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1 **Operational integration of time dependent toxicity impact category in dynamic LCA**

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11 **Abstract**

12 Life Cycle Assessment (LCA) is the most widely used method for the environmental evaluation
13 of an anthropogenic system and its capabilities no longer need to be proved. However, several
14 limitations have been pointed out by LCA scholars, including the lack of a temporal dimension.
15 The objective of this study is to develop a dynamic approach for calculating the time dependent
16 impacts of human toxicity and ecotoxicity within LCA. A new framework is proposed, which
17 includes dynamic inventory and dynamic impact assessment. This study focuses on the
18 dynamic fate model for substances in the environment, combined with the USEtox[®] model for
19 toxicity assessment. The method takes into account the noisy and random nature of substance
20 emissions in function of time, as in the real world, and uses a robust solver for the dynamic
21 fate model resolution. No characterization factors are calculated. Instead, a current toxicity is
22 calculated as a function of time i.e. the damage produced per unit of time, together with a time
23 dependent cumulated toxicity, i.e. the total damage produced from time zero to a given time
24 horizon. The latter can be compared with the results obtained by the conventional USEtox[®]
25 method: their results converge for a very large time horizon (theoretically at infinity). Organic
26 substances are found to disappear relatively rapidly from the environmental compartments (in
27 the time period in which the emissions occur) while inorganic substances (i.e. metals) tend to
28 persist far beyond the emission period.

29

30 **Keywords:** dynamic Life Cycle Assessment, fate model, toxicity, ecotoxicity

31

32 **Highlights:**

- 33 • A method is proposed for calculating time dependent toxicity and ecotoxicity.
- 34 • Resolution of the dynamic fate model is combined with the USEtox[®] toxicity model.
- 35 • A current toxicity and a cumulated toxicity are calculated in function of time.
- 36 • The dynamic toxicity calculation is integrated in a dynamic LCA framework.

37

38

39 **1. Introduction**

40 Life Cycle Assessment (LCA) is a method that calculates potential impacts associated with
41 products, processes and services over their entire life cycle. ISO standards 14040-14044
42 specify the guide for conducting a LCA study, i.e. the four operational steps: the definition of
43 the goal and scope, the construction of the Life Cycle Inventory (LCI) based on mass and
44 energy balances over the whole system life cycle, the Life Cycle Impact Assessment (LCIA)
45 based on various impact calculation models, and the interpretation step (ISO, 2006a; ISO,
46 2006b). Currently LCA is the most widely used methodology for evaluating the environmental
47 performance of any anthropogenic system. Its capabilities no longer need to be proved but
48 several limitations have been pointed out by LCA scholars. Among them, the lack of a temporal
49 dimension is intrinsically related to the LCA background. In a state of the art review,
50 Finnveden et al. (2009) argued that “the LCI results are also typically unaccompanied by
51 information about the temporal course of the emission or the resulting concentrations in the
52 receiving environment... The impacts, which can be calculated under such boundary
53 conditions, thus represent the sum of impacts from emissions released years ago, from

54 emissions released today and from emissions released sometime in the future.” Here, two
55 levels can be distinguished, which are related to the LCI and LCIA calculation steps in LCA.

56 Another time dependent aspect concerns the prospective evolution of systems over time, e.g.
57 changes at the level of technologies or economic sectors. Such issues are resolved either by
58 considering different scenarios at different time periods or by a radically different methodology
59 i.e. Consequential LCA. This aspect is beyond the scope of this work, which focuses on the
60 time dependency of inventory and impacts in Attributional LCA. Including the time dimension
61 in LCA models is a challenge that has been taken up only recently and very little research is
62 currently in progress.

63 The time dimension in the LCI step has been studied by Beloin-Saint-Pierre et al. (2014).
64 These authors developed an approach called Enhanced Structure Path Analysis, in which
65 environmental interventions (elementary flows, i.e. emissions and natural resources
66 consumed) are distributed over time by considering the convolution product between temporal
67 distributions related to the processes flows and temporal distributions related to elementary
68 flows. However, this method still lacks a full and complete relationship with an LCA database.

69 To the best of our knowledge, only Tiruta-Barna et al. (2016) have provided a dynamic method
70 for LCI, dealing with the complex supply chain and processes presented in an LCA study and
71 linking the method to traditional LCA tools (databases). It enables easier implementation of
72 temporal characteristics by LCA practitioners. In a recent study, Shimako et al. (2016) applied
73 this method to bioenergy production from microalgae by calculating temporal LCI and coupling
74 them with a temporal model of climate change.

75 In fact most studies dealing with temporal aspects in LCA are dedicated to climate change
76 impact. For example, Cherubini et al. (2011) performed a calculation considering dynamic
77 carbon removal by the biomass, which is a step prior to the calculation of the climate change
78 impact. However, dynamic results for midpoint or endpoint climate change impact are not given
79 as the calculated results are integrated in a single unit-based index. Levasseur et al. (2010)

80 and Kendall (2012) studied time dependency in climate change impact by calculating temporal
81 characterization factors (CF) for substances and applying them to dynamic emissions.
82 Nonetheless, the authors focused on the LCIA step and modelled simple systems that did not
83 present a complex network of processes (and emissions) as most LCA studies do. The fixed
84 time step and simple input of data for the LCI did not allow the application of a more complex
85 and complete dynamic LCI in their methods.

86 In traditional LCA, the mass of the emitted substance is proportionally linked to the impact by
87 using characterization factors as proportionality constants, even though the fate of chemicals
88 in the environment is determined by time-dependent processes such as mass transfer and
89 chemical reactions, which produce non-linear distributions of remaining mass of substances in
90 environment. An infinite time horizon is generally used for the calculation of CF for toxicity
91 impact. This assumption is important for taking all long lasting impacts into account. However,
92 predicting impacts for eternity is also illogical. Also, the consideration of an infinite time horizon
93 may hide the potential impacts occurring over short periods of time in the assessment of a
94 system, because of the different nature of substances considered in the assessment
95 (Huijbregts et al., 2001). The evidence of such shortcomings determined LCA scholars to
96 consider CFs for different time horizons. For toxicity calculations, Huijbregts et al. (2000a,
97 2000b, 2001) proposed characterization factors based on the USES-LCA model, which
98 comprises fate, exposure and effect calculations. CFs for 20, 100 and 500 years were
99 calculated to be in accordance with the horizon times used in global warming potentials as it
100 was considered that they provided a useful interval for policy decisions.

101 Another method, proposed by Hellweg et al. (2003), tackles the lack of time influence by
102 applying a discounting method, which considers that toxicity impact diminishes with time.
103 Calculation of time dependent CFs was also the approach proposed by Lebailly et al. (2014)
104 by evaluating the dynamics of substance fate in the environment. They used the USEtox[®]
105 model and calculated the dynamic behaviour of substances for an initial unit load of substance
106 by solving the fate model for these particular conditions. These authors calculated

107 characterization factors at different time steps (starting from the initial emission), and used
108 them for a temporal evaluation of the freshwater ecotoxicity of metals. They applied this
109 method to the use of zinc as a fertilizer in agriculture in order to assess the temporal behaviour
110 of the impact. Although it implements dynamics in the fate calculation for metals, the study
111 lacks information on organic substances and, also, it does not implement complex, temporal
112 LCIs, which may present dynamic features related to unit processes and supply chains
113 involved in the life cycle of processes.

114 In conventional LCA, several toxicity models have been developed and used over the years.
115 The Life Cycle Initiative (<http://www.lifecycleinitiative.org/>) programme of the United Nations
116 Environment Program (UNEP) and the Society for Environmental Toxicology and Chemistry
117 (SETAC) developed the USEtox[®] consensual toxicity model for LCA. USEtox[®] development
118 was based on the comparison of several toxicity models and on experts' recommendations
119 (Jolliet et al. 2006; Ligthart et al. 2004; McKone et al. 2006). USEtox[®] provides toxicity
120 characterization factors for human toxicity and freshwater ecotoxicity that are recommended
121 by LCA scholars.

122 The objective of this study is to develop a dynamic approach for calculating time dependent
123 toxicity and ecotoxicity impacts within LCA. The USEtox[®] model was chosen and adapted to
124 include the time dimension. In the first part of the paper, the theoretical development is
125 presented. Then, the method is applied to a testbed case, i.e. grape production, in order to
126 emphasize the results of the proposed framework. This testbed case was chosen for a variety
127 of reasons: i) agriculture employs potentially hazardous substances in the different production
128 stages, so a temporal analysis of the LCI and environmental impacts is justified; ii) various
129 substances are emitted into the environment by agricultural operations, i.e. metals and organic
130 compounds with different types of harmful effects on humans and ecosystems.

131

132

133 **2. Method**

134 **2.1. Toxicity Impact Assessment – USEtox[®] method**

135 This subsection gives a brief presentation of the principles of the toxicity calculation methods
136 in LCA, particularly for the USEtox[®] method. The toxicity calculation methods usually follow
137 the approach used in methods for assessing chemical risk to human and ecosystem health,
138 based on three steps following the causal chain: i) evaluation of the fate of chemicals in the
139 environment, which leads to different concentrations/quantities of substances in different
140 environmental compartments; ii) evaluation of the exposure of humans or ecosystems to a
141 given substance, and iii) the effects that exposure might have on human or ecosystem health
142 (Hauschild et al., 2008). Specific modelling approaches characterize each step, and have
143 given rise to commonly used LCIA methods like IMPACT 2002 (Jolliet et al., 2003; Pennington
144 et al., 2005), ReCiPe (Goedkoop et al., 2008) or USEtox[®] (Hauschild et al., 2008). All the
145 methods cited are based on a similar framework consisting of the calculation of
146 characterization factors for substances as the result of multiplying a fate factor, an exposure
147 factor and an effect factor together, each of them being the result of one of the three
148 corresponding modelling steps cited above (Huijbregts et al, 2005a and 2005b).

149 Rosenbaum et al. (2007) proposed a framework in which the characterization factor was
150 calculated as the product of matrices representing fate, exposure and effect factors:

151
$$\mathbf{CF}_s = \mathbf{EF}_s \cdot \mathbf{XF}_s \cdot \mathbf{FF}_s \quad (1)$$

152 where the index *s* represents the substance of concern, **CF** is the characterization factor vector
153 in which each row represents a compartment, **FF** is the fate factor matrix representing the
154 environmental removal and transport processes of a certain substance in the different
155 environmental media, **XF** is the exposure factor matrix representing the increase in human
156 consumption of a particular substance based on the increase of the substance concentration
157 in a certain medium (for human toxicity) or the bioavailability of a certain substance (for
158 ecotoxicity), **EF** is the effect factor matrix, which express the effect on humans or ecosystems

159 per unit of concentration (Rosembaum et al., 2007). The USEtox[®] calculation tool (available at
160 <http://www.usetox.org/>) is based on this flexible matrix algebra.

161 Finally, for toxicity impact calculations, the characterization factor is multiplied by the
162 aggregated environmental intervention of certain substance over its entire life cycle:

$$163 \quad n_{s,i} = CF_{s,i} g_{s,i} \quad (2)$$

164 where index *i* represents the emission compartment, *g* represents the environmental
165 intervention (aggregated mass, which is the result of the LCI step) and *n* is the toxicity impact
166 value for a certain substance *s* emitted in compartment *i*.

167 2.1.1. Fate modelling

168 Fate modelling uses a concept developed in the 1980s (described in many publications, e.g.
169 Mackay, 2002; Van de Meent, 1993), which considers the environment as connected, well
170 mixed, homogeneous boxes (named environmental media or compartments). The
171 mass/concentration of a substance varies with time due to transport between compartments,
172 reaction processes (e.g. degradation), and removal (immobilization in different media). In this
173 model, the mass balance of a substance in the environment is described by a system of
174 ordinary differential equations (ODE):

$$175 \quad \frac{d\mathbf{m}_s}{dt} = \mathbf{K}_s \mathbf{m}_s + \mathbf{g}_s \quad (3)$$

176 where **K** is the square matrix of rate constants (related to removal, degradation and transport
177 processes) in each compartment *i* (day⁻¹), **m** is the mass vector of substance *s* in the
178 respective environmental compartments (kg), **g** is the vector of emission flows in each
179 compartment (kg day⁻¹), *t* is time.

180 The nested multimedia fate concept is also used in LCIA methods but in the very simplified
181 condition of equilibrium or steady state. Physically the fate factor (day) represents the

182 persistence of a chemical in the environment. It is mathematically defined as the resident mass
 183 (kg) in a certain compartment per unit of constant flow (kg.day⁻¹) emitted into the environment.
 184 In terms of the ODE system (equation 3) that signifies no variation of the
 185 concentrations/masses, in all compartments:

$$186 \quad \frac{dm_s}{dt} = 0 = \mathbf{K}_s \mathbf{m}_s + \mathbf{g}_s \quad \text{then} \quad \mathbf{FF}_s = \frac{\mathbf{m}_s}{\mathbf{g}_s} = -\mathbf{K}_s^{-1} \quad (4)$$

187 The USEtox[®] 2.0 model is based on the steady-state condition described by equation (4). The
 188 following scales and compartments are defined (Hauschild et al., 2008): global scale (air,
 189 freshwater, ocean, natural soil, agricultural soil), continental scale (rural air, freshwater, sea
 190 water, natural soil, agricultural soil), local scale (urban air, household indoor air and industrial
 191 indoor air).

192 2.1.2. Exposure modelling in USEtox[®]

193 The exposure factor represents the relationship between the quantity of substance present in
 194 a certain compartment and its intake by humans. It can be divided into direct (i.e. direct
 195 consumption of an environmental compartment) and indirect exposure (e.g. meat, dairy
 196 produce, vegetables, etc.), represented respectively by equations 5 and 6 (Rosebaum et al.,
 197 2007).

$$198 \quad XF_{s, xp, i}^{\text{direct}} = \frac{IR_{xp, i} \cdot P}{\rho_i \cdot V_i} \quad (5)$$

$$199 \quad XF_{s, xp, i}^{\text{indirect}} = \frac{BAF_{s, xp, i} \cdot IR_{xp} \cdot P}{\rho_i \cdot V_i} \quad (6)$$

200 where XF^{direct} (day⁻¹) represents the average direct intake rate of the polluted medium i via
 201 direct ingestion. The parameter ρ is the bulk density of medium i (kg .m⁻³), V (m³) is the volume
 202 of medium i related to the exposure pathway xp, IR (kg.day⁻¹) is the ingestion rate of medium

203 i via exposure pathway xp at population level and P is the population head count. For $XF^{indirect}$
204 (day^{-1}), IR ($kg.day^{-1}$) represents the individual intake rate of food substrate correlated to
205 pathway xp and $BAF=C_{xp}/C_i$ ($kg.kg^{-1}$) is the bioaccumulation factor (the steady state
206 concentration ratio between food substrate corresponding to exposure pathway xp and
207 compartment i). For ecotoxicity, the exposure factor represents the relationship between the
208 quantity of the substance in environmental compartments and its available fraction (truly
209 dissolved fraction) (Rosenbaum et al., 2011).

210 2.1.3. Effect modelling in USEtox®

211 The effect factors represent the relationship between the intake quantity and the possible
212 negative health effect of substances for living organisms. The effect factor for humans (cancer
213 and non-cancer effects) can be calculated by equation 7. A linear dose-response function was
214 assumed for each disease endpoint and intake route (Rosenbaum et al., 2011).

$$215 \quad EF_s = \frac{0.5}{ED50_s} \quad (7)$$

216 where EF is the effect factor for humans ($cases.kg^{-1}$) for substance s, ED50 is the lifetime daily
217 dose resulting in a probability of effect of 0.5 (Henderson et al., 2011).

218 The effect factor for ecotoxicity ($PAF.m^3.kg^{-1}$) represents the change in the Potentially Affected
219 Fraction (PAF) of species due to change in concentration:

$$220 \quad EF_s = \frac{0.5}{HC50_{s,EC50_s}} \quad (8)$$

221 where HC50 is defined by the hazardous concentration at which half of the target population
222 is exposed above its EC50 (concentration for which 50% of the population is affected)
223 (Henderson et al., 2011).

224

225 **2.2. Time consideration in toxicity impact assessment**

226 Among the factors included in a toxicity calculation, the fate is the one for which the dynamic
227 aspects are the most evident. It is well-known that the fate of substances in the environment
228 depends on their nature. Organic substances can be degraded by the environment, which
229 leads to their disappearance. On the other hand, inorganic substances (metals) tend to be
230 persistent and stay in different compartments for a long time (Hauschild et al., 2008). It is
231 important to account for the dynamic behaviour of substances in the environment by
232 considering all the phenomena involved, such as mass transfer, degradation of substances,
233 removal, etc., as described by the mass balance system of equations (equation 3). Therefore,
234 considering the steady state condition, as is the case in conventional LCA, may lead to loss of
235 consistency. The dynamic mass balance model provided, once adapted, can be resolved by
236 numerical methods. It should be noted that the environmental intervention \mathbf{g} (equation 3)
237 represents emission flows with complex temporal behaviour which requires a rigorous
238 resolution approach. The input data \mathbf{g} can be defined as a time dependent function in an
239 analytical manner or as numerical values at given times. Moreover, the rate-constants matrix
240 \mathbf{K} contains values of different orders of magnitude (in day^{-1}) which signify the combination of
241 slow and rapid kinetics, with very different slopes. This condition imposes the use of finite
242 difference solvers with a very narrow discretization of the time dimension that has to be
243 investigated, or solvers with variable, adaptive, time steps. In this work, the Python odeint
244 integrator (SciPy Python library) was employed to solve initial value problems. It automatically
245 switches between an Adams predictor-corrector method for non-stiff problems and a backward
246 differentiation formula method for stiff problems. In this work, the mass balance model in
247 equation (3) was used with the specific data provided by the USEtox[®] model, i.e. kinetic
248 constants, exposure and effect factors for the defined environmental scales and
249 compartments.

250 The result of the ODE is a vector of 13 elements that represents the current masses of
251 substance s in each compartment i at a specific time t . By the end of the calculation, a mass

252 vector (13 values corresponding to each compartment) is obtained for each discrete time value.
 253 For the toxicity results, following the matrix approach proposed by Rosenbaum et al. (2007),
 254 each mass vector is multiplied by the exposure matrix (**XF**) and effect matrix (**EF**):

$$255 \quad \mathbf{n}_{\text{human},s}(\mathbf{t}) = \mathbf{m}_s(\mathbf{t}) \times \mathbf{XF}_{\text{human},s} \times \mathbf{EF}_{\text{human},s} \quad (9)$$

256 $\mathbf{n}_{\text{human}}(\mathbf{t})$ is the vector that represents human toxicity (cancer and non-cancer, cases.day⁻¹) for
 257 a certain substance s in different compartments, at a given moment t in time.

$$258 \quad \mathbf{n}_{\text{eco},s}(\mathbf{t}) = \mathbf{m}_s(\mathbf{t}) \times \mathbf{XF}_{\text{eco},s} \times \mathbf{EF}_{\text{eco},s} \quad (10)$$

259 $\mathbf{n}_{\text{eco}}(\mathbf{t})$ represents the ecotoxicity, (PAF.m³.day).day⁻¹, due to an emission into a specific
 260 compartment for a certain substance s at a given moment in time t .

261 The result for the aggregation of all substances s and compartments i , for a given time t , is
 262 given by equations (11) and (12) for human and eco-toxicity, respectively.

$$263 \quad \mathbf{n}_{\text{human}}(\mathbf{t}) = \sum_s \sum_i \mathbf{n}_{\text{human},s,i}(\mathbf{t}) \quad (11)$$

$$264 \quad \mathbf{n}_{\text{eco}}(\mathbf{t}) = \sum_s \sum_i \mathbf{n}_{\text{eco},s,i}(\mathbf{t}) \quad (12)$$

265 The cumulated values, $n_{\text{human,cumul}}$ (cases) and $n_{\text{eco,cumul}}$ (PAF.m³.day), for human toxicity and
 266 ecotoxicity can be calculated using equations (13) and (14) respectively.

$$267 \quad n_{\text{human,cumul}} = \int_{t=t_0}^{\text{HT}} \mathbf{n}_{\text{human}}(\mathbf{t}) dt \quad (13)$$

$$268 \quad n_{\text{eco,cumul}} = \int_{t=t_0}^{\text{HT}} \mathbf{n}_{\text{eco}}(\mathbf{t}) dt \quad (14)$$

269 where t_0 represents the time of the first emission released into the environment, HT is the time
270 horizon for which the impact is investigated.

271 The objective of this work is the adaptation of USEtox[®] steady-state model for a dynamic
272 representation of the chemicals fate. The USEtox[®] 2.0 physical parameters were used without
273 modifications. Nevertheless, the authors are aware about the limitations and simplifications in
274 the LCIA methods. The chemicals fate in environment reveals much more complexity than that
275 described by the multimedia fate models used in LCIA. Examples of influence factors are: local
276 characteristics of environmental media which depend, besides the geological parameters, on
277 specific climate factors and biota (e.g. Hertwich, 2001a; Daly and Wania 2004), chemical
278 speciation and its dependence on the above cited factors (Gandhi et al, 2011), and global
279 modifications at long term of all these parameters. Obviously, a more accurate representation
280 should consider time and region dependent transport and kinetic parameters in a more
281 complex nested multimedia.

282 Dynamic aspects can also be found in exposure and effect factors. Exposure of organisms to
283 a specific pollutant during a long time period may lead to high mortality and morbidity in the
284 first years. However, it may also lead to a genetic adaptation of organisms or a structural
285 change in the species composition of the ecosystem, decreasing mortality and morbidity
286 (Heijungs et al., 2004). Temporal aspects may also occur in the indirect intake of pollutants via
287 the food chain, which normally delays the moment of pollutant intake with respect to the current
288 pollution state. However, these processes are not considered in this study as the prediction of
289 such behaviour is complex and uncertain, and remains beyond the scope of this work. Here,
290 the conventional exposure model (equations 5, 6), and linear dose-response functions
291 (equations 7, 8) are used.

292 **2.3. Integration in a Dynamic LCA framework - DyPLCA**

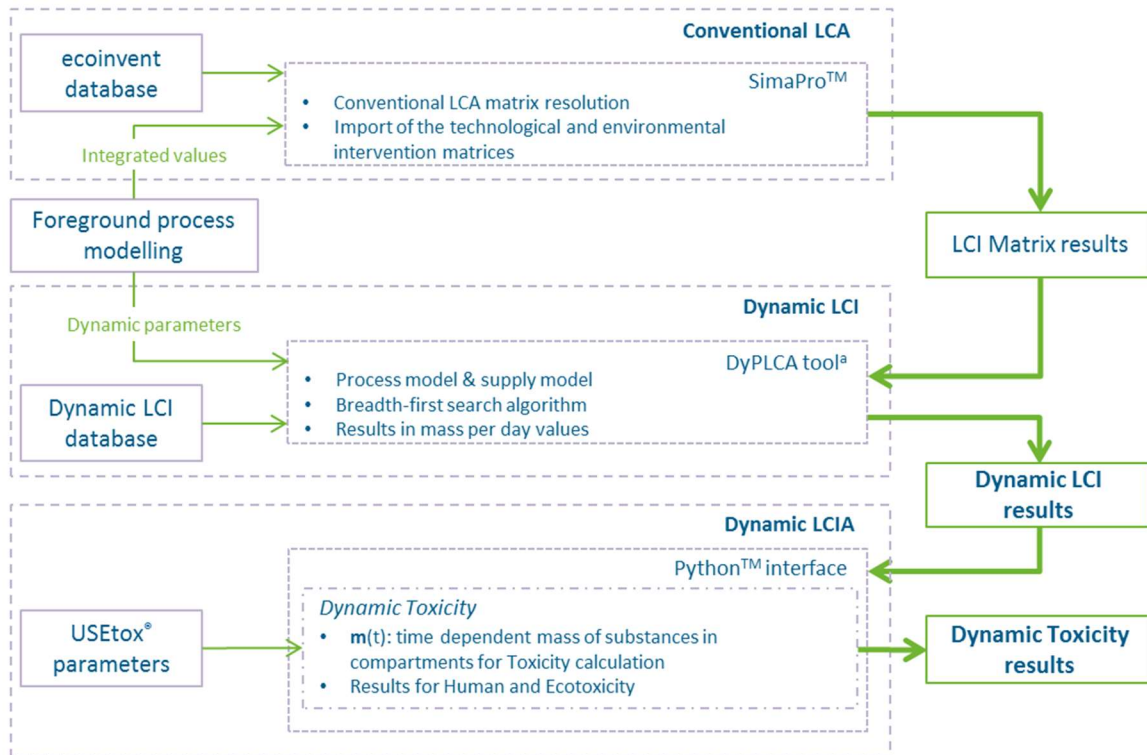
293 Introducing the time dimension into the LCIA step, in particular for toxicity calculation, is not
294 sufficient to provide a relevant temporal assessment in LCA. A reliable time dependent LCI

295 must be set up. Recently, a novel conceptual and computational framework for including time
296 dependency in LCI was proposed by Tiruta-Barna et al. (2015). This method considers the
297 temporal behaviour of the foreground processes and of the supply chain. It takes temporal
298 characteristics such as residence time of processes, lifetime of infrastructures, delivery
299 scheduling of products and latent time in the supply chain into account (more details in the
300 Supplementary Information document SI-S6). Each process is characterized by a production
301 flow function and an emission flow function. In order to distribute the environmental
302 interventions over time, the life cycle network of processes is described as a graph in which
303 the nodes represent the processes and the arcs the exchange of products. For the computation
304 of the time-resolved environmental interventions, a tracking (graph search) algorithm is
305 implemented in a Web software named DyPLCA (<http://dypzca.univ-lehavre.fr/>). In terms of
306 results, the new approach provides time dependent LCI expressed as: i) a time function for
307 individual emissions (or resource consumption) for individual processes, ii) an aggregated time
308 function for a given environmental intervention. The results are obtained in the form of
309 numerical data for discrete time values, over the time span of the life cycle under study (i.e.
310 past activities in background, present and future activities for fore- and background processes,
311 e.g. 100 years). The proposed approach and tool are generic and fully compatible with all
312 dynamic LCIA methodologies and were recently used with a dynamic climate change approach
313 by Shimako et al. (2016).

314 Three different tools were interconnected in order to obtain a modelling and computational
315 framework for dynamic toxicity in LCA (Figure 1). SimaPro® LCA software was used for the
316 traditional LCI resolution. This software delivers the LCI results in matrix form: a technological
317 matrix and an environmental intervention matrix (emissions by compartments and processes).
318 Those results were then used in the DyPLCA platform together with all the temporal
319 characteristics of processes and supply chains (defined by the practitioner prior to calculation).
320 This tool delivered a time vector and the associated emissions vector ($\text{kg}\cdot\text{day}^{-1}$) in different
321 environmental compartments, which were then used in the dynamic toxicity model proposed

322 by this study. A Python program treats data interpolation, choice of time step for calculation,
 323 and sends the data to the ODE solver together with all the necessary USEtox[®] parameters,
 324 then retrieves and treats the toxicity results. The complete dynamic framework was applied to
 325 a testbed case.

326



327

328 Figure 1- General framework for the calculation of a dynamic LCA

329

330 **2.4. Practical application to a testbed case**

331 The process of “grape production, GLO” in version 3.2 of the ecoinvent database was
 332 considered as testbed case in order to exemplify the dynamic evaluation of toxicity using
 333 USEtox[®]. Conventional and dynamic LCA were performed and the results were compared.

334 2.4.1. Conventional Life Cycle Assessment of grape production

335 *Goal and scope definition*

336 From an LCA point of view, the objective of this study is to evaluate the toxicity impacts for the
337 production of 1 kg of grapes (the functional unit). Cradle to gate boundaries are considered
338 following the ecoinvent dataset “grape production, GLO” with attributional allocation.

339 This dataset (presented in SI-S3) covers the processes starting from the initial maintenance of
340 the vineyard just after the previous crop, to the harvest and storage of the grapes produced,
341 and includes fertilizer acquisition and application, pesticide acquisition, electricity use and
342 irrigation. More details can be found in Stoessel et al. (2012).

343 *Life cycle inventory*

344 Global geography (GLO) is the only geography available in ecoinvent 3.2 and was chosen for
345 this study. For this reason, several improvements were necessary to match agricultural
346 practices better at regional scale. Regarding organic substance emissions, few substances
347 could be found in the “grape production” dataset. The emissions were accounted for in the
348 process “pesticides, unspecified” in the technosphere. However, some important pesticides
349 currently used in agriculture were not considered. In Europe, France was the main agricultural
350 pesticides producer in 2013. It ranked second for absolute sales of pesticides, with a share of
351 almost 19% in 2014, and ranked third for grape production (Eurostat, 2016). In this sense, the
352 French market was chosen to represent the quantities of pesticides to be taken into account.
353 For this purpose, the dataset “pesticide, unspecified” and the emission “pesticide, unspecified”
354 were modified to fit the values available for the French market (MEDDE, 2016 - French national
355 sales data base - provides the French market distribution for pesticides). For this study, only
356 34 compounds were selected, corresponding to 55% of the French market in 2014 (Table 1).

357

358 Table 1 – Share of pesticides in French market - substances that contribute more than 0.5%
359 to the market (classified by their abundance in 2014).

Substance	2013	2014	Substance USEtox[®] name	Substance ecoinvent name
Sulfur	19.7%	17.9%	n.a.	Sulfur
Glyphosate	14.3%	13.4%	Glyphosate	Glyphosate
Mancozeb	5.24%	7.02%	Mancozeb	Mancozeb
Metam-sodium	3.12%	3.31%	Methyldithiocarbamic acid, Na salt	Metam-sodium
Prosulfocarb	2.16%	3.27%	Prosulfocarb	
s-Metolachlor	0.00%	2.89%	Metolachlor	Metolachlor
Chlormequat	2.78%	2.84%	Chlormequat	Chlormequat
Isoproturon	2.10%	2.48%	Isoproturon	Isoproturon
Folpet	2.49%	2.31%	Folpet	Folpet
Chlorothalonil	2.12%	2.03%	Chlorothalonil	Chlorothalonil
Iron sulphate	2.17%	1.98%	n.a.	n.a.
Paraffin oil	1.49%	1.69%	n.a.	n.a.
Chlorotoluron	1.89%	1.63%	Chlortoluron	Chlorotoluron
Metiram	1.65%	1.55%	Metiram	Metiram
Pendimethalin	1.28%	1.32%	Pendimethalin	Pendimethalin
Copper from copper sulphate; Copper from tetracopper tricalcium sulphate	1.39%	1.21%	Cu(II)	Copper
Metaldehyde	1.72%	1.18%	Metaldehyde (tetramer)	Metaldehyde
Aclonifen	1.30%	1.16%	Aclonifen	Aclonifen
Dimethenamid	1.08%	1.09%	Dimethenamid	Dimethenamid
MCPA	1.36%	1.05%	MCPA - Sodium salt	MCPA
Metazachlor	1.25%	1.00%	Metazachlor	Metazachlor
Napropamide	1.00%	0.91%	n,n-Diethyl-2-(1- naphthalenyloxy)propana mide	Napropamide
2,4-d	0.96%	0.89%	2-(2,4- dichlorophenoxy)acetic acid	2,4-D

Prochloraz ; Prochloraz manganese	1.02%	0.86%	Prochloraz	Prochloraz
Prothioconazol	0.96%	0.84%	n.a.	Prothioconazol
Tebuconazole	0.81%	0.80%	Tebuconazole	Tebuconazole
Metamitron	0.85%	0.78%	Metamitron	Metamitron
Pronamide	0.64%	0.73%	Pronamide	Pronamide
Amitrol	0.64%	0.68%	Amitrole	
Mineral oils	0.30%	0.61%	n.a.	n.a.
Copper from copper hydroxide	0.72%	0.61%	Cu(II)	Copper
Thiram	0.64%	0.55%	Thiram	Thiram
Imidacloprid	0.45%	0.52%	Imidacloprid	Imidacloprid
Boscalid	0.64%	0.52%	n.a.	n.a.

360 n.a. = not applied

361 *LCIA*

362 The application case focuses on human toxicity and ecotoxicity impacts generated by the
363 substances emitted in the life cycle. The USEtox[®] 2.0 method was used for the conventional
364 LCIA. In conventional LCIA toxicity impacts are calculated in steady-state condition, i.e. for an
365 infinite time horizon.

366 2.4.2. Dynamic toxicity assessment

367 *Dynamic LCI*

368 As noted in subsection 2.3, a certain number of temporal parameters are needed in order to
369 compute dynamic LCI. The duration of one production cycle of grape is taken to be 12 months
370 in permanent culture, the period defined as starting in January of each year. The lifetime of the
371 production field is regarded as 25 years as recommended by Bordelon et al., 2000. The main
372 application of pesticides takes place between April and July and they are applied every 7-14
373 days in general (Bordelon et al., 2000). For this study, an interval of 7 days was chosen. Direct
374 emissions (i.e. N₂O) of soil fertilisation to the air are considered to occur continuously during
375 the production cycle. Fertilizers and pesticides are considered to be delivered to the process

376 of grape production twice a year. The process related to the application of fertilizer, “fertilizing,
377 by broadcaster”, has the same temporal characteristics as the pesticides application. For this
378 study, the harvest month was set as September, as it usually occurs between August and
379 October. The grape produced is stored for 2 months (Nemecek and Kägi, 2007) after the
380 harvest and irrigation was considered to be continuous between April and October.

381 Based on this information, the temporal characteristics of processes involved in the life cycle
382 of grape production were defined in the dynamic LCI method proposed by Tiruta-Barna et al.
383 (2015) (listed in SI-S6). The inventory quantitative data fromecoinvent and the temporal
384 parameters were used with the DyPLCA tool in order to build the temporal LCI.

385 *Dynamic LCIA*

386 Here only toxicity and ecotoxicity impacts were evaluated using the dynamic approach
387 developed in section 2.2.

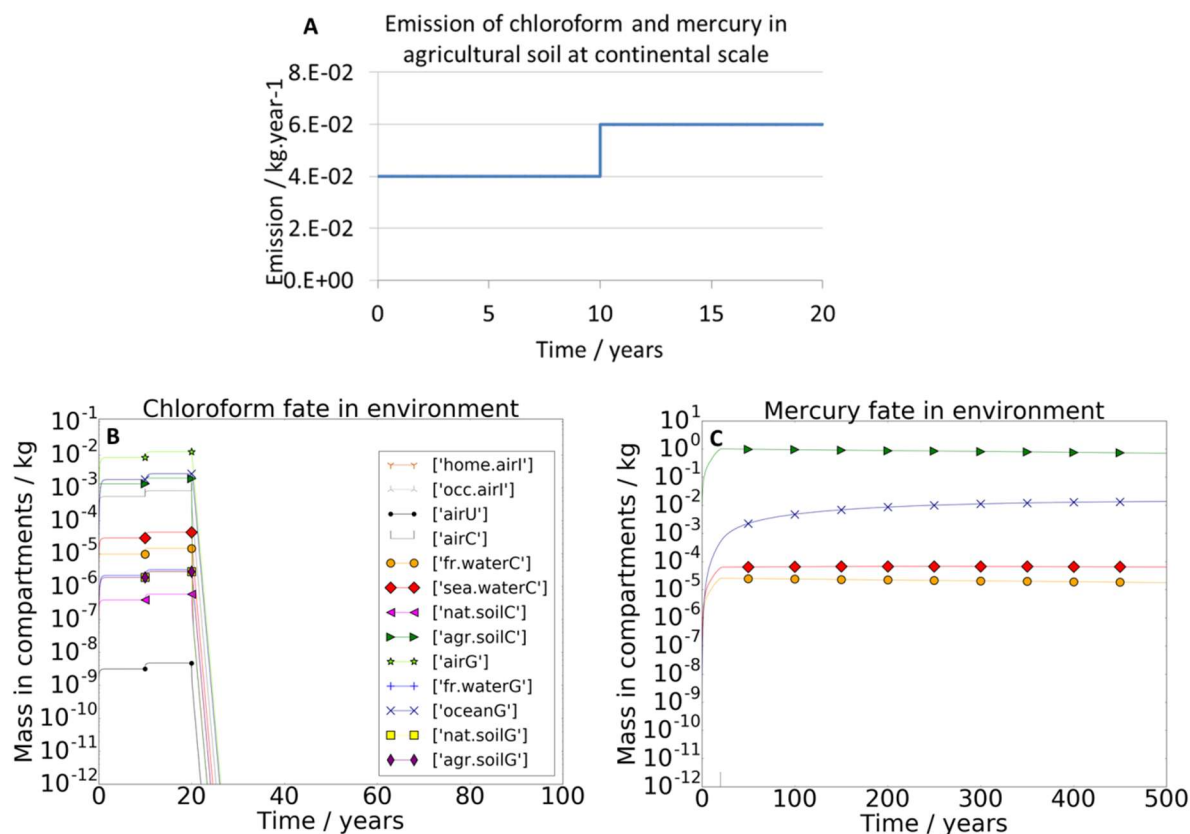
388

389 **3. Results and Discussion**

390 This section is structured in two sub-sections. In the first part the feasibility of the new method
391 and the comparison with the conventional method is discussed through two simple examples.
392 The second part presents and discusses the results for the testbed case.

393 **3.1. Discussion of the dynamic toxicity approach**

394 An organic substance (chloroform) and an inorganic one (mercury) were analysed here. For
395 each substance, an emission was considered over 20 years in the agricultural soil
396 compartment, described by a simple step behaviour (Figure 2.A): 0.04 kg.year⁻¹ constant flow
397 during the first 10 years, then a constant flow of 0.06 kg.year⁻¹ between years 10 and 20. The
398 total mass of emission is 1kg (time integral of the emission flow).



399

400 Figure 2 – (A) Emission profile of chloroform and mercury into agricultural soil at continental
 401 scale. (B) Chloroform fate in environment over 100 years and (C) Mercury fate in environment
 402 over 500 years. Legend: home.airI = household indoor air, occ.airI = industrial indoor air, airU
 403 = urban air, airC = continental rural air, fr.waterC = continental freshwater, sea.waterC =
 404 continental sea water, nat.soilC = Continental natural soil, agr.soilC = Continental agricultural
 405 soil, airG = global air, fr.waterG = Global freshwater, oceanG = ocean, nat.soilG = Global
 406 natural soil, agr.soilG = Global agricultural soil.

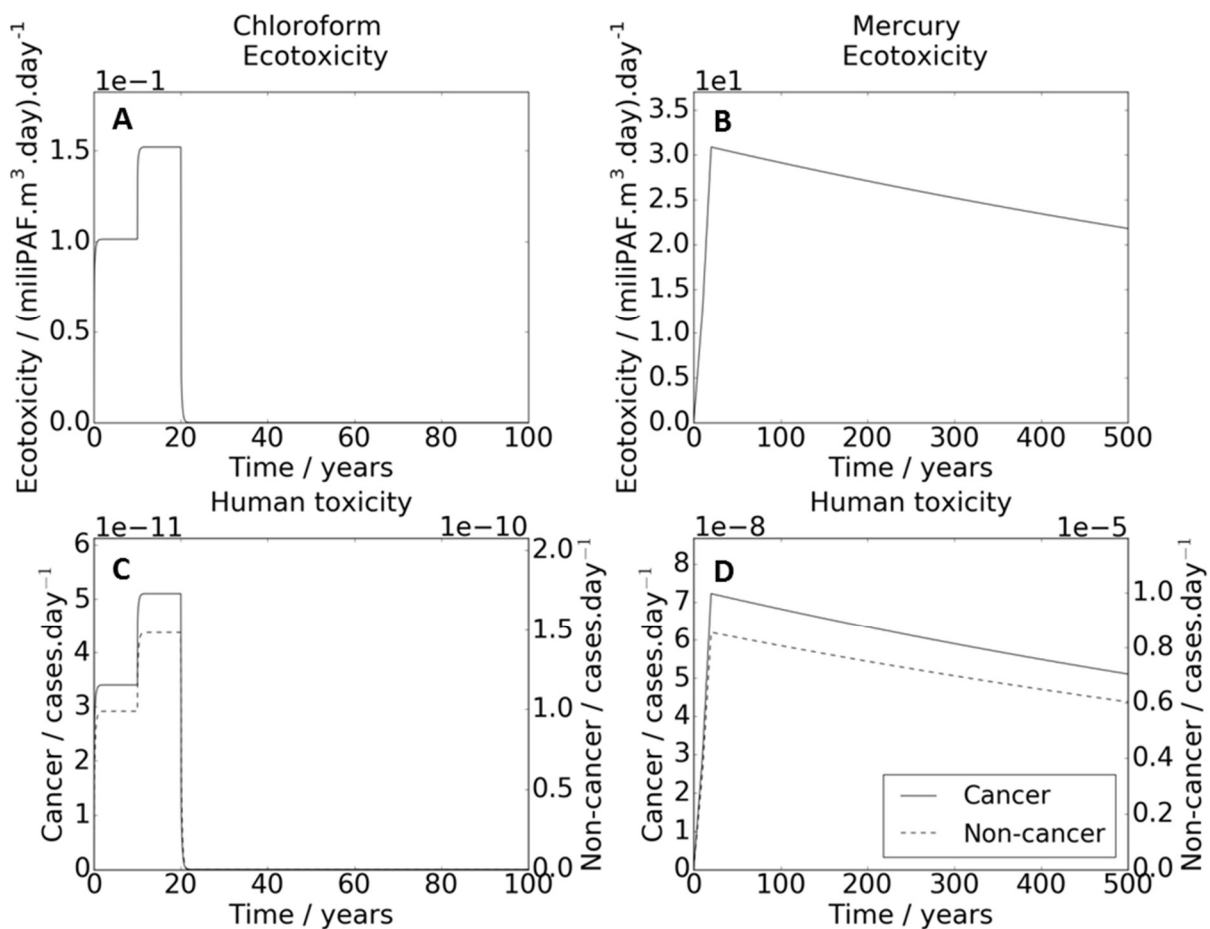
407

408 In order to convert the dynamic emission into a dynamic toxicity calculation, the first step is to
 409 calculate the fate of the substance. Figures 2.B and 2.C show the current mass of chloroform
 410 and mercury in the environmental compartments, for a calculation time of 100 years and 500
 411 years respectively. The very different behaviours found for the two substances depend on the
 412 different mechanisms included in the USEtox[®] model. Accordingly, the remaining mass of

413 chloroform drops considerably after the last emission around year 25. For non-persistent
 414 organic substances, kinetics of removal and degradation usually present a high order of
 415 magnitude, which explains the fast depletion of chloroform in the environment. The dynamics
 416 of mercury removal in the environment is still slow and the sum of the remaining mass of
 417 mercury in all compartments at year 500 represents 71% of the total emitted mass. It should
 418 be noted that, after an accumulation during the emission period, the mass decreases in the
 419 emission compartment (agricultural soil) while it increases in others, e.g. ocean. All transfer
 420 and removal processes are slow, explaining the slow, long-term evolution of mercury
 421 quantities.

422 Figure 3 shows the current dynamic toxicity impacts ($n_{\text{human}}(t)$, $n_{\text{eco}}(t)$ – equations 11, 12),
 423 calculated for 100 years in case of chloroform and for 500 years in case of mercury.

424



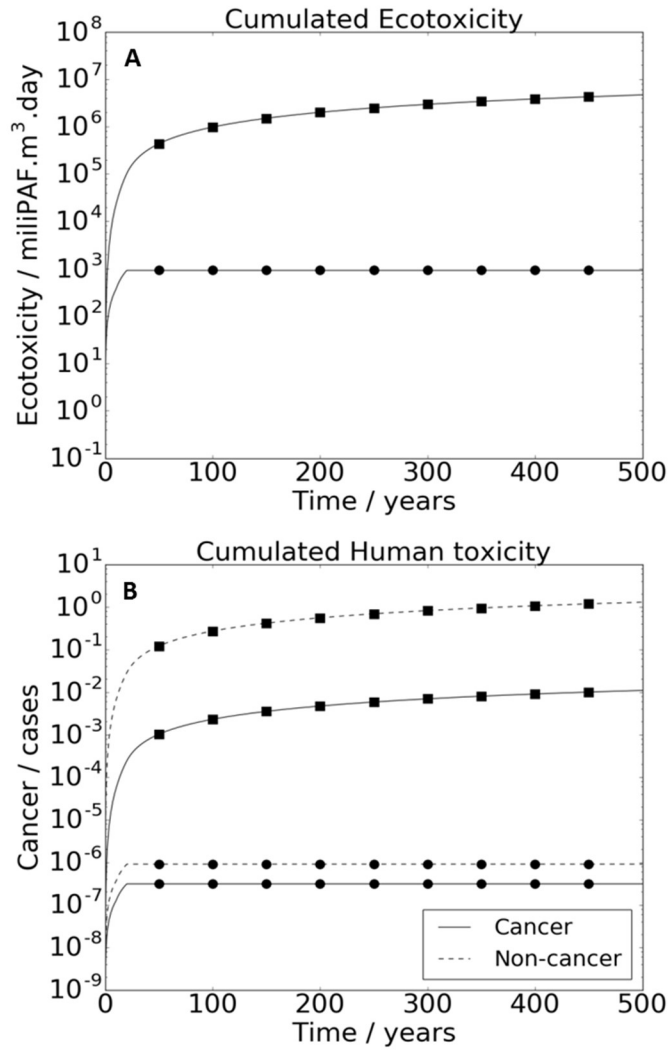
425

426 Figure 3 - Current dynamic toxicity impacts calculated for 100 years in case of chloroform and
427 for 500 years in case of mercury. Ecotoxicity (n_{eco}) for chloroform (A) and mercury (B); Human
428 toxicity (n_{human}) for chloroform (C) and mercury (D).

429

430 For both substances, the shapes of ecotoxicity (Figures 3.A and 3.B) and human toxicity curves
431 (Figures 3.C and 3.D) are similar to those obtained for the mass in the fate calculation (Figure
432 2), which is explained by the fact that the dynamic aspects are related only to the fate step.
433 Exposure and effect steps, being considered independent of time, are characterized by
434 constant values. In case of chloroform, the value of toxicity drops considerably after about 20
435 years from the first emission, leading to the conclusion that toxicity impact occurs for the time
436 frame in which the emissions exist.

437



438

439 Figure 4 - Cumulated dynamic toxicity calculated over 500 years for chloroform emission (●)
 440 and mercury emission (■) (mission during 20 years). Ecotoxicity $n_{eco,cumul}$ - A; Human toxicity
 441 $n_{human,cumul}$ - B

442

443 Figure 4 shows the values of cumulated toxicity (equations 13, 14), for chloroform and mercury,
 444 for a time horizon of 500 years. This kind of result should be interpreted as the total impact
 445 generated from time zero to a given time horizon HT, and, for sufficiently large HT, the results
 446 should be similar to those calculated by the conventional method (USEtox®, infinite HT).

447 In case of chloroform (non-persistent substance) ecotoxicity and human toxicity stabilize after
 448 the end of the emission period. In case of mercury, the cumulated toxicity is still increasing
 449 significantly as the substance remains in the environment for a long period. In conclusion, the
 450 dynamic method demonstrates that mercury generates toxicity in the long term as a
 451 consequence of its persistence in the environment, with a variable intensity culminating at the
 452 end of the emission period (maximum of mass accumulation in the emission compartment).

453 Table 2 shows the conventional toxicity results and the cumulated values (obtained for 100
 454 and 500 years integration time) obtained from the dynamic toxicity model, for both analysed
 455 substances. In case of chloroform, the values found through the dynamic evaluation are similar
 456 to those obtained from the conventional (infinite time horizon) method, thus validating the
 457 structure of dynamic calculations for toxicity. In the case of mercury, the results for 500 year
 458 time horizon are lower than the conventional results. This can be explained by the fact that the
 459 chosen time horizon might not be sufficient to reach the complete removal of the substance.
 460 However, it can be noted that the value tends to the traditional toxicity value when HT is
 461 increased.

462

463 Table 2 – Toxicity results for the emission of chloroform and mercury.

464

465

		Conventional	Dynamic 100 years	Dynamic 500 years
Mercury	Remaining mass (kg)		9.4E-01	7.2E-01
	Ecotoxicity, cumulated (miliPAF.m ³ .day)	1.6E+07	9.8E+05	4.7E+06
	Cancer toxicity, cumulated (cases)	3.7E-02	2.3E-03	1.1E-02
	Non cancer toxicity, cumulated (cases)	4.3E+00	2.7E-01	1.3E+00
Chloroform	Remaining mass (kg)		0.0E+00	0.0E+00
	Ecotoxicity, cumulated (miliPAF.m ³ .day)	9.3E E+02	9.3E+02	9.3E+02

Cancer toxicity, cumulated (cases)	3.1E-07	3.1E-07	3.1E-07
Non cancer toxicity, cumulated (cases)	9.0E-07	9.0E-07	9.0E-07

466

467 As a general conclusion, the behaviour of different substances is determined by the transport
468 and reaction processes in the fate step. The rate constants of these processes are gathered
469 in the constants matrix **K** (available with the USEtox[®] tool). All of them are compartment and
470 substance sensitive. When steady state conditions are considered in the toxicity calculation,
471 important information is lost or hidden. The equilibrium state in conventional LCA leads to
472 overestimation of CFs for toxicity, especially for persistent substances. This aspect of the
473 pollutant persistence and its associated toxicity is not visible in conventional LCIA methods,
474 i.e. it is not possible to evaluate if toxicity acts for a short period affecting people for several
475 years (as in the case of chloroform) or for a long period affecting several generations (example
476 of mercury).

477 Lebailly et al. (2014) also proposed a dynamic freshwater ecotoxicity assessment for metals
478 in LCA. After studying the behaviour of several metals, the authors reached the same
479 conclusion as the present work: the integrated toxicity approaches the conventional value for
480 large time spans, depending on the substance and compartment. However, in their method,
481 the behaviour of non-persistent organic substances was not investigated. Concerning
482 methodological aspects, their method is based on the time dependent calculation of CFs by
483 solving equation (3) for an initial unit load of substance (i.e. a pulse input, $g = 1\text{kg}$ at $t = \text{zero}$
484 and $g=0$ for $t>0$). CFs (instantaneous and cumulated) were calculated with a 1-year time step.
485 Then, ecotoxicity impact (instantaneous and cumulated) was calculated at a given HT using
486 the sum of the products $g(t)*CF(HT-t)$. The method proposed by Lebailly et al. (2014) differs
487 from our method by the mathematical approach chosen for resolving the dynamic fate model.

488 Given that $g(t)$ is expected to be noisy with a complex shape representing the emission of a
489 substance by many processes shifted in time, over a large time span covering the life cycle of

490 a system, the most rigorous approach is to directly solve the ODE system, which was carried
491 out in the present work.

492 The second solution could be to consider the mathematical properties of a linear system, i.e.
493 the convolution product between an impulse response function of the system and the input
494 perturbation signal. In our case, the system is the environment, the perturbation input signal is
495 a substance entering the environment (a temporal emission $g(t)$), and the impulse response
496 function IRF is the response of the environment (all environmental mechanisms taken
497 together) at a pulse unit input ($g=1$ at $t=0$, $g=0$ for $t>0$), i.e. a particular initial condition. This
498 approach is similar to that of Lebailly et al. (2014): the CFs(t) represent IRFs, and the toxicity
499 calculation procedure they propose corresponds to a convolution product. Well before Labailly
500 et al, Hertwich (2001b) proposed, in a context different from LCA, to solve dynamic multimedia
501 fate models by using the convolution approach, combined, in addition, with the Laplace
502 transforms of equations and source function $g(t)$ in order to avoid numerical integration
503 (possible only if $g(t)$ is analytically defined by a function).

504 The toxicity results obtained by the different mathematical methods presented (direct
505 resolution of ODE and convolution approach) should be very similar, within the limit of inherent
506 errors induced by the numerical resolution. However, given the behavioural complexity of the
507 systems studied in the context of LCA, the convolution approach is more limiting while it
508 requires specific mathematical conditions to be respected.

509 As regards the practicability of either of these approaches, again due to the complexity of the
510 g function, the direct integration of dynamic mass balances is more practical and easier to
511 handle in a modelling platform where dynamic LCI and dynamic impact calculations are
512 coupled (as described in paragraph 2.3 and shown in Figure 1). In addition, if the toxicity model
513 should evolve by adding more dynamic phenomena, variable parameters in time and space,
514 or spatial dimension, the direct resolution of a complex system of differential equations remains
515 the only solution. Moreover, the calculation of time dependent CFs becomes unnecessary

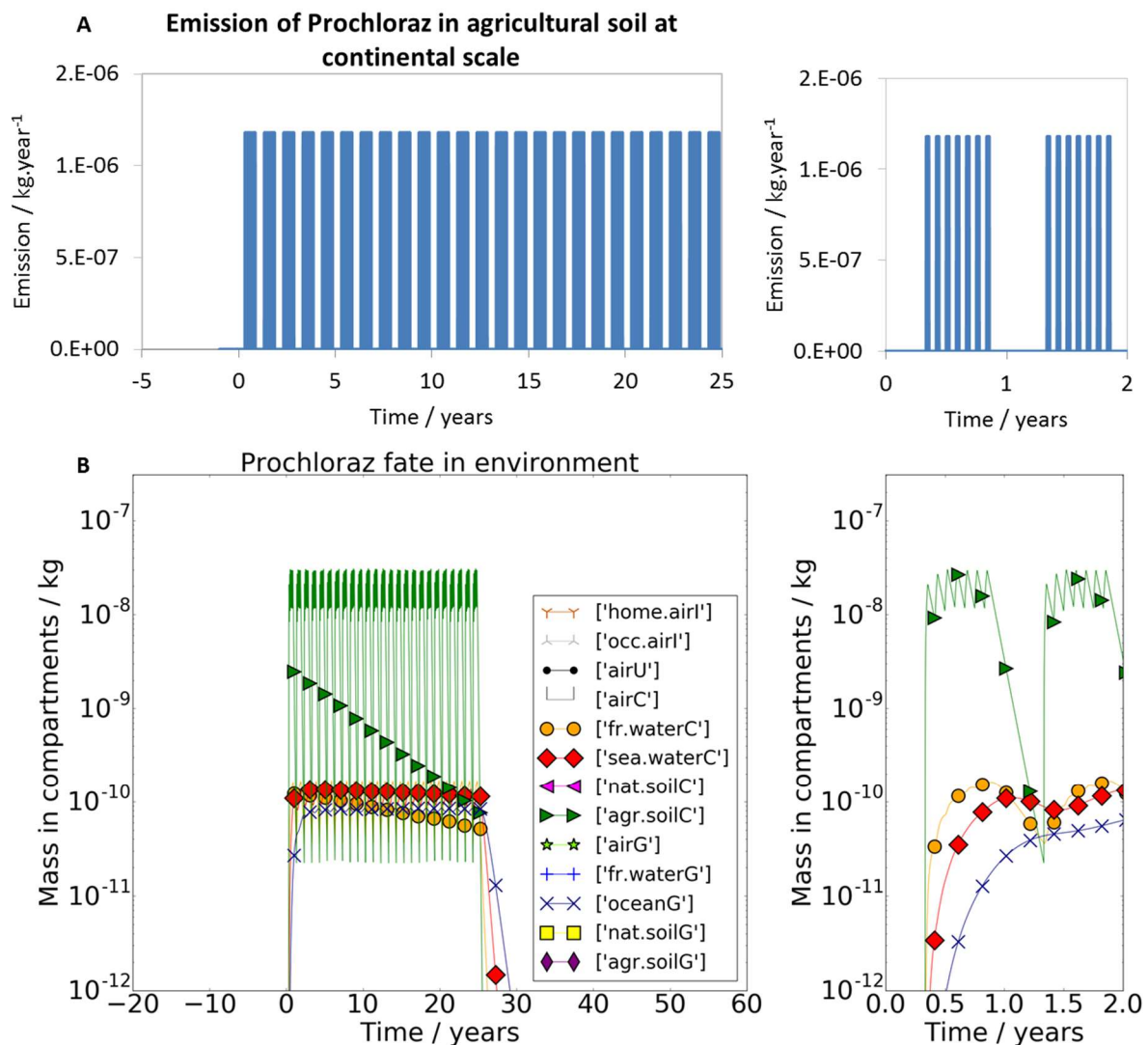
516 since the large number of values (many thousands for a single substance, depending on the
517 granulometry of the time scale) make it unfeasible to use them in the spirit of conventional LCA
518 (where only a single CF characterizes a substance/compartment pair). CF was a concept
519 introduced in LCA for the sake of simplicity, in order to gather, in a single constant, the
520 contributions of many environmental mechanisms and phenomena involved in the
521 impact/damage generation. Thus in the dynamic context, characterization factors lose their
522 sense and utility. This is why they are not used in the present study.

523 **3.2. Testbed case results**

524 First of all, the “grape production” process was modelled in SimaPro® and the matrix of
525 environmental interventions was extracted. The data from SimaPro® was then used in DyPLCA
526 together with the necessary temporal parameters, resulting in a table containing 742 columns
527 representing substances and compartments, with, in rows, the discrete values of
528 environmental interventions (LCI) for each time step. The time span covered the lifetime of the
529 main process (grape production, 25 years) and 1 year before for background processes (year
530 -1). The time step in the DyPLCA inventory used for this project was 0.5 days.

531 Then, data harmonization between the ecoinvent and USEtox® databases was performed.
532 Environmental compartments in ecoinvent are not defined in the same manner as in USEtox®.
533 Thus, the adaptation of compartments led to a different number of combinations with the
534 emitted substances (see SI - S1 and S2 for more details). Moreover, the name and chemical
535 speciation of substances are not the same in the ecoinvent and USEtox® databases, e.g.
536 metals do not have an oxidation number in ecoinvent but they do in USEtox®. Speciation is
537 one of the most important items of information for toxicity assessment. Finally, a total of 671
538 substance/compartment combinations were considered in this testbed case, covering
539 emissions over the whole life cycle. The results obtained from DyPLCA, with harmonized
540 nomenclature, were then used for dynamic toxicity calculation. The same harmonization was
541 used for conventional LCI in order to calculate toxicity with steady-state USEtox®.

542 For the sake of clarity, only the results for two selected substances are presented here together
 543 with results for organics and inorganics. All numerical results correspond to the functional unit,
 544 i.e. 1kg grape production. Figure 5.A presents the emission profile of one chosen substance,
 545 prochloraz, identified as one of the most impacting pesticide in this application, while figure 5.B
 546 shows its current mass (kg) in different compartments in function of time. The emission profile
 547 obtained after computing the dynamic LCI with DyPLCA tool, has peaks corresponding to the
 548 periods of application to the vines (see zoom side of the figure). These cycles can be well
 549 distinguished also on graph 5.B as the pesticide is relatively rapidly degraded in agricultural
 550 soil and no major accumulation takes place from one cycle to another.



552 Figure 5 – Case of the prochloraz – results for 1kg grape production. (A): Emission into
553 agricultural soil at continental scale with zoom between years 0 and 2. (B): Mass distribution
554 in different compartments with zoom between years 0 and 2. Legend: home.airI = household
555 indoor air, occ.airI = industrial indoor air, airU = urban air, airC = continental rural air, fr.waterC
556 = continental freshwater, sea.waterC = continental sea water, nat.soilC = Continental natural
557 soil, agr.soilC = Continental agricultural soil, airG = global air, fr.waterG = Global freshwater,
558 oceanG = ocean, nat.soilG = Global natural soil, agr.soilG = Global agricultural soil.

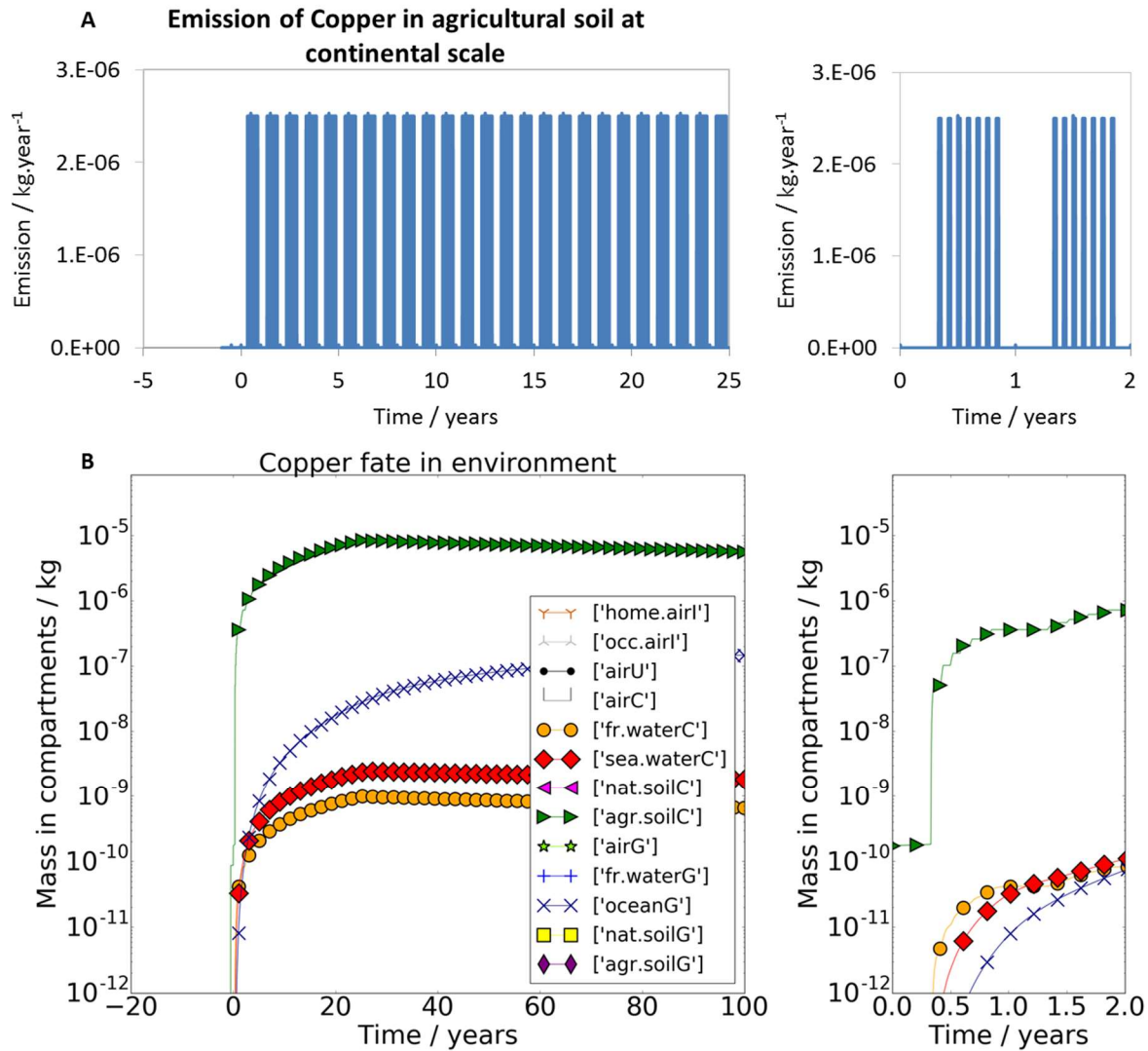
559

560 It should be noted that emissions could occur in the life cycle of the process under study before
561 it started to produce. For example, the production of grapes requires chemicals that are
562 produced before the agricultural process. The start time of the grape production is noted $t=0$
563 but background processes had already been working before this time. Therefore, a negative
564 part of the time axis was employed to point out the existence of background emissions in the
565 past.

566 Figure 6 shows the emission profile (6.A) and the fate (6.B) of copper, another compound
567 present in pesticide products. The remaining mass is predominantly in agricultural soil at
568 continental scale due to the slow transfer towards the other compartments and the very slow
569 removal. The mass in this compartment increases until the last emission and then decreases
570 slowly. About 64% of the mass still remains in the environment by the year 100 and 9% by the
571 year 500.

572 The observed behaviours of the two substances shown similarities to those discussed in
573 section 3.1, i.e. non-persistent organic compounds and persistent metals. Calculated dynamic
574 toxicities follow the fate profile as discussed in section 3.1 (toxicity results presented in SI-S7).

575



576

577 Figure 6 – Case of copper - results for 1kg grape production. (A): Emission profile into
 578 agricultural soil at continental scale with zoom between years 0 and 2. (B): Mass distribution
 579 in different compartments with zoom between years 0 and 2. Legend: home.airI = household
 580 indoor air, occ.airI = industrial indoor air, airU = urban air, airC = continental rural air, fr.waterC
 581 = continental freshwater, sea.waterC = continental sea water, nat.soilC = Continental natural
 582 soil, agr.soilC = Continental agricultural soil, airG = global air, fr.waterG = Global freshwater,
 583 oceanG = ocean, nat.soilG = Global natural soil, agr.soilG = Global agricultural soil.

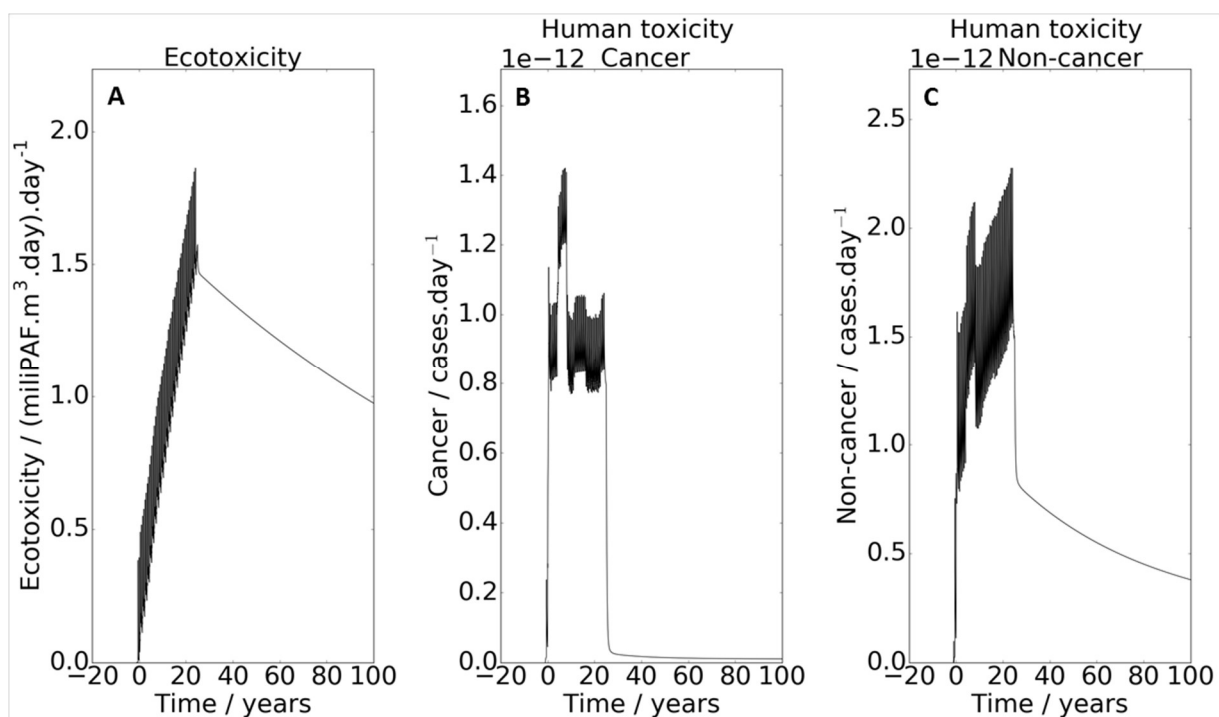
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585

586 Figure 7 presents the results obtained for ecotoxicity in $\text{PAF}\cdot\text{m}^3\cdot\text{day}\cdot\text{day}^{-1}$ (fig 7.A) and human
 587 toxicity, as cancer (fig 7.B) and non-cancer (fig 7.C) in $\text{cases}\cdot\text{day}^{-1}$, in function of time, for all
 588 substances emitted by the life cycle system. A highly variable toxicity profile is observed in the
 589 first 25 years (which is the lifetime of the foreground process), as a cumulated effect of organics
 590 and inorganics. After the end of emissions, the toxicity values drop to those of the remaining
 591 metals, and then decrease slowly following the fate of the metals.

592

593



594

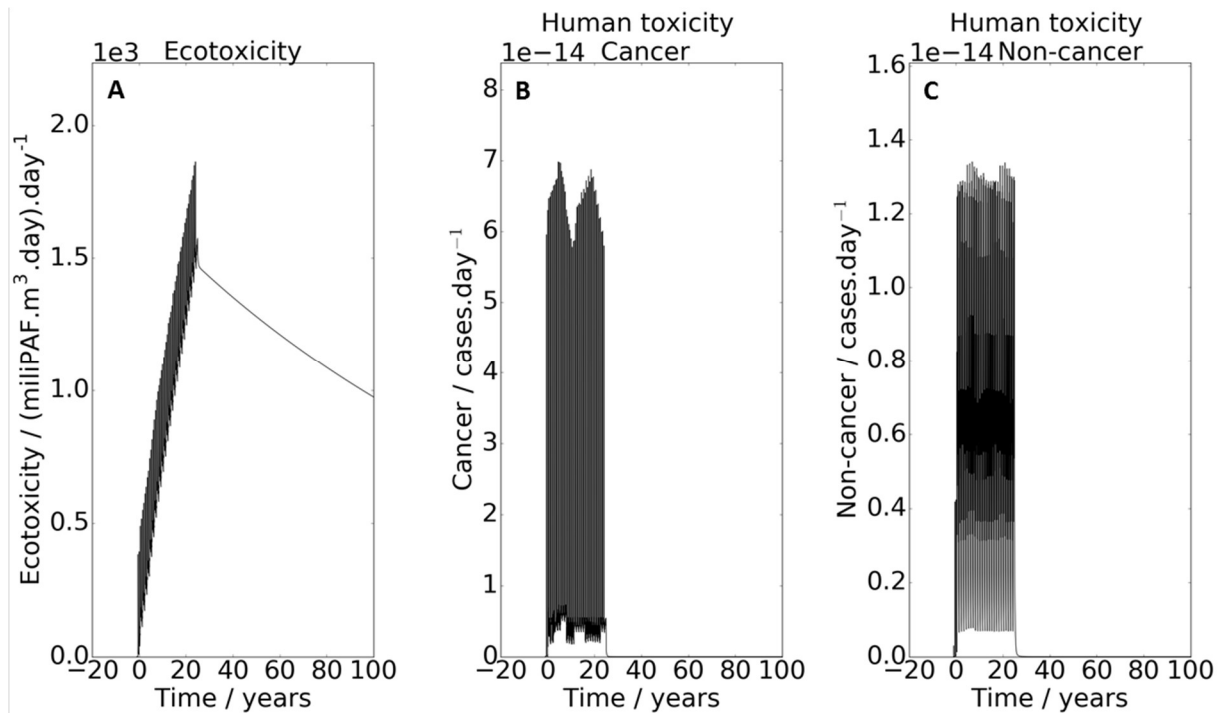
595 Figure 7– Current toxicity for the production of 1 kg of grapes. (A) Ecotoxicity $n_{\text{eco}}(t)$; (B) Cancer
 596 and (C) Non-cancer Human toxicity $n_{\text{human}}(t)$.

597

598 Human toxicity and ecotoxicity were also calculated separately for organic and inorganic
 599 substances. Regarding the current ecotoxicity and human toxicity of organic substances
 600 (Figure 8 A, B and C), marked variations can be noted during the emission period as a result
 601 of the substance fate. As previously discussed and shown in the case of prochloraz, the fate

602 of organic substances is driven not only by the emission profile but also by rapid removal and
603 transfer processes. For the organic substances the impact is high during the emission period.

604



605

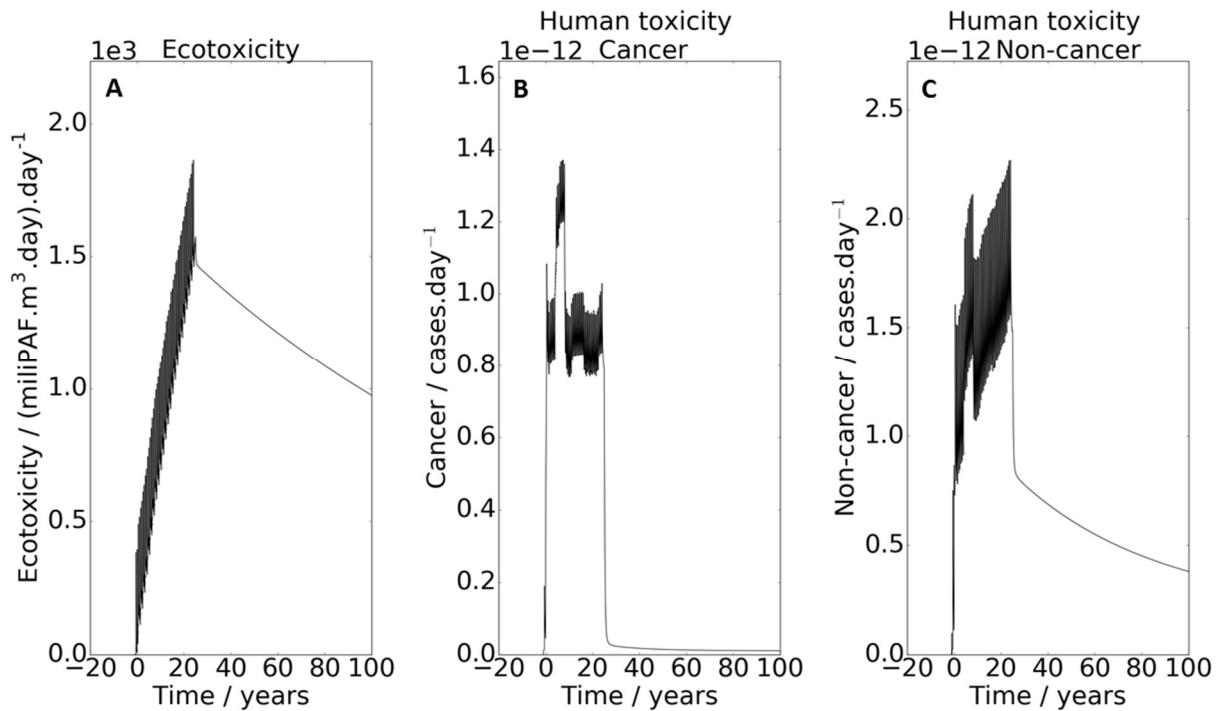
606 Figure 8 – Current Ecotoxicity $n_{eco}(t)$ (A), Cancer (B) and Non-cancer (C) Human toxicity
607 $n_{human}(t)$ of organic substances for the production of 1 kg of grapes

608

609 Regarding the human toxicity and the ecotoxicity of inorganic substances (Figure 9 A, B and
610 C), a large increase can be noted throughout the lifetime of the vineyard, due to the
611 accumulation of substances in agricultural soil as a result of their slow inter-compartment
612 transfer and very slow removal (high persistence). After that period, toxicities slowly decrease
613 asymptotically in time.

614

615



616

617 Figure 9 – Current Ecotoxicity $n_{eco}(t)$ (A), Cancer (B) and Non-cancer (C) Human toxicity
 618 $n_{human}(t)$ of metals for the production of 1 kg of grapes

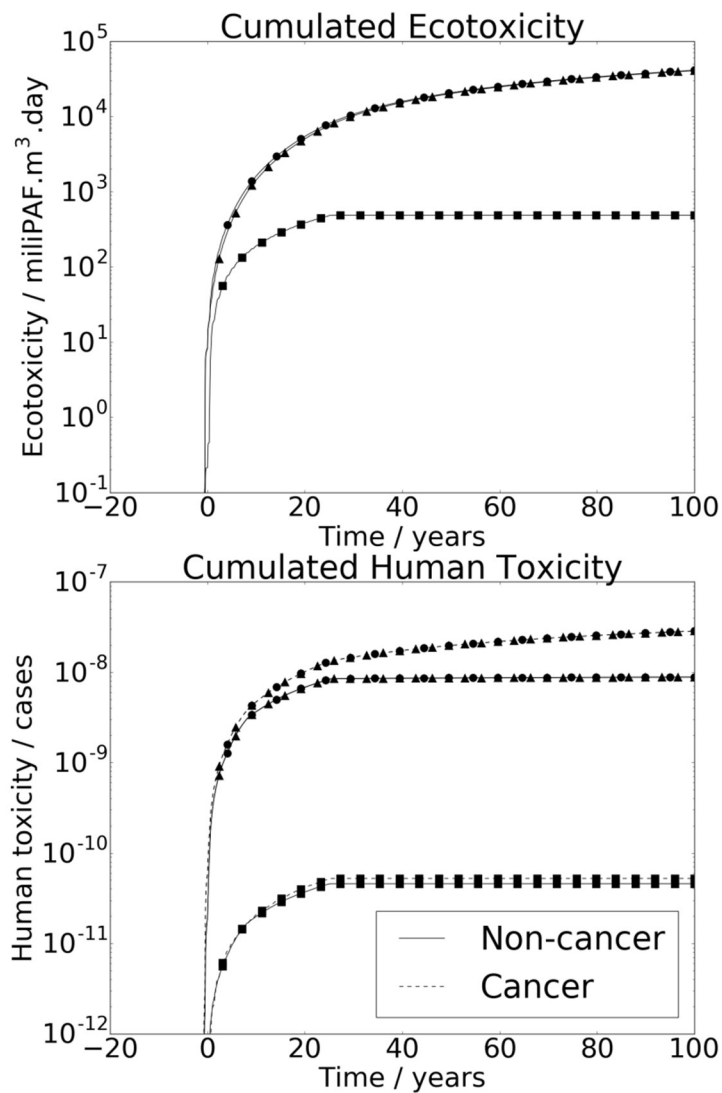
619

620 Figure 10 shows the cumulated ecotoxicity in $PAF.m^3.day$ (fig 10.A) and the cumulated human
 621 toxicity, as cancer and non-cancer in cases (fig 10.B), over the time horizon, for all substances
 622 considered together, for organics and inorganics. Cumulated ecotoxicity and non-cancer
 623 human toxicity increased progressively with time due to the higher contribution of persistent
 624 inorganics. Cancer human toxicity increased strongly during the emission of pollutants and
 625 more slowly in the long term. The explanation is the contribution of less persistent inorganics
 626 with a high toxicity potential, such as arsenic or mercury (see SI - S5).

627

628

629



630

631 Figure 10 – Cumulated dynamic ecotoxicity $n_{eco,cumul}$ (A) and human toxicity $n_{human,cumul}$ (B) of
 632 all environmental interventions (●), organic substances (■) and metals (▲) for the production
 633 of 1 kg of grapes.

634

635 Cumulated toxicity for organic substances reflects their fate well. The order of magnitude of
 636 the cumulated values for toxicity of organic substances is negligible compared to the cumulated
 637 values of toxicity for all substances considered in the testbed case. Toxicity results for inorganic
 638 substances show values very close to those obtained for all substances which highlights the
 639 importance of inorganic substances in the toxicity impact assessment for this testbed case.

640 Table 3 presents the cumulated values for human toxicity and ecotoxicity, calculated over the
 641 time horizons of 100 and 500 years.

642

643 Table 3 –Conventional (infinite time horizon) and dynamic (time horizons of 100 and 500 years)
 644 cumulated toxicity impacts for organic, inorganic and all substances emitted in the grape
 645 production testbed case

	Cumulated impact	Conventional	Dynamic 100 years	Dynamic 500 years
Organic	Ecotoxicity (PAF.m ³ .day)	4.8E-01	4.8E-01	4.8E-01
	Cancer toxicity (cases)	5.7E-11	4.6E-11	4.6E-11
	Non-cancer toxicity (cases)	5.6E-11	5.2E-11	5.2E-11
Inorganic	Ecotoxicity (PAF.m ³ .day)	1.8E+02	4.1E+01	9.9E+01
	Cancer toxicity (cases)	1.2E-07	8.8E-09	1.0E-08
	Non-cancer toxicity (cases)	2.0E-07	2.8E-08	5.5E-08
All substances	Ecotoxicity (PAF.m ³ .day)	1.8E+02	4.1E+01	9.9E+01
	Cancer toxicity (cases)	1.2E-07	8.8E-09	1.0E-08
	Non-cancer toxicity (cases)	2.0E-07	2.9E-08	5.5E-08

646

647

648 When comparing the dynamic and conventional approaches for organic substances, a
 649 difference of about 20% can be observed in the case of human cancer toxicity. This difference
 650 may come from the inventory steps in conventional and dynamic LCI, which presented about
 651 10% of difference. For metals, the gap between dynamic and conventional toxicity results
 652 decreases as the time horizon increases. In this work USEtox[®] was chosen as the database
 653 because it is highly recommended by LCA scholars. However, it should be noted that several
 654 data used for inorganic substances are of poor relevance (named interim values) and the
 655 results should be interpreted with caution.

656 When only the organic substances were evaluated, the following individual contribution results
657 have been found (Table 4, more results in SI-S7). The pesticide that had most influence for
658 ecotoxicity was metam with a contribution of 32% in the dynamic and conventional methods;
659 for dynamic human cancer toxicity, pronamide contributed with 12% in the dynamic method
660 and 10% in the conventional method; for human non-cancer toxicity prochloraz contributed
661 with 16% in the dynamic method and 15% in the conventional method.

662

663 Table 4 – Contribution of distinct pesticides on dynamic (cumulated toxicity at 100 years) and
664 conventional (infinite time horizon) toxicity impacts generated by all organic substances.
665 Results for human toxicity (Cancer and Non-cancer) and ecotoxicity (Eco) impacts for the
666 production of 1 kg of grape.

Substance	Dynamic (100 years)			Conventional		
	Cancer	Non-cancer	Eco	Cancer	Non-cancer	Eco
Folpet	0.1%	0.2%	8.0%	0.1%	0.2%	8.1%
Thiram	0.0%	0.4%	1.9%	0.0%	0.4%	1.9%
Imidacloprid	0.0%	10.2%	0.7%	0.0%	9.3%	0.7%
Napropamide	0.0%	1.8%	0.1%	0.0%	1.7%	0.1%
Chlorothalonil	0.1%	2.5%	15.0%	0.1%	2.3%	15.2%
Pronamide	12.7%	4.7%	0.2%	10.2%	4.3%	0.2%
Pendimethalin	0.0%	4.7%	2.9%	0.0%	4.3%	2.9%
Metolachlor	0.0%	4.9%	3.7%	0.0%	4.5%	3.7%
Prochloraz	9.9%	16.1%	0.9%	7.7%	14.6%	0.9%
Mancozeb	0.0%	14.1%	14.4%	0.0%	13.0%	14.4%
Metiram	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
MCPB	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Glyphosate	0.0%	15.0%	1.0%	0.0%	0.0%	0.0%
Chlormequat	0.0%	11.4%	0.0%	0.0%	10.5%	0.0%
2,4-D	0.0%	9.0%	0.0%	0.0%	8.2%	0.0%
Metam-sodium dihydrate	0.0%	0.0%	31.7%	0.0%	0.0%	31.5%

Chlortoluron	0.0%	0.0%	0.3%	0.0%	0.0%	0.3%
Isoproturon	0.0%	0.0%	3.1%	0.0%	0.0%	3.1%
Metamitron	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Metazachlor	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Aclonifen	0.0%	0.0%	7.2%	0.0%	0.0%	7.2%
Dimethenamid	0.0%	0.0%	6.5%	0.0%	0.0%	6.5%

667

668

669 In this testbed case, cumulated toxicity and ecotoxicity are dominated by the inorganic
670 persistent substances, for which conventional methods may give overestimated impact results,
671 as also discussed in section 3.1. The more the HT tends to infinity the closer the value of
672 cumulated toxicity comes to the values of a conventional LCA. In contrast, current toxicity
673 diminishes with HT. In other words, the population and ecosystems are less affected by the
674 residual pollution but they suffer the greatest damage in a restricted period corresponding to
675 the end of lifetime of the system (about one generation is strongly affected). These results
676 emphasize the importance of the current impact evaluation as a measure of the intensity of
677 possible damage at a given time.

678 Another aspect concerns the distribution in time of the activity of different processes involved
679 in the life cycle of grape production. The dynamic LCI-LCIA approach allows to observe that
680 the main toxicity impact occurs in the present and future time. The explanation is that all
681 chemicals and other commodities are produced and used during the lifetime of the foreground
682 process and no important infrastructure was built in the past. The impact generated in the past
683 by background processes, previously to vineyard activity, is very small when compared to the
684 current impact (past impact is hardly visible on the negative time axis on all figures). However,
685 inorganic substances emissions from the past activities generate persistent impact for the
686 present and future time.

687 From a LCA – decision making point of view, dynamic evaluation provides complementary
688 information helping at discriminating comparable scenarios and at proposing solutions for
689 impact mitigation. For equal conventional impact results, time dependent behaviour of toxicity
690 can be different for the compared scenarios. For example, scenario B has more metals
691 contribution than A (all equal otherwise). Impact at the human lifetime scale could be lesser in
692 case of B as the time horizon is a very important parameter for potential cumulated impact in
693 case of persistent chemicals. Scenario B could be preferable for short durations like the
694 vineyard lifetime. Solutions for changing the land destination could be envisioned in order to
695 avoid a sensitive use (e.g. for food production) in the future.

696 The existence of variations with different amplitudes on the toxicity curves (figures 5-9)
697 suggests that dynamic toxicity simulation can be used as a forecast tool for, e.g. identifying
698 optimal situations where certain activities should be (temporarily) stopped or, at the contrary,
699 launched, at regional level. For example, to not use a specific substance during the years with
700 forecasted high toxicity pics, or to stop the sensitive use of a certain water resource for a given
701 period, etc.

702

703 **4. Conclusions**

704 In this study, a mathematical implementation of dynamic toxicity assessment based on the
705 USEtox[®] model was presented. In addition, the study developed a dynamic LCA framework,
706 combining dynamic LCI modelling and toxicity impact evaluation over time. The feasibility of
707 such an approach was demonstrated via a testbed case on grape production.

708 The main features of the dynamic toxicity calculator can be summarized as follows. The
709 dynamic toxicity model is based on the resolution of the dynamic fate model in USEtox[®].
710 Exposure and effect factors are unchanged and considered constant in time. Characterization
711 factors are no longer needed as current toxicity and cumulated toxicity are directly calculated
712 in function of time.

713 Instead of using CFs, the dynamic mass balance equations were directly integrated, the
714 behaviour of different substances being determined by the transport and reaction processes
715 in the fate step. The computational method should consider the possibility of a noisy and
716 random shape for the emission function. Therefore, the odeint integrator (Scipy Python), a
717 robust method for ODE resolution that is compatible with stiff systems, was employed in the
718 present work.

719 The toxicity calculator can be easily coupled with a dynamic LCI tool, in our case DyPLCA,
720 thus providing a complete dynamic LCA framework.

721 Regarding the expected results of a dynamic approach, the following outcomes can be
722 mentioned.

723 The current toxicity ($\text{cases}\cdot\text{day}^{-1}$) allows the intensity of the impact at a given time to be
724 evaluated and the critical periods with regard to the potential impact to be identified. The
725 evolution of toxicity in time is similar to the substance fate profile (mass in compartments
726 versus time).

727 The cumulated toxicity (cases) represents the total damage generated over a given time
728 horizon. This result was compared with the conventional toxicity value. It should be noted that
729 the cumulated toxicity reaches the conventional toxicity value for large time horizons
730 (theoretically at infinite time).

731 Significantly different behaviours were observed when persistent and non-persistent
732 substances were compared. Non-persistent (generally organic) substances deployed almost
733 all their hazard potential during their emission period and disappeared more or less rapidly due
734 to degradation or transfer to sink compartments (removal). In contrast, persistent substances
735 accumulated in environmental compartments during the emission period and their toxicity
736 potential remained high after the cessation of emission, affecting many human generations.
737 However, a calculation of toxicity at equilibrium (infinite time in conventional method)
738 overestimated the total impact at the time scale of a human life.

739 The results obtained by the conventional method - which fixes an arbitrary time horizon - made
740 no distinction between persistent and non-persistent pollutants. In contrast, dynamic
741 calculations of toxicity and generally dynamic LCA brought out important information about the
742 period when the potential hazard becomes critical, allowing mitigation of pollution issues, which
743 is not the case in conventional LCA. Dynamic LCI – LCIA can be used as a forecast tool by
744 simulating different scenarios in function of time, identifying optimal situations and scheduling
745 the activities, helping in this way decision making. Combination of both dynamic aspects, LCI
746 (share of environmental interventions in time, i.e. the functioning of life cycle processes) and
747 LCIA (environmental mechanisms and specificities of substances), allows thus to obtain
748 detailed case specific information on potential hazard/environmental impact.

749

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