Science of the Total Environment xxx (xxxx) xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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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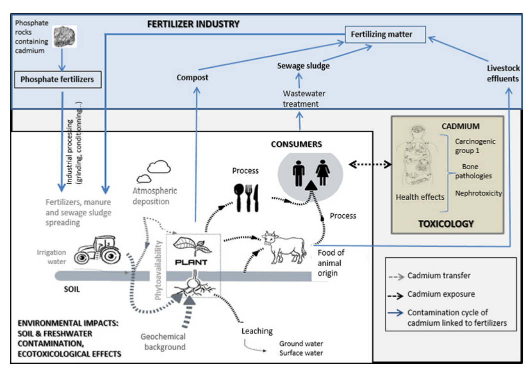
HIGHLIGHTS

- A mass-balance approach was applied to French fertilized agricultural soils.
- Cadmium concentrations in soils and plants were assessed.
- Impact of reducing cadmium in mineral phosphate fertilizers on risk was assessed.
- Cadmium limits in fertilizers were recommended to reduce its cadmium exposure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 July 2020
Received in revised form 23 October 2020
Accepted 24 October 2020
Available online xxxx

Editor: Henner Hollert

Keywords:
Cadmium
Fertilizing materials
Soil contamination
Food contamination

ABSTRACT

Cadmium is a ubiquitous and highly toxic contaminant that can cause serious adverse effects. The European Food Safety Authority (EFSA) and the French Agency for Food, Environmental and Occupational Health & Safety (ANSES) have shown that the risk related to food contamination by cadmium cannot be ruled out in Europe and France. Fertilizing material is one of the main sources of cadmium contamination in the food chain on which regulators can play to reduce cadmium exposure in the population. The aim of this work was to develop a mass-balance approach integrating the various environmental sources of cadmium to estimate the effects of a decrease in cadmium concentrations in crop fertilizers on dietary exposure and on the health risk. This approach led to a predictive model that can be used as a decision-making tool. Representative and protective fertilization scenarios associated with controlled cadmium levels in mineral phosphate fertilizers were simulated and converted into cadmium fluxes. Cadmium inputs from industrial mineral phosphate fertilizers were then compared with cadmium brought by the application of manure, sewage sludge and farm anaerobic digest, at the levels typical of French agricultural practices. Regardless of the fertilizer and scenario used, a flux lower than

Abbreviation: fertilizers, include organic, inorganic and organo-mineral fertilizers intended to ensure or improve plant nutrition, and organic, inorganic and organo-mineral soil amendments that improve the physical, chemical and biological properties of soils.

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https://doi.org/10.1016/j.scitotenv.2020.143374

Human exposure
Risk assessment

2 g Cd.ha^{-1}.year^{-1} reduces both the accumulation in soils and the transfer of cadmium in the food chain. It corresponds to a cadmium content of 20 mg.kg $P_2O_5^{-1}$ or less in mineral phosphate fertilizers. Modelling the transfer of cadmium from the soil to consumed food made it possible to propose cadmium limits in fertilizers applied in France. In a global context of ecological transition to promote human health, this research will help risk managers and public authorities in the regulatory decision-making process for the reduction of environmental cadmium contamination and human exposure.

1. Introduction

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

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

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

European (EFSA, 2012) and French (ANSES 2011a and b) studies have shown that the risk related to Cd dietary exposure cannot be ruled out for a part of the population. In the second French Total Diet Study (TDS) (ANSES 2011a), the health-based guidance value (HBGV) defined by EFSA in 2009 was exceeded in 0.6% of adults and 14.9% of children over 3 years old. This exceedance of the EFSA HBGV was also observed in younger children in the first French infant TDS, up to 29% of children aged 13 to 36 months and 36% of children aged 7 to 12 months (ANSES 2016). In both French TDSs (ANSES 2011a and b, 2016) and at the European level (EFSA 2012), the major contributors to Cd exposure are cereals and cereal products, vegetables, potatoes and related products.

One possible means to reduce exposure is to act on the main food contributors (i.e. such as cereals, vegetables, potatoes), primarily by reducing their levels of contamination at the source or after production using regulatory measures. Limiting exposure requires the implementation or enhancement of Cd management by controlling environmental releases or processes and/or fixing regulatory thresholds (or reduction of these thresholds if they already exist) to limit the contamination levels of foods identified as the main contributors. However, strengthening regulations on the maximum level of Cd allowed in food can have a low impact on reducing human exposure due to the ubiquitous Cd contamination according to Jean et al. (2015). It is therefore recommended to take further action on environmental sources and food contamination routes, particularly in regard to fertilizer inputs, identified as the main source of soil and food contamination (see Fig. 1)

In France, mineral phosphate fertilizers have been identified as the main source of Cd in agricultural soils in arable farming regions (Belon et al. 2012). Phosphate fertilization is adjusted according to the estimated plant phosphorus needs and the availability of phosphorus in the soil. However, there is a sore lack in agronomic field data. Depending on the Cd concentration and the amounts of fertilizer used for phosphate fertilization, mineral phosphate fertilizers represent a little more than half of the Cd inputs in French agricultural soils (Belon et al. 2012). Mineral phosphate fertilizers are made from natural phosphate rocks, which can contain Cd, sometimes in quite high concentrations, according to the nature of the rock material and geographical area from which the rocks are extracted. In sedimentary rocks, for instance, Cd concentrations can reach up to 150 mg Cd.kg^{-1} rocks (Roberts 2014). Igneous rocks such as Kola deposits in Russia, contain lower Cd concentrations, less than 2 mg Cd.kg^{-1}. Nevertheless, sedimentary rocks in Morocco have a Cd content greater than 25 mg Cd.kg^{-1}, e.g. in Bou Craa (32–43 mg Cd.kg^{-1}) or Youssoufia (4–51 mg Cd.kg^{-1}) deposits (Roberts 2014). In France, there are no natural phosphate deposits, and phosphate rocks are imported. In addition to the use of mineral phosphate fertilizers in France, livestock manure contributes significantly to soil inputs in livestock-farming regions, and represents about 25% of the total inflow Cd to agricultural soils (Belon et al. 2012).

In France, many efforts have already been made to reduce soil Cd inputs from fertilizers. Regulations have been enacted with safety criteria defined for marketing authorisations (MA) for fertilizers and growing media. According to the instructions that accompany the MA application (guide No 50644#01, Ministère de l'Agriculture et de la Pêche 2001), the average annual Cd flux brought to the soil in a 10 year period must not exceed 15 g Cd. ha^{-1}. year^{-1}. Moreover, the French standard NF U 42-001-1 currently set a regulatory maximum limit for mineral phosphate fertilizers at 90 mg Cd. kg^{-1} per unit mass of phosphoric anhydride (P_2O_5) equivalent. Although there were defined by REGULATION (EC), n.d Regulation (EC) No 2003/2003, no Cd limit had been previously established for this fertilizer at the European level. In 2016, the European Commission (European Commission 2016) revised the regulation on EU fertilizing products (Regulation (EU) No 2019/1009 repealing Regulation (EC) No 2003/2003) to propose new limit values for contaminants in EU-labelled fertilizers including Cd, taking into account their adverse effects on humans and the environment. Several Cd levels were discussed for the use of mineral phosphate fertilizers (European Commission 2016). A Cd concentration of 60 mg Cd.kg $P_2O_5^{-1}$ was adopted, in view of a potential application of this regulation in 2022 (Regulation (EU) No 2019/1009).

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

This original approach linked soil quality, plant quality and dietary exposure to derive and check Cd limits in mineral phosphate fertilizers to protect human and environmental health. The model was first

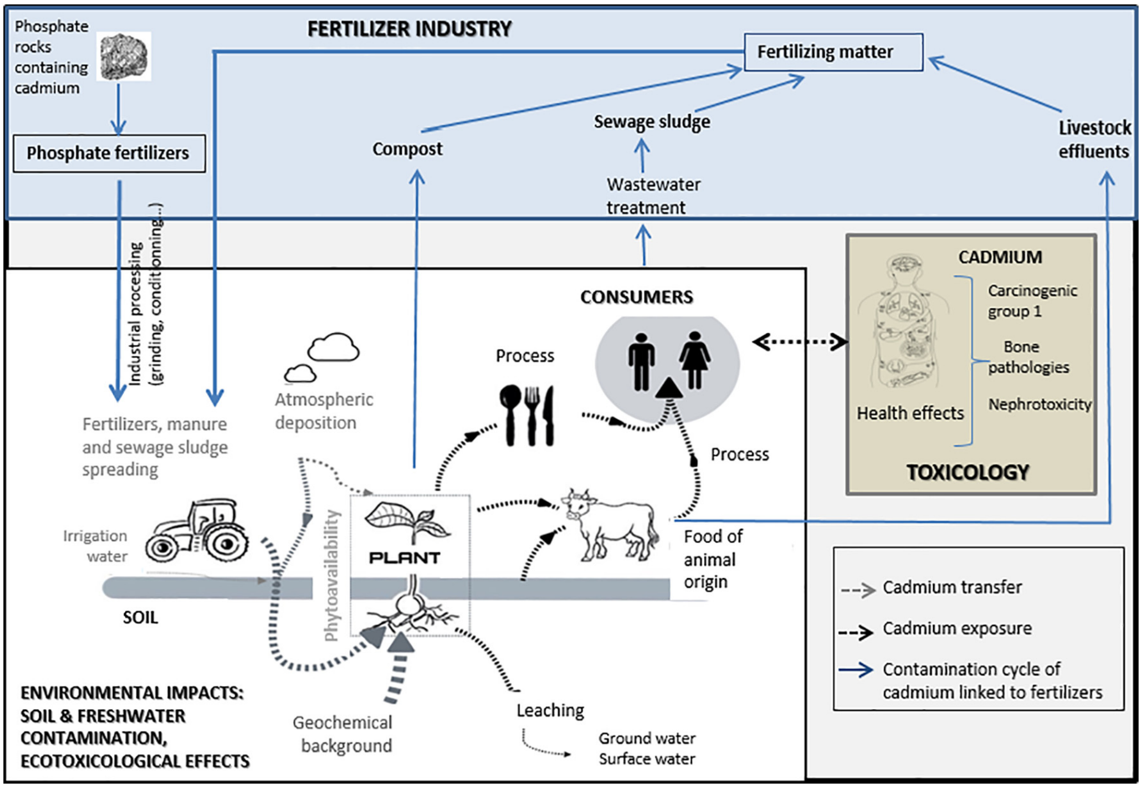

Fig. 1. Graphical abstract.

developed for the major source of Cd input (i.e. mineral phosphate fertilizers) and for the two major field crops contributing to human exposure to Cd, namely wheat and potatoes (ANSES 2011a, 2011b, 2016). The model was then adapted to other organic fertilizers when scientific data were available.

2. Materials and methods

2.1. Input data for the model

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

2.1.1. Soil data

Data came from the French soil quality monitoring network (*Réseau de Mesures de la Qualité des Sols*, RMQS) which is a systematic grid (16 km × 16 km) covering all of mainland France with 2240 sites (Arrouays et al. 2002; Arrouays et al. 2020). This network is representative of the French territory, covering a broad spectrum of climatic, soil and land-use conditions (croplands, permanent grasslands, woodlands, orchards and vineyards, natural or weakly anthropogenic lands). Every 15 years at each site, soil samples are taken, measurements are carried out and observations are made. The first campaign occurred from 2000 to 2010 in mainland France. At these sites, the soil organic carbon (SOC) content, particle-size distribution, pH, main total trace elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Tl, Zn) and soil densities were determined for the 0–30- and 30–50-cm layers. Samples for laboratory analyses were taken from a bulked sample of 25 core samples from unaligned sampling in a 400 m^2 square area. The entire dataset is available on request and the statistical distribution of the results can be downloaded from the INRAE dataverse (Saby et al., 2019).

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

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

2.1.2. Cd inputs due to atmospheric deposition

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

2.1.3. Cd inputs from irrigation water

Cd concentrations from irrigation water were calculated by combining the irrigation quantity of each crop with the Cd concentration in the irrigation water. The quantity of irrigation water for each crop was modelled by applying a triangular distribution to the French ARVALIS research institute database (ARVALIS 2011 and 2013). A truncated normal distribution was applied to the data from the geochemical atlas of

Europe linked to the FOREGS database (FOREGS 2005 and 2006) to model Cd concentrations in irrigation water.

2.1.4. Rainwater quantity

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

2.1.5. Agricultural yields

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

2.1.6. Cd concentrations in food

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

2.1.7. Food consumption

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

2.2. Fertilization scenarios and Cd input via mineral phosphate fertilizers

2.2.1. Crop fertilization

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

2.2.2. Phosphate fertilization

Representative mineral phosphate fertilizer plans for French agricultural soils were modelled. They were linked to protective scenarios of Cd input selected for the risk assessment. The fertilization plans most likely to add Cd to agricultural soils were selected. They were associated with low phosphorus concentrations in soils (i.e. one-third of the soils in France (Delmas et al. 2015, Saby et al. 2016) according to the phosphorus requirements of plants. Phosphate fertilizations plans based on annual applications and applications every 3 years of phosphate mineral fertilizer intake were included in the predictive model. Realistic but representative and reduced-Cd phosphate fertilization plans were simulated for an annual phosphate application of 80 and 100 kg P_2O_5.ha^{-1} for wheat and for the potatoes/wheat/wheat rotation. Phosphate fertilization plans with two years without fertilization were tested applying 100 and 180 kg P_2O_5.ha^{-1} for wheat and for the potatoes/wheat/wheat rotation. Although realistic, these scenarios can be considered as worst case scenarios, because in France the mean phosphorus application rates on wheat and potato crops are 53 kg.ha^{-1} P_2O_5 and 84 kg.ha^{-1} P_2O_5 respectively (Sterckeman et al. 2018a).

2.2.3. Cd concentrations tested in mineral phosphate fertilizers

Cd concentrations in mineral phosphate fertilizers proposed in the French and European regulations were studied. The level of 90 mg Cd.kg $P_2O_5^{-1}$ set by the French standard NF U 42–001–1 was used here and considered as the ‘reference scenario’. The reduced Cd concentrations already discussed at the European level (European Commission 2016) for a harmonized European regulation on mineral phosphate fertilizers with 60, 40 and 20 mg Cd.kg $P_2O_5^{-1}$ were selected here, including the level adopted in Regulation (EU) No 2019/1009. For organo-mineral fertilizers, the European Commission also proposed a plan with application EC-labelled fertilizer with 60 mg Cd.kg $P_2O_5^{-1}$, then 3 years after application a reduction of this threshold to 40 mg Cd.kg $P_2O_5^{-1}$ and finally after 12 years to 20 mg Cd.kg P_2O_5 $^{-1}$ (European Commission, 2016). This scenario was also studied in our work.

2.2.4. Cd fluxes due to mineral phosphate fertilizers.

The phosphate application doses were matched with various Cd levels in phosphate fertilizers to determine annual Cd fluxes in agricultural soils via phosphate fertilizers, expressed in g.ha^{-1}.year^{-1}. Table 1 gives the scenarios and their associated names according to the phosphate fertilizer plans (pH), the phosphate input dose related to the plant requirements for a wheat monoculture crop (b) or a potatoes/wheat/wheat rotation (bp), and the modelled Cd concentration, e.g. Ph/80b/90 indicates a phosphate fertilizer plan with an application of 80 kg P_2O_5.ha^{-1} for wheat monoculture and a Cd input of 90 mg Cd.kg $P_2O_5^{-1}$. Accordingly, our reference scenarios are Ph/80b/90, pH/100b/90, Ph/100 bp/90, Ph/180 bp/90. The reduced-Cd scenarios model 60, 40, 20 mg Cd.kg $P_2O_5^{-1}$ at fixed and degressive (e.g. reduction 3 years after first application, then again 12 years thereafter) levels. Coupling the application dose with the Cd content to be tested according to the fertilization plan (wheat monoculture or rotation) resulted in 20 fertilization plan scenarios to be tested in the model. These scenarios gave Cd fluxes varying from 0.67 to 9 g Cd.ha^{-1}.year^{-1} (Table 1).

2.3. General model

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

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

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

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

	Phosphate fertilization plan (Ph) scenario (Ph/fertilizer dose/Cd level)	Quantity of fertilizer applied (kg P_2O_5.ha^{-1})	Cd concentration in fertilizer (mg.kg $P_2O_5^{-1}$)	Cd inflow to the soil (g.ha^{-1})	Annual Cd flux (g.ha^{-1}.$year^{-1}$)
Annual application for wheat monoculture	Ph/80b/90	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	Ph/100b/90	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	Ph/100 bp/90		90	9	9
	Ph/100 bp/60		60	6	6
	Ph/100 bp/40		40	4	4
	Ph/100 bp/20	100	20	2	2
	Ph/100 bp/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	Ph/180 bp/90		90	16.20	5.40
	Ph/180 bp/60		60	10.80	3.60
	Ph/180 bp/40		40	7.20	2.40
	Ph/180 bp/20	180	20	3.60	1.20
	Ph/180 bp/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)

Underlined: reference scenarios.
* :Degressive cadmium concentration scenarios modelled over a 99-year period.

$$[Cd]_{soil,i} = [Cd]_{soil,i-1} + \frac{(cadmiuminflows - cadmiumoutflows)}{W_{soil}} \quad (1)$$

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

The annual amount of Cd leaching was calculated by determining the Cd concentration in the soil solution using on the formula

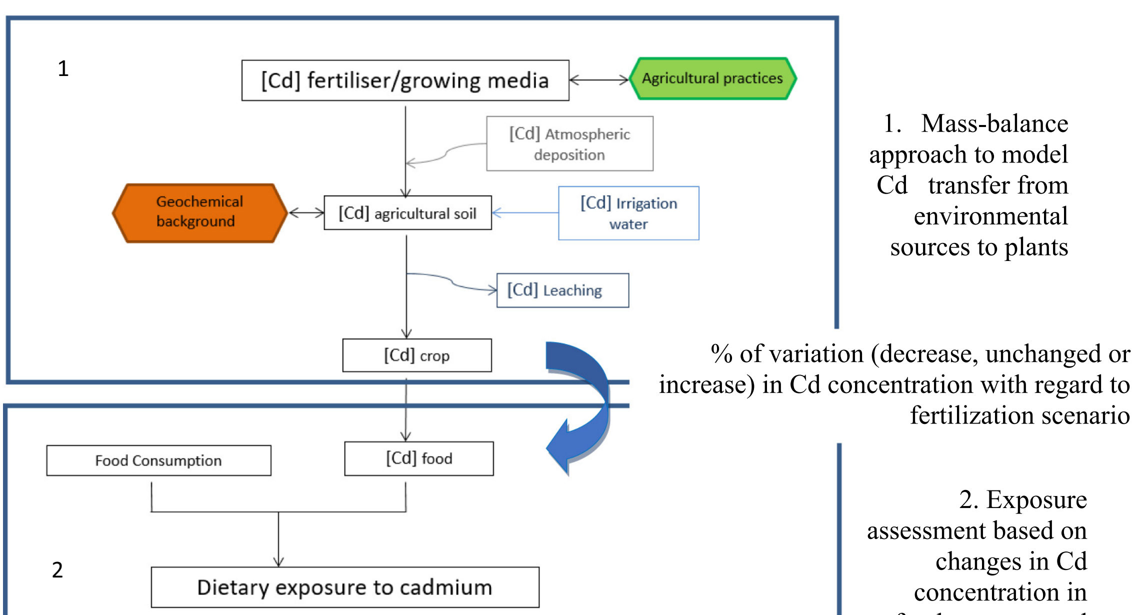

Fig. 2. Schematic of the strategy for modelling cadmium exposure and risk using a mass-balance approach integrating environmental sources of cadmium and fertilization scenarios.

elaborated by De Vries (2011 and 2013) (Table S1). We also determined the volume of soil solution removed from the soil layer considered (30 cm) each year. This volume was estimated as a percentage of the volume of water the plot receives each year, assuming that 30% of this water is irrigation water and the rest (70%) rainwater.

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

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

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

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

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

3. Results

3.1. Environmental contamination and consumer exposure

3.1.1. Mass-balance modelling results

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

Probabilistic parameterisation of the mass-balance approach allowed a presentation of a distribution of percentage variation in Cd concentration in the matrix over time. We used boxplots to explore and visualise two fertilizations plans of interest. Fig. 3 presents the plan with the greatest Cd accumulation over time in soil, plants and leachates associated with wheat monoculture receiving an annual application of 80 kg $P_2O_5.ha^{-1}.year^{-1}$ (pH/80b/90, pH/80b/60, pH/80b/40 and Ph/80b/20). As of 10 years and thereafter, Cd content increases significantly in soils and plants over time (about 10% variation) in line with increasing Cd concentrations in fertilizers, from 40 to 90 $mg.kg^{-1}$ P_2O_5. The mean rate of increase in Cd concentration reaches up to 64% in plants and 72% in leachates over the 99-year period for the Ph/80b/90 reference scenario, representing the current French regulatory threshold of 90 mg Cd.kg $P_2O_5^{-1}$. Cd content in soils and plants are contained only at a level of 20 mg $Cd.kg^{-1}$ P_2O_5 in this fertilization plan.

The potato/wheat/wheat rotation fertilization plan of 180 kg $P_2O_5.ha^{-1}.year^{-1}$ with a two-year hiatus in fertilization (Ph/180 bp/90, Ph/180 bp/60, Ph/180 bp/40 and Ph/180 bp/20) showed the greatest decrease in Cd accumulation in the soil and reduction in its transfer to plants and leachate among all simulations over time (Fig. 4). In contrast to maintaining the current French regulatory threshold of 90 mg Cd.kg $P_2O_5^{-1}$ in the Ph/180 bp/90 reference scenario, the decrease in Cd input by reducing Cd concentrations as much as possible in mineral phosphate fertilizers tends to limit its accumulation in French agricultural soils and its transfer to plants and leachate over time. Based on the distributions and the mean Cd concentration (Fig. 4), a significant reduction in the transfer of Cd to wheat (grain) and potato was observed as of 10 years for phosphate fertilizers with contents equal or less than 40 mg Cd.kg $P_2O_5^{-1}$. This decrease was enhanced for the even lower fertilizer Cd content of 20 mg Cd.kg $P_2O_5^{-1}$. In this latter plan, a decrease greater than 25% of Cd accumulation in French agricultural soils and its transfer is reached over the 99-year period with the distribution of percentage variation in Cd concentration in matrices at the 25th percentile using a set of French soil combinations. Compared with the first year of application, a greatest mean percentage of reduction in Cd concentration in matrices (21%) was observed at the lowest simulated Cd concentration (20 $mg.kg^{-1}$ P_2O_5) over the 99-year period (Table 2). The reduction in the Cd concentration in plants depending on the action at the source of Cd was more pronounced for wheat grain than for potato tuber.

The trends observed in Table 2 and Figs. 3 and 4 show that, at the two highest Cd concentrations (60 and 90 mg Cd.kg $P_2O_5^{-1}$), Cd accumulates in the soil and a significant proportion is transferred to plants and leaching water over time, regardless of the fertilization plan in wheat monoculture or potato/wheat/wheat rotation, with or without a two-year hiatus in fertilization. *A contrario*, with a decrease in Cd concentration to 20 mg Cd.kg $P_2O_5^{-1}$ in the commercial mineral phosphate fertilizer, Cd accumulation in soils and in its transfer to plants and leachate stabilises and even decreases: see scenarios Ph/80b/20, pH/100b/20, Ph/100 bp/20, Ph/180 bp/20, with an average Cd transfer decrease of up to −18% after 99 years (Table 2). Cd is preferentially transferred into leaching water than into the soil and plant matrices. Lower Cd concentrations decreased this transfer to the ground water and surface water.

When realistic fertilizer application scenarios were tested using the degressive Cd model (pH/80b/60–40-20, pH/100b/60–40-20, Ph/100 bp/60–40-20, Ph/180 bp/60–40-20), Cd transfer to the plant and to leaching water is reduced, and the soils gradually become less contaminated. For example, Fig. 5 shows this trend for Ph/180 bp/60–-40-20, representative of agricultural conditions in France. In this scenario, Cd is reduced by, on average, 16% in soils and wheat grain, 13% in potatoes and of 20% in leachate over 99 years, reaching a Cd concentration in mineral phosphate fertilizers of 20 mg Cd.kg $P_2O_5^{-1}$ in 15 years.

3.1.2. Effects of soil characteristics on cd transfer

Fig. 6 illustrates, as an example in a more exposed situation, the variation in Cd concentration depending on soil pH for a wheat monoculture fertilization plan with an annual application of 80 kg $P_2O_5.ha^{-1}.year^{-1}$ between the first year of application and after 99 years.

Table 2
Mean percentage (%) variation in Cd concentration in matrices (soil, wheat grain/or potatoes and leachate) over a 99-year period (10, 20, 60 and 99 years) compared with the first year of application of the mineral phosphate fertilizer with a control Cd content (90, 60, 40 and 20 mg.kg^{-1} P_2O_5) 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
Ph/80b/90	+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
Ph/100b/90	+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
Ph/100 bp/90	+8	+16	+44	+66	+8	+15	+44	+67	+6	+14	+34	+48	+13	+11	+37	+58
Ph/100 bp/60	+4	+8	+23	+35	+4	+8	+23	+36	+3	+7	+18	+26	+10	+3	+16	+28
Ph/100 bp/40	+1	+3	+8	+13	+1	+3	+8	+13	+1	+2	+6	+10	+8	−2	+3	+7
Ph/100 bp/20	−1	−2	−6	−9	−1	−2	−6	−9	−1	−2	−5	−7	+5	−7	−11	−13
Ph/100 bp/60–40 — 20*	+2	+2	-2	−5	+2	+2	−3	−6	+2	+1	−2	−5	+8	−2	−7	−10
Ph/180 bp/90	+3	+6	+16	+26	+3	+6	+18	+28	+2	+5	+14	+20	+9	+1	+11	+20
Ph/180 bp/60	+1	+1	+4	+7	+1	+2	+5	+8	+1	+1	+4	+6	+6	−3	−1	+2
Ph/180 bp/40	−1	−2	−3	−5	−1	−1	−3	−4	−1	−1	−3	−4	+5	−7	−8	−10
Ph/180 bp/20	−2	−5	−12	−17	−2	−5	−12	−18	−2	−4	−10	−14	+3	−10	−17	−21
Ph/180 bp/60-40-20*	−1	−3	−11	−16	−1	−2	−11	−16	−1	−3	−9	−13	+5	−7	−15	−20

Underlined: reference scenarios.
* : degressive cadmium concentration scenarios modelled over a 99-year period.

There is a risk of Cd accumulation in acid, neutral or alkaline soils as well as of Cd transfer to plants for mineral phosphate fertilizers with a Cd content greater than 40 mg Cd.kg $P_2O_5^{-1}$ for the following soils:

- soils with pH < 6.5, representing 50% of the agricultural soils in France (Saby et al., 2019);
- soils with pH >7.5, representing 30% of the agricultural soils in France (Saby et al., 2019).

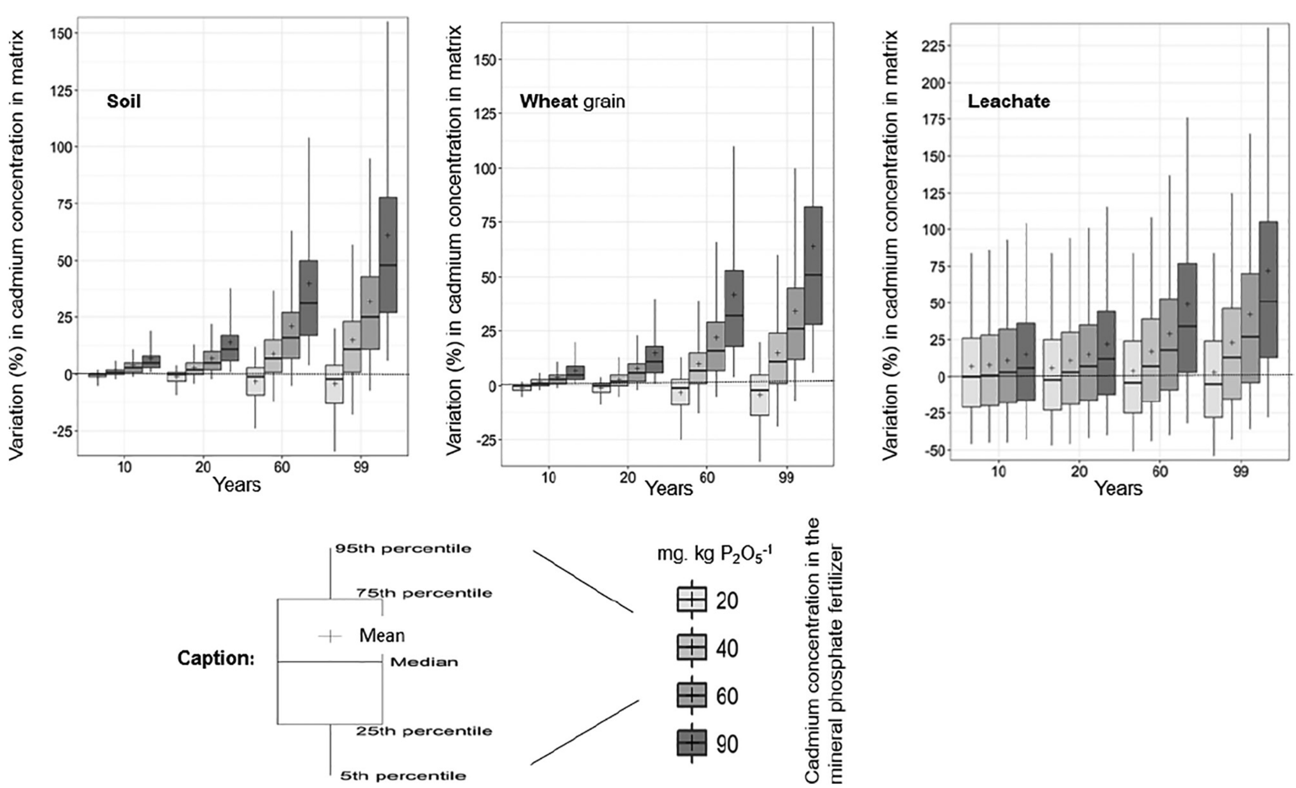

Fig. 3. Variation in Cd concentrations in matrices (soil, wheat grain, leachate) (expressed as percentages) at 10, 20, 60 and 99 years compared with the first year of application, based on mean and percentiles (P05, P25, P50, P75, P95) of Cd concentration in matrices, according to the wheat monoculture fertilization plan of 80 kg P_2O_5.ha^{-1} year^{-1} simulating a constant Cd content of 90, 60, 40 and 20 mg Cd.kg $P_2O_5^{-1}$ in the phosphate fertilizer (Ph/80b/90, Ph/80b/60, Ph/80b/40 and Ph/80b/20 fertilization plans) over a 99-year period.

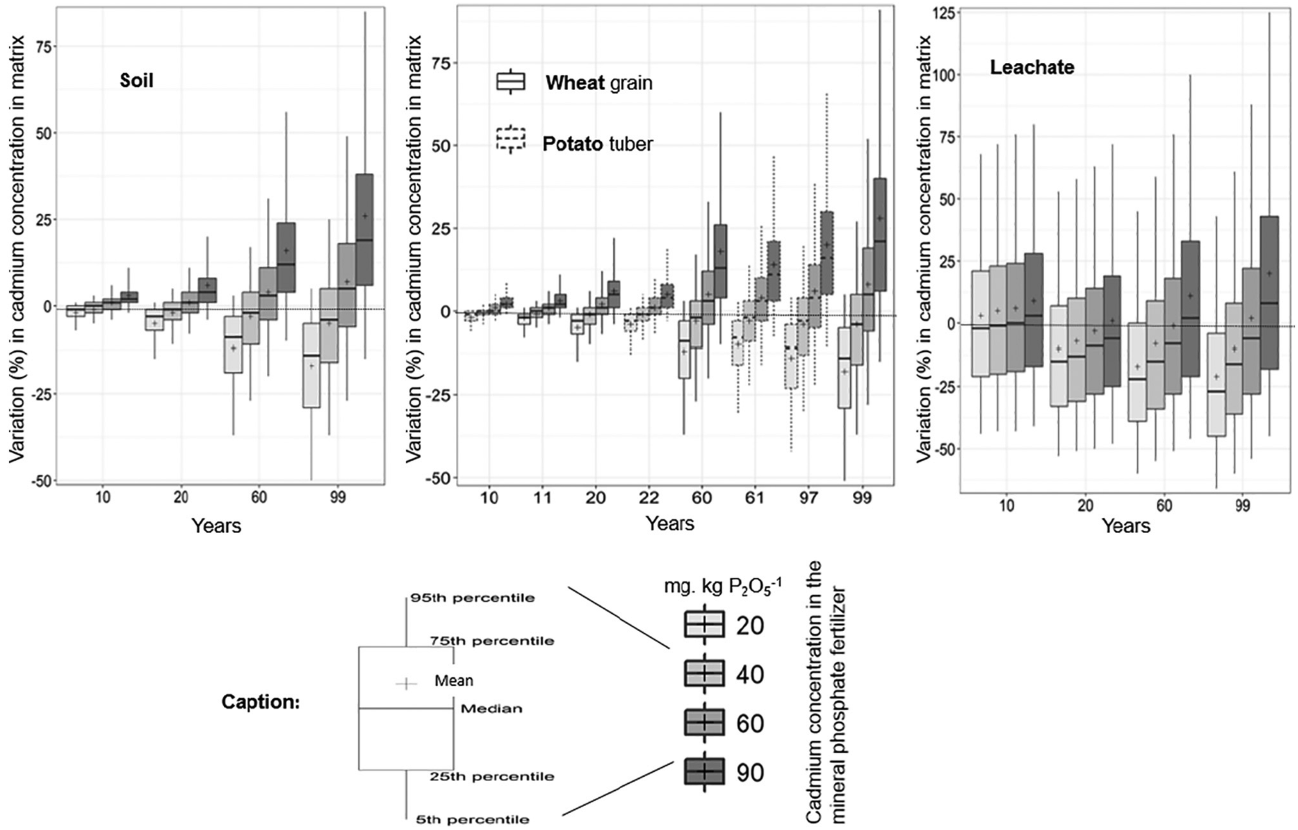

Fig. 4. Variation in Cd concentration in matrices (soil, wheat grain and potatoes, leachate) (expressed as percentages) after 10, 20, 60 and 99 years compared with the first year of application, based on the means and percentiles (P05, P25, P50, P75, P95) of Cd concentration in matrices, according to the potato/wheat/wheat rotation fertilization plan of 180 kg P_2O_5 .ha^{-1}.year^{-1} with a two year hiatus in fertilization, simulating a constant fertilizer Cd content of 90, 60, 40 and 20 mg Cd. kg $P_2O_5^{-1}$ over a 99-year period (Ph/180 bp/90, Ph/180 bp/60, Ph/180 bp/40, Ph/180 bp/20 fertilization plans).

3.1.3. Health risk assessment for the consumer.

Fig. 7 shows the percentages of adults and children exceeding the Cd HBGV intake of 0.35 μg.kg bw^{-1}.d^{-1} for different scenarios (ANSES 2019) under the UB hypothesis. Compared with the starting scenario corresponding to current exposure levels (ANSES 2011a), the reduced-Cd scenarios (20 mg Cd.kg $P_2O_5^{-1}$), on a constant or degressive basis (pH/80b/20, Ph/180 bp/20, Ph/100b/60–40-20 and Ph/180 bp/60–40-20 scenarios), lead to a lower exceedance of the HBGV. Nevertheless, the risk remains significant in adults and children, for whom the percentage exceeded 12% even after 99 years. Only the Ph/180 bp/20 and Ph/180 bp/60–40-20 scenarios show a significant decrease in this percentage in children after 99 years.

In the reference scenarios corresponding to the current French regulatory threshold of 90 mg Cd.kg $P_2O_5^{-1}$ in mineral phosphate fertilizers

Fig. 5. Variation in Cd concentration in matrices (soil, wheat grain and potatoes, leachate) (expressed as percentages) after 10, 20, 60, 99 years compared with the first year of application, based on the mean and percentiles (P05, P25, P50, P75, P95) of Cd concentration in matrices, according to the potato/wheat/wheat rotation phosphate fertilization plan with 180 kg P_2O_5. ha^{-1}.year^{-1} including a two year hiatus in fertilization and using degressive fertilizer Cd concentrations over a 99-year period (Ph/180 bp/60–40 − 20).

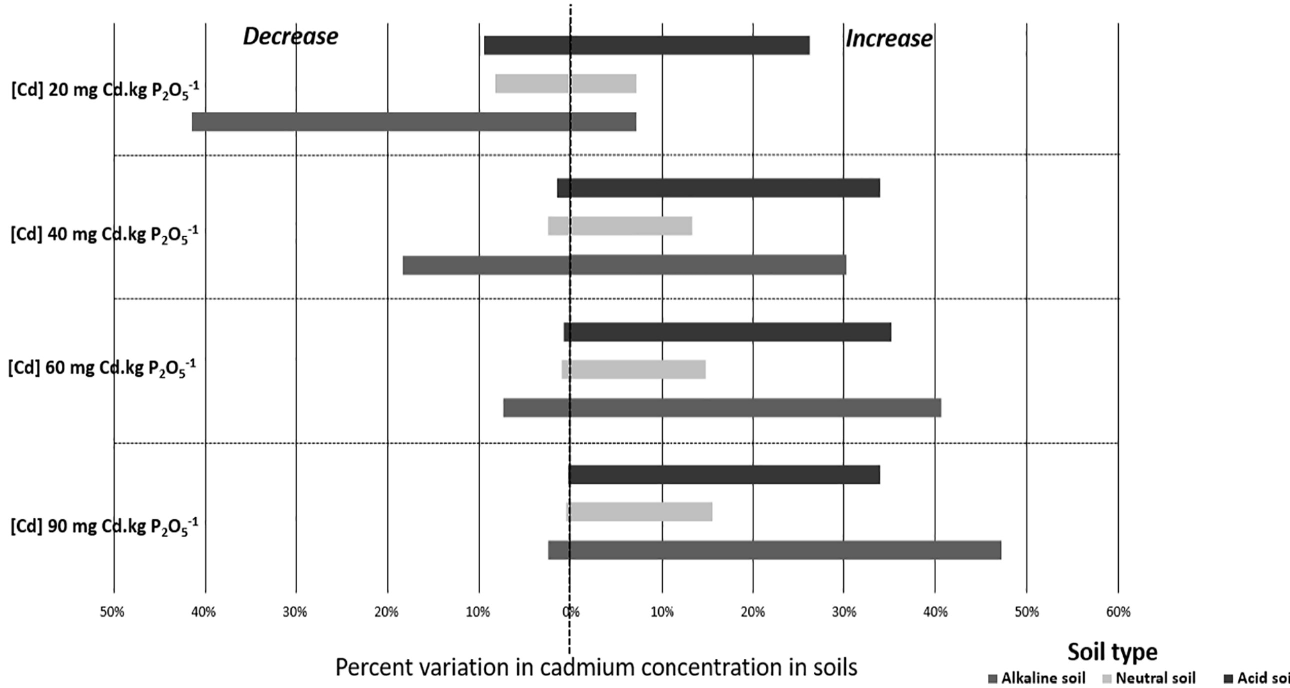

Fig. 6. Variation (%) of cadmium concentration in French agricultural soils, as a function of their pH (acid, neutral or alkaline) and the cadmium concentration of mineral phosphate fertilizers spread (90, 60, 40 and 20 mg Cd.kg $P_2O_5^{-1}$) between the 1st year of application and the 99-year period for a fertilization plan corresponding to a wheat monoculture at 80 kg P_2O_5.ha^{-1}.year^{-1}.

(pH/80b/90 and Ph/100 bp/90), the percentages of exceedance are significantly higher than in the starting scenario ($p < 0.05$). For adults, this increase is significant after 60 or 99 years of projection. In these situations, the percentage of children in which HBGV is exceeded doubles after the projected 99 years, while for one-third or more, it is not be possible to rule out a risk.

In fertilization plans associated with a fertilizer Cd content of 20 mg Cd kg $P_2O_5^{-1}$ (constant or degressive Cd content scenarios), an exceedance of the HBGV in adults and children is undeniably observed, but with a significant reduction after 99 years.

3.2. Comparison of Cd fluxes via fertilizing materials

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

Fig. 8 shows the results of Cd accumulation in French agricultural soils and its transfer to plants and leachates over the 99-year period obtained using fluxes from different fertilizing materials according to wheat monoculture agricultural practises in France. Cd accumulation in the soil and its transfer to wheat grains decreases following fertilization plans with an annual flux varying from 0.67 to 2 g Cd.ha^{-1}.year^{-1}. This decrease is attributed to the use of farm anaerobic digestates with a mean Cd concentration of 0.70 mg.kg^{-1} of dry matter (DM) and mineral phosphate fertilizers with a Cd content of 20 mg Cd.kg $P_2O_5^{-1}$. The condition without added Cd from agronomic inputs (Cd inputs only come from atmospheric deposition and irrigation water, in addition to the geochemical background) was also tested.

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

4. Discussion

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

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

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

Six and Smolders (2014) updated the mass-balance approach initiated in 2002 by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) by integrating the inventory of Cd inputs to agricultural soils in the EU 27 + Norway (EU27 + 1) with recent data on atmospheric deposition, phosphate fertilizers, sludge, lime and manure applications for soils used for arable production of cereal and potato crops. However, they used mean estimates of input variables. Thus, although their assumptions were realistic and encompassed the majority of current situations, their assessment can be improved by taking into account the variability of input data and local situations in

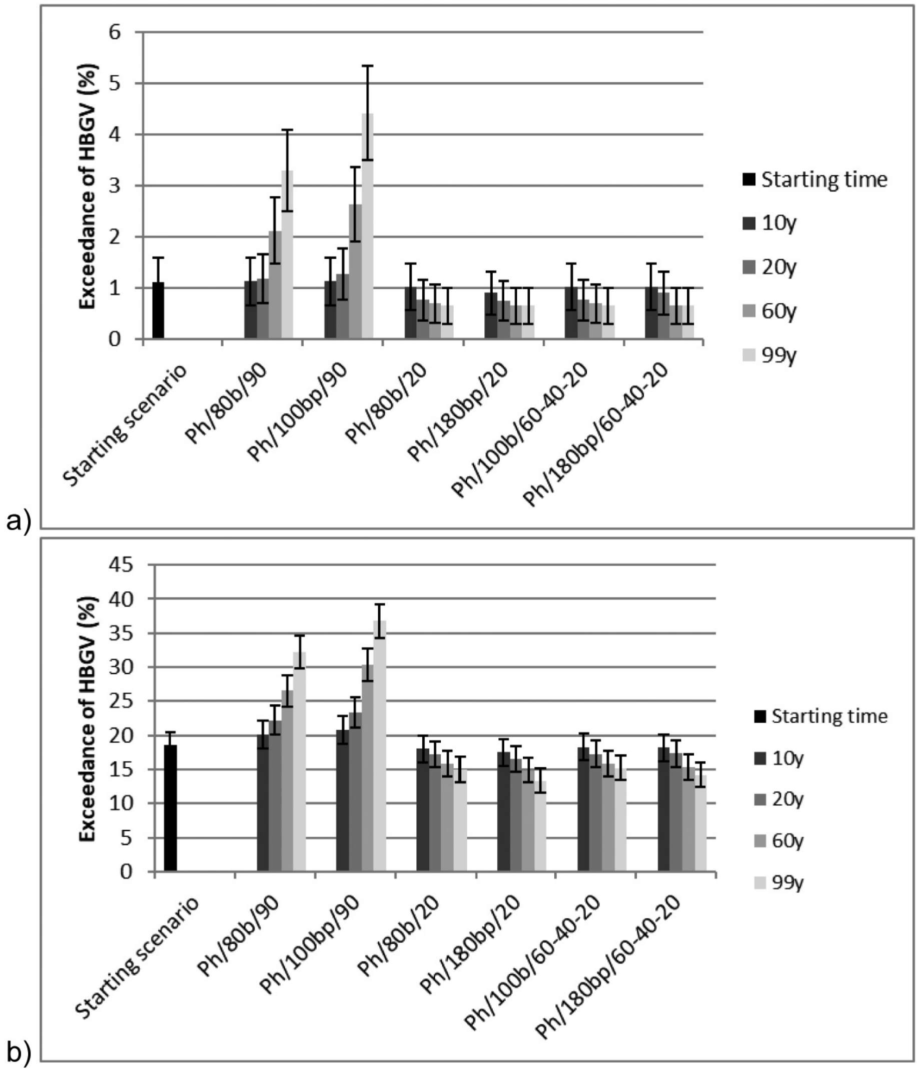

Fig. 7. Percentage of cases exceeding the health-based guidance value (HBGV) of 0.35 μg Cd.kg $bw^{-1}.d^{-1}$ and 95% confidence interval ($CI_{95\%}$) in the different scenarios, for French adults (a) and children (b), under the upper bound (UB) hypothesis.

particular the ones corresponding to Cd overexposure through particular soil/ plant/input combinations, as explored here in this study. Römkens et al. (2017) and Sterckeman et al. (2018a, 2018b) implemented the mass-balance approach with the integration of data focusing on a more precise geographical scale respectively at the European regional level and in France by integrating soil variability. However, their approach focused only on Cd transfer in soil and plants and did not study their impact on food products. Furthermore, previous

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

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

* DM: dry matter.

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

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

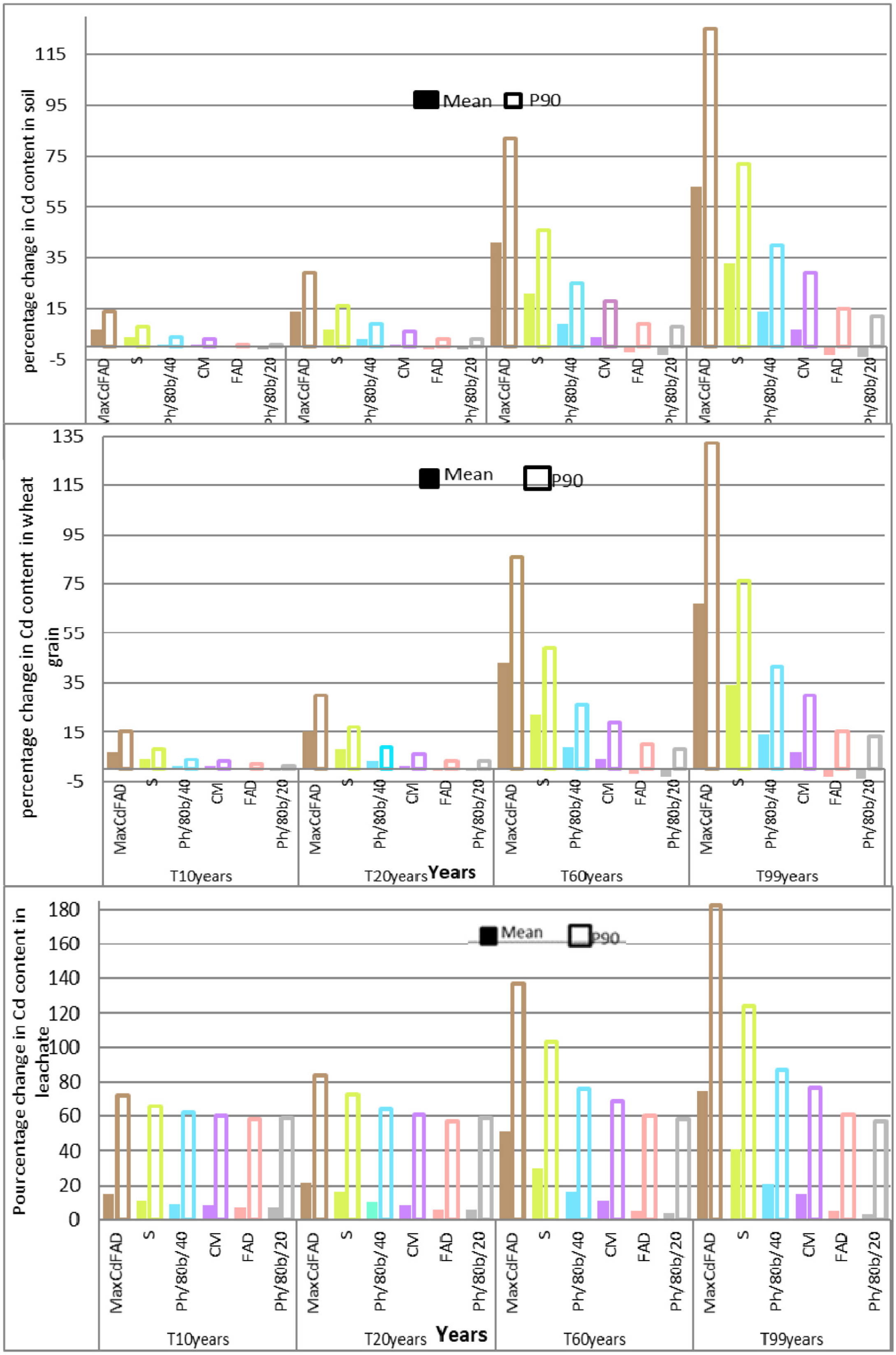

Fig. 8. Variations (%) in the mean and 90 percentile (P90) Cd contents in French agricultural soils, wheat grain and leachate matrices over a 99-year period (10, 20, 60, 99 years) compared with the first year of application and according to application of fertilizing materials based on a wheat monoculture plan.

studies have already expressed the need for a joint assessment of the trends of accumulation of Cd in soil and the general dietary exposure of the population to Cd (Rietra et al. 2017; KEMI, 2011).

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

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

For example, simulated plant Cd concentrations at the start of the simulations (median of 0.07 mg $Cd.kg^{-1}$ in wheat grains and 0.04 mg $Cd.kg^{-1}$ in potatoes) were of the same order of magnitude as those measured by the French monitoring programs during the 2010–2015 period (median of 0.02 mg $Cd.kg^{-1}$ in both crops) and that reported at the European level (median of 0.02 mg $Cd.kg^{-1}$ for the two crops (EFSA, 2009). Also, Cd concentrations derived for leachates at the start of the simulations were quite similar to the data reported in Six and Smolders (2014). Our model provided a mean maximum leached Cd content for each simulation of 2.4 g $Cd.ha^{-1}.year^{-1}$, whereas Six and Smolders (2014) reported a mean leaching rate in Europe of 2.56 g Cd. $ha^{-1}.year^{-1}$. Our models were thus appropriate for conducting a quantitative health risk assessment.

Moreover, our model gave mean estimates of the progressive decrease in Cd accumulation in soils over time at the lowest Cd concentration (20 mg Cd.kg $P_2O_5^{-1}$), with −17% over a 99-year period. These estimates are close to those obtained by Six and Smolders (2014): −20% to −14% with a medium fertilizer Cd concentration between 0 and 40 mg Cd.kg $P_2O_5^{-1}$.

Here, our model included several uncertainties that can be reduced by including additional supplementary data that remain to be acquired. For example, we only considered wheat and potatoes, because they were identified as major contributors to consumer Cd exposure through food products (EFSA, 2012, ANSES 2011a, 2011b, 2016). Because fertilizers are applied to crops other than wheat and potatoes, the assessment can be extended to other routes of Cd transfer from soils to food products of plant and animal origin. Moreover, other trace elements present in the soil can compete with Cd for uptake by plants (Dharma-wardana 2018). Some of these elements, namely Zn and Se, are known to interfere with Cd toxicity. For instance, Zn clearly inhibits Cd uptake and bioavailability in many plant species (Chaney 2012). A review of the role of ion competition (Cu, Se, Zn, etc.) on Cd toxicity and Cd uptake by plants suggests that they depend on element concentrations and plant genotype (Qin et al. 2020). Furthermore, Kikuchi et al. (2003) and JECFA (2004) stressed that the gastro-intestinal absorption of Cd is influenced by Zn and other ions. Such interactions, inhibitions or synergies may influence the resulting toxicity. However, we here used as a reference point a HBGV set for cadmium, which is based on epidemiological data (ANSES 2019). Therefore, this HBGV includes the interactions with other trace elements provided through the general consumer diet. Nevertheless, the comparison of the effect of the studied scenarios on dietary exposure to Cd remains valid. In addition, parameters related to climate, soil typology, agricultural practices, agricultural inputs (particularly fertilizers of organic origin (which had large amounts of missing data) and food habits were considered to be constant over the 99-year period because the data to take into account the evolutions of these parameters were not available.

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

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

In fine, our approach is a predictive tool that can be used to propose safe and sanitary Cd levels according to the Cd concentrations in a product placed on the market whose Cd content can be controlled, or according to Cd fluxes regardless of fertilizer type and/or the total fertilizers applied to arable soils. Through the combination of Cd concentration and fertilizer application dose as input data, reasoning finally in Cd fluxes is of interest to the farmer and the regulator, regardless of the fertilizing materials used. The estimation of fluxes can quantitatively and temporally monitor the Cd inputs with regard to the sustainable management of Cd inputs in agricultural soils and crops in a context of agroecological transition.

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

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

Our work simulated different Cd concentrations in commercial mineral phosphate fertilizers based on protective fertilization plans applied in the case of French agricultural soils, for which extensive field data is available in the RMQS. Our approach modelled the Cd effects on the environment and consumer health by using different mineral phosphate fertilizations plans playing different Cd concentrations (90, 60, 40 or 20 mg Cd.kg $P_2O_5^{-1}$ as constant or degressive over a 99-year period), giving Cd fluxes varying between 0.67 and 9 g Cd. $ha^{-1}.an^{-1}$. In comparison with a reference scenario using the French threshold (90 mg Cd.kg $P_2O_5^{-1}$), results from our study showed the need to take measures to reduce Cd inputs at the source. In regard to environmental and consumer safety, measures need to include restrictions on Cd concentrations, either by using the lowest possible concentration of 20 mg Cd.kg $P_2O_5^{-1}$ in the product commercialized or not exceeding flux of 2 g Cd. $ha^{-1}.year^{-1}$. Stabilization, and eventually a decrease in Cd levels in soils, plants and leachates over time was confirmed for Ph/80b/20, pH/100b/20, Ph/100 bp/20, Ph/180 bp/20 fertilization plans using lowest Cd concentration and the Ph/80b/60–40-20, Ph/100b/60–40-20, Ph/100 bp/60–40-20, Ph/180 bp/60–40-20 fertilizations plans progressively reducing the Cd concentration in mineral phosphate fertilizers to 20 mg Cd.kg $P_2O_5^{-1}$ over 15 years. These fertilization plans do not exceed a Cd flux of 2 g Cd. $ha^{-1}.year^{-1}$. Dropping below this level appears essential to stop the increase in the part of the population likely to be overexposed to Cd through food. Although results of exposures exceeded the oral HBGV, those results showed that if no action is taken to reduce the Cd content in mineral phosphate fertilizers, the risk will increase over time due to Cd accumulation. Because fertilizers are applied to many crops and not only potatoes and wheat, it is likely that the effects observed following a reduction of Cd-containing fertilizer application would have a favourable impact on all crops and consequently on dietary exposure.

Anyway, the application of mineral phosphate fertilizers with contents higher than 40 mg Cd.kg $P_2O_5^{-1}$ (linked to Cd fluxes greater than 2 g Cd. $ha^{-1}.year^{-1}$, see Table 1) is incompatible with the typology of the receiving agricultural soil. A risk of Cd accumulation in soils is observed through an analysis of soils characteristics on Cd transfer by the model. According to Cd concentrations of 90, 60 and 40 mg Cd.kg $P_2O_5^{-1}$ in mineral phosphate fertilizer, our probabilistic simulations showed great variation in the Cd concentration in soils based on a variety of cases, including unfavourable and protective local situations (for example, soils low in phosphorus requiring higher fertilization). According to soil characteristics (e.g. pH > 7) and soil uses (e.g. cultivated soils that are currently amended), Römkens et al. (2017) predict large Cd accumulation which can exceed 30% in soils: in that study, both the strong Cd fluxes and high pH favour the soil pollution. In presence of alkaline soils, our results also indicated trends of Cd to be immobilised by precipitation regardless of the Cd content of the mineral phosphate fertilizers tested. As demonstrated by our simulation, the reduction in Cd at the source can be efficient even in acidic soils. In effect, the effect of pH on Cd bioavailability results in a significant reduction in transfer in the presence of purified soil over the time, particularly at the lowest Cd concentration in mineral phosphate fertilizers. Acidic soils favour the Cd transfer to plants (Tremel-Schaub and Feix 2005), thus they are considered as 'at-risk soils' in terms of crops and therefore human exposure. We also observed a slightly more marked Cd transfer in wheat grain than in potatoes, a crop that requires phosphorus. In potatoes, the phyto-available Cd fraction will be directly taken up and transferred to the tuber, whereas in wheat, there is less translocation of Cd from roots to grain. Rotational fertilization scenarios reduced Cd accumulation over time and Cd transfer to plants and leachates is more marked for a rotation plan of 180 kg $P_2O_5.ha^{-1}.year^{-1}$ with a two-year pause in fertilization, due to a lower annual Cd input. Otherwise, a comparison of the mass balances showed that Cd transfer is greater in leachates than in soil and plant matrices. These transfers to ground water and surface water contributing to diffuse and generalised environmental contamination must be limited as much as possible in light of the resulting environmental and health consequences. In addition, this water may be subsequently used for crop irrigation. Lowering Cd inputs via controlled fertilizer application preserves the quality of the environment, specifically in regard to leaching water.

Our work opened by the comparison of modelling Cd inputs via mineral phosphate fertilizers and other fertilizing materials based on available data. For example, we modelled a wheat monoculture fertilization plan applied to French agricultural soils. Spreading sewage sludge, cattle manure or anaerobic digestates, whose Cd concentration is low, can lead to a Cd flux of up to 7.50 g Cd. $ha^{-1}\cdot year^{-1}$, due to a high amount of fertilizer applied to the soil. The comparison indicated that irrespective of the type of fertilizer, a Cd flux of less than 2 g $Cd.ha^{-1}.year^{-1}$ better protected the environment (soil, plants) and consequently the related final food products. Hence, an annual Cd flux not exceeding 2 g $Cd.ha^{-1}.year^{-1}$ regardless of the type (fertilizer/soil amendment, organic/mineral origin, etc.) and total quantity of fertilizer(s) added to French agricultural soils may help control the pollution of agricultural soils, contamination of agricultural production and thus the associated dietary exposure. A Cd content equal to or less than 20 mg Cd.kg $P_2O_5^{-1}$ in mineral phosphate fertilizer products that can be regulated at the source would ensure that this annual flux of 2 g $Cd.ha^{-1}.year^{-1}$ is not exceeded. Moreover regarding human exposure to metals, given the growing urban populations around the world and the frequent significant pollution events (Dumat et al. 2019; Natasha et al. 2019), it is crucial to avoid insofar as possible the introduction of new persistent metals into the environment and their accumulation in the food chain.

4.3. How agroecology practices can promote human health

In France, the current standard threshold of 90 mg Cd.kg $P_2O_5^{-1}$ in mineral phosphate fertilizer sustains the Cd contamination cycle and thus human Cd exposure, despite having taken steps to limit Cd contamination by this fertilizer inputs. Currently, the new harmonized EU Regulation (EU) 2019/1009 on the market of EU-labelled fertilizers is moving for that their content of cadmium should therefore be limited in such products. This regulation establishes that the Cd level in an organo-mineral fertilizer must not exceed 60 mg Cd.kg $P_2O_5^{-1}$. However, maintaining a threshold of 60 mg Cd.kg $P_2O_5^{-1}$ does not stimulate a rapid reversal of the current upward trend. Limiting applications to a concentration of 20 mg Cd.kg $P_2O_5^{-1}$ in an organo-mineral fertilizer, perhaps in a degressive Cd decrease over a 15-year period, would be more beneficial and better protect the environment and human health.

Other ways (currently not explored for economic reasons) to promote soil quality is to select phosphate rock deposits based on Cd concentration criteria and to optimise decadmiation processes. Setting a limit on annual fluxes (equal or less to 2 g $Cd.ha^{-1}.year^{-1}$) would be more favourable for the management of fertilizer application and soil quality to obtain improvements. Specifically, in France, the oldest threshold Cd fluxes stipulated in the existing national regulations (instructions that accompany the MA application (guide No 50644#01)) of 15 g $Cd.ha^{-1}.year^{-1}$ (Ministère de l'Agriculture et de la Pêche 2001) must be cut back by a factor of 7 to reach the level we recommend here. Our recommendation of a threshold flux limit of 2 g $Cd.ha^{-1}.year^{-1}$ for applied fertilizers, regardless of their nature and quantity, would be more efficient to control soil and plant contamination. This threshold is important for the last link in the food chain: human consumers. This level would also be more convincing in France, for which one-third of agricultural soils are at risk for cadmium accumulation (Delmas et al. 2015; Saby et al. 2016).

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

Given the temporary effectiveness of trapping techniques, it is necessary to continue to decrease the limit value below 60 mg Cd.kg $P_2O_5^{-1}$ for mineral phosphate fertilizers (towards a value equal to or lower than 20 mg Cd.kg $P_2O_5^{-1}$) and the development of decadmiation techniques relating to their production. The introduction of Cd fluxes limits or reduces Cd fluxes with respect to the French administrative guidance value (Ministère de l'Agriculture et de la Pêche 2001), enhancing the management of Cd inputs into soils on a larger scale.

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

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

To promote sustainable agriculture and the agri-food system at the global scale, both improving the quality of fertilizers and amendments and optimising the applied quantities (considering the plant cycle, using green manure crops and other agroecological practices) are therefore crucial steps. The development of numerous urban agriculture projects involving different stakeholders constitutes an efficient vector for ecology education and enhances the links between consumers and local and organic produce farmers (Dumat 2019).

5. Conclusions and perspectives.

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

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

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

Given the ubiquitous nature of Cd and the need to reduce its environmental contamination cycle and long-term dietary exposure to this element, it is important to control Cd fluxes via fertilizers. A Cd flux lower than 2 g $Cd.ha^{-1}.year^{-1}$ from the application of fertilizers, corresponding to a Cd content of 20 mg.kg $P_2O_5^{-1}$ or less in mineral phosphate fertilizers, ensures better protection of environmental and human health. Within a century, a protective concentration of 20 mg.kg $P_2O_5^{-1}$ in a potato/wheat/wheat rotation fertilizer plan of 180 kg $P_2O_5.ha^{-1}.year^{-1}$ with a two-year no-fertilizer period can lead to a mean Cd reduction of up to 17% in French agricultural soils, 18% in wheat grain, 14% in potatoes and 21% in leachates. This reduction is essential to limit Cd accumulation in soils such that consumer exposure, mainly via food, does not exceed the health threshold values.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We are grateful to the ANSES Expert Panels on “Health reference values”, “Fertilizers and growing media” and “Assessment of the physical and chemical risks in foods” for proofreading and validating this work. We are grateful to the INFOSOL-INRAE research unit for providing and authorising the use of French soil data.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.143374.

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