Modeling of ^{137}Cs migration in soils using an 80-year soil archive: role of fertilizers and agricultural amendments

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ABSTRACT

An 80-year soil archive, the 42-plot experimental design at the INRA in Versailles (France), is used here to study long-term contamination by ^{137}Cs atmospheric deposition and the fate of this radioisotope when associated with various agricultural practices: fallow land, KCl, $NH_4(NO_3)$, superphosphate fertilizers, horse manure and lime amendments. The pertinence of a simple box model, where radiocaesium is supposed to move downward by convectional mechanisms, is checked using samples from control plots which had been neither amended, nor cultivated since 1928. This simple model presents the advantage of depending on only two parameters: α, a proportional factor allowing the historical atmospheric ^{137}Cs fluxes to be reconstructed locally, and k, an annual loss coefficient from the plow horizon. Another pseudo-unknown is however necessary to run the model: the shape of historical ^{137}Cs deposition, but this function can be easily computed by merging several curves previously established by other surveys. A loss of ~1.5% per year from the plow horizon, combined with appropriate fluxes, provides good concordance between simulated and measured values. In the 0–25 cm horizon, the residence half time is found to be ~18 yr (including both migration and radioactive decay). Migration rate constants are also calculated for some plots receiving continuous long-term agricultural treatments. Comparison with the control plots reveals significant influence of amendments on ^{137}Cs mobility in these soils developed from a unique genoform.

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1. Introduction

Knowledge of the behavior of ^{137}Cs at terrestrial interfaces is of great environmental and/or geological interest as this radio-isotope can be used as a chronostratigraphical marker in sediments (e.g. Zuo et al., 1991), and as a tool to quantify soil erosion rates (Ritchie and McHenry, 1990; Walling and He, 1999; Sanchez-Cabeza et al., 2007). In addition, the identification and quantification of parameters governing its post-depositional downward migration in soils allow long-term risks in terms of radiological impacts to be evaluated: soil *via* root uptake can become a source of contamination for agricultural products (Gonze and Bréchignac, 2000; Bréchignac et al., 2002); the external radiation dose from radionuclides contained in soil also depends on the vertical distribution within the soil profile (Arapis et al., 1999). Low vertical mobility extends potential resuspension of contaminated and respirable dust into the air. In contrast, downward migration represents potential risk of groundwater contamination. Radiocaesium mobility is known to depend to a large extent on the presence and nature of clay minerals, particularly illite (Cornell, 1993; Staunton and Levacic, 1999), but other parameters such as soil type, soil chemistry, organic carbon content, biological activity and climatic conditions have also been identified as acting variables. For example, it has been suggested that the sorption of ^{137}Cs decreases with increasing organic matter content (Dumat et al., 1997; Nakamaru et al., 2007), although such relationships are not yet fully understood (Staunton and Levacic, 1999).

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In addition to numerous studies focusing on the chemical availability of caesium in soils applying chemical extraction schemes (e.g. Krouglov et al., 1998; Bunzl et al., 1998; Forsberg et al., 2001), downward migration in soils has been investigated by modeling ^{137}Cs depth distributions, determined at the time of sampling, by using either convection equations alone (Palágyi and Palágyiová, 2003), or a combination of convection and diffusion equations (Bossew and Kirchner, 2004). Some refinements taking into account the different states of ^{137}Cs in the soil matrix, clay content, etc. have also been proposed (Faroussi et al., 2007). The convection model is basically rendered using a serial compartmental scheme, where the soil is split into a set of N horizontal and connected layers (Kirchner, 1998; Chibowski and Zygmunt, 2002). Each compartment is considered as a box characterized by its own downward transport rate, k_i. In other words, the amount of radionuclides reaching the underlying compartment per unit of time is proportional (k_i positive factor) to the pool present within the layer. Mobility along the soil profile is simulated by a series of differential equations of the first order, one for each compartment. Fitting the equations to the measured activities allows the different k_i values to be calculated. In such an approach, back-transport is precluded, activities are considered uniform within each compartment, and transport rate values are presumed to be linear and time-invariant. When convection–diffusion equations are preferred, a constant diffusion factor is introduced. Whatever the model, parameter values depend on the function describing radionuclide fallout over time. If historical ^{137}Cs deposition is not available, a single pulse into the surface soil horizon is sometimes considered. This simplification is reasonable in contaminated areas such as Central or Eastern Europe, where Chernobyl-derived fallout predominates over global nuclear bomb-derived inputs (Chibowski and Zygmunt, 2002; Hrachowitz et al., 2005). When studies integrate the complex history of ^{137}Cs fallout, continuous deposition is approximated by a series of single depositions (Hölgye and Maly, 2000).

Despite the wide variety of approaches developed to study the vertical translocation of ^{137}Cs in soils, predictions deduced from dynamic models are seldom validated because the opportunity to access samples covering an appropriate time-scale is rare, except for some exceptional long-term experiments operated in dedicated facilities under close-to-real controlled conditions especially designed for simulations (Forsberg et al., 2000; Bréchignac et al., 2000). In the present study, we investigated the effectiveness of a simple convective model to describe ^{137}Cs migration in surface soil samples from the 80-year soil archive of the INRA 42-plot experimental design, located in Versailles (France). This sample-set constitutes a valuable archive to study historical atmospheric fallout, and hence, mobility-controlling parameters for various pollutants, as was recently demonstrated for common lead (Semlali et al., 2004). In addition to non-amended, non-cultivated control plots, the 42-plot design includes 16 replicate plots which are annually treated with various mineral fertilizers and agricultural amendments; all soils being developed from one unique genoform. Consequently, this scheme offers an outstanding opportunity to check the influence of agricultural practices on ^{137}Cs migration, by eliminating the variability commonly related to soil nature.

2. Materials and methods

2.1. The site

In 1928, the French "Central Agronomy Station" and the "Soil Laboratory" of the Institute, which became INRA in 1946, created a long-term agronomic experiment in the Gardens of Versailles Palace, located about 20 km south-west of Paris. This experimental site was originally designed to study long-term effects of the main N, P, and K fertilizers as well as organic matter and lime amendments on the composition and physical properties of Neoluvisols (loamy Aquic Hapludalf) developed in eolian loess deposits, typical of the Paris Basin (Burgevin and Henin, 1939). In these soils,

the clay fraction is dominated by illite–smectite mixed-layer minerals and minor amounts of illite–mica and kaolinite (Pernes-Debuyser et al., 2003). The experimental design comprises 42 plots of 2.0 m × 2.5 m, maintained as bare soils. Ten plots have never been fertilized or amended. They represent the control. The other plots have received 16 treatments: either mineral fertilizers with mono or bivalent cations (Na^+, K^+, NH_4^+, Ca^{++}) or organic (manure, dried blood) or lime ($CaCO_3$, CaO) amendments. These treatments produced notable acidifying, neutral or basic effects on the physicochemistry of the soils (Pernes-Debuyser and Tessier, 2002a,b). From 1929 to 1970, one or more sampling campaigns were carried out each year; since the 1970s, sampling has taken place every two or three years. Sampling consists in collecting 1 kg of soil from each plot, which is then air-dried, ground to < 2 mm and stored in hermetically closed glass vials. In 1992, horizons at 25–50 cm, 50–75 cm and 75–100 cm were also sampled from selected plots.

2.2. Methods

The ^{137}Cs activity was measured by g-spectrometry (at 661 keV) in an intrinsic high-purity germanium well detector (Ortec Ametek, Inc, USA) at the Universities of Bordeaux and Geneva. The spectrometers were installed underground, inside a heavy shielding composed of archeological lead. Counting efficiency was determined with a standard of known activity with the same geometry as for samples. Powders were counted for 3–6 days to obtain satisfactory counting statistics. Results for control and amended plots are reported in Tables 1 and 2, respectively.

Table 1
^{137}Cs activity in control plots P11, P32 and P34 (in plow horizons, except for 1992) decay-corrected for the sampling date.

Year of collection	Plot ID	^{137}Cs (Bq kg^{-1})	$\pm 1\sigma$
1945	P11	NM	–
	P32	<0.4	–
1948	P32	<0.4	–
1950	P32	<0.4	–
1952	P11	<1.8	–
	P32	0.5	–
1955	P11	<1.5	–
	P32	0.7	0.2
1957	P32	2.3	0.2
1958	P32	2.5	0.4
1960	P11	7.4	1.9
	P32	6.0	0.5
1962	P11	5.5	1.3
	P32	4.7	0.5
1963	P11	9.7	1.8
	P32	9.0	0.8
1964	P32	13.3	0.8
1966	P32	11.2	0.7
	P34	11.2	0.7
1968	P11	11.7	1.1
	P34	9.8	0.5
	P32	10.7	0.7
1972	P11	10.8	1.5
	P34	11.0	0.6
	P32	9.6	0.6
1977	P11	10.0	0.9
	P32	9.3	0.6
1980	P11	9.5	0.9
	P32	8.3	0.5
1981	P32	7.3	0.5
	P34	7.1	0.5
1982	P34	8.6	0.5
1987	P11	8.6	0.4
	P32	8.4	0.4
	P34	8.9	0.4
1991	P11	8.1	0.9
	P34	7.0	0.4
	P32	6.9	0.4
1992	P11 (25–50 cm)	3.2	0.5
	P11 (50–75 cm)	<0.8	–
	P11 (75–100 cm)	NM	–
1997	P34	6.0	0.4
1998	P11	5.3	0.5
1999	P11	6.3	0.6
2002	P11	5.7	0.3
	P32	5.0	0.3
	P34	5.5	0.3

NM: not measurable.

Table 2
^{137}Cs activity in selected plots receiving fertilizers and amendments (in plow horizons), decay-corrected for the sampling date (2002).

Agricultural treatment	Plot ID	^{137}Cs (Bq kg^{-1})	$\pm 1\sigma$
(NH$_4$)NO$_3$	P6	5.5	0.5
	P20	6.7	0.6
Horse manure	P10	5.8	0.5
	P12	7.1	0.9
Lime (CaO)	P26	4.3	0.6
	P40	4.9	0.5
Superphosphate (P$_2$O$_5$)	P27	5.7	0.8
	P38	3.5	0.4
KCl (K$_2$0)	P23	3.8	0.6
	P47	4.6	0.5

3. Results and discussion

3.1. Describing the dynamic model applied to the control plots

The case of the control plots of the 42-plot experimental design is much simpler than generally observed for natural fields: (i) no amendments were applied; (ii) uptake by plants need not be considered as the plots were not cultivated during the period of sampling; (iii) lateral runoff can reasonably be ignored because the slope is negligible and because plots are isolated from one another by plastic boards. As a result, the temporal evolution of the ^{137}Cs pool within the 0–25 cm plow horizon, P_{Cs}, is expected to depend on atmospheric fallout (F_{atm}), radioactive decay ($F_{desint.}$), and exit from the system by downward migration to the underlying horizons (F_{out}):

$$\frac{dP_{Cs}}{dt}(t) = F_{atm}(t) - F_{desint.}(t) - F_{out}(t) \tag{1}$$

This equation becomes:

$$\frac{dP_{Cs}}{dt}(t) = F_{atm}(t) - \lambda_{Cs} \times P_{Cs}(t) - k \times P_{Cs}(t) \tag{2}$$

where λ_{Cs} represents the disintegration constant, and k, a positive factor expressed in yr^{-1}, the proportion of ^{137}Cs leaving the plow layer by downward migration. Instead of running this first order differential model, it is much easier to discretize mechanisms at an annual step. When ^{137}Cs deposition starts at the year t_0, the ^{137}Cs pool per unit surface in soil corresponds to the annual atmospheric flux (AF$_{atm}$) per surface unit:

$$P_{Cs}(t_0) = AF_{atm}(t_0). \tag{3}$$

Each year, the ^{137}Cs pool is augmented by new fluxes but part of the ^{137}Cs already present in the plow layer disappears by decay and downward migration, so that at time t_n, the ^{137}Cs pool in the plow layer becomes:

$$P_{Cs}(t_n) = AF_{atm}(t_n) + P_{Cs}(t_{n-1})e^{-(k+\lambda)(t_n-t_{n-1})} \tag{4}$$

Since hereafter the step is considered as annual, Eq. (4) simplifies to become:

$$P_{Cs}(t_n) = AF_{atm}(t_n) + P_{Cs}(t_{n-1})e^{-(k+\lambda)} \tag{5}$$

Instead of expressing the amount of ^{137}Cs in terms of a pool per surface unit within the plow layer, it can be reformulated in terms of activity (A_{Cs}) within the 0–25 cm horizon:

$$A_{Cs}(t) = \frac{P_{Cs}(t)}{hd_a} \tag{6}$$

where h and d_a are the thickness and the bulk density of the plow horizon, respectively.

3.2. Feeding the model

If annual atmospheric fluxes of ^{137}Cs for the last 60 years, in other words the AF$_{atm}(t)$ function, were available at the INRA site, the k-factor would be the only unknown parameter of the above set of equations and its value could be directly assessed by adjusting the model to experimental data. In our case, direct monitoring of ^{137}Cs deposition, by the Commissariat à l'Energie Atomique (CEA) located 15 km from our site, is only available from 1970 onward (Barker and Bouisset, 2001). This data set was recently complemented by Renaud and Louvat (2004), who estimated ^{137}Cs deposition from mean air activity concentration, amount of rainfall, and deposition velocity for the station of Le Vésinet, in the Paris area, from 1961 to 1978. As the ^{137}Cs fallout of the late 1950s is not documented, it is necessary to supplement the record by other data. This operation, however, requires great care as the magnitude of ^{137}Cs fallout is known to be strongly related to the local annual amount of rainfall (Schuller et al., 2002; Renaud and Louvat, 2004; Huh and Su, 2004; Sigurgeirsson et al., 2005). Interestingly for our purpose, fallout resulting from the large nuclear bomb tests (>500 kt TNT equivalent) of the late 1950s and early 1960s derived almost entirely from ^{137}Cs injected primarily into the stratosphere, transferred into the troposphere, and hence deposited to the ground. With a residence time of particles in the stratosphere of approximately 15–18 months (see reference Warneke et al., 2002 and reference therein), radioisotopes were well mixed and deposition was observed globally, though affecting mostly the mid-latitudes of the hemisphere where the tests occurred. The deposition history is therefore expected to follow approximately the same pattern everywhere (Smith et al., 1997), at least when sites are close to each other and far from the testing zones. Atmospheric deposition fluxes measured at Milford Haven (UK) from 1955 onwards (EML, 2000), ^{137}Cs specific activity determined in about 50 grass samples harvested at the Rothamsted site (UK) from 1945 to 1990 (Warneke et al., 2002) and estimates made by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 1982) can be merged together with the Orsay and Le Vésinet documentation to produce a composite curve ($t \rightarrow f(t)$) describing the shape of historical ^{137}Cs atmospheric fallout in Versailles (Fig. 1a). In practice, the Orsay and Rothamsted curves were adjusted to the Milford Haven flux record by using least square methods for the periods where series overlap (Fig. 1b). The year 1986 is nevertheless an exception and must be taken alone. Unlike nuclear weapon tests, the explosion and fire at the Chernobyl nuclear power plant reactor released radioactive elements into the troposphere. The heaviest particles deposited rapidly while the smallest ones were windborne over long distances. Between April 30th and May 5th, the 'radioactive cloud' crossed France, mainly in the east (Roussel-Debel et al., 2007). Radioactive fallout was largely controlled by the occurrence, intensity and nature of wet deposition during this short period, leading to considerable heterogeneity (Renaud et al., 2003; Pourcelot et al., 2003). Here, ^{137}Cs flux measured at Orsay in 1986 ($\sim$355 Bq m^{-2}) is taken as a basis for modeling because it constitutes the most realistic value for Versailles, but the pertinence of this value must be checked later. Finally, intensity of fluxes at Versailles, AF$_{atm}(t)$, can be drawn by multiplying the $f(t)$ function (except for 1986) by a factor α, which represents an adjustment of the composite curve:

For $t \in [1945, 2004]$, except 1986:

$$AF_{atm}(t) = \propto f(t), \tag{7}$$

For $t = 1986$ (Orsay value):

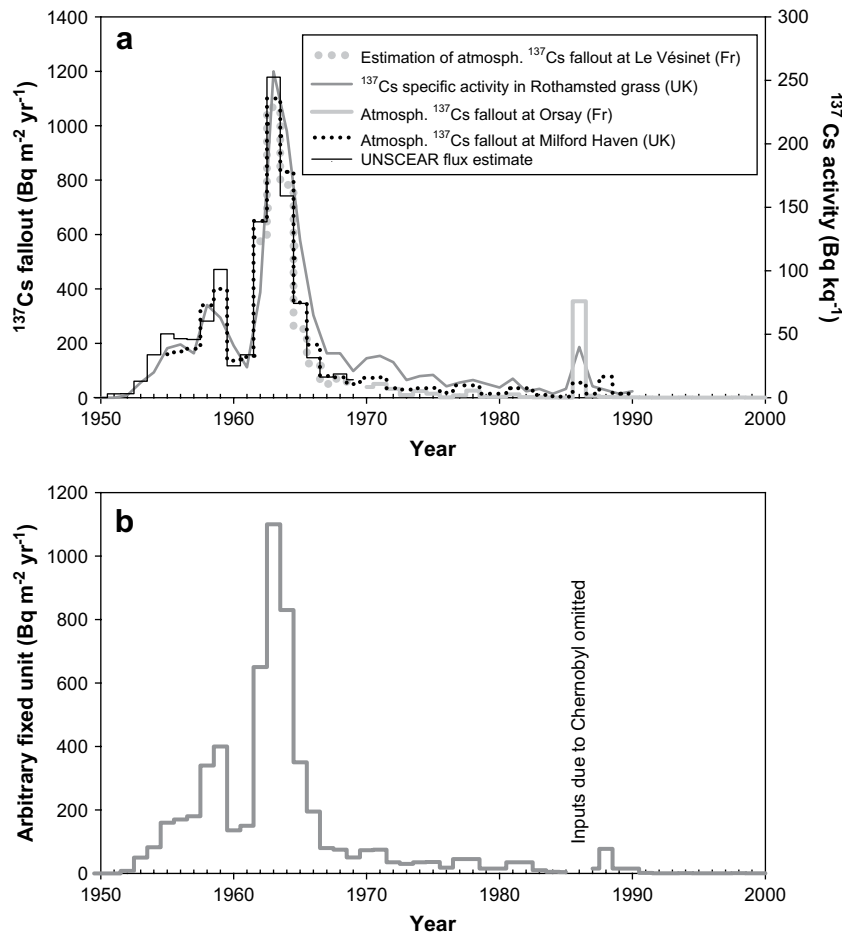$$AF_{atm}(1986) = 355 \text{ Bq m}^{-2} \tag{8}$$

Fig. 1. (a) ^{137}Cs specific activity in Rothamsted grass, expressed in Bq kg^{-1} (Warneke et al., 2002), annual atmospheric ^{137}Cs fallout at Orsay, expressed in Bq m^{-2} yr^{-1} (Barker and Bouisset, 2001), and at Milford Haven from 1957 to 1991 (EML, 2000), estimate of ^{137}Cs deposition for Paris (UNSCEAR, 1982) and Le Vésinet (Renaud and Louvat, 2004). (b) Composite curve (see text for construction) used as surrogate for ^{137}Cs input fluxes at the INRA site from 1950 to 2000, to within a factor α. The y-axis was arbitrarily fixed to coincide with the ^{137}Cs fluxes measured at Milford Haven.

3.3. Running the model

To sum up, the set of equations modeling the evolution of ^{137}Cs activity in the plow horizon of the Versailles soils from 1945 to 2004 is governed by several variables which are summarized in Table 3; two of them are unknown (α, necessary to obtain the ^{137}Cs fluxes, and k, the annual loss from the plow horizon by downward migration). In our case, the condition of uniformity of ^{137}Cs activity within the 0–25 cm horizon required for a convection model is reasonably respected as this layer is annually homogenized by plowing. The point is therefore to find, at least at first, a domain in which the combination of α and k matches the field data. The fitting error, FE, is computed by summing the square of the deviations between the observed, ^{137}Cs$_{meas.}(i)$, and the modeled values, ^{137}Cs$_{mod.}(i)$, weighted by the inverse of the error related to activity measurements, $w(i)$:

$$FE = \sum_{i=1}^{n} w_i(^{137}Cs_{meas.}(t_i) - {}^{137}Cs_{mod.}(t_i))^2 \qquad (9)$$

where $t_1, \ldots, t_n$ correspond to the time for which collected samples have been analyzed. This parameter, which has to be minimized, is graphically represented in a 2-D space by contour lines after multiple calculations using α (as x-axis) and k (as y-axis) varying within the intervals 0–1.5 and 0–0.027 yr^{-1}, respectively (Fig. 2a). The ability of the model to match the data is illustrated by

the five positions shown. For each coordinate (α,k), modeled ^{137}Cs activity has been computed through time and graphically confronted to activity observed in natural conditions (Fig. 2 b–f). For the b–e close-ups, fluxes and/or losses are either too high or too low, so that significant divergences are noticed. Only position f exhibits a good concordance. It is worth noticing that ^{137}Cs flux value assumed for 1986 on the basis of the survey carried out at Orsay (355 Bq m^{-2}) produces an increase in modeled ^{137}Cs activity quite coherent with results from the field. Fig. 2a suggests the existence of a unique solution ($\alpha \sim 0.95$; $k \sim 0.015$ yr^{-1}). However, it must be kept in mind that significant errors are associated both to ^{137}Cs activity obtained from the field samples and to the determination of the $f(t)$ function describing the shape of the ^{137}Cs fluxes. It is therefore more reasonable to consider at this stage a domain solution rather than a single position. This is why the 25–50 cm, 50–75 cm, and 75–100 cm horizons of the P11 control plot, sampled in 1992, were also measured, in order to better constrain α- and k-values. On the basis of the 1991 collection, the ^{137}Cs inventory in 1992 within the 0–25 cm plow horizon was about 2200 Bq m^{-2}, while below there was a total activity of approximately 1000 Bq m^{-2} (Table 1, Fig. 3). Below 50 cm, and more particularly below 75 cm, ^{137}Cs was no longer measurable, suggesting that all the ^{137}Cs that reached the ground had been inventoried by coring the experimental plot to a depth of 1 m. The ratio between the ^{137}Cs pools below and within the plow horizon, designated b hereafter, was therefore 0.45 in 1992. This provides an

Table 3
Summary of the known data and unknowns used to run the model.

Name	Parameter	Value
Known (measured or calculated)		
h	Plow depth	25 ± 2 cm
d_a	Bulk density	1.25 Mg m^{-3}
λ_{Cs}	Disintegration constant of ^{137}Cs	0.0229 yr^{-1}
$f(t)$	Shape of temporal evolution of ^{137}Cs input	Obtained by combining different curves
Unknown		
α	Coefficient applied to $f(i)$ to obtain annual fluxes	Sought value
k	Coefficient of annual loss from 0 to 25 cm horizon also called migration rate constant in the body of the text	Sought value

additional constraint as b values can be easily simulated with varying couples of (α,k) values (Fig. 4). The value for k is around 0.015 yr^{-1}, in good agreement with the assessments previously performed, on the basis of the temporal evolution of ^{137}Cs activity within the plow layer. For $\alpha \sim 0.95$ and $k \sim 0.015$ yr^{-1}, calculations give 2196 Bq m^{-2} within the plow horizon and 972 Bq m^{-2} below, quite similar to measured values (cf. Fig. 3).

The residence half time in the 0–25 cm plow horizon due to migration processes only ($t = \ln 2/k$) and the apparent migration rate to the underlying layer ($v = h/t$) can now be estimated at 46 yr and 0.54 cm yr^{-1}, respectively. It is clear that, at the INRA site, the mobility of ^{137}Cs is enhanced by annual plowing, which mechanically incorporates contaminated surface soils in depth.

Despite this mixing, a value of $k = 0.015$ yr^{-1} indicates that the migration rate is less than that of radioactive decay ($\lambda_{Cs} = 0.023$ yr^{-1}). By combining both constants, an overall residence half time of about 18 yr is obtained. Such an estimate falls within the range of values (3.6–29 yr, average ~ 10 yr) recently assessed on the basis of several measurements of ^{137}Cs activity in agricultural and meadow topsoils monitored from 1990 to 2004 (Roussel-Debel et al., 2007). The absence of erosion and of export due to harvesting at the INRA site could explain why the overall residence half time computed at Versailles lies in the upper range of the previously reported values.

A value of $\alpha = 0.95$ means that the ^{137}Cs fluxes at Versailles (average annual rainfall ~ 650 mm) were just slightly lower than those monitored at Milford Haven (average annual rainfall ~ 750 mm), obviously excluding Chernobyl-derived deposition. The ^{137}Cs inventory in soils from 1988 (Chernobyl excluded) is estimated at 2370 ± 150 Bq m^{-2} on the basis of the mean annual precipitation using the relation empirically established by Mitchell et al. (1990). This value is lower than 3000 Bq m^{-2} computed for Versailles using $\alpha = 0.95$. Our model also provides a sum of total fallout occurring between 1962 and 1969 of 3210 Bq m^{-2}, which is in very good agreement with calculations made by Renaud and Louvat (2004) for the same period at the site of Le Vésinet, located at about 10 km from Versailles: 2980 Bq m^{-2}. The sum of ^{137}Cs deposition at Versailles for the period 1945–2004 is approximately 5750 Bq m^{-2} (uncorrected for decay); the Chernobyl deposition represents only about 350 Bq m^{-2} of this total.
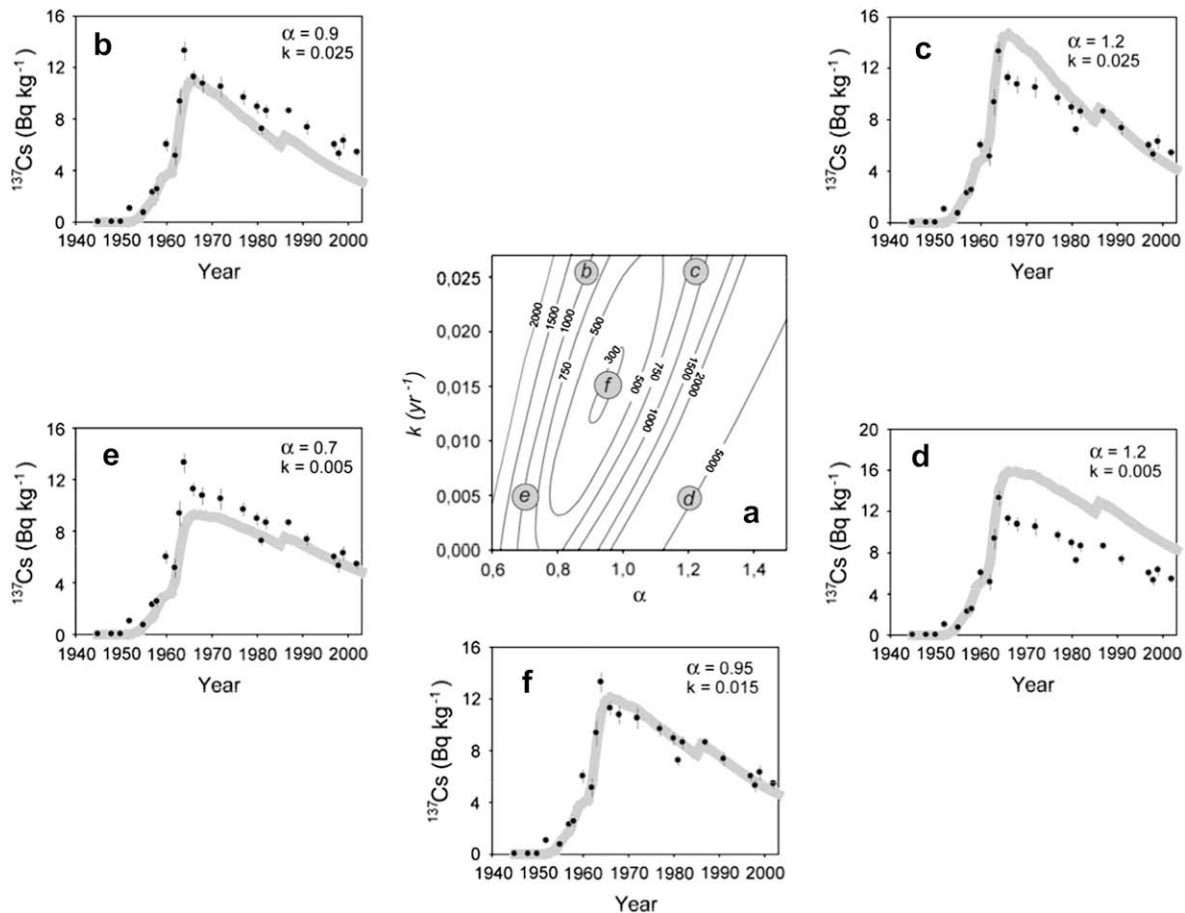

Fig. 2. (a) Fit error for ^{137}Cs activity reported on a k versus α diagram. The lower the value, the better the concordance between modeled and field data. Modeled and observed ^{137}Cs activity is represented by a grey line and closed circles, respectively, in five close-ups (b–f) for various combinations of a and k.
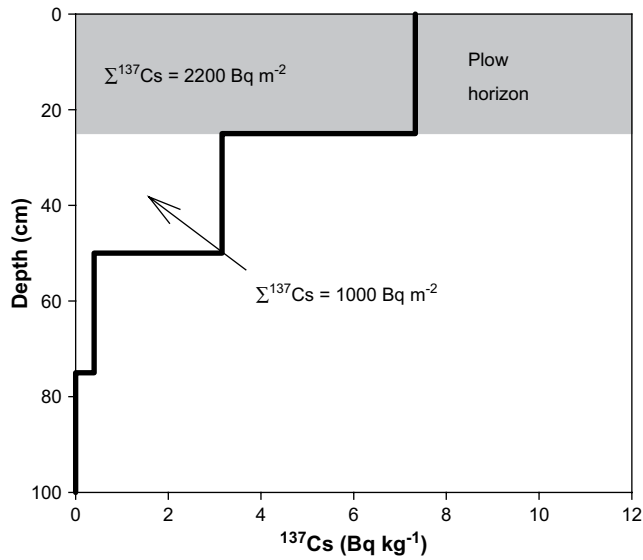
Fig. 3. ^{137}Cs depth distributions in the P11 plot cored in 1992 (activity corrected to the date of sampling). ^{137}Cs inventories, expressed in Bq m^{-2} are also reported for the plow horizon and below.

3.4. Influence of fertilizers and amendments

When applying the model to plots receiving long-term fertilization and/or amendments (Table 2), the calculated k-factors differed approximately fourfold (Fig. 5), in the following order:

$$k_{KCl} > k_{Ca0} \approx , k_{superphosphate} \geq k_{control} > k_{NH_4NO_3} \approx k_{manure}$$

This wide variety of radiocaesium mobility illustrates the role of characteristic properties which developed in the soils of the 42-plot experiment over time, such as differences in clay mineralogy, organic matter content, CEC, pH and physical properties (Pernes-Debuyser and Tessier, 2002a,b, 2004). Indeed, with time, the long-term agricultural treatments have led to a wide variety of physicochemical characteristics (Table 4): pH (4.2–8.2), CEC (7.6–18.7) and organic carbon (5.1–31.8 g kg^{-1}). Although these long-term treatments have influenced both the chemical and physical properties in the surface layers, further insights may yet be highlighted by our results. The highest k-factor is calculated for the KCl-fertilized plot. The KCl-plot displays physicochemical characteristics rather similar to those of the control plot, but Pernes-Debuyser et al. (2003) showed an increasing illite-like behavior of the clay fraction. This mineralogical evolution was related to K-retrogression in smectitic layers, increasing the proportion of illite in the illite–smectite inter-layered phyllosilicates. Since both K
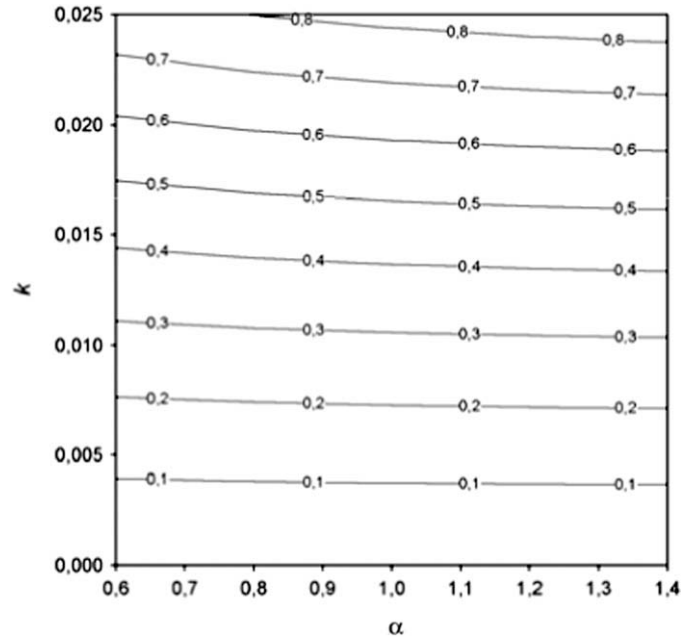

Fig. 4. Simulated ratio between the ^{137}Cs pools below and within the plow horizon (b parameter) for α and k varying from 0.6 to 1.4 and from 0 to 0.025 yr^{-1}, respectively. Calculations were performed for 1992. The 1992 field value of b was approximately 0.45.

and Cs displays high affinity for interfoliar exchangeable sites of illitic clay minerals (Staunton and Levacic, 1999; Seaman et al., 2001), and since these sites are predominantly occupied by K, the ^{137}Cs entering these soils migrate more easily in comparison to the control plot.

The lowest k-factors are observed for the manure-amended plot and that fertilized with NH$_4$NO$_3$. A striking difference for the manure plot was its high organic matter content and CEC value (Table 4). Although manure was shown to provide high amounts of potassium leading to an illitization of the clay fraction as in case of the KCl-plot (Pernes-Debuyser et al., 2003), the incorporation of organic matter increases the amount of negative charges, obviously favoring perennial sorption of ^{137}Cs. This result is however divergent with respect to many other studies which highlight the role of organic matter to favor Cs mobility (Staunton and Levacic, 1999; Chibowski and Zygmunt, 2002; Nakamaru et al., 2007). In case of the NH$_4$NO$_3$ plot, according to work of Giannakopoulou et al. (2007) the low pH (4.5) would be unfavorable to Cs sorption, in contradiction with the low k-factors observed in Fig. 5. In the present work, the long-term NH$_4$NO$_3$ gifts seem to produce impacts on the physical properties, rather than chemical consequences,
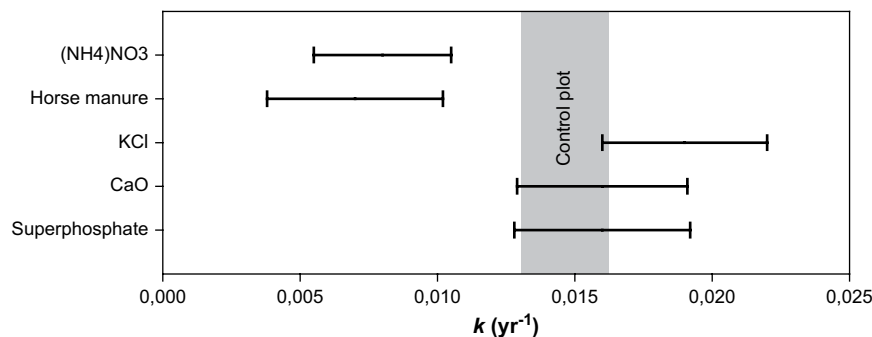

Fig. 5. Mean values of k (computed from data listed in Table 2) for the experimental plots amended with (NH$_4$)NO$_3$, horse manure, KCl, CaO and superphospate. Error margins are given at 1σ. The k-value for the control plots is represented by a grey box for purposes of comparison.

Table 4
Clay content, total organic carbon content, cationic exchange capacity, pH in the 0–25 cm horizon of control and amended plots 70 yr after the beginning of the experiment (Pernes-Debuyser and Tessier, 2002a,b).

Plot ID	Type of amendment	Amount amended	Year of coll.	Clay $(g\,kg^{-1})$	TOC $(g\,kg^{-1})$	CEC $(cmol + kg^{-1})$	pH water
Initial conditions (1929)							
P11	Control plot	–	1929	19.4	16	15.3	6.3
After 70 years of experiment							
P11	Control plot	–	1999	18.4	7.1	8.7	5.6
P6	$(NH_4)NO_3$	$150\,kg\,ha^{-1}\,yr^{-1}$	1999	17.5	7.3	7.6	4.5
P12	Horse manure	$100\,t\,ha^{-1}\,yr^{-1}$	1999	20.1	31.8	18.7	7.8
P26	Lime (CaO)	$1\,t\,ha^{-1}\,yr^{-1}$	1999	16.9	5.8	13.6	8.2
P27	Superphosphate (P_2O_5)	$200\,kg\,ha^{-1}\,yr^{-1}$	1999	16.7	5.3	11.3	7.1
P37	KCl $(K_2 0)$	$250\,kg\,ha^{-1}\,yr^{-1}$	1999	18.9	5.1	10.2	6.3

For comparative purposes, values are also given for the soil at the start of the experiment (after Burgevin and Henin, 1939).

since NH_4^+ is known to have a disaggregating effect on soil structure (Bresson and Boiffin, 1990). Hence, the explanation of the low k-factor can be related to the formation of soil crusting at the surface of plots after rainfall events, particularly in acidified plots (Bresson and Boiffin, 1990). This crust formation and its duration strongly reduce both water infiltration in acid plots and drainage of ^{137}Cs in the soil solution towards subsurface horizons.

Intermediate values of k-factors were observed for the CaO and superphosphate-amended plots. Both treatments provide large amounts of Ca and lead to nearly neutral or basic soil pH (Table 4). The predominance of Ca on the cation exchange complex ensures a soil structure favorable to rainwater infiltration, but at the same time a pH ≥ 7 was shown to be favorable to the creation of variable charges on clay minerals and organic matter (Pernes-Debuyser and Tessier, 2002b), increasing the sorption of ^{137}Cs (Giannakopoulou et al., 2007). Hence, as a compromise, the k-factors for these two treatments are of the same order as those calculated for the control plot (Fig. 5).

4. Conclusion

This study takes advantage of a long-term soil experiment, which allows modeled results to be verified against measured time series. Even if the model applied is simple, compared with previously published works, it appears that with a migration rate from the plow horizon to underlying layers of 1.5% per year ($k = 0.015\,yr^{-1}$) and an appropriate ^{137}Cs flux history, the data modeled almost perfectly fit both (i) the evolution of ^{137}Cs activity in all control plots from 1945 to 2002, and (ii) the ^{137}Cs depth distribution in 1992. This undoubtedly indicates the pertinence of the compartmental modeling approach, at least in superficial soil layers. Although plowing obviously extends downward migration, radioactive decay remains the dominant process of activity decline within the mixed soil horizon. Combining disintegration and mobility, a residence half time within the topmost 25 cm of approximately 18 yr is obtained. For plots with long-term fertilizations and/or amendments, interpretation is complicated by the great number of physicochemical variables subsequently affected by treatments, but significantly different k-values can be straightforwardly compared, since all plots developed from the same genoform.

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