Predicting the transfer of radiocaesium from organic soils to plants using soil characteristics

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Abstract

A model predicting plant uptake of radiocaesium based on soil characteristics is described. Three soil parameters required to determine radiocaesium bioavailability in soils are estimated in the model: the labile caesium distribution coefficient ($k_{dl}$), K$^+$ concentration in the soil solution ($m_K$) and the soil solution→plant radiocaesium concentration factor (CF, Bq kg$^{-1}$ plant/Bq dm$^{-3}$). These were determined as functions of soil clay content, exchangeable K$^+$ status, pH, NH$_4^+$ concentration and organic matter content. The effect of time on radiocaesium fixation was described using a previously published double exponential equation, modified for the effect of soil organic matter as a non-fixing adsorbent. The model was parameterised using radiocaesium uptake data from two pot trials conducted separately using ryegrass (\textit{Lolium perenne}) on mineral soils and bent grass (\textit{Agrostis capillaris}) on organic soils. This resulted in a significant fit to the observed transfer factor (TF, Bq kg$^{-1}$ plant/Bq kg$^{-1}$ whole soil) ($P < 0.001, n = 58$) and soil solution K$^+$ concentration ($m_K$, mol dm$^{-3}$) ($P < 0.001, n = 58$). Without further parameterisation the model was tested against independent radiocaesium uptake data for barley ($n = 71$) using a database of published and unpublished information covering contamination time periods of 1.2–10 years (transfer factors ranged from 0.001 to 0.1). The model accounted for 52\% ($n = 71, P < 0.001$) of the observed variation in log transfer factor. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Radiocaesium; Plant uptake; Soil; Model
1. Introduction

In May 1986, radiocaesium ($^{137}$Cs, $^{134}$Cs) from the Chernobyl accident was deposited over large areas of Europe, Belarus, Ukraine and Russia. It was generally found that radiocaesium remained bio-available in many regions. In the UK for example, sheep grazing in upland areas still attain activity concentrations of radiocaesium which exceed the UK and EC limit of 1000 Bq kg$^{-1}$ fresh weight. Failure to predict this long-term availability of radiocaesium was partly due to differences between the organic, acidic soils with a low clay and nutrient (K) status which received most of the UK deposition and the lowland clay-rich mineral soils on which most previous Cs studies had been conducted (Kirk & Staunton, 1989). Problems of elevated food chain contamination by radiocaesium in the long term may therefore be confined to areas with a high incidence of organic soils (e.g. Cumbria, North Wales). Thus a model which is able to account for the effect of organic matter, and other soil properties, when estimating trends in radiocaesium transfer to food products, may be a valuable tool for assessing post-accident management options.

Radiocaesium bioavailability is strongly influenced by soil properties such as K status and clay content (Smolders, Van der Brande & Merckx, 1997; Absalom, Young & Crout, 1995). Absalom et al. (1999) presented a semi-mechanistic model which predicts activity concentrations of radiocaesium in plants for stipulated soil-Cs contact times, utilising readily available soil characteristics: %clay, exchangeable K$^+$, initial soil radiocaesium content. The model was developed using data describing plant uptake of $^{137}$Cs from a range of mineral soils (Smolders et al., 1997). Subsequently a further study has been conducted on mainly organic soils (Sanchez et al., 2000). In this paper we present a revised radiocaesium uptake model which accounts explicitly for the effect of organic matter on caesium sorption by soil and uptake by plants. The model has been parameterised using data from Cs-uptake trials on both mineral and organic soils to provide a more generally applicable simulation of radiocaesium dynamics.

2. Model description

The model of Absalom et al. (1999) assumed that Cs sorption occurred exclusively on the soil clay fraction. The distribution of sorbed and solution $^{137}$Cs was described by a labile $^{137}$Cs distribution coefficient ($k_{dl}$, dm$^3$ kg$^{-1}$) which was estimated as a function of soil clay and exchangeable K$^+$ contents. Plant uptake of radiocaesium was described by a concentration factor (CF, Bq kg$^{-1}$ plant/Bq dm$^{-3}$ soil solution) which was related to solution K$^+$ concentration ([mK$^+$], moles dm$^{-3}$).

The model presented here represents a significant extension to that of Absalom et al. (1999) as it accounts for the effect of organic matter on $^{137}$Cs sorption and hence uptake. Radiocaesium uptake by plants is again determined from a concentration factor (CF) defined as the ratio of radiocaesium activity concentration in the plant ($C_{s_{plant}}$) to that in soil solution ($C_{s_{sol}}$). However, the activity concentration of radiocaesium in solution is estimated from a distribution coefficient, $k_{dl}$, which varies
in relation to the organic and inorganic constituents of the soil and the concentrations of $K^+$ and $NH_4^+$ in soil solution, $[m_K]$ and $[m_{NH4}]$. Sorption of $^{137}Cs^+$ is described using a two-component ‘assemblage model’ (Lofts & Tipping, 1998) in which adsorption on humus is entirely ‘indifferent’ while labile $Cs^+$ on clay is held ‘specifically’ and is progressively transferred to a non-labile pool (‘fixed’) in collapsed clay interlayers. Time-dependent fixation of radiocaesium is described by a two-component first-order kinetic process as described previously (Absalom et al., 1999). Thus, the model depends upon readily available soil data: exchangeable $K^+$, humus, clay content and pH value and on soil–Cs contact time. Fig. 1 shows the relationship between conceptual pools of radiocaesium in the current model.

2.1. Activity concentration of radiocaesium in plants

Plant activity concentration ($Cs_{plant}$, Bq kg$^{-1}$) is calculated from the product of a concentration factor (CF, dm$^{-1}$ kg$^{-1}$) and the radiocaesium activity concentration in soil solution ($Cs_{sol}$, Bq dm$^{-3}$)

$$Cs_{plant} = CF \times Cs_{sol}.$$ (1)
The use of Eq. (1) requires the prediction of the activity concentration of radiocaesium in soil solution and the value of CF. Smolders et al. (1997) showed that the CF for radiocaesium uptake by ryegrass may be related to \([m_k]\) subject to a limiting minimum value of \([m_k]\). Absalom et al. (1999) adopted this approach and termed the limiting value of \([m_k]\), \(k_{\text{lim}}\). The use of a similar relationship was tested in this work but it was found that the inclusion of the \(k_{\text{lim}}\) parameter did not affect the model fit, therefore the simple linear relationship shown in Eq. (2) was used.

\[
\log[\text{CF}] = k_1 - k_2 \log(m_k),
\]

where \(k_1\) and \(k_2\) are unknown empirical constants.

\subsection{2.2. Soil solution K\(^+\) concentration, \([m_k]\)]

Calcium and magnesium are the main competitors for K\(^+\) adsorption on “indifferent” exchange sites in most soils. The Gapon exchange coefficient \((k_G)\) describes the relative selectivity of a sorbing surface for a pair of cations. As Ca and Mg normally dominate the pool of exchangeable cations, \((\text{Ca}_x + \text{Mg}_x)\) may be approximated by the difference between the effective cation exchange capacity \((\text{CEC}, \text{cmol}_c \text{ kg}^{-1})\) and exchangeable K\(^+\) \((K_{\text{soil}}^x, \text{cmol}_c \text{ kg}^{-1})\). In the context of radiocaesium adsorption, it may be reasonable to assume that there are just two types of exchange surfaces: humus and clay. Thus \(m_k\) (mol dm\(^{-3}\)) may be expressed in terms of an equilibrium between K\(^+\) sorbed on humus or on clay

\[
[m_k] = \frac{K_x^{\text{humus}} \times \sqrt{[m_{\text{Ca}+\text{Mg}}]}}{k_G^{\text{humus}} \times (\text{CEC}^{\text{humus}} - K_x^{\text{humus}})} = \frac{K_x^{\text{clay}} \times \sqrt{[m_{\text{Ca}+\text{Mg}}]}}{k_G^{\text{clay}} \times (\text{CEC}^{\text{clay}} - K_x^{\text{clay}})}
\]

where \(K_x\) is the exchangeable K\(^+\) content (cmol\(_c\) kg\(^{-1}\)) and \([m_{\text{Ca}+\text{Mg}}]\) and \([m_k]\) are the corresponding ion concentrations in solution (mol dm\(^{-3}\)). Values of the Gapon exchange coefficients \((k_G^{\text{humus}}\) and \(k_G^{\text{clay}}\)) were derived as part of the primary parameterisation, using two data sets described in the following sections. The combined concentration of \((\text{Ca}^{2+} + \text{Mg}^{2+})\) is described as a linear function of pH:

\[
-\log_{10}[m_{(\text{Ca}+\text{Mg})}] = k_3 - k_4 \times \text{pH}.
\]

The values of \(k_3\) and \(k_4\) are given in Table 1. Thus \(m_{(\text{Ca}+\text{Mg})}\) varies between 0.001 and 0.009 moles dm\(^{-3}\) at pH values of 2 and 8, respectively. To account for proton competition for specific adsorption on organic sites (mainly carboxyl groups), CEC\(^{\text{humus}}\) (cmol\(_c\) kg\(^{-1}\) organic matter) is also pH-dependent (Eq. (5)).

\[
\text{CEC}^{\text{humus}} = k_5 + k_6 \times \text{pH}.
\]

Helling, Chesters and Corey (1964) studied the effect of pH on the contribution of clay and organic matter to the overall soil CEC. Sixty soils were evaluated representing 34 soil series, at six pH values, ranging from 2.5 to 8. For the 60 soils, the average CEC of organic matter \((\text{CEC}^{\text{humus}})\) was observed to vary between 36 cmol\(_c\) kg\(^{-1}\) (at pH 2.5) and 213 cmol\(_c\) kg\(^{-1}\) (at pH 8). A significant \((P < 0.01)\) linear relationship was found...
Table 1
Values of both fitted and independent (*) model parameters used in Eqs. (2)-(14); (±) values represent standard errors of parameters

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Value</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>2.57 ± 0.1</td>
<td>2</td>
</tr>
<tr>
<td>(k_2)</td>
<td>1.56 ± 0.32</td>
<td>2</td>
</tr>
<tr>
<td>(k_G^{lay})</td>
<td>3.18 ± 0.44</td>
<td>3, 7</td>
</tr>
<tr>
<td>(k_G^{humus})</td>
<td>2.32 ± 0.1</td>
<td>3, 7</td>
</tr>
<tr>
<td>(k_7)</td>
<td>4.167 ± 0.27</td>
<td>8, 9</td>
</tr>
<tr>
<td>(k_8)</td>
<td>0.043 ± 0.017</td>
<td>10</td>
</tr>
<tr>
<td>(k_9)</td>
<td>1.74 ± 0.17</td>
<td>10</td>
</tr>
<tr>
<td>(k_3^*)</td>
<td>3.368</td>
<td>4</td>
</tr>
<tr>
<td>(k_4^*)</td>
<td>0.16</td>
<td>4</td>
</tr>
<tr>
<td>(k_5^*)</td>
<td>-34.66</td>
<td>5</td>
</tr>
<tr>
<td>(k_6^*)</td>
<td>29.72</td>
<td>5</td>
</tr>
<tr>
<td>(k_{fast}(d^{-1})^*)</td>
<td>0.0019</td>
<td>14</td>
</tr>
<tr>
<td>(k_{slow}(d^{-1})^*)</td>
<td>0.00019</td>
<td>14</td>
</tr>
<tr>
<td>(P_{soil}^*)</td>
<td>0.814</td>
<td>14</td>
</tr>
<tr>
<td>CEC^{clay}</td>
<td>50 cmol _c kg^{-1} clay</td>
<td>6</td>
</tr>
</tbody>
</table>

between CEC^{humus} and pH. This relationship (Eq. (5)) and parameters (\(k_8\) and \(k_6\), Table 1) have been used here. In the same study, the CEC of clay was found to vary between only 38 and 64 cmol _c kg^{-1} over the pH range of 2.5–8 (averages of 60 soils); with an average of 53 cmol _c kg^{-1} clay across all pH values. This is similar to the constant value of 50 cmol _c kg^{-1} clay used by Absalom et al. (1999) following Nemeth, Mengel and Grimme (1970), to describe the CEC of clay (CEC^{clay}. Eq. (6)) and which is also adopted here.

The whole soil CEC (CEC^{soil}, cmol _c kg^{-1} soil) may be calculated by summing the CEC of the inorganic and organic components, corrected for their relative abundance

\[
\text{CEC}^{soil} = (\text{CEC}^{clay} \times \theta_{clay}) + (\text{CEC}^{humus} \times \theta_{humus}),
\]

where CEC^{clay} = 50 cmol _c kg^{-1} clay (Table 1) and \(\theta_{clay}\) and \(\theta_{humus}\) are the measured gravimetric clay and humus contents (g g^{-1}) respectively.

2.3. Partitioning of exchangeable \(K^+\) between humus and clay fractions

Eq. (3) requires an estimate of the exchangeable \(K^+\) sorbed on clay (\(K_x^{clay}, \text{cmol }_c \text{ kg}^{-1}\)) or on humus (\(K_x^{humus}, \text{cmol }_c \text{ kg}^{-1}\)). With the assumption that total exchangeable \(K^+\) (\(K_x^{soil}, \text{cmol }_c \text{ kg}^{-1}\)) makes only a small contribution to the CEC, then from (3) and a mass balance on \(K_x^{soil}\):

\[
K_x^{humus} = \frac{K_x^{soil}}{((k_G^{clay} \times \text{CEC}^{clay} \times \theta_{clay})(k_G^{humus} \times \text{CEC}^{humus})) + \theta_{humus}}.
\]
2.4. Labile $^{137}$Cs distribution coefficient, $k_{dl}$

The relationship between adsorbed and solution Cs is given by the labile $^{137}$Cs distribution coefficient ($k_{dl}$, dm$^3$ kg$^{-1}$). Due to the different nature of sorption by clay and humus fractions, separate $k_{dl}$ values for both humus ($k_{dl}^{\text{humus}}$) and clay ($k_{dl}^{\text{clay}}$) are required. These are both corrected for gravimetric humus ($\theta^{\text{humus}}$) and clay ($\theta^{\text{clay}}$) contents so that they may be summed to generate a whole soil value of $k_{dl}$ for labile radiocaesium.

Cs is strongly adsorbed at specific sites present in the clay mineral fraction, in particular the weathered edges of illitic and micaceous tactoids. These minerals, even when present in small amounts are normally adequate to sorb the trace quantities of radiocaesium resulting from deposition (Absalom et al., 1995; Hird, Rimmer & Livens, 1995). The only significant competitors for adsorption at these selective sites are potassium and ammonium. As nitrate-N is likely to dominate the inorganic nitrogen pool of aerobic agricultural soils, the role of NH$_4^+$ may be ignored in most cases. However, in the data of Sanchez et al. (2000), significant quantities of NH$_4^+$ were recorded in the organic soils studied and the effect of NH$_4^+$ is accounted for here, using observed values. The solid-solution equilibrium of radiocaesium which is specifically adsorbed in soil may be described by a ‘radiocaesium interception potential’ (RIP), (Cremers, Elsen & De Peter, 1988). The RIP of a soil is the product of its specific Cs$^+/(K^+ + NH_4^+)$ exchange constant and the content of Cs$^+$/K$^+$/NH$_4^+$-specific sites which are assumed to be occupied almost exclusively by K$^+$. Thus RIP may be defined in terms of three variables, $k_{dl}$, $m_K$ and $m_{NH4}$:

$$\text{RIP} = k_{dl} \times ([m_K] + (k_7 \times [m_{NH4}])).$$  \tag{8}

The fitted parameter $k_7$ accounts for the fact that NH$_4^+$ has been observed to compete with Cs$^+$ more strongly than K$^+$ (Cremers et al., 1988). In the original model of Absalom et al. (1999) the RIP for a whole soil was estimated from the clay content. Here, we ascribe a single (fitted) value to a clay — RIP (RIP$^{\text{clay}}$) but express the radiocaesium distribution coefficient for clay on a whole soil basis ($k_{dl}^{\text{clay}}$), thus:

$$k_{dl}^{\text{clay}} = \frac{\text{RIP}^{\text{clay}} \times \theta_{\text{clay}}}{[m_K] + (k_7 \times [m_{NH4}]).}$$  \tag{9}

where $k_7$ is a fitted parameter. The value of RIP$^{\text{clay}}$ has been observed to decrease slightly with increasing organic matter (Sanchez et al., 2000). Thus log$_{10}$(RIP$^{\text{clay}}$) is given by:

$$\log_{10}(\text{RIP}^{\text{clay}}) = -k_8 \times \left(\frac{\theta_{\text{humus}}}{\theta_{\text{clay}}}\right) + k_9.$$  \tag{10}

Eq. (10) effectively describes the effect of interaction between the two components of the assemblage model. Most studies have demonstrated that such “additivity” effects are quite modest, as discussed by Lofts and Tipping (1998). Non-specific adsorption of Cs$^+$ on clay is ignored because it will always be insignificant in comparison to the pool of specifically adsorbed Cs$^+$ described by Eq. (10).
By contrast, both K\(^+\) and Cs\(^+\) are assumed only to be adsorbed non-specifically on the organic soil fraction; this is in line with most published evidence and speciation models describing ion adsorption on organic matter (eg “WHAM”: Tipping, 1994). Thus radiocaesium is assumed to be distributed between the solid and liquid phase in the same manner as K\(^+\) so that \(k_{d0}^{\text{humus}}\) may be estimated as the ratio of exchangeable K\(^+\) adsorbed on humus (\(K_{x}^{\text{humus}}\), cmol\(_e\) kg\(^{-1}\)) to solution K\(^+\) ([\(m_{K}\]), moles dm\(^{-3}\)). Again, \(k_{d0}^{\text{humus}}\) is expressed on a whole soil basis:

\[
k_{d0}^{\text{humus}} = \frac{\theta_{\text{humus}} \times K_{x}^{\text{humus}} \times 0.01}{[m_{K}]},
\]

(11)

the adjustment factor of 0.01 arises from the conversion of cmol\(_e\) kg\(^{-1}\) to mol kg\(^{-1}\).

The overall “whole soil” \(k_{dl}\) is the sum of \(k_{d0}^{\text{humus}}\) and \(k_{d0}^{\text{clay}}\) which may then be used to estimate soil solution radiocaesium as a function of total labile radiocaesium in the soil.

\[
k_{dl} = k_{d0}^{\text{clay}} + k_{d0}^{\text{humus}}
\]

(12)

2.5. The effect of time on the bioavailability of radiocaesium

The model accounts separately for the dynamic process of Cs\(^+\) fixation within clay minerals, thus the value of \(k_{dl}\) (Eq. (12)) describes a distribution between adsorbed labile and solution activity concentrations of radiocaesium. This contrasts with the normal definition of a distribution coefficient which simply expresses the ratio of activities in the solid and solution phases and, with progressive Cs\(^+\) fixation, would increase with time.

The effect of time on \(^{137}\)Cs fixation in the soil is considered in the model of Absalom et al. (1999). Cs is divided into two pools with relative magnitudes (\(P_{fast}\)) and (1 – \(P_{fast}\)) subject to rapid and slow fixation rates, respectively (\(k_{fast}\) and \(k_{slow}\)). This approach assumed that all radiocaesium was sorbed on the clay fraction where fixation could proceed by movement of radiocaesium into the collapsed interlayers of micaceous minerals. In the model presented here, the radiocaesium adsorbed on the organic fraction is not subject to fixation. Thus the values of the two rate coefficients are modified by a factor, \(k_{dr}\), (Eq. (13)) which is the proportion of labile Cs\(^+\) adsorbed on the clay fraction:

\[
k_{dr} = \frac{k_{d0}^{\text{clay}}}{(k_{d0}^{\text{clay}} + k_{d0}^{\text{humus}})}.
\]

(13)

Thus Eq. (14) is used to calculate a dynamic factor \((D, 0–1)\) which describes the change in labile Cs\(^+\) with time. The corresponding change in solution activity concentration of radiocaesium with time is calculated from \(k_{dl}\) (Eq. (12)).

\[
D = (P_{fast}e^{-k_{d0}^{\text{humus}} \times t \times k_{dr}} + (1 – P_{fast})e^{-k_{d0}^{\text{clay}} \times t \times k_{dr}}).
\]

(14)
Table 2
Summary of properties recorded in the datasets used for model parameterisation and validation

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TF</td>
<td>0.227</td>
<td>8.83</td>
<td>0.02</td>
</tr>
<tr>
<td>Bq kg⁻¹ plant</td>
<td>(0.0018–2.62)</td>
<td>(0.039–44.1)</td>
<td>(0.0007–0.27)</td>
</tr>
<tr>
<td>Bq kg⁻¹ soil</td>
<td></td>
<td>0.41</td>
<td>0.55</td>
</tr>
<tr>
<td>Exchangeable K⁺ (cmol kg⁻¹)</td>
<td>0.69 (0.15–1.84)</td>
<td>0.41 (0.05–0.82)</td>
<td>0.55 (0.09–1.9)</td>
</tr>
<tr>
<td>Soil Organic Matter (%)</td>
<td>8.39 (3.4–35.1)</td>
<td>54.8 (6.02–96.5)</td>
<td>6.39 (0.9–58.0)</td>
</tr>
<tr>
<td>Soil clay (%)</td>
<td>12.3 (1.44–31.3)</td>
<td>14.8 (2.03–57.6)</td>
<td>16.97 (0.5–43)</td>
</tr>
<tr>
<td>pH</td>
<td>5.33 (4.92–6.95)</td>
<td>3.4 (2.39–5.98)</td>
<td>6.36 (5–8.2)</td>
</tr>
<tr>
<td>Time (years)</td>
<td>0.16</td>
<td>0.19</td>
<td>3.05 (1.2–10)</td>
</tr>
<tr>
<td>No. of observations</td>
<td>30</td>
<td>23</td>
<td>71</td>
</tr>
</tbody>
</table>

*Mean values are underlined while maximum and minimum values are given in brackets.

The values used for the rate constants, \( k_{\text{fast}} \) and \( k_{\text{slow}} \) were \( 1.9 \times 10^{-3} \) and \( 1.9 \times 10^{-4} \) d⁻¹, respectively (Absalom et al., 1999). \( P_{\text{fast}} \) is the proportion of labile Cs subject to rapid fixation at the rate \( k_{\text{fast}} \); Absalom et al. (1999) derived a value of 0.81 by fitting literature data which described temporal changes in transfer factors. Time (\( t \)) represents the period (days) of soil exposure to \(^{137}\)Cs.

3. Data sources

Table 2 summarises data used for parameterisation and validation. Two studies of radiocaesium uptake by grass were used to parameterise the model. Pot experiments were used to measure radiocaesium uptake by two grass species (Lolium perenne and Agrostis capillaris) over relatively short periods (60–72 days). The trials were conducted on both mineral soils (Smolders et al., 1997) and organic soils (Sanchez et al., 2000) following the same methodology, and the results have been combined for use in this paper. Both studies recorded various relevant parameters, including %clay, loss on ignition, exchangeable K⁺, soil solution K⁺ and \( NH_4^+ \), pH and soil solution radiocaesium activity concentration both before and after the measurement of plant radiocaesium activity concentration at harvest (Table 2).

A comprehensive database of \(^{137}\)Cs contamination of major crops has been collated by Nisbet, Woodman and Haylock (1999). This database also contains the soil...
properties required to run the model and is used here to provide independent model validation (Table 2).

4. Results and discussion

4.1. Model parameterisation

The data for the two grass pot experiments conducted with a range of mineral and organic soils (Smolders et al., 1997; Sanchez et al., 2000) included measured values of \( [m_K], k_{al} \) and transfer factor (TF, Bq kg\(^{-1}\) plant/Bq kg\(^{-1}\) whole soil). The unknown empirical constants in the model equations were derived by simultaneous fitting of Eqs. (2)–(14) to observed \( [m_K], k_{al} \) and TF data \((n = 53)\) using a Marquardt non-linear regression technique (Press, Flannery, Teukolsky & Vetterling, 1986). All model parameter values (both fitted and independent) are given in Table 1, together with the equation number to which they relate.

The sensitivity of the model fit to variation in the fitted parameters was investigated. This was undertaken by varying parameter values by 10% above and below their estimated values using a fully factorial experimental design. This required 2187 parameter value combinations. The resulting variation in the sum of squared residuals was analysed by ANOVA thereby enabling the effect of parameter interactions to be investigated. The analysis suggested that the model fit was especially sensitive to \( k_1 \), \( k_2 \), \( k_3 \times k_9 \).

Fig. 2 shows a comparison between predicted and observed values of \( \log[m_K], \log[k_{al}] \) and \( \log(TF) \), for both the previously published model for mineral soils (Figs. 2 and 2e, Absalom et al., 1999) and the revised model presented here (Figs. 2b and f). Both grass datasets (Sanchez et al., 2000; Smolders et al., 1997) were used, in combination \((n = 53)\), to parameterise the revised model. The new model fits the observed data significantly better \((F\text{-}test; \ P < 0.001)\) than the original ‘mineral soil’ model (Absalom et al., 1999). Of course the model of Absalom et al. (1999) can be re-parameterised using the extended data set employed here. Although this results in an improved fit \((F\text{-}test; \ P < 0.001)\) the revised model presented still represents a significantly improved fit \((F\text{-}test; \ P < 0.001)\) over the re-parameterised model of Absalom et al. (1999). The major difference between the two models is the clear improvement in fit of the predominantly organic soils data (Sanchez et al., 2000) when the new model is applied.

4.2. Model validation

Comprehensive independent data sets containing the soil parameters and plant radiocaesium activity concentrations required for model validation are rare. The validation data used by Absalom et al. (1999) covered a range of agricultural crop types grown almost exclusively on mineral soils (Nisbet et al., 1999). Of the cereal crops contained in this database, the crop with the most observations conducted on soils with moderate or large humus contents was barley. However, these data are not
Fig. 2. A comparison of the original (○, ●) and the extended (∆, ▲) models of radiocaesium transfer using the combined grass datasets (Table 2, n = 53) of Smolders et al. (1997) (open symbols) and Sanchez et al. (2000) (filled symbols). Comparison of measured and modelled variables include: \( -\log_{10}(m_K) \) (Figs. 2a and b), \( \log_{10}(k_d) \) (Figs. 2c and d) and \( \log_{10}(TF) \) (Figs. 2e and f).
Fig. 3. Validation of the extended soil model using an independent dataset. The data for Cs transfer factor (TF) in barley are from a variety of independent studies of various types (pot, lysimeter, field) following a range of Cs–soil contact times (1.5–10 years) (Table 2). Model parameters are those derived from two grass data sets (Table 1). The broken line represents one residual standard deviation on either side of the 1 : 1 line (n = 71, r² = 0.52, P < 0.001).

ideal for validation as organic soils are not very well represented: the maximum and minimum organic matter contents of the 71 soils included were 58 and 0.9% respectively while the mean was 6.9%, Table 2. A comparison between predicted and observed ¹³⁷Cs transfer factors (log values) for barley is given in Fig. 3 (r² = 0.52, n = 71, P < 0.001). The model was run with the parameter values established for grass. Whilst the overall trend is reproduced there is considerable scatter and several points deviate noticeably from the 1 : 1 line. In three cases the deviation between model and observation was a factor of 3 greater than the residual standard deviation (0.364) and in each case the model under-predicted the transfer factor. One of these soils was found to have a very high organic matter content (53%) in conjunction with a clay content of 16%. The other two had relatively high clay contents (34 and 31%). However an analysis of the relationship between the residuals and the soil properties across the data set as a whole revealed no significant trends which could assist in interpreting the model validation results.

Despite the limitations discussed above and in the absence of more suitable data, this limited validation provides some encouragement for the use of the new model independently of the datasets used to parameterise it. Furthermore, the barley results used here for validation were derived from a variety of experimental designs (pot, lysimeter and field), over a considerable range of time periods (1.2–10 years).

5. Conclusions

The extended model presented accounts for the effect of caesium sorption by both mineral and organic soil fractions, and time-dependent Cs fixation in clay, on plant
uptake of radiocaesium. It shares similar principles to the original model of Absalom et al. (1999) but is able to predict radiocaesium dynamics across a much wider range of soil humus contents, including moorland peat soils.

As illustrated in Fig. 2f observed transfer factors for grass in the data sets of Smolders et al. (1997) and Sanchez et al. (2000) ranged over nearly five orders of magnitude and the model was able to account for a significant proportion of the observed variation. This is an improvement over models which rely upon single transfer factor values (e.g. PATHWAY (Whicker & Kirchner, 1987), ECOSYS (Muller & Pröhl, 1993) to predict plant uptake.

It is likely that the model could be improved further. In particular, if quantitative information on clay mineralogy (e.g. illite content and surface area) was available for the soils used in radiocaesium bio-availability trials, it would be possible to model the adsorption and fixation processes on a more mechanistic basis. However, it is questionable whether such a model would be generally applicable to existing soil spatial data sets where, normally, mineralogical information is qualitative or absent. Therefore the wider application of a more mechanistic model to long-term planning and targeting intervention strategies would be difficult. Alternatively, results from more detailed plant trials and time-dependent studies could be used to investigate whether additional soil properties may be useful in improving the prediction of bioavailability with time.

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References


