confronted with other 794 datasets including recent active ingredients with the aim of improving the predictive quality.

795

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- 803
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Table 1: Snapshot of CONTRA "decision tree" tab (Bockstaller et al., 2017), showing the 1035 1036 decision tree design of the subindicator, pesticide leaching risk of contamination (RCgw_{Int}). The groundwater ubiquity index (GUS), the application period (Appli), the leaching potential of soil 1037 (LixPot) and the solubility of the active ingredient in water (Solu) were aggregated with 1038 respectively a weight of 40% for GUS and 20% for the three other variables, giving the 1039 calibrated RCgw_{in} expressed between 0 (high risk) and 10 (low risk). Some modifications were 1040 given to the decision rules yielding the final RCgw_{in} according to the explanations given in the 1041 last column. Input variables belong either to the favourable set (F) or to unfavourable set (U), 1042 1043 (see Table S3).

1044

| GUS | Ap pli | LeaPot | Solu | Calibrated RCgwlea | Correction (absolute value) | Fin al RCgw _{tea} | Explanation on correction |
|-----|--------|--------|------|-----------------------|-----------------------------------|----------------------------|---|
| F | F | F | F | 10,0 | | 10,0 | |
| F | F | F | D | 8,0 | 1 | 9,0 | if GUS is favourable, effect of solubility is reduced |
| F | F | D | F | 8,0 | | 8,0 | |
| F | F | D | D | 6,0 | 1 | 7,0 | if GUS is favourable, effect of solubility is reduced |
| F | D | F | F | 8,0 | | 8,0 | |
| F | D | F | D | 6,0 | 0,5 | 6,5 | if GUS is favourable, effect of solubility is reduced |
| F | D | D | F | 6,0 | | 6,0 | |
| F | D | D | D | 4,0 | | 4,0 | |
| D | F | F | F | 6,0 | -0,5 | 5,5 | If GUS is unfavourable, risk is increased to avoid a similar results with previous lines |
| D | F | F | D | 4,0 | 0,5 | 4,5 | If praying period is favourable (dry soil), risk is reduced |
| D | F | D | F | 4,0 | 0,5 | 4,5 | If praying period is favourable (dry soil), risk is reduced |
| D | F | D | D | 2,0 | 0,5 | 2,5 | If praying period is favourable (dry soil), risk is reduced |
| D | D | F | F | 4,0 | | 4,0 | |
| D | D | F | D | 2,0 | | 2,0 | |
| D | D | D | F | 2,0 | | 2,0 | |
| D | D | D | D | 0,0 | | 0,0 | |

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Table 2: Decision tree of the subindicator, pesticide runoff risk of contamination (RCsw_a) in case for runoff. RuPot is the runoff potential and Avai is the availability of the pesticide (see Equation 5). Input variables belong either to the favourable set (F) or to unfavourable set (U), (see Table S3).

1051

| RuPot | Avai | RCsw _{r/d} |
|-------|------|---------------------|
| F | F | 10 |
| F | U | 5.5 |
| U | F | 6.7 |
| U | U | 0 |

1052

1053 Table 3: Snapshot of CONTRA "decision tree" tab (Bockstaller et al., 2017), showing the 1054 decision tree design of the subindicator, risk of air contamination by drift (RCair_d). The type of 1055 sprayer (Sprayer), the speed sprayer (Speed), the sprayer height (Height), the use of antidrift

- nuzzle (Nuzzle) and the air pressure (Pressure) were aggregated with the same weight of 20%
- for all variables, giving the calibrated RCair_{a_1} expressed between 0 (high risk) and 10 (low risk). Some modifications were given to the decision rules yielding the final RCair_{$a_1} according to the$ explanations given in the last column. Input variables belong either to the favourable set (F) or</sub>

1060 to unfavourable set (U), (see Table S3).



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Table 4: Snapshot of CONTRA "decision tree" tab (Bockstaller et al., 2017), showing the 1064 decision tree design of the subindicator, pesticide risk for surface water (I-Phy_{ss}). The 1065 1066 contamination risk for surface water through drainage or runoff (RCswation), the contamination risk for surface water through drift (RCswa), and the toxicity variable for aquatic organisms 1067 (TOX) were aggregated with respectively a weight of 33%, giving the calibrated I-Physw 1068 expressed between 0 (high risk) and 10 (low risk). Some modifications are given to the 1069 decision rules yielding the final I-Phy_{se} according to the explanations given in the last column. 1070 Input variables belong either to the favourable set (F) or to unfavourable set (U), (see Table 1071 1072 S3).

| RC sw _{t/d} | RCsw _{dr} | Тох | Calibrated I-Phy _{sw} | Correction (absolute value) | Final I-Phy _{sw} | Explanation on correction |
|----------------------|--------------------|-----|-----------------------------------|-----------------------------------|------------------------------|---|
| F | F | F | 10 | | 10 | |
| F | F | U | 6 | | 6 | |
| F | U | F | 7 | | 7 | |
| F | U | U | 3 | -1 | 2 | Transfer for one pathway and toxicity unfavourable: decrease of 1 point to highlight the unacceptable situation for stakeholder |
| U | F | F | 7 | | 7 | |
| | - | | 2 | -1 | 2 | Transfer for one pathway and toxicity unfavourable: decrease of 1 point to highlight the unacceptable situation for stakeholder. |
| | - | | 3 | -1 | 2 | stakenoroer |
| 0 | U | F | 4 | | 4 | |
| U | U | U | 0 | | 0 | |

1074

Table 5: Snapshot of CONTRA "decision tree" tab (Bockstaller et al., 2017), showing the 1075 decision tree design calculating the final I-Phy indicator. The subindicators assessing the risk 1076 for three environmental compartments, pesticide risk respectively for groundwater (I-Phy_w), for 1077 1078 surface water (I-Phy_s) and for air (I-Phy_s) were aggregated with the same weight of 33%, giving the calibrated I-Phy expressed between 0 (high risk) and 10 (low risk). Some modifications 1079 were given to the decision rules yielding the final I-Phy according to the explanations given in 1080 1081 the last column. Input variables belong either to the favourable set (F) or to unfavourable set 1082 (U), (see Table S3). Membership functions are sinusoidal.

| I-Phy _{gw} | I-Phy _{sw} | I-Phy _{air} | Calibrated I-Phy | Correction (absolute value) | Final I-Phy | Explanation on correction |
|---------------------|---------------------|----------------------|---------------------|-----------------------------------|----------------|---------------------------|
| F | F | F | 10 | | 10 | |
| F | F | U | 6.7 | -0.7 | 6 | To set at 6 |
| F | U | F | 6.7 | -0;7 | 6 | To set at 6 |
| F | U | U | 3.3 | -1.3 | 2 | To set at 2 |
| U | F | F | 6.7 | -0.7 | 6 | To set at 6 |
| U | F | U | 3.3 | -1.3 | 2 | To set at 2 |
| U | U | F | 3.3 | -1.3 | 2 | To set at 2 |
| U | U | U | 0 | | 0 | |

1083

Table 6: theoretical example of probability test comparing classes of an indicator (in colum, class 5 shows a higher value effect than 1) with a measurement (increasing values show a higher effect). The probability is the sum of correct estimation (cases colored in green) and overestimation (cases colored in blue). The cases colored in brown are considered as underestimation.

| | | Result of measured data (in class) | | | | | | | | | | |
|--------------------------------------|-----------------|------------------------------------|------------------|------------------|-------------------|--|--|--|--|--|--|--|
| Result of Indicator (in class) | From 0 to 20 | From 20 to 40 | From 40 to 60 | From 60 to 80 | Fomr 80 to 100 | | | | | | | |
| From 8 to 0 | 20 | 8 | 8 | 9 | 2 | | | | | | | |
| From 6 to 8 | 16 | 5 | 11 | 11 | 35 | | | | | | | |

| From 4 to 6 | 3 | 1 | 12 | 22 | 3 |
|-------------|----|---|----|----|---|
| From 2 to 4 | 23 | 0 | 0 | 1 | 5 |
| From 0 to 2 | 4 | 0 | 1 | 0 | 2 |

- 1092 Table 7: correlation test between the measured data of the 3 sites and 4 transfer pathway
- and the concerned subindicator RC for the 3 versions of I-Phy. The results are in bold when
- subindicators of I-Phy3 performs better than in the previous versions.

| Component of | l- | Transferenthway | | fd0.1 | | | ftotal | | | CMP | | |
|--------------|--------------|-------------------|--------|---------|---------|---------|---------|---------|--------|---------|---------|--|
| Phy | Site | Transfer patriway | I-Phy3 | I-Phy 1 | I-Phy 2 | I- Phy3 | I-Phy 1 | I-Phy 2 | I-Phy3 | I-Phy 1 | I-Phy 2 | |
| RC gw-lea | La Jaillière | Drainage | 0.48 | 0.36 | 0.24 | 0.35 | 0.49 | 0.19 | 0.35 | 0.41 | 0.13 | |
| RC sw-r/d | La Jaillière | Saturation runoff | 0.49 | 0.44 | 0.49 | 0.27 | 0.26 | 0.28 | 0.32 | 0.38 | 0.31 | |
| RC sw-r/d | Geispitzen | Hortonien runoff | 0.66 | 0.31 | 0.32 | 0.15 | -0.15 | -0.04 | 0.35 | 0.21 | 0.34 | |
| RC gw-lea | Le Magneraud | Leaching | 0.46 | 0.3 | -0.17 | 0.17 | 0.05 | -0.11 | 0.08 | -0.01 | -0.09 | |

- 1099 Table 8: probability test (see Figure 2) for the 3 sites and 4 transfer pathways for each
- 1100 concerned subindicator RC (see Figure 3), comparing to the measured transfer of active
- ingredient In blue the probability is over 70%, in yellow, the probability is between 50% and70% and in red, between 40% et 50%



- ----

1134 Table 9: detailed probability test (see Figure 2) for the site of La Jaillière runoff for the frequency

| 1135 | of excee | of exceedance of the threshold of $0,1\mu g.L^{-1}$). | | | | | | | | | | | | |
|------|----------|--|----|----|----|-----|--|--|---|--|--|--|--|--|
| | | Fd 0.1 (%) | | | | | | | | | | | | |
| | Class | 20 | 40 | 60 | 80 | 100 | | | n | | | | | |

| | Class | 20 | 40 | 60 | 80 | 100 | | n | % |
|------|-------|----|----|----|----|-----|---------------------|-----|-----|
| | 1 | 80 | 8 | 8 | 9 | 14 | Correct | 90 | 43% |
| | 2 | 16 | 8 | 11 | 11 | 27 | overestimation | 20 | 10% |
| | 3 | 3 | 1 | z | 1 | 3 | underestimation | 97 | 47% |
| | 4 | 0 | 0 | 0 | 0 | 5 | Total | 207 | |
| 1136 | 5 | 0 | 0 | 0 | 0 | 0 | | | |
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| 1139 | | | | | | | | | |
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| 1140 | | | | | | | | | |
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| 1141 | | | | | | | | | |
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| 1142 | | | | | | | | | |
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Figure 1: Overview of the calculation of I-Phy3 with three levels of aggregation and main input variables, in blue pesticide properties, in red soil and topographic variables, in green: management variable (KOC: adsorption coefficient, DT50: half-life, Solubility: solubility in water, Ps: vapor pressure, LogKow: logarithm of the octanoal-water coefficient, time: time between spraying and runoff event). For each aggregation, a fuzzy decision tree (see Figure S2) was implemented with information on fuzzy subsets linked to each variable given in Table S2.



1154 1155 Figure 2: Repartitions of the sites used to assess predictive quality. With red bullet: sites for water quality and with blue bullets: sites for air quality 1156

| Year | Crop | Active ingredient | Corrected rate (g/ha) | % treated area | I-Phy | I-Phygw | RCgw | I-Physw | RCsw-rd | RCsw-dr | I-Phyair | RCair-vol | RCair-dr |
|------|---------------|----------------------|-----------------------------|----------------------|-------|---------|------|---------|---------|---------|----------|-----------|----------|
| 2020 | Spring barley | 2,4-MCPA | 150 | 100 | 4.6 | 4.3 | 3.6 | 6.9 | 6.6 | 10.0 | 4.7 | 6.1 | 4.9 |
| 2020 | Spring barley | clopyralid | 15 | 100 | 7.8 | 6.5 | 5.6 | 9.0 | 8.6 | 10.0 | 8.2 | 10.0 | 6.9 |
| 2020 | Spring barley | fluroxypyr | 30 | 100 | 9.0 | 8.8 | 7.0 | 9.1 | 8.5 | 10.0 | 8.8 | 10.0 | 5.8 |
| 2020 | Spring barley | éthéphon | 24 | 100 | 8.2 | 9.0 | 10.0 | 8.4 | 8.6 | 10.0 | 7.2 | 9.2 | 5.8 |
| 2020 | Spring barley | prothiocona zole | 13 | 100 | 8.3 | 9.0 | 10.0 | 8.2 | 10.0 | 10.0 | 7.7 | 10.0 | 6.9 |
| 2020 | Spring barley | fluoxastrobi ne | 6 | 100 | 7.1 | 8.3 | 10.0 | 7.3 | 9.5 | 10.0 | 7.4 | 10.0 | 7.4 |

| RCgw (weighted by treated area) | GUS | Applicati on period (day num ber) | Potential of leaching | ıl Solubility S | | |
|---------------------------------------|------|---|-----------------------------|-----------------------|--|--|
| 3.6 | 0.00 | 0.56 | 0.10 | 0.00 | | |
| 5.6 | 0.00 | 0.56 | 0.10 | 0.00 | | |
| 7.0 | 0.31 | 0.56 | 0.10 | 0.00 | | |
| 10.0 | 1.00 | 1.00 | 0.10 | 0.00 | | |
| 10.0 | 1.00 | 1.00 | 0.10 | 1.00 | | |
| 10.0 | 0.98 | 1.00 | 0.10 | 1.00 | | |



- Figure 3: the detail for one subindicator RCeso. The membership degrees of the input variables show to which extent the variable is unfavourable (close to 0) or favourable (close to 1) and
- 1168 plays a role in the determination of the risk.



Figure 4: correlation between the slope coefficient of the cumulative fluxes of a.i. used as a proxy of volatilization risk (see SM XX) and the means of RC_{vol} for 12 a.i.