Aging of nickel added to soils as predicted by soil pH and time

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HIGHLIGHTS

- The mobility of soluble Ni added to soils initially decreased rapidly followed by slower reactions.
- Most importantly, increasing soil pH increased the rate and extent of aging reactions.
- Aging of Ni added to soils can be predicted by pH and time based on semi-mechanistic models.

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ABSTRACT

Although aging processes are important in risk assessment for metals in soils, the aging of Ni added to soils has not been studied in detail. In this study, after addition of water soluble Ni to soils, the changes over time in isotopic exchangeability, total concentrations and free Ni^{2+} activity in soil pore water, were investigated in 16 European soils incubated outdoors for 18 months. The results showed that after Ni addition, concentrations of Ni in soil pore water and isotopic exchangeability of Ni in soils initially decreased rapidly. This phase was followed by further decreases in the parameters measured but these occurred at slower rates. Increasing soil pH increased the rate and extent of aging reactions. Semi-mechanistic models, based on Ni precipitation/nucleation on soil surfaces and micropore diffusion, were developed and calibrated. The initial fast processes, which were attributed to precipitation/nucleation, occurred over a short time (e.g. 1 h), afterwards the slow processes were most likely controlled by micropore diffusion processes. The models were validated by comparing predicted and measured Ni aging in three additional, widely differing soils aged outdoors for periods up to 15 months in different conditions. These models could be used to scale ecotoxicological data generated in short-term studies to longer aging times.

1. Introduction

After water-soluble Ni is added to soils, the added Ni initially partitions rapidly between solution and solid phases, then continually and slowly decreases in extractability and availability/toxicity (Oorts et al., 2007; Smolders et al., 2009) and converts to less labile forms (Ponizovsky et al., 2008; Rajaie et al., 2008; Wang et al., 2009). This process is normally defined as "aging". The slow "aging" reactions most likely are caused by the diffusion of Ni into micropores, incorporation into crystal lattices (Ford et al., 1999; Hoffmann and Stipp, 2001) or Ostwald ripening of precipitates (Scheckel et al., 2000; Nachtegaal and Sparks, 2003). The adsorption and diffusion of Ni in soils and soil components, such as Fe oxides, has been previously investigated (e.g. Barrow, 1998). In those studies, micropore diffusion mechanisms were postulated to explain the slow aging processes following an initial rapid adsorption (Brümmer et al., 1988; Barrow et al., 1989; Barrow, 1998; Axe and Trivedi, 2002; Fischer et al., 2007). This suggests that diffusion is the rate-limiting process occurring during aging. Hoffmann and Stipp (2001) studied the behavior of Ni on the surfaces of a calcite single crystal and found that surface recrystalization of Ni occurred, even in very dry environments (<5% humidity). Also, Ford

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et al. (1999) indicated that Ni, sorbed to the surface of ferrihydrite, could be incorporated into hematite and/or goethite during their formation via crystallization of ferrihydrite. In the case of Ni on Fe oxides, Arai (2008) showed by Ni K-edge X-ray absorption spectroscopy evidence for Ni^{2+} inner-sphere surface complexes via monodentate and bidentate mononuclear linkages at the iron oxyhydroxides–water interface. On the other hand, the precipitates of Ni have been shown to occur on the surface of clay minerals and Al oxides at sorption densities below a theoretical monolayer of sorbed Ni (Nachtegaal and Sparks, 2003). Furthermore, these precipitates were formed at pH values and Ni solution concentrations undersaturated with respect to the solid phases of Ni (Scheidegger et al., 1996) and led to a reduction in Ni mobility (McNear et al., 2007). It was reported that aging decreased Ni toxicity to soil microbial processes and that the changes in the Ni toxicity due to aging generally were greatest in soil with high pH (Oorts et al., 2007). This is consistent with other observations that, through aging, the largest relative decrease in soluble Ni concentrations in soils (Oorts et al., 2007) and iron oxides (Buekers et al., 2008) and decreases in isotopic exchangeability of Ni (Buekers et al., 2007) occurred in soils of higher pH.

Since long-term aging reactions modify Ni availability and toxicity over time, they are important in ecological risk assessment and development of soil quality standards (Smolders et al., 2009; McLaughlin et al., 2011). In this study, the effects of aging on Ni isotopic exchangeability, total Ni in soil pore water and pore water free Ni^{2+} activity were investigated in 16 European soils incubated outdoors for 18 months. Also semi-mechanistic models for long-term aging of soluble Ni added to soils were developed based on incubation time and soil pH. The models were validated using a separate set of soils that were aged in the field in a different region and with soils that are enriched with Ni, due to either contamination or due to the particular mineralogy of serpentine soils.

2. Materials and methods

2.1. Soil samples and treatments

A set of 16 soils covering a range of soil properties was collected throughout Europe. These soils are representative of the major soil types in the region and cover a wide range of soil properties expected to affect the bioavailability of Ni. Selected chemical and physical characteristics of the soils are reported in Table 1 and were determined by analytical procedures as described in detail by Rooney et al. (2007). Air-dried soil samples equivalent to 1.5 kg oven-dried soil (<4 mm sieved) were dosed with soluble Ni at two concentrations, which were predetermined as the total Ni concentrations that would decrease plant growth by 10% and

90% in each soil (EC10 and EC90), respectively (Rooney et al., 2007). Addition of Ni was conducted by dispensing 75 mL $NiCl_2$ solutions over the soil sample with a pipette. After Ni addition, the soils were thoroughly mixed then leached with artificial rain water following the procedure described by Oorts et al. (2006a,b) in order to avoid salt effects on metal partitioning (Stevens et al., 2003). After leaching the soil samples were incubated (aged) in pots, which were fitted with plastic liners to prevent leaching, outdoors in Canberra, Australia, where the climatic conditions are intermediate between those of southern and northern European countries (mean annual rainfall, 630 mm; mean annual maximum temperature, 20.0 °C; mean annual minimum temperature, 7.1 °C). Periodically, soil samples were collected from the pots (as a column from soil surface to bottom). All samples were air-dried and passed through a 2 mm sieve.

2.2. Soil pore water extraction and analysis

Soil samples (air-dried, two replications) were placed in 1 L glass jars and the amount of deionised water required to bring the soil water potential to pF 2.0 (log 100 cm water suction) was added and thoroughly mixed. After mixing, the wetted soil was then stored for 3 d in darkness in an incubation room at 20 °C. The soil sample was transferred to a 50 mL plastic syringe filled previously with 0.5 cm quartz wool and the soil pore water was extracted by centrifugation at 3000g for 15 min. The concentrations of Ni, pH and electrical conductivity in the soil pore water were measured immediately on an aliquot of the separated solution, with Ni concentration determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; SpectroFlame Modula, Spectro, Kleve, Germany). This analysis was performed at 0, 90, 180 and 360 d after spiking of the soils. Free Ni^{2+} concentrations in the EC10-treated soils incubated for 180 d were also determined by Donnan dialysis following the method outlined in Nolan et al. (2009).

2.3. Determination of isotopically exchangeable Ni and total Ni

The isotopically exchangeable pools (E values) of soil Ni were measured in duplicate by isotopic (^{63}Ni) dilution using water extraction followed by a resin purification step as outlined by Nolan et al. (2009). This technique has the advantages of increasing the analyte concentration and suppressing colloidal interferences (Lombi et al., 2003; Nolan et al., 2009). The E values were measured for soils spiked at both EC10 and EC90 and equilibrated for 18, 180, 360 and 540 d. The isotopic exchangeability (lability) of added Ni (E_{add}, %) expressed as a percentage of total Ni added was calculated by subtracting the E value of non-dosed (i.e. untreated) control

Table 1
Soil properties and total Ni added to soils at two toxicity effect concentrations (EC10 and EC90).

Soil No.	Soil location	pH (CaCl$_2$)	Clay (%)	Organic C (%)	CaCO$_3$ (%)	Total Ni (mg kg^{-1})	EC10 (mg kg^{-1})	EC90(mg kg^{-1})
1	Houthalen (Belgium)	3.6	0.4	1.73	<0.5	1.0	44.1	36.6
2	Zegveld (The Netherlands)	4.1	34	33.1	<0.5	26	1796	2727
3	Montpellier (France)	4.1	25.3	0.25	<0.5	16	94	311
4	Rhydtalog (UK)	4.2	12.7	12.5	<0.5	3.0	599	834
5	Jyndevad (Denmark)	4.5	1.5	1.32	<0.5	1.0	45.0	95.9
6	Kövlinge II (Sweden)	5.1	3.9	2.47	<0.5	2.0	128	266
7	Aluminusa (Italy)	5.6	46.9	0.99	<0.5	19	259	772
8	Borris (Denmark)	5.6	4.3	1.33	<0.5	3.0	95	271
9	Woburn (UK)	6.1	35.3	4.30	<0.5	39	488	1196
10	Ter Munck (Belgium)	6.7	9.6	1.09	<0.5	11	141	454
11	Souli (Greece)	7.0	33.2	0.63	1.5	81	181	610
12	Marknesse (The Netherlands)	7.6	19.9	2.52	11.5	19	303	836
13	Brécy (France)	7.5	49.2	3.67	19.1	113	439	1141
14	Cordoba 2 (Spain)	7.6	55.4	4.67	34.8	24	613	1570
15	Cordoba 1 (Spain)	7.6	19.8	3.14	21.8	18	240	608
16	Guadalajara (Spain)	7.7	17.2	3.78	29.0	11	331	825

soils from the total E value measured in the respective soils with added Ni, and then dividing by the measured Ni dose (total Ni in spiked soil minus total Ni in control soil). Total concentrations of Ni in soil were determined by ICP-OES (SpectroFlame Modula, Spectro, Kleve, Germany) following digestion with *aqua regia* (a fresh mixture (1:3) of concentrated HNO$_3$ and HCl) as described in detail by Oorts et al. (2006a,b). On average, 84% to 96% of initially added Ni was recovered, with the differences attributable to losses during the post-dosing leaching step. For analytical quality control, standard certified reference soil materials were used for determination of physic-chemical properties of soils, and for determination of total metal concentrations. As there are no certified reference standards for labile Ni in soil, an internal laboratory quality control soil was used. .

2.4. Modeling of isotopically exchangeable Ni

The E value was used for semi-mechanistic modeling of the changes in Ni lability. This parameter was chosen as the E-value technique allows a direct assessment of Ni in equilibrium with the soil solution (and therefore potentially available) and is consequently well suited to be described with a semi-mechanistic model that is based on processes that remove Ni from the exchangeable pool. Short-term adsorption reactions would not decrease the E_{add} value since the adsorbed Ni would still be isotopically exchangeable. However, the fast aging processes, which occur particularly rapidly at high pH and can lead to decreased isotopic exchangeability of added Ni (E_{add} value), can most likely be attributed to the surface precipitation/nucleation of Ni-bearing minerals in soils (Scheckel et al., 2000). This precipitation/nucleation process is considered to be related to the formation of Ni(OH)$^+$ on clay minerals and Fe oxides in soils (Brümmer et al., 1988; Scheckel et al., 2000) and can be described as follows (Ma et al., 2006a,b):

$$Y_1 = \frac{B}{10^{(pK^\circ - pH)} + 1} \times t^{C/t} \quad (1)$$

where Y_1 represents the change (%) in E_{add} value of added Ni due to the fast processes (surface precipitation/nucleation); B is a coefficient which is considered to be related to the effect of precipitation/nucleation; t is aging time (d); pK° is the first hydrolysis constant of Ni; the reciprocal power exponential equation $t^{C/t}$ (C is a constant) is used to describe the kinetics of these relatively fast processes; and pH is soil pH measured in 0.01 M CaCl$_2$.

Micropore diffusion or intraparticle surface diffusion are the main slow processes that are likely to be involved in Ni aging (Axe and Trivedi, 2002). Diffusion is a rate-limiting process in soils and is proportional, at least in the initial phase, to the $\sqrt{t}$ (Crank, 1975). Subsequently the diffusion process can be described by a simplified Elovich equation (Aharoni and Sparks, 1991). In this case the diffusion process is linearly related to the natural logarithm of time.

Taking into account the factors mentioned above and two main Ni aging processes active in soil, one semi-mechanistic model based on $\sqrt{t}$ for relative short-term aging (Sqrt-model) and another based on the natural logarithm of time for relative long-term aging (Ln-model) were developed as follows:

Sqrt-model : E_{add} value (%)

$$= A - \frac{B}{10^{(pK^\circ - pH)} + 1} \times t^{C/t} - F_1 \times \sqrt{t} \quad (2)$$

Ln-model : E_{add} value (%)

$$= A - \frac{B}{10^{(pK^\circ - pH)} + 1} \times t^{C/t} - F_2 \times \ln(t) \quad (3)$$

where A is a coefficient which represents the E value of added Ni at time zero (=100%); F_1 is a coefficient in Sqrt-model and is equal to

$600 \sqrt{D/\pi r^2}$ in which D is the diffusion coefficient and r is the radius of the spherical particle; the term D/r^2 expresses the apparent diffusion rate coefficient (Crank, 1975; Kärger and Ruthven, 1992; Ma and Uren, 1997); F_2 is a coefficient in Ln-model which is also considered to be related to the rate of micropore diffusion. The parameters in the model were optimized by minimizing the sum of the squares of the residual variation of the data points from the model.

2.5. Validation of the models

Three soils were used for validation based on their contrasting soil properties: Jyndevad (Denmark), Woburn (UK), and Cordoba II (Spain) (Table 1). Air-dried soils (<4 mm) were spiked at eight doses (0–1600 mg Ni kg^{-1} for Jyndevad and 0–4800 mg Ni kg^{-1} for Woburn and Cordoba II) with NiCl$_2$ solution. The spiked soils, contained in 10-L plastic pots, were aged at a field site in Leuven (Belgium; mean annual rainfall, 780 mm; mean annual maximum temperature, 14.3 °C; mean annual minimum temperature, 7.1 °C). Soils were sampled at 7, 165, 300 and 450 d of aging and, after each sampling, were air-dried at 25 °C, sieved through 4-mm mesh, and mixed to ensure homogeneity. More details of sample treatment can be found in Oorts et al. (2007). The concentration of total Ni in soils was again determined by boiling *aqua regia* extraction and analysis by ICP-OES (Optima 3300 DV; PerkinElmer, Norwalk, CT, USA). The E values of Ni added to the soils were determined as described above.

2.6. Statistical analyses

Statistical analyses, including analysis of variance and regression analysis were conducted using Genstat 6.1 for Windows (Genstat, 2002).

3. Results and discussion

3.1. Soil pore water

Total concentrations of Ni in soil pore waters decreased from a range of 1.43 mg L^{-1} to 64.3 mg L^{-1} in the freshly spiked soils to a range of 0.004 mg L^{-1} to 4.72 mg L^{-1} in the EC10-treated soils aged for 360 d (Fig. 1). On average, total Ni concentration decreased by 244 times (range for all soils was 14 to 1537 times) between fresh spiking (0 d) and 360 d after spiking. During the incubation outdoors, the electrical conductivity (EC) decreased and pH in pore
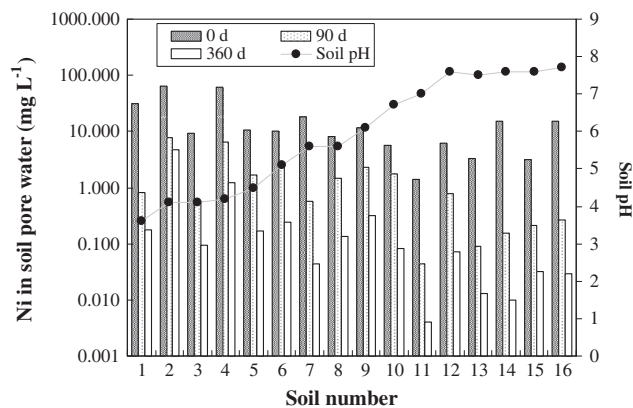

Fig. 1. Total Ni concentration in soil pore water extracted after spiking (0 d), 90 and 360 d of incubation from EC10-treated soils. Soil pH was measured in 0.01 M CaCl$_2$ (1:5 soil:solution ratio) as shown in Table 1.

water increased. For example, the mean pore water EC values in the EC10-treated soils were initially 3.51 mS cm^{-1}, these values decreased with time to 0.68 (90 d), and 0.58 mS cm^{-1} (360 d). The initial pH of soil pore water in the EC10-treated soils was on average 0.67 units lower than that in the soils incubated for 360 d. The decrease in EC and increase in pH likely contributed to the decrease in total Ni in soil pore waters. The percentage of free Ni^{2+} to total Ni in soil pore waters in the EC10-treated soils incubated for 180 d varied from 2.8% to 93% (Fig. 2), and was significantly and inversely related to soil pH (% free Ni^{2+} = 175–22.2 pH, r = 0.956, $p \leqslant 0.0001$). Similar results were found in pore water of 13 Ni-contaminated soils from Australia and Canada (Nolan et al., 2009), and even in 0.01 M CaCl$_2$ extracts in a sandy soil spiked with Ni (Weng et al., 2003) and in sludge-amended soils (Sanders and Adams, 1987). Also, pNi^{2+} ($-\log_{10}$ Ni^{2+} activity) in the EC10-treated soils incubated for 180 d varied from 3.76 to 7.13 and increased significantly with pH (pNi^{2+} = 0.788 pH + 0.749, r = 0.937, $p \leqslant 0.0001$). Even though the soils were spiked to a level of equivalent toxicity, pNi^{2+} in soil pore waters increased from 3.8 to 7.1 with increasing pH. Therefore, these data are in agreement with the fact that, at parity of free ion activity, Ni^{2+} is more toxic at higher pH. Li et al. (2009) showed that pH affected Ni toxicity through H$^+$ competition with Ni^{2+} bound to biotic ligands at pH < 7.0 and through the change of Ni species in solution at pH $\geqslant$ 7.0. When pH $\geqslant$ 7.0 both Ni^{2+} and NiHCO$_3^+$ were found to be toxic to barley root elongation.

A solubility diagram, plotted using Visual MINTEQ 3.0 (Gustafsson, 2010) calculations, was prepared to determine if the solutions were supersaturated with respect to any known pure mineral phases of Ni. In this diagram, two partial atmospheric pressures of CO$_2$ in soil pore water were assumed i.e. 0.038 and 0.00038 atm (Lindsay, 1979; Nolan et al., 2003). When viewed in comparison to Ni minerals displayed in these diagrams, the solubility products in the relatively high pH calcareous soils in this study (soil 12–16, pH 7.5–7.7) could approach the solubility products of NiCO$_3$ when the CO$_2$ partial atmospheric pressure in soils was assumed to be high i.e. 0.038 (Fig. 2). This suggests that a part of the freshly spiked Ni^{2+} may precipitate as NiCO$_3$ in high pH calcareous soils at high rates of Ni^{2+} addition and high soil CO$_2$ partial atmospheric pressure. The relatively high pH soils in this study were undersaturated with respect to Ni(OH)$_2$. However, Manceau et al. (1987) provided compelling extended X-ray absorption fine struc-

ture (EXAFS) spectroscopic evidence that Ni, in the lateritic profiles of New Caledonia was not only associated with garnierite, lithiophorite and goethite, but also with the Mn oxide – asbolane – as layers of Ni(OH)$_2$. Therefore, the possibility of Ni(OH)$_2$ precipitation cannot be excluded as we did not have solubility products for these phases. In fact, soil mineral surfaces probably act as nucleation sites for precipitating Ni^{2+}, thereby reducing the apparent solubility product in much the same way that pure clays appear to reduce solubility products by surface adsorption. As suggested for Cu (Ma et al., 2006a), it is possible that when water soluble Ni was added to these calcareous soils, the Ni ions were quickly adsorbed on solid surfaces and precipitated, with further decreases in free Ni^{2+} activity in the soils occurring due to ongoing slow reactions (such as micropore diffusion into crystal lattices).

3.2. Isotopically exchangeable Ni

In untreated control soils the average concentration of isotopically exchangeable Ni (E value) was 1.54 mg kg^{-1} with the highest value, 6.63 mg kg^{-1}, in the Zegveld soil (The Netherlands) which also has the highest organic carbon content (33.1%). For soils with EC10 treatments the E values ranged from 18.4 to 1160 mg kg^{-1} with a mean of 158 mg kg^{-1}, and for oils with EC90 treatments the E values ranged from 15.7 to 2051 mg kg^{-1} with a mean of 319 mg kg^{-1}. The mean E_{add} values as a percentage of total Ni added were 52% for EC10 treatments and 46% for EC90 treatments. There was a decreasing trend of E_{add} values (%) with increasing Ni dose, especially for calcareous soils (soil 11–16) where the mean E_{add} values (%) were 22.6% for EC10 treatments and 15.1% for EC90 treatments. Between 18 and 540 d E_{add} values decreased by up to 3-fold, with the decrease particularly marked in higher pH soils. Stepwise regression analysis was used to identify the most important factors influencing E_{add} values (%); they were found to be soil pH and incubation time. Regression equations for both EC10 and EC90 treatments, considering three different mathematical representations of elapsed time, were identified as follows:

$$E_{add} \text{ value } (\%) = 159.4 - 17.6(P \leq 0.00001)\text{pH} - 0.0107(P \leq 0.127)t \quad (\text{adjusted } R^2 = 0.763, n = 110) \quad (4)$$

$$E_{add} \text{ value } (\%) = 163.1 - 17.6(P \leq 0.00001)\text{pH} - 0.459(P \leq 0.014)\sqrt{t} \quad (\text{adjusted } R^2 = 0.771, n = 110) \quad (5)$$

$$E_{add} \text{ value } (\%) = 173.0 - 17.6(P \leq 0.00001)\text{pH} - 3.34(P \leq 0.001)\ln(t) \quad (\text{adjusted } R^2 = 0.782, n = 110) \quad (6)$$

The slope of E_{add}/pH (17.6) for Ni is higher than that (5.3–6.8) found for Cu aging (Ma et al., 2006a). In other words, the soil pH affected E_{add} value (%) for Ni much more than for Cu.

3.3. Semi-mechanistic models for E_{add} values

The semi-mechanistic models based on the processes of Ni precipitation/nucleation and micropore diffusion were used to describe the aging processes which led to the decrease in the isotopic exchangeability of Ni added to soils. When the data were fitted by the model using the Solver function in Microsoft Excel, the parameters B and C were subjected to the following constraints: $0 \leqslant B \leqslant 110$ and $0 \leqslant C \leqslant 1$, with 0.000001 precision, 5% tolerance and 0.0001 convergence. The reciprocal power exponential equation $t^{C/t}$ (C is a constant) was used to describe the fast processes of precipitation/nucleation. The parameters in the models are shown in Table 2. The regression coefficients (adjusted R^2) for the semi-mechanistic models were 0.88–0.91, higher than those
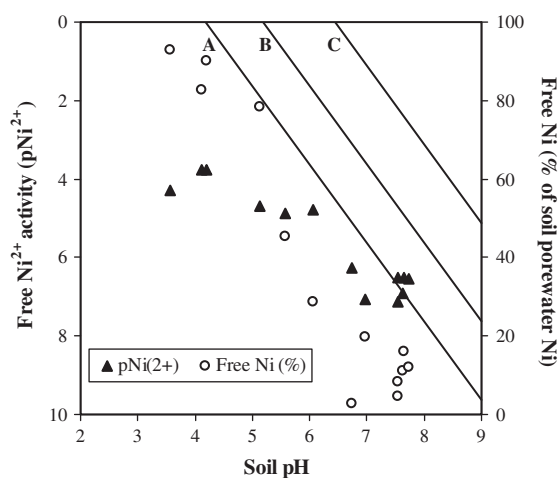

Fig. 2. Free Ni^{2+} activity (pNi^{2+}) and free Ni^{2+} as a percentage of total dissolved Ni in soil pore water in the EC10-treated soils incubated for 180 d as a function of soil pH. The solid lines are solubility limits for NiCO$_3$ assuming 0.038 (line A) and 0.00038 (line B) CO$_2$ partial atmospheric pressures and for amorphous Ni(OH)$_2$ (line C), which were calculated using Visual MINTEQ 3.0.

Table 2
Model parameters and regression coefficients (adjusted R^2) derived from 16 soils at two toxicity effect concentrations (EC10 and EC90).

	E_{add} value (%) $= 100 - \frac{B}{10^{(pK^\circ - pH)}+1} \times t^{C/t} - F_1 \times \sqrt{t}$				
Ni added	B	pK°	C	F_1	Adjusted $R^{2\dagger}$
EC10	67.9	6.45	9.11×10^{-6}	1.01	0.91[***]
EC90	74.0	6.54	1.1×10^{-5}	1.17	0.91[***]
EC10 and EC90	71.2	6.50	1.6×10^{-4}	1.08	0.91[***]
	E_{add} value (%) $= 100 - \frac{B}{10^{(pK^\circ - pH)}+1} \times t^{C/t} - F_2 \times \ln(t)$				
Ni added	B	pK°	C	F_2	Adjusted $R^{2\dagger}$
EC10	70.0	6.67	0.000	4.60	0.89[***]
EC90	64.1	6.60	0.000	4.11	0.89[***]
EC10 and EC90	67.4	6.61	0.000	4.20	0.88[***]

[†], [***] Indicates significance at $P \leqslant 0.001$.

obtained by the empirical model (0.76–0.78). Although there was a decreasing trend of E_{add} values (%) with increasing dose, the differences between the two Ni doses in both the Sqrt-model and the Ln-model were not significant and could be ignored in order to simplify the models, so that the models for EC10- and EC90-treated soils were used for validation and application. The constant C in the models was found to be small ($\leqslant$0.00016), which suggested that the fast processes, such as precipitation/nucleation, were stable within 1 h, afterwards the aging processes were controlled by the micropore diffusion processes. In the models, the values of pK° were estimated as 6.50 for the Sqrt-model or 6.61 for the Ln-model, which are lower than those reported for Ni hydrolysis in water (8.35–9.9, Hummel and Curti, 2003). This is likely due to facilitated hydrolysis of $Ni(H_2O)_6$ on the surfaces of soil solids. The apparent diffusion rate coefficient (D/r^2) estimated by the Sqrt-model (Table 2) was found to be in the order of 10^{-5} day^{-1}, which is similar to that of Zn (Ma and Uren, 1997, 2006) and Cu (Ma et al., 2006a; Zhou et al., 2008). The slow diffusion rate coefficient suggests that the diffusion of Ni into micropores was a rate-limiting process in these soils (Nye, 1979; Ma et al., 2006a).

The measured E_{add} values as a function of incubation time and soil pH and the E_{add} values estimated by the semi-mechanistic models for EC10- and EC90-treated soils are shown in Fig. 3. It can be seen that the isotopic exchangeability of Ni added to soils decreased rapidly after addition, especially at high pH. The aging rate was fast initially and then decreased with increasing incubation time. The difference between the Sqrt-model and the Ln-model was less than 8% over the study period considered. However, the Sqrt-model should be used for short-term prediction ($\leqslant$6 months) and the Ln-model for long-term prediction (>6 months) because theoretically the initial stage of the diffusion processes can be linearly related to the $\sqrt{t}$ (Crank, 1975) and the following period to the natural logarithm of time (Aharoni and Sparks, 1991).

In the model, when soil pH was <4 only slow aging processes (likely diffusion) occurred, with the fast processes (likely precipitation/nucleation) in soils insignificant (<0.3%). The isotopically exchangeable Ni species retained by soils at pH values <5 is likely to be Ni^{2+} (both in solution and sorbed). The decrease in E_{add} values (%) due to precipitation/nucleation was only 2.0% at pH 5, however, these fast processes of precipitation/nucleation were significantly increased at pH values >5 and they were estimated by the Sqrt-model to increase from 17% at pH 6, to 54% at pH 7 and 67% at pH 8.

3.4. Model validation

The measured and predicted E values (%) of Ni added at multiple rates to the independent validation soil set are shown in Table 3. In this case, the mean E values (%) of added Ni in soils with different
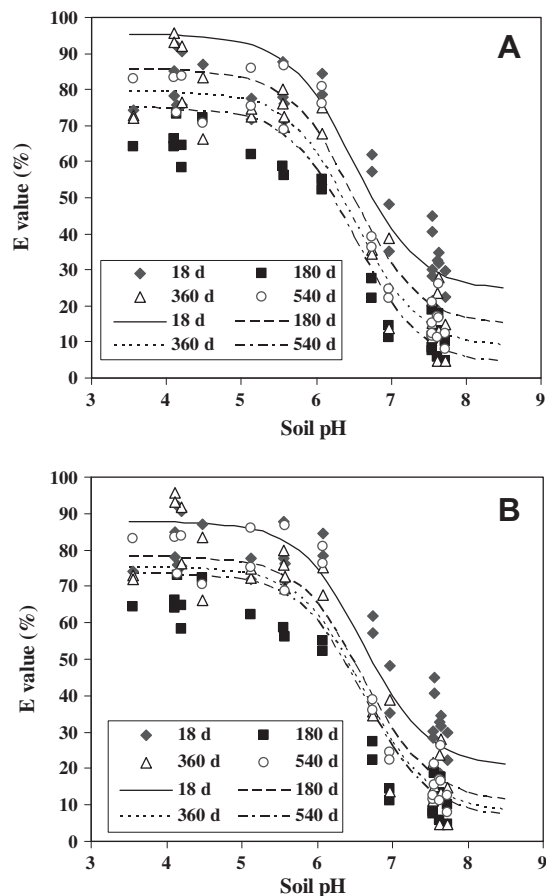

Fig. 3. The E_{add} values (% of total added Ni) measured in the EC10- and EC90-treated soils incubated for different times (symbols) and the curves predicted by the Sqrt-model (A) and the Ln-model (B).

doses of Ni were used to compare with the E values predicted by the semi-mechanistic models for EC10- and EC90-treated soils. It was found that the differences between the predicted and measured E values were less than 10%, except for the Woburn (UK) soil incubated for 300 d (Table 3). However, the predictive power of this simple model (based only on pH and time) was satisfactory. A limitation of the model is that one aging period was used for the calculation even though Ni additions in the field often occur repeatedly over time. The model is less likely to accurately predict the aging of Ni applied to soils in other forms (such as Ni in sewage sludge, organic manure, and mining wastes) because different sources of Ni, due to matrix effects, will most likely exhibit different fates in soil. For example, when the models are used for E values (expressed as percentage of labile Ni to total Ni) of field-contaminated soils reported by Nolan et al. (2009) and of agricultural and serpentine soils reported by Echevarria et al. (2006), the E values in some field soils were lower than that predicted by the models (Fig. 4), because substantial amounts of Ni in these soils originated most likely from Ni bearing minerals which have not yet weathered. Nevertheless, the results of this study demonstrate that for water soluble Ni added to soils, the change in isotopic exchangeability of added Ni with time can be predicted simply by soil pH and time. Therefore, the models derived could potentially be used to scale ecotoxicological data generated from different soils spiked with soluble Ni under different aging periods. Such an approach is in keeping with recent developments in European Union risk assessments, in which soil pH-dependent aging effects on E values have been used to adjust and correct Ni terrestrial ecotoxicity data (Smolders et al., 2009).

Table 3
Soil pH, incubation time, measured *E* values (%, mean and range) and predicted *E* values (%) of Ni added to the soils spiked with different doses of Ni and aged for 7, 165, 300 and 450 d.

| Soil No.	Location	Soil pH	Time (d)	*E* measured (%, mean and range)	*E* predicted (%)
5	Jyndevad (Denmark)	5.4	7	91.3 (75.4–100)	96.5
5	Jyndevad (Denmark)	5.4	165	89.7 (80.8–95.9)	85.5
5	Jyndevad (Denmark)	5.4	300	69.8 (63.5–80.1)	75.6
5	Jyndevad (Denmark)	5.4	450	82.8 (59.3–96.9)	73.9
9	Woburn (UK)	6.1	7	69.9 (61.0–76.5)	77.7
9	Woburn (UK)	6.1	165	70.1 (62.7–79.4)	66.8
9	Woburn (UK)	6.1	300	78.4 (70.2–87.0)	61.1
9	Woburn (UK)	6.1	450	68.3 (60.5–80.0)	59.3
14	Cordoba 2 (Spain)	7.6	7	26.3 (17.5–38.0)	30.9
14	Cordoba 2 (Spain)	7.6	165	19.4 (7.93–36.8)	19.9
14	Cordoba 2 (Spain)	7.6	300	18.7 (6.73–31.1)	14.7
14	Cordoba 2 (Spain)	7.6	450	12.9 (3.8–22.0)	13.0
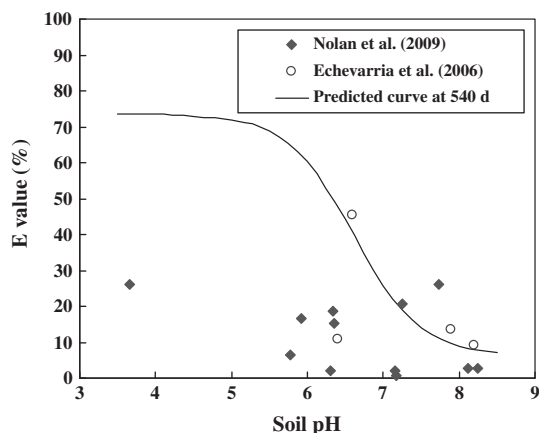
Fig. 4. The measured *E* values (% of total soil Ni) in field soils reported by Nolan et al. (2009) and Echevarria et al. (2006) and the curve of *E*~add~ values (% of total added Ni) predicted by the Ln-model at 540 d.

4. Conclusions

When water-soluble Ni was added to soils, the concentrations of Ni in soil pore water and isotopic exchangeability of Ni in soils initially decreased rapidly, then continued to decrease with time at a slower rate. Soil pH was the key parameter controlling the aging processes. Semi-mechanistic models, based on Ni precipitation/ nucleation on soil surfaces and micropore diffusion, were developed. The initial fast processes, which were attributed to precipitation/nucleation, occurred over a short time (e.g. 1 h), afterwards the slow processes were most likely controlled by micropore diffusion processes. The models were validated using three widely differing soils aged outdoors for periods up to 15 months and could potentially be used to scale ecotoxicological data generated from different soils under different aging times.

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