

The Chemical Extractability and Mobility of Ni⁶³ in Soil and Sludge

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Abstract: A sludge was conducted to attain the chemical extractability and mobility of Ni⁶³ in soil and sludge. The results of this sludge showed a variation in extractable Ni⁶³ activity with different incubation times. The extractions from the spread columns within increase in time showed, the amount of water soluble Ni⁶³ in the soil, sludge and soil mixtures decreased significantly. The percentage removal of organically bound Ni⁶³ by DTPA varied during the eight weeks, while EDTA showed a higher percentage of removal with a correlation with plant uptake. In some cases water decreased the solubility of Ni⁶³ with increasing time in soil, sludge and mixture columns. Organic matter also decreased the Ni⁶³ concentrations in all mixtures. Nitric acid digestion was used as a method of total recovery of Ni⁶³ from all columns and 86-94% of the initial Ni⁶³ was recovered in leachates from the soil and soil/sludge mixtures a greater proportion of cationic species of Ni⁶³ than non cationic species were present, but in the sludge only leachates the reverse was true after 8 weeks. Organic matter content of soil increased by incorporation of sewage sludge may help to reduce the mobility of nickel.

Key words: Chemical form, mobility, time, column, Ni⁶³

Introduction

Heavy metals in sewage sludge applied to soil may pass through the soil uncharged, form insoluble or sparingly soluble inorganic and organic compounds, be sorbed by soil colloids, cations, anions or molecules, or taken up by the plant (Alloway and Jackson, 1999). If not complexed with organic matter, metals probably exist in soil solutions predominantly as divalent cations. Many other inorganic complex ions, molecules, and ion pairs of these elements are known to occur in equilibrium with the divalent form. Recent research (Lagerwerff *et al.*, 1976) has shown that significant quantities of complexed heavy metals may exist in sewage sludges. The presence of soluble substances leached from residues and sewage sludges has received particular attention (Blakeslee, 1973). Organic matter content of sludge amended soils chelates toxic metals, such as nickel, and reduces their availability to the plant. Because organic matter confers this protection against metal toxicity, its management is very important (Keefer and Singh, 1986). It is known that chelated or complexed forms of heavy metals move more readily in soil systems than cationic forms (Hodgson *et al.*, 1966 and Norvell and Lindsay, 1972). Mobility of nickel in soils is affected by the movement of water through the profile and any factor that affects the solubility of an element must affect its movement (Alloway, 1998). Mobility of nickel in soil is definitely affected by the movement of water through the profile (Nouri, 1980). One of the most important factors affecting the mobilization and immobilization of micronutrients in soils is drainage (Alloway, 1998). When assessing heavy metal mobility, environmental factors should thus be considered, as well as determining the extent of complexed and cationic forms of heavy metals in sewage sludge to be applied to the land. Page and Pratt (1975) stated that elements which occur in solution, as anions or neutral molecules, pass through soils more readily than cations. This is because there are many more cation adsorption sites in soils than anion adsorption sites; indeed the existing anion exchange sites may be dominated with common anions such as Cl⁻. Fractionation into cationic and non-cationic forms of metals in aqueous sludge extracts may be a useful index of the

groundwater pollution hazard of the sludge.

The objectives of this study were to investigate the variations with time in the proportions of Ni⁶³ extractable from soil/sludge; to study the mobility of soluble and insoluble Ni⁶³ through different soil/sludge columns and their variation with time and the resulting implications for land applications and groundwater pollution hazards of sludge and to evaluate the total quantities and relative amounts of cationic and non-cationic species of Ni⁶³ present in the water leachate portion of sewage sludge and oil amended with sludge.

Materials and Methods

The soil and sludge samples were collected prepared in London in 1990. The isotopes ⁶³Ni²⁺ was present as nickel chloride in aqueous solution, the batch used contained 0.85 m Ci/mg nickel in 1 ml. In order to study the extractability and solubility of Ni⁶³ spiked soil/sludge, 10 g of air-dried soil/sludge treated with 10 μ Ci Ni⁶³ were placed in each of 60 beakers (100 ml volume) and allowed to equilibrate for 1 day, 1 week, 2 weeks, 4 weeks, and 8 weeks. The beakers were divided into 3 series:

- 20 beakers with 100 % soil
- 20 beakers with 100 % sludge
- 20 beakers with 50 % soil and 50 % sludge mixture.

Each sample was spiked with 10 μ Ci of Ni⁶³, left for the required equilibration period, and then treated with all of four different extractants:

1. Deionized water
2. 0.5 M acetic acid
3. 0.005 M DTPA
4. 0.05 M EDTA

After shaking for 2 hrs, the slurry was centrifuged at 1500 g for 10 min. and filtered. 1 ml of filtrate was pipetted off, added to 10 ml of scintillation fluid and counted.

In second part of the experiment, in order to study the movement of soluble and insoluble forms of Ni⁶³ in soil and sludge, a series of columns was used (Table 1). The 16 columns used were each made of seven identical glass rings

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Table 1: Series of experiment columns

Column (a)	Surface layer	-	100% soil
	Lower layers	-	100% soil
Column (b)	Surface layer	-	90/10% soil/sludge
	Lower layers	-	100% soil
Column (c)	Surface layer	-	100% sludge
	Lower layers	-	100% page
Column (d)	Surface layer	-	100% sludge
	Lower layers	-	100% soil

Table 2: Physical properties of ion exchange resin loaded

Resin type	Cation exchange	Anion exchange
Resin/name	Dowex 50	Dowex 1-X8
Resin form	H ⁺	OH ⁻
Particle size	100*200 mesh	20-50 mesh
Exchange capacity	0.7 meq/ml resin bed	-
Useful pH range	1-13	1-13

connected to form a vertical cylinder 17.5 cm tall with an internal diameter of 2.5 cm. The lower layers in each column are saturated to field capacity with deionized water for a week before the surface layer was added. Four identical columns were made up for each of the four different layer arrangements given below, so that the activity of the leachate from each type of layer arrangement could be measured at four different times. (In these experiments, the term of "leachate" is defined as the liquid coming out of the base of the column.)

Each surface layer was initially spiked with 10 µCi Ni⁶³ and left for 2 days, then transferred to the top of the column as the surface layer to act as source of mobile Ni for the profile. Each day, 20 ml of deionized water were very slowly poured into the top of the column. A circular piece of filter paper had previously been placed over the surface layer to protect the soil structure from damage. There was another filter paper between the surface and lower layers and a third at the bottom of the column covering a 0.5 mm nylon mesh which formed the base of the column.

The leachates were accumulated in a beaker at the bottom of each column. On 7th, 14th, 28th and 56th days the original beakers were replaced with empty ones so that the activity of the leachate on those days could be measured separately from that of the previously accumulated leachate.

In order to separate the Ni⁶³ into cationic and non-cationic forms, the leachate collected on the last day was treated by the batch method. The characteristics of the ion exchange resins are listed in Table 2. 5 ml of Dowex 50 (H⁺) resin were washed with deionized water for several hours to bring the pH near to neutral. The measured pH was approximately 5 for cation exchange resin before the sample was added and 5 ml of resin were added to 5 ml of leachate and the mixture shaken overnight. It was then filtered and the activity of the filtrate measured.

Another 5 ml of filtrate were similarly treated with Dowex 1 (OH⁻). This anion exchange resin was not successful in measuring Ni⁶³ activity, because it did not remove significant amount of Ni⁶³ form the leachate. Sequential treatment with Dowex 50 followed by Dowex 1 would probably have been

more successful.

At the end of the experiment, each column was separated into seven sections (Corresponding to the seven constituent rings) and each section was extracted with 20 ml of deionized water for 2 hours, filtrate activity was then measured. The residue was digested with concentrated nitric acid and filtrate activity was measured after dilution with 1 N HNO₃.

Results

Extractability of Ni⁶³: Results showing the variation in extractable Ni⁶³ activity with different incubation times (1 day, 1, 2, 4 and 8 weeks) for leachates from Ni⁶³ - spiked soil, sludge and mixtures of soil/sludge are given in Table 3 and Figs. 1 to 3. The reliability of such results depends on the specificity of each reagent used to extract the metal form. Water extraction was used to find the percentage of Ni⁶³ which was water-soluble, this solvent extracted a lower percentage on Ni⁶³ than any other used and the percentage decreased over the eight weeks period. It was lower for soil than for sludge or soil/sludge mixtures. Greater activity was found in extraction with acetic acid which removed a higher proportion of the exchangeable form of the isotope from the mixture than from soil or sludge. The acetic acid reagent would be expected to extract metals specifically adsorbed to inorganic sites as well as exchangeable Ni⁶³. The chelating agents DTPA and EDTA usually extracted more activity from soil than from sludge or soil/sludge, this suggested that a greater percentage of the inorganic Ni⁶³ spike added to sludge was fixed or complexed by the higher organic content (32 %) of the sludge than by lower organic content (4 %) of the soil. The high sludge nickel (860 µg g⁻¹) may also have interacted with the inorganic Ni⁶³ added to the soil.

Mobility of soluble and insoluble Ni⁶³: The water extraction of soluble Ni⁶³ and the nitric acid digestions were carried out on different section of columns of soil, sludge and mixtures beneath the Ni⁶³ spiked surface layer. The extractions were

Table 3: Results for variation in extractable Ni⁶³ with time from spiked soil/sludge

Time	Extractants	Radioactivity in d.m.p x 10 ²		
		Sludge	Soil	Mixture (50/50)
1 Day	H ₂ O	9.27(4.2) *	2.23(1.0)	8.81(4.0)
	CH ₃ COOH	40.41(18.2)	36.27(16.3)	61.64(27.8)
	DTPA	87.65(39.5)	96.79(43.6)	83.61(37.7)
	EDTA	98.81(44.5)	149.67.4)	121.32(54.6)
1 Week	H ₂ O	4.74(2.1)	1.31(0.59)	6.64(3.0)
	CH ₃ COOH	36.27(16.3)	31.08(14.0)	55.09(24.8)
	DTPA	63.62(28.7)	74.20(33.4)	74.67(33.6)
	EDTA	66.26(29.8)	131.41(59.2)	96.90(43.7)
2 Weeks	H ₂ O	4.21(1.9)	1.29(0.58)	5.80(2.6)
	CH ₃ COOH	34.75(15.5)	30.16(13.6)	53.07(23.9)
	DTPA	59.93(26.7)	69.53(31.3)	70.49(31.7)
	EDTA	58.27(25.9)	117.06(52.7)	93.32(42.0)
4 Weeks	H ₂ O	4.17(1.88)	1.15(0.52)	5.47(2.5)
	CH ₃ COOH	34.35(15.5)	30.13(13.6)	53.25(24.0)
	DTPA	59.38(26.7)	67.05(30.2)	68.64(30.9)
	EDTA	57.59(25.9)	106.88(48.1)	88.06(39.7)
8 Weeks	H ₂ O	4.03(1.8)	1.14(0.51)	5.55(2.5)
	CH ₃ COOH	32.87(14.8)	29.19(13.2)	49.88(22.5)
	DTPA	59.33(26.7)	64.04(28.8)	70.15(31.6)
	EDTA	57.70(26.0)	106.60(48.0)	89.43(40.3)

*The values in parenthesis expresses the recovered as a percentage of the activity of the initial Ni⁶³ spike.

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Table 4: Water extraction of Ni⁶³, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ spiked surface layer of 100% soil (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 weeks
0	122 900 ± 740*	98 790 ± 660	80 660 ± 660	67 920 ± 550
2.5	15 520 ± 260	13 730 ± 250	9 200 ± 200	5 620 ± 160
5.0	5 850 ± 160	2 430 ± 100	1 100 ± 70	750 ± 58
7.5	2 380 ± 100	1 050 ± 70	440 ± 44	315 ± 37
10.0	820 ± 60	490 ± 50	230 ± 32	67 ± 17
12.5	720 ± 56	350 ± 40	160 ± 27	40 ± 13
15.0	800 ± 60	320 ± 38	140 ± 25	18 ± 9
17.5				
Leachate activity	42 340 ± 970	43 520 ± 980	36 080 ± 900	36 870 ± 900

* These results, from 20 minutes counting, are expressed as the mean value ± standard error, at 95% confidence limit.

Table 5: Water extraction of Ni⁶³, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ spiked surface layer of 90% soil, 10% sludge (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 Weeks
0	102 800 ± 680*	80 450 ± 600	75 510 ± 580	67 370 ± 550
2.5	16 250 ± 270	15 670 ± 260	6 720 ± 170	6 440 ± 170
5.0	2 130 ± 95	650 ± 55	400 ± 40	390 ± 40
7.5	990 ± 66	235 ± 33	160 ± 27	122 ± 24
10.0	710 ± 56	220 ± 32	145 ± 25	84 ± 19
12.5	690 ± 55	230 ± 30	110 ± 22	58 ± 16
15.0	730 ± 57	245 ± 32	65 ± 17	36 ± 13
17.5				
Leachate Activity	30 250 ± 820	36 850 ± 900	35 500_890	52 220 ± 1080

* These results, from 20 minutes counting, are expressed as the mean value ± standard error, at 95% confidence limit.

Table 6: Water extraction of Ni⁶³, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ spiked surface layer of 100% sludge (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 Weeks
0	90 020 ± 630*	86 140 ± 620	61 130 ± 520	52 870 ± 490
2.5	12 840 ± 240	11 980 ± 230	10 480 ± 220	5 750 ± 160
5.0	2 310 ± 100	1 240 ± 74	1 210 ± 73	1 840 ± 90
7.5	1 410 ± 80	270 ± 35	400 ± 42	390 ± 42
10.0	80 ± 60	250 ± 33	170 ± 28	135 ± 24
12.5	700 ± 55	120 ± 23	80 ± 19	20 ± 9
15.0	710 ± 56	130 ± 24	40 ± 13	25 ± 10
17.5				
Leachate Activity	30 600 ± 820	32 980 ± 860	39 940 ± 940	48 680 ± 1040

* These results, from 20 minutes counting, are expressed as the mean value ± standard error, at 95% confidence limit.

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Table 7: Water extraction of Ni⁶³, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ spiked surface layer of 100% sludge (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 Weeks
0	88 800 ± 630 *	66 200 ± 540	60 900 ± 520	42 400 ± 430
2.5	7 130 ± 180	6 760 ± 170	6 180 ± 170	4 220 ± 140
5.0	1 120 ± 70	590 ± 50	360 ± 40	300 ± 35
7.5	1 100 ± 70	250 ± 35	120 ± 20	70 ± 18
10.0	580 ± 50	250 ± 33	58 ± 16	65 ± 17
12.5	560 ± 50	120 ± 20	42 ± 13	58 ± 16
15.0	835 ± 60	200 ± 30	70 ± 18	18 ± 9
17.5				
Leachate Activity	25 520 ± 750	29 420 ± 810	33 960 ± 870	45 550 ± 1000

* These results, from 20 minutes counting, are expressed as the mean value ± standard error, at 95% confidence limit.

Table 8: Nitric acid extraction of residual Ni⁶³ after water extraction, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ - spiked surface layer of 100% soil (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 Weeks
0	18 930	19 148	18 507	18 083
2.5	998.5	1 080.8	1244.3	1 044.9
5.0	38.3	67.5	73.4	72.4
7.5	15.4	19.7	16.8	25
10.0	5	7.4	7.8	24.1
12.5	1.4	4.2	5.8	1.1
15.0	3.6	2.7	2.7	3.4
17.5				
Total residual	19 977.8	20 330.3	19 857.8	19 253.9
Total water soluble	149	117.16	92.93	74.73
Recovered	20 126.8	20 447.46	19 950.73	19 328.63
Total Ni ⁶³ spiked	22 200	22 200	22 200	22 200
% recovery	90.7	92.1	89.9	87

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Table 9: Nitric acid extraction of residual Ni⁶³ after water extraction, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ - spiked surface layer of 90% soil (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 Weeks
0	19 890	18 969	19 034	18 596
2.5	867.2	1 254	907.1	984.6
5.0	15.9	21.95	26.8	40.32
7.5	6.85	3.95	10.97	6.6 6.85
10.0	3.95	10.97	6.6	
12.5	2.87	3.44	7.97	5.97
15.0	1.75	3.08	3.65	2.83
17.5	2.69	3.19	1.24	2.3
Total residual	19 787.26	20 258.61	19 991.73	19 630.62
Total water soluble	124.3	97.7	93.11	74.5
Recovered	19 911.56	20 365.31	20 084.84	19 713.12
Total Ni ⁶³ spiked	22 200	22 200	22 200	22 200
% recovery	89.7	91.7	90.5	88.8

Table 10: Nitric acid extraction of residual Ni⁶³ after water extraction, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ - spiked surface layer of 100% soil (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 Weeks
0	18 836	19 117	18 467	18 101.3
2.5	989.6	1 102.12	917.3	927.3
5.0	83.6	109.5	79.78	84.93
7.5	50.1	26.56	16.22	17.57
10.0	8.58	7.7	3.44	3.48
12.5	4.54	2.56	2.98	2.83
15.0	2.52	5.05	2.48	3.3
17.5				
Total residual	19 974.94	20 370.49	19 489.2	19 140.71
Total water soluble	108.79	100.13	73.51	61.03
Recovered	20 083.73	20 470.62	19 562.71	19 201.74
Total Ni ⁶³ spiked	22 200	22 200	22 200	22200
% recovery	90.5	92.2	88.1	86.5

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Table 11: Nitric acid extraction of residual Ni⁶³ after water extraction, at different heights in a column of soil (sections 2-7), leached from a Ni⁶³ - spiked surface layer of 100% sludge (section 1), at different times

Column depth (cm)	Radioactivity in d.p.m. × 10 ³			
	1 Week	2 Weeks	4 Weeks	8 Weeks
0	19 969	19 714	19 009	18 427
2.5	769.7	1 062.9	1 416.5	696.25
5.0	28.58	64.89	43.53	280.7
7.5	7.52	9.6	7.79	10.99
10.0	7.02	5.44	2.31	3.5
12.5	5.79	2.12	1.3	1.17
15.0	4.17	1.23	1.56	1.02
17.5				
Total residual	20 791.78	20 860.18	20 481.99	19 420.63
Total water soluble	100.12	74.37	67.73	74.13
Recovered	20 891.9	20 934.55	20 549.72	19 467.76
Total Ni ⁶³ spiked	22 200	22 200	22 200	22 200
% recovery	94.1	94.3	92.6	87.7

Table 12: Distributions and ionic forms of Ni⁶³ activity, leached from soil/sludge column of Ni⁶³ - spiked surface of Ni⁶³ - spiked surface layer, with time

		Surface layer (1)		Lower layers (2)	
		Column (a)	100% soil	100% soil	100% soil
		Column (b)	90% soil, 10% sludge	100% soil	100% soil
Column (c)	100% sludge		100% soil		
Column (d)	100% sludge		100% sludge		
Radioactivity in d.p.m.					
		Cumulative activity	Activity on the last day	Cationic form	Anionic and Neutral form
1 Week	a	42 340	5 630	3 510 (62.3)*	(37.7)
	b	30 250	5 270	3 490(66.2)*	(33.8)
	c	30 600	5 020	2 840(56.6)	(43.4)
	d	25 520	3 190	900(28.2)	(71.8)
2 Weeks	a	43 520	4 680	3 140(67.1)	(32.9)
	b	36 850	4 600	3 600(78.3)	(21.7)
	c	32 980	4 850	3 240(66.8)	(33.2)
	d	29 420	3 430	1 630(47.5)	52.5)
4 Weeks	a	36 080	3 630	2 480(68.3)	(31.7)
	b	36 850	4 370	3 080(70.5)	(29.5)
	c	32 980	4 480	3 210(71.7)	(28.3)
	d	29 420	3 770	1 850(49.1)	(50.9)
8 Weeks	a	36 870	2 710	2 130(78.6)	(21.4)
	b	52 220	3 020	1 860(61.6)	(38.4)
	c	48 680	2 580	1 390(53.9)	(46.1)
	d	45 550	3 880	2 040(52.6)	(47.4)

*Numbers in parentheses expressed as a percentage of total activity on the last day.

carried out on the columns 1, 2, 4 and 8 weeks after spiking. The results are given in Tables 4 to 7 (Fig. 4). The soluble Ni⁶³ activity significantly decreased within each column over 8 weeks and markedly decreased with depths. The activities of the leachate (Fig. 5) from each column

generally increased with time, except for the soil column, indicating that the mobility of Ni⁶³ leached into the amended soil columns was affected by the movement of water through the profile. The water extraction of column sections showed that the 100 % soil column had the highest soluble Ni⁶³

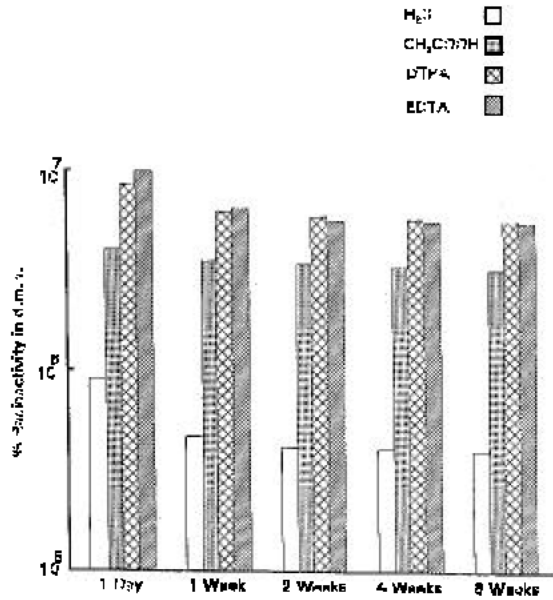


Fig. 1: Variations in extractable Ni⁶³ with time from spiked sludge

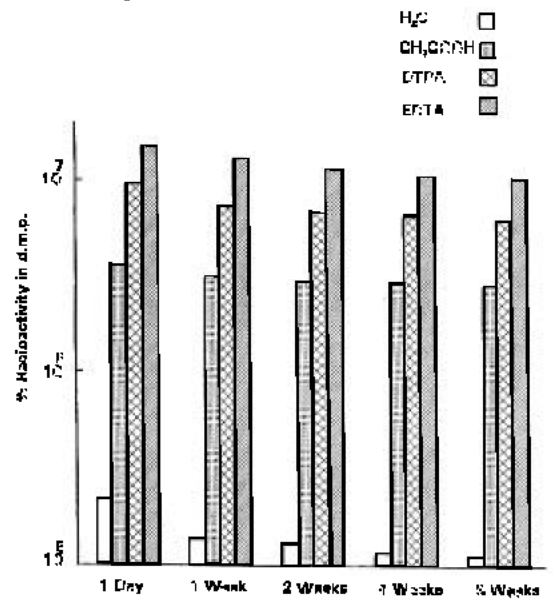


Fig. 2: Variations in extractable Ni⁶³ with time from spiked soil

concentration and the 100 % sludge column, the lowest. The concentrate nitric acid digestion of residual Ni⁶³ was done sequentially after water extraction (Tables 8 to 11 and Fig. 6). The Tables also show the activities of total residual Ni⁶³, total water-soluble Ni⁶³ and initial Ni⁶³ spiked into the surface layer (22.2×10^6 dpm), and the recovered Ni⁶³ activities for all the experiment. In general, much more insoluble Ni⁶³ activity was recovered than water extractable Ni⁶³ activity in each column, the soluble Ni⁶³ activity was about 0.5 % of the total spiked activity, while the recovered insoluble Ni⁶³ activity was about

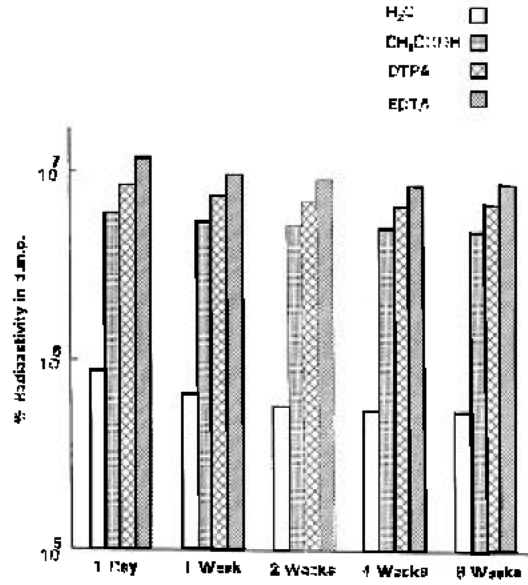


Fig. 3: Variations in extractable Ni⁶³ with time from spiked soil-sludge mixtures (50/50)

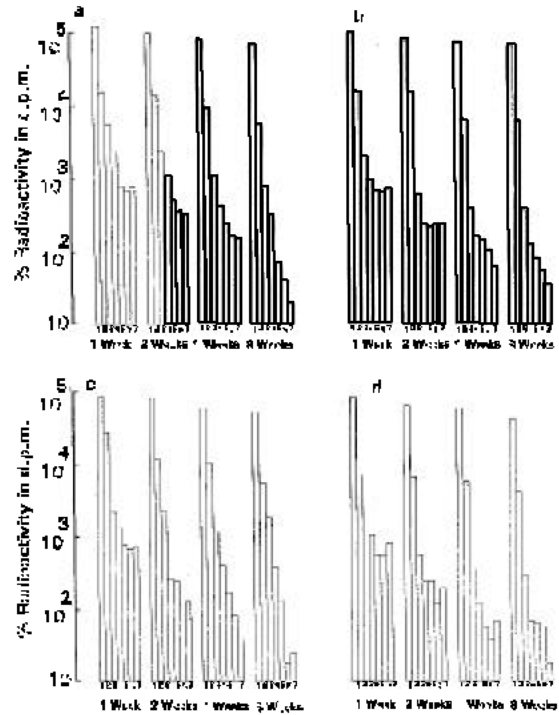


Fig. 4: Water extraction of Ni⁶³, at seven different heights in various soil/sludge columns, leached from a Ni⁶³-spiked surface layer, at different times

- Surface layer (1)
- | | |
|------------------------|---------------|
| a 100% soil | c 100% sludge |
| b 90 soil + 10% sludge | d 100% sludge |
- Lower layers (2-7)
- | | |
|-------------|---------------|
| a 100% soil | c 100% soil |
| b 100% soil | d 100% sludge |

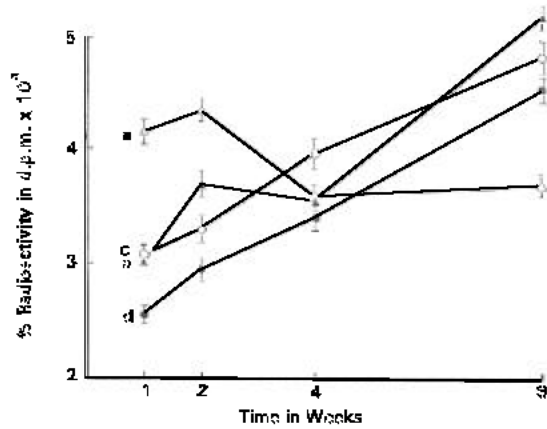


Fig. 5: Leachate radioactivity with time
 Surface layer (1) Lower layers (2-7)
 a. 100% soil 100% soil
 b. 90% soil + 10% sludge 100% soil
 c. 100% sludge 100% soil
 d. 100% sludge 100% sludge

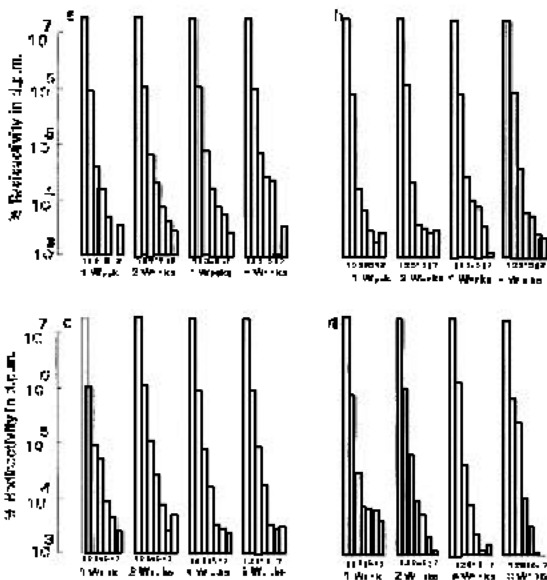


Fig. 6: Nitric acid extraction of residual Ni⁶³ after water extraction, at seven different heights in various soil/sludge columns, leached from a Ni⁶³-spiked surface layers, at different times

Surface layer (1)
 a. 100% soil b. 90% soil + 10% sludge
 c. 100% sludge d. 100% sludge
 Lower layer (2-7)
 a. 100% soil b. 100% soil
 c. 100% soil d. 100% sludge

90 % of the total. There were no significant relationships between the insoluble Ni⁶³ activities recovered from different columns. The recovered activity was irregularly constant for all columns, but the percentage of Ni⁶³ recovered from 100 % soil showed a significant continual decrease with time (from

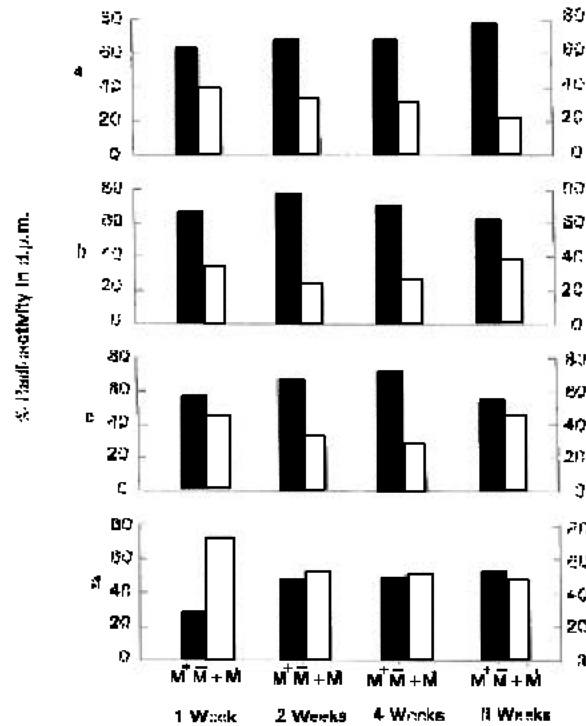


Fig. 7: Ionic forms of Ni⁶³ activity, leached from soil/sludge columns of Ni⁶³ - spiked surface layers, with time

Surface layers (1) Lower layers (2)
 (a) 100% soil 100% soil
 (b) 90% soil, 10% sludge 100% soil
 (c) 100% sludge 100% soil
 (d) 100% sludge 100% sludge

90.7 % to 87 % over 8 weeks) as did that from 100 % sludge (94.1 % to 87.7 %). For soil/sludge mixtures the decrease was irregular. Fig. 5 shows the leachate activities for all four column during the 8 weeks of leaching. Column (c), with 100 % sludge as only the surface layer, and (d), with 100 % sludge in all layers, showed a significant increase in activity by the end of 8 weeks. Column (b), with 90/10 % soil/sludge in the surface layer and 100 % soil beneath, showed an increase after 2 weeks and then a decrease by the fourth week, followed by a marked increase to the highest level of activity by the end of 8 weeks, Column (a), 100 % soil, were different to the others, after 1 week the activity had increased but then markedly decreased by the end of 4 weeks and showed little further change after 8 weeks.

Presence of Ni⁶³ in cationic or anionic forms: The changes, over time, in the ionic forms of Ni⁶³ leached from the soil/sludge columns with Ni⁶³-spiked surface layers are given in Table 12 (Fig. 7). The relative amounts of these forms are expressed as percentages of the total activity on the last day (Table 12). Of the two ion exchange resins used (Dowex 50 and Dowex 1, Table 2) only Dowex 50 removed appreciable amounts of Ni⁶³ from the leachates, indicating that at least some of the Ni⁶³ was present in cationic form. The results also suggested that the percentage of Ni⁶³ in cationic form in the sludge was less than the percentage in cationic form in the soil or mixtures. The activity of cationic forms in 100 % soil

columns (a) increased significantly with time, therefore the non-cationic form must have decreased. The non-cationic activity in the 100 % sludge was initially higher than the cationic and decreased with time, whereas the cationic was initially lower but increased significantly.

Discussion

The results of the extractions of Ni⁶³ from the spiked columns indicated that with increasing time, the amount of water soluble Ni⁶³ in the soil, sludge and mixtures decreased significantly. There could be several reasons, such as the chelation of inorganic nickel to organic compounds, and increase in pH with time, and immobilization of nickel through microbial action (Alloway, 1995). The presented data indicated that a very small fraction of the total Ni⁶³ was present in the water phase. The water solubility of Ni⁶³ appeared to be greater in sludge and sludge treated soil than in soil alone for all incubation times. During the eight weeks the water-soluble percentage varied from 4.2 to 1.8 for sludge, 4 to 2.5 for mixtures and 0.51 to 1.0 for soil. Lindsay (1972) noted that water soluble nickel present in sludge is found at a considerably greater concentration than that present in soil systems. Stover *et al.* (1976), Alloway and Jackson (1991) stated that water solubility of nickel was shown to vary considerably in differences sludge, which implies differences in sludge properties. The proportions of exchangeable Ni⁶³ were measured with an organic acid, acetic acid, they appeared higher in mixtures of soil/sludge than in sludge and soil separately. The percentages for mixtures varied from 8 to 5, for sludge 2 to 8 and for soil 3 to 2. The greater proportion of exchangeable nickel in sludge treated soil (mixture) helped to explain the relatively high mobility of nickel in soil-plant systems. The acetic acid reagent would be expected to extract metals specifically adsorbed to inorganic sites as well as the exchangeable metal. Stover *et al.* (1976) found that acetic acid was quite unsatisfactory for selective extraction of adsorbed metals because it dissolved metal carbonate and some sulfides. Chelating agents such as DTPA and particularly EDTA removed most of the Ni⁶³ bound to organic matter (Essington and Mattigod, 1991). The results of the extractions showed that the soil had most organically bound Ni⁶³ during the whole 8 weeks, even though the organic matter content of this soil was relatively low (4 % L.O.I.). In contrast, the sludge, with nearly eight times more organic matter (32 % L.O.I.), had much lower levels of organically bound Ni⁶³. Stover *et al.* (1976) indicated that the amount of nickel extracted by EDTA (about 32 %) showed that carbonates may play an important role in the complexation of nickel. In this work the percentage removal of organically bound Ni⁶³ by DTPA, during the eight weeks varied from 6 to 8 for soil, 7 to 6 for mixtures and 5 to 7 for sludge. EDTA showed a higher percentage removal as follows 67.4 to 48 for soil, 6 to 3 for mixtures and 44.5 to 62 for sludge. In general, EDTA removed more Ni⁶³ than DTPA, although Ni⁶³ removal by the latter has been found to correlate with plant uptake in some cases. The water extraction of Ni⁶³, leached from the Ni⁶³-spiked surface layers, which was carried out at different times and on sections at different heights in the columns, indicated that the solubility of Ni⁶³ significantly decreased with increasing time in soil, sludge and mixture columns. The solubility of Ni⁶³ also decreased markedly with depths in all the columns. Flemming and Murphy (1968) noted that while the nature of the soil parent material is the major factor determining the general element status of soils, the distribution of the element within the profile is a function of soil character. Increasing the organic matter by adding sludge to the soil also decreased the

Ni⁶³ concentrations in all columns, indicating fixation or complexation of Ni⁶³ by organic matter. The highest percentage of water soluble Ni⁶³ was recovered from the soil column, whereas the lowest from the sludge column. Nitric acid digestion was used as a method of total recovery of Ni⁶³ from the different columns, 86 to 94 % of the total initial Ni⁶³-spiked was recovered. Lagerwerff *et al.* (1976) reported that the changes in heavy metal leachability and extractability from sewage sludge were defined as functions of the combined impact of different weathering processes such as drying, hydrolysis and oxidation. The chelation of soluble Ni⁶³ by organic matter was depended upon time, while chelation of insoluble Ni⁶³ was not, in the former case there was a significant decrease in Ni⁶³ recovery with time, and the latter was irregularly constant. In the leachates from the soil and soil/sludge mixtures there was a greater proportion of cationic species of Ni⁶³ than non-cationic species, but in the sludge only leachates the reverse was initially true but after eight weeks cationic species formed the greatest proportion here as well. Thus, increasing the organic matter content of soil by incorporation of sewage sludge might help to reduce the mobility of nickel and its availability to food crops.

The successful use of the cation exchange resin, Dowex 50, supports the concept that in most of the soil columns, or at least in the sludge columns, part of the soluble or at least in the sludge columns, part of the soluble or exchangeable Ni⁶³ was present as the cation, or as a cationic complex. Shewry and Peterson (1976) indicated the presence of cationic forms of nickel in serpentine soils by using Dowex 50. The advantages of using the present batch ion exchange methods become apparent since the swelling characteristics (Smith, 1974) and slow kinetics of uptake of cations in column ion exchange methods make them more difficult to employ than the conventional ion exchange resins. When ion exchange techniques are used in the field, batch methods are very much more convenient than column methods (Hart and Davies, 1976).

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