TOTAL RECOVERABLE SELENIUM AND OTHER ELEMENTS BY HNO_3 AND $HClO_4$ DIGESTION AND OTHER SOIL CHARACTERIZATION DATA FROM WOOLEY VALLEY UNITS 3 AND 4 WASTE ROCK DUMPS AND DAIRY SYNCLINE LEASE AREA SOILS, SOUTHEAST IDAHO

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ABSTRACT

As part of a series of geoenvironmental studies on the mobilization, reaction pathways, transport, and fate of selenium (Se) and other potentially toxic elements in southeast Idaho phosphate mining areas, composite soil samples were collected along vegetation and soil sampling transects established on the Wooley Valley units 3 and 4 waste rock dumps. Soil samples were also collected along vegetation sampling transects established in the Dairy Syncline lease area to serve as pre-mining baseline data. Total recoverable element concentrations in the soil samples were determined by digestion in concentrated HNO_3 + $HClO_4$. Mean or median scintillometer readings, several element concentrations (e.g., Na, Ca, Sr, Cr, Mo, Ni, Cu, Zn, Cd, P, As, S, and Se), soil pH, and total N were all significantly higher in Wooley Valley Unit 4 Waste Rock Dump soils than in Dairy Syncline lease area soils. The soil chemical analyses and the weathering and disturbance histories of the sedimentary deposits and soils have important implications concerning Se mobility and thus management of waste rock dumps and soil stockpiles to minimize Se bioaccumulation in the environment. Recently disturbed, but relatively unweathered sedimentary deposits with high Se concentrations (new waste rock dumps) have the highest potential for Se mobilization. Undisturbed materials have the lowest potential for Se mobilization either because they have not been exposed to an oxidizing environment (e.g., deeper-lying phosphatic shales) or they have already been exposed to weathering for long periods of time (e.g., overburden soils on upper slopes and ridge-tops such as the Dairy Syncline lease area). Older waste rock dumps (e.g., Wooley Valley) and older soil stockpiles represent an intermediate state in weathering and disturbance history. Therefore, to minimize Se oxidation and mobility during material handling it would be best to stockpile overburden soils in a dry environment, to not expose waste rock at the surface of the dumps, and to use topsoils and subsoils with the lowest Se concentrations to cap waste rock dumps.

INTRODUCTION

Background

The U. S. Geological Survey (USGS) has studied the Permian Phosphoria Formation and related rock units in southeast Idaho and the Western U.S. Phosphate Field through much of the twentieth century. In response to a request by the Bureau of Land Management (BLM), a new series of resource and geoenvironmental studies was undertaken by the USGS in 1998. Integrated, multidisciplinary research studies are currently addressing issues such as (1) resource and reserve estimation of phosphate in selected 7.5-minute quadrangles; (2) elemental, mineralogical, and petrochemical characteristics; (3) mobilization and reaction pathways, transport, and fate of potentially toxic elements associated with the occurrence, development, and societal use of phosphate; (4) geophysical signatures; and (5) improved understanding of the depositional origin. To carry out these studies, the USGS has formed collaborative research relationships with two federal agencies, the U.S. Bureau of Land Management (BLM) and the U.S. Forest Service (FS), who are responsible for land management and resource conservation on public lands, and with five companies currently leasing or developing phosphate resources in southeast Idaho. The five companies include Agrium U.S. Inc. (Rasmussen Ridge phosphate mine), Astaris LLC (Dry Valley phosphate mine), J. R. Simplot Company (Smokey Canyon phosphate mine), Rhodia Inc. (Wooley Valley phosphate mine – inactive), and Monsanto Company (Enoch Valley phosphate mine). Because raw data acquired during the project will require time to interpret, the data are released in USGS open-file reports for prompt availability to other workers. Open-file reports associated with this series of resource and geoenvironmental studies are submitted to each of the Federal and industry cooperators for technical review; however, the USGS is solely responsible for the data contained in the reports.

As part of the geoenvironmental studies on the mobilization, reaction pathways, transport, and fate of potentially toxic elements, composite soil samples were collected along vegetation and soil sampling transects established on the Wooley Valley units 3 and 4 waste rock dumps. Soil samples were also collected along vegetation sampling transects established in the Dairy Syncline lease area to serve as pre-mining baseline data. This report presents total recoverable (by HNO_3 + $HClO_4$ digestion) element concentration data from these soil samples as well as some ancillary soil characterization data useful in interpreting the mobility and fate of trace elements in soils.

Although phosphatic shales contain many potentially toxic trace elements (e.g., V, Mo, Cr, Ni, Zn, Cd, and Se), the element of most concern at present is Se. Elevated levels (up to 2000 ug/L) of Se have been found in drainage waters leaching phosphate mining waste rock dumps (Piper and others, 2000), and several incidents of livestock deaths have been linked to Se toxicosis. Although other element concentrations are presented in this report, the discussion will focus on Se because of its potential toxicity and relatively high geochemical mobility.

Location and General Geology

The Wooley Valley phosphate mining area is located about 25 km northeast of Soda Springs, Idaho (T7S R43E) in an area of southeastern Idaho that has had extensive phosphate mining during the past several decades. The Dairy Syncline lease area is located about 25 km east of Soda Springs, Idaho (T9S R44E) on a ridge at the head of Wilde Canyon between Big Basin and Slug Creek. The general location of the Wooley Valley area is shown on a map in Herring and Amacher (2001).

Service (1966) provided an evaluation of the western phosphate industry in Idaho and a brief description of the mining history, ore occurrence, and geology. More detailed discussion of the Phosphoria Formation in the Western Phosphate Field is found in McKelvey and others (1959). Gulbrandsen and Kier (1980) discussed general aspects of the large and rich phosphorus resources in the Phosphoria Formation in the vicinity of Soda Springs. Gulbrandsen (1966, 1975, and 1979) summarized bulk chemical compositional data for various lithologies of the phosphatic intervals in the Phosphoria Formation.

METHODS

Sample Collection

Transects for sampling soils and above-ground live vegetation were established on the slopes and terraces of lifts 1 through 4 of Wooley Valley Unit 4 Waste Rock Dump (see photograph of Unit 4 Waste Rock Dump in Herring and Amacher, 2001). Additional details concerning construction of the dump are found in Herring and Amacher (2001). For each transect, an arbitrary starting point was marked with a chaining pin at the southeastern edge of each slope and terrace of the waste rock dump. Transects on the lift slopes followed the slope contours while transects on the lift terraces ran parallel to the lift slopes.

At selected points along each transect, scintillometer readings were taken and soil samples were collected from the top 15 cm of the waste rock material using a bucket auger. The soil samples were collected adjacent to the above-ground vegetation that was sampled (Herring and Amacher, 2001). The soil samples collected along a given transect were composited in a plastic pail and thoroughly mixed. A subsample was taken and stored in a labeled, plastic-lined soil sample bag. Distances along each transect were measured with a hip chain and the GPS location of each sampling site was recorded.

A composite soil sample was also collected from the slope of Wooley Valley Unit 3 Waste Rock Dump adjacent to the haul road. Soil samples were not collected from the fenced top of the unit 3 dump because it was overgrazed and the soil trampled so that undisturbed soil and plant samples could not be obtained.

To obtain pre-mining baseline data on the trace element content of undisturbed soils and trace element accumulation by above-ground biomass of native plant species, soil and plant sampling transects were also established across the Meade Peak Phosphatic Shale member of the Permian Phosphoria Formation in the Dairy Syncline lease area. Four transects were established. The first transect began in the underlying Grandeur dolostone, crossed the Meade Peak, and ended on a Rex chert outcrop on a ridge above the valley floor. The second transect, began in a Rex chert – Meade Peak transition zone, crossed the Meade Peak parallel to a forest road, and ended in Grandeur dolostone. The third and fourth transects had the same starting point adjacent to a forest road, ran along an old exploration trench in the Meade Peak, and ended in Rex chert. The third transect ran through the native vegetation above and adjacent to the exploration trench and the fourth transect ran along the side-wall of the exploration trench. Distances along each transect were measured with a hip chain. The GPS location of each transect starting point was recorded.

At selected points along transects 1, 2, and 3, scintillometer readings were taken and a sample of the top 15 cm of soil was collected with a bucket auger. At transect 4, scintillometer readings were taken and the exposed subsoil comprising the side-wall of the exploration trench was sampled using a trowel. The soil samples were placed in labeled plastic-lined soil sample bags and returned to the laboratory for analysis.

Sample Preparation

The soil samples were air-dried at ambient temperature. Stable soil aggregates were then crushed using a ceramic mortar and pestle and each soil sample was sieved through a 2-mm stainless steel sieve to remove coarse fragments. The weights of the coarse fragment and <2-mm size fractions were recorded. A well-mixed representative subsample of each soil sample was placed in a glass scintillation vial with a steel pin and mixed on a motor-driven roller for 4 days to further pulverize the samples to < 100 mesh.

Sample Analysis

A 0.500-g sample of each soil was digested in 20 mL of a mixture of concentrated HNO_3 and $HClO_4$ (3.5:1 ratio) on a hot plate at low heat until the white fumes of $HClO_4$ were visible. At this point the undigested mineral residue has a bleached white or gray color. Digestion vessels were 125-mL conical beakers with small funnels placed in the mouths of the beakers to promote refluxing of the acid mixture. A digest blank consisting of the acid mixture without soil was also heated to fumes of $HClO_4$. After cooling, the digests were transferred to 50-mL volumetric flasks by rinsing with small volumes of 1% HCl. The flasks were filled to volume with deionized water, mixed, and transferred to plastic storage bottles. Element concentrations in the digests were determined by inductively coupled plasma – atomic emission spectrophotometry (ICP-AES). Because some of the element concentrations (e.g., Al, Ca, Fe, Mg, and P) were above the linear range of the instrument, the digests were also diluted 1:10 with deionized water and again analyzed by ICP-AES. The ICP-AES was calibrated with working standards and instrument performance was monitored with independent solution check standards of known element concentrations from a commercial source. These standards serve as an instrument calibration check and do not measure digestion efficiency or element recoveries. Although the HNO_3 + $HClO_4$ digestion method will generally extract most trace elements in soils, it cannot provide a complete digestion of all soil minerals. Therefore, elements extracted by this method should be considered total recoverable by HNO_3 + $HClO_4$ digestion rather than a true total.

Some ancillary soil characterization data were collected including 1:1 soil-water pH (Thomas, 1996), total carbon (TC) by combustion furnace (Nelson and Sommers, 1996), total organic carbon (TOC) by dichromate oxidation with heating (Nelson and Sommers, 1996), total inorganic carbon (TIC) calculated from TC - TOC, and total nitrogen by combustion furnace (Bremner, 1996).

Data Analysis

Scintillometer readings, element concentrations, and ancillary soil characterization data for the composited soil samples from Wooley Valley Units 3 and 4 Waste Rock Dumps were plotted versus location (lift number slope or terrace). Scintillometer readings, element concentrations, and ancillary soil characterization data for the Dairy Syncline lease area soil samples were plotted versus distance along the transects. Box plots comparing the distribution of data for Wooley Valley Unit 4 with the Dairy Syncline lease area were also prepared. For normally distributed data, an analysis of variance was run to compare mean values from Wooley Valley Unit 4 with mean values from the Dairy Syncline lease area. For non-normally distributed data, a Kruskal-Wallis analysis of variance on ranks was run to compare median values from the Wooley Valley Unit 4 Waste Rock Dump with median values from the Dairy Syncline lease area. Data from Wooley Valley Unit 3 were omitted from the analysis of variance because only one composite sample was collected from this area.

RESULTS

Sample identifications, locations, and scintillometer readings associated with the sampling sites are listed in table 1. Total recoverable (conc. HNO_3 + conc. $HClO_4$) element concentrations in the soil samples in mg/kg are listed in table 2 and ICP performance data are documented in table 3. Two different ICP performance standards were analyzed – one with the undiluted sample set and the other with the diluted sample set. All measured element concentrations were within performance limits for the standard run with the undiluted sample set, whereas measured K, Mo, and Na concentrations were slightly below performance limits for the standard run with the diluted sample set. Because the data from the undiluted sample set was used for these elements, the lower concentrations obtained in the analysis of the diluted sample set are moot. Ancillary soil characterization data are found in table 4.

Mean ± standard error scintillometer readings along each transect on the units 3 and 4 waste rock dumps are plotted in figure 1. Element concentrations in the composite soil samples collected along each transect on the units 3 and 4 waste rock dumps are shown as bar graphs in figures 2 through 10. Ancillary soil characterization data from these same transects are plotted in figures 11 and 12. Figure 13 shows the association between total recoverable Se in the composite soil samples and mean scintillometer readings along each transect.

Scintillometer readings along the Dairy Syncline lease area transects are plotted in figure 14. Element concentrations and ancillary soil characterization data from selected locations along each transect are plotted in figures 15 through 27. Soil samples were not collected at every location along the plant sampling transects at which plant samples and scintillometer readings were taken. Instead, soil samples were collected at only some of the locations to keep sample analysis costs within budget.

Box plots comparing the distribution of scintillometer readings, element concentrations, and ancillary soil characterization data at Wooley Valley Unit 4 Waste

Rock Dump and Dairy Syncline lease area are shown in figures 28 through 40. Mean or median values of each measured variable along with results of the analysis of variance comparing Wooley Valley Unit 4 Waste Rock Dump with the Dairy Syncline lease area are shown in table 5. Mean values are reported for normally distributed data while median values are reported for non-normally distributed data.

Although a full discussion and interpretation of these and other data will appear in the scientific literature at some later date, some of the more significant findings are summarized below.

Wooley Valley Unit 3 and 4 Waste Rock Dumps

- Scintillometer readings, concentrations of many elements (e.g., Na, Mg, Ca, Sr, Cr, Mo, Ni, Cu, Zn, Cd, Pb, P, As, S, and Se), total carbon and TOC, and total N tended to decrease moving upslope on the Unit 4 Waste Rock Dump from lift 1 to lift 4 (figs. 1, 2, 3, 4, 6, 7, 9,10, and 12). Since these elements tend to be associated with the phosphatic shales, this suggests that the exposed surfaces of lifts 1 and 2 contain more waste shale and less of other rock types than lifts 3 and 4. Most of the Se in the unit 4 dump appears to be concentrated in the upper terrace of lift 1 and the slope of lift 2 (fig. 10). This is also the area of the dump where the highest concentrations of Se in the above-ground portion of sampled vegetation were found (Herring and Amacher, 2001).

- Mn, Fe, Co, and Al concentrations tended to increase moving upslope on the Unit 4 Waste Rock Dump from lift 1 to lift 4 (figs. 5, 6, and 8). Soil pH increased from lift 1 to lift 3 and decreased at lift 4 (fig. 11). Potassium and Al concentrations were higher in lift slope soils than in terrace soils (figs. 2 and 8).

- Unit 4 Waste Rock Dump soils contain much higher levels of Mo, Ni, Zn, Cd, and Se than Unit 3 Waste Rock Dump soils in the areas sampled (figs. 4, 6, 7, and 10).

- The strong association of total recoverable Se with scintillometer readings (fig. 13) suggests that a scintillometer may be used as a reconnaissance tool to delineate areas of potentially high Se concentrations and accumulation by vegetation.

Dairy Syncline Lease Area

- Scintillometer readings were higher in soils developed in the Meade Peak Phosphatic Shale Member of the Permian Phosphoria Formation than in soils overlying Grandeur dolostone and Rex chert (fig. 14).

- Concentrations of several elements (e.g., Na, Ca, Sr, Cr, Zn, Cd, B, and P) tended to be higher in soils developed in the Meade Peak Phosphatic Shale

Member of the Permian Phosphoria Formation than in soils overlying Grandeur dolostone and Rex chert (figs. 15, 16, 17, 20, 21, and 22).

- No detectable Se (by ICP-AES) was found in the A horizon of soils sampled in the Dairy Syncline lease area (except at the starting point of transect 3 at the exploration trench). However, Se was found in the subsoil from the side-wall of the exploration trench (transect 4 in fig. 23).

Comparison of Wooley Valley Unit 4 Soils with Dairy Syncline Lease Area Soils

- Mean or median scintillometer readings, several element concentrations (e.g., Na, Ca, Sr, Cr, Mo, Ni, Cu, Zn, Cd, P, As, S, and Se), soil pH, and total N were all significantly higher in Wooley Valley Unit 4 Waste Rock Dump soils than in Dairy Syncline lease area soils (table 5 and figs. 28, 29, 30, 31, 33, 34, 36, 37, 38, and 40)

- Mean or median Ba, Mn, Fe, Co, and Al concentrations were significantly higher in Dairy Syncline lease area soils than in Wooley Valley Unit 4 Waste Rock Dump soils (table 5 and figs. 30, 32, 33, and 35).

DISCUSSION

The waste rock dumps at Wooley Valley and at other locations were constructed from a variety of materials including overburden soils, phosphatic shales that are too low in P concentrations to be economically useful with current technologies (e.g., middle waste shales), and related sedimentary deposits such as cherts, limestones, and dolostones. The waste rock also represents sedimentary deposts with a range of weathering histories ranging from deeper-lying, unweathered (unoxidized) phosphatic shales to more weathered (oxidized) near-surface sedimentary deposits (Herring and others, 1999, 2000a, 2000b, 2000c). In contrast, soils developed over the Meade Peak Member and related sedimentary units represent the most weathered geologic components on the landscape, particularly those on upper slopes or along ridge-tops where higher precipitation (more leaching) leads to more weathering.

Compositional differences between waste rock dumps constructed of sedimentary deposits (e.g., Wooley Valley Unit 4) and undisturbed soils overlying the sedimentary units are easily explained by weathering history. The waste rock dumps constructed primarily from less weathered sedimentary deposits contain higher concentrations of relatively geochemically mobile elements (such as Se) than the more strongly weathered soils overlying those undisturbed rock units. Furthermore, the more highly weathered overburden soils have lower pH levels and higher concentrations of elements (e.g., Mn, Fe, Al) associated with minerals more resistant to weathering (e.g., metal oxides) than the waste rock dump soils. Also, no detectable Se was found in the topsoil of these soils, but instead occurred in the subsoils, which is consistent with the weathering history of these soils. Higher Se levels also tend to be found in the deeper-lying, unweathered phosphatic shales than in the more weathered near-surface sedimentary deposits (Herring and others, 1999, 2000a, 2000b, 2000c).

The weathering history of the sedimentary deposits and soils developed from them is summarized in table 6. At one end of the weathering spectrum lie the unweathered, deeper-lying phosphatic shales and at the other end are the more strongly weathered soils overlying these deposits. Also shown in table 6 is the disturbance history of these geologic materials ranging from the undisturbed sedimentary deposits and soils in place to recently disturbed materials used to construct waste rock dumps and soil stockpiles.

The soil chemical analyses and the weathering and disturbance histories of the sedimentary deposits and soils have important implications concerning Se mobility and management of waste rock dumps and soil stockpiles to minimize Se bioaccumulation in the environment. Recently disturbed, but relatively unweathered sedimentary deposits with high Se concentrations have the highest potential for Se mobilization (new waste rock dumps). The high potential for Se mobilization of these sedimentary rocks was confirmed by passive leaching experiments (Desborough and others, 1999). Desborough and others (1999) found that significant amounts of Se were leached from phosphatic shales reacted with pH 5 deionized water for 48 h. Selenium concentrations in the leachate were strongly correlated with sulfate and the highest levels of Se and sulfate were leached from rocks crushed to < 0.5 mm. Selenium in leachates reacted with 11 waste rock samples was positively correlated with Mg, Ca, and Fe in the leachate and with Se, Cd, and pyrite levels in the rock. Selenium concentrations on the order of 180 ug/L were found in leachates reacted for 48 h with two waste rock samples containing 95 and 180 mg/kg Se.

Undisturbed materials have the lowest potential for Se mobilization either because they have not been exposed to an oxidizing environment (e.g., deeper-lying phosphatic shales) or they have already been exposed to weathering for long periods of time (e.g., overburden soils on upper slopes and ridge-tops such as the Dairy Syncline lease area). Older waste rock dumps (e.g., Wooley Valley) and older soil stockpiles represent an intermediate state in weathering and disturbance history, but still have a high potential for Se mobilization as shown by the relatively high concentrations of Se found in seeps at the base of the dumps (up to 2000 ug/L)(Piper and others, 2000).

Overburden subsoils that contain Se concentrations much lower than the sedimentary units from which they developed may still represent a Se hazard to the environment after they are disturbed because then they would be exposed to a new oxidizing environment. Thus, to minimize Se oxidation and mobility during material handling it would be best to stockpile overburden soils in a dry environment, to not expose waste rock at the surface of the dumps, and to use topsoils and subsoils with the lowest Se concentrations to cap waste rock dumps. Other reclamation issues dealing with using plant species to minimize Se accumulation will be addressed elsewhere.

The Se concentrations presented in this report and those in other cited reports are total or total recoverable Se values and do not provide any information on the forms of Se found in the soils or sedimentary deposits. Selenium mobility and bioavailability is in part dependent on the forms of Se in the environment (McNeal and Balistrieri, 1989). Data are needed on the mineral forms and associations (e.g., sorbed to iron oxides) and chemical species (e.g., selenide (Se(-II)), elemental (Se(0)), selenite (Se(IV)), and selenate (Se(VI))) of Se in the sedimentary deposits, soils, and sediments in southeastern Idaho to provide a more accurate assessment of the mobility, bioaccumulation potential, and fate of Se in that environment. Methods are now available to provide data on the solid phase speciation of Se in soils and sediments (Martens and Suarez, 1997).

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Table 1. Soil sample identifications, locations, and scintillometer readings from Wooley Valley units 3 & 4 waste rock dumps and Dairy Syncline lease area.

WUSP Sample Number	Date Collected	Transect or Site Location	Transect Site No	Transect Distance m	GPS readings Latitude	GPS readings Longitude	Scintillometer Reading cps
		Wooley Valley Unit 4					
WPTU4L1S	07/07/99	Lift 1 lower slope composite (4 sites)					
			WVU4L1LS1-1	40	42.821050	-111.398233	230
			WVU4L1LS1-2	90	42.821467	-111.397883	145
			WVU4L1LS1-3	140	42.821817	-111.397633	125
			WVU4L1LS1-4	193	42.822317	-111.397367	120
WPTU4L1T	07/07/99	Lift 1 upper terrace composite (4 sites)					
			WVU4L1UT1-1	35	42.819967	-111.397350	125
			WVU4L1UT1-2	80	42.820283	-111.396983	175
			WVU4L1UT1-3	123	42.820567	-111.396750	170
			WVU4L1UT1-4	169	42.820933	-111.396367	180
WPTU4L2S	07/07/99	Lift 2 slope composite (4 sites)					
			WVU4L2S1-1	35	42.819100	-111.396700	170
			WVU4L2S1-2	73	42.819317	-111.396350	135
			WVU4L2S1-3	117	42.819583	-111.395950	160
			WVU4L2S1-4	178	42.819983	-111.395383	105
WPTU4L2T	07/07/99	Lift 2 terrace composite (4 sites)					
			WVU4L2T1-1	30	42.817933	-111.396367	180
			WVU4L2T1-2	88	42.818033	-111.395900	370
			WVU4L2T1-3	132	42.818617	-111.395533	360
			WVU4L2T1-4	176	42.818900	-111.395167	115
WPTU4L3S	07/06/99	Lift 3 slope composite (3 sites)					
			WVU4L3S1-1	52	42.817400	-111.394500	125
			WVU4L3S1-2	90	42.817617	-111.394117	110
			WVU4L3S1-3	138	42.817883	-111.393683	115
WPTU4L3T	07/06/99	Lift 3 terrace composite (3 sites)					
			WVU4L3T1-1	36	42.817167	-111.394067	135
			WVU4L3T1-2	75	42.817433	-111.393717	130
			WVU4L3T1-3	128	42.817717	-111.393317	120
WPTU4L4S	07/06/99	Lift 4 slope composite (3 sites)					
			WVU4L4S1-1	22	42.816667	-111.392317	120
			WVU4L4S1-2	55	42.816750	-111.392000	90
			WVU4L4S1-3	98	42.817017	-111.391617	70
WPTU4L4T	07/06/99	Lift 4 terrace composite (3 sites)					
			WVU4L4T1-1	30	42.815917	-111.392033	130
			WVU4L4T1-2	70	42.816150	-111.391650	130
			WVU4L4T1-3	125	42.816467	-111.391083	115
		Wooley Valley Unit 3					
WPTU3S	07/08/99	Slope composite (4 sites)					
			WVU3S1-1	32	42.850667	-111.421767	48
			WVU3S1-2	68	42.851817	-111.422017	110
			WVU3S1-3	102	42.850883	-111.420917	54
			WVU3S1-4	136	42.851367	-111.420667	115
		Dairy Syncline Lease Area					
WPTDST11	07/09/99	Ridge above valley floor	DS1-1	0	42.610800	-111.335950	35
		Ridge above valley floor	DS1-2	20			50
		Ridge above valley floor	DS1-3	40			60
WPTDST14	07/09/99	Ridge above valley floor	DS1-4	60			65
		Ridge above valley floor	DS1-5	82			70
		Ridge above valley floor	DS1-6	105			60
WPTDST17	07/09/99	Ridge above valley floor	DS1-7	138			35
WPTDST21	07/09/99	Along road at top of ridge	DS2-1	0	42.626450	-111.353850	33
WPTDST22	07/09/99	Along road at top of ridge	DS2-2	20			50
WPTDST23	07/09/99	Along road at top of ridge	DS2-3	40			90
		Along road at top of ridge	DS2-4	60			50
WPTDST25	07/09/99	Along road at top of ridge	DS2-5	80			40
WPTDST31	07/09/99	Top of exploration trench	DS3-1	0	42.625817	-111.352617	125
		Top of exploration trench	DS3-2	20			78
WPTDST33	07/09/99	Top of exploration trench	DS3-3	46			85
		Top of exploration trench	DS3-4	69			48
WPTDST35	07/09/99	Top of exploration trench	DS3-5	90			40
		Side of exploration trench	DS4-1	0	42.625817	-111.352617	150
WPTDST42	07/09/99	Side of exploration trench	DS4-2	30			125
WPTDST43	07/09/99	Side of exploration trench	DS4-3	50			120
WPTDST44	07/09/99	Side of exploration trench	DS4-4	70			115
WPTDST45	07/09/99	Side of exploration trench	DS4-5	90			125
WPTDST46	07/09/99	Side of exploration trench	DS4-6	115			75

Table 2. Total recoverable (conc. HNO_3 + conc. $HClO_4$) element concentrations in Wooley Valley units 3 & 4 waste rock dumps and Dairy Syncline lease area soil sample.

WUSP Sample Number	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Sr	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
WPTU4L1S	15571	27.7	371	108	131979	58.6	1.8	1315	126.4	14420	4950	7622	111	25.9	1222	222.1	51176	13.1	4006	61.5	691	1023
WPTU4L1T	12961	25.9	320	98	147179	58.5	1.8	1102	130.4	14460	4434	8781	126	28.9	1404	295.8	57436	9	6130	139.3	581	1389
WPTU4L2S	18061	27.8	366	121	134479	46.3	0.7	1412	104.5	15590	6401	9304	93	33.8	1415	264.7	47646	5	4446	118.6	507	1373
WPTU4L2T	10121	15.9	78	65	187779	74.8	0.1	477	84.9	10740	2376	3518	101	14.9	1586	157.7	81436	10.5	2932	67.8	534	1213
WPTU4L3S	22231	17.6	722	164	111679	33	4.1	771	67.8	15760	6358	3229	391	14.1	1409	132.2	46176	6.4	2030	34.2	409	708
WPTU4L3T	12021	24.4	150	104	129179	31.4	2.4	1222	113.8	15260	4030	4553	152	36.7	961	284.6	45206	6.7	3794	64.6	616	1119
WPTU4L4S	23811	14.3	271	131	84619	23.8	3.9	670	60.2	16120	6269	4465	225	12	729	113.5	34156	5.8	1448	26.8	290	554
WPTU4L4T	16351	17.3	110	95	104179	40.3	3	563	83.2	15730	3899	2424	192	15.4	699	141.7	43786	8.8	2145	41.2	390	763
WPTU3S	28651	13.6	334	154	38789	13.5	5.9	612	54.6	15940	6279	2750	182	2.7	669	34.6	17246	3.2	665	0.8	215	236
WPTDST11	13681	4.3	32	168	5007	2.4	7.2	22	7.2	8692	3380	1903	798	0.8	140	14.1	948	9	238	0	27	90
WPTDST14	25921	4.8	102	362	17649	20.1	7	87	14	16420	6400	4154	621	2	410	22.3	5337	10.8	408	0	99	330
WPTDST17	28381	9.7	32	353	8221	17.8	9.7	73	15.8	17720	6465	4238	994	1.7	253	26.3	2516	12.1	307	0	55	264
WPTDST21	23701	5.2	15	274	6177	11.9	9	67	12.9	19050	4371	3695	989	2.1	124	26.5	1605	10.2	258	0	47	291
WPTDST22	30821	4.6	59	277	10319	14.4	7.3	70	9.8	19070	5625	4364	601	1.6	423	17.7	3777	13.2	144	0	50	368
WPTDST23	32891	6.5	190	288	38219	11.5	7.3	200	11.8	18690	5375	4241	200	0.5	532	23.4	17606	8.9	161	0	179	211
WPTDST25	27391	6.6	43	188	5580	3.6	7.4	47	8.2	15630	3929	4049	360	0.4	328	13.6	1258	9.1	131	0	31	176
WPTDST31	23361	6.9	311	247	69379	17.8	4.5	215	10.4	14910	4511	3166	440	2.9	834	24.1	30466	16.5	576	7.8	228	276
WPTDST33	26431	6	91	208	38829	21.6	5.7	180	13.1	16730	4842	3691	483	2.5	286	31.3	16426	14.8	237	0	133	370
WPTDST35	27771	6.6	56	270	9489	19.3	7.5	165	17.1	18740	6470	3794	790	4.3	300	30.8	1813	13.4	405	0	75	525
WPTDST42	31061	17	319	200	45729	8.7	6.9	608	48.8	23270	6551	3724	259	5.2	725	70.4	20016	5.4	752	2.5	342	338
WPTDST43	25681	19.9	379	138	83939	12.3	2	1272	122.7	20200	6291	2589	32	8.5	1025	81	37616	2	993	13.7	572	328
WPTDST44	32041	10.4	240	187	57579	29.2	2.6	585	40	18190	6859	3689	186	7	591	63	24916	4.1	476	4.6	298	542
WPTDST45	27951	8.4	207	201	43999	30.6	8.4	203	18.9	16440	6108	3836	433	3.6	491	35.1	17746	5.8	310	1.5	152	497
WPTDST46	31821	10.9	74	180	5285	3	14.9	296	18.6	27150	7918	3875	513	9.1	296	53.7	2370	3.5	106	0	41	283
Blank	28	0	30	0	35	0	0	1	0	8	13	12	0	0	38	0.2	0	0.4	5	0	0	1

Table 3. ICP-AES performance data.

	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Detection Limit	4	8	2	0.4	0.2	0.6	1.2	2	4	2	40
	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L
Check standards											
Measured (undiluted samples)	780	371	260	769	93.2	156	944	480	74.8	1129	183
Certified value	797	388	242	791	94.6	167	954	493	86.6	1240	183
Performance limits	654-940	291-458	198-301	649-933	88-103	137-197	782-1130	404-581	71-102	1020-1460	167-199
Measured (diluted samples)	1125	714	507	307	46.2	260	349	782	772	1657	**27.4**
Certified value	1120	744	494	329	48.1	266	347	809	801	1830	31.9
Performance limits	917-1320	558-878	405-583	270-388	44.8-52.6	218-314	284-409	663-955	657-945	1500-2160	29.0-34.9

	Mg	Mn	Mo	Na	Ni	Pb	S	Se	Sr	Zn
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Detection Limit	0.2	0.2	2	6	4	6	15	10	0.6	0.4
	Mg	Mn	Mo	Na	Ni	Pb	S	Se	Sr	Zn
	mg/L	ug/L	ug/L	mg/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L
Check standards										
Measured (undiluted samples)	34.3	526	525	202	2395	582	78.4	1430	237	1270
Certified value	34.3	571	548	213	2490	605	77.5	1480	256	1340
Performance limits	31.4-37.0	468-674	449-646	200-225	2050-2940	496-714	68.4-83.8	1110-1750	210-302	1100-1580
Measured (diluted samples)	17.0	2154	**19.4**	**133**	1559	461	13.3	603	36.1	177
Certified value	17.5	2250	25.9	159	1580	469	12.9	617	38.1	175
Performance limits	16.0-18.9	1850-2660	21.2-30.6	149-168	1300-1870	385-553	11.2-14.2	463-728	31.2-44.9	144-207

Table 4. Ancillary soil characterization data for Wooley Valley units 3 & 4 waste rock dumps and Dairy Syncline lease area.

WUSP Sample Number	Coarse Fragments > 2 mm %	pH	Total Carbon %	Total Organic Carbon %	Total Inorganic Carbon %	Total Nitrogen %
WPTU4L1S	48.93	6.71	5.48	4.59	0.89	0.52
WPTU4L1T	42.12	6.88	6.76	5.90	0.86	0.63
WPTU4L2S	49.26	6.95	6.22	4.34	1.88	0.56
WPTU4L2T	53.18	7.11	2.69	2.11	0.58	0.23
WPTU4L3S	43.17	6.96	3.28	2.97	0.31	0.38
WPTU4L3T	34.85	7.11	4.92	3.61	1.31	0.58
WPTU4L4S	50.44	6.96	3.52	3.30	0.22	0.35
WPTU4L4T	41.67	6.59	3.58	2.88	0.70	0.42
WPTU3S	43.36	6.74	0.95	0.85	0.10	0.22
WPTDST11	14.06	5.70	4.90	4.72	0.18	0.23
WPTDST14	39.92	6.19	5.58	4.86	0.72	0.33
WPTDST17	49.71	6.19	4.08	4.02	0.06	0.25
WPTDST21	38.59	5.99	4.09	3.50	0.59	0.20
WPTDST22	42.96	5.29	2.93	2.68	0.25	0.12
WPTDST23	36.24	5.36	1.61	1.31	0.30	0.11
WPTDST25	38.90	5.52	4.01	3.65	0.36	0.12
WPTDST31	37.53	5.31	4.25	3.91	0.34	0.21
WPTDST33	28.47	5.69	2.85	2.58	0.27	0.17
WPTDST35	61.54	6.17	8.98	7.60	1.38	0.44
WPTDST42	36.49	6.20	0.98	0.96	0.02	0.27
WPTDST43	44.25	6.40	0.95	0.79	0.16	0.35
WPTDST44	16.89	6.03	1.46	1.24	0.22	0.18
WPTDST45	36.67	6.43	2.78	3.00	-0.22	0.15
WPTDST46	47.24	6.26	1.03	0.90	0.13	0.09

Table 5. Mean ± standard error or median scintillometer readings, element concentrations, and ancillary soil characterization data for soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area. Mean values not followed by the same letter are significantly different ($p<0.01$). Median values not followed by the same letter are significantly different ($p<0.01$) according to the Kruskal-Wallis analysis of variance on ranks.

Parameter	Units	Wooley Valley Unit 4 (n = 8)	Dairy Syncline Lease Area (n = 15)
Scintillometer	Cps	130 a (n = 28)	65 b (n = 23)
Na	mg/kg	1178 ± 120 a	451 ± 66 b
K	mg/kg	4840 ± 510 a	5673 ± 321 a
Mg	mg/kg	4509 a	3794 a
Ca	%	12.89 ± 1.09 a	2.97 ± 0.68 b
Sr	mg/kg	520 a	99 b
Ba	mg/kg	111 ± 10 a	236 ± 17 b
Cr	mg/kg	936 a	180 b
Mo	mg/kg	20.6 a	2.5 b
Mn	mg/kg	174 ± 35 a	513 ± 75 b
Fe	%	1.54 a	1.82 b
Co	mg/kg	2.1 a	7.3 b
Ni	mg/kg	202 ± 26 a	35.6 ± 5.5 b
Cu	mg/kg	94.7 a	14.0 b
Zn	mg/kg	1018 ± 111 a	326 ± 32 b
Cd	mg/kg	43.3 a	14.4 b
Pb	mg/kg	8.2 ± 1.0 a	9.3 ± 1.1 a
B	mg/kg	296 a	91 a
Al	%	1.60 a	2.78 b
P	%	4.69 a	0.53 b
As	mg/kg	21.4 ± 2.0 a	8.5 ± 1.2 b
S	mg/kg	3363 a	307 b
Se	mg/kg	63.0 a	0.0 b
Coarse fragments	%	45.5 ± 2.1 a	38.0 ± 3.1 a
pH		6.91 ± 0.06 a	5.92 ± 0.10 b
Total carbon	%	4.25 a	2.93 a
Total organic carbon	%	3.46 a	3.00 a
Total inorganic carbon	%	0.78 a	0.25 a
Total nitrogen	%	0.46 ± 0.05 a	0.22 ± 0.03 b

Table 6. Relationship of weathering and disturbance history of phosphatic shales, related sedimentary deposits, and overburden soils to potential for Se mobilization.

	Weathering history & tendency →					
Disturbance history	Unweathered	Lightly weathered	Moderately weathered	More strongly weathered	↓	Potential for Se mobilization
Undisturbed	Deeper phosphatic shale deposits	Near-surface sedimentary deposits[1]		Soil developed over sedimentary deposits		
Older disturbances		Old waste rock dumps		Old soil stockpiles[2]		
Recently disturbed	New waste rock dumps			New soil stockpiles[2]		
	← Potential for Se mobilization					

[1] Grandeur dolostone, Rex chert, etc.
[2] Old and new soil stockpiles are topsoil and subsoil overburden removed during phosphate rock mining and stockpiled for use in waste rock dump reclamation. New soil stockpiles have been recently removed from their original position on the landscape and stockpiled in a new weathering environment. Old soil stockpiles are those that have been subjected to weathering for at least several years.

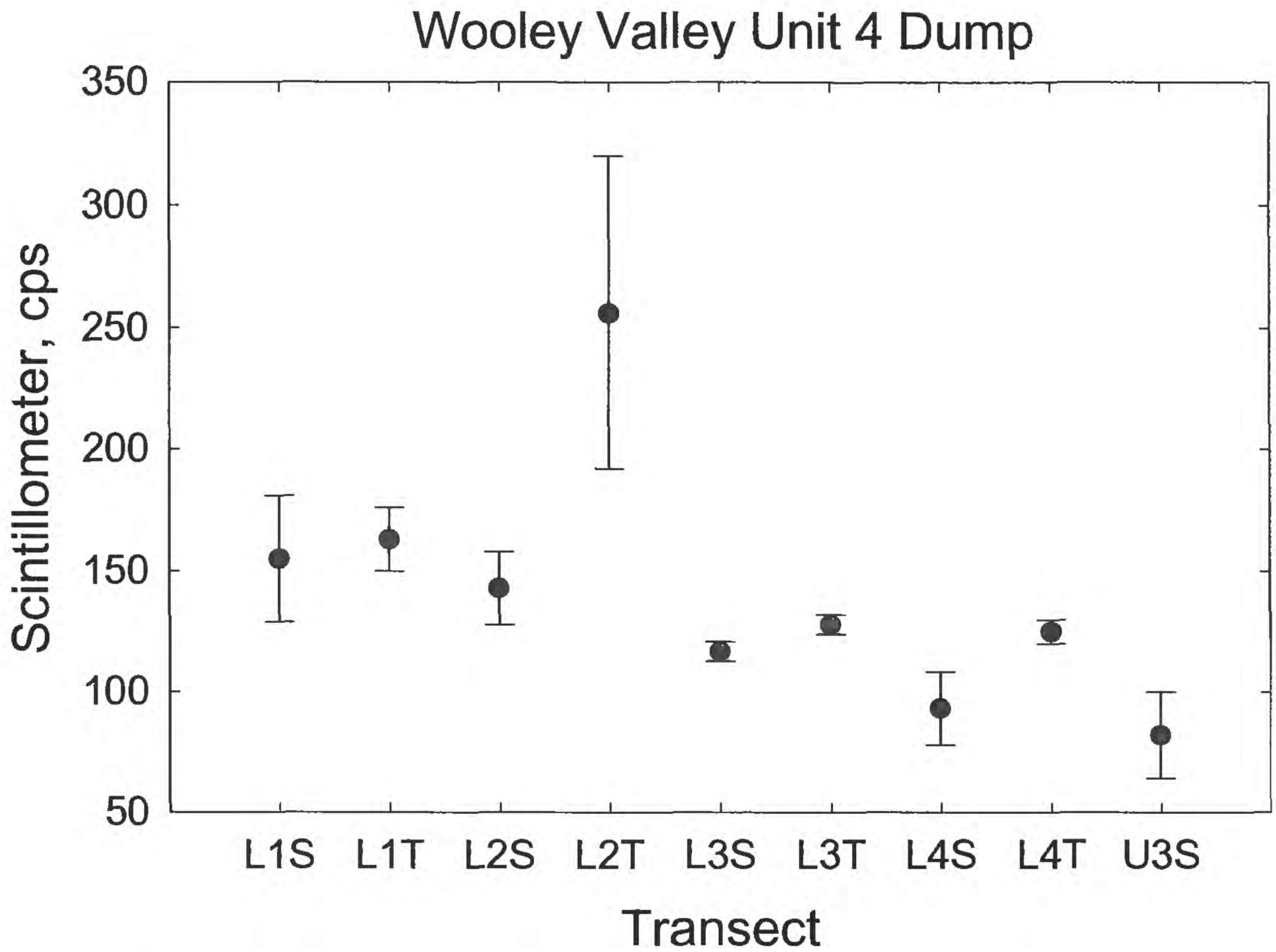

Figure 1. Mean ± standard error scintillometer readings along sampling transects on the slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

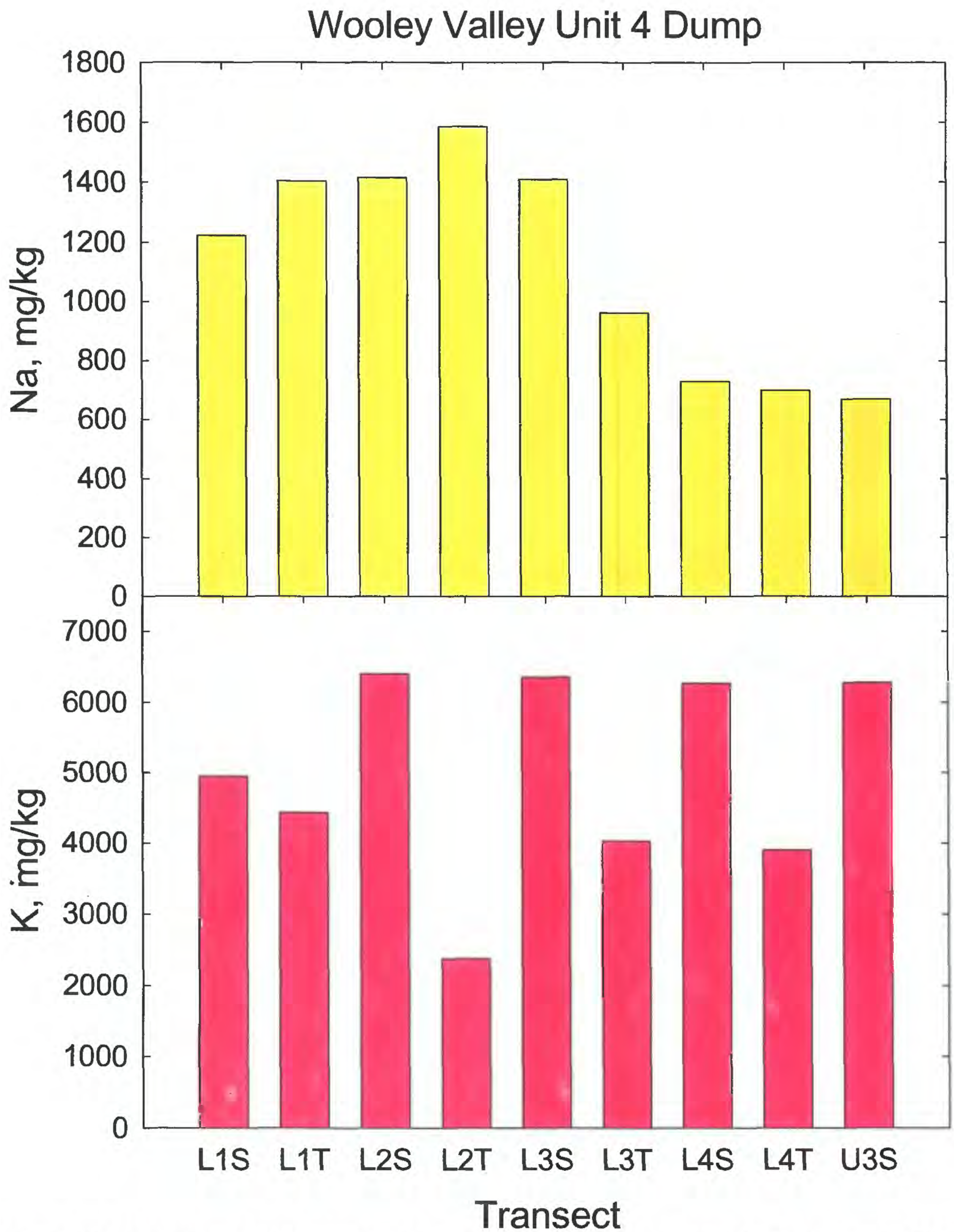

Figure 2. Total Na and K in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

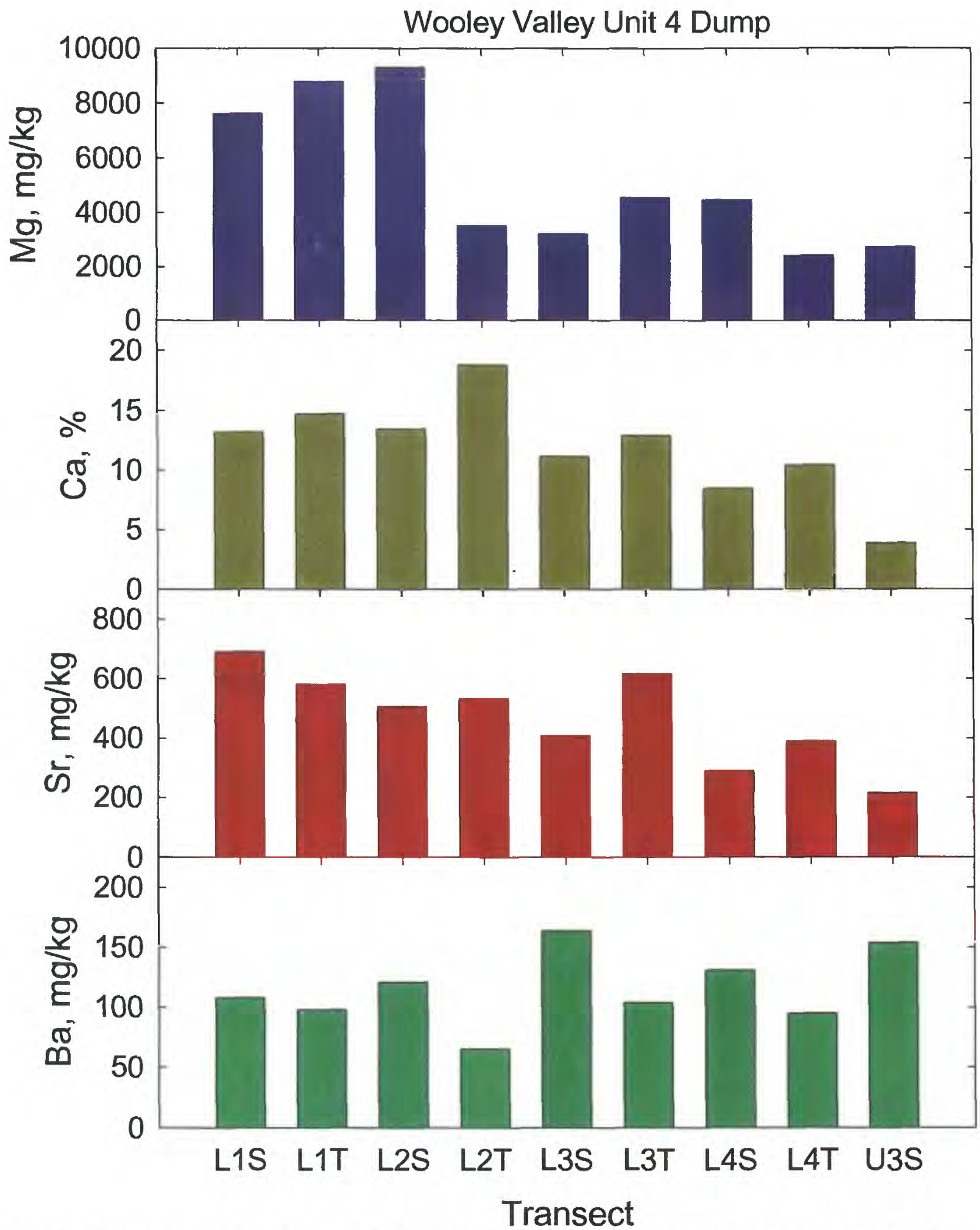

Figure 3. Total Mg, Ca, Sr, and Ba in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

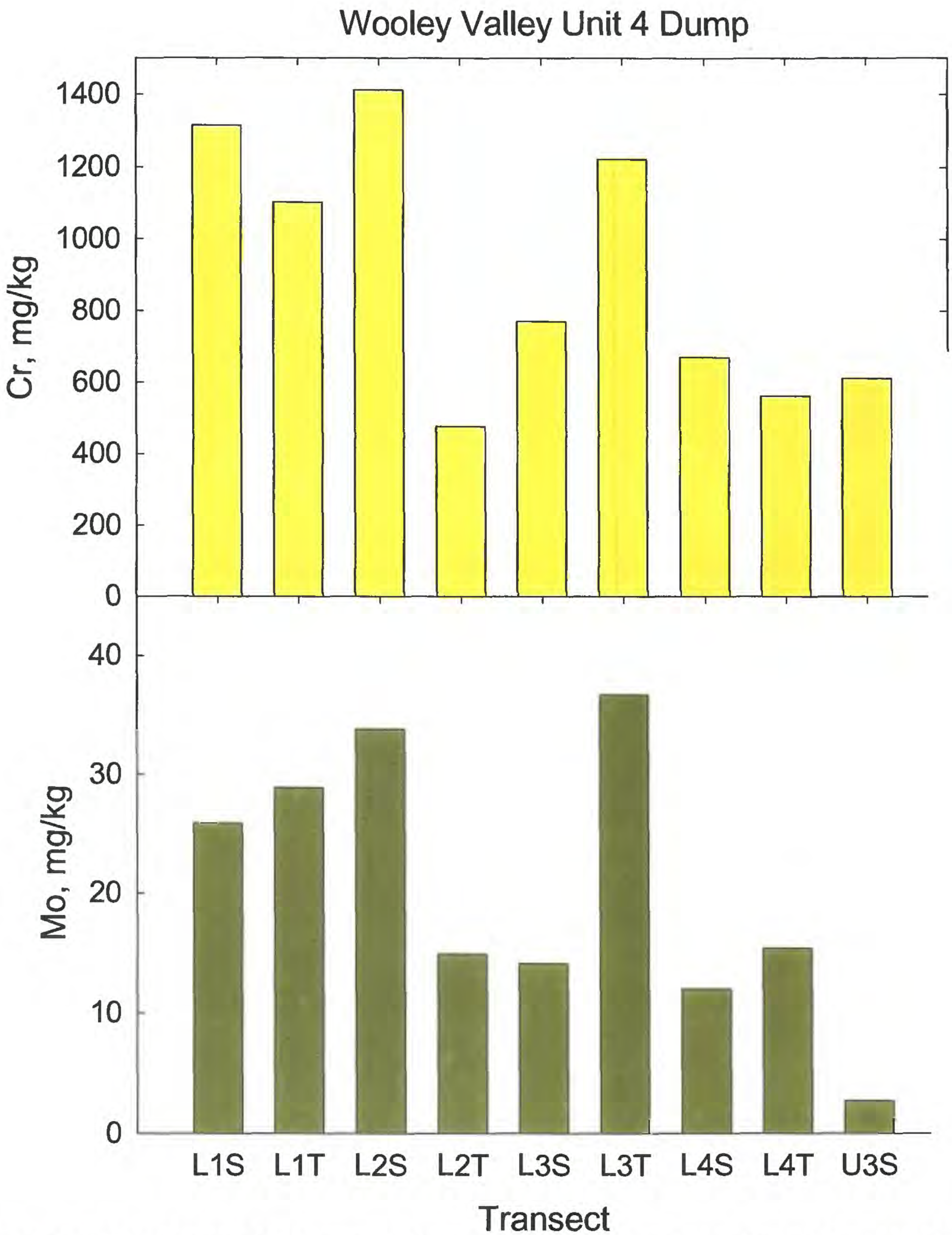

Figure 4. Total Cr and Mo in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

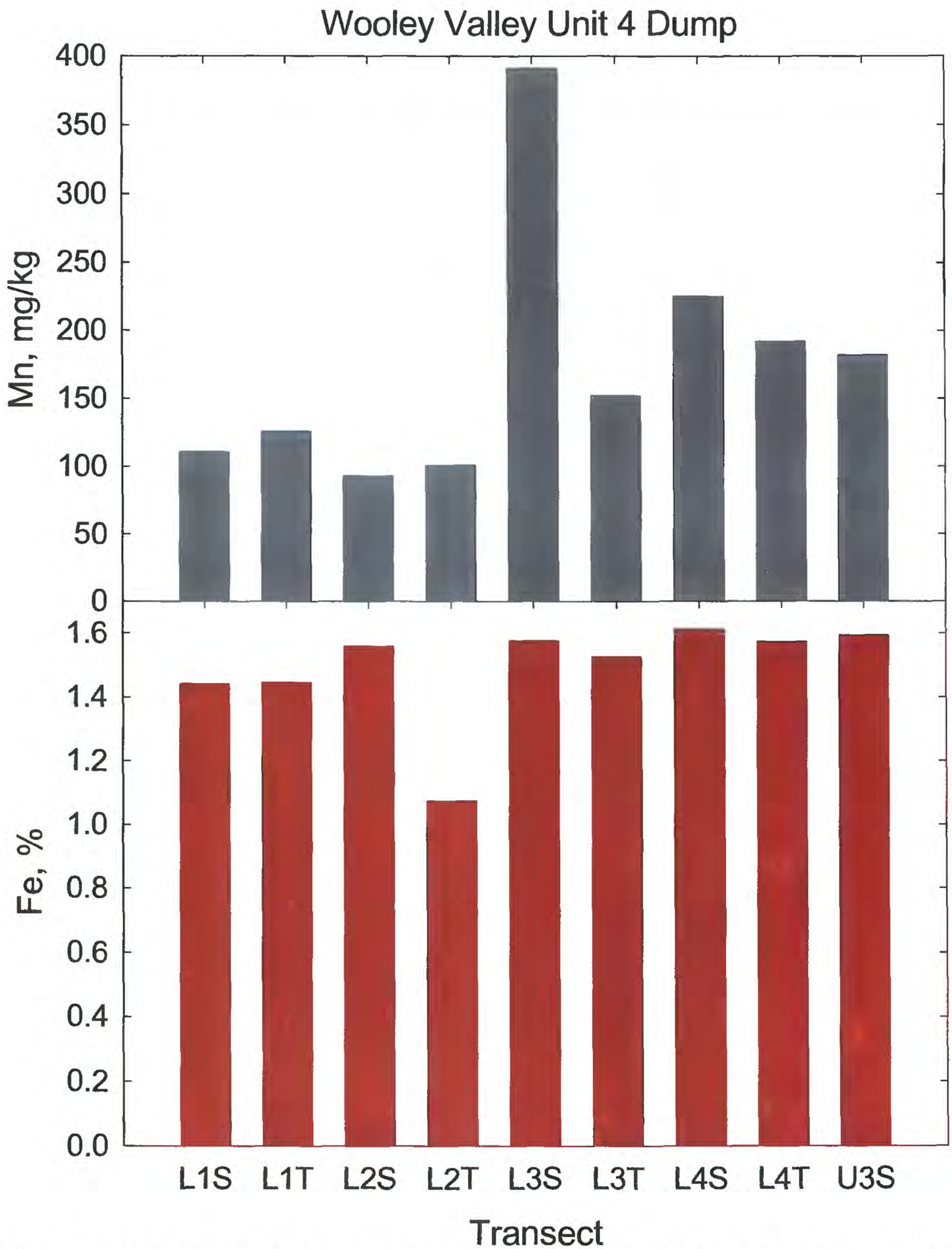

Figure 5. Total Mn and Fe in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

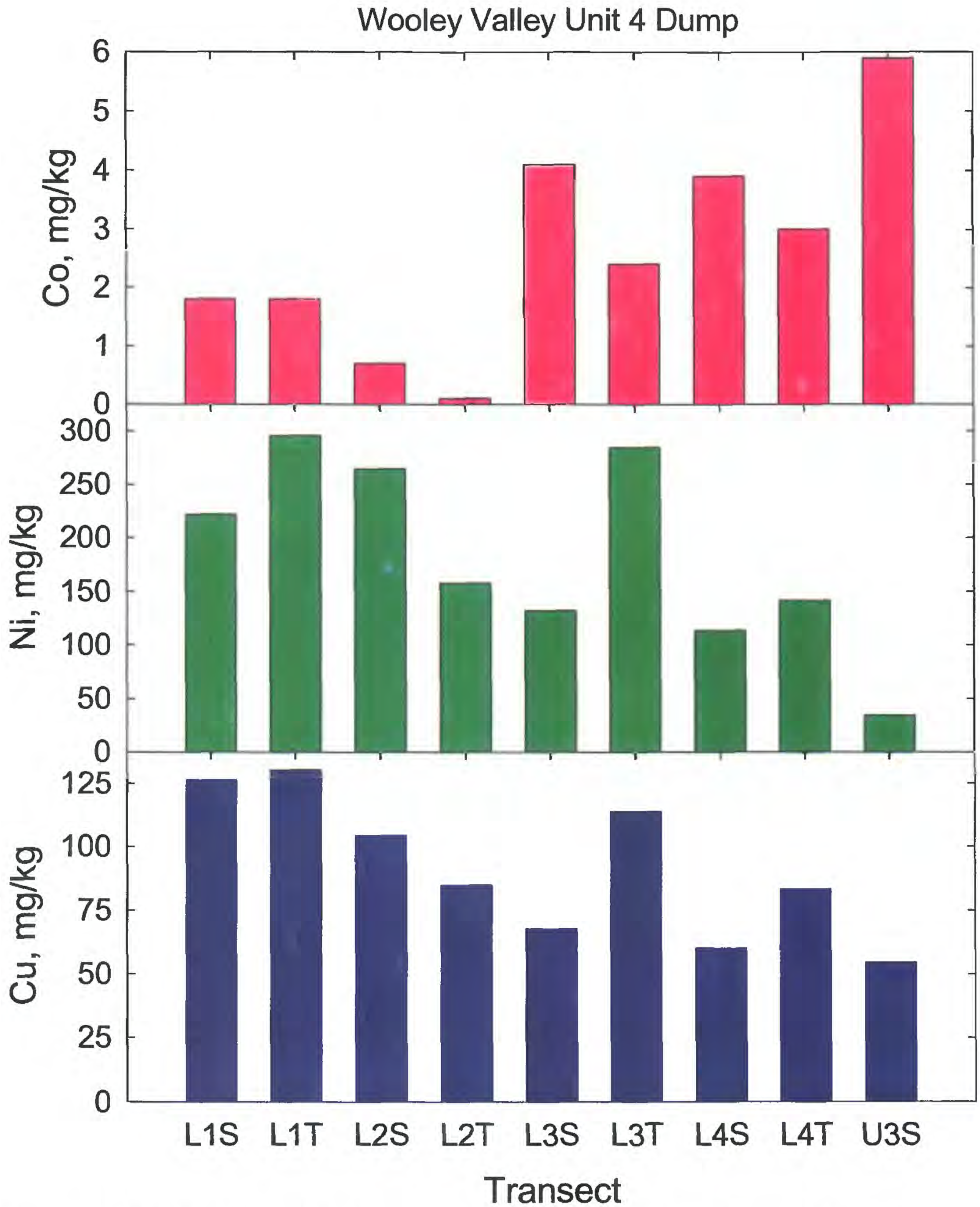

Figure 6. Total Co, Ni, and Cu in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

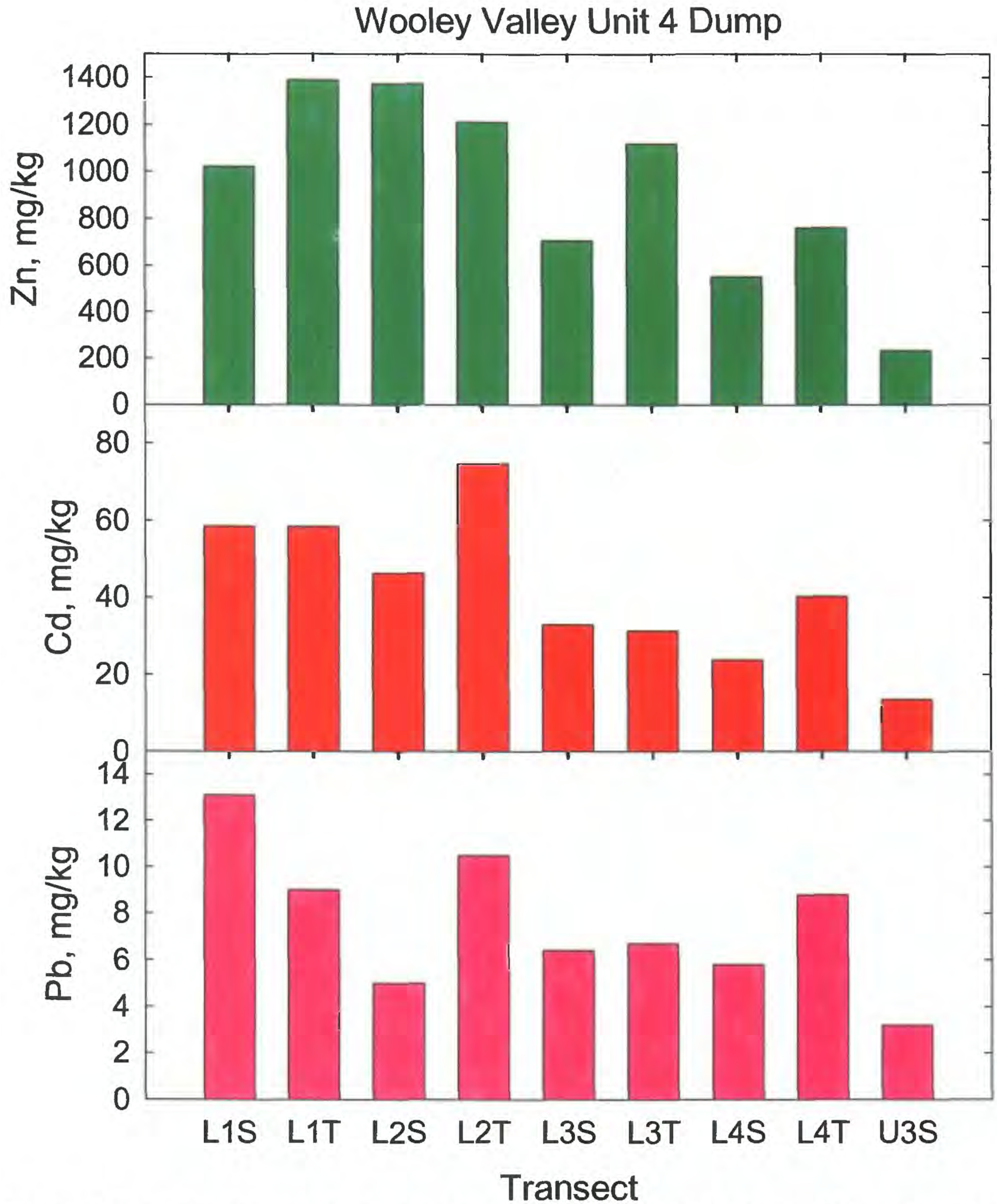

Figure 7. Total Zn, Cd, and Pb in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

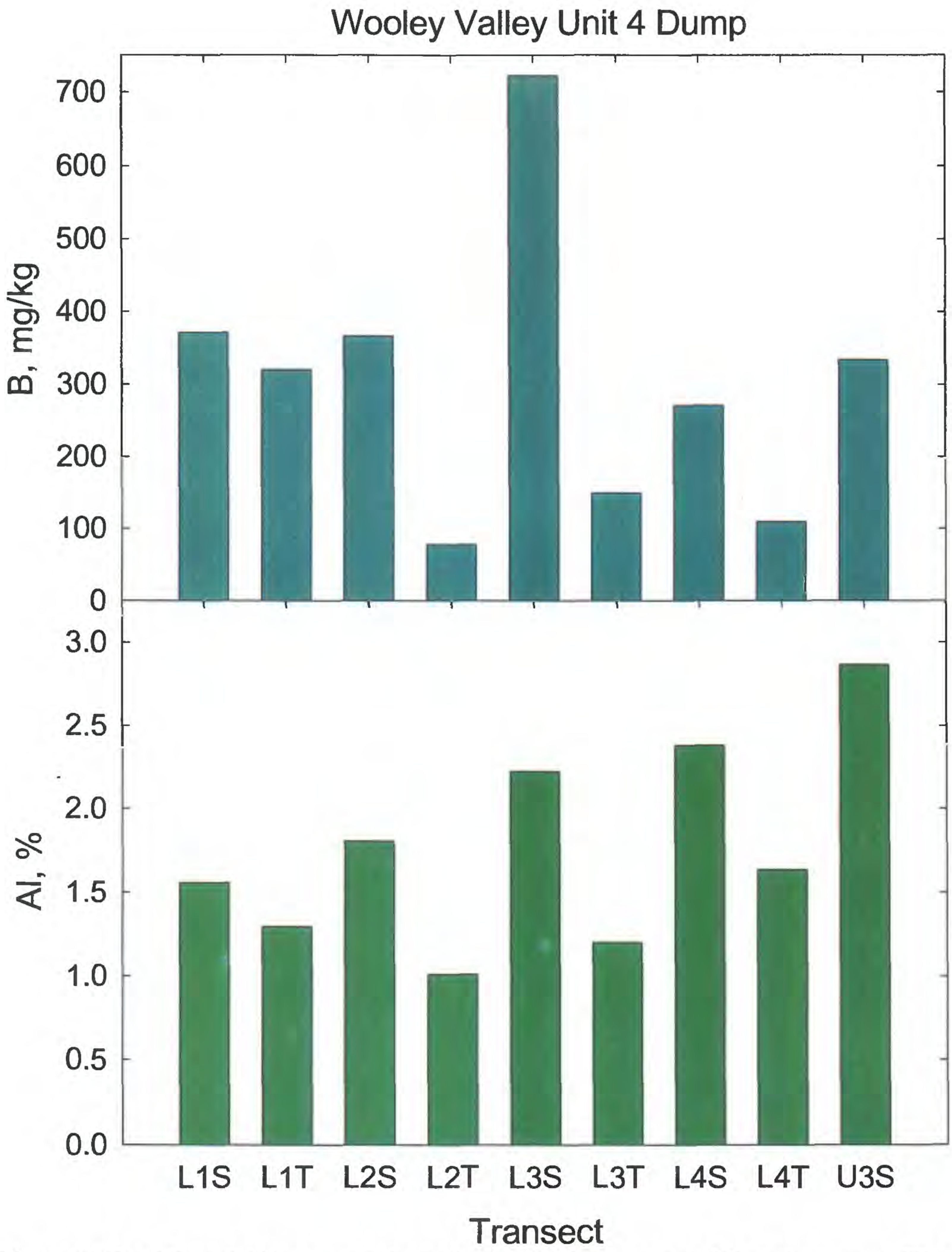

Figure 8. Total B and Al in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

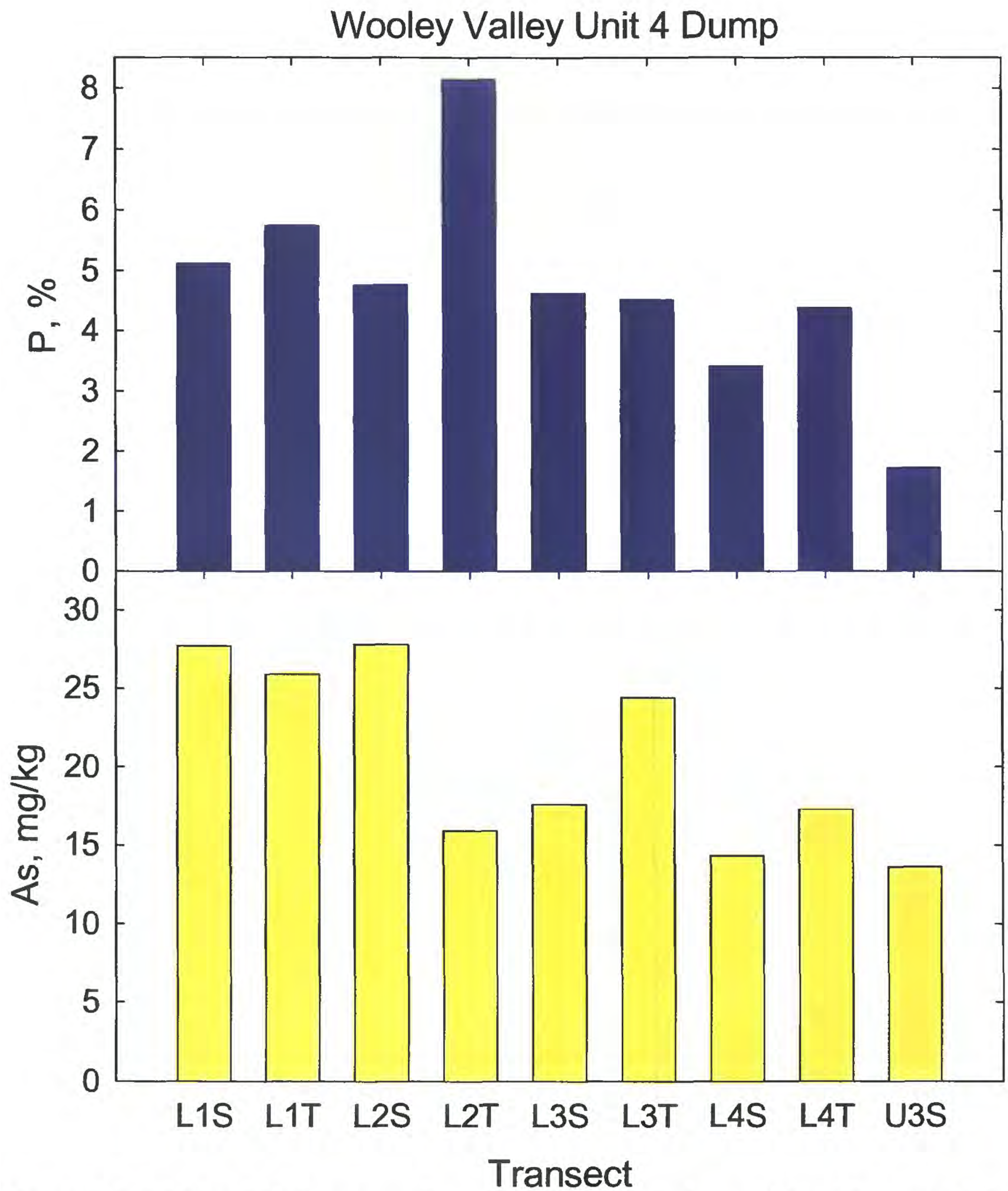

Figure 9. Total P and As in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

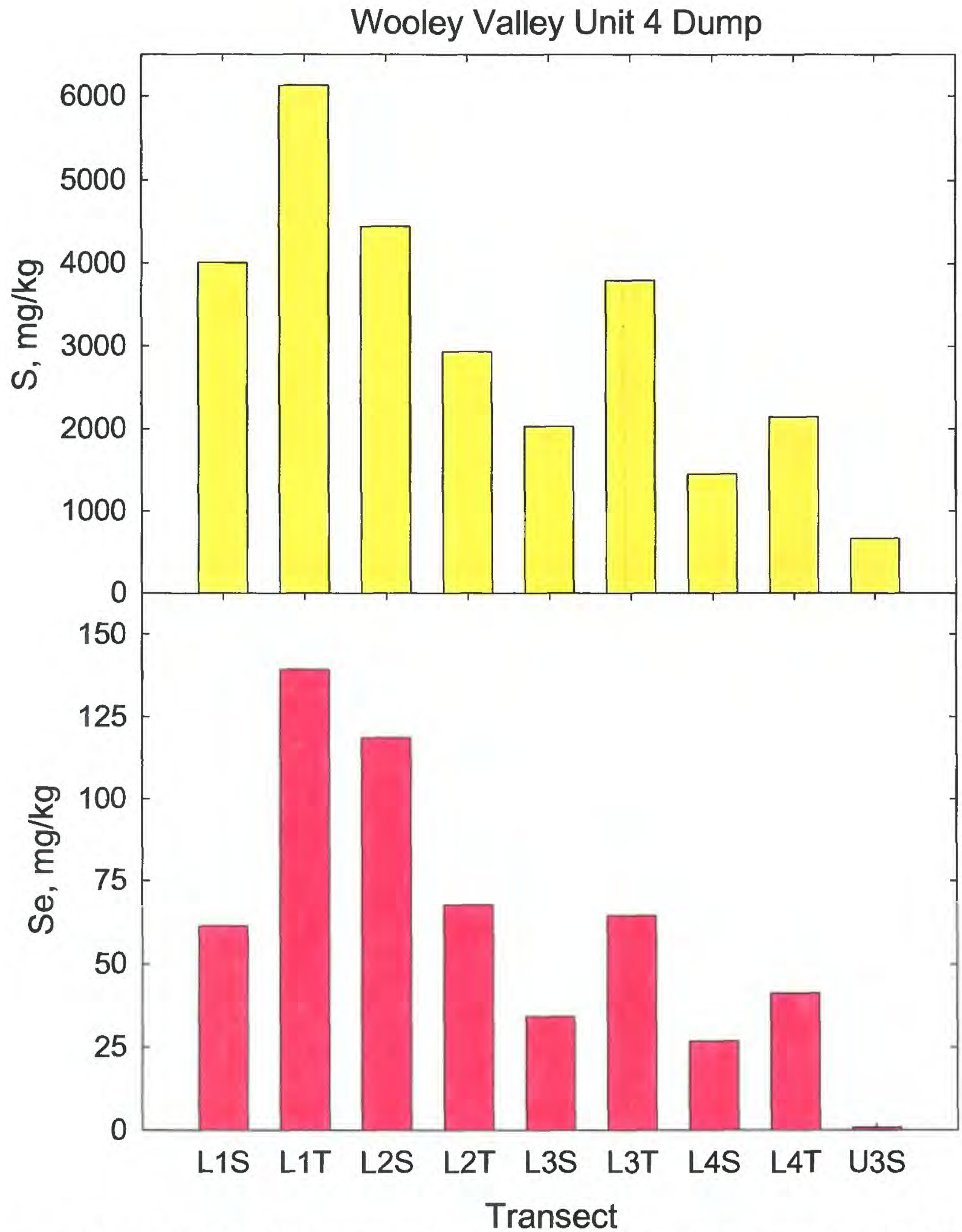

Figure 10. Total S and Se in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

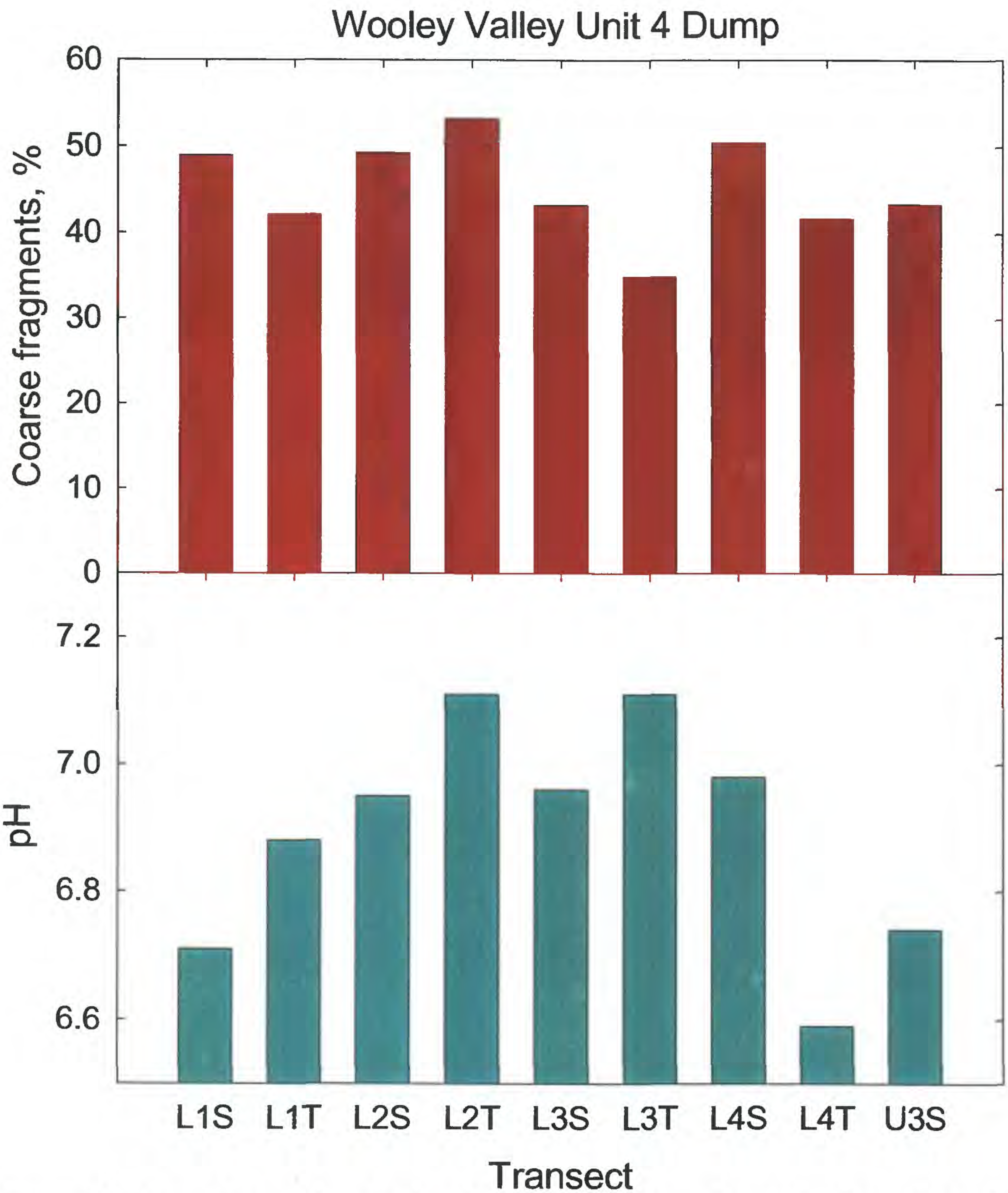

Figure 11. Coarse fragment content and pH of composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

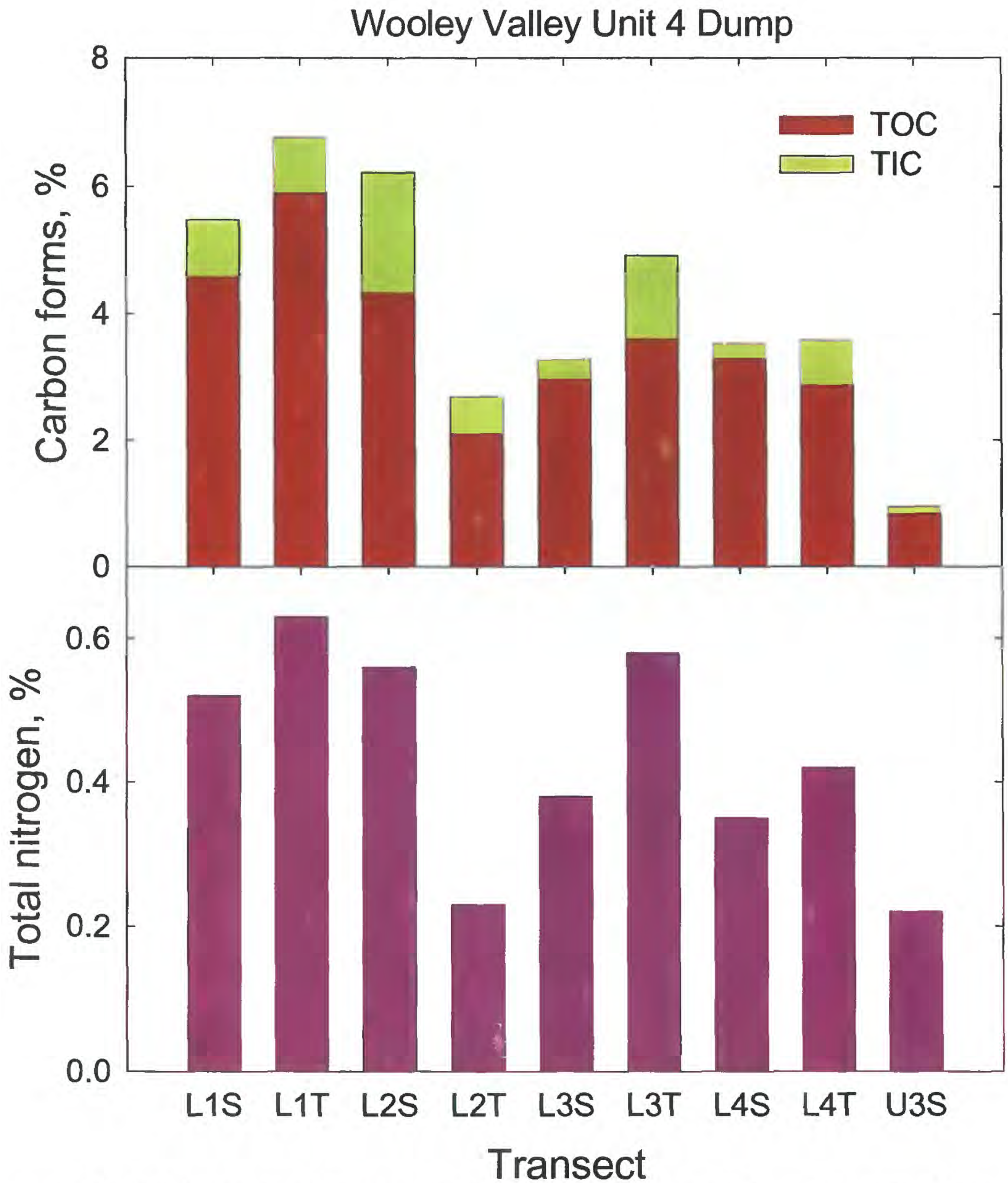

Figure 12. Total organic and inorganic C and total N in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

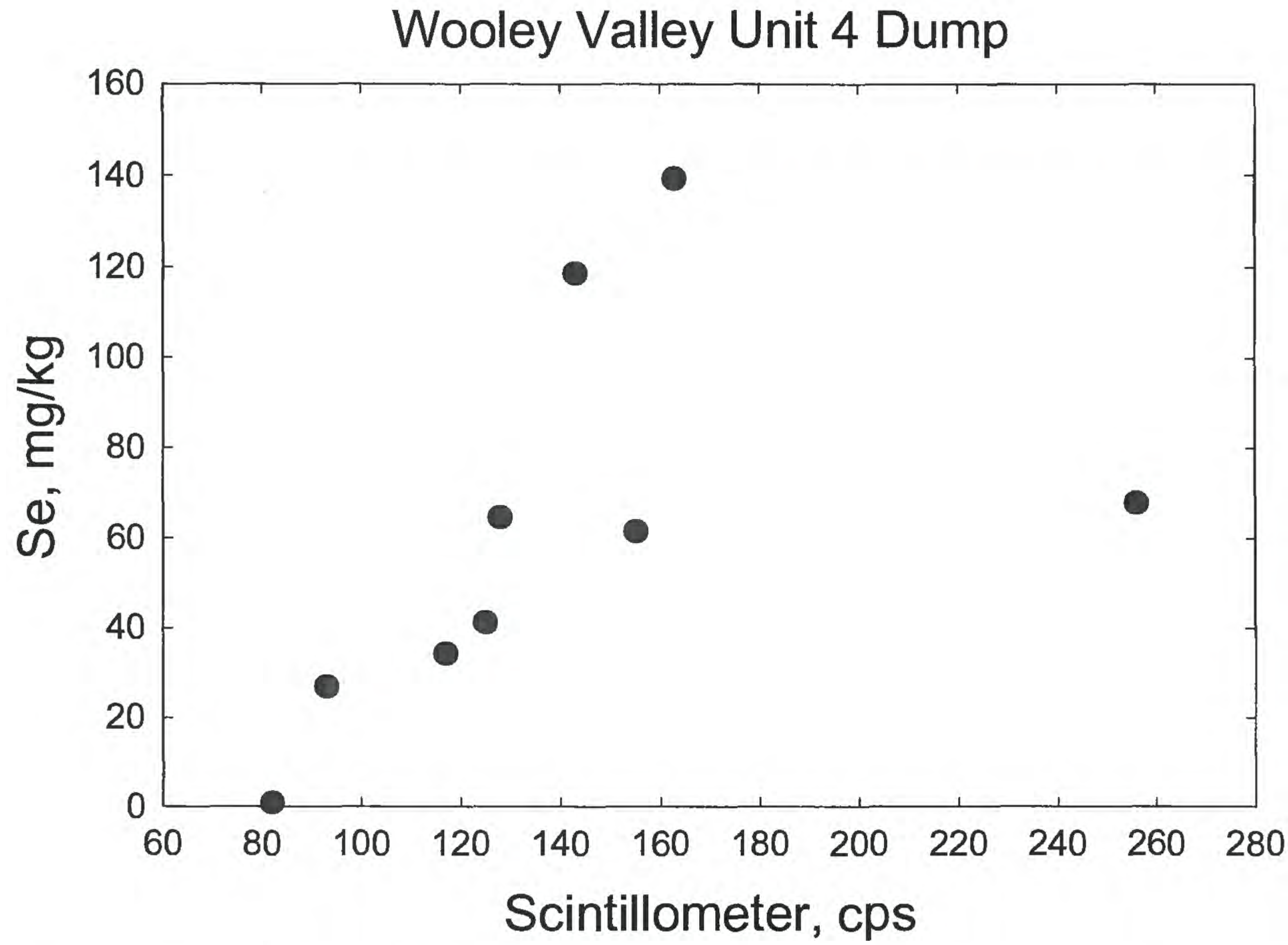

Figure 13. Relationship of total Se to scintillometer readings in composite soil samples from slopes (S) and terraces (T) of lifts 1 through 4 (L1, L2, L3, L4) at Wooley Valley Unit 4 Waste Rock Dump and the slope of Unit 3 Waste Rock Dump.

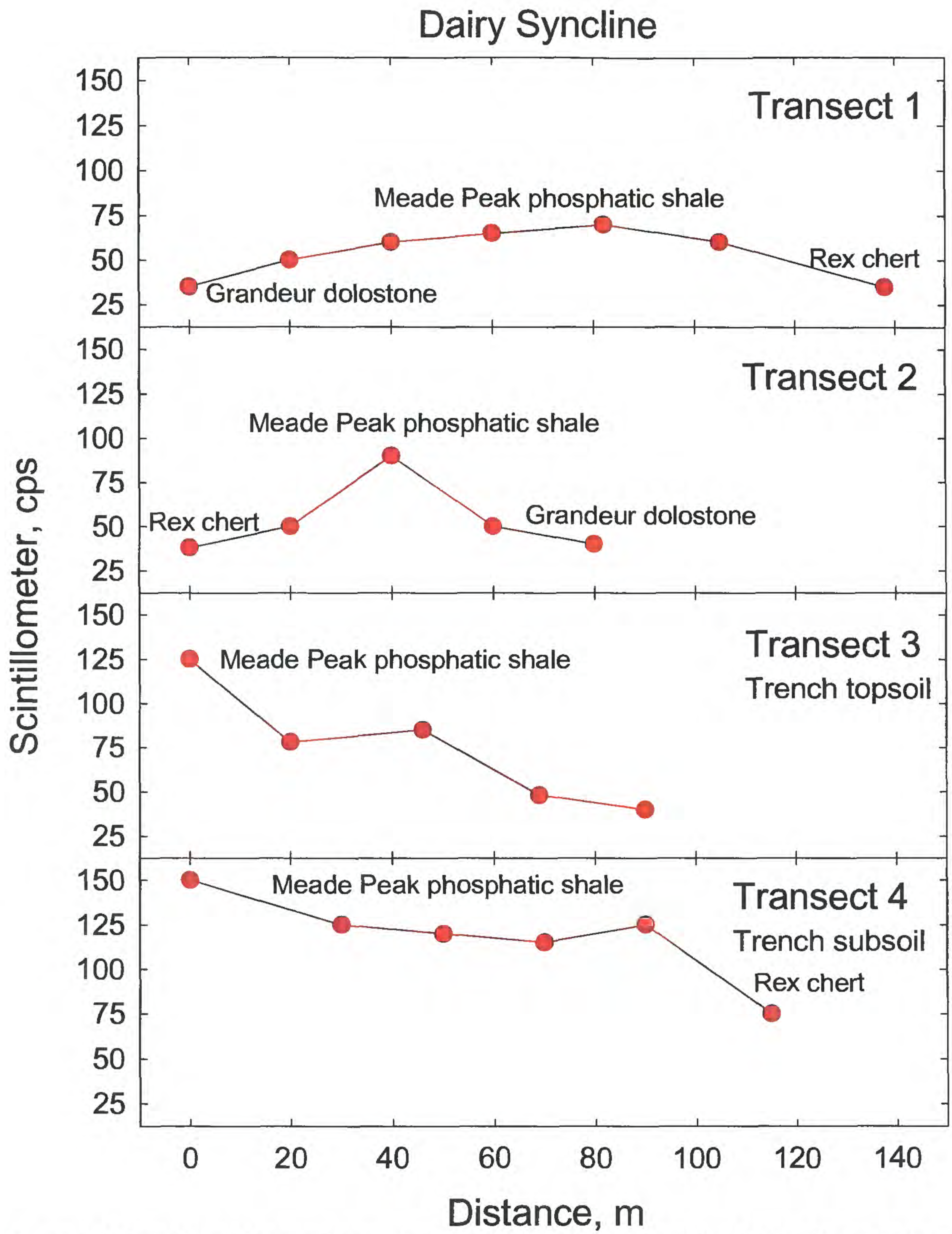

Figure 14. Scintillometer readings along sampling transects in the Dairy Syncline lease area.

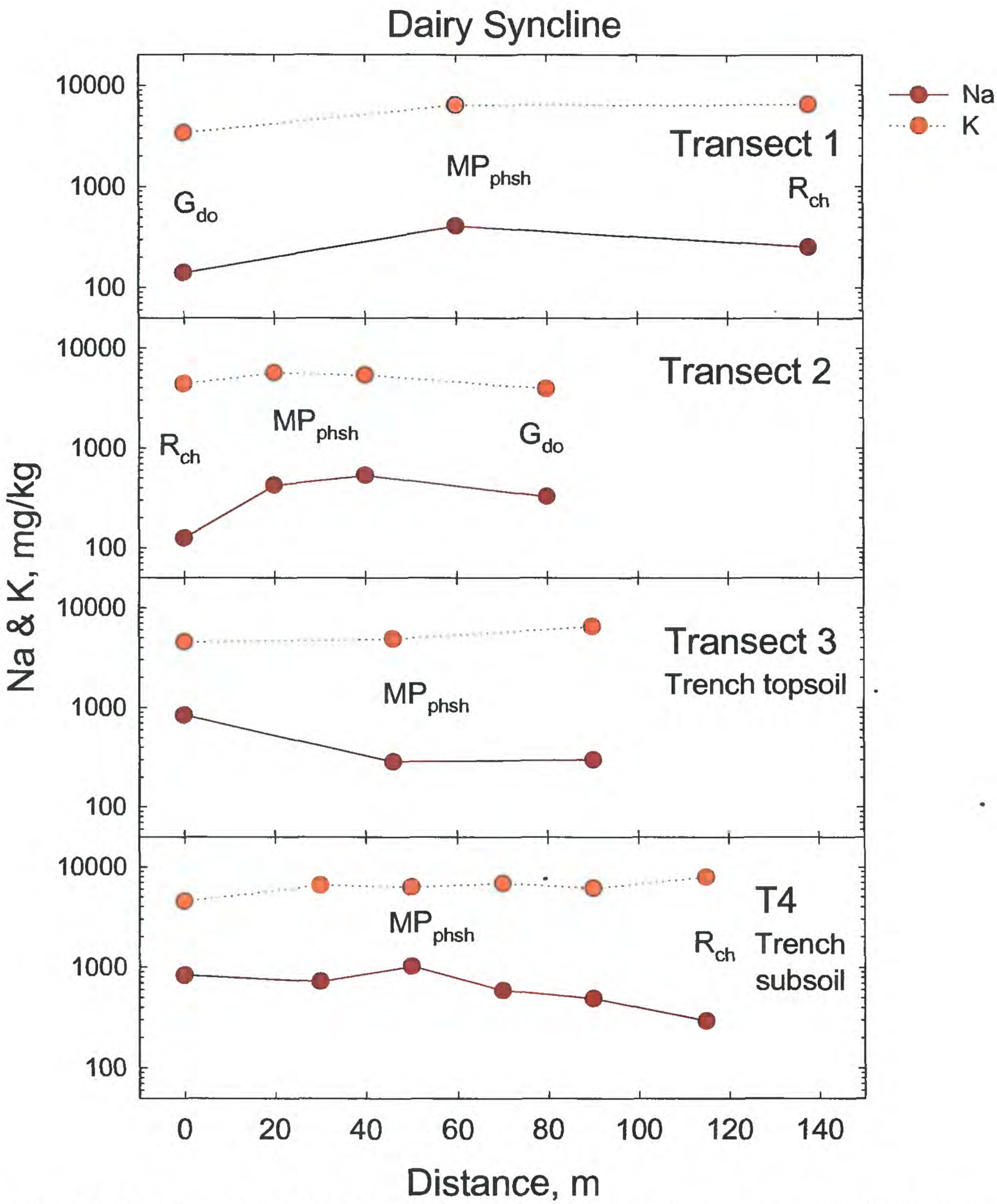

Figure 15. Total Na and K in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

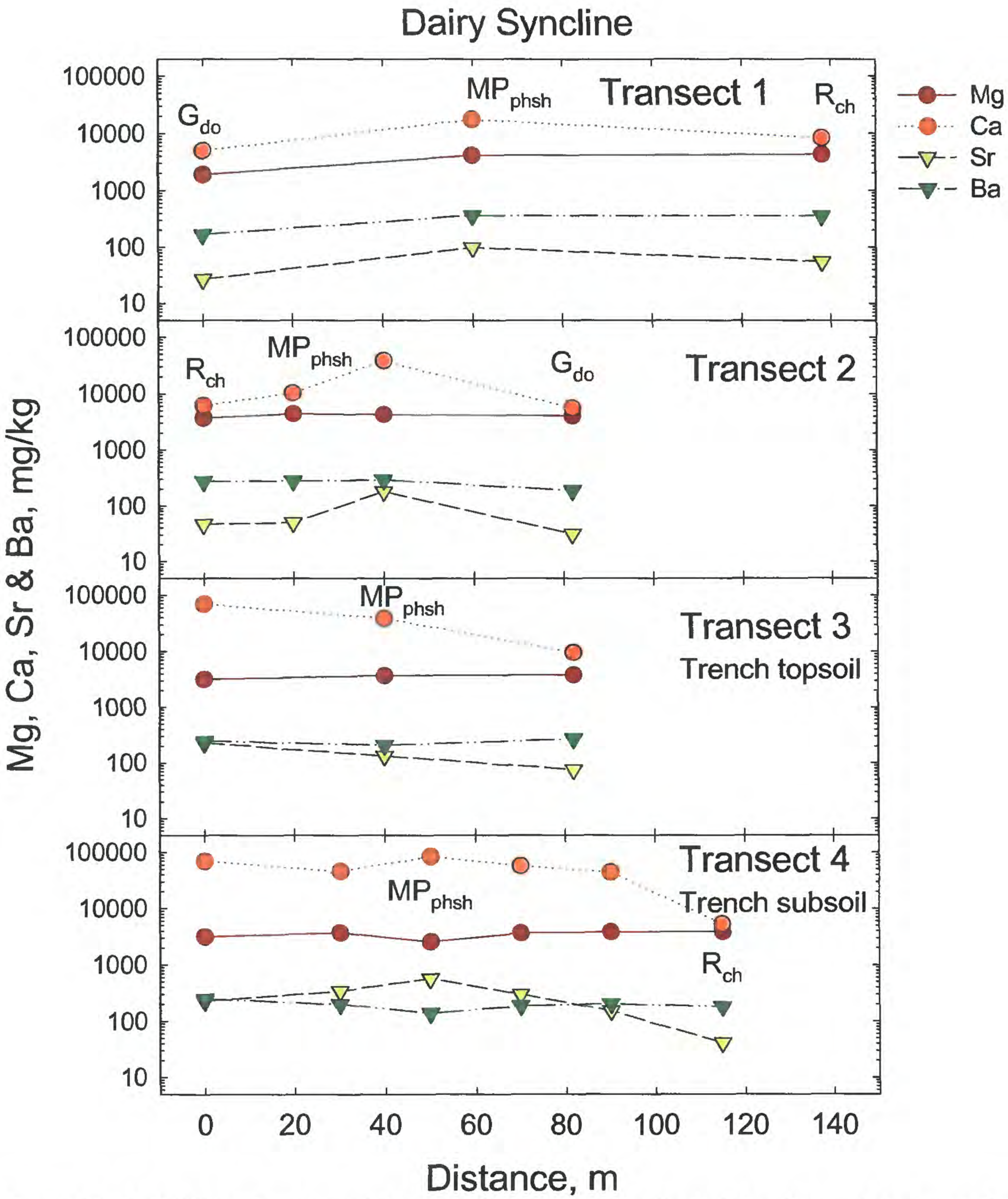

Figure 16. Total Mg, Ca, Sr, and Ba in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

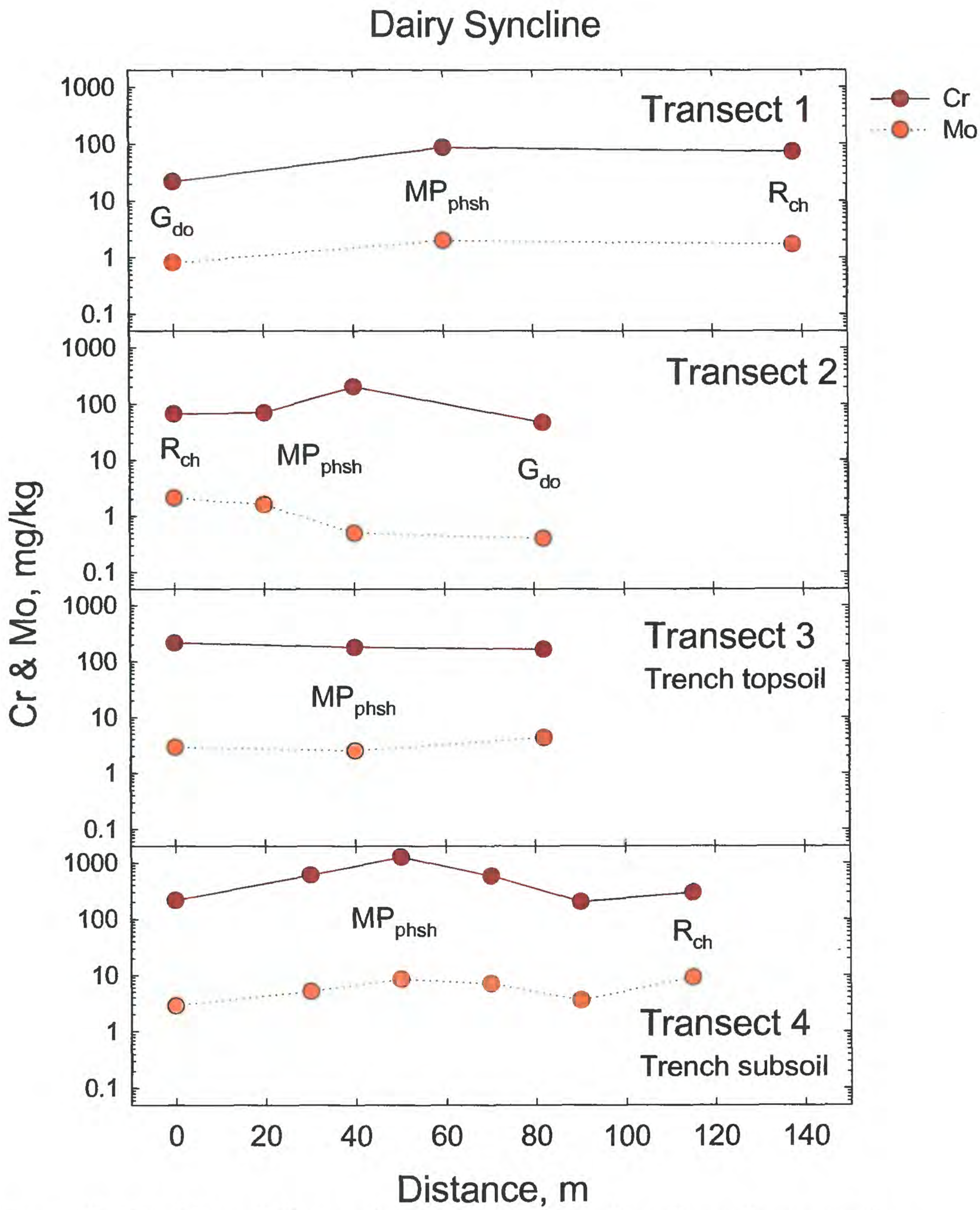

Figure 17. Total Cr and Mo in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

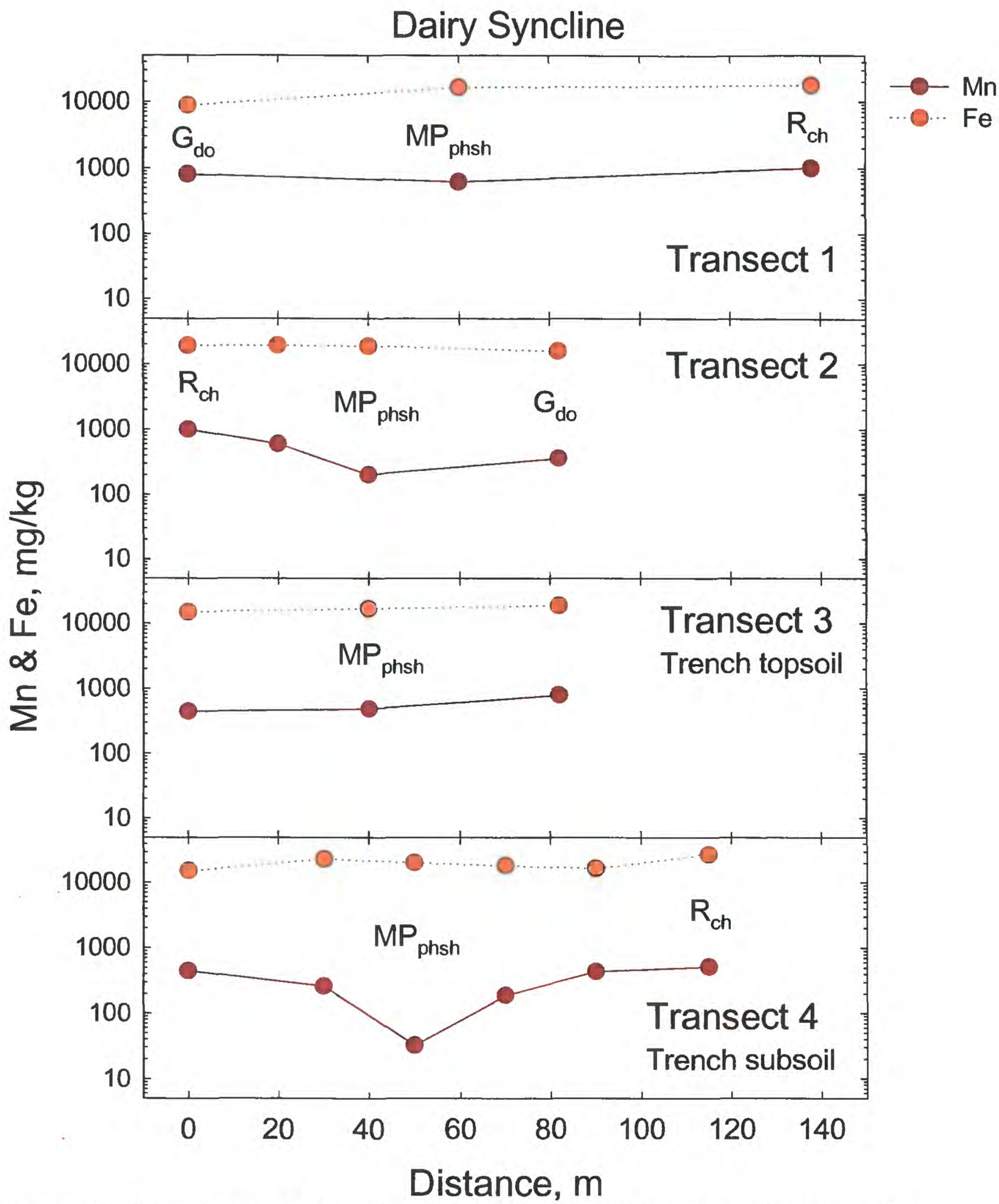

Figure 18. Total Mn and Fe in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

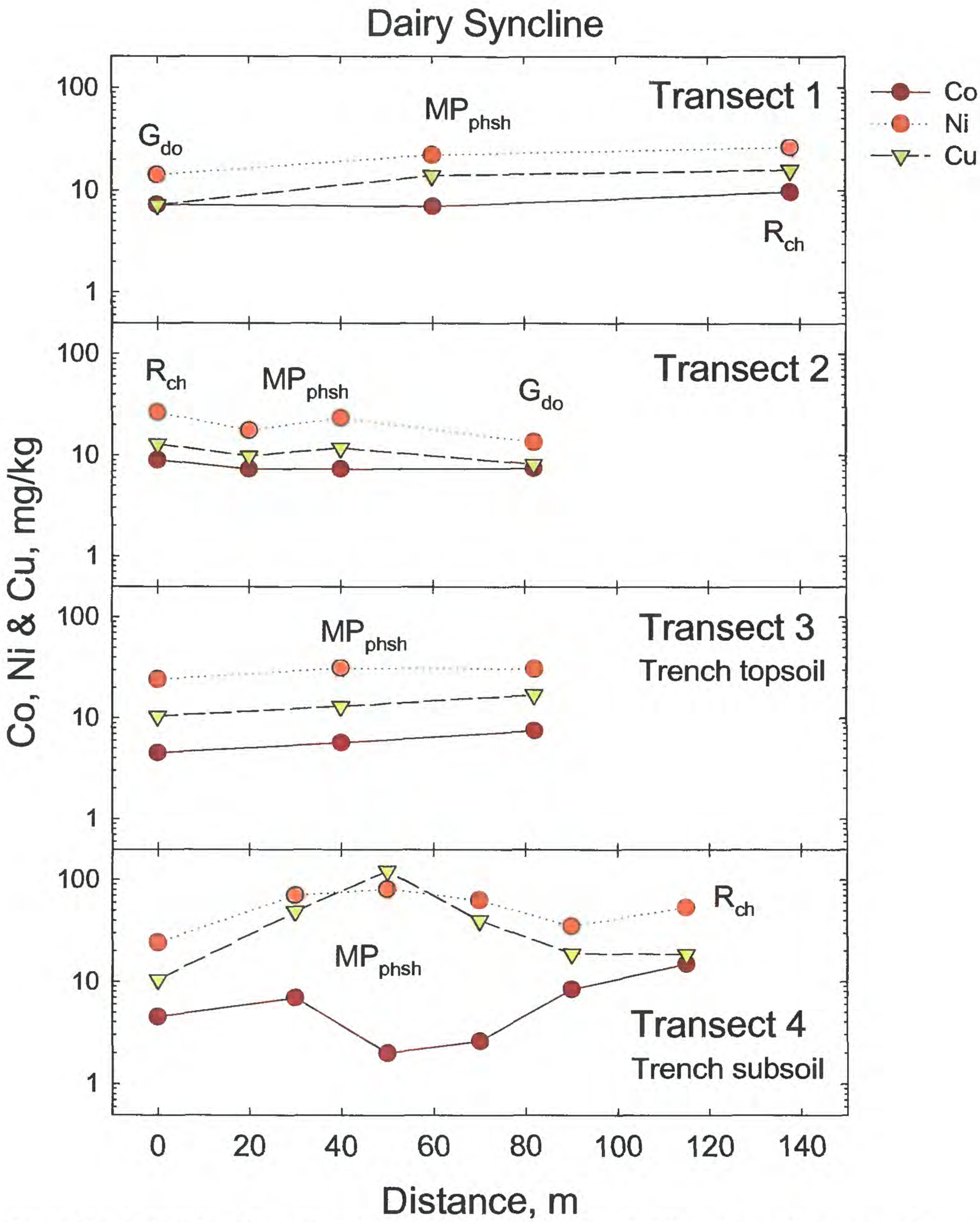

Figure 19. Total Co, Ni, and Cu in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

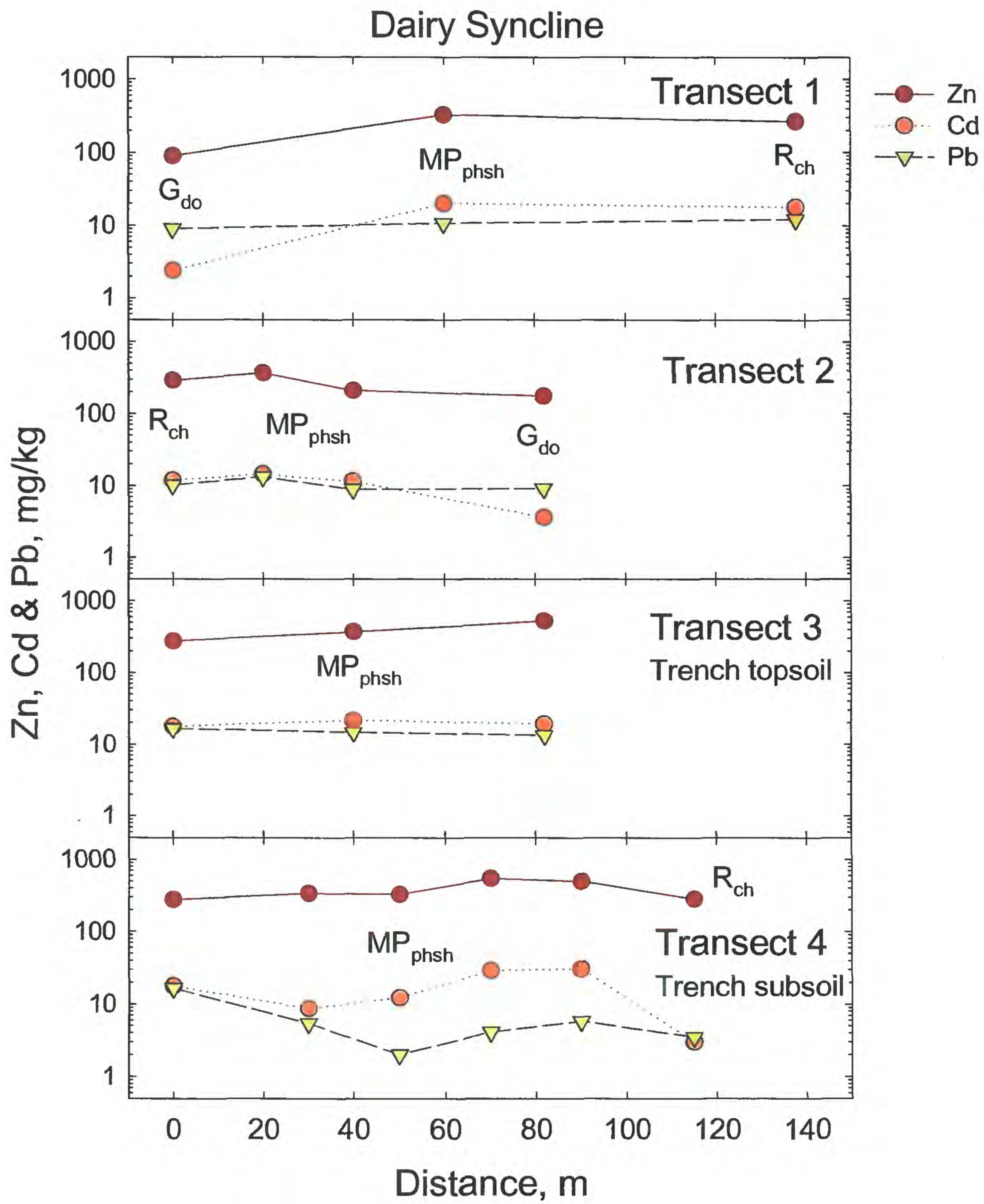

Figure 20. Total Zn, Cd, and Pb in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

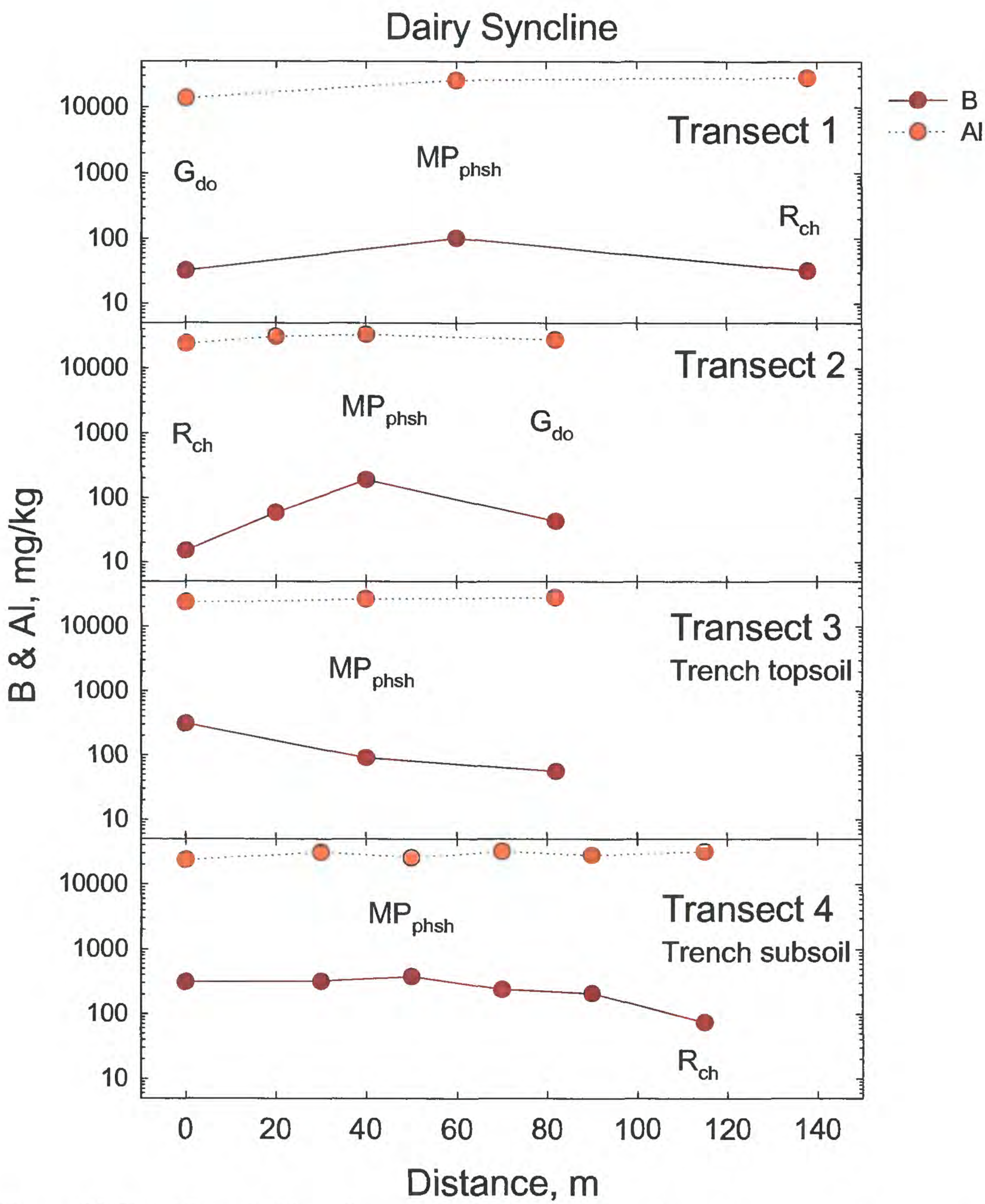

Figure 21. Total B and Al in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

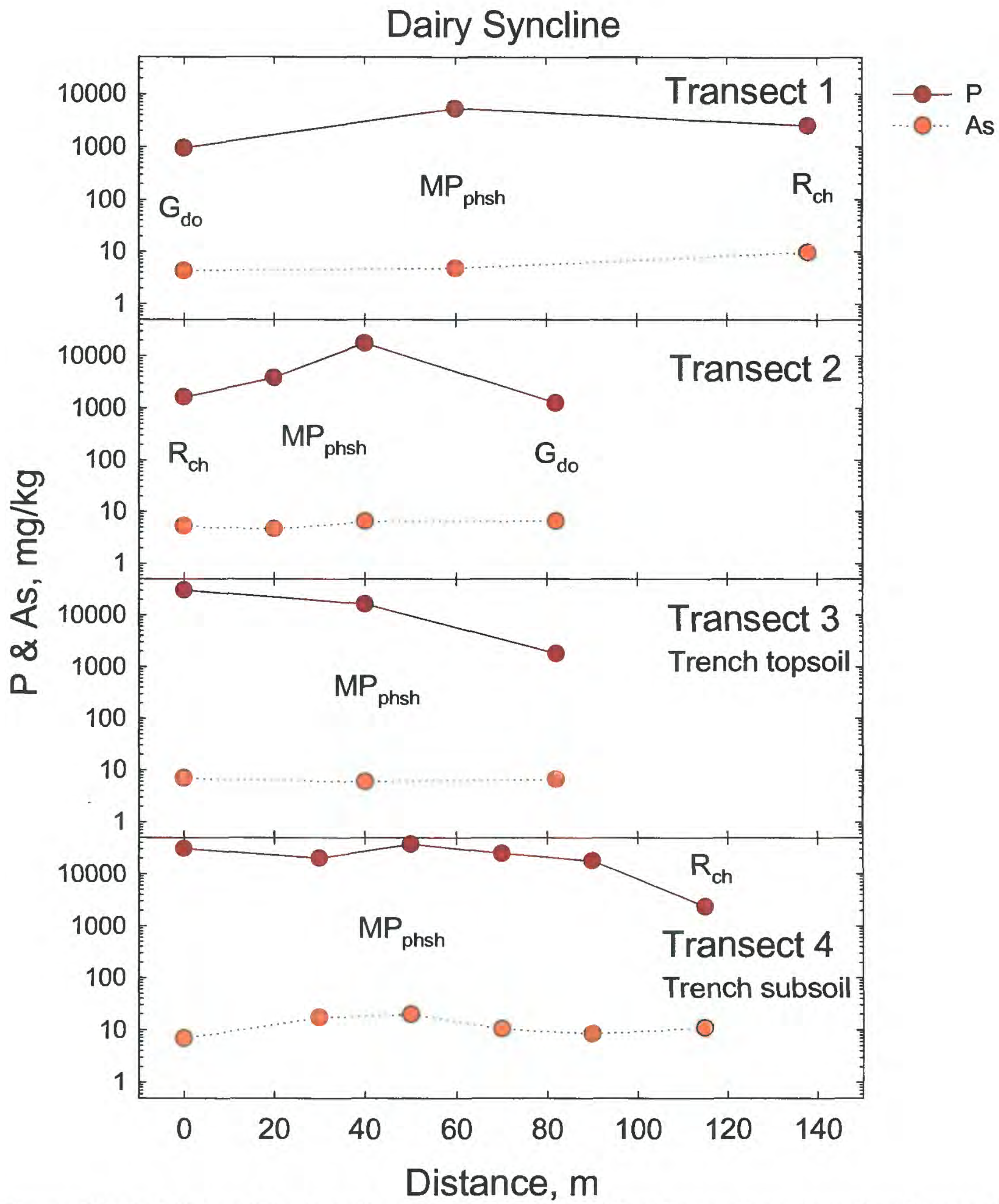

Figure 22. Total P and As in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

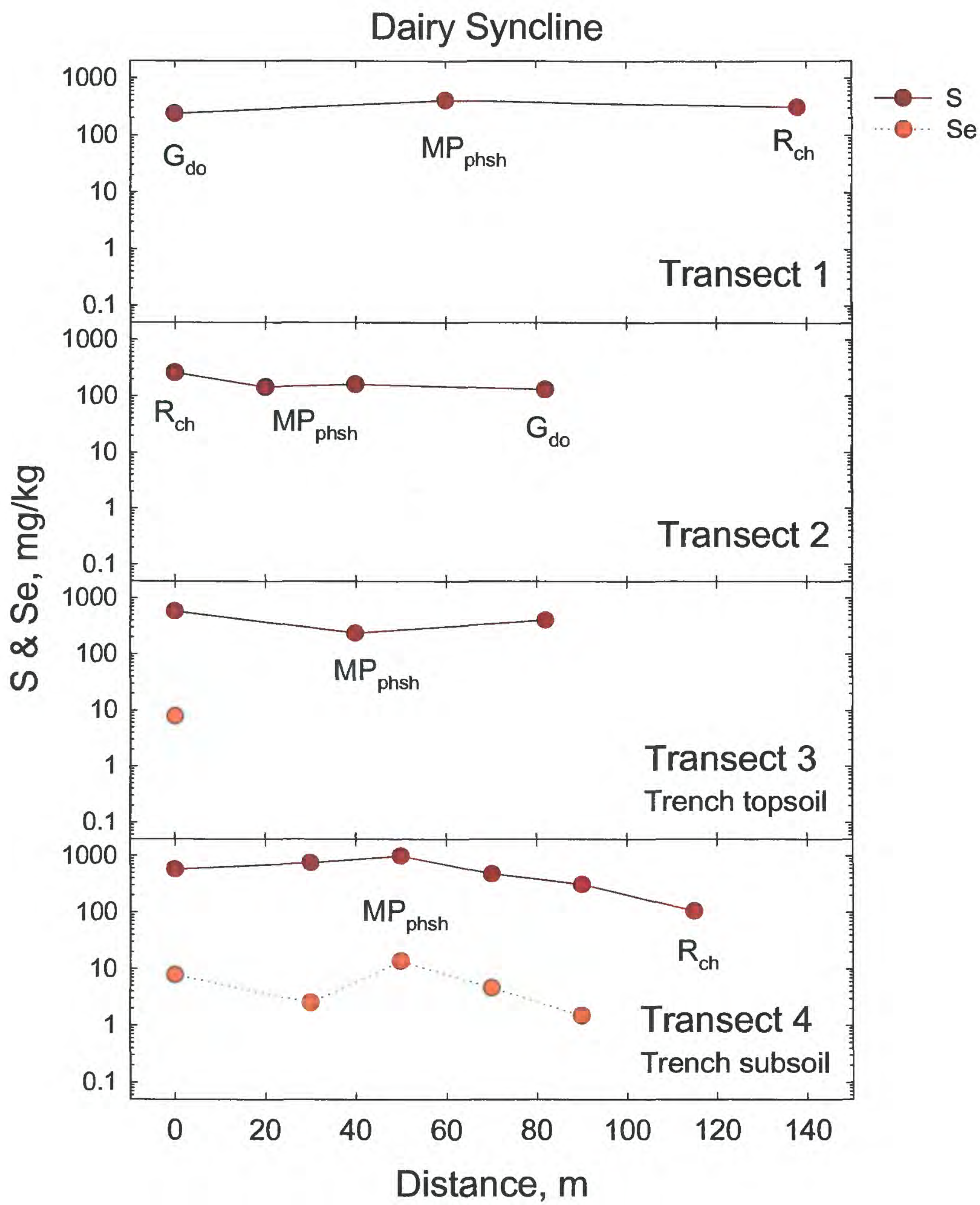

Figure 23. Total S and Se in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

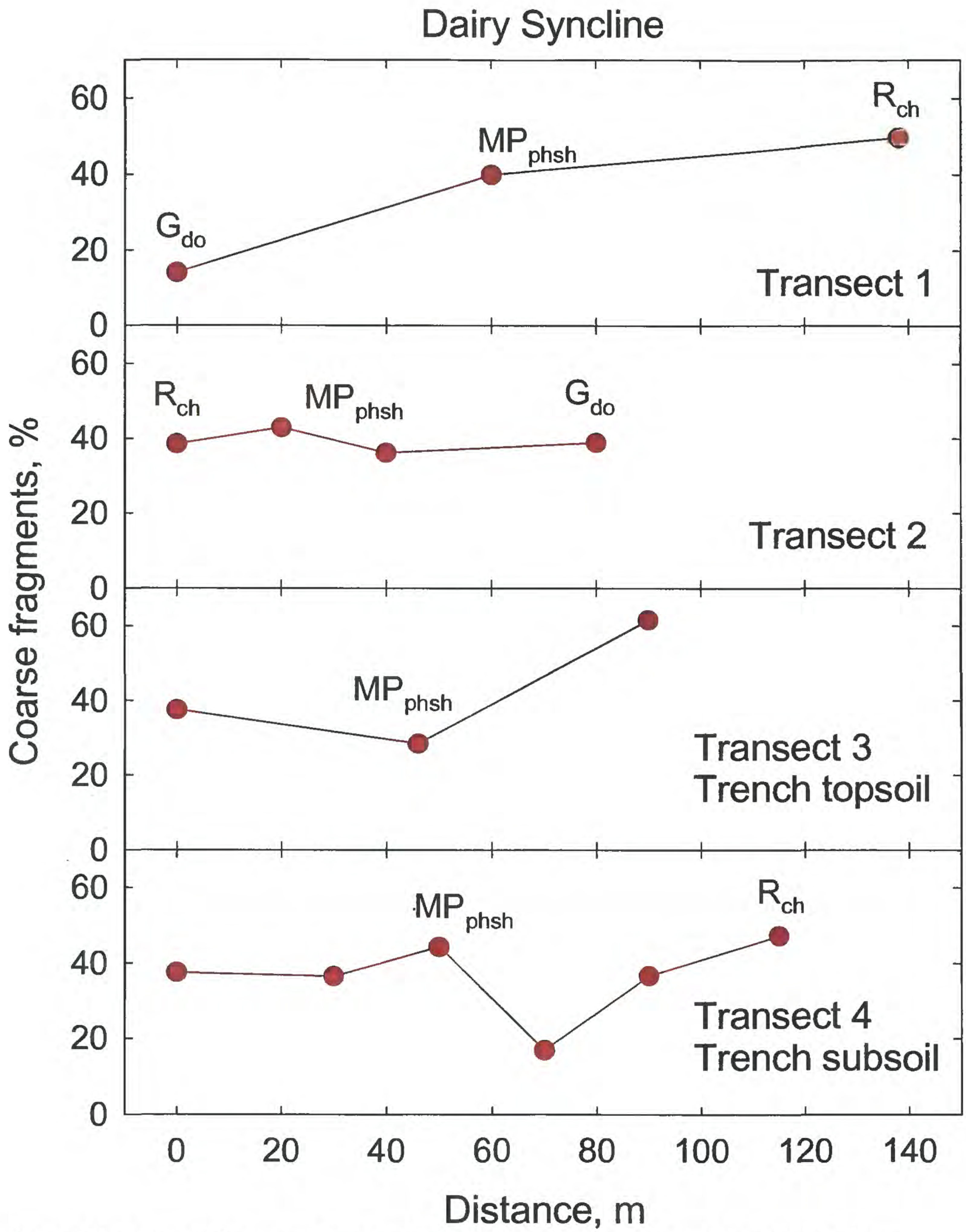

Figure 24. Coarse fragment content of soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

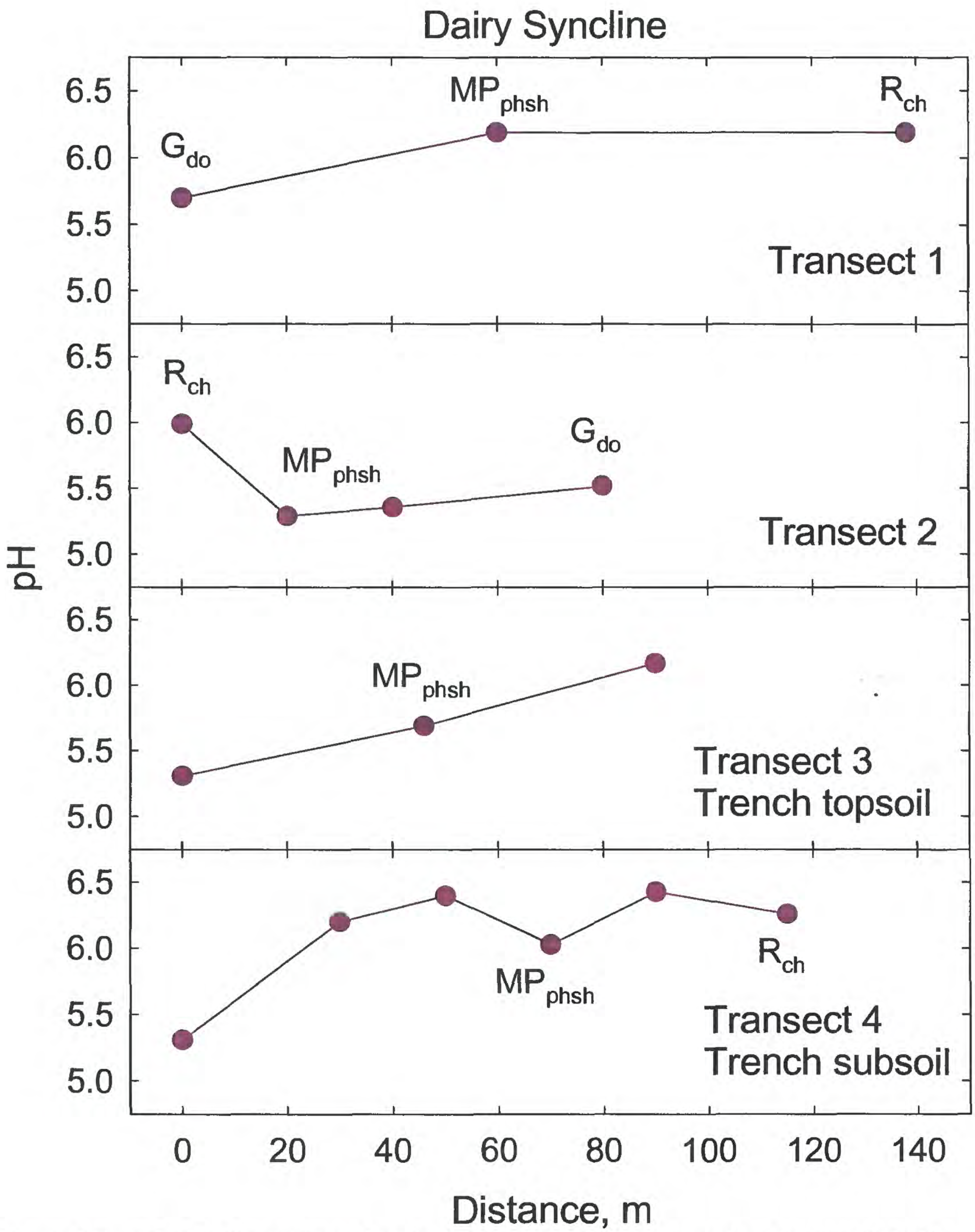

Figure 25. pH of soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

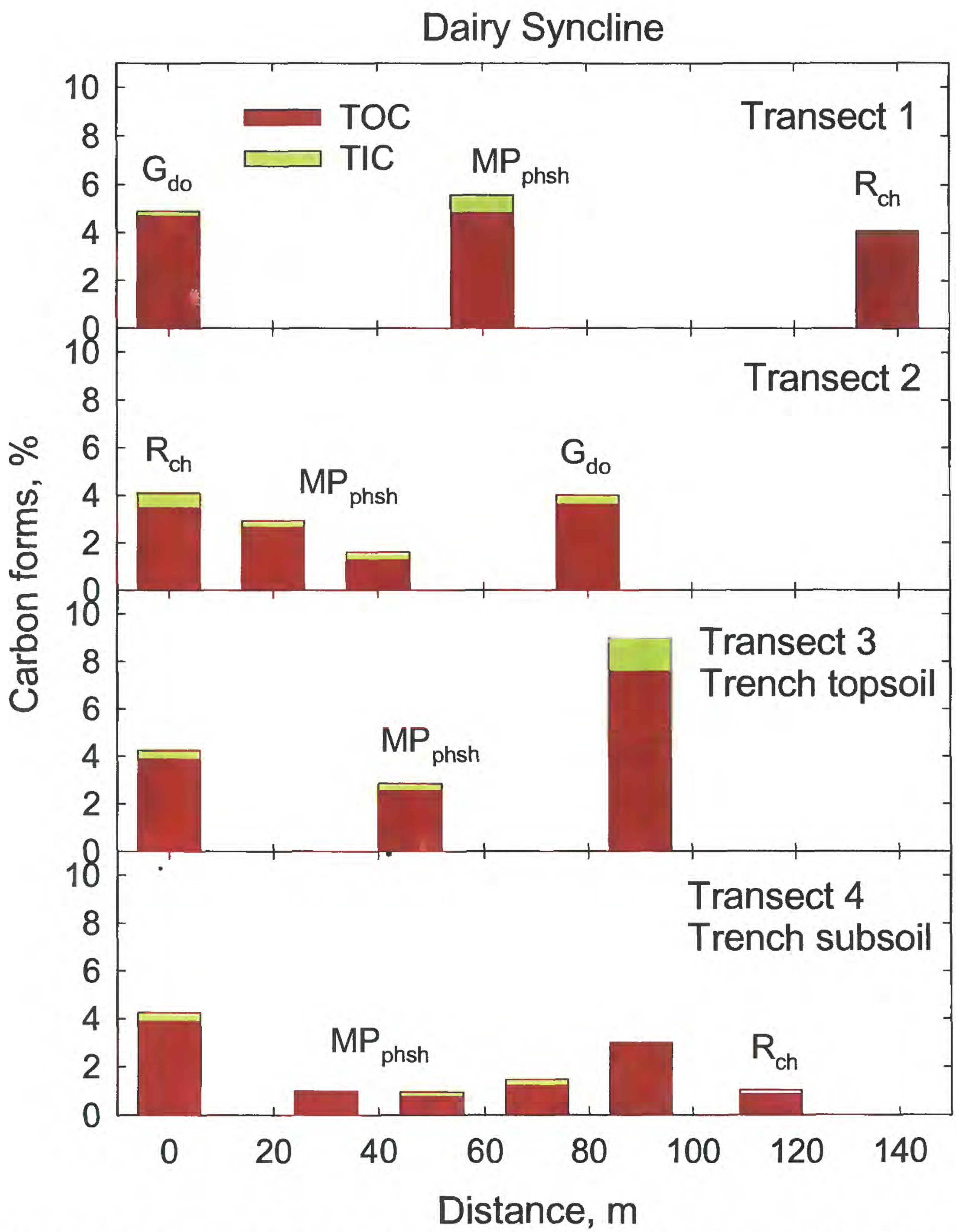

Figure 26. Total organic and inorganic carbon in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

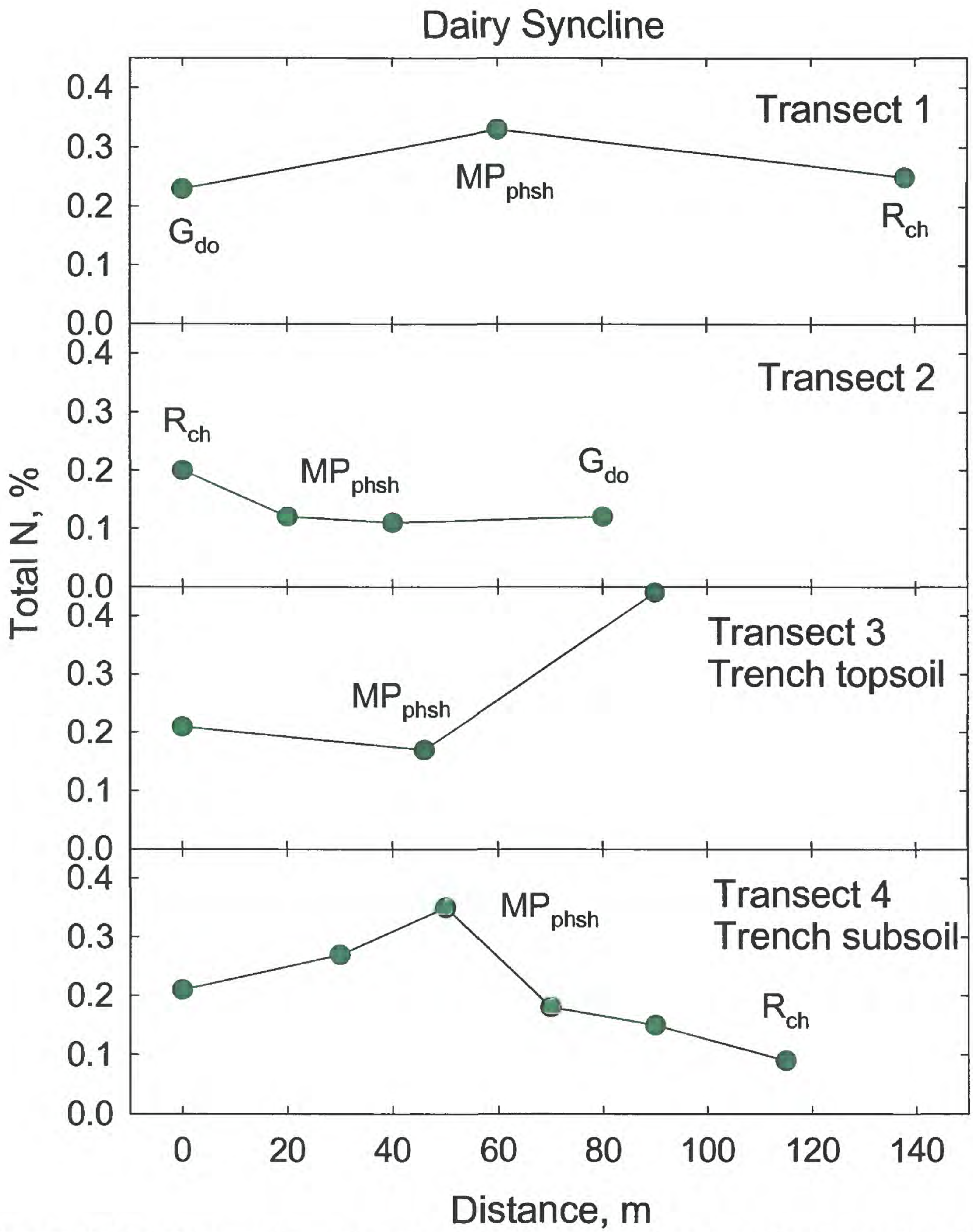

Figure 27. Total N in soil samples at selected locations along sampling transects in the Dairy Syncline lease area.

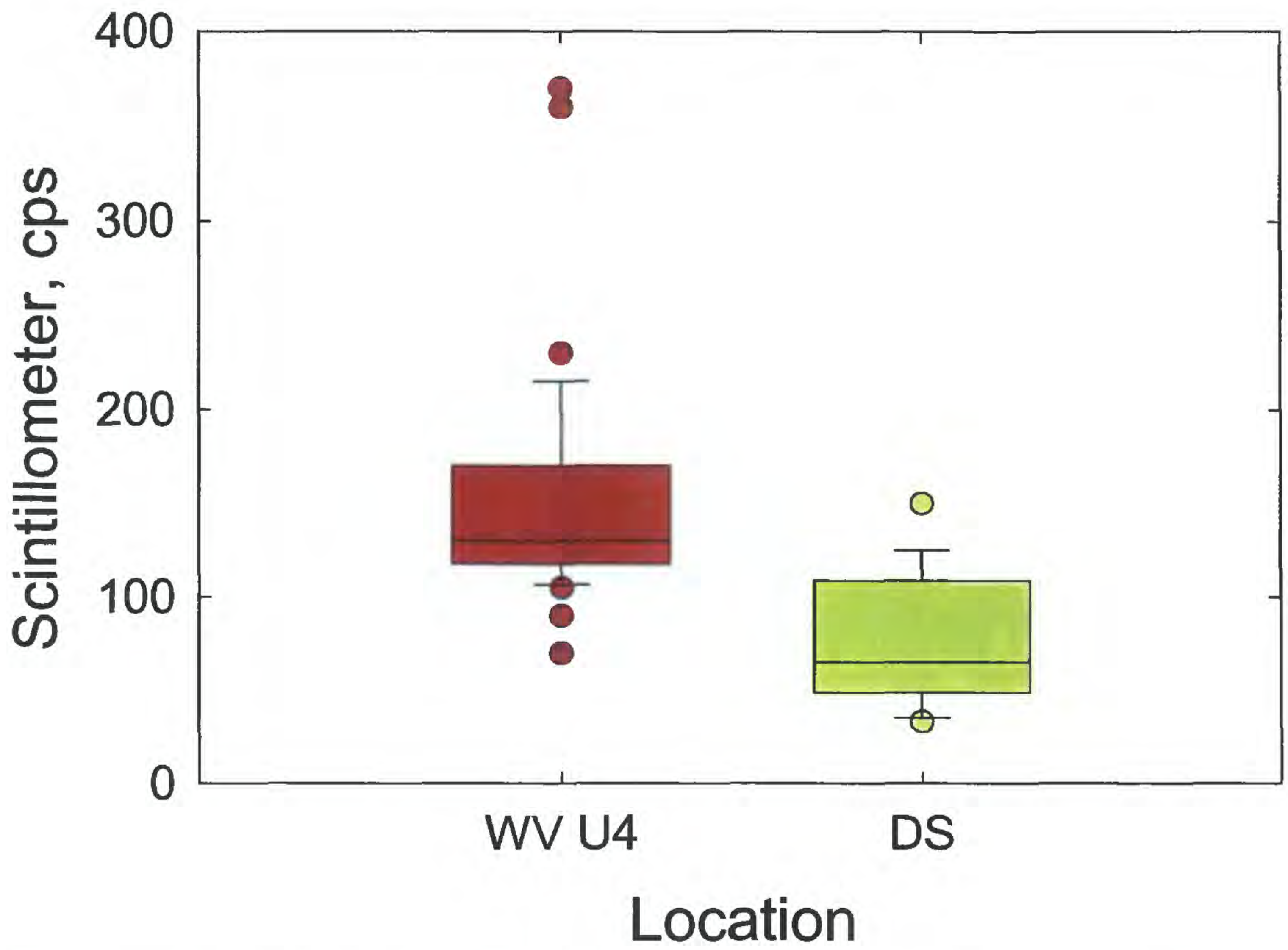

Figure 28. Box plots of scintillometer readings from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

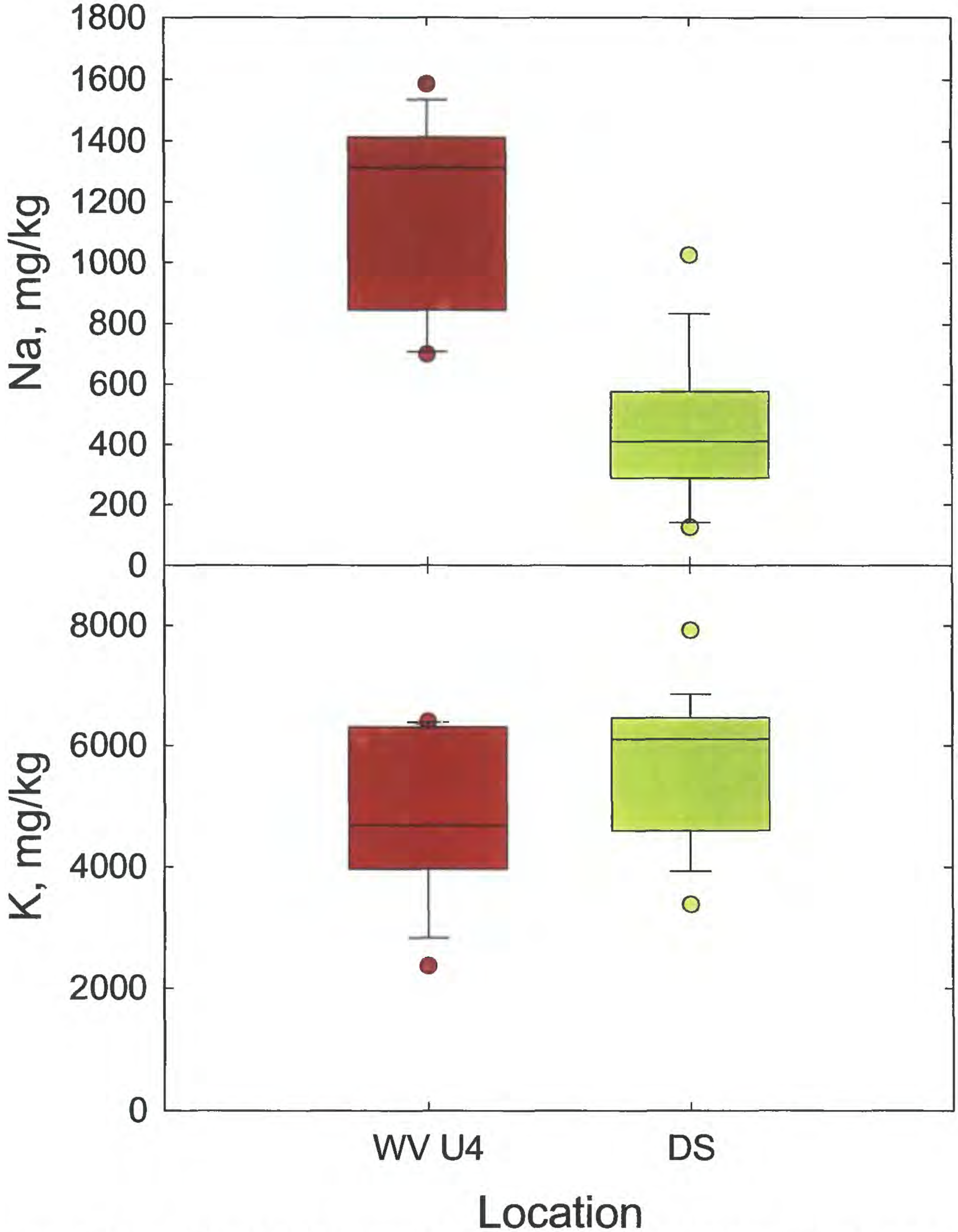

Figure 29. Box plots of total Na and K in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

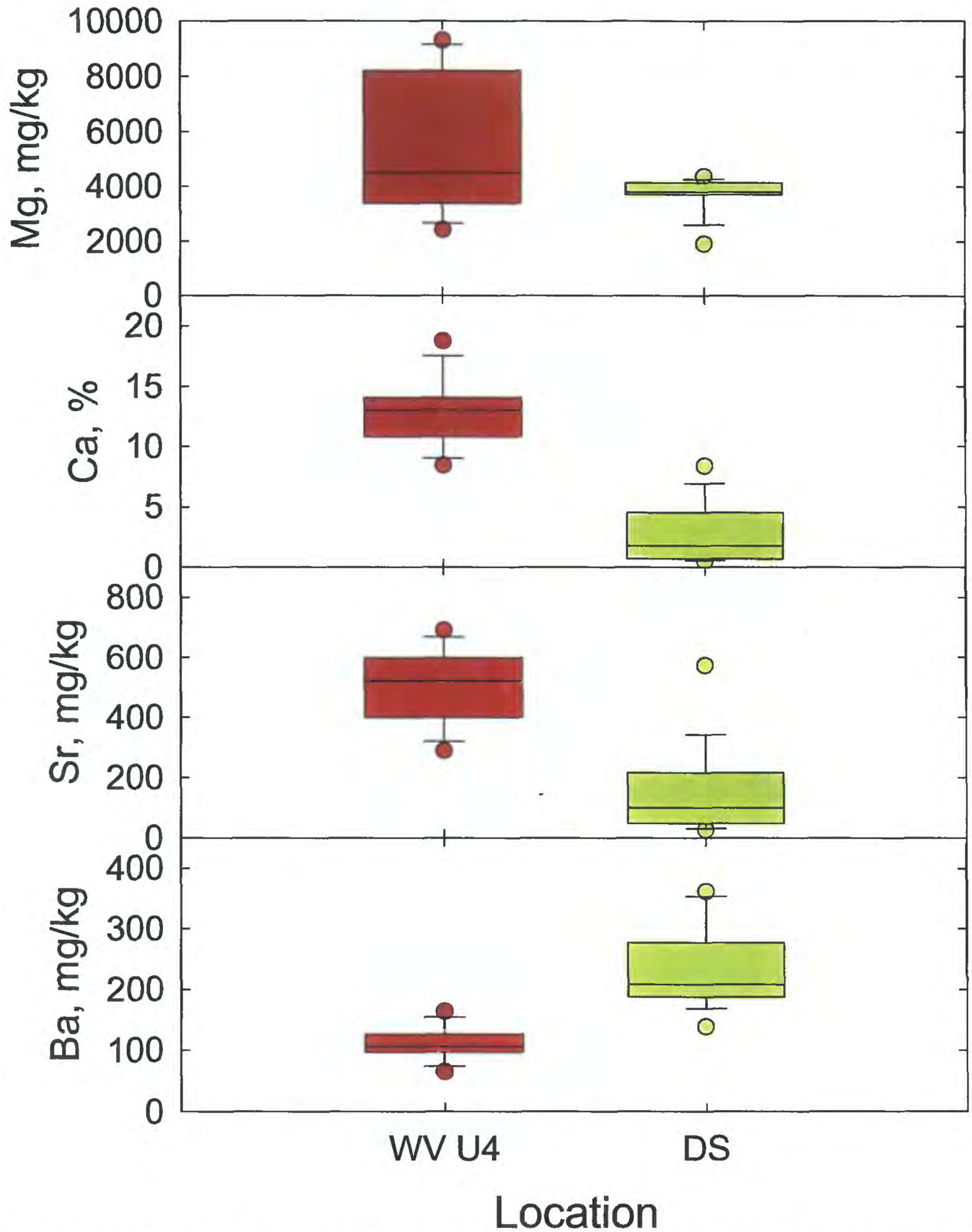

Figure 30. Box plots of total Mg, Ca, Sr, and Ba in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

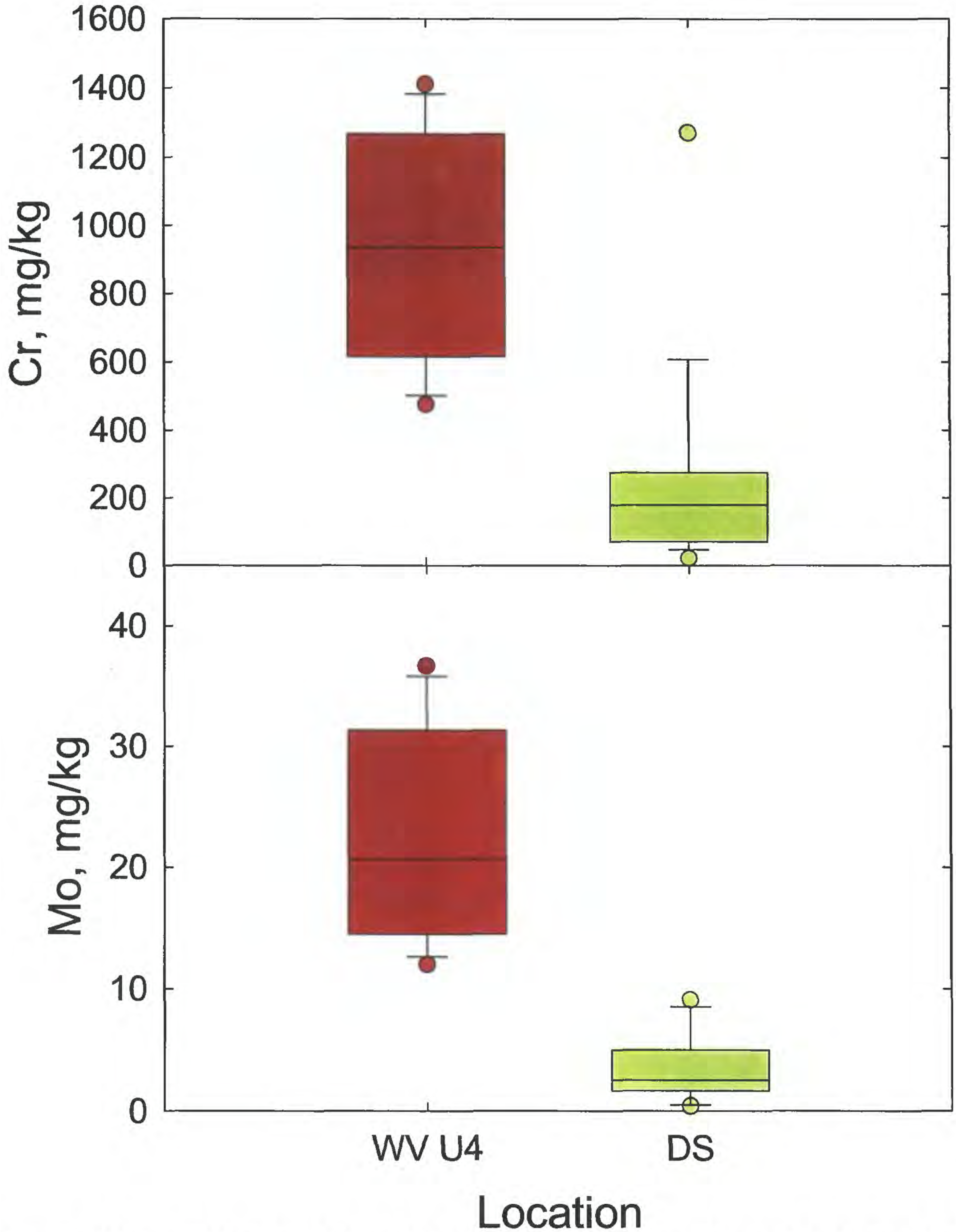

Figure 31. Box plots of total Cr and Mo in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

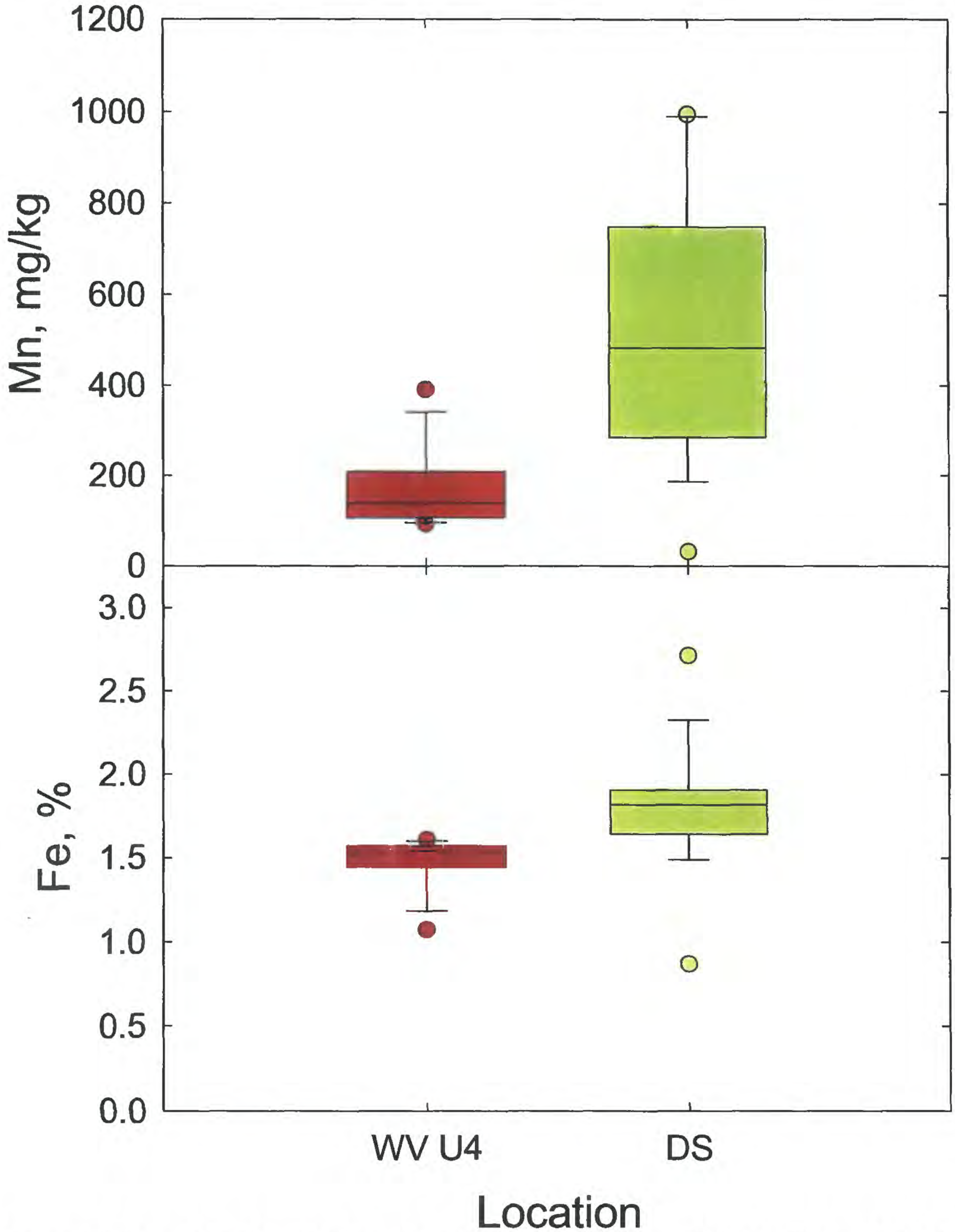

Figure 32. Box plots of total Mn and Fe in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

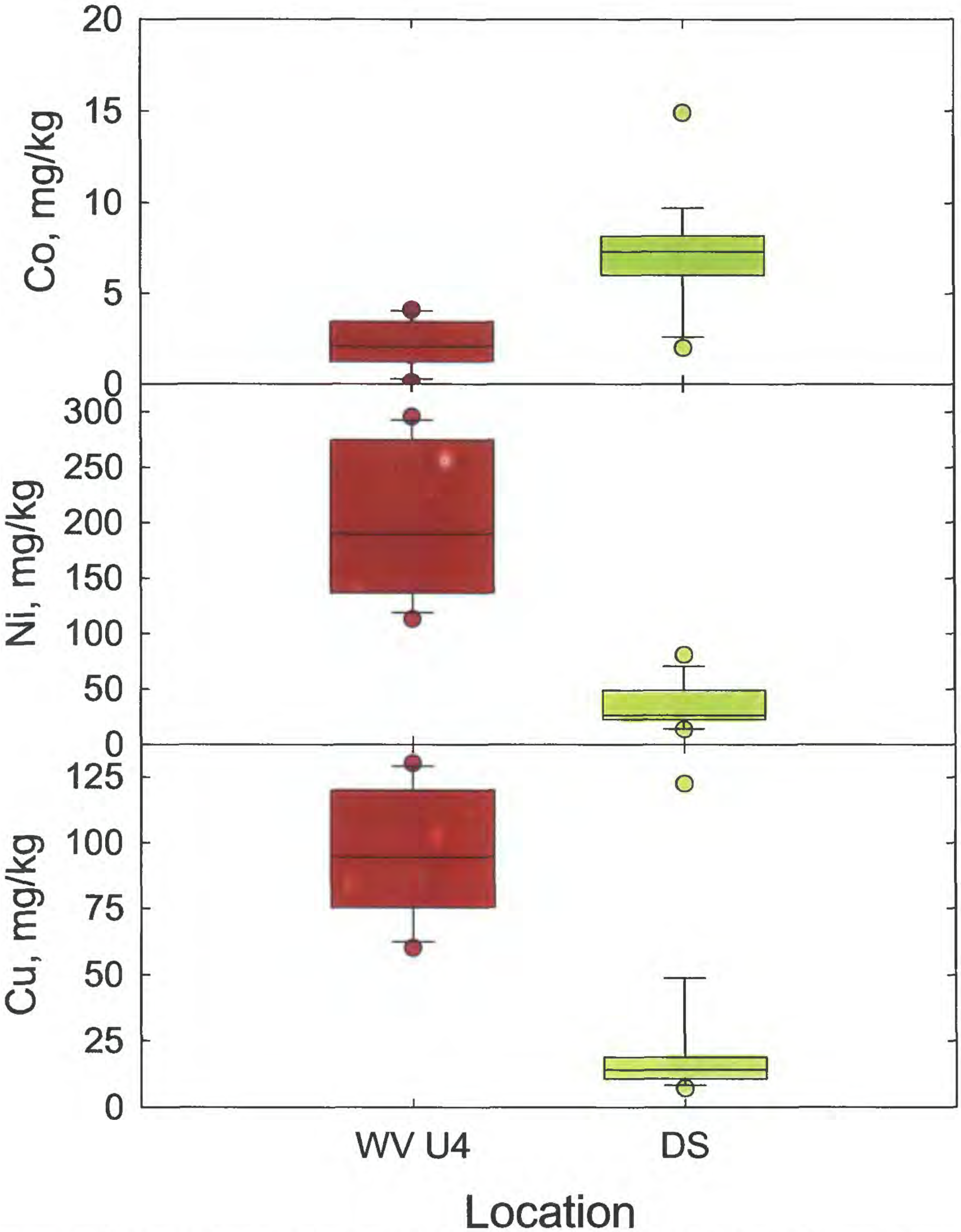

Figure 33. Box plots of total Co, Ni, and Cu in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

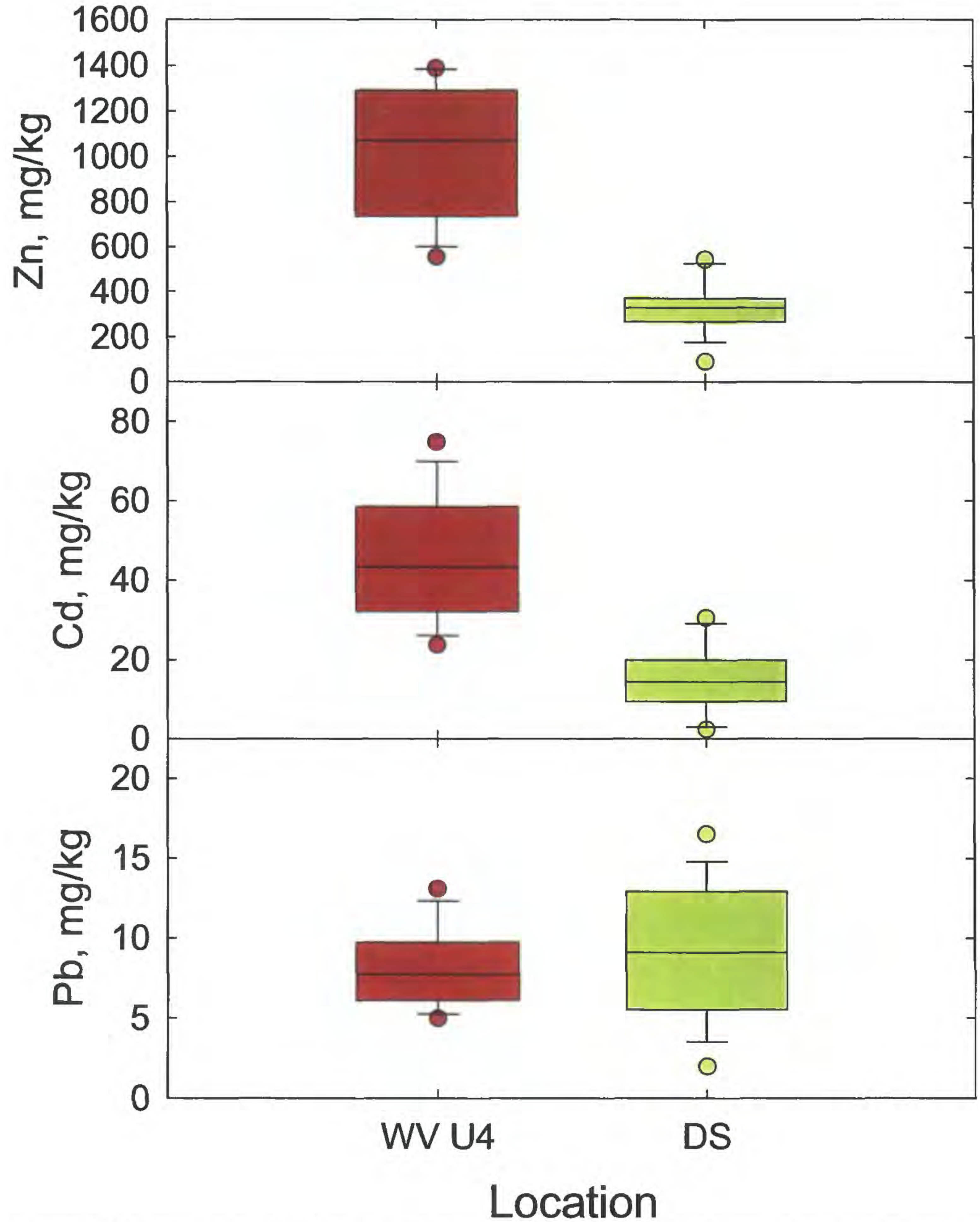

Figure 34. Box plots of total Zn, Cd, and Pb in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

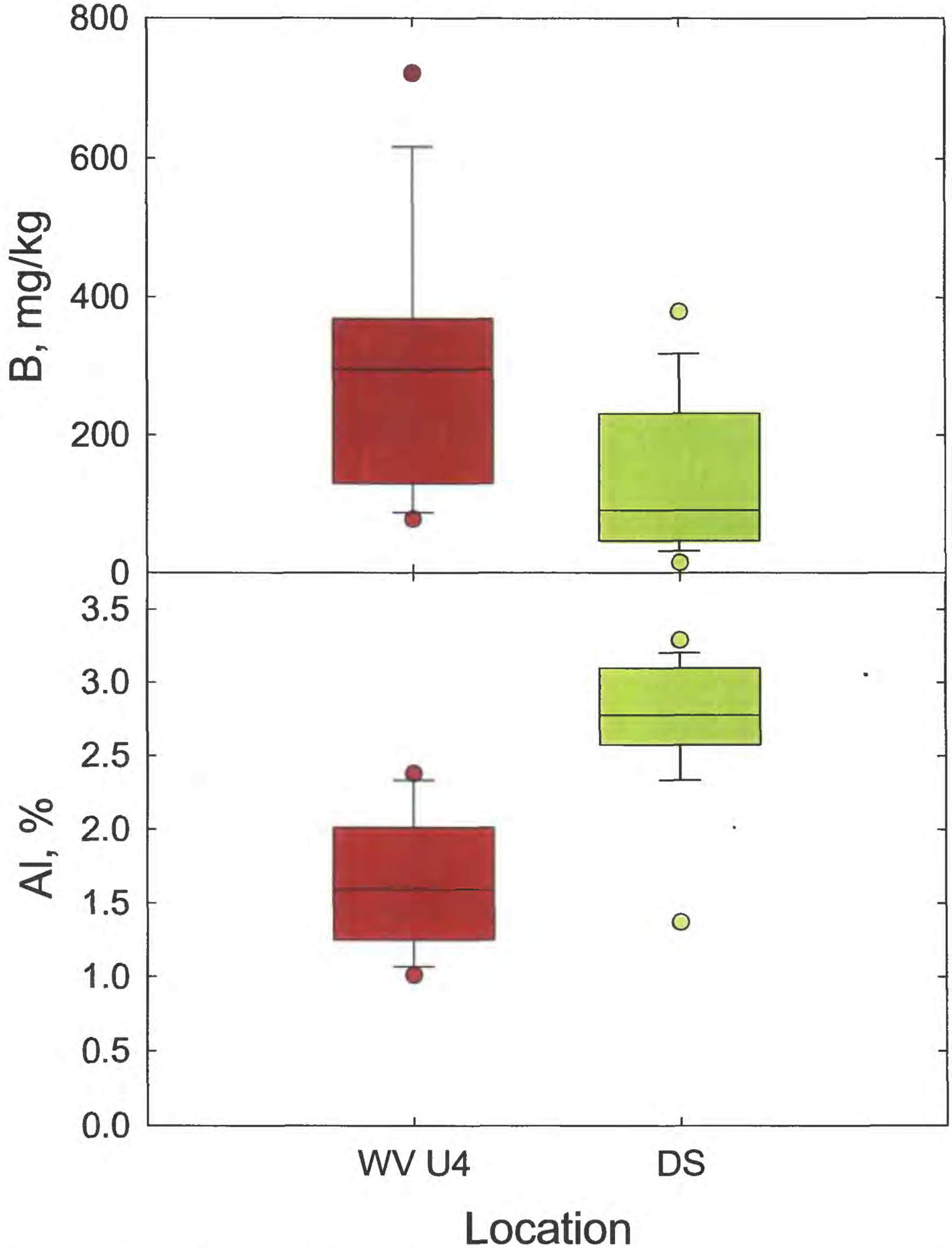

Figure 35. Box plots of total B and Al in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

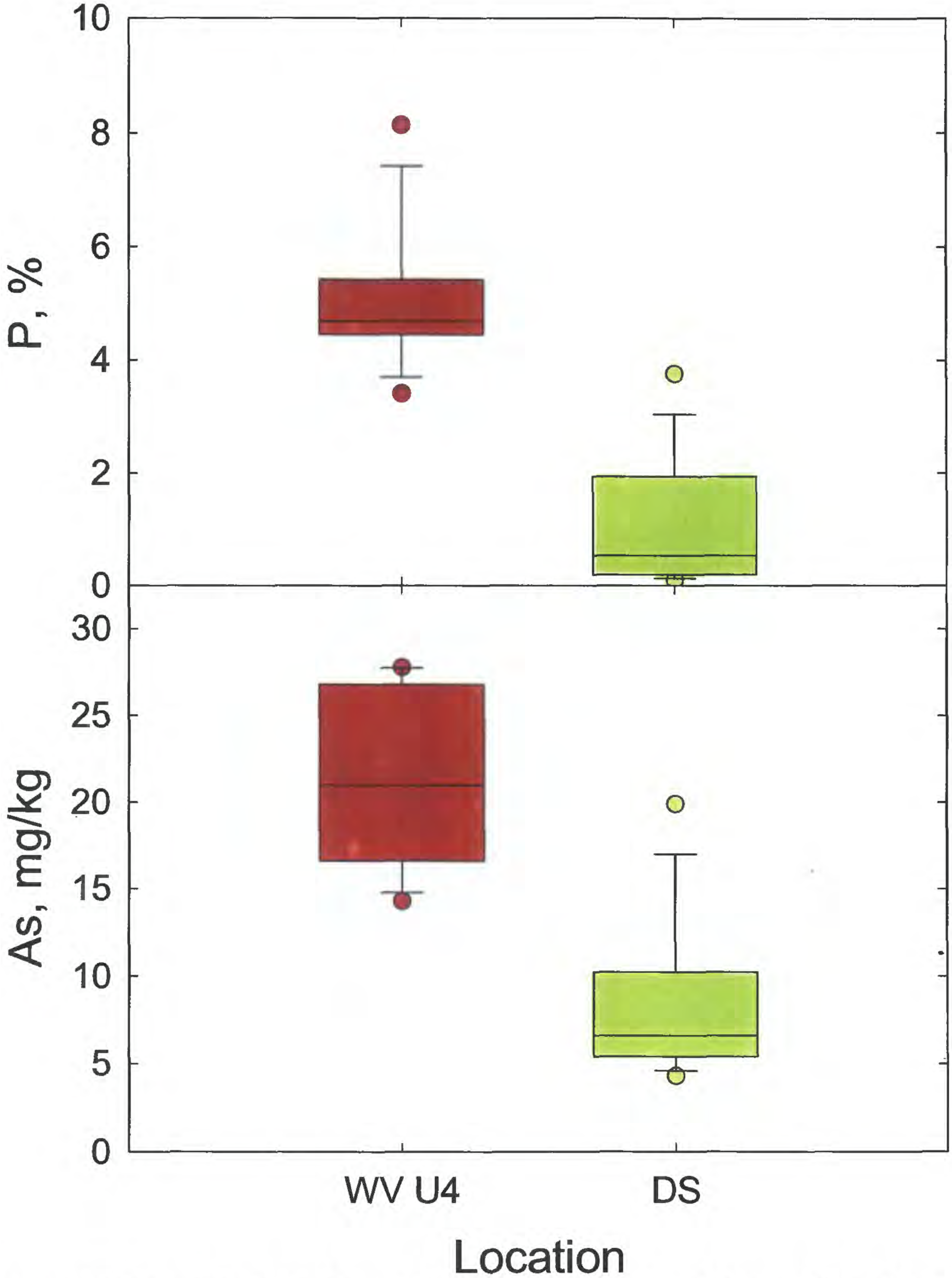

Figure 36. Box plots of total P and As in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

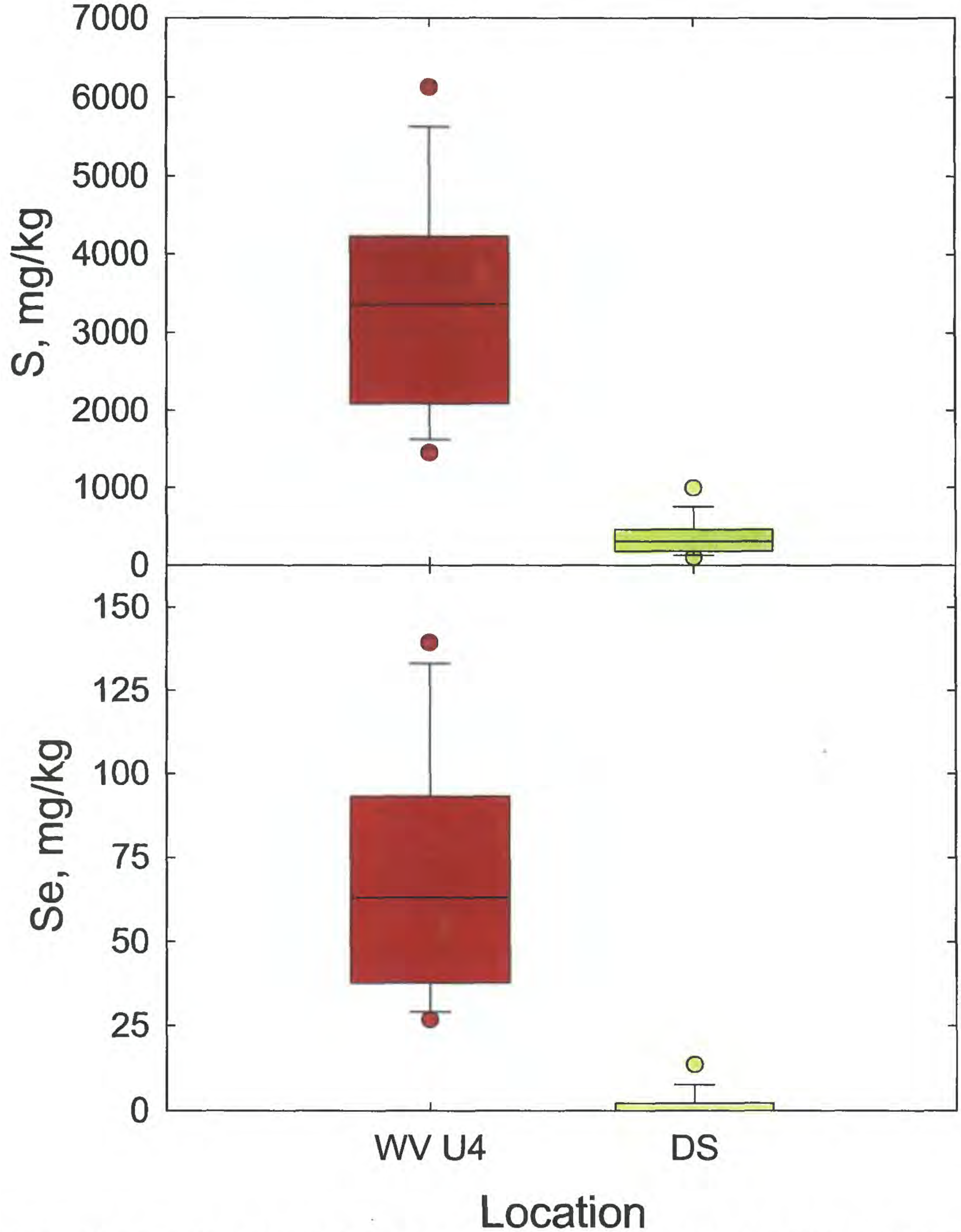

Figure 37. Box plots of total S and Se in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

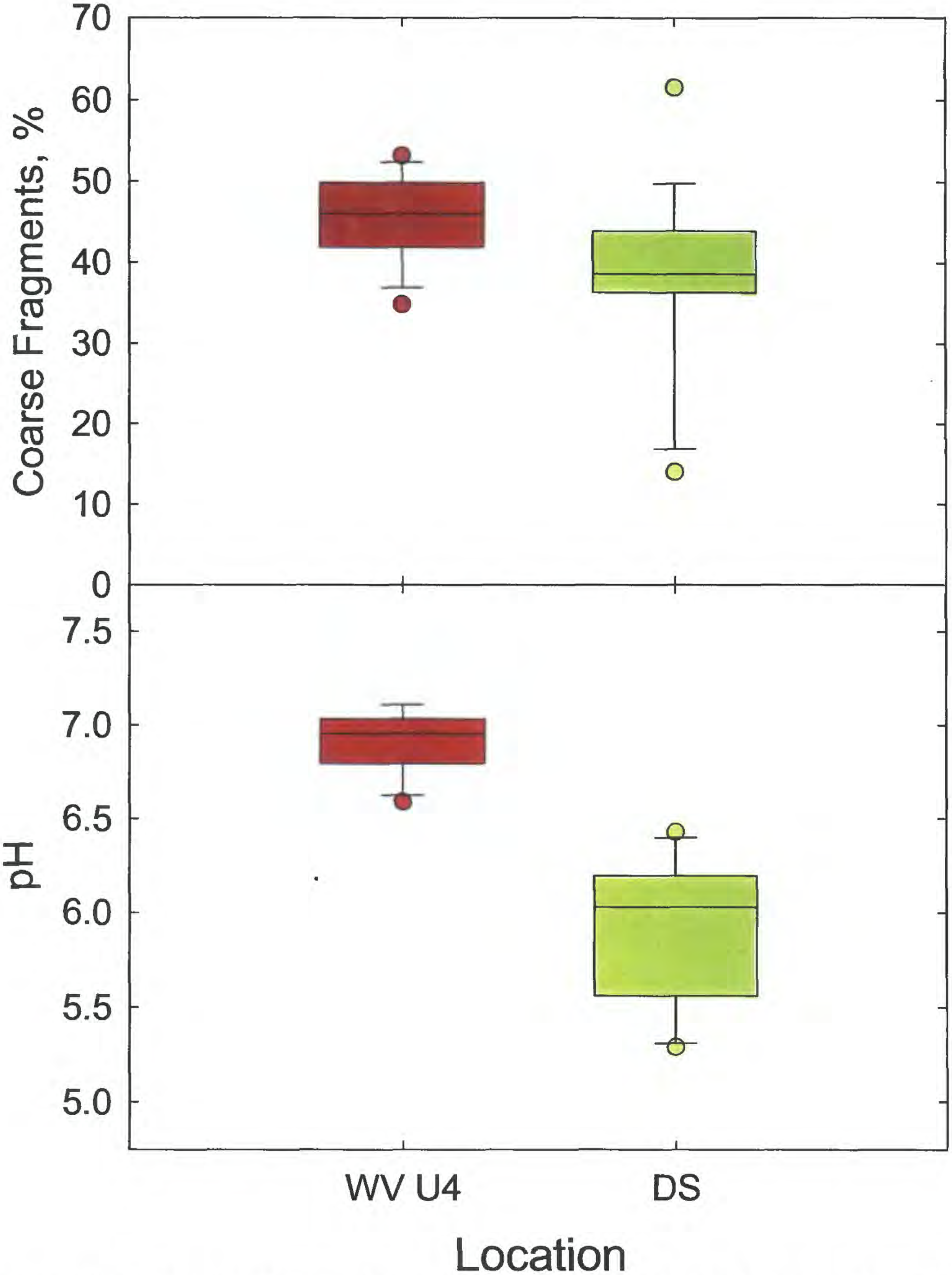

Figure 38. Box plots of coarse fragment content and pH of soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

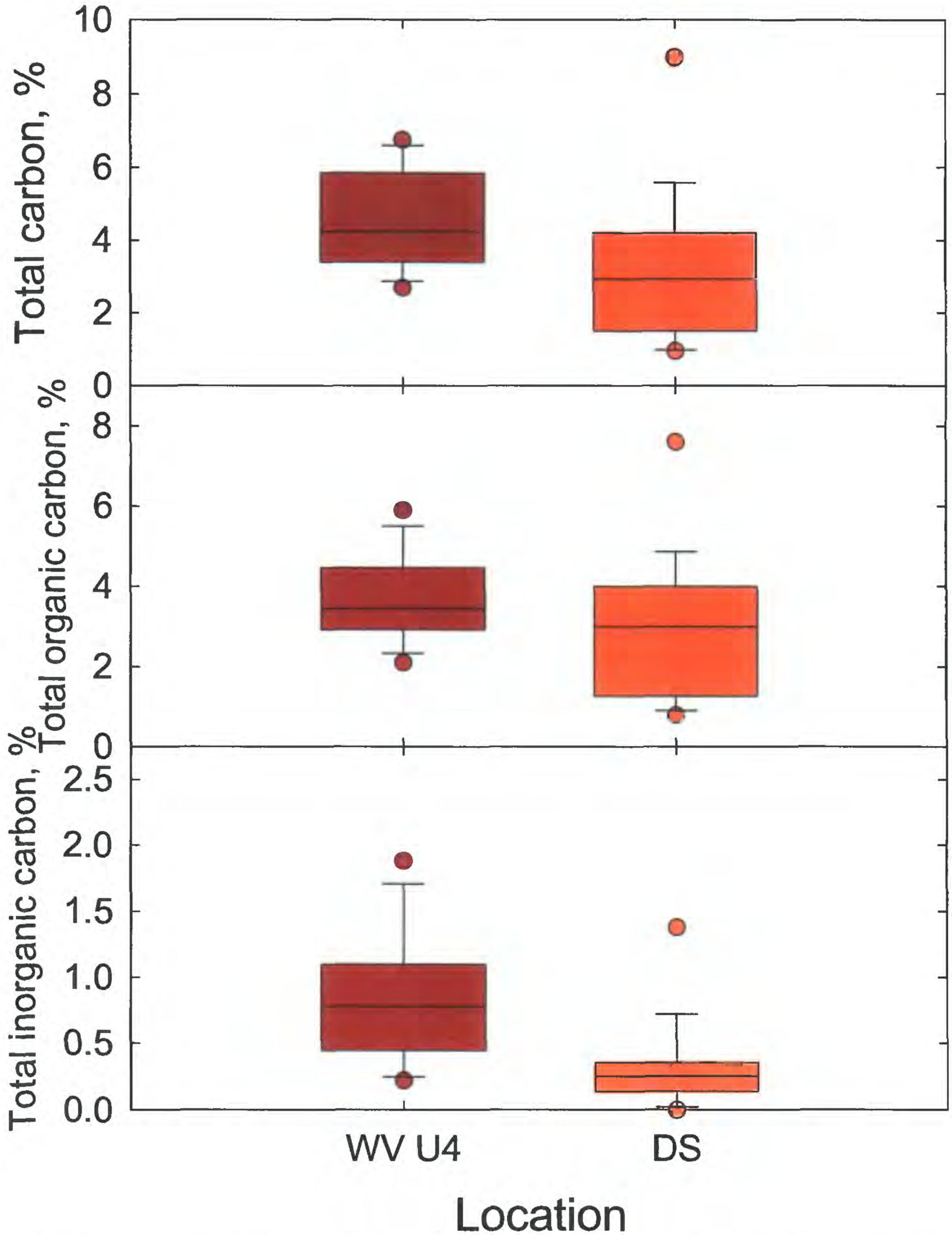

Figure 39. Box plots of total C, total organic C, and total inorganic C in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.

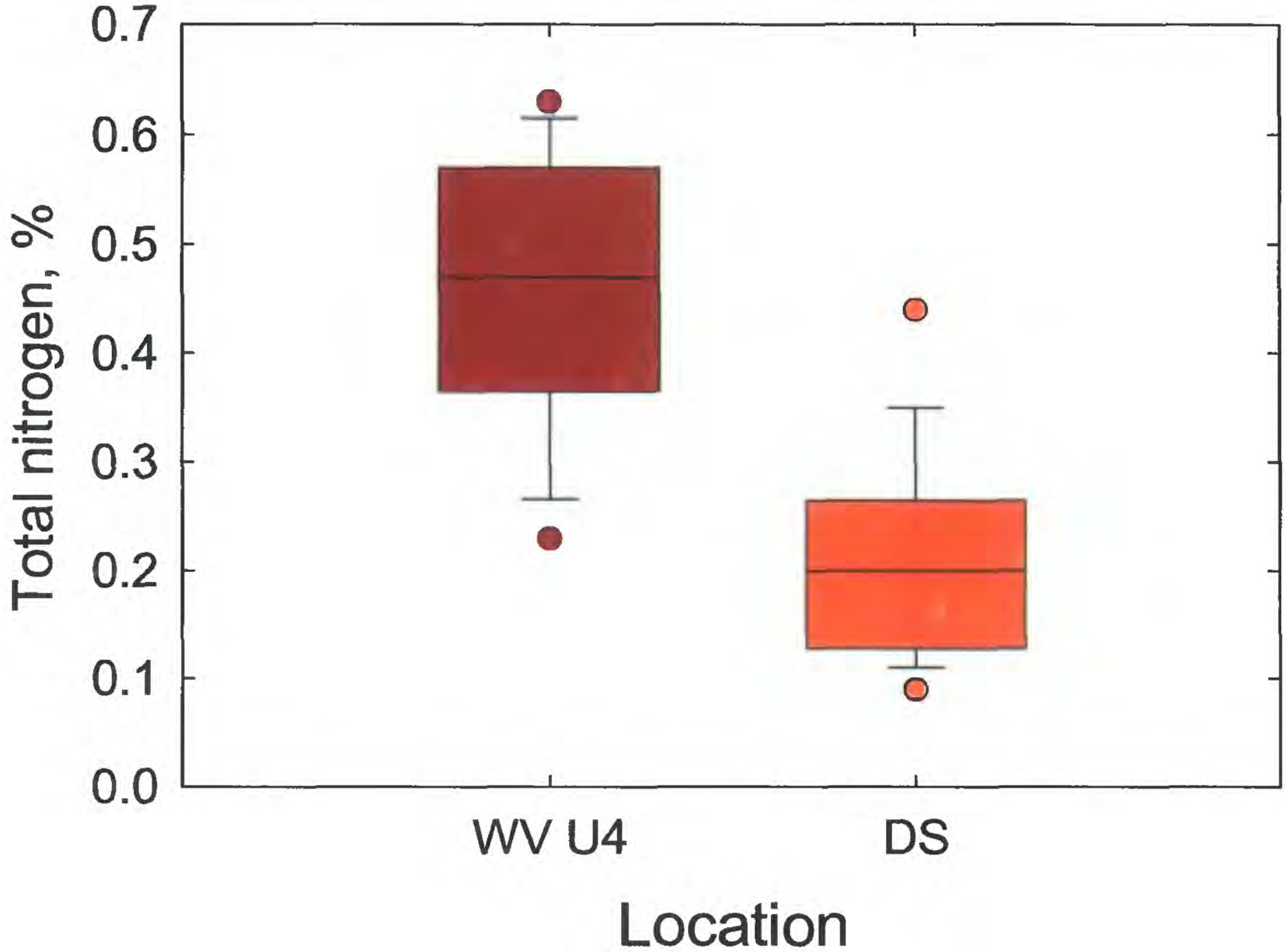

Figure 40. Box plots of total N in soil samples from Wooley Valley Unit 4 Waste Rock Dump and Dairy Syncline lease area.