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Mass balance approach to assess the impact of cadmium decrease in mineral phosphate fertilizers on health risk: the case-study of French agricultural soils

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KEYWORDS

Cadmium, fertilizing materials, soil contamination, food contamination, human exposure, risk assessment

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31 Abbreviation, specific definition: fertilisers (UK) = fertilizers (US) include organic, inorganic
32 and organo-mineral fertilizers intended to ensure or improve plant nutrition, and organic,
33 inorganic and organo-mineral soil amendments that improve the physical, chemical and
34 biological properties of soils.

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57 **Abstract**

58 Cadmium is a ubiquitous and highly toxic contaminant that can cause serious adverse effects.
59 The European Food Safety Authority (EFSA) and the French Agency for Food, Environmental
60 and Occupational Health & Safety (ANSES) have shown that the risk related to food
61 contamination by cadmium cannot be ruled out in Europe and France. Fertilizing material is
62 one of the main sources of cadmium contamination in the food chain on which regulators can
63 play to reduce cadmium exposure in the population. The aim of this work was to develop a
64 mass-balance approach integrating the various environmental sources of cadmium to estimate
65 the effects of a decrease in cadmium concentrations in crop fertilizers on dietary exposure and
66 on the health risk. This approach led to a predictive model that can be used as a decision-making
67 tool. Representative and protective fertilization scenarios associated with controlled cadmium
68 levels in mineral phosphate fertilizers were simulated and converted into cadmium fluxes.
69 Cadmium inputs from industrial mineral phosphate fertilizers were then compared with
70 cadmium brought by the application of manure, sewage sludge and farm anaerobic digest, at
71 the levels typical of French agricultural practices. Regardless of the fertilizer and scenario used,
72 a flux lower than $2 \text{ g Cd.ha}^{-1}.\text{year}^{-1}$ reduces both the accumulation in soils and the transfer of
73 cadmium in the food chain. It corresponds to a cadmium content of $20 \text{ mg.kg P}_2\text{O}_5^{-1}$ or less in
74 mineral phosphate fertilizers. Modelling the transfer of cadmium from the soil to consumed
75 food made it possible to propose cadmium limits in fertilizers applied in France. In a global
76 context of ecological transition to promote human health, this research will help risk managers
77 and public authorities in the regulatory decision-making process for the reduction of
78 environmental cadmium contamination and human exposure.

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82 **1. Introduction**

83 Even at low concentrations, cadmium (Cd) is a highly toxic ubiquitous trace element (EFSA,
84 2009). Environmental Cd levels result partly from its natural occurrence in the earth's crust and
85 mainly from anthropogenic inputs related to industrial, agricultural and transport activities
86 (EFSA, 2009).

87 In humans, Cd is widely distributed in the body, where it accumulates over time, with a
88 biological half-life ranging from 10 to 30 years (EFSA, 2009). Cd is mainly found and stored
89 in the liver and kidneys (EFSA, 2009; ATSDR, 2012). Prolonged human oral exposure to Cd
90 induces nephropathy, bone diseases, reproductive disorders and an increased risk of cancer for
91 several organs (lung, prostate and kidneys) (EFSA, 2009). Cd and its compounds are considered
92 as "carcinogenic to humans" (group 1) by the International Agency for Research on Cancer
93 (IARC, 2012).

94 Excluding smoking, exposure to Cd in the general population is mainly through diet (EFSA,
95 2009, 2012). Cd enters the food chain primarily through transfer from soils to crops (EFSA,
96 2009). Plant roots uptake Cd at a rate that is essentially driven by the chemical species of the
97 element, with soluble Cd ions being more readily assimilated than insoluble the complexes that
98 Cd can form with inorganic and organic soil constituents. Physico-chemical properties of the
99 soil may also play important roles. For instance, when soil pH decreases, Cd bioavailability
100 increases. Soil-plant transfer of Cd also depends on plant features (species, developmental
101 stage, plant organ, etc.) (Tremel-Schaub and Feix, 2005). Its persistence and the increase in
102 anthropogenic bioavailable forms in the environment and cultivated soils particularly poses a
103 serious human health problem that demands investigation (Shahid *et al.*, 2017)

104 European (EFSA, 2012) and French (ANSES, 2011a and b) studies have shown that the risk
105 related to Cd dietary exposure cannot be ruled out for a part of the population. In the second
106 French Total Diet Study (TDS) (ANSES, 2011a), the health-based guidance value (HBGV)

107 defined by EFSA in 2009 was exceeded in 0.6% of adults and 14.9% of children over 3 years
108 old. This exceedance of the EFSA HBGV was also observed in younger children in the first
109 French infant TDS, up to 29% of children aged 13 to 36 months and 36% of children aged 7 to
110 12 months (ANSES, 2016). In both French TDSs (ANSES, 2011a and b, 2016) and at the
111 European level (EFSA 2012), the major contributors to Cd exposure are cereals and cereal
112 products, vegetables, potatoes and related products.

113 One possible means to reduce exposure is to act on the main food contributors (i.e. such as
114 cereals, vegetables, potatoes), primarily by reducing their levels of contamination at the source
115 or after production using regulatory measures. Limiting exposure requires the implementation
116 or enhancement of Cd management by controlling environmental releases or processes and/or
117 fixing regulatory thresholds (or reduction of these thresholds if they already exist) to limit the
118 contamination levels of foods identified as the main contributors. However, strengthening
119 regulations on the maximum level of Cd allowed in food can have a low impact on reducing
120 human exposure due to the ubiquitous Cd contamination according to Jean *et al.* (2015). It is
121 therefore recommended to take further action on environmental sources and food contamination
122 routes, particularly in regard to fertilizer inputs, identified as the main source of soil and food
123 contamination.

124 In France, mineral phosphate fertilizers have been identified as the main source of Cd in
125 agricultural soils in arable farming regions (Belon *et al.*, 2012). Phosphate fertilization is
126 adjusted according to the estimated plant phosphorus needs and the availability of phosphorus
127 in the soil. However, there is a sore lack in agronomic field data. Depending on the Cd
128 concentration and the amounts of fertilizer used for phosphate fertilization, mineral phosphate
129 fertilizers represent a little more than half of the Cd inputs in French agricultural soils (Belon
130 *et al.*, 2012). Mineral phosphate fertilizers are made from natural phosphate rocks, which can
131 contain Cd, sometimes in quite high concentrations, according to the nature of the rock material

132 and geographical area from which the rocks are extracted. In sedimentary rocks, for instance,
133 Cd concentrations can reach up to 150 mg Cd.kg⁻¹ rocks (Roberts, 2014). Igneous rocks such
134 as Kola deposits in Russia, contain lower Cd concentrations, less than 2 mg Cd.kg⁻¹.
135 Nevertheless, sedimentary rocks in Morocco have a Cd content greater than 25 mg Cd.kg⁻¹, e.g.
136 in Bou Craa (32-43 mg Cd.kg⁻¹) or Youssoufia (4-51 mg Cd.kg⁻¹) deposits (Roberts, 2014).
137 In France, there are no natural phosphate deposits, and phosphate rocks are imported. In
138 addition to the use of mineral phosphate fertilizers in France, livestock manure contributes
139 significantly to soil inputs in livestock-farming regions, and represents about 25% of the total
140 inflow Cd to agricultural soils (Belon *et al.*, 2012).

141 In France, many efforts have already been made to reduce soil Cd inputs from fertilizers.
142 Regulations have been enacted with safety criteria defined for marketing authorisations (MA)
143 for fertilizers and growing media. According to the instructions that accompany the MA
144 application (guide No 50644#01, Ministère de l'Agriculture et de la Pêche, 2001), the average
145 annual Cd flux brought to the soil in a 10 year period must not exceed 15 g Cd. ha⁻¹. year⁻¹.
146 Moreover, the French standard NF U 42-001-1 currently set a regulatory maximum limit for
147 mineral phosphate fertilizers at 90 mg Cd. kg⁻¹ per unit mass of phosphoric anhydride (P₂O₅)
148 equivalent. Although there were defined by Regulation (EC) No 2003/2003, no Cd limit had
149 been previously established for this fertilizer at the European level. In 2016, the European
150 Commission (European Commission, 2016) revised the regulation on EU fertilizing products
151 (Regulation (EU) No 2019/1009 repealing Regulation (EC) No 2003/2003) to propose new
152 limit values for contaminants in EU-labelled fertilizers including Cd, taking into account their
153 adverse effects on humans and the environment. Several Cd levels were discussed for the use
154 of mineral phosphate fertilizers (European Commission, 2016). A Cd concentration of 60 mg
155 Cd.kg P₂O₅⁻¹ was adopted, in view of a potential application of this regulation in 2022
156 (Regulation (EU) No 2019/1009).

157 At the interface between risk assessment and regulatory level, the present study aims to define
158 protective Cd limit levels in mineral phosphate fertilizers intended to be applied. To do so, a
159 predictive support model was built to evaluate the evolution of Cd content in French agricultural
160 soils over time, the resulting contamination of crop production and associated dietary exposure
161 and human health risk with respect to Cd inputs. This predictive model was based on a mass-
162 balance approach (equilibrium calculation between the input and output pathways of Cd in
163 agricultural soils) combined with a dietary exposure assessment.

164 This original approach linked soil quality, plant quality and dietary exposure to derive and
165 check Cd limits in mineral phosphate fertilizers to protect human and environmental health.
166 The model was first developed for the major source of Cd input (i.e. mineral phosphate
167 fertilizers) and for the two major field crops contributing to human exposure to Cd, namely
168 wheat and potatoes (ANSES, 2011a, 2011b, 2016). The model was then adapted to other
169 organic fertilizers when scientific data were available.

212 **2. Materials and methods**

213 2.1 Input data for the model

214 Data used as input parameters for the mass-balance approach applied to French agricultural
215 soils involved soil data, Cd concentrations in fertilizers, rainwater quantity, agricultural yields
216 and Cd concentrations due to atmospheric deposition and irrigation water. Table S1 in
217 supplementary materials describes the data sources and distributions used to model this data,
218 their range of values and the equations used to estimate some model parameters from the data.
219 It also indicates if the variability between plot and year was included or not and how uncertainty
220 was dealt with.

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223 *Soil data*

224 Data came from the French soil quality monitoring network (*Réseau de Mesures de la Qualité*
225 *des Sols*, RMQS) which is a systematic grid (16 km × 16 km) covering all of mainland France
226 with 2240 sites (Arrouays *et al.*, 2002; Arrouays *et al.*, 2020). This network is representative of
227 the French territory, covering a broad spectrum of climatic, soil and land-use conditions
228 (croplands, permanent grasslands, woodlands, orchards and vineyards, natural or weakly
229 anthropogenic lands). Every 15 years at each site, soil samples are taken, measurements are
230 carried out and observations are made. The first campaign occurred from 2000 to 2010 in
231 mainland France. At these sites, the soil organic carbon (SOC) content, particle-size
232 distribution, pH, main total trace elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Tl, Zn) and
233 soil densities were determined for the 0–30- and 30–50-cm layers. Samples for laboratory
234 analyses were taken from a bulked sample of 25 core samples from unaligned sampling in a
235 400 m² square area. The entire dataset is available on request and the statistical distribution of
236 the results can be downloaded from the INRAE dataverse (Saby *et al.*, 2019).

237 The concentration of Cd in French soils was mapped across France (Marchant *et al.*, 2010), the
238 mean and median values for Cd in the top soil (0–30 cm) were respectively 0.30 and 0.20 mg.kg⁻¹
239 dry mass. For modelling, the Cd geochemical background, which represents the Cd present in
240 the soil at the beginning of the simulation, was taken from this dataset restricted to current Cd
241 levels in French agricultural soils (i.e. cultivated soils and grasslands, other land uses being
242 excluded as non-cultivated with no fertilizer applications). This dataset provided the empirical
243 distribution of Cd levels associated with the geochemical background in French agricultural
244 soils. All other parameters needed for modelling (i.e. apparent soil density, concentrations of
245 organic matter, clay, carbon, and soil pH) came from the same RMQS dataset including 2059
246 agricultural soils.

247 Our models took the diversity of soil composition found in France into account by randomly
248 sampling one RMQS site in the dataset, represented by a vector, including its Cd geochemical
249 background, concentrations of organic matter, clay, carbon, and soil pH.

250 *Cd inputs due to atmospheric deposition*

251 The Cd concentration due to atmospheric deposition on French agricultural soils came from the
252 empirical distribution proposed in Belon *et al.* (2012).

253 *Cd inputs from irrigation water*

254 Cd concentrations from irrigation water were calculated by combining the irrigation quantity
255 of each crop with the Cd concentration in the irrigation water. The quantity of irrigation water
256 for each crop was modelled by applying a triangular distribution to the French ARVALIS
257 research institute database (ARVALIS, 2011 and 2013). A truncated normal distribution was
258 applied to the data from the geochemical atlas of Europe linked to the FOREGS database
259 (FOREGS, 2005 and 2006) to model Cd concentrations in irrigation water.

260 *Rainwater quantity*

261 Rainwater quantity was integrated in the model by using the empirical distribution from data of
262 the Agri4cast resources portal (JRC): Agri4Cast Resources Portal. Gridded Agro-
263 Meteorological Data in Europe. Available at
264 <https://agri4cast.jrc.ec.europa.eu/DataPortal/Index.aspx?o=> for the 2005-2015 period of
265 precipitations in France.

266 *Agricultural yields*

267 Yields specific to each crop were simulated from a triangular distribution applied to data from
268 the French ARVALIS research institute (ARVALIS, 2013).

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271 *Cd concentrations in food*

272 Concentration in foods came from the second French TDS, in which Cd was analysed in 1319
273 food composite samples representative of the whole diet of the population and prepared “as
274 consumed” (Millour *et al.*, 2011). Left-censored data were managed by calculating a lower
275 bound (LB) and an upper bound (UB) hypothesis by adapting WHO recommendations (WHO,
276 2013). In the LB approach, non-detected results and detected-but-non-quantified results were
277 respectively replaced by zeros and by the limit of detection (LOD). In the UB approach, non-
278 detected results were replaced by the LOD and detected-but-non-quantified results were
279 replaced by the limit of quantification (LOQ). Because the quantification rate was high, results
280 were similar under both hypotheses, and only the UB approach is presented in the present work
281 as recommended by the WHO (2013).

282 *Food consumption*

283 Consumption data came from the French national and individual food consumption survey
284 (INCA2) (Dubuisson *et al.*, 2010; Lioret *et al* 2010). In this survey, food and beverage
285 consumption was assessed through a 7 consecutive day record for a random sample of the
286 French population drawn using a multistage cluster sampling technique. Individual body
287 weights were also measured. For this study, data from 1918 adults aged 18-79 years and 1444
288 children aged 3-17 years were used.

289 2.2 Fertilization scenarios and Cd input via mineral phosphate fertilizers

290 *Crop fertilization*

291 Wheat was studied in monoculture or in rotation with potatoes over three years
292 (potatoes/wheat/wheat) following common agricultural practices of French fertilizations plans
293 as recommended by the *Comité Français d'Etude et de Développement de la Fertilisation*.
294 *Raisonnée* (COMIFER, 2009) and ARVALIS (ARVALIS, 2018).

295 *Phosphate fertilization*

296 Representative mineral phosphate fertilizer plans for French agricultural soils were modelled.
297 They were linked to protective scenarios of Cd input selected for the risk assessment. The
298 fertilization plans most likely to add Cd to agricultural soils were selected. They were associated
299 with low phosphorus concentrations in soils (i.e. one-third of the soils in France (Delmas *et al.*,
300 2015, Saby *et al.*, 2016) according to the phosphorus requirements of plants. Phosphate
301 fertilizations plans based on annual applications and applications every 3 years of phosphate
302 mineral fertilizer intake were included in the predictive model. Realistic but representative and
303 reduced-Cd phosphate fertilization plans were simulated for an annual phosphate application
304 of 80 and 100 kg P₂O₅.ha⁻¹ for wheat and for the potatoes/wheat/wheat rotation. Phosphate
305 fertilization plans with two years without fertilization were tested applying 100 and 180 kg
306 P₂O₅.ha⁻¹ for wheat and for the potatoes/wheat/wheat rotation. Although realistic, these
307 scenarios can be considered as worst case scenarios, because in France the mean phosphorus
308 application rates on wheat and potato crops are 53 kg.ha⁻¹ P₂O₅ and 84 kg.ha⁻¹ P₂O₅ respectively
309 (Sterckeman *et al.*, 2018a).

310 *Cd concentrations tested in mineral phosphate fertilizers*

311 Cd concentrations in mineral phosphate fertilizers proposed in the French and European
312 regulations were studied. The level of 90 mg Cd.kg P₂O₅⁻¹ set by the French standard NF U 42-
313 001-1 was used here and considered as the 'reference scenario'. The reduced Cd concentrations
314 already discussed at the European level (European Commission, 2016) for a harmonised
315 European regulation on mineral phosphate fertilizers with 60, 40 and 20 mg Cd.kg P₂O₅⁻¹ were
316 selected here, including the level adopted in Regulation (EU) No 2019/1009. For organo-
317 mineral fertilizers, the European Commission also proposed a plan with application EC-labelled
318 fertilizer with 60 mg Cd.kg P₂O₅⁻¹, then 3 years after application a reduction of this threshold

319 to 40 mg Cd.kg P₂O₅⁻¹ and finally after 12 years to 20 mg Cd.kg P₂O₅⁻¹ (European commission,
320 2016). This scenario was also studied in our work.

321 *Cd fluxes due to mineral phosphate fertilizers*

322 The phosphate application doses were matched with various Cd levels in phosphate fertilizers
323 to determine annual Cd fluxes in agricultural soils via phosphate fertilizers, expressed in g.ha⁻¹
324 ¹.year⁻¹. Table 1 gives the scenarios and their associated names according to the phosphate
325 fertilizer plans (Ph), the phosphate input dose related to the plant requirements for a wheat
326 monoculture crop (b) or a potatoes/wheat/wheat rotation (bp), and the modelled Cd
327 concentration, e.g. Ph/80b/90 indicates a phosphate fertilizer plan with an application of 80 kg
328 P₂O₅.ha⁻¹ for wheat monoculture and a Cd input of 90 mg Cd.kg P₂O₅⁻¹. Accordingly, our
329 reference scenarios are Ph/80b/90, Ph/100b/90, Ph/100bp/90, Ph/180bp/90. The reduced-Cd
330 scenarios model 60, 40, 20 mg Cd.kg P₂O₅⁻¹ at fixed and degressive (e.g. reduction 3 years after
331 first application, then again 12 years thereafter) levels. Coupling the application dose with the
332 Cd content to be tested according to the fertilization plan (wheat monoculture or rotation)
333 resulted in 20 fertilization plan scenarios to be tested in the model. These scenarios gave Cd
334 fluxes varying from 0.67 to 9 g Cd.ha⁻¹.year⁻¹ (Table 1).

335 2.3 General model

336 The model developed to estimate the effect of reduced Cd in fertilizers on consumer exposure
337 and risk over time comprised two steps (Figure 2). The first step modelled the transfer of Cd
338 from environmental sources (irrigation water, soil, atmospheric deposition and fertilizers) to
339 plants. It was based on a probabilistic parameterisation of a mass-balance approach and made
340 it possible to study the effect of reducing Cd in fertilizers on the Cd concentration in plants,
341 according to the expected Cd concentration in the fertilizer. The second step assessed the effect
342 of reduced Cd on consumer exposure and risk. It studied the potential percentage of decrease
343 in Cd levels in food according to the various reduced-Cd (protective) scenarios.

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2.3.1 Mass-balance approach to model Cd transfer from environmental sources to plants

348 *Mass-balance approach to estimate Cd in soil in year i*

349 Cd concentrations in soil were estimated using a mass-balance approach linked to different
350 sources of Cd in agricultural soil and its elimination. This approach was based on the method
351 proposed by Six and Smolders (2014), and implemented for specific French soils as described
352 in Sterckeman *et al.* (2018a, b). The soil Cd concentration in year i, $[Cd]_{soil,i}$ (mg.kg⁻¹), was
353 calculated by adding the soil Cd concentration in soil at year i-1 $[Cd]_{soil,i-1}$ (mg.kg⁻¹) to Cd
354 inflows (mineral phosphate fertilizer, atmospheric deposition and irrigation water) minus Cd
355 outflows (elimination by leaching and plant transfer) divided by the mass of the 0–30cm layer
356 per hectare (W_{soil}) (kg.m⁻³) (Eq. (1)).

$$357 \quad [Cd]_{soil,i} = [Cd]_{soil,i-1} + \frac{(cadmium\ inflows - cadmium\ outflows)}{W_{soil}} \quad (1)$$

358

359 *Cd transfer in plant and leaching*

360 Modelling of cadmium outflows from agricultural soil to plants (wheat grain and potato) was
361 based on the integration of transfer equations from Franz *et al.* (2008) and Ran *et al.* (2016),
362 given in Table S1. These equations were selected on the basis of the following criteria: (i) a
363 non-industrial origin of soil Cd contamination, (ii) a pertinent correlation coefficient and (iii)
364 the possibility to include the parameters of the equation using available French soil input data
365 presented in section 2.1. The equations specifically took into account crop uptake factors linked
366 to soil physico-chemical characteristics with distributions of soil organic matter concentrations,
367 clay and carbon and also soil pH.

368 The annual amount of Cd leaching was calculated by determining the Cd concentration in the
369 soil solution using on the formula elaborated by De Vries (2011 and 2013) (Table S1). We also
370 determined the volume of soil solution removed from the soil layer considered (30 cm) each
371 year. This volume was estimated as a percentage of the volume of water the plot receives each
372 year, assuming that 30% of this water is irrigation water and the rest (70%) rainwater.

373 *Simulations over 99 years integrating variability and uncertainty*

374 Cd concentrations in soil, wheat grains, potatoes and leachate were simulated over 99 years
375 using Monte Carlo simulations. For a given fertilization plan, 10,000 plots were simulated to
376 account for the diversity of plots in France. To simulate one plot, a vector containing the Cd
377 concentration related to the geochemical background, concentrations of organic matter, clay
378 and carbon, and soil pH was selected from the RMQS dataset, which allowed us to integrate
379 correlations observed between these parameters in the French plots. For parameters such as
380 rainwater quantity, agricultural yields or irrigation water quantity, which varied from plot to
381 plot and from year to year, variability was accounted for by randomly selecting a value per plot
382 and per year in their associated distributions. Increases or decreases in Cd concentrations were
383 then calculated on the modelling period for the 10,000 plots. A sensitivity analysis on the
384 number of simulated plots was performed and showed that simulating 10,000 plots was
385 sufficient to obtain stable results. The mass balance for each simulation was also verified. The
386 algorithm was programmed using R software (version 3.4.0, 21-04-2017). The means and
387 percentiles of Cd concentrations in soil, plants (wheat grains and potato) and leachate over time
388 for all plots are given in tables and graphs. Differences in concentrations in the different
389 matrices (soil, plant or leachate) between years were also analysed in regard to the Cd content,
390 soil pH and whether the Cd concentration between the first year of application and the 99 year
391 increased or decreased.

392

393 2.3.2 Exposure and risk assessment based on changes in Cd concentration in food as
394 consumed

395 French exposure to Cd was first calculated by combining consumed quantities from the INCA
396 2 study with the Cd concentration in food from the TDS considering all food items
397 contaminated by Cd. The resulting exposure was considered as the ‘starting scenario’.

398 Then, variations in Cd concentrations over time expressed as a mean percentage decrease or
399 increase in plants based on the fertilization scenarios were applied to the mean Cd
400 contamination of soft and durum wheat- and potato-based foods of the TDS, using the method
401 described in Jean *et al.* (2015). Corresponding consumer exposure levels for each fertilization
402 scenario were assessed. Reduced-Cd scenarios were compared with both the reference scenario
403 (French regulatory Cd cadmium concentration in mineral phosphate fertilizer) and the starting
404 scenario.

405 Mean, standard deviation (SD) and 95th percentiles of exposure (P95) were calculated for adult
406 and child populations, for each scenario and each period (10, 20, 60 and 99 years). In addition,
407 the health risk linked with each exposure was assessed by calculating the percentage of
408 individuals exceeding the HBGV, with its 95% confidence interval (CI_{95%}). In the present work,
409 a HBGV for Cd by ingestion of 0.35 µg.kg bw⁻¹.d⁻¹ was used on the basis of a physiologically
410 based toxicokinetic model modelling lifelong exposure to Cd and considering the effects on
411 bones as critical effects (ANSES, 2019).

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418 **3. Results**

419 3.1 Environmental contamination and consumer exposure

420 3.1.1 Mass-balance modelling results

421 Table 2 presents the mean Cd variation for the various scenarios modelled.

422 Probabilistic parameterisation of the mass-balance approach allowed a presentation of a
423 distribution of percentage variation in Cd concentration in the matrix over time. We used
424 boxplots to explore and visualise two fertilizations plans of interest. Figure 3 presents the plan
425 with the greatest Cd accumulation over time in soil, plants and leachates associated with wheat
426 monoculture receiving an annual application of 80 kg P₂O₅.ha⁻¹.year⁻¹ (Ph/80b/90, Ph/80b/60,
427 Ph/80b/40 and Ph/80b/20). As of 10 years and thereafter, Cd content increases significantly in
428 soils and plants over time (about 10% variation) in line with increasing Cd concentrations in
429 fertilizers, from 40 to 90 mg.kg⁻¹ P₂O₅. The mean rate of increase in Cd concentration reaches
430 up to 64% in plants and 72% in leachates over the 99-year period for the Ph/80b/90 reference
431 scenario, representing the current French regulatory threshold of 90 mg Cd.kg P₂O₅⁻¹. Cd
432 content in soils and plants are contained only at a level of 20 mg Cd.kg⁻¹ P₂O₅ in this fertilization
433 plan.

434 The potato/wheat/wheat rotation fertilization plan of 180 kg P₂O₅.ha⁻¹.year⁻¹ with a two-year
435 hiatus in fertilisation (Ph/180bp/90, Ph/180bp/60, Ph/180bp/40 and Ph/180bp/20) showed the
436 greatest decrease in Cd accumulation in the soil and reduction in its transfer to plants and
437 leachate among all simulations over time (Figure 4). In contrast to maintaining the current
438 French regulatory threshold of 90 mg Cd.kg P₂O₅⁻¹ in the Ph/180bp/90 reference scenario, the
439 decrease in Cd input by reducing Cd concentrations as much as possible in mineral phosphate
440 fertilizers tends to limit its accumulation in French agricultural soils and its transfer to plants
441 and leachate over time. Based on the distributions and the mean Cd concentration (Figure 4), a

442 significant reduction in the transfer of Cd to wheat (grain) and potato was observed as of 10
443 years for phosphate fertilizers with contents equal or less than 40 mg Cd.kg P₂O₅⁻¹. This
444 decrease was enhanced for the even lower fertilizer Cd content of 20 mg Cd.kg P₂O₅⁻¹. In this
445 latter plan, a decrease greater than 25% of Cd accumulation in French agricultural soils and its
446 transfer is reached over the 99-year period with the distribution of percentage variation in Cd
447 concentration in matrices at the 25th percentile using a set of French soil combinations.
448 Compared with the first year of application, a greatest mean percentage of reduction in Cd
449 concentration in matrices (21%) was observed at the lowest simulated Cd concentration (20
450 mg.kg⁻¹ P₂O₅) over the 99-year period (Table 2). The reduction in the Cd concentration in plants
451 depending on the action at the source of Cd was more pronounced for wheat grain than for
452 potato tuber.

453 The trends observed in Table 2 and Figures 3 and 4 show that, at the two highest Cd
454 concentrations (60 and 90 mg Cd.kg P₂O₅⁻¹), Cd accumulates in the soil and a significant
455 proportion is transferred to plants and leaching water over time, regardless of the fertilization
456 plan in wheat monoculture or potato/wheat/wheat rotation, with or without a two-year hiatus in
457 fertilization. *A contrario*, with a decrease in Cd concentration to 20 mg Cd.kg P₂O₅⁻¹ in the
458 commercial mineral phosphate fertilizer, Cd accumulation in soils and in its transfer to plants
459 and leachate stabilises and even decreases: see scenarios Ph/80b/20, Ph/100b/20, Ph/100bp/20,
460 Ph/180bp/20, with an average Cd transfer decrease of up to -18% after 99 years (Table 2). Cd
461 is preferentially transferred into leaching water than into the soil and plant matrices. Lower Cd
462 concentrations decreased this transfer to the ground water and surface water.

463 When realistic fertilizer application scenarios were tested using the degressive Cd model
464 (Ph/80b/60-40-20, Ph/100b/60-40-20, Ph/100bp/60-40-20, Ph/180bp/60-40-20), Cd transfer to
465 the plant and to leaching water is reduced, and the soils gradually become less contaminated.
466 For example, Figure 5 shows this trend for Ph/180bp/60-40-20, representative of agricultural

467 conditions in France. In this scenario, Cd is reduced by, on average, 16% in soils and wheat
468 grain, 13% in potatoes and of 20% in leachate over 99 years, reaching a Cd concentration in
469 mineral phosphate fertilizers of 20 mg Cd.kg P₂O₅⁻¹ in 15 years.

470 3.1.2 Effects of soil characteristics on Cd transfer

471 Figure 6 illustrates, as an example in a more exposed situation, the variation in Cd concentration
472 depending on soil pH for a wheat monoculture fertilization plan with an annual application of
473 80 kg P₂O₅.ha⁻¹.year⁻¹ between the first year of application and after 99 years.

474 There is a risk of Cd accumulation in acid, neutral or alkaline soils as well as of Cd transfer to
475 plants for mineral phosphate fertilizers with a Cd content greater than 40 mg Cd.kg P₂O₅⁻¹ for
476 the following soils:

477 - soils with pH < 6.5, representing 50% of the agricultural soils in France (Saby *et al.*,
478 2019);

479 - soils with pH >7.5, representing 30% of the agricultural soils in France (Saby *et al.*,
480 2019).

481 3.1.3 Health risk assessment for the consumer

482 Figure 7 shows the percentages of adults and children exceeding the Cd HBGV intake of 0.35
483 µg.kg bw⁻¹.d⁻¹ for different scenarios (ANSES, 2019) under the UB hypothesis. Compared with
484 the starting scenario corresponding to current exposure levels (ANSES, 2011a), the reduced-
485 Cd scenarios (20 mg Cd.kg P₂O₅⁻¹), on a constant or degressive basis (Ph/80b/20, Ph/180bp/20,
486 Ph/100b/60-40-20 and Ph/180bp/60-40-20 scenarios), lead to a lower exceedance of the HBGV.
487 Nevertheless, the risk remains significant in adults and children, for whom the percentage
488 exceeded 12% even after 99 years. Only the Ph/180bp/20 and Ph/180bp/60-40-20 scenarios
489 show a significant decrease in this percentage in children after 99 years.

490 In the reference scenarios corresponding to the current French regulatory threshold of 90 mg
491 Cd.kg P₂O₅⁻¹ in mineral phosphate fertilizers (Ph/80b/90 and Ph/100bp/90), the percentages of

492 exceedance are significantly higher than in the starting scenario ($p < 0.05$). For adults, this
493 increase is significant after 60 or 99 years of projection. In these situations, the percentage of
494 children in which HBGV is exceeded doubles after the projected 99 years, while for one-third
495 or more, it is not possible to rule out a risk.

496 In fertilization plans associated with a fertilizer Cd content of $20 \text{ mg Cd kg P}_2\text{O}_5^{-1}$ (constant or
497 degressive Cd content scenarios), an exceedance of the HBGV in adults and children is
498 undeniably observed, but with a significant reduction after 99 years.

499

500 3.2 Comparison of Cd fluxes via fertilizing materials

501 Cd fluxes via mineral phosphate fertilizers were compared with those via sewage sludge, cattle
502 manure and anaerobic digestates currently used in France for soil improvement. The inclusion
503 of these fertilizing materials is based on the availability of data giving results for common
504 French agronomic practices for wheat monoculture fertilization plans. Compared with Cd
505 fluxes derived for mineral phosphate fertilizers (Table 1), the fluxes for these organic fertilizers
506 are almost equivalent (0.67 to $9 \text{ g Cd.ha}^{-1}\text{.year}^{-1}$ for mineral phosphate fertilizers *versus* 1.75 to
507 $7.50 \text{ g Cd.ha}^{-1}\text{.year}^{-1}$ for organic fertilizers). Cd inputs to soils from applications of organic
508 fertilizers are mainly attributed to high application quantities, because the Cd concentrations in
509 these organic materials are generally low or intermediate compared with inorganic fertilizers as
510 shown in Table 3.

511 Figure 8 shows the results of Cd accumulation in French agricultural soils and its transfer to
512 plants and leachates over the 99-year period obtained using fluxes from different fertilizing
513 materials according to wheat monoculture agricultural practises in France. Cd accumulation in
514 the soil and its transfer to wheat grains decreases following fertilization plans with an annual
515 flux varying from 0.67 to $2 \text{ g Cd.ha}^{-1}\text{.year}^{-1}$. This decrease is attributed to the use of farm
516 anaerobic digestates with a mean Cd concentration of 0.70 mg.kg^{-1} of dry matter (DM) and

517 mineral phosphate fertilisers with a Cd content of 20 mg Cd.kg P₂O₅⁻¹. The condition without
518 added Cd from agronomic inputs (Cd inputs only come from atmospheric deposition and
519 irrigation water, in addition to the geochemical background) was also tested.

520 Results (not shown) show that the levels in the three media considered are below and close to
521 the lowest Cd dose in a mineral phosphate fertilizer (i.e. Ph/80b/20; Figure 8).

522

523 **4. Discussion**

524 Our results indicate that limiting the inputs of persistent and bioavailable Cd in the environment
525 — particularly in agricultural soils used to produce food — is a prerequisite to reducing
526 contamination in the food chain and thus human exposure to Cd and subsequent health risk.

527

528 4.1 Mass-balance and consumer exposure combining approaches to assess the Cd risk via the 529 application of fertilizers to cultivated soils

530 As required by the European Regulation project (European Commission, 2016), our
531 methodology explored the link between the evolution of Cd contamination in soils and plants
532 and the ultimate consumer exposure from food intake in a health risk assessment context. Thus,
533 our assessment addresses the effects of actions at the source, through the use of representative
534 environmentally and protective fertilization plans. The model also comprehensively addressed
535 the accumulation of Cd over time in various compartments (soil, plants and leachates) and the
536 possible health effects for consumers.

537 Six and Smolders (2014) updated the mass-balance approach initiated in 2002 by the Scientific
538 Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) by integrating the inventory
539 of Cd inputs to agricultural soils in the EU 27 + Norway (EU27 + 1) with recent data on
540 atmospheric deposition, phosphate fertilizers, sludge, lime and manure applications for soils

541 used for arable production of cereal and potato crops. However, they used mean estimates of
542 input variables. Thus, although their assumptions were realistic and encompassed the majority
543 of current situations, their assessment can be improved by taking into account the variability of
544 input data and local situations in particular the ones corresponding to Cd overexposure through
545 particular soil/ plant/input combinations, as explored here in this study. Römken *et al.* (2017)
546 and Sterckeman *et al.* (2018a, b) implemented the mass-balance approach with the integration
547 of data focusing on a more precise geographical scale respectively at the European regional
548 level and in France by integrating soil variability. However, their approach focused only on Cd
549 transfer in soil and plants and did not study their impact on food products. Furthermore,
550 previous studies have already expressed the need for a joint assessment of the trends of
551 accumulation of Cd in soil and the general dietary exposure of the population to Cd (Rietra *et*
552 *al.*, 2017; KEMI, 2011).

553 Based on probabilistic parameterisation in a mass-balance approach, our model made it possible
554 to simulate Cd transfer from agricultural soils to food consumed by the French population and
555 account for variability in French soils, local specificities and agricultural practices. This
556 approach has the advantage of being based on reliable input parameters drawn from currently
557 available data. If country-specific data on soil typology and the contamination of foods
558 consumed are available, our approach can be extended to other European and non-European
559 countries. This approach can also be developed to study other contaminants or metals, such as
560 lead (Pb), and their evolution in the case of polluted soils or population overexposure.

561 Our model, based on realistic scenarios of Cd inputs to the soil, provided estimations of Cd
562 concentrations in plants (wheat and potatoes) and leachates consistent with those observed in
563 Europe.

564 For example, simulated plant Cd concentrations at the start of the simulations (median of 0.07
565 mg Cd.kg⁻¹ in wheat grains and 0.04 mg Cd.kg⁻¹ in potatoes) were of the same order of

566 magnitude as those measured by the French monitoring programs during the 2010-2015 period
567 (median of 0.02 mg Cd.kg⁻¹ in both crops) and that reported at the European level (median of
568 0.02 mg Cd.kg⁻¹ for the two crops (EFSA, 2009). Also, Cd concentrations derived for leachates
569 at the start of the simulations were quite similar to the data reported in Six and Smolders (2014).
570 Our model provided a mean maximum leached Cd content for each simulation of 2.4 g Cd.ha⁻¹
571 ¹.year⁻¹, whereas Six and Smolders (2014) reported a mean leaching rate in Europe of 2.56 g
572 Cd.ha⁻¹.year⁻¹. Our models were thus appropriate for conducting a quantitative health risk
573 assessment.

574 Moreover, our model gave mean estimates of the progressive decrease in Cd accumulation in
575 soils over time at the lowest Cd concentration (20 mg Cd.kg P₂O₅⁻¹), with -17% over a 99-year
576 period. These estimates are close to those obtained by Smolders and Six (2014): -20% to -14%
577 with a medium fertilizer Cd concentration between 0 and 40 mg Cd.kg P₂O₅⁻¹.

578 Here, our model included several uncertainties that can be reduced by including additional
579 supplementary data that remain to be acquired. For example, we only considered wheat and
580 potatoes, because they were identified as major contributors to consumer Cd exposure through
581 food products (EFSA, 2012, ANSES, 2011a,b, 2016). Because fertilizers are applied to crops
582 other than wheat and potatoes, the assessment can be extended to other routes of Cd transfer
583 from soils to food products of plant and animal origin. Moreover, other trace elements present
584 in the soil can compete with Cd for uptake by plants (Dharma-wardana, 2018). Some of these
585 elements, namely Zn and Se, are known to interfere with Cd toxicity. For instance, Zn clearly
586 inhibits Cd uptake and bioavailability in many plant species (Chaney, 2012). A review of the
587 role of ion competition (Cu, Se, Zn, etc.) on Cd toxicity and Cd uptake by plants suggests that
588 they depend on element concentrations and plant genotype (Qin *et al.*, 2020). Furthermore,
589 Kikuchi *et al.* (2003) and JECFA (2004) stressed that the gastro-intestinal absorption of Cd is
590 influenced by Zn and other ions. Such interactions, inhibitions or synergies may influence the

591 resulting toxicity. However, we here used as a reference point a HBGV set for cadmium, which
592 is based on epidemiological data (ANSES, 2019). Therefore, this HBGV includes the
593 interactions with other trace elements provided through the general consumer diet.
594 Nevertheless, the comparison of the effect of the studied scenarios on dietary exposure to Cd
595 remains valid. In addition, parameters related to climate, soil typology, agricultural practices,
596 agricultural inputs (particularly fertilizers of organic origin (which had large amounts of
597 missing data) and food habits were considered to be constant over the 99-year period because
598 the data to take into account the evolutions of these parameters were not available.

599 Because data on leaching in French agricultural soils were missing, Cd transfer via leachates
600 was estimated from an Australian environment using the equation derived in De Vries *et al.*,
601 (2011, 2013). Sterckerman *et al.* (2018a) indicated that the accuracy of mass can be improved
602 with a better assessment of Cd leaching. Their study of six scenarios of agricultural practices
603 in France demonstrated the consequences of the calculated results on the proportion of leached
604 Cd in the mass balance, with different factors affecting the outflow of leached Cd (Sterckerman
605 *et al.*, 2018a). However, in our study, the input data related to the calculation of Cd transfer via
606 leaching were based on a situation maximalist in the context of a health risk assessment.

607 Another difficulty was to estimate the real proportion of bioavailable Cd relative to the
608 application of fertilizers. Our models assumed that total Cd was fully bioavailable as a
609 conservative, protective hypothesis. Through soil characteristics (pH, carbonates, etc.) included
610 in transfer equations, Cd distribution was considered and then indirectly as Cd speciation.
611 However, Cd speciation actually depends on soil characteristics.

612 *In fine*, our approach is a predictive tool that can be used to propose safe and sanitary Cd levels
613 according to the Cd concentrations in a product placed on the market whose Cd content can be
614 controlled, or according to Cd fluxes regardless of fertilizer type and/or the total fertilisers
615 applied to arable soils. Through the combination of Cd concentration and fertilizer application

616 dose as input data, reasoning finally in Cd fluxes is of interest to the farmer and the regulator,
617 regardless of the fertilizing materials used. The estimation of fluxes can quantitatively and
618 temporally monitor the Cd inputs with regard to the sustainable management of Cd inputs in
619 agricultural soils and crops in a context of agroecological transition.

620

621 4.2 Recommendation of Cd limits in fertilizers to reduce soil, plant and related food chain 622 contamination

623 Our study examined the effects of actions to reduce the source of Cd inputs identified in
624 agricultural activities and over time. In support of a sustainable food system and in an effort to
625 preserve the environment, this study was at the interface of a risk assessment approach and
626 implementation of regulations with regard to putting EC-marked fertilizers on the market.
627 Ultimately, to reduce consumer exposure to Cd, one efficient action is to reduce the Cd level of
628 a controlled product, such as mineral phosphate fertilizers, the main source of Cd inputs in
629 agricultural soils (Belon *et al.*, 2012).

630 Our work simulated different Cd concentrations in commercial mineral phosphate fertilizers
631 based on protective fertilization plans applied in the case of French agricultural soils, for which
632 extensive field data is available in the RMQS. Our approach modelled the Cd effects on the
633 environment and consumer health by using different mineral phosphate fertilizations plans
634 playing different Cd concentrations (90, 60, 40 or 20 mg Cd.kg P₂O₅⁻¹ as constant or degressive
635 over a 99-year period), giving Cd fluxes varying between 0.67 and 9 g Cd. ha⁻¹.an⁻¹. In
636 comparison with a reference scenario using the French threshold (90 mg Cd.kg P₂O₅⁻¹), results
637 from our study showed the need to take measures to reduce Cd inputs at the source. In regard
638 to environmental and consumer safety, measures need to include restrictions on Cd
639 concentrations, either by using the lowest possible concentration of 20 mg Cd.kg P₂O₅⁻¹ in the
640 product commercialized or not exceeding flux of 2 g Cd. ha⁻¹.year⁻¹. Stabilization, and

641 eventually a decrease in Cd levels in soils, plants and leachates over time was confirmed for
642 Ph/80b/20, Ph/100b/20, Ph/100bp/20, Ph/180bp/20 fertilization plans using lowest Cd
643 concentration and the Ph/80b/60-40-20, Ph/100b/60-40-20, Ph/100bp/60-40-20, Ph/180bp/60-
644 40-20 fertilizations plans progressively reducing the Cd concentration in mineral phosphate
645 fertilizers to 20 mg Cd.kg P₂O₅⁻¹ over 15 years. These fertilization plans do not exceed a Cd
646 flux of 2 g Cd. ha⁻¹.year⁻¹. Dropping below this level appears essential to stop the increase in
647 the part of the population likely to be overexposed to Cd through food. Although results of
648 exposures exceeded the oral HBGV, those results showed that if no action is taken to reduce
649 the Cd content in mineral phosphate fertilizers, the risk will increase over time due to Cd
650 accumulation. Because fertilizers are applied to many crops and not only potatoes and wheat,
651 it is likely that the effects observed following a reduction of Cd-containing fertilizer application
652 would have a favourable impact on all crops and consequently on dietary exposure.

653 Anyway, the application of mineral phosphate fertilizers with contents higher than 40 mg Cd.kg
654 P₂O₅⁻¹ (linked to Cd fluxes greater than 2 g Cd. ha⁻¹.year⁻¹, see Table 1) is incompatible with
655 the typology of the receiving agricultural soil. A risk of Cd accumulation in soils is observed
656 through an analysis of soils characteristics on Cd transfer by the model. According to Cd
657 concentrations of 90, 60 and 40 mg Cd.kg P₂O₅⁻¹ in mineral phosphate fertilizer, our
658 probabilistic simulations showed great variation in the Cd concentration in soils based on a
659 variety of cases, including unfavourable and protective local situations (for example, soils low
660 in phosphorus requiring higher fertilization). According to soil characteristics (e.g. pH > 7) and
661 soil uses (e.g. cultivated soils that are currently amended), Römken *et al.* (2017) predict large
662 Cd accumulation which can exceed 30% in soils: in that study, both the strong Cd fluxes and
663 high pH favour the soil pollution. In presence of alkaline soils, our results also indicated trends
664 of Cd to be immobilised by precipitation regardless of the Cd content of the mineral phosphate
665 fertilizers tested. As demonstrated by our simulation, the reduction in Cd at the source can be

666 efficient even in acidic soils. In effect, the effect of pH on Cd bioavailability results in a
667 significant reduction in transfer in the presence of purified soil over the time, particularly at the
668 lowest Cd concentration in mineral phosphate fertilizers. Acidic soils favour the Cd transfer to
669 plants (Tremel-Schaub and Feix, 2005), thus they are considered as 'at-risk soils' in terms of
670 crops and therefore human exposure. We also observed a slightly more marked Cd transfer in
671 wheat grain than in potatoes, a crop that requires phosphorus. In potatoes, the phyto-available
672 Cd fraction will be directly taken up and transferred to the tuber, whereas in wheat, there is less
673 translocation of Cd from roots to grain. Rotational fertilization scenarios reduced Cd
674 accumulation over time and Cd transfer to plants and leachates is more marked for a rotation
675 plan of $180 \text{ kg P}_2\text{O}_5 \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ with a two-year pause in fertilisation, due to a lower annual Cd
676 input. Otherwise, a comparison of the mass balances showed that Cd transfer is greater in
677 leachates than in soil and plant matrices. These transfers to ground water and surface water
678 contributing to diffuse and generalised environmental contamination must be limited as much
679 as possible in light of the resulting environmental and health consequences. In addition, this
680 water may be subsequently used for crop irrigation. Lowering Cd inputs via controlled fertilizer
681 application preserves the quality of the environment, specifically in regard to leaching water.
682 Our work opened by the comparison of modelling Cd inputs via mineral phosphate fertilizers
683 and other fertilising materials based on available data. For example, we modelled a wheat
684 monoculture fertilization plan applied to French agricultural soils. Spreading sewage sludge,
685 cattle manure or anaerobic digestates, whose Cd concentration is low, can lead to a Cd flux of
686 up to $7.50 \text{ g Cd} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$, due to a high amount of fertilizer applied to the soil. The comparison
687 indicated that irrespective of the type of fertilizer, a Cd flux of less than $2 \text{ g Cd} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ better
688 protected the environment (soil, plants) and consequently the related final food products.
689 Hence, an annual Cd flux not exceeding $2 \text{ g Cd} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ regardless of the type (fertilizer/soil
690 amendment, organic/mineral origin, etc.) and total quantity of fertilizer(s) added to French

691 agricultural soils may help control the pollution of agricultural soils, contamination of
692 agricultural production and thus the associated dietary exposure. A Cd content equal to or less
693 than 20 mg Cd.kg P₂O₅⁻¹ in mineral phosphate fertilizer products that can be regulated at the
694 source would ensure that this annual flux of 2 g Cd.ha⁻¹.year⁻¹ is not exceeded. Moreover
695 regarding human exposure to metals, given the growing urban populations around the world
696 and the frequent significant pollution events (Dumat *et al.*, 2019; Natasha *et al.*, 2019), it is
697 crucial to avoid insofar as possible the introduction of new persistent metals into the
698 environment and their accumulation in the food chain.

699 4.3 How agroecology practices can promote human health

700 In France, the current standard threshold of 90 mg Cd.kg P₂O₅⁻¹ in mineral phosphate fertilizer
701 sustains the Cd contamination cycle and thus human Cd exposure, despite having taken steps
702 to limit Cd contamination by this fertilizer inputs. Currently, the new harmonized EU
703 Regulation (EU) 2019/1009 on the market of EU-labelled fertilizers is moving for that their
704 content of cadmium should therefore be limited in such products. This regulation establishes
705 that the Cd level in an organo-mineral fertilizer must not exceed 60 mg Cd.kg P₂O₅⁻¹. However,
706 maintaining a threshold of 60 mg Cd.kg P₂O₅⁻¹ does not stimulate a rapid reversal of the current
707 upward trend. Limiting applications to a concentration of 20 mg Cd.kg P₂O₅⁻¹ in an organo-
708 mineral fertilizer, perhaps in a degressive Cd decrease over a 15-year period, would be more
709 beneficial and better protect the environment and human health.

710 Other ways (currently not explored for economic reasons) to promote soil quality is to select
711 phosphate rock deposits based on Cd concentration criteria and to optimise decadmiation
712 processes. Setting a limit on annual fluxes (equal or less to 2 g Cd.ha⁻¹.year⁻¹) would be more
713 favourable for the management of fertilizer application and soil quality to obtain improvements.
714 Specifically, in France, the oldest threshold Cd fluxes stipulated in the existing national
715 regulations (instructions that accompany the MA application (guide No 50644#01)) of 15 g

716 Cd.ha⁻¹.year⁻¹ (Ministère de l'Agriculture et de la Pêche, 2001) must be cut back by a factor of
717 7 to reach the level we recommend here. Our recommendation of a threshold flux limit of 2 g
718 Cd.ha⁻¹.year⁻¹ for applied fertilizers, regardless of their nature and quantity, would be more
719 efficient to control soil and plant contamination. This threshold is important for the last link in
720 the food chain: human consumers. This level would also be more convincing in France, for
721 which one-third of agricultural soils are at risk for cadmium accumulation (Delmas *et al.*, 2015,
722 Saby *et al.*, 2016).

723 The results showed that a Cd content below 1 mg Cd.kg⁻¹ of dry matter (DM) in organic
724 fertilizers would comply with this flux of 2 g Cd.ha⁻¹.year⁻¹ (the mean Cd concentration is 0.7
725 mg.kg⁻¹DM for farm anaerobic digestates). Although France has introduced a regulatory Cd
726 threshold in digestate of 3 mg.kg⁻¹DM by a French decree of 13 June 2017, this limit is not
727 sufficient according to our simulations to reduce the accumulation of Cd in soils and crops, and
728 to respect a Cd flux of 2 g Cd.ha⁻¹.year⁻¹. However, the average Cd contents observed in
729 anaerobic digestion digestates in France (0.7 mg.kg⁻¹DM) respect this flux. In view of the
730 difficulty of controlling Cd concentrations in organic fertilizers, providing a Cd limit in this
731 type of input source may lead to limitations on their agricultural reuse. Their redirection towards
732 other means of disposal or reuse methods (landfilling in storage centres, incineration, anaerobic
733 digestion, etc.) may also constitute sources of pollution that need to be controlled. The benefit
734 of reducing Cd concentrations in mineral phosphate fertilizers was particularly noted for acidic
735 soils, which promote Cd solubility and therefore phytoavailability. However, the pH of these
736 acidic soils can be increased by liming (adding alkaline soil amendments) to limit Cd transfer
737 to crops. Nevertheless, liming is not a sustainable alternative for avoiding Cd transfer to food.
738 Such liming practices have short-term benefits, but can represent a medium- and long-term
739 hazards, because there is no guarantee that the increase in pH will be sustainable. On the
740 contrary, the soil processes at work will tend to restore the original physico-chemical balances

741 and lower the pH again, which in the long term may promote transfers from soil to crops and
742 leaching water. Liming cannot therefore be a substitute for an active policy of reducing Cd on
743 agricultural soils.

744 Given the temporary effectiveness of trapping techniques, it is necessary to continue to decrease
745 the limit value below 60 mg Cd.kg P₂O₅⁻¹ for mineral phosphate fertilizers (towards a value
746 equal to or lower than 20 mg Cd.kg P₂O₅⁻¹) and the development of decadmiation techniques
747 relating to their production. The introduction of Cd fluxes limits or reduces Cd fluxes with
748 respect to the French administrative guidance value (Ministère de l'Agriculture et de la Pêche,
749 2001), enhancing the management of Cd inputs into soils on a larger scale.

750 Given this ubiquitous contaminant, limiting fluxes will be more effective when combined with
751 the reduction of the contamination cycle by controlling Cd inputs of all fertilizers and by
752 reducing the contribution of all other types of inputs.

753 Sterckerman *et al.* (2018 a and b) observed that an over-fertilization of agricultural crops can
754 induce long-term Cd accumulation in French soils. They highlighted that soil quality can be
755 improved with a combination of good practices regarding phosphate fertilization and limiting
756 Cd content in mineral phosphate fertilizers, along with a progressive decrease in Cd content in
757 mineral phosphate fertilizers consistent with the proposal related to the revision of the EU
758 fertilizer regulation. Their study indicated that the use of organic farming and fertilizers of
759 organic origin can also lead to an evolution of cadmium in the soil in a similar way to that of
760 conventional agriculture by applying good practices.

761 To promote sustainable agriculture and the agri-food system at the global scale, both improving
762 the quality of fertilizers and amendments and optimising the applied quantities (considering the
763 plant cycle, using green manure crops and other agroecological practices) are therefore crucial
764 steps. The development of numerous urban agriculture projects involving different stakeholders

765 constitutes an efficient vector for ecology education and enhances the links between consumers
766 and local and organic produce farmers (Dumat, 2019).

767

768 **Conclusions and perspectives**

769 Cd combined hazard and exposure characteristics support the importance of health assessment
770 work focused on exposure to this substance.

771 To preserve human health, reducing Cd exposure is recommended, by acting in particular on
772 the level of environmental contamination, especially via mineral phosphate fertilizers and more
773 widely via all fertilizing materials. Results derived from our predictive model provide a
774 scientific support for environmental management and public policy decision-making. At the
775 interface of applied research, risk assessment, expert assessment and regulatory decision-
776 making, the proposed model based on a mass-balance approach made it possible to determine
777 the maximum Cd level in mineral phosphate fertilizers to control and reduce Cd soil pollution,
778 crop contamination and dietary exposure in consumers, as well as occupational exposure (albeit
779 indirect) in the fertilizer industry. Perspectives for research include a better understanding and
780 more data on leachates, phytoavailability, Cd speciation and characterisation of organic
781 fertilizers.

782 Moreover, our model can be extended to other countries using their data and fertilization plans.
783 It can be also a tool for further studies and be extended to the assessment of other contaminants
784 identified in polluted sites and soils.

785 Given the ubiquitous nature of Cd and the need to reduce its environmental contamination cycle
786 and long-term dietary exposure to this element, it is important to control Cd fluxes via
787 fertilizers. A Cd flux lower than $2 \text{ g Cd}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ from the application of fertilizers,
788 corresponding to a Cd content of $20 \text{ mg}\cdot\text{kg P}_2\text{O}_5^{-1}$ or less in mineral phosphate fertilizers,
789 ensures better protection of environmental and human health. Within a century, a protective

790 concentration of 20 mg.kg P₂O₅⁻¹ in a potato/wheat/wheat rotation fertilizer plan of 180 kg
791 P₂O₅.ha⁻¹.year⁻¹ with a two-year no-fertiliser period can lead to a mean Cd reduction of up to
792 17% in French agricultural soils, 18% in wheat grain, 14% in potatoes and 21% in leachates.
793 This reduction is essential to limit Cd accumulation in soils such that consumer exposure,
794 mainly via food, does not exceed the health threshold values.

795

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8 Title of the manuscript: "***Mass balance approach to assess the impact of cadmium decrease in mineral
9 phosphate fertilizers on health risk: the case-study of French agricultural soils***".

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13 List of Tables:

14 - **Table 1.** Representative and protective scenarios of mineral phosphate fertilizer inputs with
15 regard to cadmium contamination in French agricultural soils, used for wheat monoculture
16 crops or potato/wheat/wheat crop rotations

17 - **Table 2.** Mean percentage (%) variation in Cd concentration in matrices (soil, wheat grain/or
18 potatoes and leachate) over a 99-year period (10, 20, 60 and 99 years) compared with the first
19 year of application of the mineral phosphate fertilizer with a control Cd content (90, 60, 40 and
20 20 mg.kg⁻¹ P₂O₅) as a function of the phosphate fertilization plan

21 - **Table 3.** Cd inputs related to applications of organic fertilizers tested in the model

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Table.

33 **Table 1.** Representative and protective scenarios of mineral phosphate fertilizer inputs with
 34 regard to cadmium contamination in French agricultural soils, used for wheat monoculture crops
 35 or potato/wheat/wheat crop rotations

	Phosphate fertilization plan (Ph) scenario (Ph/fertilizer dose/Cd level)	Quantity of fertilizer applied (kg P ₂ O ₅ .ha ⁻¹)	Cd concentration in fertilizer (mg.kg P ₂ O ₅ . ⁻¹)	Cd inflow to the soil (g.ha ⁻¹)	Annual Cd flux (g.ha ⁻¹ .year ⁻¹)
Annual application for wheat monoculture	<u>Ph/80b/90</u>	80	90	7.20	7.20
	Ph/80b/60		60	4.80	4.80
	Ph/80b/40		40	3.20	3.20
	Ph/80b/20		20	1.60	1.60
	Ph/80b/60-40-20*		60 (Year 1-3) 40 (Year 4-15) 20 (Year 16-99)	4.80 (Year 1-3) 3.20 (Year 4-15) 1.60 (Year 16-99)	4.80 (Year 1-3) 3.20 (Year 4-15) 1.60 (Year 16-99)
Application every three years for wheat monoculture	<u>Ph/100b/90</u>	100	90	9	3
	Ph/100b/60		60	6	2
	Ph/100b/40		40	4	1.33
	Ph/100b/20		20	2	0.67
	Ph/100b/60-40-20*		60 (Year 1-3) 40 (Year 4-15) 20 (Year 16-99)	6 (Year 1-3) 4 (Year 4-15) 2 (Year 16-99)	2 (Year 1-3) 1.33 (Year 4-15) 0.67 (Year 16-99)
Annual application for a potato/wheat/wheat rotation	<u>Ph/100bp/90</u>	100	90	9	9
	Ph/100bp/60		60	6	6
	Ph/100bp/40		40	4	4
	Ph/100bp/20		20	2	2
	Ph/100bp/60-40-20*		60 (Year 1-3) 40 (Year 4-15) 20 (Year 16-99)	6 (Year 1-3) 4 (Year 4-15) 2 (Year 16-99)	6 (Year 1-3) 4 (Year 4-15) 2 (Year 16-99)
Application every three years for a potato/wheat/wheat rotation	<u>Ph/180bp/90</u>	180	90	16.20	5.40
	Ph/180bp/60		60	10.80	3.60
	Ph/180bp/40		40	7.20	2.40
	Ph/180bp/20		20	3.60	1.20
	Ph/180bp/60-40-20*		60 (Year 1-3) 40 (Year 4-15) 20 (Year 16-99)	3.60 (Year 1-3) 7.20 (Year 4-15) 10.80 (Year 16-99)	3.60 (Year 1-3) 2.40 (Year 4-15) 1.20 (Year 16-99)

36 Underlined: reference scenarios

37 *: degressive cadmium concentration scenarios modelled over a 99-year period

38 **Table 1.** Mean percentage (%) variation in Cd concentration in matrices (soil, wheat grain/or
 39 potatoes and leachate) over a 99-year period (10, 20, 60 and 99 years) compared with the first
 40 year of application of the mineral phosphate fertilizer with a control Cd content (90, 60, 40 and
 41 20 mg.kg⁻¹ P₂O₅) as a function of the phosphate fertilization plan

Phosphate fertilization plan	Matrix															
	Soil				Crop plant								Leachate			
					Wheat grain				Potato tuber							
	Period (year)				Period (year)				Period (year)				Period (year)			
	10	20	60	99	10/11	20	60	99	10	22	61	97	10	20	60	99
<u>Ph/80b/90</u>	+7	+14	+40	+61	+7	+15	+42	+64	-	-	-	-	+15	+22	+49	+72
Ph/80b/60	+4	+7	+21	+32	+4	+8	+22	+34	-	-	-	-	+11	+15	+29	+42
Ph/80b/40	+2	+3	+9	+15	+2	+3	+10	+15	-	-	-	-	+8	+11	+18	+23
Ph/80b/20	-1	-1	-3	-4	-1	-1	-3	-4	-	-	-	-	+7	+6	+4	+3
Ph/80b/60-40-20 *	+2	+2	0	-2	+2	+2	0	-2	-	-	-	-	+10	+7	+6	+6
<u>Ph/100b/90</u>	+1	+2	+6	+11	+1	+2	+7	+11	-	-	-	-	+8	+10	+16	+19
Ph/100b/60	0	-1	-1	0	0	-1	-1	0	-	-	-	-	+7	+7	+6	+7
Ph/100b/40	-1	-2	-6	-8	-1	-2	-6	-8	-	-	-	-	+5	+5	+2	-1
Ph/100b/20	-2	-4	-11	-15	-2	-4	-11	-16	-	-	-	-	+5	+3	-5	-7
Ph/100b/60-40-20 *	-1	-3	-9	-14	-1	-3	-10	-15	-	-	-	-	+7	+5	-2	-8
<u>Ph/100bp/90</u>	+8	+16	+44	+66	+8	+15	+44	+67	+6	+14	+34	+48	+13	+11	+37	+58
Ph/100bp/60	+4	+8	+23	+35	+4	+8	+23	+36	+3	+7	+18	+26	+10	+3	+16	+28
Ph/100bp/40	+1	+3	+8	+13	+1	+3	+8	+13	+1	+2	+6	+10	+8	-2	+3	+7
Ph/100bp/20	-1	-2	-6	-9	-1	-2	-6	-9	-1	-2	-5	-7	+5	-7	-11	-13
Ph/100bp/60-40-20 *	+2	+2	-2	-5	+2	+2	-3	-6	+2	+1	-2	-5	+8	-2	-7	-10
<u>Ph/180bp/90</u>	+3	+6	+16	+26	+3	+6	+18	+28	+2	+5	+14	+20	+9	+1	+11	+20
Ph/180bp/60	+1	+1	+4	+7	+1	+2	+5	+8	+1	+1	+4	+6	+6	-3	-1	+2
Ph/180bp/40	-1	-2	-3	-5	-1	-1	-3	-4	-1	-1	-3	-4	+5	-7	-8	-10
Ph/180bp/20	-2	-5	-12	-17	-2	-5	-12	-18	-2	-4	-10	-14	+3	-10	-17	-21
Ph/180bp/60-40-20 *	-1	-3	-11	-16	-1	-2	-11	-16	-1	-3	-9	-13	+5	-7	-15	-20

42 Underlined: reference scenarios

43 *: degressive cadmium concentration scenarios modelled over a 99-year period

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45 **Table 3.** Cd inputs related to applications of organic fertilizers tested in the model

Fertilization scenario	Mean Cd concentration in fertilizing matter (mg.kg ⁻¹ DM*)	Total amount of nitrogen (kg.t ⁻¹ DM*)	Amount of fertilizing matter applied at the Nitrate Directive threshold of 170 kg N.ha ⁻¹ (t DM*.ha ⁻¹ .year ⁻¹)	Cd flux added to the soil in one application (g.ha ⁻¹ .year ⁻¹)
Sewage sludges (S)	1.60	Not applicable	3**	4.80
Cattle manure (CM)	0.30	20	8.50	2.55
Farm anaerobic digestate (FAD)	0.70	68	2.50	1.75
Max Cd farm anaerobic digestate (MaxCdFAD) ***	Regulatory Cd threshold in digestate	Total amount of nitrogen (kg.t ⁻¹ DM)	Amount of fertilizing material applied at the threshold of 170 kgN.ha ⁻¹ (t DM.ha ⁻¹ .year ⁻¹)	Cd flux added to the soil in one application (g.ha ⁻¹ .year ⁻¹)
	3	68	2.50	7.50

46 (From Plateau (2001), Brittany Chamber of Agriculture *et al.* (2007), IRSTEA and SOLAGRO (2012), Benoît *et al.* (2014), Wolf Environnement
47 (2001))

48 * DM: dry matter

49 ** For sewage sludge, the maximum threshold authorised by the regulations was used, because the amounts of nitrogen and the physical nature of
50 the sludge (liquid, paste or solid) can vary. We started from the maximum application threshold authorised by the regulations (3 t DM.ha⁻¹.year⁻¹).

51 *** The proposed calculations include the Cd concentration proposed in the market authorisation specifications and the use of agricultural biogas
52 digestates as fertilizer (regulated by a French decree of 13 June 2017)

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7

8 Title of the manuscript: " **Mass balance approach to assess the impact of cadmium decrease in mineral
9 phosphate fertilizers on health risk: the case-study of French agricultural soils**".

10 Authors: G. Carne, S. Leconte, V. Sirot, N. Breysse, P-M Badot, A. Bispo, I.Z Deportes, C. Dumat, G.
11 Rivière, A. Crépet

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20 wheat monoculture fertilization plan of 80 kg P₂O₅.ha⁻¹.year⁻¹ simulating a constant Cd content of
21 90, 60, 40 and 20 mg Cd.kg P₂O₅⁻¹ in the phosphate fertilizer (Ph/80b/90, Ph/80b/60, Ph/80b/40
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27 year⁻¹ with a two year hiatus in fertilization, simulating a constant fertilizer Cd content of 90,
28 60, 40 and 20 mg Cd. kg P₂O₅⁻¹ over a 99-year period (Ph/180bp/90, Ph/180bp/60, Ph/180bp/40,
29 Ph/180bp/20 fertilization plans)

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31 (expressed as percentages) after 10, 20, 60, 99 years compared with the first year of application,
32 based on the mean and percentiles (P05, P25, P50, P75, P95) of Cd concentration in matrices,
33 according to the potato/wheat/wheat rotation phosphate fertilization plan with 180 kg P₂O₅.ha⁻¹.
34 year⁻¹ including a two year hiatus in fertilization and using degressive fertilizer Cd
35 concentrations over a 99-year period (Ph/180bp/60-40-20)

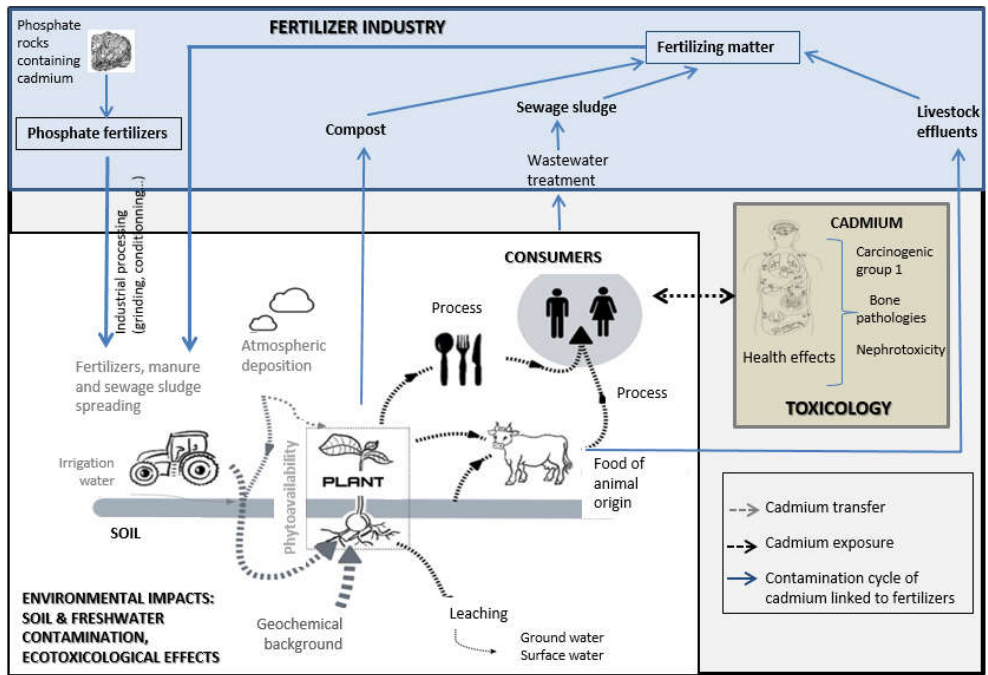
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38 40 and 20 mg Cd.kg P₂O₅⁻¹) between the first year of application and after 99 years for a wheat
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- 43 - **Figure 8.** Variations (%) in the mean and 90 percentile (P90) Cd contents in French agricultural
44 soils, wheat grain and leachate matrices over a 99-year period (10, 20, 60, 99 years) compared
45 with the first year of application and according to application of fertilizing materials based on a
46 wheat monoculture plan
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49 FIGURES.

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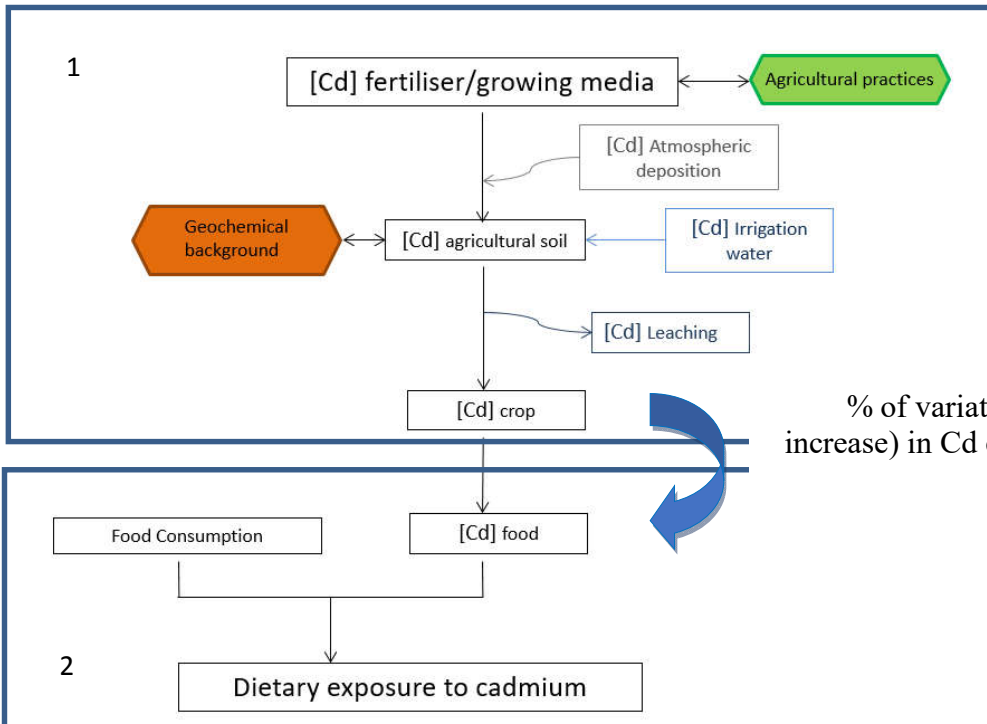


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53 **Figure 1.** Graphical Abstract

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1. Mass-balance approach to model Cd transfer from environmental sources to plants

% of variation (decrease, unchanged or increase) in Cd concentration with regard to fertilization scenario

2. Exposure assessment based on changes in Cd concentration in food as consumed

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57 **Figure 2.** Schematic of the strategy for modelling cadmium exposure and risk using a mass-balance
 58 approach integrating environmental sources of cadmium and fertilization scenarios

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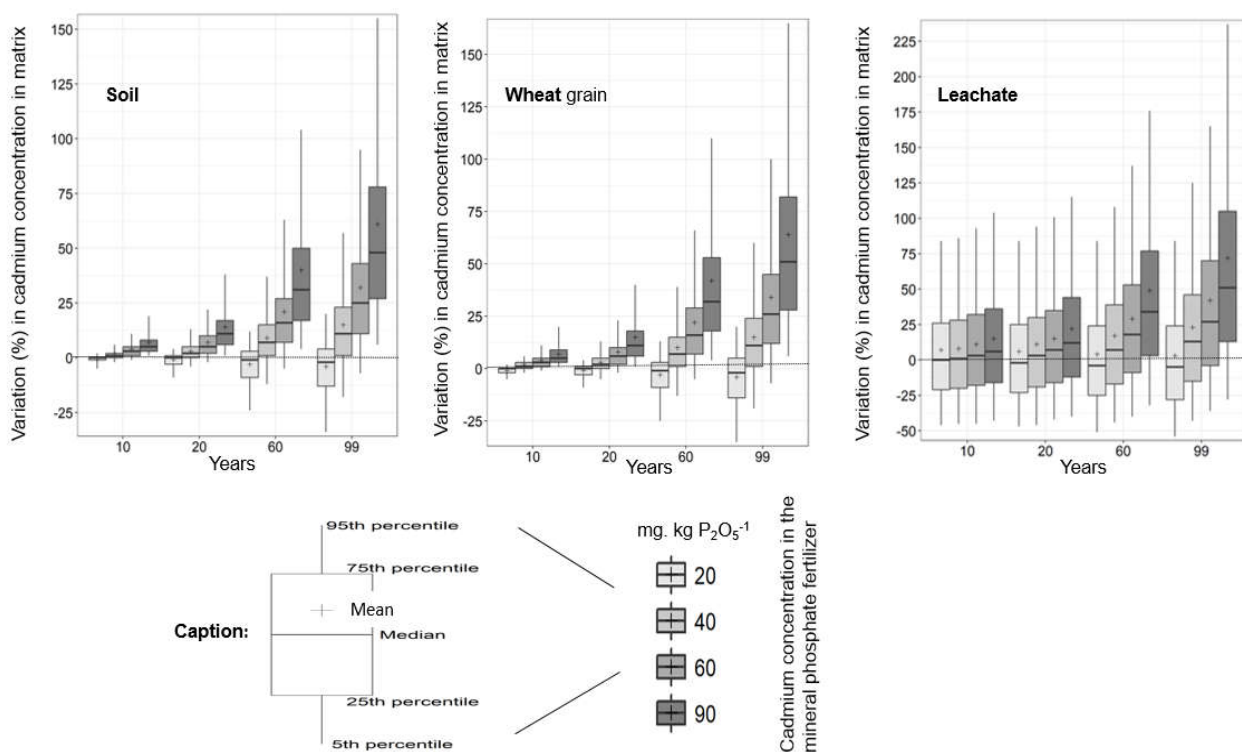
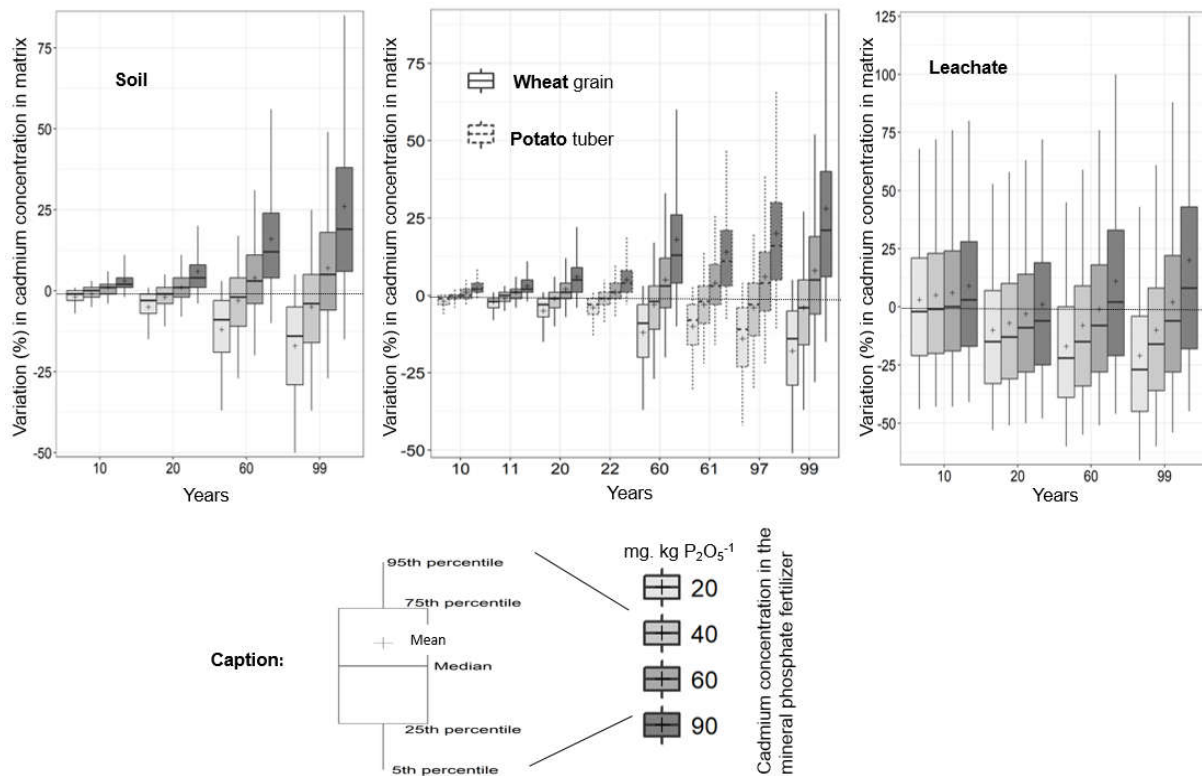


Figure 3. Variation in Cd concentrations in matrices (soil, wheat grain, leachate) (expressed as percentages) at 10, 20, 60 and 99 years compared with the first year of application, based on mean and percentiles (P05, P25, P50, P75, P95) of Cd concentration in matrices, according to the wheat monoculture fertilization plan of 80 kg P₂O₅.ha⁻¹year⁻¹ simulating a constant Cd content of 90, 60, 40 and 20 mg Cd.kg P₂O₅⁻¹ in the phosphate fertilizer (Ph/80b/90, Ph/80b/60, Ph/80b/40 and Ph/80b/20 fertilization plans) over a 99-year period

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Caption:

95th percentile
75th percentile
+ Mean
Median
25th percentile
5th percentile

mg. kg P₂O₅⁻¹
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Cadmium concentration in the mineral phosphate fertilizer

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96 **Figure 4.** Variation in Cd concentration in matrices (soil, wheat grain and potatoes, leachate) (expressed
 97 as percentages) after 10, 20, 60 and 99 years compared with the first year of application, based on the
 98 means and percentiles (P05, P25, P50, P75, P95) of Cd concentration in matrices, according to the
 99 potato/wheat/wheat rotation fertilization plan of 180 kg P₂O₅ .ha⁻¹.year⁻¹ with a two year hiatus in
 100 fertilization, simulating a constant fertilizer Cd content of 90, 60, 40 and 20 mg Cd. kg P₂O₅⁻¹ over a 99-
 101 year period (Ph/180bp/90, Ph/180bp/60, Ph/180bp/40, Ph/180bp/20 fertilization plans)

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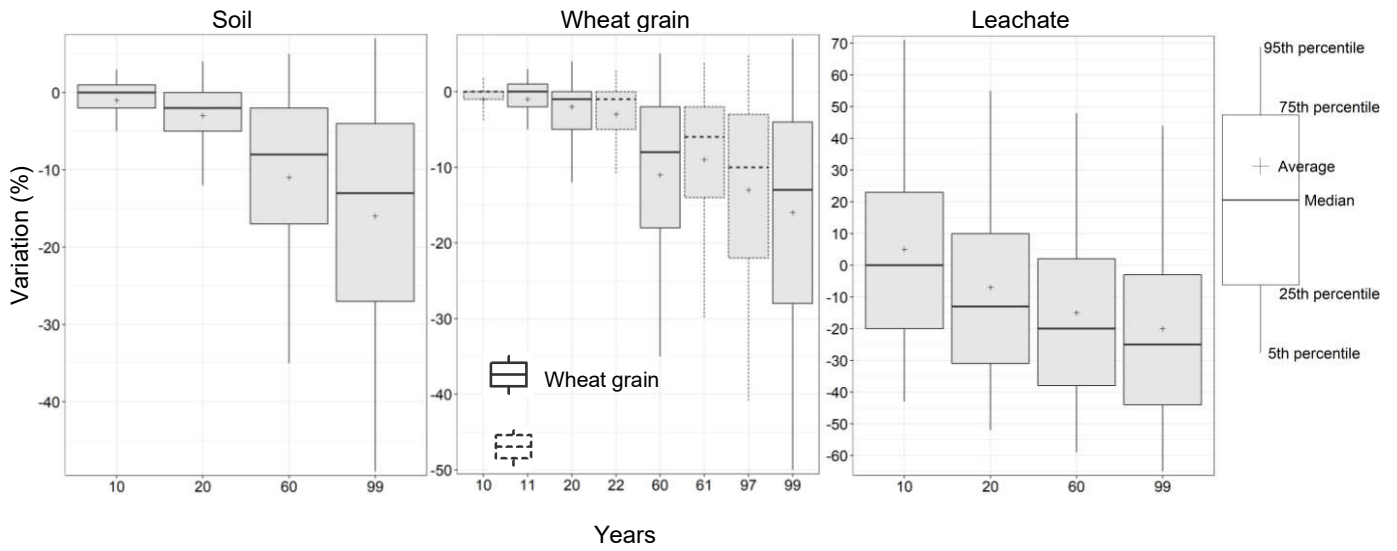
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111 **Figure 5.** Variation in Cd concentration in matrices (soil, wheat grain and potatoes, leachate) (expressed
 112 as percentages) after 10, 20, 60, 99 years compared with the first year of application, based on the
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 114 potato/wheat/wheat rotation phosphate fertilization plan with 180 kg P₂O₅.ha⁻¹.year⁻¹ including a two
 115 year hiatus in fertilization and using degressive fertilizer Cd concentrations over a 99-year period
 116 (Ph/180bp/60-40-20)

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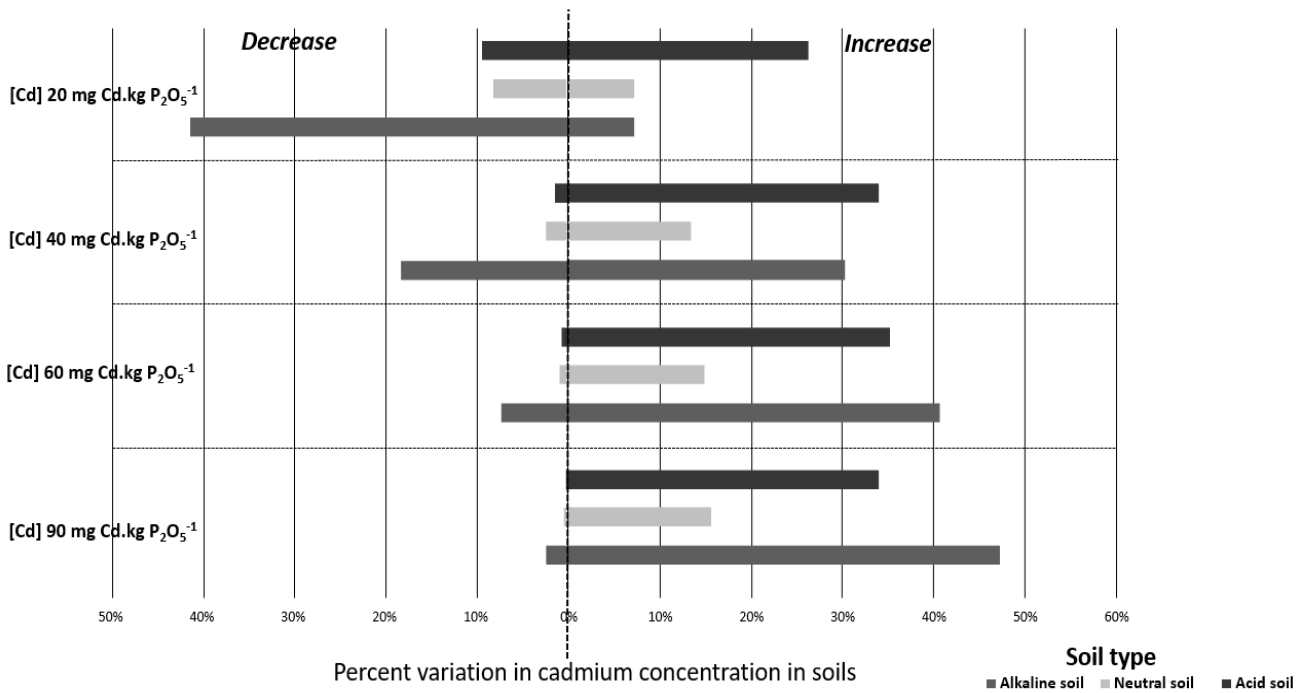
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132 **Figure 6.** Variation (%) of cadmium concentration in French agricultural soils, as a function of their pH
 133 (acid, neutral or alkaline) and the cadmium concentration of mineral phosphate fertilizers spread (90,
 134 60, 40 and 20 mg Cd.kg P₂O₅⁻¹) between the 1st year of application and the 99-year period for a
 135 fertilization plan corresponding to a wheat monoculture at 80 kg P₂O₅.ha⁻¹.year⁻¹

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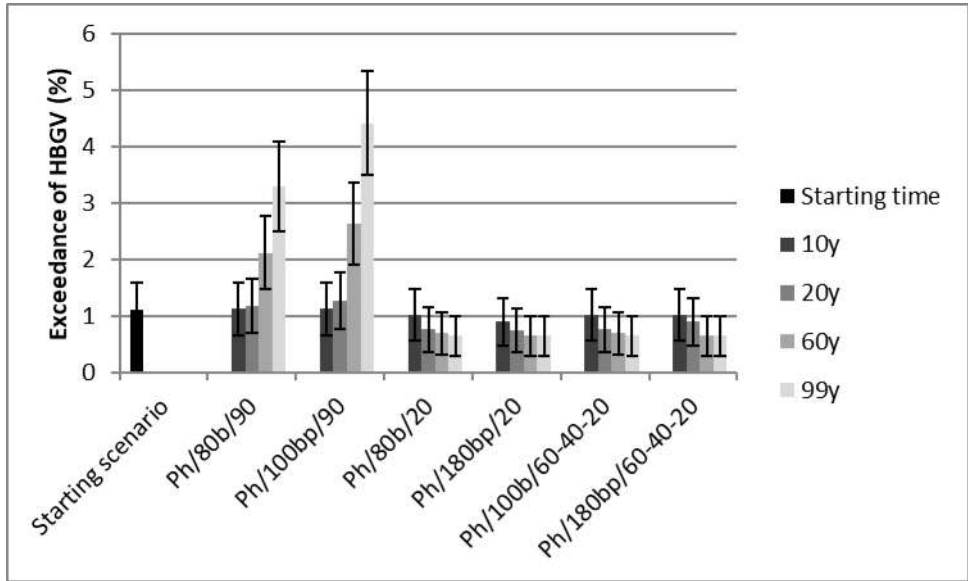
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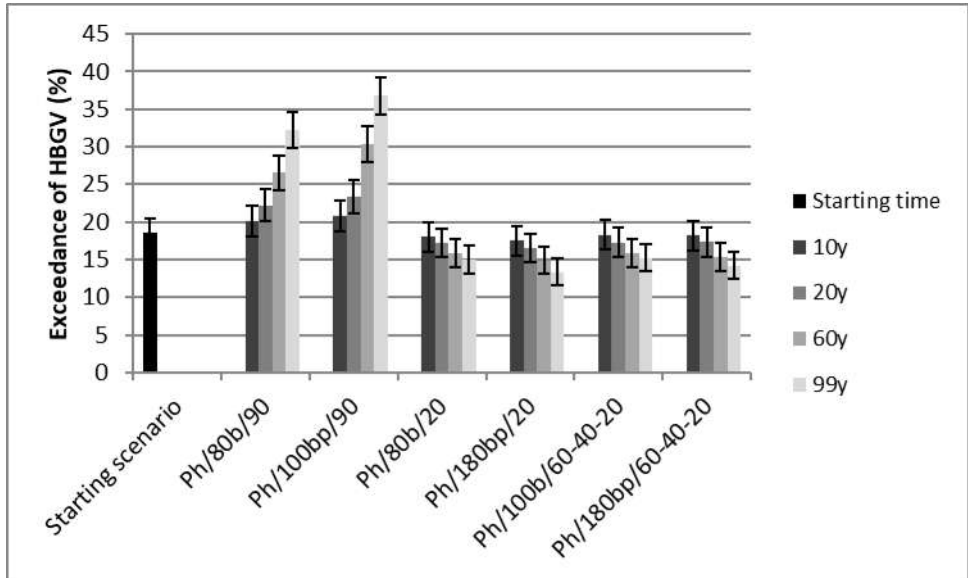
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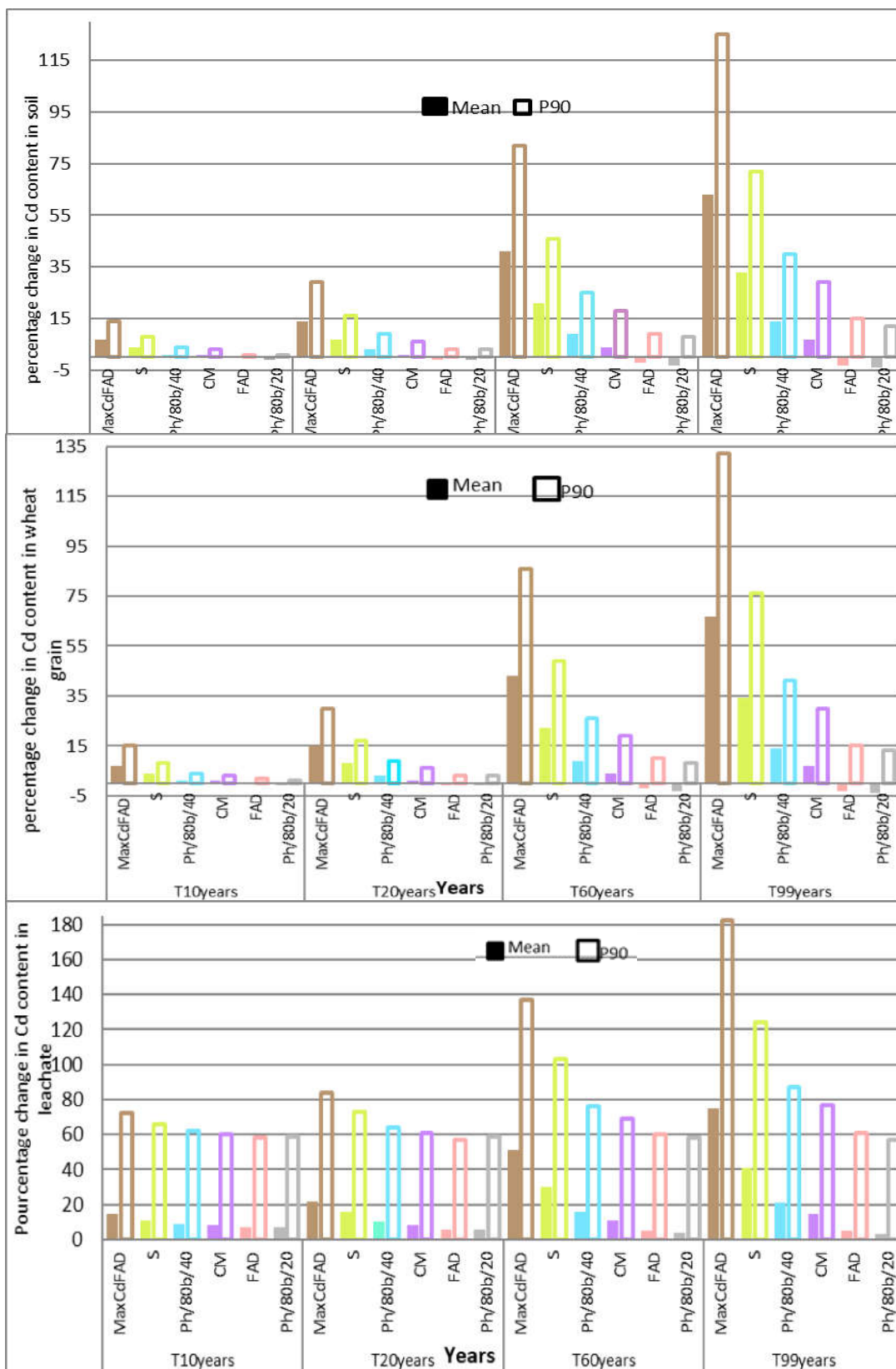
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154 and 95% confidence interval ($\text{CI}_{95\%}$) in the different scenarios, for French adults (a) and children (b),
155 under the upper bound (UB) hypothesis

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180 plan

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