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Nd-Sr isotopic and trace element geochemistry of river sediments and soils in a fertilized catchment, New South Wales, Australia

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Abstract—Neodymium and strontium isotopes and a suite of trace elements have been used to distinguish between the various sources of particulate loads and soils in a major catchment of the Murray-Darling drainage system, the largest river in Australia. One of the goals was to estimate additions of Sr and rare earth elements of anthropogenic (fertilizer) origin to the natural catchment sources to the soils and streams. Among possible sediment sources, Tertiary basalts and Paleozoic metagraywackes have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ and highest ϵ_{Nd} , whereas Paleozoic metapelitic rocks have negative ϵ_{Nd} and the highest $^{87}\text{Sr}/^{86}\text{Sr}$. Phosphate fertilizers have strongly negative ϵ_{Nd} and $^{87}\text{Sr}/^{86}\text{Sr}$ similar to Tertiary seawater. Soils formed on basalt and metagraywacke have compositions that are shifted toward higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower ϵ_{Nd} than their parent rocks. REE patterns and elemental ratios such as Nd/P are also distinctive between fertilizer and natural catchment sources.

Reservoir sediment from the upper catchment have isotopic and trace element compositions that confirm that the dominant source of stream particulates is from basalt soils in the steep upland part of the catchment. Mixing calculations based on isotopic and elemental compositions for reservoir sediment in the upper catchment are consistent with less than 0.2% bulk addition by mass of fertilizer to the natural sediment source. The isotopic compositions of soils in less easily eroded portions of the upper catchment reflect the addition of a component to the soil which is interpreted to be wind-blown dust, derived either from Paleozoic granitoids that dominate the lower regions of the catchment or from more distal westerly sources. Sediment from the lower catchment requires that the dominant source below the reservoir is derived from Paleozoic granitoid and metapelitic rocks of the New England fold belt. The lower catchment sediments show no definitive evidence of either basalt or fertilizer input. Natural sources dominate the particulate loads in these streams. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

Phosphate fertilizers have been implicated in the occurrence of toxic blue-green algal (cyanobacteria) blooms in many Australian rivers during low flow conditions. Phosphorus is considered to be a limiting nutrient to algal growth, and circumstances leading to elevated levels of P are considered to be a major contributing cause of algal blooms (Hecky and Kilham, 1988). In turbid rivers such as those which predominate in Australia, P is overwhelmingly associated with the particulate load (Caitcheon et al., 1995). Understanding the possible sources of P to rivers is consequently a problem that involves tracing the sources of the sediment itself. Because P is monoisotopic, direct stable isotope tracing using this element is impossible. In this paper, radiogenic isotope and trace element geochemical techniques have been used as tracers of the particulate loads of rivers.

The isotopic abundances of naturally occurring radiogenic neodymium and strontium varies between different rock, sediment and soil types. Because of the long half-lives of their parent nuclides ^{87}Rb (4.89×10^{10} years) and ^{147}Sm (1.06×10^{11} years), the isotopic ratios $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are effectively constant over the time scale of recent surficial processes. Nd and Sr isotopes are therefore powerful tracers of the sources of the particulate and dissolved loads of rivers (Goldstein and Jacobsen, 1987, 1988a; Palmer and Edmond,

1992; Andersson et al., 1994; Allégre et al., 1996; Dupré et al., 1996; Edmond et al., 1996). In igneous rocks, much of the Nd and Sr is partitioned into the same phases that contain P, particularly the mineral apatite or volcanic glass (Hofmann and White, 1982; McDonough et al., 1985; Sun and McDonough, 1989; Price et al., 1991). Chemical weathering may serve to change the Sr and Nd isotopic compositions of weathered relative to unweathered materials by preferential weathering of primary minerals with different Rb/Sr and Sm/Nd, such as plagioclase, pyroxene or amphibole (Graustein and Armstrong, 1983; Aberg et al., 1989; Graustein, 1990; Price et al., 1991; Blum et al., 1993; Miller et al., 1993; Douglas et al., 1995; Taylor and Blum, 1995; Borg and Banner, 1996; Bullen et al., 1996, 1997). When liberated during chemical weathering, these elements are either released to solution, taken up in new minerals, or trapped by adsorption onto the surface of particles.

Phosphate fertilizers are widely applied in agricultural areas of Australia to counteract the naturally low available P content of most soils. Most phosphate fertilizers are produced from phosphorites or from guano deposits from a variety of locations around the world, such as continental margin deposits in Jordan, west Africa and the southeastern U.S.A., or from ocean islands in the Pacific Ocean (Nauru Island) or Indian Ocean (Christmas Island), and therefore represent an additional possible source of Nd and Sr in catchments. These fertilizers should retain isotopic and elemental abundances characteristic of their sources, which may be distinct from the natural sources in the catchment. Thus, geochemical tracing using Sr and Nd

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isotopes can in some cases be used to investigate anthropogenic as well as natural sources to streams (Martin and McCulloch, 1995; Négrel and Deschamps, 1996).

It has been suggested that the Nd isotopic compositions of soils predominantly reflect the provenance of the components of the soil (Borg and Banner, 1996), whereas their Sr isotopic compositions can also be affected by preferential weathering and cation exchange processes (Miller et al., 1993; Borg and Banner, 1996; Bullen et al., 1997). Because the suspended load of rivers is derived from material which has been subjected to a combination of physical and chemical weathering, it is reasonable to assume that, as for soils, suspended sediments should have Nd isotopic compositions that reflect their source components, whereas their Sr isotopic compositions will be affected by weathering and exchange processes in addition to source variations.

Trace elements, particularly the rare earth elements (REEs), have been used extensively to investigate the processes involved in weathering. Although the REEs in many weathering studies have shown little fractionation, there are subtle differences which can develop, predominantly an enrichment in the light REE (LREE) in the residual and neoformed solid phases of weathering and soil formation (e.g., Nesbitt, 1979; Duddy, 1980; Nesbitt et al., 1980; Sawka et al., 1986; Eggleton et al., 1987; Banfield and Eggleton, 1989; Braun et al., 1993; Prudêncio et al., 1993; Daux et al., 1994; Rasmussen and Glover, 1994; Schaltegger et al., 1994; Öhlander et al., 1996; Rasmussen, 1996). Furthermore, riverine dissolved loads are generally enriched in heavy REE (HREE) when compared to the suspended loads (Goldstein and Jacobsen, 1988b; Brookins, 1989; Elderfield et al., 1990; Wood, 1990; Sholkovitz, 1992, 1995; Johannesson et al., 1996), due to the greater stability of HREE in solution. The REE patterns of the particulate loads of rivers therefore reflect both the sources and their integrated weathering history. Other trace elements, such as U (Periáñez and Martínez-Aguirre, 1997; Zielinski et al., 1997), Mo, and Cd, are enriched in phosphate fertilizers relative to most natural sources and may also be used to trace their influence in surficial materials.

In this study, Nd and Sr isotopes and trace elements are used to investigate the provenance of riverine sediments in a headwater catchment and the lower reaches of the Namoi River of southeastern Australia. The effects of fertilizer addition on the isotopic and trace element composition of the sediments is assessed, and the results are related to the sources of particulate P to rivers. The sources contributing to the soils in the upper catchment are also discussed.

2. SAMPLES AND ANALYTICAL METHODS

The catchment area under primary consideration in this study is that of the Chaffey Reservoir. Located in northern New South Wales (Fig. 1a) the Peel River has its headwaters in the Great Dividing Range and flows into Chaffey Reservoir approximately 25 km downstream. The reservoir has experienced problems with toxic blue-green algal (cyanobacteria) blooms since its completion in 1979 (Caitcheon et al., 1995). Below the reservoir, the Peel River flows inland to join the Namoi River, which itself flows into the Barwon-Darling River, part of the largest river system in Australia.

Chaffey Reservoir catchment is comprised of two dominant lithologic types (Fig. 1b) (Caitcheon et al., 1995). Tertiary basaltic rocks are present as the caprock of the Liverpool Ranges, and outcrop exclusively in the southern and western upland part of the catchment. Lower in the catchment, the most abundant rocks are mid to late Paleozoic metasedimentary rocks. Soils have formed on both rock types. In the field, soils are broadly categorized as "basaltic" or "metasedimentary" on the basis of the lithology of the nearest outcrops or physical characteristics (color and texture), and they will be referred to in this way throughout the paper.

The sampling locations are shown in Fig. 1. Samples of soils and rocks from the catchment, sediments from cores taken in Chaffey reservoir, and a suspended sediment sample from the Namoi River near its confluence with the Barwon River were collected by researchers from the Division of Water Resources at CSIRO. In most cases, rock and soil samples from the same locality were analyzed. The soils were separated into coarse ($>63 \mu\text{m}$) and fine ($<63 \mu\text{m}$) size fractions. As the main purpose of this study was to investigate the sources of the reservoir sediment, which has a grain size of $<20 \mu\text{m}$, only the fine size fractions of the soils were analyzed for their Nd-Sr isotope and trace element compositions. Two additional soil samples were composites taken from several sites in the catchment. The composite soils were combined and homogenized and then separated into size fractions. The 2–10 μm size fraction of the metasedimentary soil composite and the $<2 \mu\text{m}$ size fraction of the basaltic soil composite were analyzed. Because these composites are averages of a number of localities in the catchment, they should provide a reasonable estimate of the spatially averaged isotopic composition of the different soil types in the catchment. The Chaffey reservoir sediments were taken from cores located at different sites in the reservoir. The 10–12 cm interval of the core nearer to the inlet and the 0–2 cm interval of the more centrally located core were analyzed.

Some areas of the Chaffey Reservoir catchment, particularly in the western side and the lowlands, have had phosphate fertilizer applied to them for over 40 years (Caitcheon et al., 1995). The levels of fertilizer use for 1984–1995 (as compiled by the Landholders of the Chaffey Catchment: T. Donnelly, pers. comm.) are shown in Fig. 1b. A group of the fertilizers with variable phosphorus concentration (Table 1) that have been used in the catchment were analyzed to assess their importance as sources of trace elements and P to the reservoir sediments and soils.

Rock, soil and sediment samples were analyzed for their Nd and Sr isotope compositions and trace element concentrations. Most of these samples had been processed and analyzed previously for their major element compositions (J. Olley and G. Caitcheon, pers. comm.). In addition, the mineralogy of three basaltic soils, three metasedimentary soils and one of the Chaffey reservoir sediments were determined by XRD in the Geology Department at the ANU. Samples of 50–100 mg

Fig. 1. (a) Maps showing the locations of the Namoi catchment within the Murray-Darling Basin of Australia and the Chaffey Reservoir catchment within the Namoi. (b) Maps of Chaffey Reservoir catchment. Sampling locations are shown in both (a) and (b). Symbols are: basalt (closed circle), metasedimentary rock (closed square), basaltic soil (open circle), sedimentary soil (open square), Chaffey Reservoir sediments (cross), and Namoi river sediment (inverted triangle). Half filled circles and squares indicate sites where both soil and rock were sampled. Small, unnumbered symbols indicate localities of samples that were combined to make soil composites. Inset maps of Chaffey catchment show the location of basaltic outcrop (in black) in the upper catchment (after Caitcheon et al., 1995) and the application rates of fertilizer for the years 1984–1994 (compiled by T. Donnelly, 1995, from data provided by the Landholders of the Chaffey Catchment).

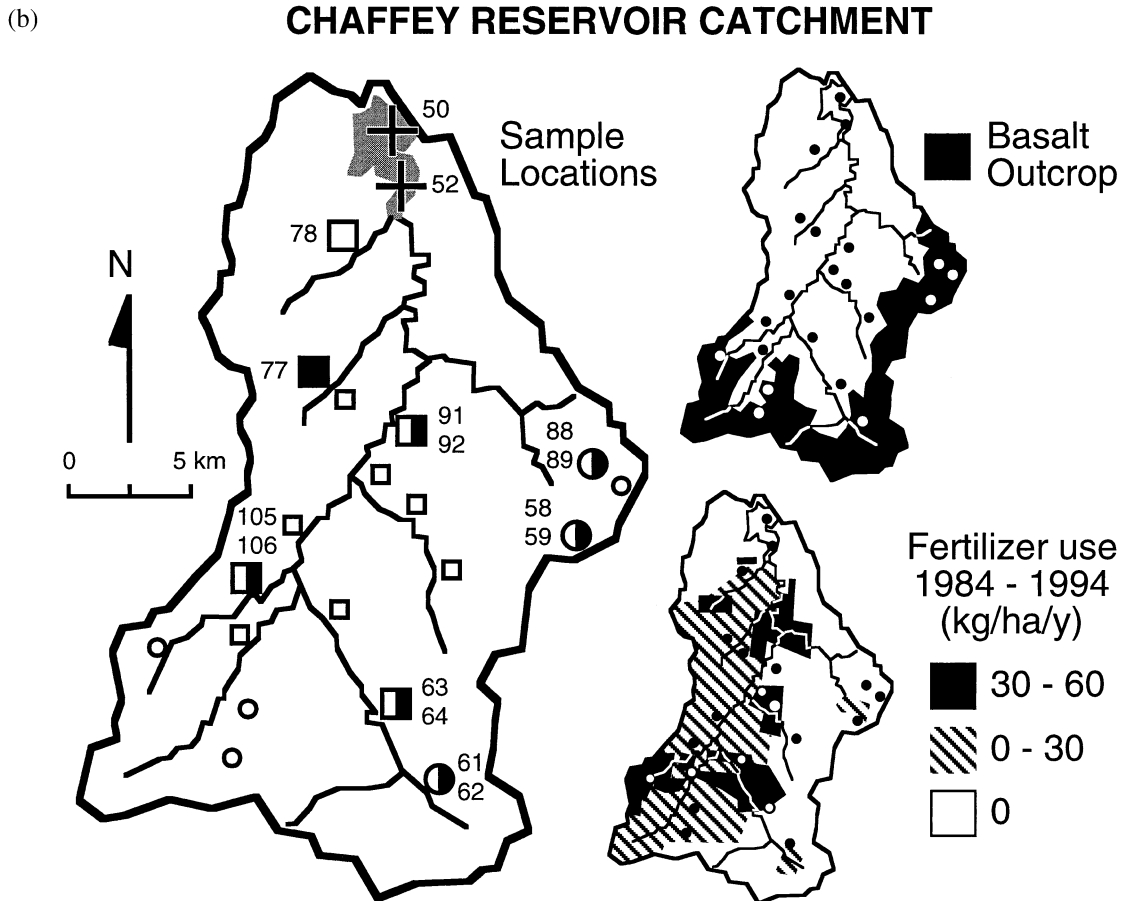
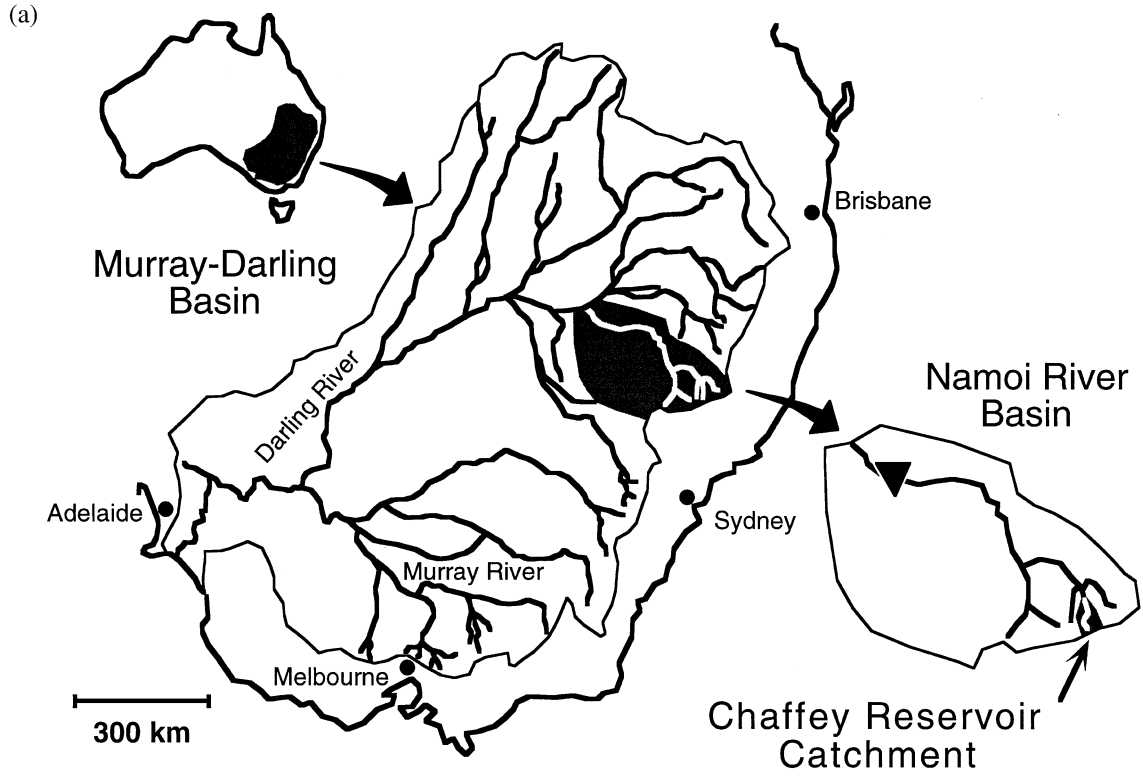


Table 1. Major and trace element and isotope data for Namoi catchment rocks, soils, and sediments, and fertilizers.

Sample# Type	CM93059 basalt	CM93062 basalt	CT93089 basalt	CM93064 metapelite	CT93077 metagraywacke	CM93092 metagraywacke	CM93106 metapelite
Li	7.05	5.26	7.78	79.0	15.0	14.8	39.7
Ti	13829	13120	9371	9280	3379	8811	5712
Zn	93.0	91.0	111	131.3	47.4	103.1	56.3
Rb	27.1	14.65	5.53	118.9	34.1	15.7	77.5
Sr	863	860	335	293	401	245	131
Y	25.9	24.1	20.8	43.45	7.96	26.97	20.64
Zr	214.5	160.5	95.7	270.3	72.4	98.7	169.6
Nb	81.9	50.8	21.6	13.92	3.8	2.56	9.7
Mo	0.413	0.515	0.542	0.459	0.322	0.272	0.141
Cd	0.0906	0.053	0.044	0.104	0.0052	0.0494	0.0657
Ba	408	336	209	485	473	288	237
La	35.8	23.4	10.3	31.72	9.71	7.93	15.27
Ce	67.6	45.9	20.5	59.8	23.2	19.2	44.6
Pr	7.96	5.50	2.66	8.91	3.19	2.80	4.30
Nd	30.6	22.0	11.8	35.3	13.0	13.2	16.7
Sm	6.27	4.98	3.27	7.89	2.87	3.69	3.88
Eu	2.11	1.73	1.20	1.979	0.827	1.244	0.885
Gd	5.97	5.08	3.74	7.41	2.44	4.18	3.63
Tb	0.859	0.777	0.629	1.20	0.349	0.689	0.593
Dy	4.73	4.38	3.78	7.30	1.76	4.33	3.48
Ho	0.922	0.872	0.778	1.55	0.311	0.932	0.717
Er	2.44	2.35	2.14	4.56	0.785	2.75	2.02
Yb	2.08	1.98	1.81	4.44	0.593	2.51	1.95
Lu	0.3	0.286	0.266	0.671	0.088	0.376	0.29
Hf	4.28	3.31	2.27	6.70	2.10	2.57	4.10
Ta	5.60	3.02	1.29	1.111	0.318	0.159	0.758
Pb	2.23	2.13	1.13	19.4	11.4	4.06	11.4
Th	4.46	2.59	1.2	10.63	1.95	1.27	4.6
U	1.22	0.728	0.397	2.31	1.42	0.52	1.55
SiO ₂	44.06	45.30		60.72	68.22	60.3	60.84
Al ₂ O ₃	14.18	14.54		17.04	15.31	16.32	16.84
Fe ₂ O ₃	12.24	11.99		7.41	3.17	7.12	6.93
MgO	9.66	9.63		2.08	0.90	2.50	1.85
CaO	9.16	9.42		1.43	0.42	1.66	0.74
MnO ₂	0.19	0.20		0.007	0.04	0.14	0.09
Na ₂ O	2.45	2.58		2.02	5.24	5.33	1.42
K ₂ O	1.24	0.86		2.14	2.48	0.39	2.48
P ₂ O ₅	0.74	0.46	0.22 ^a	0.15	0.14	0.31	0.15
LOI	4.06	3.20		6.14	3.52	4.75	7.85
⁸⁷ Sr/ ⁸⁶ Sr	0.703228	0.703330	0.703446	0.712373	0.705374	0.705658	0.714830
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512935	0.512897	0.512953	0.512426	0.512847	0.512882	0.512369
ε _{Nd} (0)	5.79	5.06	6.14	-4.13	4.08	4.76	-5.24

were spiked with mixed ⁸⁴Sr-⁸⁵Rb and ¹⁵⁰Nd-¹⁴⁷Sm spikes, dissolved in teflon bombs using a mixture of nitric and hydrofluoric acids, and separated using cation exchange chromatography. Nd and Sr isotopic compositions were determined on the Finnigan MAT 261 thermal ionization mass spectrometer at the Research School of Earth Sciences. Usual in-run precisions of better than ±0.00002 were obtained on ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios. Sr isotope ratios were normalized to ⁸⁶Sr/⁸⁸Sr = 0.1194. The NBS-987 Sr standard analyzed during the course of the study gave an average value of 0.710197 ± 34 (2 σ, n = 4). Repeat analyses of the nNd-1 standard over the course of this study gave an average ¹⁴³Nd/¹⁴⁴Nd of 0.512188 ± 7 (2 σ, n = 7).

Concentrations of REEs, Rb, Sr and other selected trace elements were determined on a VG PQ2 ICP-MS, using methods outlined by Eggins et al. (1997). Separate splits of approximately 100 mg were digested and then taken up in 2% nitric acid. Chemical procedural blanks for both the TIMS and ICP-MS procedures were insignificant for all the elements determined. The internal standard solution, used as a drift monitor, and added to a level of 5 wt.% of the final solution, contains ⁶Li, ¹¹⁵In, ¹⁴⁷Sm, ¹⁶⁹Tm, and ²⁰⁹Bi, ⁸⁴Sr, ¹⁰³Rh, natural Re, and ²³⁵U. An in-house rock standard (a Kilauea East Rift basalt) and the international rock standard BHVO-1 were analyzed at the start of and interspersed through the session and used as calibration standard and accuracy monitor. In addition, one of the samples was run repeatedly

during the session and used as an external drift monitor. Uncertainties in the concentrations are better than 5% for all the elements reported.

Several samples were subjected to one or two leaching procedures. The first leachate solution consisted of a mixture of 4 mL 0.1 N HCl and 0.1 mL 30% H₂O₂. This solution was allowed to react with approximately 200 mg of sample powder for 2 hours (at ~40°C), and then the solids were removed by centrifugation. In a few cases, the residual solids were subjected to a subsequent leach with 1N HCl, that was gently warmed (to ~40°C) on a hotplate for 1 h and allowed to sit overnight at room temperature before centrifuging. Leachate solutions were split; about half was taken for Nd and Sr isotopic composition and the remainder analyzed for trace elements by the procedures described above. Concentrations for the leachates are reported relative to the original powder mass. The leaching procedure is not intended to simulate natural weathering processes within the catchment but to give an indication of the relative solubility of the elements in the samples.

3. RESULTS

3.1. Rocks

Elemental concentrations and Nd-Sr isotopic compositions of the rock, soil and sediment samples are listed in Table 1. The

Table 1. (Continued)

Sample# Type	CM93058/1 basaltic soil 0–6 cm	CM93061/1 basaltic soil 0–6 cm	CM93088/1 basaltic soil 0–5 cm	59 composite basaltic soil <2 μm	CM93063/1 metased soil 0–6 cm	CT93078/1 metased soil 0–6 cm	CM93091/1 metased soil 0–5 cm	CM93105/1 metased soil 0–6 cm	69 ss comp metased soil 2–10 μm
Li	0.861	6.63	2.21		22.8	37.4	30.9	38.1	37.3
Ti	26829	18844	11355		6395	4969	8419	5974	7133
Zn	123	179	175		59.7	117	39.6	126.8	144
Rb	25.1	28.1	12.58	40.3	38.5	53.0	16.2	78.3	82.3
Sr	76.0	305	95.1	256	63.0	182	35.0	104	152
Y	20.2	24.9	177		16.0	28.4	21.7	20.3	24.4
Zr	498	193	184		222	181	234	235	137
Nb	109	71.1	41.1		11.3	7.75	10.3	11.3	9.90
Mo	0.486	0.263	0.27		0.373	1.07	0.354	0.254	0.874
Cd	0.19	0.111	0.0694		0.0956	0.127	0.0612	0.0811	0.121
Ba	200	341	185		158	270	182	228	312
La	33.25	26.12	80.57		10.4	17.2	10.5	12.9	19.0
Ce	60.6	42.8	56.7		22.6	36.4	16.1	29.3	39.7
Pr	6.98	6.25	23.6		2.62	4.80	3.20	3.16	4.75
Nd	25.2	24.6	105	23.0	9.80	19.9	13.2	12.4	18.5
Sm	4.97	5.51	30.1	4.95	2.15	4.60	3.16	2.87	4.00
Eu	1.38	1.89	10.7		0.517	1.18	0.749	0.697	1.02
Gd	4.4	5.38	32.6		2.13	4.43	3.16	2.80	3.71
Tb	0.667	0.817	5.41		0.376	0.731	0.53	0.498	0.617
Dy	3.7	4.58	31		2.36	4.32	3.33	3.21	3.82
Ho	0.717	0.874	6.01		0.525	0.925	0.702	0.706	0.802
Er	1.93	2.3	15.7		1.61	2.68	2.09	2.20	2.30
Yb	1.67	1.87	11.4		1.71	2.53	2.00	2.24	2.24
Lu	0.242	0.266	1.67		0.261	0.396	0.318	0.367	0.350
Hf	9.88	3.69	4.25		5.15	4.52	5.63	5.71	3.59
Ta	5.87	4.15	2.74		0.845	0.56	0.765	0.930	0.719
Pb	11.3	8.40	7.07		7.90	12.5	4.20	13.2	25.5
Th	8.09	3.24	4.55		3.86	5.39	2.73	5.72	6.88
U	2.52	1.00	1.13		1.09	1.24	0.850	1.48	1.68
SiO ₂	52.28	51.27	52.58	50.43	80.56	62.95	80.65	68.41	70.94
Al ₂ O ₃	16.68	15.01	19.25	22.57	9.84	15.92	9.62	15.98	14.37
Fe ₂ O ₃	17.40	13.05	13.79	11.92	3.22	6.29	3.04	6.75	5.00
MgO	0.71	2.96	1.17	3.23	0.48	1.29	0.46	1.40	0.83
CaO	0.85	3.11	1.27	2.29	0.39	2.02	0.42	0.62	0.72
MnO ₂	0.52	0.18	0.21	0.39	0.08	0.11	0.05	0.09	0.13
Na ₂ O	0.40	1.78	0.73	1.80	1.10	1.81	1.00	1.10	1.48
K ₂ O	0.46	1.45	0.52	1.23	1.10	1.88	0.78	2.12	1.57
P ₂ O ₅	0.42	0.69	0.40	0.51	0.16	0.23	0.11	0.21	0.23
LOI	5.75	6.97	7.55	3.35	2.01	6.59	2.43	2.18	3.42
⁸⁷ Sr/ ⁸⁶ Sr	0.707916	0.703718	0.705253	0.705603	0.711783	0.708446	0.708457	0.714784	0.709646
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512647	0.512875	0.512872	0.512754	0.512322	0.512511	0.512513	0.512356	0.512501
$\epsilon_{\text{Nd}}(0)$	0.18	4.62	4.56	2.26	-6.16	-2.48	-2.44	-5.50	-2.67

Nd-Sr isotopic data (Fig. 2) encompass a large range for the different rock and soil types. The Tertiary basalts are all isotopically very similar and have the lowest measured ⁸⁷Sr/⁸⁶Sr (0.70323–0.70345) and highest ¹⁴³Nd/¹⁴⁴Nd (0.51290–0.51295) in the catchment. These isotopic compositions are similar to other Tertiary basalts in eastern Australia (McDonough et al., 1985; Ewart et al., 1988; Price et al., 1991; O'Reilly and Zhang, 1995). The Paleozoic metasedimentary rocks have higher ⁸⁷Sr/⁸⁶Sr and lower ¹⁴³Nd/¹⁴⁴Nd than the basalts and fall into two categories. One group, referred to hereafter as metagraywackes, has isotopic compositions similar to other metamorphosed graywacke sandstones in the New England fold belt (Hensel et al., 1985), that are composed of volcanic detritus. The second group of metasedimentary rocks, referred

to hereafter as metapelites, has more extreme Sr-Nd isotopic compositions that are typical of upper crustal derived pelitic sediments (Hensel et al., 1985).

The REE patterns of the rocks are shown in Fig. 3 normalized to the values in Post-Archean Australian Shale (PAAS; McLennan, 1989). The basalts all have very similar amounts of HREE with variable degrees of LREE depletion (Fig. 3a). The metasediments are LREE depleted and much more variable in HREE (Fig. 3b). One metagraywacke (sample 77) has a relative HREE depletion, whereas the other metasedimentary rocks have HREE enrichment. (Note: Specific samples will be referred to hereafter by the last two or three digits of their sample number designation in Table 1.) All the rocks have a positive Eu anomaly (Eu/Eu*, defined as $\text{Eu}_{\text{norm}}/(\text{Sm}_{\text{norm}} \times \text{Gd}_{\text{norm}})^{0.5}$)

Table 1. (Continued)

Sample# Type	CT93050/6	CM93052/1	DR94051-55						
	Chaffey sed 10-12 cm	Chaffey sed 0-2 cm	Namoi River sediment	F#1 fertilizer	F#3 fertilizer	F#5 fertilizer	F#12 fertilizer	F#13 fertilizer	F#22 fertilizer
Li	15.3	15.0	29.5	3.07	0.440	0.440	107	1.34	0.624
Ti	14335	13995	6817	212	297	189	1165	68.0	224
Zn	131	138	95.3	90.5	263	248	289	46.3	372
Rb	18.7	25.7	68.5	8.72	0.241	0.490	22.6	3.88	0.839
Sr	394	247	134	46.7	243.7	179	1028	18.1	145
Y	28.6	30.7	31.3	86.0	5.23	16.5	229	33.2	10.7
Zr	184	177	199	154	7.76	23.6	67.6	8.02	4.37
Nb	50.7	41.6	20.8	0.700	1.09	0.700	3.54	0.303	0.748
Mo	1.07	0.23	0.786	11.5	7.42	0.877	25.9	4.38	4.50
Cd	0.062	0.0958	0.0476	2.18	8.94	12.0	5.43	1.04	11.6
Ba	327	266	301	6.74	30.1	10.1	71.7	2.55	8.10
La	25.2	22.4	27.6	9.99	1.55	6.77	86.7	2.91	4.67
Ce	52.1	44.3	59.0	11.9	2.30	8.53	124	3.34	7.11
Pr	6.44	5.88	7.33	1.65	0.213	1.37	17.8	0.474	0.922
Nd	26.3	24.0	28.8	7.36	0.932	5.64	75.4	2.09	3.94
Sm	5.93	5.70	6.15	2.16	0.203	1.18	17.4	0.651	0.818
Eu	2.03	1.82	1.49	0.59	0.0513	0.271	3.82	0.181	0.186
Gd	5.86	5.82	5.55	3.65	0.262	1.36	18.6	1.16	0.925
Tb	0.909	0.891	0.886	0.643	0.0419	0.210	2.99	0.219	0.148
Dy	5.20	5.26	5.21	4.83	0.282	1.33	18.9	1.69	0.926
Ho	1.03	1.07	1.07	1.37	0.0744	0.324	4.56	0.489	0.220
Er	2.74	2.90	3.02	4.79	0.228	0.976	13.6	1.79	0.617
Yb	2.33	2.53	2.80	7.64	0.258	0.852	15.4	2.98	0.579
Lu	0.340	0.375	0.427	1.39	0.0447	0.138	2.62	0.554	0.091
Hf	3.92	3.78	4.78	0.233	0.170	0.465	1.141	0.133	0.083
Ta	2.93	2.47	1.38	0.025	0.081	0.0616	0.22	0.0092	0.043
Pb	16.4	7.70	18.3	1.58	0.951	3.30	14.47	0.703	2.40
Th	3.29	3.28	9.08	8.14	0.375	0.886	15.5	3.09	0.909
U	0.982	0.889	1.96	186	37.6	29.9	349	81.1	33.1
SiO ₂	51.56	54.67	59.64						
Al ₂ O ₃	17.94	15.52	16.58						
Fe ₂ O ₃	12.74	12.36	7.84						
MgO	3.18	2.60	1.78						
CaO	3.63	2.88	1.11						
MnO ₂	0.23	0.21	0.11						
Na ₂ O	1.65	1.82	0.9						
K ₂ O	1.03	1.24	1.52						
P ₂ O ₅	0.43	0.43	0.17	46.1	19.3	12.7	48.4	21.3	16.4
LOI	5.12	5.97	9.06						
⁸⁷ Sr/ ⁸⁶ Sr	0.704043	0.704583	0.708791	0.708800	0.708071	0.709022	0.708782	0.708573	0.709020
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512847	0.512805	0.512513	0.512304	0.512346	0.512246	0.512279	0.512305	0.512300
ε _{Nd} (0)	4.08	3.26	-2.44	-6.51	-5.7	-7.65	-7	-6.5	-6.59

* Trace element concentrations in ppm, major elements (G. Caitcheon, pers. comm., except fertilizer P) in %. $\epsilon_{Nd}(0) = ((^{143}Nd/^{144}Nd)_{\text{measured}} / (^{143}Nd/^{144}Nd)_{\text{CHUR}} - 1) \times 10^4$, and $(^{143}Nd/^{144}Nd)_{\text{CHUR}} = 0.512638$. ^aestimated from data in the literature (McDonough et al., 1985, Hensel et al., 1985 and references therein).

for PAAS normalized concentrations, e.g., McLennan, 1989), reflecting a relative enrichment in plagioclase feldspar compared to typical upper crust.

3.2. Soils

Both the basaltic and metasedimentary soils have a large range of isotopic composition. Figs. 4a and 4b show the Nd and Sr isotopic compositions of soils compared to rocks taken from the same locality. For one basalt rock/soil (61/62) and one metapelite rock/soil pair (105/106), the Nd and Sr isotopic compositions are nearly identical to the rock from the same locality. The other soils, both basaltic and metasedimentary, are displaced toward significantly lower ¹⁴³Nd/¹⁴⁴Nd compared to

the rocks from the same locality. The soils related to the basalts and metagraywacke have significantly higher ⁸⁷Sr/⁸⁶Sr than the associated rock, whereas the soils related to the metapelite has a similar but slightly lower ⁸⁷Sr/⁸⁶Sr than the associated rock. The <2 μm fraction of the basalt soil composite falls within the isotopic range defined by the <64 μm fractions of the individual surface soil samples (Fig. 2). Similarly, the 2-10 μm fraction of the metasedimentary soil composite has Nd and Sr isotopic compositions that are within the range defined by the individual surface soil samples.

The mineralogy of six soil samples is given in Table 2. All the soils contain kaolinite, with the exception of basalt soil 61, which contains montmorillonite and talc. Albitic feldspar was

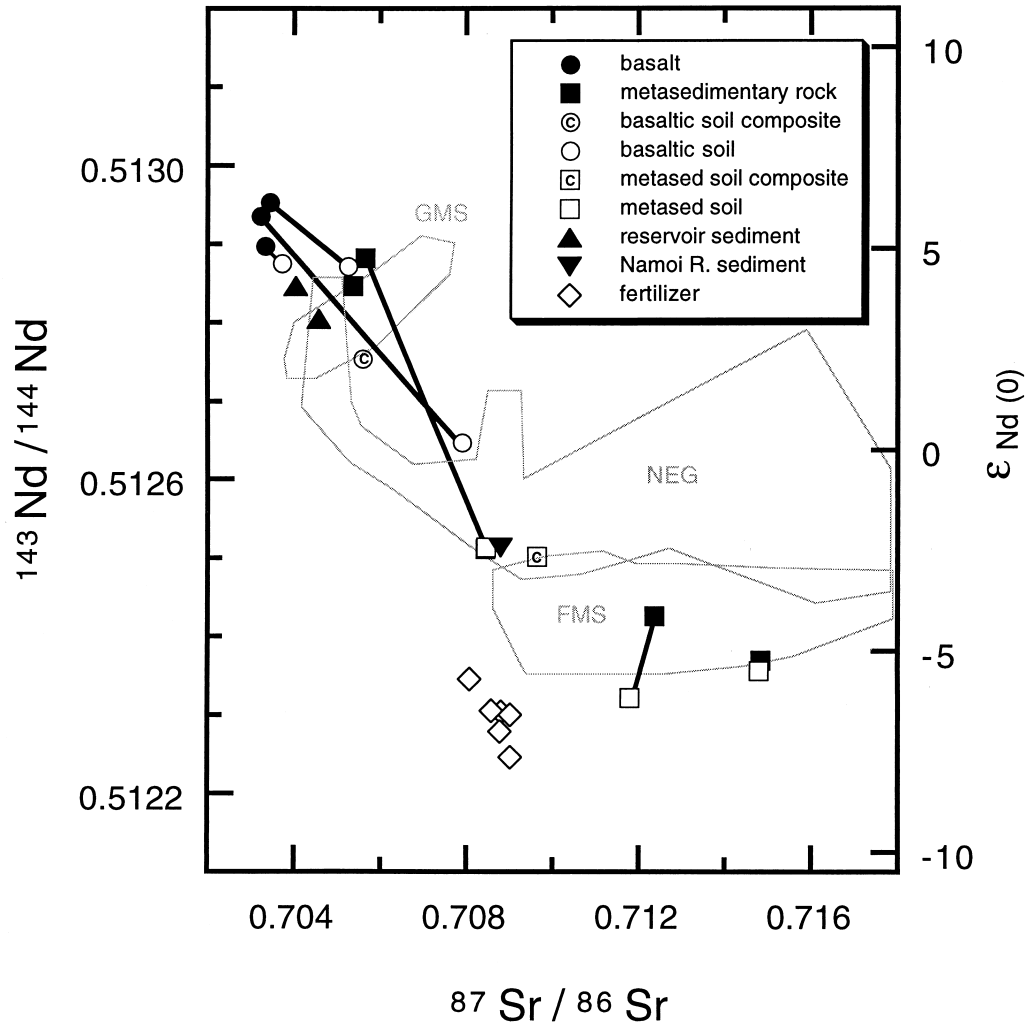


Fig. 2. Variation diagram of Nd versus Sr isotopic composition in rock, soil and sediment samples from the Namoi catchment and fertilizers used in the catchment. Lines connect rock and soil samples taken from the same locality. Outlined fields show isotopic compositions of New England granitoids (NEG), metapelitic rocks (FMS) and metagraywackes (GMS) from the New England fold belt (Hensel et al., 1985).

present in all the soils except for basalt soil 58, the only sample in which hematite was identified. Noteworthy is the fact that basalt soil samples 58 and 88 contain quartz, whereas basalt soil 61 does not. The quartz present in these two basaltic soils is unlikely to have been derived from the parental basalts and is evidence that these soils contain some externally derived material. All the metasedimentary soils contain mica. Quartz is not present in metasedimentary soil 105. Metasedimentary soils 63 and 91 have the same mineralogy despite their very different isotopic compositions.

Two of the basalt soils have very similar REE patterns, that resemble the parent rocks but have a slightly more negative slope to the HREEs (Fig. 3c). They also show a relative decrease in Ce concentrations. Basalt soil 88 is quite unusual in its REE pattern, because it is highly enriched relative to basalt 89. The observed REE pattern found in this soil is similar to anomalous REE enrichments that have been reported to occur in some weathered basalts from Victoria (Price et al., 1991),

where it has been attributed to the concentration and fixation of the REEs into secondary phosphate minerals during chemical weathering. The metasedimentary soils and soil composite have very similar REE patterns (Fig. 3d), with a slight peak at Eu and a slight enrichment of HREE over LREE. The HREEs are fairly flat to either slightly positively or slightly negatively sloped.

3.3. Sediments

The Chaffey reservoir sediments are isotopically similar to the basalts and metagraywackes, i.e., they have low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 2). Interestingly, the reservoir sediments have Nd-Sr isotopic compositions closer to that of the basalts than does the basaltic soil composite. The two reservoir sediments show subtle differences in isotopic composition and chemistry that could be related to either authigenic mineral precipitation or to differences in detrital mineralogy. Surface

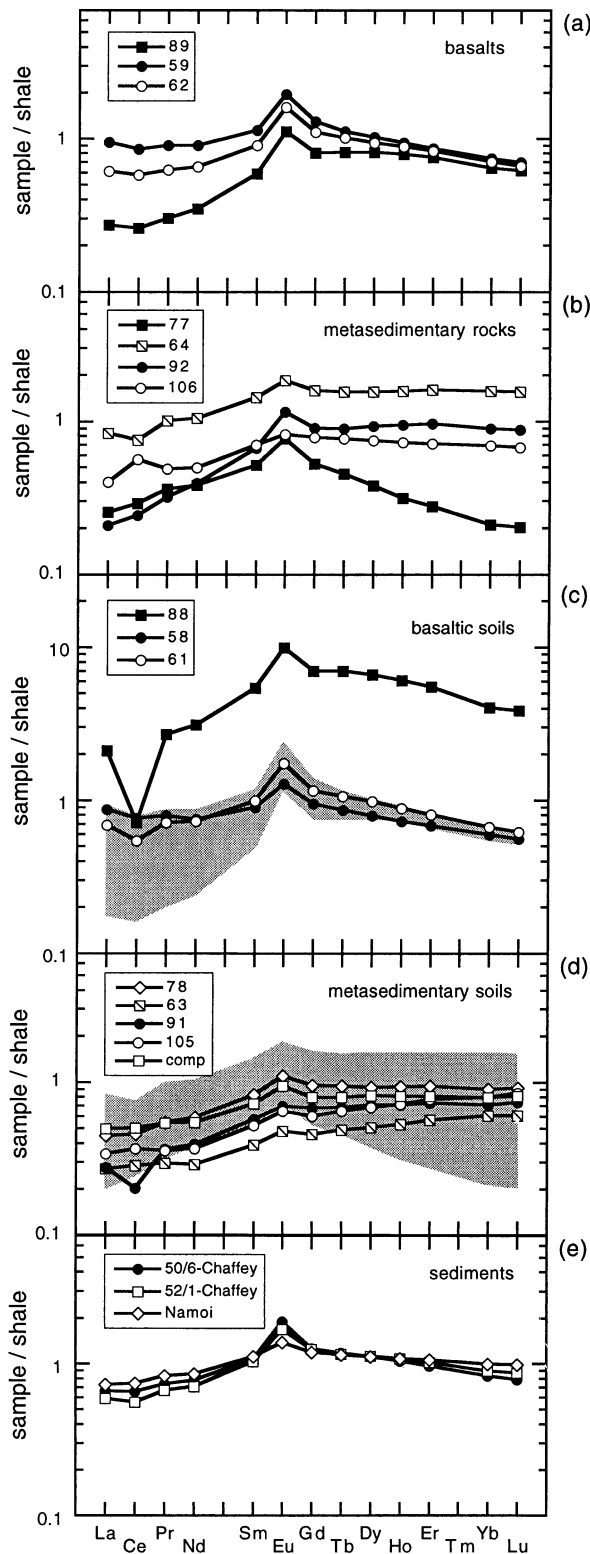


Fig. 3. (a–e) REE patterns for basalts, metasedimentary rocks, basaltic soils, metasedimentary soils and river and reservoir sediments, normalized to the concentrations in PAAS shale (McLennan, 1989). Soils (c,d) and rocks (a,b) from the same locality are shown by the same symbol style. Shaded fields outlining the ranges for the basalts are shown in (c) and for the metasedimentary rocks in (d).

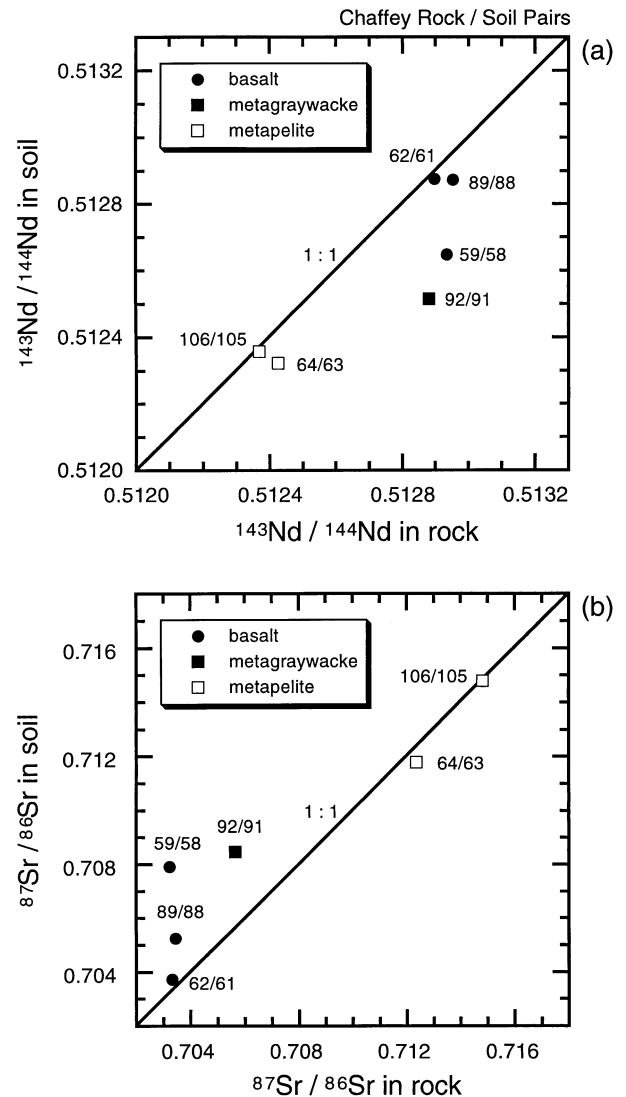


Fig. 4. (a) Nd and (b) Sr isotopic composition of soils versus rocks from the same locality, with a 1:1 reference line. Soil with the same isotopic composition as the underlying bedrock can be formed entirely by in situ weathering with minimal isotopic fractionation; displacement from the 1:1 line requires either preferential removal of isotopically distinct mineral phases or introduction of components.

(0–2 cm depth) sediment sample 52/1 has higher Na, K and Rb concentrations, Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than deeper sample 50/6 (10–12 cm depth), which has higher Ca, Sr and Al concentrations (Table 1). These features, combined with their generally low Sr isotopic compositions, probably reflect differences in the amount or composition of plagioclase feldspar and mica in the sediment. XRD analysis of sample 52/1 indicates the presence of montmorillonite, mica, kaolinite, quartz and albitic feldspar. The major element chemistry and mineralogy, combined with the fact that authigenic phases were not found in the reservoir sediment analyzed, indicate that the slight isotopic and chemical variations reflect differences in the mineralogy of the detritus that is deposited near to the mouth of the Peel River compared to the more distal sediments.

Table 2. Mineralogy of soil and sediment samples.

Sample#	Type	Mineralogy
CM93058/1	Basaltic soil	qtz, kaol, hem
CM93061/1	Basaltic soil	mont, talc, alb
CM93088/1	Basaltic soil	kaol, qtz, alb
CM93063/1	Metasedimentary soil	kaol, mica, qtz, alb
CM93091/1	Metasedimentary soil	qtz, kaol, alb, mica
CM93105/1	Metasedimentary soil	verm, mica, kaol, alb
CM93052/1	Reservoir sediment 0–2 cm	mont, mica, kaol, qtz, alb

* Results of qualitative XRD scans, in approximate order of abundance. qtz = quartz; kaol = kaolinite; hem = hematite; mont = montmorillonite; alb = albitic feldspar; verm = vermiculite.

The Namoi River suspended sediment was collected well downstream of Chaffey Dam. This sample has a Sr-Nd isotopic composition that is very different from the Chaffey sediment and is similar to the metasedimentary soils in Chaffey catchment and the granitoids and metapelitic rocks of the region (Fig. 2).

The Chaffey reservoir and Namoi river sediments have REE patterns (Fig. 3e) that are all generally quite similar. Compared to the soils, they have generally slightly higher REE contents, a more pronounced positive Eu anomaly, and negatively sloped HREE patterns. Goldstein and Jacobsen (1988b) have also observed that river water suspended loads have REE patterns that differ from average shales. Négrel and Deschamps (1996) found that soils in a basalt-dominated catchment in France were enriched in LREE compared to bedload sediments, opposite to what is observed in Chaffey.

3.4. Fertilizers

Compositional data for the fertilizers are given in Table 1. Their Nd-Sr isotopic compositions are shown in Fig. 2. In contrast to the basalts, metasedimentary rocks and soils in this area, the phosphate fertilizers have rather uniform Nd and Sr isotopic compositions. The fertilizers have an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70871 (range of 0.70807 to 0.70902) and ϵ_{Nd} values averaging -6.7 (-5.7 to -7.6). For comparison, a phosphate fertilizer analyzed by Borg and Banner (1996) has an $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70889 and ϵ_{Nd} of -7.5 , within the range observed in this study. This latter fertilizer was produced from a source in Florida (J. Banner, pers. comm.). The fertilizers used in Australia have their sources mostly from Pacific and Indian ocean islands, with a small proportion obtained from Florida (T. Donnelly, pers. comm.). The Nd isotopic variations in the fertilizers most likely reflect the difference in the ocean basins from which they were derived (Piepgras and Wasserburg, 1980; Shaw and Wasserburg, 1985; Grandjean et al., 1987; Goldstein and Jacobsen, 1987). The Sr isotopic composition of the fertilizers are within the range observed for Tertiary seawater, with the level of isotopic variability probably reflecting differences in the age of the marine source or addition of non-marine (dust?) Sr to the fertilizer or its precursor rock.

In contrast to the natural materials in the drainage basin, the fertilizers have a very wide range in concentration of both Nd and Sr, from 0.93–75 ppm (average 16 ppm) and 18–1028 ppm (average 277 ppm), respectively. The phosphate fertilizer analyzed by Borg and Banner (1996) has 520 ppm Sr and 36.8 ppm

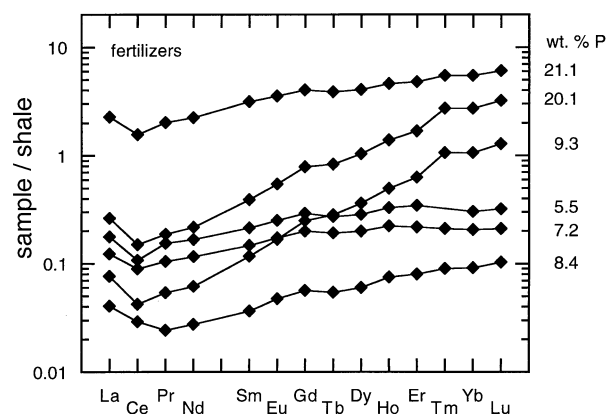


Fig. 5. Shale-normalized rare earth element patterns of phosphate fertilizers sold in the Namoi catchment. The P concentration of each fertilizer is shown next to the sample.

Nd, within our observed range. The range in concentration may be due to differences in elemental behavior during chemical processing of phosphorite or guano to make fertilizer, or it may be due to differences in the original materials. Grandjean et al. (1987) report Sr concentrations of 425–4752 ppm in fish remains that comprise phosphorites. These Sr concentrations are higher but cover a similar order of magnitude range observed in the fertilizers, suggesting that as much as 90% of the Sr is removed from phosphorite during fertilizer production, possibly by concentration into its phosphogypsum residue.

REE (Fig. 5) and Sr (Table 1) concentrations are highest in the fertilizers with the highest P concentration, and in general decrease with decreasing P concentration. This suggests that these elements are mainly associated with the phosphate component of the fertilizer and that the non-phosphate components of the fertilizer act simply to dilute their REE concentrations. The general similarity between the relative abundance levels in the phosphate fertilizers and phosphorites (Goldberg et al., 1963; Grandjean et al., 1987; Grandjean and Albarède, 1989) suggests that little fractionation between REE and P takes place during the manufacture of fertilizer. Five of the six fertilizer samples have a negative Ce anomaly, reflecting the derivation of their precursor phosphate from Ce-depleted oxic seawater (Goldstein and Jacobsen, 1988b; Elderfield et al., 1990; Sholkovitz et al., 1994). Eu anomalies are not present in any of the fertilizers, and four of the six fertilizers have positively sloped HREE patterns, very different from any of the natural samples from the catchment. The fertilizers with the lowest P content differ from the others, having a fairly flat REE pattern, but they also have normalized LREE abundances that are lower than the HREEs.

3.5. Leaching Experiments

In an attempt to better constrain the relative solubility of elements in the rocks and soils, a series of leaching experiments was undertaken. The first leachates of the rock and soil samples contain between 15 and 66% of the REE present in the bulk samples (Fig. 6), and show a relative depletion in HREE relative to LREE. The Nd isotopic compositions of the

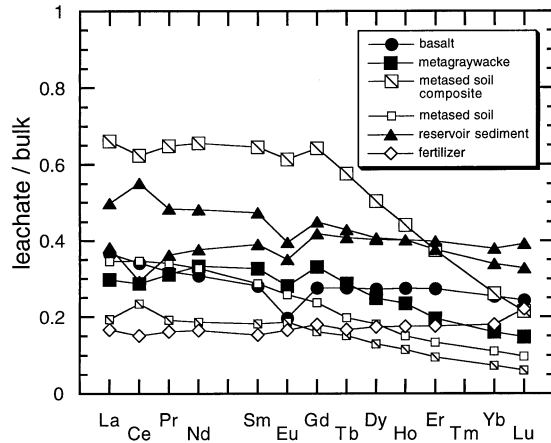


Fig. 6. REE patterns showing the concentration in leachates (larger symbols = first leachate, smaller symbols = second leachate) normalized to the bulk sample. The first leachates of the rocks and soils contain a larger fraction of LREEs than HREEs, the reservoir sediment leachate contains more HREE than LREE, and the fertilizer leachate did not preferentially solubilize any of the REEs.

leachates are nearly identical to the unleached samples (Fig. 7a). Leachates of the basalt and metagraywacke have Sr isotopic compositions that are somewhat higher than the rocks, but leachates of the soils are very similar to the unleached samples (Fig. 7b). A larger percentage of Nd (31–66%) and other REE than of Sr (4–25%) was removed in the first leachates (Tables 1 and 3). There is no carbonate in the soil samples to act as a readily dissolvable host mineral for Sr, which may account for relatively low solubility of Sr observed here. The high solubility of the REEs, particularly the LREEs, in the leachates might reflect the dissolution of apatite in the HCl-containing leaching solution, but then Sr, which is also concentrated in apatite, would be expected to be very soluble. The phases hosting the leachable REE therefore probably contain little Sr, and are most likely to be clay minerals or other secondary phases that are rich in REEs (Banfield and Eggleton, 1989). The high level of REE solubility observed here is also likely to be due to the low pH of the leaching solutions applied compared to most natural waters preventing readsorption of REE onto residual phases (e.g., Sholkovitz, 1989).

The fertilizer with the highest REE concentrations (F#12) was subjected to the same leaching procedure described for the rocks and soils. The leachate Nd and Sr isotopic compositions are indistinguishable from the bulk sample (Fig. 7), as would be expected for a recently chemically processed and homogenized material. The REEs were leached from the fertilizer with little fractionation (Fig. 6), but a somewhat lower fraction of total REEs (e.g., 16% of Nd) was leached from the fertilizer than from the natural samples. On the other hand, a larger fraction of Sr (38%) was leached from the fertilizer compared to the natural samples.

4. DISCUSSION

4.1. Elemental Solubility and the Cause of Isotopic Shifts in the Weathering Environment

A potential complicating factor in making source attributions on the basis of Sr-Nd isotopes is the effect of differential

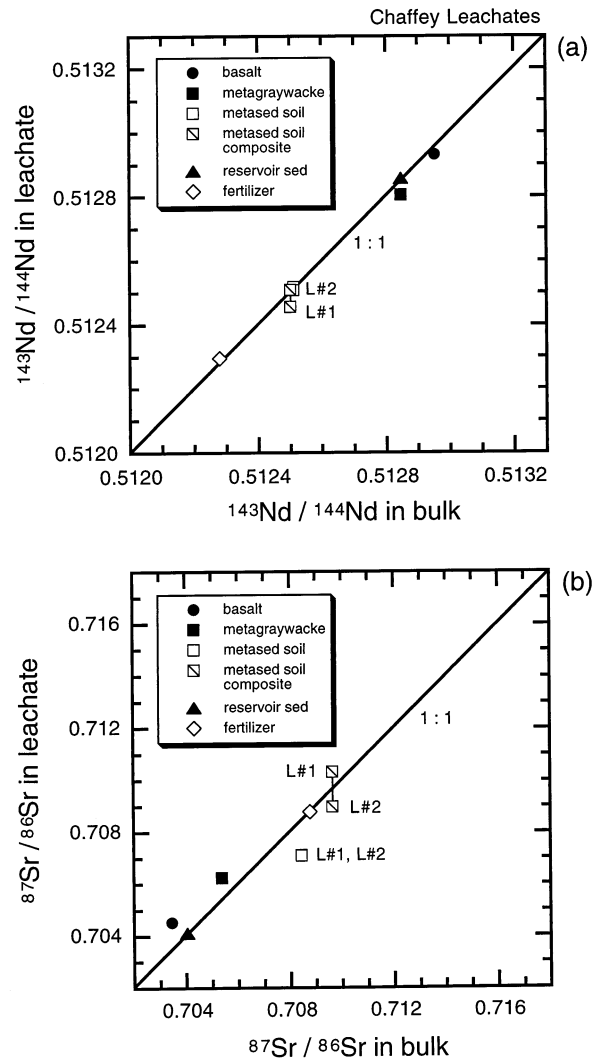


Fig. 7. (a) Nd and (b) Sr isotopic composition of leachates compared to bulk samples fall very close to a 1:1 reference line, suggesting that there is little isotopic change associated with leaching.

elemental solubility resulting from preferential weathering of mineral phases which have distinctive isotopic compositions. Isotopic variability in a rock arises in ancient samples due to in situ radiogenic production of ^{87}Sr or ^{143}Nd in minerals with different Rb/Sr and Sm/Nd ratios. Older rocks, particularly those containing minerals with high and variable parent/daughter ratios, develop significant inter-mineral isotopic variability; this is the principal behind the mineral isochron. Because the minerals in a rock weather at different rates, the isotopic composition of the Sr and Nd released to solution may therefore differ significantly from the whole rock values. Similarly, the insoluble residue of weathering (ultimately soil or sediment) may also in principle differ in isotopic composition from the fresh whole rock. The issue of elemental solubility and its possible associated isotopic shifts due to preferential mineral weathering can be addressed using the isotopic and trace element systematics of the rocks, soils, and sediments and the results of the leaching experiments.

Table 3. Results of leaching experiments.

Element	CT93089	CT93077	69	69	CT93078/1	CT93078/1	CT93050/6	CT93050/6	F12 L#1 fertilizer leachate
	L#1	L#1	L#1	L#2	L#1	L#2	L#1	L#2	
	basalt leachate	metagraywacke leachate	metasedimentary 1st leachate	soil composite 2nd leachate	metasedimentary soil		Chaffey Reservoir sediment		
Li	0.89	2.68	5.80	7.33		4.30	2.27	3.55	2.88
Ti	31.5	69.4	35.9	31.8		28.1	77.7	242	103
Zn	19.7	13.2	49.3	79.1		48.2	18.2	59.7	89.4
Rb	2.24	0.51	4.69	13.31		4.22	0.78	6.23	7.24
Sr	35.3	16.2	35.2	17.8		15.8	96.6	68.5	394
Y	6.23	2.16	11.20	2.39		3.91	13.2	10.9	32.9
Zr	0.74	0.10	0.21	0.27		1.35	0.39	1.11	10.4
Nb	0.402	0.048	0.017	0.016		0.018	0.127	0.022	0.163
Mo	0.050	0.115	0.241	0.026		0.014	0.125	0.0064	6.48
Cd	0.0160	0.0055	0.0409	0.0671		0.0226	0.0152	0.0376	3.54
Ba	78.2	35.1	83.4	45.9		36.2	56.3	55.5	6.9
La	3.76	2.88	12.5	3.66		5.92	9.6	12.5	14.4
Ce	7.00	6.64	24.7	9.25		12.6	15.2	28.7	18.7
Pr	0.845	0.991	3.08	0.907		1.63	2.33	3.11	2.86
Nd	3.62	4.30	12.1	3.44		6.48	9.88	12.6	12.4
Sm	0.92	0.94	2.58	0.73		1.32	2.31	2.80	2.65
Eu	0.236	0.232	0.625	0.190		0.304	0.709	0.801	0.630
Gd	1.03	0.806	2.38	0.596		1.05	2.45	2.63	3.34
Tb	0.173	0.100	0.355	0.093		0.144	0.370	0.389	0.496
Dy	1.03	0.437	1.92	0.49		0.78	2.09	2.11	3.28
Ho	0.213	0.073	0.353	0.091		0.138	0.413	0.413	0.793
Er	0.584	0.153	0.859	0.218		0.355	1.09	1.03	2.39
Yb	0.459	0.095	0.583	0.163		0.278	0.882	0.79	2.77
Lu	0.0646	0.013	0.075	0.021		0.038	0.133	0.111	0.576
Hf	0.0177	0.0065	0.0135	0.0107		0.0608	0.0207	0.0453	0.172
Ta	0.0033	0.0009	0.0024	0.0014		0.0014	0.0052	0.0023	0.0190
Pb	0.172	3.27	4.33	12.19		9.06	0.94	12.28	0.65
Th	0.075	0.073	0.248	2.291		2.000	0.032	1.699	1.128
U	0.149	0.136	0.230	0.104		0.110	0.235	0.237	141
⁸⁷ Sr/ ⁸⁶ Sr	0.704532	0.706241	0.710319	0.708980	0.707098	0.707085	0.704101		0.708779
¹⁴³ Nd/ ¹⁴⁴ Nd	0.51293	0.51280	0.51246	0.51251	0.51252	0.51251	0.51286	0.51284	0.51230
ε _{Nd} (0)	+5.7	+3.2	-3.6	-2.5	-2.3	-2.6	+4.2	+4.0	-6.7

* All concentrations are in ppm relative to the mass of powder leached.

As a first way of estimating the chemical effects of the production of soil from parent rocks, it is useful to compare concentrations of elements that are considered to be relatively immobile in the weathering environment. Ti, Zr, Hf, Th (Table 1), and REEs (Fig. 3) are present in similar concentrations in the reservoir sediment and basaltic soils, and their concentrations in both are high compared to the rocks, suggesting that these elements have been concentrated by removal of more soluble components from the sediment sources. During weathering, soluble phases are dissolved but Nd (REEs) remain behind, either because they were not present in the soluble phases or they were immediately reprecipitated in another, less soluble form after being liberated from the soluble phase. This should lead to Nd isotopes being nearly invariant during weathering-related dissolution. Sr exhibits a different behavior, as it is generally considered to be quite soluble in the weathering environment and would not be precipitated in many secondary phases. The Chaffey Reservoir sediments have Sr concentrations that are higher than the metasedimentary soils and two of the four basalt soils, but the soils themselves have very low Sr concentrations relative to the rocks (Table 1). The removal of a large fraction (up to 90%) of the original Sr present in the rocks during their conversion into soils is consistent with these

observations and thus could, in principle, result in Sr isotopic shifts, if the soluble mineral components have variable Rb/Sr ratios. Concentration arguments alone are not enough to resolve the issue.

Next, it is useful to compare the leachate results with the bulk rocks and soils. The leachate fractions of the rocks and soils (Fig. 7a) have very similar Nd isotopic compositions to the bulk samples. This further supports the hypothesis that the Nd isotopic composition of these samples would not be changed much by selective mineral dissolution. The results of the leaching experiments can also be used to quantify the extent to which removal of Sr to solution during weathering might have affected the Sr isotopic composition of the residual material. The ⁸⁷Sr/⁸⁶Sr of the first leachates of the basalt, metagraywacke and metasedimentary soil composite were higher than the bulk samples (Fig. 7b), implying that the more soluble Sr in these samples is more radiogenic. Similar Sr isotopic relationships have been reported for leaching experiments on granites by Irber et al. (1998). By mass balance, the ⁸⁷Sr/⁸⁶Sr of the residua of the leaching experiments were lowered by <0.001. In the case of the other metasedimentary soil, the first leachate was less radiogenic in Sr than the bulk sample, and suggests that the ⁸⁷Sr/⁸⁶Sr of this soil residuum would tend to

be increased very slightly by weathering. The calculated Sr isotopic changes are quite small relative to the large range in $^{87}\text{Sr}/^{86}\text{Sr}$ in the catchment materials. Because the leaching techniques applied here were more severe than natural conditions, we consider that weathering would have a minimal effect on the Sr isotopic composition of residual sediments and soils in Chaffey reservoir catchment.

Still another means to assess whether weathering-related isotopic changes have occurred in Chaffey reservoir catchment involves a simple comparison of the rock-soil pairs. For both basalt rock-soil pair 61/62 and metapelite rock-soil pair 105/106, the soil and associated rock have nearly identical isotopic compositions (Fig. 4a and b), and their REE patterns are very similar (Fig. 3 a–d). Although relatively immobile elements (such as Ti) have been enriched and more soluble elements (such as Sr) removed from rocks 62 and 106 during their conversion to soils 61 and 105, for these soils there has not been a significant change in the Nd or Sr isotope of the weathering residua produced relative to their associated rocks. These results are consistent with the production of these two soils by in situ weathering and pedogenesis. The fact that the remaining soils have Sr and Nd isotopic compositions that differ from their associated rocks could be taken as evidence that more extreme levels of in situ weathering resulted in preferential dissolution of minerals with isotopic compositions different from the whole rocks. However, consideration of the leachate-residue mass balance shown above suggests that this is unlikely.

As the isotopic shifts observed in the majority of the soils cannot be readily explained by simple in situ weathering, it is reasonable to consider that they may have been produced by weathering in a system that was not closed relative to inputs of externally-derived or “exotic” material to the soil. One way to address this possibility more thoroughly is by a direct comparison of the Sm-Nd isochron systematics of the parent rocks and their related soils. Even if Nd has been fractionated to some extent from Sm during chemical weathering, the isochron analysis makes it possible to answer the question of whether the soils in Chaffey Reservoir catchment can have been formed entirely by in situ pedogenesis or whether they must contain an externally derived, “exotic” source.

A Sm-Nd isochron diagram for the basaltic rocks and associated basaltic soils is shown in Fig. 8a. The basaltic rocks of the Liverpool Ranges are estimated to be Early Oligocene (Wellman and McDougall, 1974; Coenraads, 1990; Sutherland et al., 1993); reference isochrons for the basaltic whole rocks are shown for an age of 36 Ma. Because of the long half-life of Sm, the young age of the basalts and their low $^{147}\text{Sm}/^{144}\text{Nd}$ ratios, there has been little opportunity for any of the minerals in these rocks to have developed Nd isotopic compositions that are very different from the initial at the time of crystallization. It is possible to assess whether preferential weathering has removed some of the components from the rock using the isochron diagram. In the simplest case of no Sm-Nd fractionation during weathering, any residual mineral phase will plot directly on the isochron. In any case, a soil that was derived entirely by in situ pedogenesis from these young basalts must have a $^{143}\text{Nd}/^{144}\text{Nd}$ which is essentially equal to or only slightly greater than the initial isotopic composition from the isochron.

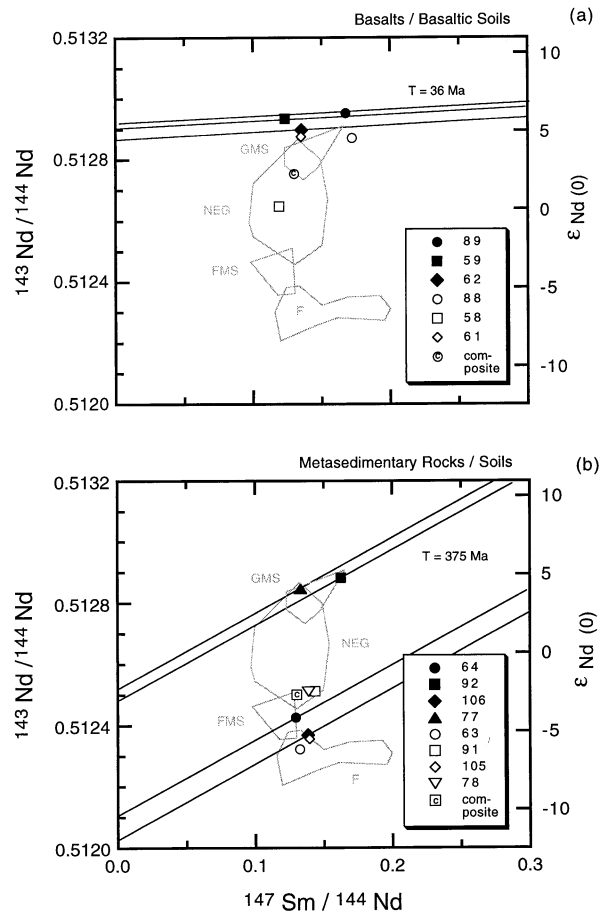


Fig. 8. Sm-Nd isochron diagrams for basalts (a) and metasedimentary rocks (b) from Chaffey Reservoir catchment. The lines are reference isochrons for the age of the rocks (36 Ma for basalts, 375 Ma for metasedimentary rocks), which gives the possible isotopic composition of phases weathering out of the rock. Basalt soil 61 and metasedimentary soil 105 have isotopic compositions that are consistent with an entirely in situ soil forming process. The remaining soils plot below the $^{143}\text{Nd}/^{144}\text{Nd}$ expected for their $^{147}\text{Sm}/^{144}\text{Nd}$ ratios, indicating that in situ weathering of the bedrocks can not be the only source of the soils and suggest that addition of components such as the regional granitoids (NEG) and metapelites (FMS) or fertilizer (F) could be involved.

Basaltic soil 61 plots very close to the isochron defined by its associated basalt 62, having similar $^{147}\text{Sm}/^{144}\text{Nd}$ as well as $^{143}\text{Nd}/^{144}\text{Nd}$. Basaltic soil 88 is more significantly displaced from the isochron, and both basaltic soil 58 and the basaltic soil composite have $^{143}\text{Nd}/^{144}\text{Nd}$ that are lower than the initial isotopic composition of the rock (Fig. 8a). The very important conclusion which can be drawn from these results is that most of these basaltic soils could not have been derived exclusively from the weathering of their basaltic parent rock.

The isochrons for the metasedimentary rocks (Fig. 8b) have been constructed for their Paleozoic age (calculated for 375 Ma). Because of the older age of these rocks, the possible range of acceptable Nd isotopic compositions is greater than for the case of the basaltic soils, but the same relationships hold. (Note that, although detrital minerals in the metasedimentary rocks may not have completely equilibrated at the metamorphic age, on the basis of the regional geology the detritus is no older than

about 500 Ma, and the slope of their isochron would not be much different than for 375 Ma.) Comparison of the metasedimentary rock-soil pairs illustrates three cases. For metapelite rock-soil pair 105/106, the soil plots on the Sm-Nd isochron defined by the rock and therefore can be explained entirely by a process of in situ soil production. The other metasedimentary soils have similar $^{147}\text{Sm}/^{144}\text{Nd}$ ratios to the metasedimentary rocks, but have significantly lower $^{143}\text{Nd}/^{144}\text{Nd}$. Especially noteworthy is the case of metagraywacke 92 in comparison with soil 91. In situ pedogenesis alone could not have produced these soils from the type of parent rock previously assigned to them in the field on the basis of color and proximity. The addition of at least one additional, "exotic" or imported component to the soils is therefore required by their Sm-Nd isotope systematics.

In summary, there is no evidence to suggest that elemental solubility during chemical weathering of the rocks in Chaffey Reservoir catchment resulted in a major shift in Nd or Sr isotopes of the resulting soils and sediments. In two cases the soils have the same isotopic compositions as their parent rocks and could have been produced entirely by in situ weathering and pedogenesis. On the basis of the isochron systematics for the other soils that differ in isotopic composition from their parent rocks, the shift is interpreted to be due to incorporation of externally derived material rather than to chemical weathering. It is shown below that the nature of the "exotic" component in the soils, as well as the relative contributions of different soils and fertilizers to reservoir and river sediments, can be traced using their Nd-Sr isotopes, in conjunction with their trace element compositions.

4.2. An "Exotic" Component in the Soils

The externally derived component causing the observed Nd-Sr isotope shifts in most of the soils in Chaffey catchment must be relatively similar to the native rock types, so as not to affect drastically the chemical composition of the soils, and yet it must contain enough Nd and Sr to cause a shift in isotopic compositions. Fluvial or eolian transport of dust from outside the boundary of the catchment or application of phosphate fertilizers are possible ways to introduce an "exotic" component to the soils. However, as the Tertiary basalts are present at the highest elevation in the catchment, the basaltic soils are unlikely to contain a fluvial component unless the drainage patterns have drastically changed since the inception of soil production. In addition, the shifts toward lower $^{143}\text{Nd}/^{144}\text{Nd}$ in the metasedimentary soils cannot be explained by incorporation of fluvially transported basaltic material, which has high $^{143}\text{Nd}/^{144}\text{Nd}$. We will therefore consider further only eolian and fertilizer sources of the "exotic" component in the soils.

The application of phosphate fertilizers such as those analyzed in this study would not affect the major element composition of the soils other than increasing their P content. (We note that the other reported major elements in the fertilizers are S and N, which were not analyzed in the catchment samples). Due to the much lower $^{143}\text{Nd}/^{144}\text{Nd}$ in the fertilizers relative to the rocks, fertilizer addition would decrease the $^{143}\text{Nd}/^{144}\text{Nd}$ of the soils relative to the parent rock, provided that the Nd remained bound to the soil particles. There are a number of reasons to believe that this would be the case. First, the soils all

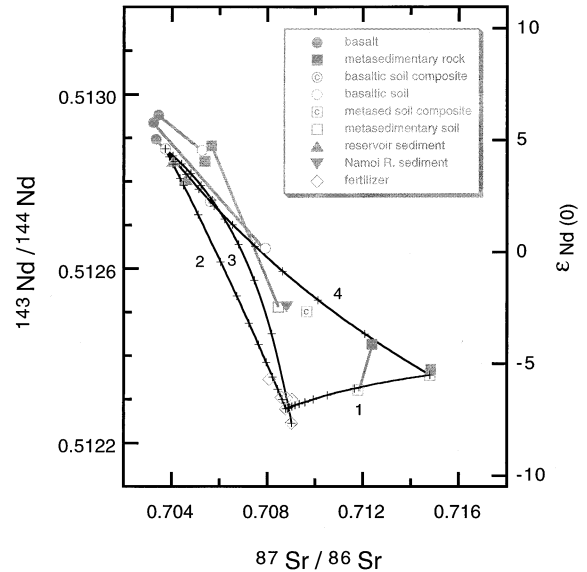


Fig. 9. Two component mixing lines in Nd-Sr isotope space, with samples from the Namoi catchment shown in the background. Mixing curves shown are: 1 = metasedimentary soil 105 + fertilizer F#12; 2 = basalt soil 61 + fertilizer F#12; 3 = basalt soil 61 + fertilizer F#5; 4 = basalt soil 61 + metasedimentary soil 105. Ticks indicate mixing proportions in 10% increments.

have significantly higher concentrations of Nd (18.5–23 ppm) than the rocks (11.8–13 ppm), as has also been observed by Borg and Banner (1996), suggesting a process of enrichment. In addition, the low concentration of Nd in filtered waters from the catchment (Martin and McCulloch, 1995, and unpublished data) agrees with abundant other evidence that Nd is only slightly soluble in near neutral waters (Goldstein and Jacobsen, 1988b; Brookins, 1989; Elderfield et al., 1990; Wood, 1990; Sholkovitz, 1992, 1995; Erel and Stolper, 1993; Hall et al., 1995; Johannesson et al., 1996). Furthermore, the results of the strong leaching experiment for the fertilizer showed that less Nd was removed relative to the natural catchment samples, suggesting that a net enrichment of Nd could occur in soils subjected to fertilizer application. Therefore, it might be expected that the soils would be sensitive to Nd isotopic shifts due to fertilizer application. For example, addition of 10% by mass of fertilizer F#12 to metasedimentary soil 105 would result in isotopic compositions similar to soil 63 (curve 1 in Fig. 9).

However, consideration of the actual mass balance shows that, unless fertilizer is applied at very high rates for long periods of time, the Nd isotopic composition will not be significantly affected, due to the generally similar concentration levels of Nd in the fertilizer and rocks. The isotopic and compositional relations are illustrated in Fig. 10. Because the Nd/P ratios of the native materials of the catchment are significantly higher than the ratio in the fertilizers, bulk mixing between the two will first become apparent as lowering of the Nd/P ratio of the mixture. The rocks, soils and sediments of Chaffey reservoir sediment have similar Nd/P ratios, suggesting that there has been little fractionation of this ratio during soil formation. The mixing curves shown illustrate that as little as 1% fertilizer addition in bulk to the sediment would be identifiable as a decrease in Nd/P ratio. To see if this is

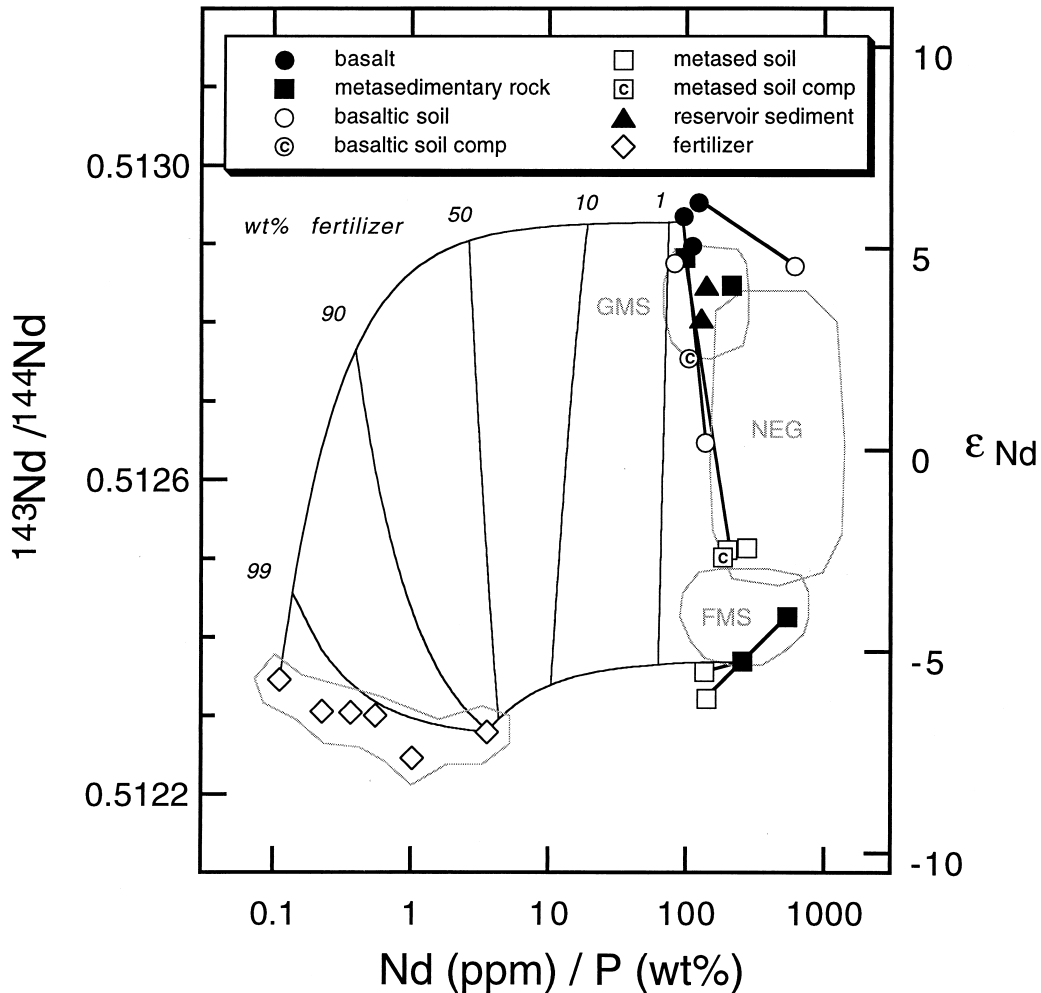


Fig. 10. Plot of $^{143}\text{Nd}/^{144}\text{Nd}$ vs. Nd/P for samples from Chaffey reservoir and fertilizers. Soils that form by weathering-related loss of soluble elements increase in Nd concentration but will not change Nd/P ratio (provided P and Nd have similar solubility) or Nd isotopic composition. The bulk mixing relations between the average fertilizer and basaltic soil are shown, with mixing proportions indicated. Because the Nd/P ratios of rocks, soils and sediments are at least a factor of 20 lower than that of the fertilizers, even as little as 1% fertilizer addition should be readily distinguished. There is no systematic trend of decreasing Nd/P with decreasing $^{143}\text{Nd}/^{144}\text{Nd}$ for the Chaffey Reservoir sediment and the soils compared to the rocks in the catchment, suggesting that there is little fertilizer incorporated in the sediment and soils.

plausible, we considered a mass balance for a fertilizer application rate of 60 kg per hectare per year, the maximum rate in the catchment, using the fertilizer with 75 ppm Nd, the highest measured concentration, for the last 40 years. If the fertilizer was mixed to a depth of 10 cm and the soil has a bulk density of 1 g/cm^3 , the increase in Nd concentration of the soil would be 0.18 ppm. Compared to the soil concentrations of 18.5–23 ppm, this would be less than 1% increase in Nd concentration, and would produce little change in the Nd isotopic composition (Fig. 10). If the fertilizer P becomes fixed into the soil, this level of fertilizer addition would raise the P content of the soil by 60%, due to the very high P content of the fertilizer, resulting in a dramatic lowering of the Nd/P ratio in the soil. This is not observed in the basalt-basalt soil pairs, nor in the metagraywacke-soil pair. An additional consideration is the fact that the metasedimentary rock-soil pair 105/106, from a

fertilized area, has no Nd isotopic difference and very similar Sr isotopes. These observations lead us to suggest that where isotopic differences are observed in the soils relative to their parent rocks, it has not been brought about by fertilizer incorporation.

Preferential solubility or plant uptake of P from fertilizer (with subsequent export) would tend to increase the Nd/P ratio of the mixing endmember relative to the fertilizer, but the ratio would have to be increased by at least a factor of 10–15 in order to explain the measured Nd/P ratio of the sedimentary soils. The largest increase in Nd/P ratio observed for soil/rock pairs in this study is a factor of 5 (for pair 88/89). Price et al. (1991) have described increases in Nd/P of up to a factor of 8 which they interpret to be due to anomalous enrichment of the REEs by formation of secondary phosphate minerals during basalt weathering. Other elements that are present in the fertil-

izers in high concentration, such as Cd, Zn and U, would be expected to increase the soil concentration but are not systematically higher in samples with low Nd/P ratio (Table 1). These results therefore agree with the isotopic evidence that fertilizer can only be of very minor importance as an exotic component in the sediments and soils.

Eolian dust is considered the most likely candidate for the transported, "exotic" component in the Chaffey catchment soils. It is well known that wind-blown dust has been deposited off the eastern margin of Australia, during both wet and arid periods (McTainsh and Boughton, 1993). On the basis of the isotopic data set presented here, it is not possible to determine the exact location of the wind-blown source (i.e. derived from nearby or long-travelled), but the isotopic results do allow for these possibilities to be assessed. The $^{143}\text{Nd}/^{144}\text{Nd}$ and Sm/Nd ratio of the soils (Table 1, Fig. 8) compare favorably with some of the granitoid and metapelitic rocks of the New England fold belt (Hensel et al., 1985), which would be present nearby and within the boundaries of the Namoi catchment itself. This means that the dominant source of REEs (up to nearly 100%) in the soils could be from a regionally derived eolian component. Another possible source of eolian material to the soils could be from areas which are distal to the Namoi, such as Australian loess and dust samples from southern and western Australia that were analyzed for their isotopes by Grousset et al. (1992). These samples have $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512037–0.512447, overlapping the range in the Chaffey soils, and $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.72182–0.76336, which is much higher than any of the Chaffey samples. Isotopic mass balance calculations using this range of loess and dust as end-member mixing compositions would result in about 10% of the Sr and 15% of the Nd in the basaltic soil composite being derived from the eolian component and the remainder from the weathering of the basalt.

In summary, the shift in Nd and Sr isotopic compositions of the soils relative to their bedrock sources may reflect the addition of windblown components from the west, the dominant wind direction in this region of Australia. However, the similarity of the Chaffey catchment sedimentary soils to the Namoi sediment supports the suggestion that there is some internal recycling between riverine and eolian deposition within the greater Namoi catchment. The results of this study further demonstrate the potential of Nd and Sr isotopes to investigate eolian transport of soil components (e.g., Borg and Banner, 1996), even in complex terrains.

4.3. Chaffey Reservoir Sediment Sources

The Chaffey reservoir sediment can be considered to be made up of a minimum of two sources, one of which is isotopically similar to the young basalts and the other more isotopically similar to typical upper crust. From the above discussion of the Nd-Sr systematics of the soils in the Chaffey reservoir catchment, there appear to be two regolith regimes in the catchment that may be distinguished on the basis of geochemistry and topography. Low gradient erosional remnants (tablelands), such as are present along the eastern boundary of the catchment, can be identified by the isotopic difference between the rocks and soils caused by eolian dust deposition. In these areas the soils (such as basalt soil 88) can also obtain

anomalous REE enrichments by prolonged weathering enrichment of immobile elements (Price et al., 1991). On the other hand, high gradient areas that are actively eroding, such as the headwaters of the Peel River (site 61/62), can be identified by the isotopic similarity of the soil and rock and the lack of major fractionations among the least soluble elements in the soils. It is reasonable to consider the actively eroding areas of the catchment as the prime source of the sediment deposited in Chaffey reservoir.

Indeed, comparison of the isotopic compositions (Fig. 2) of the Chaffey reservoir sediment with the soils in the catchment confirms that basaltic soils similar to those near the headwaters of the Peel River (sample 61) must be the dominant source of sediment to Chaffey reservoir. In particular, basalt-derived components are the only source materials with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than the reservoir sediment. The metagraywackes would also provide sediment with basalt-like Nd isotopic compositions, but they do not have appropriate Sr isotopic compositions. The REE patterns of the Chaffey reservoir sediments (Fig. 3), particularly the negative slope of the HREEs, also suggests their affinities with the basalts. Furthermore, the presence of montmorillonite in both Chaffey surface sediment sample 52/1 and basalt soil 61 provides additional support that much of the sediment reaching the reservoir is derived from actively eroding areas such as the Peel River headwaters.

Thus, the isotopic data in combination with the mineralogy, trace element concentrations and REE patterns of the rocks, soils and sediment (Fig. 3) have demonstrated that basalt-derived material which has been physically (but not strongly chemically) weathered provides a significant fraction of the reservoir sediment. This conclusion agrees well with the suggestion made on the basis of the major element chemistry that basalt-derived material is the dominant contributor to the reservoir sediment (Caitcheon et al., 1995). Furthermore, on the basis of isotope systematics the basaltic soils do not contribute equally from across the catchment. This is made evident by the fact that the basaltic soil composite, which may be considered to be a reasonable spatial average of the basaltic soils, and both of the individual basaltic soils interpreted to have a significant eolian component are isotopically less basalt-like than are the reservoir sediments. Thus, the isotope results demonstrate that preferential erosion is taking place from high gradient areas such as the basaltic headwaters of the Peel River to provide the majority of the reservoir sediment.

On the basis of isotopes alone, some limits can be placed on the maximum amount of fertilizer input to the Chaffey reservoir sediments. For example, addition of 2–5% of fertilizer F#12 or 10–25% of fertilizer F#5 to basalt soil 61 would result in isotopic compositions similar to the results for the two Chaffey reservoir sediments (curves 2 and 3 in Fig. 9). However, this addition would also have effects on the trace element concentrations of the sediment, as was discussed above for the soils. Thus, although a simple mixture of basalt and fertilizer satisfies the isotopic constraints for the Chaffey reservoir sediment, the trace element concentrations, particularly U, Cd, Zn and P, are not satisfied by the large amount of fertilizer required by such a model.

In order to accommodate the trace elements as well as the isotopes and to further assess the possible extent of fertilizer addition, a minimum of three components must be used. For

example, reasonable natural catchment components would be basalt soil 61 and metasedimentary soil 105, the most isotopically distinct soils in the catchment, and those that are considered to be from net erosional areas on the basis of their isotopic similarity to their parent rocks (Fig. 9). Fertilizer F#5 is reported to be the most used fertilizer in the catchment, and fertilizer F#12 has the highest trace element concentrations, so these are also reasonable endmember components. A least squares regression of these components was performed using a subset of the elements analyzed. Elements were chosen on the basis of being distinctive of one of the endmembers: Ti and Nb are very enriched in basalt soil 61; Li, Rb, Zr are in high concentrations in metasedimentary soil 105, and high levels of Zn, Mo, Cd, U are present in fertilizers F#5 and F#12 (Table 1).

For the 10–12 cm reservoir sediment (50/6), the result from least squares regression is close to 0% of F#5 or F#12 fertilizer component, within uncertainties, and was therefore essentially identical to a two-component mixture between the natural catchment sources (curve 4 in Fig. 9). For the 0–2 cm reservoir sediment sample (52/1), calculated proportions are 75% basalt soil and 25% metasedimentary soil, with 0.13% of fertilizer F#5. The results of the regression analysis are consistent with the earlier observation that the differences in isotopes, chemistry and mineralogy of the reservoir sediments require differences in their detrital sources.

Using the mixing proportions determined from the regression, the concentrations for the remaining elements, as well as Nd–Sr isotopic compositions for the mixtures, were calculated. The difference between the calculated and measured results are plotted versus the measured concentrations for Chaffey reservoir sediments in Fig. 11. The fit is good for relatively mobile as well as immobile trace elements, even for elements that range in concentration by six orders of magnitude. The isotopic compositions also fit well using the regression parameters. Because metasedimentary soils can provide the high $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$ ratio source and also satisfy the trace element concentrations, a more reasonable upper limit to the fertilizer component of approximately 0.2% of the mix is calculated as a bulk percentage.

4.4. Namoi River Sediment Sources

The Namoi sediment plots in a completely different portion of Sr–Nd isotope space from the Chaffey reservoir sediment (Fig. 2) and appears to have little or none of the basalt or metagraywacke components that characterize the upstream Chaffey reservoir sediment. Rather, the Namoi sediment appears to be very similar to the metasedimentary soils from Chaffey catchment, which are themselves derived from metapelites and granitoids that are typical of the New England fold belt (Hensel et al., 1985). This implies that the basaltic sources of the upper catchment are rapidly overwhelmed by the granitoid and metapelitic sources in the lower catchment, despite the greater relief in the basalt-dominated portions of the catchment. This may be due to the present-day practice of extensive damming, which would tend to capture the sediment in basalt-dominated catchments such as Chaffey. Whether the lack of a basalt signature in the lower Namoi suspended sediment is a long-lived feature or has only arisen since the dam

construction might be resolved by the analysis of pre-dam sediment deposits.

The P concentration of the lower Namoi suspended sediment is a factor of 2.5 lower than that found in the basalt-dominated Chaffey reservoir sediment. There are anecdotal reports that algal blooms occurred throughout the Darling River basin prior to recent land clearing and damming (or fertilizer usage on a large scale). Because the basalts are a naturally rich source of P, their delivery to the lower Namoi might have been a cause of algal blooms at that time. Our results indicate that there is no such basalt source at the present time providing P-rich sediment to the lower Namoi. Thus another source of P to the river seems to be required, which may include fertilizers. Because of the large range in Sr and Nd isotopic compositions observed in New England Fold Belt rocks, it is difficult to calculate a mass balance that includes a possible fertilizer contribution. Therefore, although our isotope and elemental data do not require a fertilizer source in the Namoi river sediment, we cannot completely rule out its presence at this time.

These findings have important implications for the source of P in rivers, given the role of P as a limiting nutrient in algal blooms. In catchments such as the Chaffey, where natural sources high in phosphorus dominate the suspended sediment load, the problem of excess P is unlikely to be solved by reducing fertilizer usage within the catchment. Rather, excess P can more likely be reduced by improving land management practices, in particular by adopting strategies to minimize erosion. The situation in the lower Namoi is less clear-cut, however, and illustrates that each catchment must be assessed individually considering factors such as geology, geochemistry, geomorphology, and land use and fertilizer application history.

5. CONCLUSIONS

Nd and Sr isotopic compositions and trace elements have been used to investigate the sources contributing to the suspended loads of the Namoi River and one of its tributaries and the soils in its upper catchment. Soils in the upper catchment have been derived by a combination of in situ weathering and pedogenesis and eolian transport, depending strongly on the local topography. A significant amount of wind-blown dust component has been incorporated into basaltic soils in low gradient erosional remnants (tablelands) of the upper catchment. The Sr–Nd isotopes and trace elements of the rocks and soils indicate that Tertiary basalts from the river headwaters provide the dominant source of sediment in a reservoir located in the upper catchment, with Paleozoic metasediments providing the remainder. Localities where soils are isotopically similar to rocks are most likely in erosional rather than depositional areas and are therefore the prime sources for river sediment. Sediment from the lower catchment is similar to metasedimentary soils in the upper catchment and shows little evidence for long-distance transport of P-rich basalt soil in the river system at the present time. The increasingly dominant influence of granitoids and metapelites from the New England Fold Belt is observed in suspended sediment from the lower portion of the catchment. The influence of phosphate fertilizer in the soils and sediments is minimal, amounting to 0.2% incorporated as a bulk component in the upper catchment reservoir sediment. Increases in the concentration of trace elements that are asso-

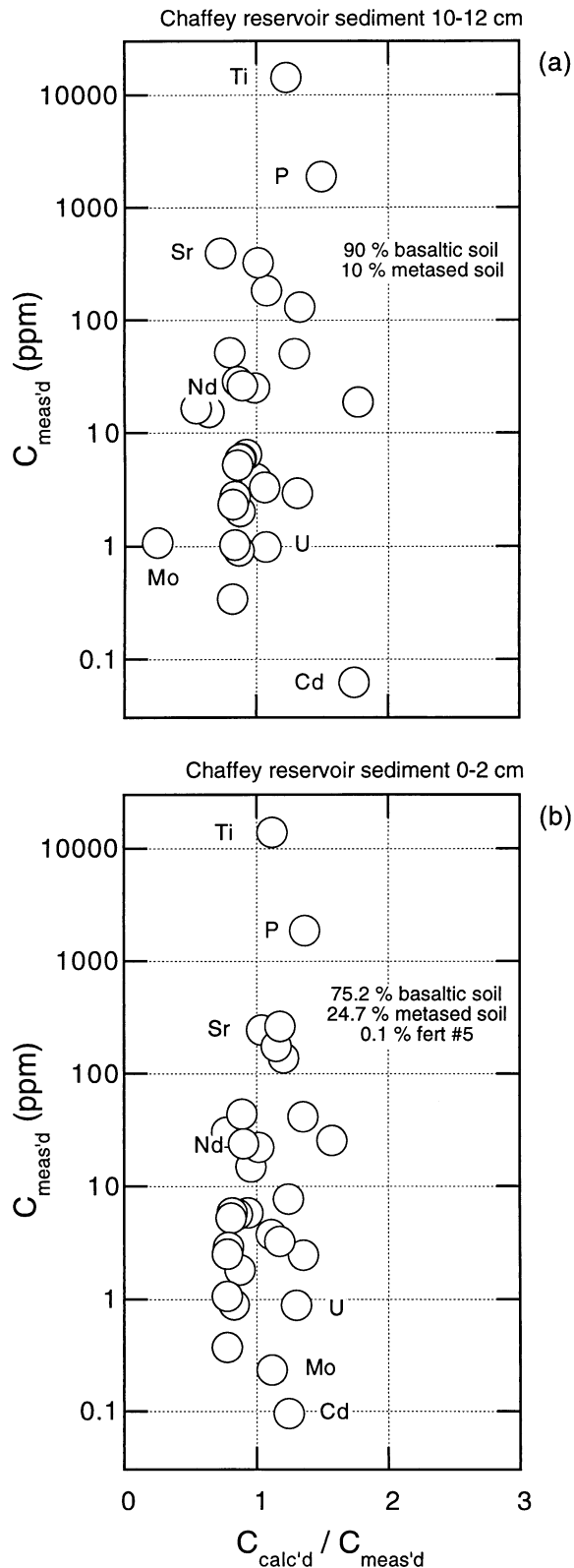


Fig. 11. Plot showing the deviation of the calculated versus measured concentration of trace elements in the Chaffey Reservoir sediments, for a multi-component mixture of basalt soil 61, metasedimentary soil 105, and fertilizer F#5.

ciated with fertilizer or changes in related elemental ratios such as Nd/P, used in conjunction with isotopic variations, may be used to assess the relative importance of fertilizer incorporation into soils and river sediments. Although Sr was soluble during weathering and transport, Sr isotopes, in conjunction with Nd isotopes and trace element geochemistry, provide important constraints on sources and processes in these catchments.

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