

Bioavailabilities of radionuclides and non-radiological contaminants in sediment containing uranium mill tailings

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Abstract: A study was undertaken to investigate contaminant bioavailability in sediment following the addition of uranium mill tailings. Tailings from Ranger Uranium Mine and surface sediments from the Magela floodplain were examined. Tailings buffered pH strongly over the range pH 2.9–5.7 and particularly above pH 3.6. Self-neutralisation of acidified tailings occurred over 2 days and amounted to 0.5–0.8 pH units. Distributions of metals and radionuclides in the solid phases of tailings and sediment were investigated using sequential extraction. In sediment, Mn and Sr reported mainly in exchangeable form while Al, Cr, Cu, Fe, Ni, Pb and U were associated with an oxidisable phase implying an association with organic matter and/or sulphide. Most Ba, Cd and Zn was associated with an easily-reducible fraction. With few exceptions, namely Ba, Sr and Cd, a negligible proportion of metals in tailings was exchangeable and most was found in the residual fraction. Around 30% of total Mn and Pb was in an easily-reducible phase. Over 70% of total ^{226}Ra was exchangeable in tailings and around 35% in sediment. Tailings were added to sediment at various rates and incubated at room temperature for 2 months under water-saturated, oxic and suboxic conditions. The aqueous phase of these mixtures was then separated and the solid phase treated to remove exchangeable forms. Incubation of mixtures of sediment and tailings resulted in the fixing of Cd, Ni, Pb and Zn but small increases occurred in labile Cu and Sr. Anaerobic conditions promoted labile Ba, Sr, Fe and Mn but lowered the concentrations of Cd and Pb. Adding tailings to sediment increased labile Mn and Pb but lowered Fe and Sr. Between 70–86% of labile ^{226}Ra and 72–98% of labile U was fixed but labile ^{210}Pb showed modest increases of as much as 1000 Bq/kg when 40% tailings were present. The concentration of labile U and activities of labile ^{226}Ra and ^{210}Pb were proportional to the addition of tailings but redox conditions only influenced U with anaerobic conditions favouring its fixing in a non-labile form. The increase in labile ^{210}Pb , which was contrary to the net fixing of authigenic Pb, was ascribed to the establishment of isotopic equilibrium by exchange between ^{210}Pb and ^{208}Pb .

1 INTRODUCTION

Ranger Uranium Mine (RUM), operated by Energy Resources of Australia Ltd. (ERA), is situated in the Alligator Rivers Region of the Northern Territory, Australia. The Ranger Project Area, comprising 78 km², is surrounded by Kakadu National Park which has World Heritage listing. Mining by open pit and the processing of ore began in 1981. In January 2000, new Federal Environmental Requirements for RUM came into operation which require that the tailings in the dam are transferred to the mined-out pits on the cessation of mining operations. Prior to this date, the former Environmental Requirements allowed the company the option of rehabilitating tailings in an above-grade repository (ie the tailings dam) subject to certain criteria being met.

After milling, mineralised rock is leached with concentrated sulphuric acid in the presence of pyrolusite, or by Caro's acid, and the pregnant liquor then undergoes solvent extraction and calcination to form U_3O_8 . Waste in the form of tailings is neutralised to pH 4.8-5.0 using lime and pumped to a repository. Until 1996, tailings were deposited in a 107 ha tailings dam with a capacity of $15Mm^3$ and are now placed in a mined-out pit. Typically, over 90% of native U is won with the residual U in tailings associated with recalcitrant minerals such as brannerite (Fordham, 1993). Almost all of the radionuclide burden is transferred to the tailings. For example, around 95% of ^{226}Ra , ^{210}Po and ^{210}Pb is leached by acid treatment but is then distributed largely to gypsum and jarosite phases (Snodgrass et al., 1982).

The work contained in this paper examines some biogeochemical aspects of a speculative breach of an above-grade tailings repository at RUM by describing solid-phase speciation of radionuclides and metals in sediment and tailings and how this might change once tailings and sediment are mixed and deposited in a wetland environment. Previous work (Wasson, 1992) showed that in the event of a breach, tailings would be deposited over a timescale in excess of 1000 y in the wetlands of the Mudginberri Corridor and the southern Magela Floodplain which form part of the Magela Creek catchment. Estimates of the proportion of tailings deposited in sediment on the floodplain range from 0.4% (assuming tailings erode at a similar rate to the surrounding Koolpinya landscape) to 4% at an accelerated 3.5 fold rate (Wasson, 1992). Pathway analysis of radionuclide dispersal in tailings (Akber, 1993) has indicated that the most critical factor determining radiation dose to the public from eroded tailings would likely come from the consumption of aquatic food sources. However, prediction of dose is complex since variability and seasonal change in the chemical environment will influence the bioavailabilities of contaminants. Further, superimposed upon a suite of possible chemical processes which might influence the fate of contaminants in a wetland system are the influences of sedimentation, diagenesis, and biological uptake and cycling over an undefined period of time. Hence, an estimate of public dose from eroded tailings must derive from an understanding of the chemistry of tailings and depositional environment, an assessment of the residence times, forms and labilities of the radionuclides the tailings contain, and the sediment–water column–plant–animal transfer factors involved.

2 EXPERIMENTAL

A sample (20 L) of fresh, limed tailings was obtained from the process stream at Ranger. At the time, Caro's acid was being used as an oxidant to treat ore. The pH of the tailings was 5.70 ± 0.01 and the solids content was $32.5 \pm 1.0\%$. The acid buffering properties of tailings were determined by rapidly titrating a known mass of tailings slurry with 0.01 M HCl. Tailings buffered acidity strongly over the range pH 2.9–5.7, and particularly pH 3.6–5.7, which represents a pH range over which progressive acidification leads to the solution of oxyhydroxide solids

including hematite, ferrihydrite and aluminium hydroxide under oxidising conditions (Brookins, 1988). All three of these minerals are either assumed to be or have been noted as components of tailings at Ranger (Wasson, 1992; Fordham, 1993). Other dominant minerals such as quartz, muscovite and pyrites (Wasson, 1992; Fordham, 1993) which resist dissolution by acid treatment during ore milling will provide surfaces for H⁺ exchange and contribute to pH buffering. The recovery of pH by limed tailings subsequently acidified was examined over 2 days. Following a fast recovery of 0.5–0.8 pH units over 4 h, further increase was more gradual reflecting a kinetically slower rate of neutralisation. When Fordham (1993) examined pH recovery of unlimed acidified tailings at pH 1.8, fast kinetics led to pH 3.6 over the first 32 days with a much slower increase to pH 3.9 over the next 111 days. Self-neutralisation has been ascribed mainly to the breakdown of the brucite layer in chlorite (Fordham, 1993).

All other work involved air-dry tailings. Before the tailings underwent sequential extraction, they were washed thoroughly with deionised water (1:10 solids:solution ratio) and the supernatants discarded until a conductivity of <50 µS/cm was achieved. Surface sediment (0-10 cm) was obtained under saturated conditions from two locations representing a backflow billabong in the Mudginberri corridor and the Magela floodplain which are approximately 10 and 25 km from RUM. The wet sediments (1:1 volume ratio) had a pH of 5.77 and 4.42 and conductivities of 111 and 293 µS/cm respectively. Both sediments had a moderately high organic matter content (19.6% and 15.3% loss on ignition respectively) and a moderately high cation exchange capacity of around 20 cmol₊/kg.

The chemical forms in which solids hold metals may be delineated by sequential extraction of which a variety of schemes exist (Kersten & Förstner, 1995). The procedure used here is described by Kong & Liu (1995). However, the method was modified to exclude the first extractant, NH₄CH₃COO, which specifically removes exchangeable metals. A summary of the specificity of each extractant is summarised in Table 1.

Table 1 Role of extractants in the sequential extraction scheme for metals

Extractant	Speciation in the solid phase
1M NaOOCCH ₃	exchangeable, specifically sorbed and carbonate-bound
0.1M NH ₂ OH.HCl	easily reducible phases (eg MnO _x and freshly precipitated Fe oxyhydroxides)
0.2M (NH ₄ COO) ₂ .H ₂ O	weakly crystalline oxyhydroxides that are moderately reducible
30% H ₂ O ₂	organic matter and sulphides
conc. HNO ₃	Residue

Duplicate samples of <2 mm air-dry sediment and six replicates of tailings were extracted sequentially. Solutions were analysed for Al, Ba, Cd, Cu, Fe, Mn,

Ni, Pb, Sr, U and Zn. The identical procedure was also followed on the same number of replicates to obtain extract solutions for radionuclide determinations.

Tailings were added to air-dry sediment at the rate of 0, 4, 10 and 40% of total mass which, in each case, was 5 g. Quadruplicate treatments were prepared in 50 ml HDPE centrifuge tubes, and each set, consisting of 8 samples (ie. 2 sediments x 4 treatments) placed in a rack. *Milli-Q* deionised water (30 ml) was then added to each tube, shaken and the level marked on each tube with a pen. Each tube was stoppered through which a glass Pasteur pipette was placed to reach below the overlying solution. Each set of tubes was connected, by plastic tubing to each pipette, to a manifold with a valve for each line. Small aquarium pumps served each rack via the manifold. Duplicate treatments were then placed in a fume cupboard at room temperature to provide an oxidising environment whereby ambient air was continuously pumped through the mixtures of tailings and sediments. The remaining two sets of treatments were placed in a glove box at room temperature, evacuated and attached to a supply of high purity N₂ to provide a reducing environment by bubbling ambient N₂ through each tube.

During the course of the experiment, which lasted 2 months, evaporative losses were compensated for by adding deionised water. At the end of the experiment, the tubes were centrifuged and the solutions (hereafter referred to as water extracts) analysed for Fe²⁺, pH, EC, metals (as listed before) and radionuclides. The treatments were then extracted by 1M sodium acetate (NaAc). After centrifuging, the supernatants were analysed for metals and radionuclides.

The preparation of samples for γ -ray spectrometry was based on methods by Pfitzner (1994) and Paulka & Akber (1996) and analysis followed the procedure of Murray et al. (1987). Metals were analysed by ICPMS or ICPAES. Ferrous iron was determined using phenanthroline (APHA, 1989).

3 RESULTS AND DISCUSSION

Given their different modes of occurrence, Island billabong and Magela floodplain sediments showed a strong correspondence in the concentration of individual metals reporting in each fraction (Table 2 & Figure 1). Excluding the residual fraction, three groups of metals in sediment were discerned on the basis of dominant form; an exchangeable fraction (ie Mn and Sr), an easily reduced (oxyhydroxide) fraction (ie Ba, Cd and Zn) and an oxidisable fraction (Al, Cr, Cu, Fe, Ni, Pb and U). Commonly, <20% of total metal was found in the residual fraction. Exceptions were Al (~30%) and Cu (~50%). Radionuclide activities in both sediments were typical of natural background levels (Table 2).

With few exceptions, a negligible proportion of total metal in tailings was exchangeable and in all cases most was found in the residual fraction (Figure 1). This is not surprising given that U ore, from which tailings are derived, is subjected to a concentrated acid leach. The metals which showed a significant presence (arbitrarily >10%) in exchangeable form were Ba, Sr and Cd. Both Ba and Sr form insoluble sulphate salts having a K_{sp} of 1×10^{-10} and 3×10^{-7}

Table 2 Mean total metal concentrations (mg/kg) and radionuclide activities (Bq/kg) in tailings and sediment

Metal	Tailings	Island	F ^l plain	Metal	Tailings	Island	F ^l plain
Al	3344±435	2528	2578	Mn	75±2	58	60
Ba	121±7	18	19	Ni	61±5	11	12
Cd	0.04±0.02	0.07	0.06	Pb	7.3±0.5	8.9	9.5
Cr	23±3	10	11	Sr	1.6±0.1	6.6	6.5
Cu	175±16	5.3	4.8	U	306±16	4.0	3.8
Fe	3946±482	8427	8567	Zn	132±12	20	22
²²⁶ Ra	27225±3520	28±6	36±5	²¹⁰ Pb	20920±1428	58±14	80±21

respectively (Aylward & Findlay, 1984). Unlike other metals, Ba was found to be almost equally distributed between phases (Figure 1). This may imply a source of BaSO₄ in tailings whose solubility was kinetically limited. The mass of Sr in a saturated solution of SrSO₄ is over two orders of magnitude greater than Ba for the corresponding salt and is therefore less likely to cause a residual effect over a sequence of extractants. Cadmium concentrations in each phase were very low.

A relatively large proportion of Mn and Pb in tailings were found in the hydroxylamine fraction (Figure 1). This is expected because hydroxylamine specifically targets easily-reducible MnO_x which is a common product of weathering in soil and rock and Pb is known to have affinity for MnO_x surfaces (Hem, 1978; McKenzie, 1980).

The majority (72%) of ²²⁶Ra in tailings was exchangeable with negligible activity in the oxalate and peroxide fractions (Table 3). Of the remainder, 11% and 15% reported in the hydroxylamine and residual fractions respectively. Most ²¹⁰Pb was recovered in the hydroxylamine and residual fractions (Table 3) in keeping with the pattern shown by authigenic Pb (Figure 1).

Table 3 Mean extractabilities (% of total) of ²²⁶Ra and ²¹⁰Pb in tailings and sediment

Fraction	Tailings		Island		Floodplain	
	²²⁶ Ra	²¹⁰ Pb	²²⁶ Ra	²¹⁰ Pb	²²⁶ Ra	²¹⁰ Pb
NaAc	72	5	35	–	23	21
H ^l amine	11	40	23	–	13	4
Oxalate	<1	4	5	18	15	14
Peroxide	1	4	15	82	12	41
Residual	15	47	23	–	38	20

Addition of tailings to sediment increased (P<0.01) pH but its liming effect was more apparent under oxidising conditions which led to a lower (P<0.001) mean pH compared to reducing conditions. With the exception of Al, Fe and Mn, concentrations of metals in the water extract were very low in the order of 10¹–10² µg per kg solid phase. Redox affected the concentration of Cu (P<0.05), Fe, Pb and U (P<0.001) but not Mn. Iron (II) concentration was doubled under reducing conditions but higher concentrations of Cu, Pb and U were shown in

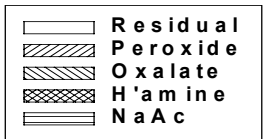
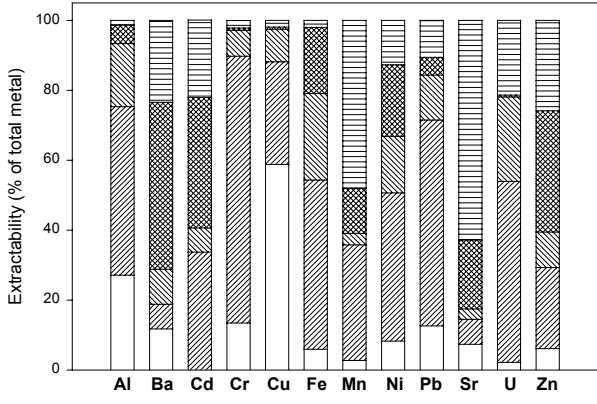
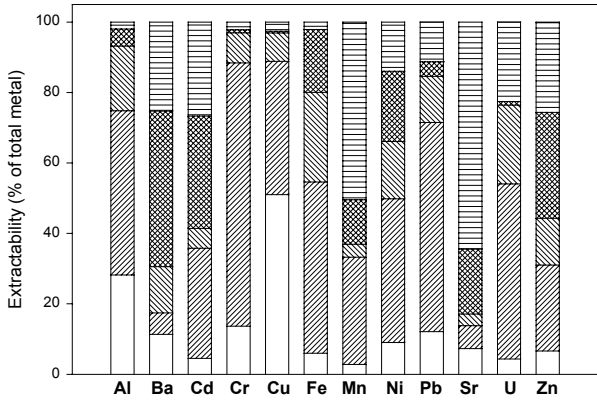
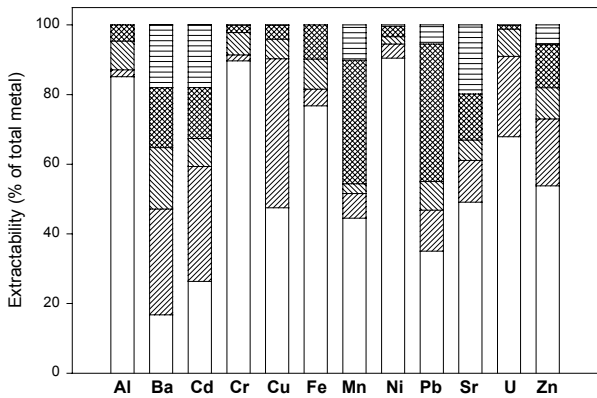


Figure 1 Mean extractabilities of metals from tailings (top) and Island billabong (middle) and floodplain (bottom) sediments

solution under oxidising conditions. Whilst Cd concentration was inversely proportional to tailings addition, U concentration and ^{226}Ra activity increased. At a tailings addition of 40% w/w, ^{226}Ra reached activities of 20–40 Bq/kg.

Compared to the water extract, the greater proportion of metals and radionuclides were contained in a NaAc extractable phase. Hence, the results from incubating sediment and tailings are summarised by accounting for a labile (water + NaAc) fraction (Figure 2). The addition of tailings to sediment increased ($P < 0.001$) labile Mn, Ni, Pb, ^{226}Ra and ^{210}Pb in the order $\text{Ni} < \text{Mn} < \text{Pb} < \text{U} < ^{226}\text{Ra} < ^{210}\text{Pb}$ but decreased ($P < 0.001$) Fe and Sr. Anaerobic as opposed to aerobic treatment led to higher ($P < 0.001$) concentrations of labile Fe and Mn but lower ($P < 0.001$) concentrations of labile Cd, Pb and U.

In terms of the labilities of its non-radiological contaminants and its total metal concentrations, Ranger tailings appear relatively benign. While the total concentrations of Ni, Zn, Ba, and Cu in tailings exceed background levels in surface sediment by about 5, 5, 7 and 30 fold respectively (Table 2), with the exception of Ba (data not given), negligible portions are associated with a labile, NaAc-extractable phase (Figure 1). The key question, however, is whether the labilities of contaminants change once tailings are mixed with sediment and, if so, the implications to ecological and human health. In Figure 2, observed treatment effects can be compared to an expected effect based upon no change to the concentrations of NaAc-extractable metals in tailings and sediment prior to mixing and incubation. Of particular importance are the chemical transformations that metal oxyhydroxides undergo in response to changes in redox potential and pH since their surfaces and mineral lattices host metals in sorbed and occluded forms.

Substantial increases in labile Fe and Al occurred but the pattern to these increases were specific to the sediment, redox treatment and, in the case of Fe, were directly related to the proportion of tailings mixed with sediment (Figure 2). The very close agreement between the observed and the ‘no change’ relationships for Fe in the oxidised floodplain sediment could imply that redox poised at a potential at or above the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple. Moreover, this may suggest this treatment remained oxic according to definitions provided by Sposito (1989) in contrast to the ‘oxidised’ Island billabong sediment which produced a net increase in labile Fe.

The behaviour of Mn appeared different between the sediments. At the end of the incubation experiment, Mn was found to be fixed in the floodplain sediment treatments in a manner inversely proportional to the addition of tailings (Figure 2) but in the treatments containing Island billabong sediment, there was net production of labile Mn with little or no tailings effect. Irrespective of redox treatment, Cd, Ni, Pb and Zn were fixed by incubation with the relative effect greatest for Pb (Figure 2). For Ni, labile concentrations in the Island billabong sediment treatments approached the ‘no change’ value at 40% tailings (ie $\sim 1000 \mu\text{g}/\text{kg}$) but around 50% was fixed in the floodplain sediment treatments. Overall between 5–50% of the labile Zn initially present was fixed but there was a net

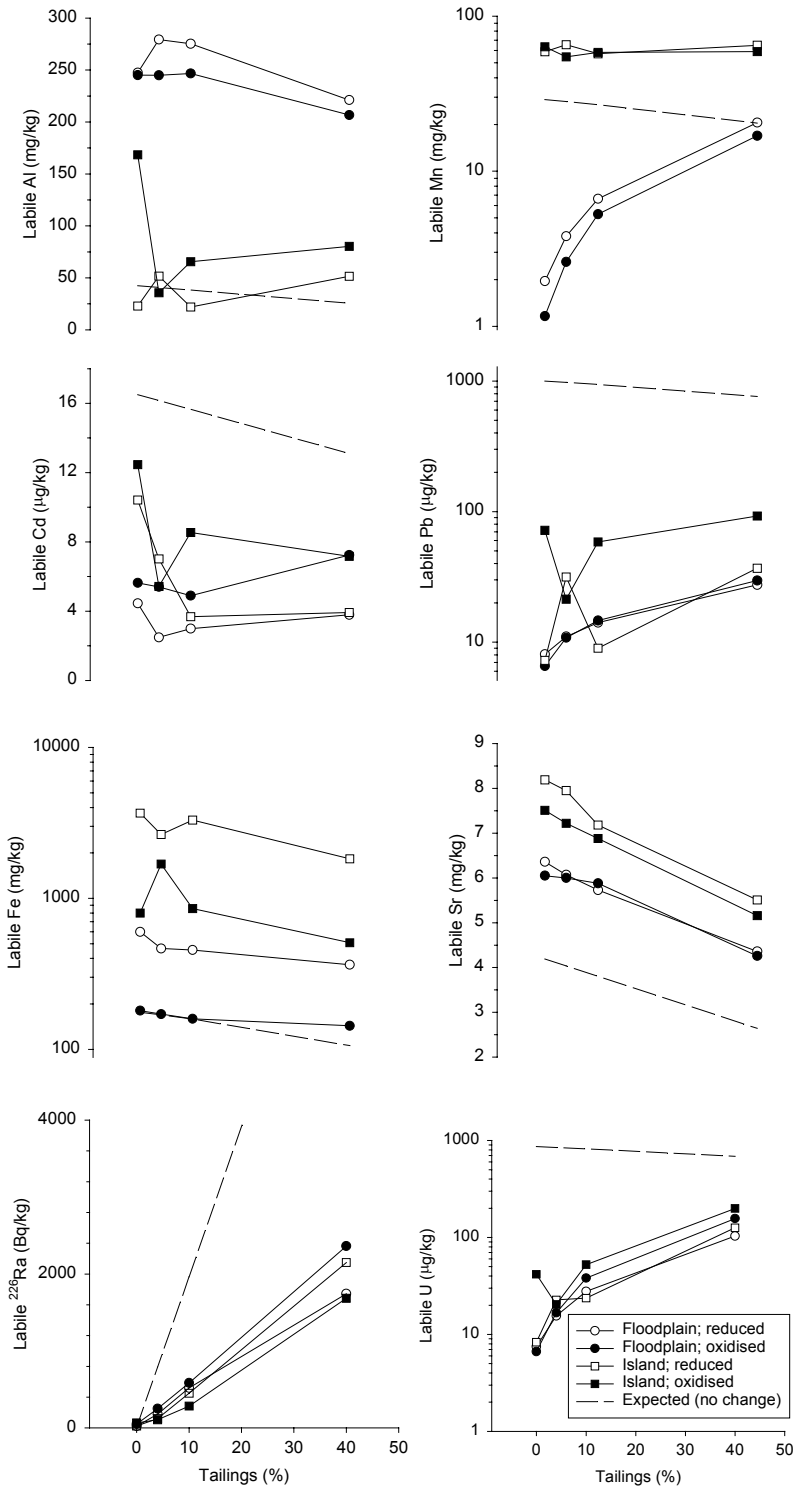
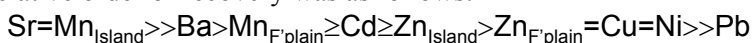
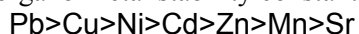


Figure 2 Concentrations of labile metals in mixtures of sediment and tailings (see text for an explanation of the 'no change' line)

release of Cu (1.5–4 fold) (data not given) and Sr (1.5–2 fold) (Figure 2). Virtually all of the total Sr in both sediment treatments and Mn in the Island billabong sediment treatments were accounted for in the labile phase following incubation but the recovery of heavy metals, especially Pb, Cu and Ni was very low. The relative order of recovery was as follows:



The data suggests that the reductive processes undergone in the Island billabong sediment were intense but in conjunction with the release of Sr stresses the relative weakness by which both these ions are complexed by humic material in these organically-rich sediments. Kabata-Pendias & Pendias (1984) have summarised the order of organo-metal stability constants as follows;



which shows good agreement with the relative order of metal recovery in labile form.

The findings contained here agree generally with those of Willett (1992) who examined changes in the distribution of metals by sequential extraction of a range of Magela floodplain sediments mixed and incubated with tailings (0, 0.4 and 4% w/w). In Willett's work, decreases in bioavailable forms of Pb and Zn (principally exchangeable and reducible fractions) and an increase in bioavailable Cu were also found. Willett (1992) attributed the increase in bioavailable Cu to the contribution made by the oxidisable fraction of tailings containing chalcopyrite which makes up a dominant fraction of the total as previously noted in Figure 1.

On the basis of activity, the addition of even small proportions of tailings to sediment would be expected to result in large increases in total activity over background levels but of greater relevance is how this translates into changes in the labilities of radionuclides. In this regard, discussion is restricted to U (^{238}U), ^{226}Ra and ^{210}Pb because these were the only radionuclides having measurable activities in either water-extractable or exchangeable forms following incubation with sediment.

Initially, the addition of tailings to sediment led to increases in reducible and oxidisable U, exchangeable ^{226}Ra and reducible ^{210}Pb (Table 2 & Figure 1). However, by the end of the incubation period the greater part of labile U (72–98%) and ^{226}Ra (70–86%) had been fixed (Figure 2). In contrast to U, ^{226}Ra and authigenic Pb (^{208}Pb), there was net release of labile ^{210}Pb in all the treatments except the reduced floodplain sediment (data not given) suggesting that the chemical/mineralogical associations of ^{210}Pb and ^{208}Pb were different.

There have been relatively few studies in which solid phase speciation of ^{210}Pb has been compared to stable isotopes of Pb in the natural environment using sequential extraction. Cooper et al (1981) found generally that higher proportions of ^{210}Pb compared to authigenic Pb were exchangeable in naturally contaminated sediment and that a high efficiency of extraction by acetic acid implied the potential for ^{210}Pb to migrate (Vos et al., 1983). However, other findings suggest that over 30 years and despite strongly acidic conditions Pb, U

and ^{226}Ra did not leach below 10 cm of a tailings–sediment interface (Jeffrey et al. 1988).

Differences in the chemical behaviour of authigenic as opposed to radiogenic Pb in tailings are to be expected because their extraction during milling is likely to be different. Most authigenic Pb in unweathered Ranger ore is associated with sulphides which will not be taken up by sulphuric acid during milling and hence are likely to remain relatively unaltered in fresh tailings. In contrast, a greater proportion of radiogenic Pb in ore is likely to enter solution, not only because it is closely associated with U-bearing minerals targeted by the milling process, but because some of the ^{210}Pb has already become more mobile as a result of the radioactive decay process. This in turn infers a greater extractability of radiogenic Pb and its sorption by freshly precipitated minerals such as oxyhydroxides and gypsum formed during milling and incorporated into tailings. However, the most probable explanation for the increase in the availability of ^{210}Pb is its isotopic exchange with ^{208}Pb . The total concentration of ^{208}Pb is around 10^6 fold greater and unlikely to be in isotopic equilibrium with ^{210}Pb in fresh tailings. During incubation, the replacement of ^{208}Pb by ^{210}Pb on exchange sites would have been favoured, particularly if a greater proportion of ^{210}Pb was in a potentially labile form, giving rise to an apparent increase in NaAc-extractable ^{210}Pb .

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Przyswajalność biologiczna radionuklidów i nieradiologicznych zanieczyszczeń w osadach zawierających odpady z kopalni uranu

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Streszczenie: Podjęto badania przyswajalności biologicznej substancji zanieczyszczających w osadach odpadów z kopalni uranu. Badano odpady z kopalni uranu Ranger i osady powierzchniowe z równiny zalewowej Magela. Odpady silnie buforowały pH w zakresie pH 2.9-5.7, a zwłaszcza powyżej pH 3.6. Samoneutralizacja kwaśnych odpadów następowała po 2 dniach i sięgała 0,5-0,8 jednostek pH. Dystrybucję metali i radionuklidów w fazach stałych i osadach badano stosując ekstrakcję sekwencyjną. W osadach Mn i Sr występowały głównie w formie wymiennej, podczas gdy Al, Cr, Cu, Fe, Ni, Pb i U związane były z fazą utleniającą się, co wskazywało na ich powiązanie z substancją organiczną i/lub siarczkami. Większość Ba, Cd i Zn związana była z frakcją wysoce podatną na redukcję. Z kilkoma wyjątkami, mianowicie Ba, Sr i Cd, nieznaczna część metali była w opadzie wymienna i większość znajdowała się we frakcji resztkowej. Około 30% całości Mn i Pb znajdowało się w fazie wysoce podatnej na redukcję. Ponad 70% ²²⁶Ra było wymiennych w odpadach a około 35% w osadach. Odpady były dodawane do osadów w różnym stopniu i

utrzymywane w temperaturze pokojowej przez 2 miesiące w warunkach nasycenia wodą, tlenowych i podtlenowych. Faza wodna tych mieszanin była następnie oddzielona a z fazy stałej usunięto formy wymienne. Inkubacja mieszaniny osadu i odpadów doprowadziła do związania Cd, Ni, Pb i Zn, ale mały wzrost odnotowano w labilności Cu i Sr. Warunki anaerobowe były korzystne dla labilnych Ba, Sr, Fe i Mn, ale obniżyły z kolei koncentracje Cd i Pb. Dodanie odpadów do osadu podwyższyło zawartość labilnych Mn i Pb, ale obniżyło Fe i Sr. Około 70-86% labilnego ^{226}Ra i 72-98% labilnego U zostało związanych, ale labilny ^{210}Pb wykazał umiarkowany wzrost wielkości rzędu 1000 Bq/kg przy 40% zawartości odpadów. Koncentracja labilnego U i aktywność labilnego ^{226}Ra i ^{210}Pb były proporcjonalne do dodawania odpadów, lecz warunki redukujące wpływały tylko na U przy warunkach anaerobowych korzystnych dla jego wiązania w formie nielabilnej. Wzrost labilnego ^{210}Pb , który był przeciwny do wiązania autogenicznego Pb, przypisano ustanowieniu równowagi izotopowej poprzez wymianę między ^{210}Pb i ^{208}Pb .