5 Contaminant Fate and Transport

This chapter presents information on the fate and transport of the contaminants discussed in Chapter 4. The fate and transport discussion is based on site observations and measurements, as well as analytical tests run on selected samples collected during the RI field investigations. The discussion of fate and transport is focused on the principal COPCs at the site.

5.1   Mechanisms of Contaminant Migration

This section identifies the general physical and chemical processes of the primary contaminant release and migration mechanisms at the RDM.

5.1.1   Wind Transport and Deposition

Contaminants contained in or adsorbed to tailing/waste rock, flotation tailings, and/or soil can be transported within and offsite as windblown particles. The potential for Aeolian (wind) transport of contaminated particles is dependent on snow cover, vegetative cover, soil moisture, and grain size distribution of the soil exposed to wind action.

No field studies were performed during the RI field investigations to quantify off-site transport of contaminants via this mechanism. However, it is assumed that this contaminant migration mechanism is relatively unimportant at the RDM based on the following:

- The ground surface at the site is covered with snow for approximately seven months of the year.
- Much of the ground surface at the site is vegetated.
- Much of the surface that is not vegetated consists of coarse-grained material.

5.1.2   Leaching of Inorganic Elements

Leaching is the process by which contaminants are released from solid phase into the aqueous phase under the influence of dissolution and desorption processes. The potential for leaching of contaminants is related to the solubility of the contaminant, the amount of water (rain and snowmelt) percolating through the soil or waste horizon, soil pH and reduction/oxidation (redox), and microbiological activity.

Leaching of contaminants from surface and near-surface soil horizons to subsurface soil horizons and/or groundwater is occurring at the RDM. Several analytical tests were performed on RI samples to evaluate the leaching potential of selected site-related contaminants.

5.1.2.1 Synthetic Precipitation Leaching Procedure
The EPA SPLP was developed to evaluate mobility of organic and inorganic constituents in materials using a batch leach approach. The SPLP is generally regarded as the preferred technique for evaluating potential metals leaching of mine waste materials. Selected samples of surface and subsurface soil types were tested using the SPLP and analyzing the leached material for TAL inorganic elements. Results of the SPLP tests are presented in Chapter 4. Key findings of these results are discussed below.

Antimony
Antimony SPLP results were evaluated by comparing SPLP concentrations to total antimony concentrations and soil type (as designated in Chapter 3). Key findings are illustrated in Figures 5-1 through 5-4) and summarized below.

- The soil types that exhibited the highest SPLP concentrations at the RDM are tailings/waste rock, followed by flotation tailings.
- Tailings/waste rock exhibited the highest SPLP concentrations, ranging up to 75,300 µg/L, with most results below 20,000 µg/L. Tailings/waste rock SPLP concentrations are generally proportional to total antimony concentrations.
- Flotation tailings SPLP results ranged up to 3,660 µg/L and are generally proportional to total antimony concentrations.
- Native and disturbed native soils generally have lower total and SPLP concentrations.
- A sample of tailings (calcine material, sample 10OP01SS) exhibited total and SPLP antimony concentrations of 3,520 mg/kg and 1,950 µg/L, respectively. The ratio of SPLP concentration to total antimony concentration in this sample is lower than for tailings/waste rock and flotation tailings samples.

Collectively, these observations suggest that tailings/waste rock, particularly the waste rock component, constitutes a significant source of antimony leaching at the RDM. Similar ratios of SPLP to total antimony between tailings/waste rock and flotation tailings suggest a common source of total and leachable antimony in these waste types. This is consistent with information in historical mining operations reports, which indicate that stibnite is commonly collocated with cinnabar in Red Devil Mine ore. Attempts were made to separate it from cinnabar prior to retorting, including separation of waste rock containing abundant stibnite. The flotation process was employed only during the final stage of mine operations. Reportedly, flotation was used after 1969 to beneficiate the ore, producing cinnabar and stibnite concentrates (Buntzen and Miller 2004). Flotation tailings exhibit total antimony concentrations that are generally low relative to tailings/waste rock, indicat-

ing that separation by flotation was at least partially successful. Much of the antimony in the tailings (calcine material) sample, which exhibits a relatively lower leachability, is likely antimony trioxide generated from furnacing.

Arsenic

Arsenic SPLP results were evaluated by comparing SPLP concentrations to total arsenic concentrations and soil type. Key findings are illustrated in graphs, provided in Figures 5-5 through 5-8, and summarized below:

- The soil types exhibiting the highest SPLP arsenic concentrations at the RDM are tailings/waste rock and tailings (calcine material).
- Tailings/waste rock exhibited the highest SPLP concentrations, ranging up to 6,000 µg/L. The SPLP concentration of one tailings (calcine material) sample (10OP01SS) is 4,430 µg/L.
- Flotation tailings SPLP arsenic results ranged up to 2,310 µg/L, corresponding to a total arsenic concentration of 9,880 mg/kg.
- Native and disturbed native soils generally have relatively lower total and SPLP concentrations.
- SPLP arsenic concentrations are generally proportional to total arsenic concentrations for tailings/waste rock from the Pre-1955 Main Processing Area, and for tailings/waste rock from the Post-1955 Main Processing Area.
- Both SPLP and total arsenic concentrations are generally higher for tailings/waste rock from the Post-1955 Main Processing Area than tailings/waste rock from the Pre-1955 Main Processing Area. Furthermore, the ratio of SPLP to total arsenic is generally higher for tailings/waste rock from the Post-1955 Main Processing Area than the Pre-1955 Processing Area.
- The ratio of SPLP to total arsenic concentrations for flotation tailings is low relative to the ratios for tailings/waste rock from both the Pre-1955 and Post-1955 Main Processing Areas.
- A sample of tailings (calcine material, sample 10OP01SS) exhibited total and SPLP arsenic concentrations of 4,430 mg/kg and 5,340 µg/L, respectively. The ratio of SPLP concentration to total arsenic concentration in this sample is similar to those for tailings/waste rock from the Post-1955 Main Processing Area.
- A sample of presumed stockpiled ore exhibited a SPLP arsenic concentration of 440 µg/L, corresponding to a total arsenic concentration of 7,310 mg/kg. The ratio of SPLP to total arsenic is very low compared to those for tailings/waste rock and is similar to those for flotation tailings and waste rock.
- With several exceptions, disturbed native soils and weathered bedrock in the surface mined area and sluiced overburden exhibit lower total and SPLP arsenic concentrations than tailings/waste rock and flotation tailings. The ratios of SPLP to total arsenic are generally low compared to tailings/waste rock and flotation tailings.

Collectively, the observations noted above suggest that tailings/waste rock, particularly the tailings (calcines) component, is a significant source of arsenic leaching at the RDM. Tailings/waste rock from the Post-1955 Main Processing Area appear more leachable than tailings/waste rock at the Pre-1955 Main Processing Area. Relatively low ratios of SPLP to total arsenic for flotation tailings suggest that these materials are a less significant source of leaching at the RDM. Similarities between the ratios of SPLP to total arsenic for flotation tailings and presumed stockpiled ore materials suggest a common source of total and leachable arsenic in these waste types, likely realgar and orpiment. The comparatively low ratios of SPLP to total arsenic for disturbed native soils in the Surface Mined Area and sluiced overburden suggest that these materials are not a significant source of arsenic leaching at the RDM.

Mercury

Mercury SPLP results were evaluated by comparing SPLP concentrations to total mercury concentrations and soil type (as designated in Chapter 3). Key findings are illustrated in graphs provided in Figures 5-9 through 5-12, and summarized below.

- Tailings/waste rock exhibited the highest SPLP mercury concentrations, ranging up to 356 µg/L, corresponding to a total mercury concentration of 2,370 mg/kg (estimated). All but four of the 73 samples analyzed for SPLP mercury had SPLP concentrations of 40 µg/L or lower, with total mercury concentrations ranging up to 1,620 mg/kg.
- The highest flotation tailings SPLP mercury concentration was 7.42 µg/L.
- Native and disturbed native soils generally have lower total and SPLP mercury concentrations.
- A sample of tailings (calcine material, sample 10OP01SS) exhibited total and SPLP mercury concentrations of 170 mg/kg and 4.8 µg/L (estimated), respectively. The ratio of SPLP concentration to total mercury concentration in this sample is fairly low.

Collectively, the observations noted above suggest that mercury in tailings/waste rock and flotation tailings is considerably less leachable than antimony or arsenic. This is consistent with information regarding site operations. Cinnabar, the highly insoluble ore mineral at the mine, is likely the primary mercury phase in waste rock. Tailings are expected to have had most of the mercury removed from them by the thermal processing in furnaces or retorts. Mercury mobility is further evaluated using a selective sequential extraction procedure, discussed below.

5.1.2.2   Toxicity Characteristic Leaching Procedure

The EPA TCLP was designed to evaluate the mobility of organic and inorganic constituents in a sanitary landfill. Selected samples of surface and subsurface soil types were evaluated for TCLP metals. Results of the TCLP tests are presented in Chapter 4 and briefly summarized below.

Arsenic

Arsenic SPLP results were evaluated by comparing SPLP concentrations to total arsenic concentrations and soil type. Key findings are illustrated in graphs provided in Figures 5-13 and 5-14, and summarized below

- The soil types exhibiting the highest TCLP arsenic concentrations at the RDM are tailings/waste rock and tailings (calcine material).
- Tailings/waste rock TCLP concentrations for samples in the Pre-1955 Main Processing Area included one result of 6,970 µg/L, one result of 2,800, and the remainder at concentrations of 1,000 µg/L or less.
- Tailings/waste rock TCLP concentrations for samples in the Post-1955 Main Processing Area ranged as high as 15,700 µg/L, with most results between 5,000 and 10,000 µg/L.
- The TCLP concentration of one tailings (calcine material) sample (10OP01SS) was 29,100 µg/L.
- Flotation tailings TCLP arsenic results ranged up to 2,800 µg/L, corresponding to a total arsenic concentration of 9,880 mg/kg.
- Native and disturbed native soils generally have relatively lower total and SPLP concentrations.
- TCLP arsenic concentrations are generally proportional to SPLP concentrations (discussed above) for samples that were tested by both procedures.

Collectively, the observations noted above further suggest that tailings/waste rock, particularly the tailings (calcines) component, is a significant source of arsenic leaching at the RDM. Tailings/waste rock from the Post-1955 Main Processing Area appear more leachable than tailings/waste rock at the Pre-1955 Main Processing Area. As with the SPLP results, relatively low ratios of TCLP to total arsenic for flotation tailings suggest these materials are a less significant source of leaching at the RDM. The tailings (calcines, sample 10OP01SS) material appears particularly leachable by TCLP.

Mercury

Mercury TCLP results were all below 78.5 µg/L, with most concentrations values below 10 µg/L. These values are all significantly less than the RCRA regulatory limit of 200 µg/L. TCLP mercury results are generally proportional to SPLP results for samples that were analyzed by both procedures.

5.1.3 Groundwater Transport

In general, inorganic contaminants can migrate directly into groundwater from sources that lie within the saturated zone or from sources or by leaching from overlying source materials. Transport of contaminants in groundwater is governed by the processes of advection, hydrodynamic dispersion (including mechanical dispersion and molecular diffusion), sorption/desorption, solution and dissolution, and recharge.

Transport of contaminants in groundwater is occurring at the RDM. Contaminants in groundwater were detected in monitoring wells at locations hydraulically downgradient of known contaminant sources areas (see Chapter 4). Contaminant migration in groundwater at the RDM is complex. The contaminant migration pathways lie within fractured bedrock and overlying materials that locally consist of disturbed and undisturbed native soils, tailings/waste rock, and flotation tailings. The three-dimensional framework of these materials at the RDM is locally complex and includes localized low-permeability zones that result in perching and other possible compartmentalization of the groundwater regime, as discussed in Section 3.2. The configuration of bedrock fracture flow pathways also is complex. The system of underground mine workings at the site likely has a strong effect on groundwater flow pathways in bedrock, and possibly the shallow subsurface as well, particularly in the vicinity of the seep along Red Devil Creek. The full nature of the impact of underground mine workings on groundwater flow and chemistry is not understood.

Groundwater is locally subject to impacts from contaminants in tailings/waste rock, flotation tailings, and contaminated soils. The greatest impacts from these sources on groundwater was observed where the materials occurred within the saturated zone. Where the water table elevation may vary, such waste materials could potentially be subjected to repeated wetting/drying cycles, which would likely promote mobilization of contaminants. Where the waste materials are above the water table, contaminants from these sources have locally migrated downward toward groundwater.

Ultimately, contaminated groundwater within the site flows to the Red Devil Creek valley and emerges as surface water in Red Devil Creek or flows down the valley to the Kuskokwim River.

5.1.4 Erosion and Mass Wasting

Erosion includes the physical processes by which moving surface water transports solid materials. In general, mass wasting is the downslope movement of soil and rock under the influence of gravity; it includes creep, slides, debris flows, slumps, rock flows, rockfalls, and block glides. Generally, the potential for transport by erosion is dependent on the surface area of exposed materials subjected to erosion; the size, shape, and density of the grains; the cohesiveness of the material, and the frequency and magnitude of precipitation/runoff events.

Erosion and mass wasting of contaminated soils, tailings/waste rock, and flotation tailings are relatively important contaminant release and migration mechanisms at the RDM. Observations made during the RI field investigations indicate that erosion and mass wasting of tailings/waste rock in the Main Processing Area are occurring. These processes are discussed further below.

Within the Post-1955 Main Processing Area, rills and gullies within the tailings/waste rock areas indicate erosion of these materials and transportation to Red Devil Creek.

The steep embankments of Red Devil Creek in the vicinity of the former culvert and road crossing are subject to mass wasting. The stream embankment in this area is steep and underlain by exposed tailings/waste rock. The stream bed in this area includes tailings/waste rock, some of which likely entered the creek by mass wasting. Tailings/waste rock and/or soil and fill and debris materials associated with the former culvert and road crossing likely underlie the stream bed to some depth in this area. No soil borings were installed within the stream bed to assess conditions beneath the stream bed. However, in soil boring 11MP29SB, installed near Red Devil Creek in this area, tailings/waste rock extended from the surface to a depth of approximately 16 feet bgs, approximately 2 feet below the elevation of the bed of Red Devil Creek. The stream bed substrate in the area of the former culvert/road crossing and the high gradient section of the creek extending downstream from this area are likely subject to erosion by downcutting due to the relatively high stream gradient.

Materials that enter Red Devil Creek by erosion and mass wasting have been in the past, and presently are, subject to surface water transport downstream within Red Devil Creek (discussed further below). Some of the materials transported down Red Devil Creek to its mouth have been in the past, and likely still are, deposited in the Red Devil Creek delta. These materials may be subject to further erosion by Red Devil Creek as it flows over the delta, and by the Kuskokwim River. Similarly, sluiced overburden that was historically deposited in the Dolly Sluice and Rice Sluice deltas is presently subject to erosion by the Kuskokwim River.

5.1.5 Surface Water Transport

Surface water transport processes include transport of dissolved and suspended particulate phase materials and bed load transport. Materials transported as suspended load are deposited at locations downstream under low energy conditions. These processes are discussed below.

5.1.5.1 Suspended and Dissolved Phase Transport

Surface water transport of contaminants involves the physical movement of dissolved or suspended particulate phase chemicals with the flow direction of surface water systems.

Suspended phase transport of particulates is primarily dependent on flow velocity and turbulence, grain size and shape, and grain density. Temporal changes in the flow regime, especially flow velocity, determine whether particulate materials at a given location are subject to erosion or deposition at a given time. Materials that are deposited under one set of conditions may be subject to subsequent entrainment and transport under another set of conditions. At the RDM, particle density is likely a significant factor for some mine waste materials due the relatively high specific gravity of cinnabar (8.1) and stibnite (4.56), and other minerals that make up a portion of waste rock and flotation tailings. Grains that make up or contain a significant proportion of these minerals will be less prone to erosion and suspend-

ed transport than native material grains of similar size and shape that do not contain appreciable amounts of these minerals.

Dissolved phase chemicals enter surface water by influx of groundwater under gaining flow conditions, and by dissolution and/or desorption of chemicals from rock and mineral particles in contact with the surface water. In general, the magnitude of surface water dissolved transport is dependent on groundwater influx and tendency of contaminants to dissolve or desorb from the bed sediments.

At the RDM, surface water transport of contaminants has historically occurred. Tailings/waste rock and other materials that entered the Red Devil Creek channel were historically transported, and likely locally deposited downstream within the creek, as evidenced by the occurrence of tailings/waste rock in the Red Devil Creek channel (see Red Devil Creek sediment results, presented in Chapter 4). Some of the materials were transported within Red Devil Creek downstream to its mouth in the Kuskokwim River. Some of that material was deposited in the Red Devil Creek delta, and some of the material was further transported by the Kuskokwim River downstream. Transport of overburden from the surface mined area by sluicing resulted in the Dolly and Rice Sluice deltas. Results of Kuskokwim River sediment samples indicate that some transportation of materials from Red Devil Creek, and likely the Dolly and Rice Sluice deltas, has occurred. Some of the deposited materials make up the bed load, which is discussed below.

RI results indicate that surface water transport is occurring presently at the RDM. Contaminants are migrating by groundwater into Red Devil Creek along gaining reaches and are being transported downstream by surface water. Contaminants also are likely dissolving or desorbing from stream bed sediments and being transported downstream. Particulates are being transported downstream by suspended phase transport within Red Devil Creek and the Kuskokwim River. These processes are discussed specifically for antimony, arsenic, mercury, and methylmercury below.

Contaminant Loading

Based on contaminant concentrations in surface water samples collected on August 26 and 27, 2001, and stream discharge rates measured on August 18, 2011, contaminant loading in surface water was estimated. Results are presented in Table 5-1.

Table 5-1 Surface Water Loading, August 2011 - Antimony, Arsenic, Mercury, and Methylmercury (kg/day)

Station ID	RD03	RD10	RD04	RD05	RD12	RD09	RD06	RD07	RD08
Sample ID	11RD03 SW	11RD10S W	11RD04 SW	11RD05 SW	11RD12 SW	11RD09S W	11RD06 SW	11RD07 SW	11RD08 SW
Total Antimony	0.015	0.026	0.25	0.014	1.24	1.84	2.70	3.11	3.24
Total Arsenic	0.008	0.014	0.16	0.45	0.45	1.07	1.42	1.49	1.37
Total Mercury	4.50E-05	5.77E-05	2.97E-04	2.77E-05	1.43E-03	4.56E-03	3.57E-03	3.72E-03	4.20E-03
Methylmercury	9.01E-07	1.08E-06	1.16E-06	2.73E-07	1.81E-06	1.90E-06	2.33E-06	2.61E-06	2.11E-06

Antimony, Arsenic, Mercury, and Methylmercury

During the RI surface water sampling events, surface water in Red Devil Creek exhibited generally increasing total and dissolved antimony, arsenic, and mercury concentrations along Red Devil Creek within and downstream of the Main Processing Area (from sample stations RD10 and RD11 downstream).

Total concentrations of antimony and arsenic were only slightly higher than the dissolved concentrations at each sample location throughout most of the stream in both 2010 and 2011, indicating that transport of antimony and arsenic in Red Devil Creek surface water is dominated by dissolved phase transport. Total concentrations of mercury were significantly higher than the dissolved concentrations at each sample location in both 2010 and 2011, indicating that mercury transport in surface water in Red Devil Creek is dominated by particulate phase. These results are likely attributable to mercury's strong tendency to bind to organic carbon, including organic particulates, in aqueous environments.

At the seep (location RD05), both total and dissolved concentrations of arsenic were higher than in Red Devil Creek surface water locations upstream and downstream in 2010 and 2011. These concentrations and the arsenic loading estimate (see Table 5-1, above) suggest that the seep and associated groundwater entering Red Devil Creek via baseflow is a significant source of arsenic to Red Devil Creek. Total and dissolved concentrations of antimony were lower in the seep sample (location RD05) than in Red Devil Creek at locations upstream and downstream in 2010 and 2011. These comparatively low concentrations and a low estimated loading suggest that the seep and associated groundwater entering Red Devil Creek via baseflow is not a significant source of antimony to the creek. Dissolved mercury concentrations were lower in the seep samples than in adjacent creek samples. However, total mercury concentrations in the seep samples were similar to the total mercury concentrations in the adjacent stream samples.

Methylmercury concentrations in Red Devil Creek surface water generally increase downstream from the beginning of the Main Processing Area through about station RD06, and slightly decrease further downstream. Generally, methylmercury in water is promoted by the presence of ionic mercury and high concentrations of sulfate and dissolved organic carbon (e.g., Rytuba 2001). In Red Devil Creek RI surface water samples, methylmercury concentrations are generally positively correlated with both total and dissolved mercury concentrations and with sulfate concentrations in all surface water samples collected during the RI. The highest methylmercury concentrations were detected in one sample from the seep location (RD05). The comparatively high methylmercury concentrations in the spring sample are attributable to the relatively high sulfate concentrations in these samples.

Increases in surface water loading along the length of Red Devil Creek are likely attributable in large part to groundwater migration into the stream along gaining

reaches. Within the lower portion of Red Devil Creek outside of the Main Processing Area, increasing contaminant concentrations and loading downstream is likely attributable to a combination of localized groundwater impacts and entrainment and dissolution/desorption of contaminants in channel bed sediment. Groundwater along this gaining section flows through tailings/waste rock beneath and near the creek channel and likely dissolved/desorbs inorganic elements from these materials prior to emerging into the stream as baseflow. Stream water flows over bed sediments that include tailings/waste rock and may dissolve/desorb inorganic elements from the materials as well as entrain particulates that contain higher concentrations of these inorganic elements.

Kuskokwim River Surface Water Transport

Tailings/waste rock and sluiced overburden materials that were deposited during mining operations in the Red Devil Creek delta and the Dolly and Rice Sluice deltas are subject to surface water erosion and transport within the Kuskokwim River. Suspended load would be deposited within lower energy environments within the river. The Kuskokwim River is a highly dynamic system, with widely varying river level, discharge rate, and flow velocity. As such, changes in these factors should result in significant variation in erosion, transport, and deposition conditions both spatially and temporally. Results of sediment sampling indicate that sediments are impacted by contaminants from the RDM at locations downriver of the Red Devil Creek and delta and Dolly and Rice Sluice deltas. A portion of these sediments likely represents material that was transported by suspended load and deposited under lower energy conditions. Some of the material also represents bed load, discussed further below.

5.1.5.2 Bed Load Transport

In general, sediment bed load transport is the process by which solid materials are moved downstream by moving water—including movement by rolling, sliding, and saltation—and deposited in a downstream location. Bed load transport is primarily dependent on sediment grain size and shape, flow velocity, and stream or river bed morphlogy (including bottom slope), and particle density. As with suspended load transport (discussed above), particle density is likely a significant factor at the RDM because of the relatively high specific gravity of cinnabar and stibnite in waste rock. Clasts that make up or contain a significant proportion of cinnabar or stibnite will be less prone to bed load transport than clasts of similar size and shape that do not contain appreciable amounts of these minerals, including some native soils and alluvium.

At the RDM, transport of contaminants by bed load has historically occurred. Large grains (sand and gravel) or tailings/waste rock and other materials that entered the Red Devil Creek channel were historically transported as bed load and deposited within the creek and the Kuskokwim River. Some of that material was deposited in the Red Devil Creek delta, and some of the material was further transported by bedload in the Kuskokwim River to locations downstream.

Sediment bed load transport of contaminants from the RDM is likely an important migration mechanism in Red Devil Creek and the Kuskokwim River. Tailings/waste rock within the Red Devil Creek channel and delta, sluiced overburden within the Dolly and Rice Sluice deltas, and any of these materials within the Kuskokwim River are expected to be further transported as bed load, particularly under relatively high energy conditions such as occur during spring breakup or intense rainfall events.

5.2 Speciation of Mercury and Arsenic

5.2.1 Methylmercury

Selected sediment, surface water, and groundwater samples were analyzed for methylmercury to evaluate the bioavailability of mercury in these media. Results of methylmercury analyses are presented in Chapter 4. Discussion of methylmercury in surface water is presented in Section 5.1.5.1. Results for sediment collected in Red Devil Creek and along the shoreline of the Kuskokwim River are presented below.

Red Devil Creek Sediment

The highest concentration of methylmercury detected in Red Devil Creek sediment samples was 7.02 nanograms per gram (ng/g), detected at upstream sample location RD02. The remaining creek sediment samples had concentrations of 1 ng/g or less. The seep sediment sample collected at RD05 had a concentration of 12.7 ng/g. Methylmercury concentrations showed no readily discernible increase with an increase in total mercury concentrations but were generally proportional to percent fines in all samples and to percent total organic carbon (TOC) in all samples except the seep sample. This is generally expected because mercury tends to bind strongly to organic carbon and clay particles.

Kuskokwim River Sediment

The highest concentration of methylmercury detected in Kuskokwim River sediment samples was 2.64 ng/g, detected at shoreline sample location KR15. The rest of the samples contained methylmercury at concentrations of 1.45 ng/g or less. Concentrations of methylmercury showed no readily discernible increase with an increase in total mercury concentrations, percent fines, or percent TOC.

5.2.2 Mercury Selective Sequential Extraction

Methylmercury is the most bioavailable form of mercury. Methylation of mercury and its uptake is a complicated process governed by several variables. Mercury speciation plays a large role in determining how much of the mercury released from mine sources may become available for methylation in downstream aquatic environments. For example, elemental mercury and ionic mercury are more readily methylated than other forms of mercury. Speciation also dictates how much mercury is bioavailable for the direct ingestion exposure pathway, as well as influencing the mobility of mercury in the environment.

Information on mercury species in ore materials at the RDM indicates that cinnabar is the dominant mercury mineral. Extended X-ray adsorption fine structure spectroscopy studies of mercury mine wastes indicate that the mercury species metacinnabar (m-HgS), corderoite ($Hg_3S_2Cl_2$), schuetteite ($HgSO_4$ -H20), and mercury chlorides are likely to form during the roasting of mercury ores, and each of these species is more soluble than cinnabar (Rytuba 2002).

An SSE technique was employed to approximate relative proportions of water soluble, stomach acid (weak acid) soluble, organo-complexed, strong complexed, and mineral bound forms of mercury in selected RDM soil and sediment samples. Although this technique does not identify exact mineral or oxidation state, it does differentiate between and quantify groups of mercury species based upon their solubility behavior. Each sequential extraction step dissolves a less soluble fraction. A summary of the selective extraction technique and typical mercury species identified by each extraction step is provided below.

Step	Extractant	Fraction Description	Typical Compounds
F0	De-ionized Water	Volatile	Hg_0
F1	De-ionized Water	Water soluble	$HgCl_2$, $HgSO_4$ (salts)
F2	pH 2 HCl/HOAc	Stomach acid soluble (weak acid)	HgO
F3	1 M KOH	Organo-complexed	Hg-humics, Hg_2Cl_2
F4	12 M HNO_3	Strong complexed	mineral lattice, Hg_2Cl_2, Hg_0
F5	Aqua Regia (concentrated HCl and HNO_3)	Mineral bound/cinnabar	HgS, m-HgS, HgSe, HgAu
F6	Hydrofluoric Acid	Mineral bound	Hg-silicates

5.2.2.1   Soil

Surface and subsurface soil, including tailings/waste rock, waste rock, flotation tailings, sluiced overburden, fill, and a variety of disturbed and undisturbed native soils were analyzed by mercury SSE. Results are presented in Chapter 4 and briefly summarized below.

Mercury SSE results were compared to total mercury concentrations and soil type. The comparably less soluble SSE fractions F5 and F6, which include cinnabar, and mercury silicates, generally made up most of the mercury in samples with higher concentrations of total mercury, including tailings/waste rock, waste rock, and flotation tailings. High proportions of F5 and F6 were also observed in other samples of other soil types, including weathered bedrock and a variety of disturbed and undisturbed native soil types and sluiced overburden.

The comparably more soluble SSE fractions F0 through F4 were dominant in a limited number of samples, all of which exhibited comparatively very low total mercury concentrations. In samples where fractions F0 through F4 made up 60

percent or more of total mercury, the total mercury concentrations were 6.6 mg/kg or less. Samples in which fractions F0 through F4 made up 20 percent or more of the total mercury exhibited total mercury concentrations of 55.4 mg/kg or less.

5.2.2.2   Sediment
Selected sediment samples from Red Devil Creek and the Kuskokwim River were analyzed by mercury SSE. Results are presented in Chapter 4 and briefly summarized below.

In Red Devil Creek sediment samples, the comparably more soluble SSE fractions F0 through F4 were collectively observed in a fairly high proportion only in samples with comparatively low total mercury concentrations.

In Kuskokwim River sediment samples, the less soluble fractions F5 and F6 were dominant in three of the four samples. The fourth sample, with fractions F0 through F4 comprising 71 percent of the total, had a low total mercury concentration of 0.52 mg/kg (estimated).

5.2.3 Arsenic Speciation
Arsenic typically exists in the environment in two valence states: arsenic (III), or arsenite; and arsenic (V), or arsenate. The toxicity of arsenic compounds varies based on valence state, form (inorganic or organic), physical state (gas, solution, or powder) and factors such as solubility, particle size, rates of absorption and elimination, and presence of impurities. Inorganic arsenic, usually in arsenic (III) form, is generally more toxic than organic arsenic. The toxicity of arsenic (III) is several times greater than that of arsenic (V) due to greater cellular uptake. However, at equivalent intracellular levels, arsenic (III) and arsenic (V) compounds are equally toxic.

Arsenate and arsenite are the two forms of arsenic typically found in groundwater. Arsenic mobility in groundwater is largely controlled by two general types of processes: 1) adsorption and desorption reactions, and 2) solid-phase precipitation and dissolution reactions. Arsenic adsorption and desorption reactions are affected by pH, redox reactions, presence of competing anions, and solid-phase structural changes at the atomic level. Precipitation and dissolution are controlled by solution chemistry, including pH, redox state, and solid chemical composition.

In general, arsenate is predominant under oxidizing conditions, and arsenite is predominant under reducing conditions. Within the range of pH of most groundwater, arsenate is in the form of oxyanions $H_2AsO_4^-$ or $HAsO_4^{2-}$, and arsenite is in the form of the neutrally charged species $H_3AsO_3^0$ (Hem 1985). The tendency of these species to adsorb to solid-phase surfaces in water varies in part because of these differences in charge.

Adsorption and Desorption
Arsenate and arsenite both adsorb to surfaces of a variety of aquifer solid phase materials, including iron oxides, aluminum oxides, and clay minerals. Arsenate

adsorbs strongly to iron oxide surfaces in acidic and circum-neutral pH water (Waychunas et al. 1993). However, under alkaline pH conditions, arsenate tends to desorb from iron oxide surfaces. Arsenite adsorption to iron oxide surfaces is generally weaker than for arsenate under typical environmental pH conditions. Adsorption of arsenite to iron oxide surfaces tends to decrease as pH increases within the range of pH 6 to pH 9.

Redox reactions also may control adsorption and desorption of arsenic because redox affects arsenic speciation. For example, reduction of arsenate to arsenite may result in increased arsenic mobility because arsenite is generally less strongly adsorbed than is arsenate.

Dissolution and Precipitation

Arsenic contained within solid phases, either as a primary structural component or as an impurity, is released when those solid phases dissolve. Similarly, arsenic precipitates out of solution when solid phases containing arsenic form. For example, arsenic often co-precipitates with iron oxide (Waychunas et al. 1993). As such, iron oxide may act as an arsenic source or a sink in water.

High concentrations of arsenic often are associated with iron oxides and sulfide minerals (Thornton 1996). Iron oxides frequently dissolve under reducing conditions and precipitate under oxidizing conditions. Sulfide minerals generally are unstable under oxidizing conditions and may precipitate under reducing conditions. Therefore, transfer of arsenic between these solid phases and water by precipitation and dissolution reactions may be a significant factor in the concentration and mobility of arsenic in water.

RDM Surface Water

Surface water samples collected from Red Devil Creek and the seep were analyzed for arsenate, arsenite, and total inorganic arsenic. Results are presented in Chapter 4. Arsenate and arsenite make up approximately 100 percent of the total inorganic arsenic for all samples. The proportion of arsenate to total inorganic arsenic ranged from 72 to 90 percent in Red Devil Creek samples. The proportion of arsenate in the seep sample was 31 percent. Total arsenic in the seep sample was 1,030 µg/L, and dissolved arsenic was 856 µg/L.

RDM Groundwater

Selected groundwater samples collected from monitoring wells were analyzed for arsenate, arsenite, and total inorganic arsenic. Results are presented in Chapter 4. Arsenate and arsenite make up approximately 100 percent of the total inorganic arsenic for all samples. The proportion of arsenate to total inorganic arsenic ranged from approximately 3 to 100 percent. Arsenate made up 95 percent or more of total inorganic arsenic in all but one sample, with total and dissolved arsenic concentrations greater than 37 µg/L. The sample from monitoring well MW10 contained total and dissolved arsenic at 96.9 and 92.1 µg/L, respectively. Arsenite made up 97 percent of total inorganic arsenic in this sample.

RDM Soil

Selected surface and subsurface soil samples were analyzed for arsenate, arsenite, and total inorganic arsenic. Results are presented in Chapter 4. The proportion of arsenate to total inorganic arsenic ranged from approximately 60 to 98 percent, with arsenate comprising 80 percent or more of total inorganic arsenic all but three samples.

Red Devil Creek Sediment

Selected sediment samples from Red Devil Creek and the seep at station RD05 were analyzed for arsenate, arsenite, and total inorganic arsenic. Results are presented in Chapter 4 and summarized below.

Total arsenic concentrations of creek sediment samples ranged from 32.5 mg/kg (at station RD11, located upstream of the Main Processing area), to 3,610 mg/kg (at station RD12). Total arsenic in the seep sediment sample, consisting of yellowboy material, was 130,000 mg/kg. Arsenate was the dominant arsenic species in all stream sediment samples, comprising between 87 and 98 percent of total inorganic arsenic, as well as the seep sample, in which arsenate made up 97 percent of total inorganic arsenic.

Kuskokwim River Sediment

Selected sediment samples from the Kuskokwim River were analyzed for arsenate, arsenite, and total inorganic arsenic. Results are presented in Chapter 4 and summarized below.

Total arsenic concentrations of the selected sediment samples ranged from 17.5 to 1,790 mg/kg. The dominant arsenic species is arsenate. The percent arsenate of total inorganic arsenic for most of the samples, with all of the higher concentration samples containing more than 90 percent arsenate. Arsenite percentages were higher in samples with lower total inorganic arsenic concentrations.

5.3   Bioavailability of Arsenic

The results of soil samples analyzed for arsenic bioavailability are presented in Tables 4-17, 4-18, 4-20, and 4-23. Arsenic bioavailability samples were collected from seven of the soil types introduced in Section 3.1.3 and specified in the tables contained in Appendix A. Arsenic bioavailability results ranged from 2.7 percent to 68.1 percent in the soil samples.

Figure 5-15 presents a chart showing arsenic bioavailability results compared to total arsenic results by soil type. The data indicate there is no strong correlation between total arsenic concentrations and arsenic bioavailability. However, the data indicate:

- Flotation tailings generally have lower arsenic bioavailability than other surface materials at the site; and

- Soil containing thermally processed tailings (T/WR soil type) generally have higher arsenic bioavailability than the flotation tailings and most native soils types.

Based on these observations, it can be concluded that arsenic in thermally processed tailings material and some native soils has a higher potential for biota uptake than other site surface materials. Arsenic bioavailability is further addressed in the human health risk assessment in Section 6.1.
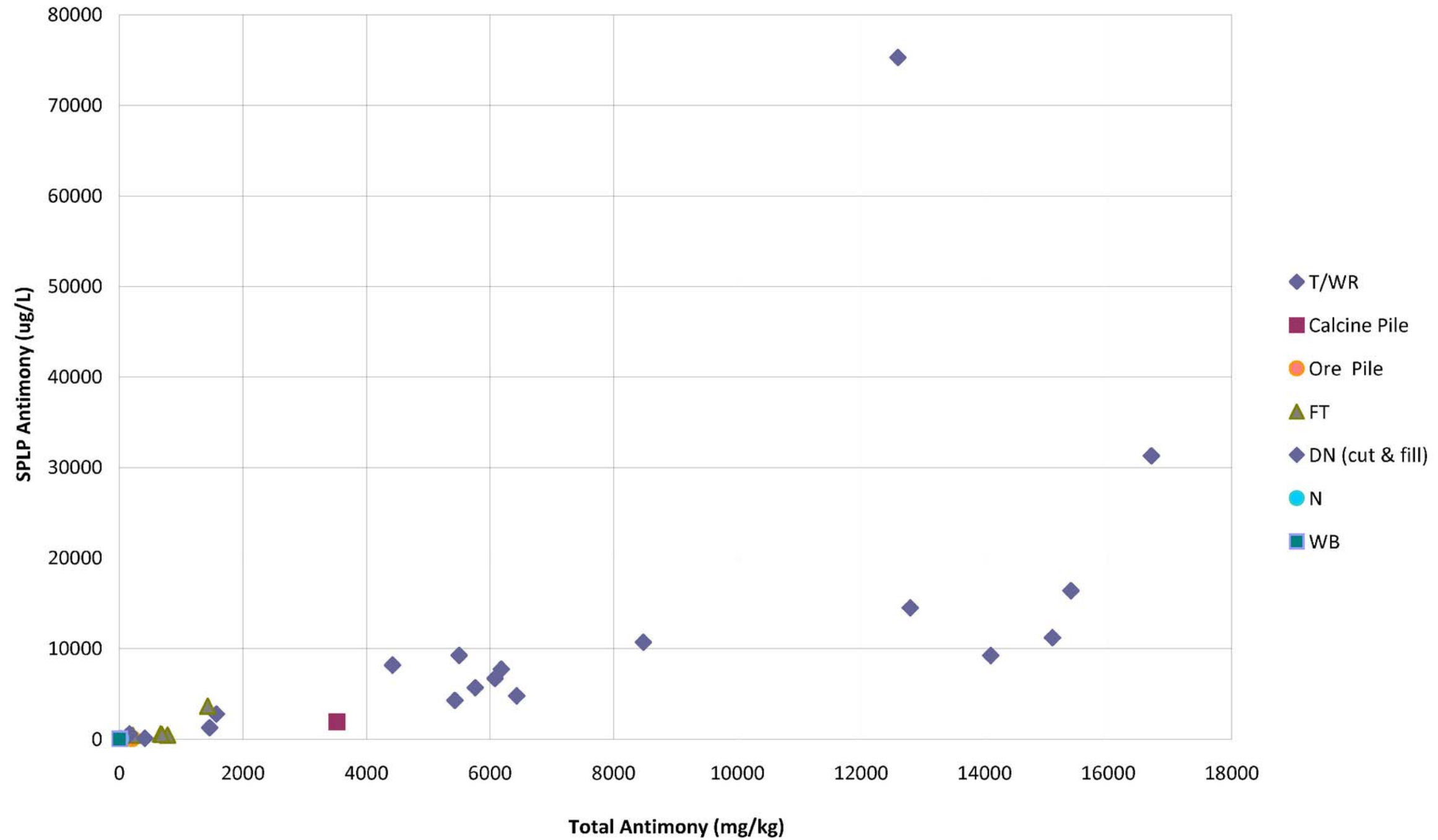
**Figure 5-1 Antimony - SPLP vs. Total
Pre-1955 Main Processing Area**
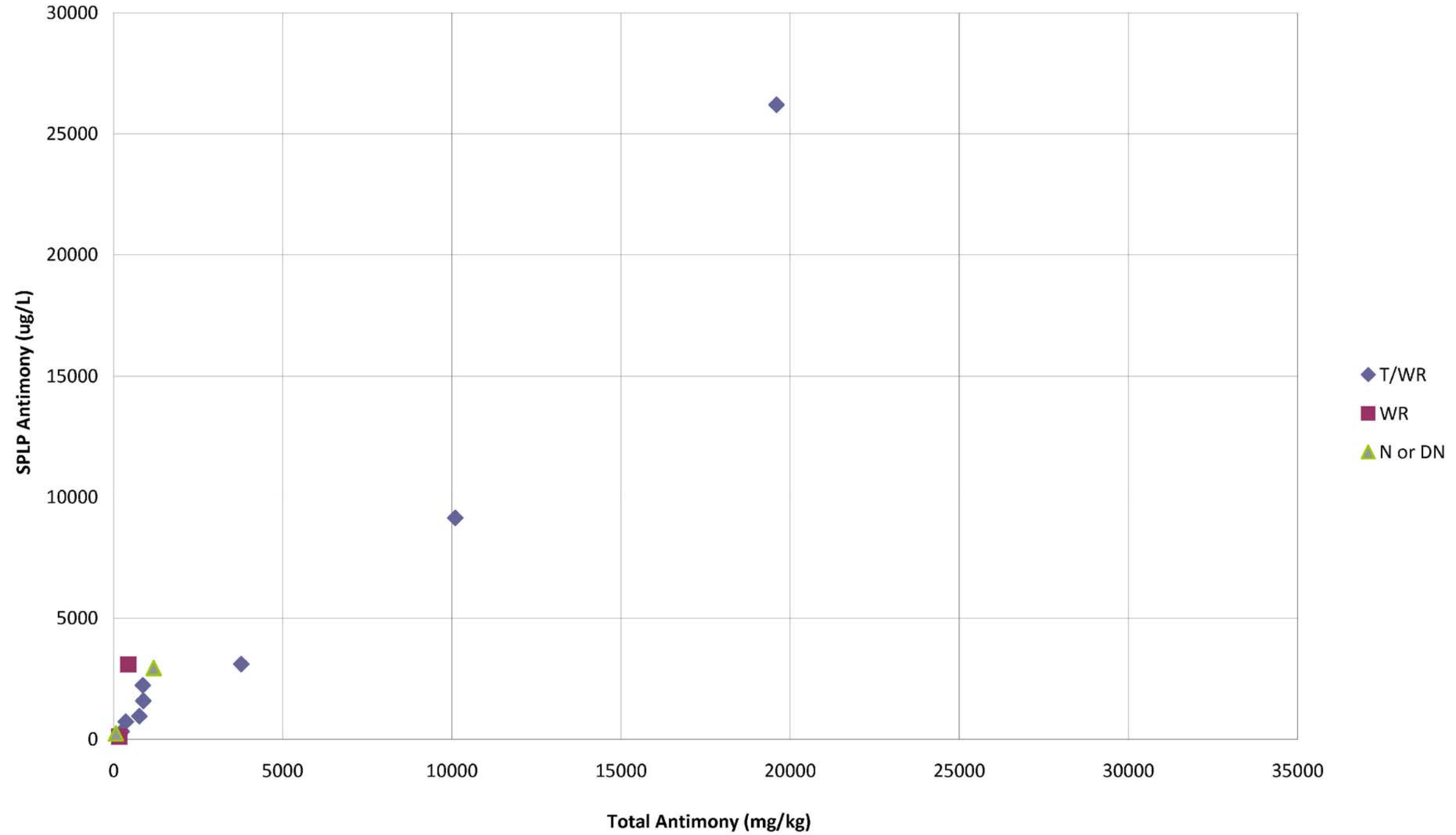
RED DEVIL MINE

Red Devil, Alaska

Figure 5-1
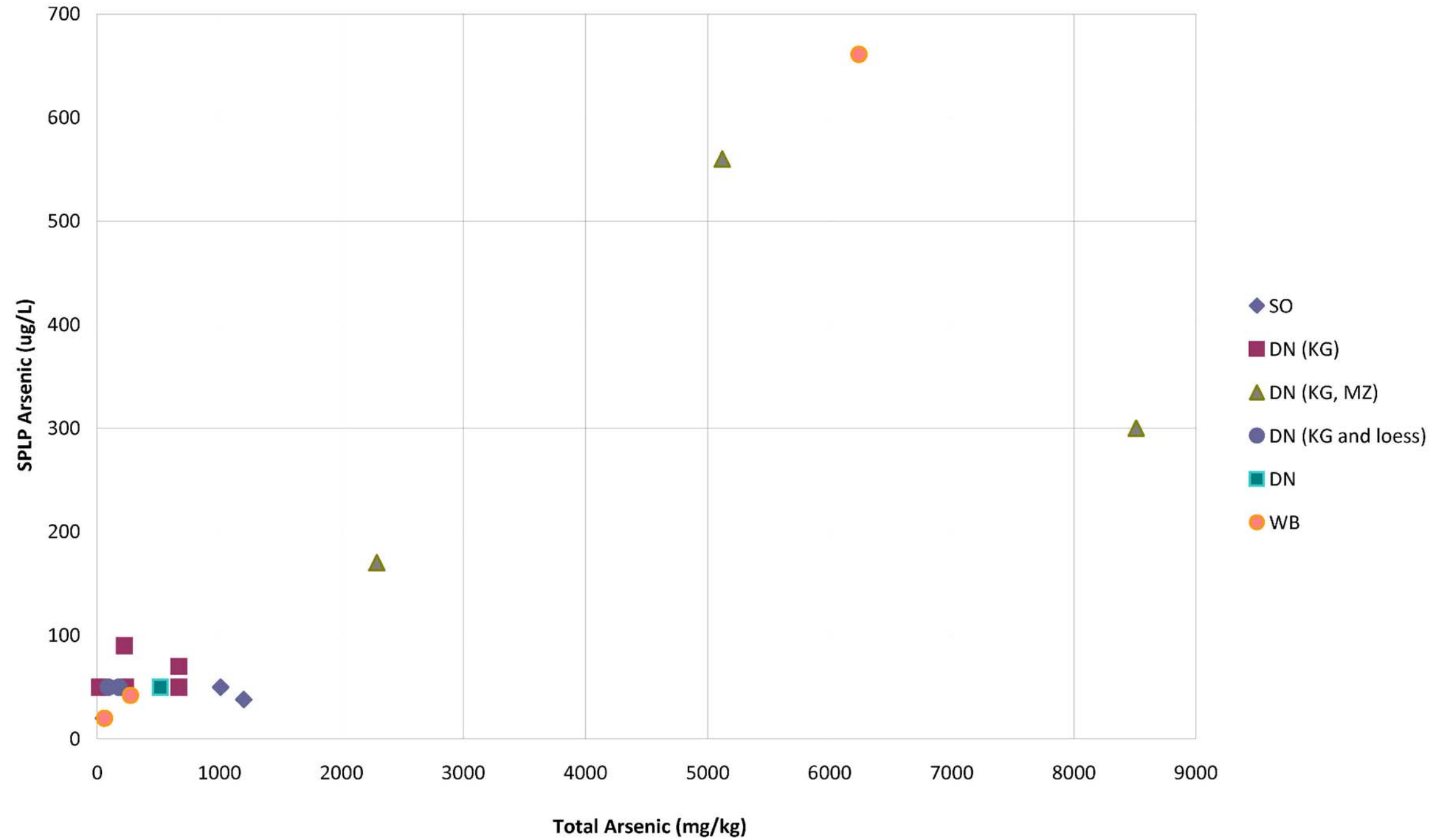Antimony - SPLP vs. Total
Pre-1955 Main Processing Area

Figure 5-2 Antimony - SPLP vs. Total
Post-1955 Main Processing Area

RED DEVIL MINE

Red Devil, Alaska

Figure 5-2
Antimony - SPLP vs. Total
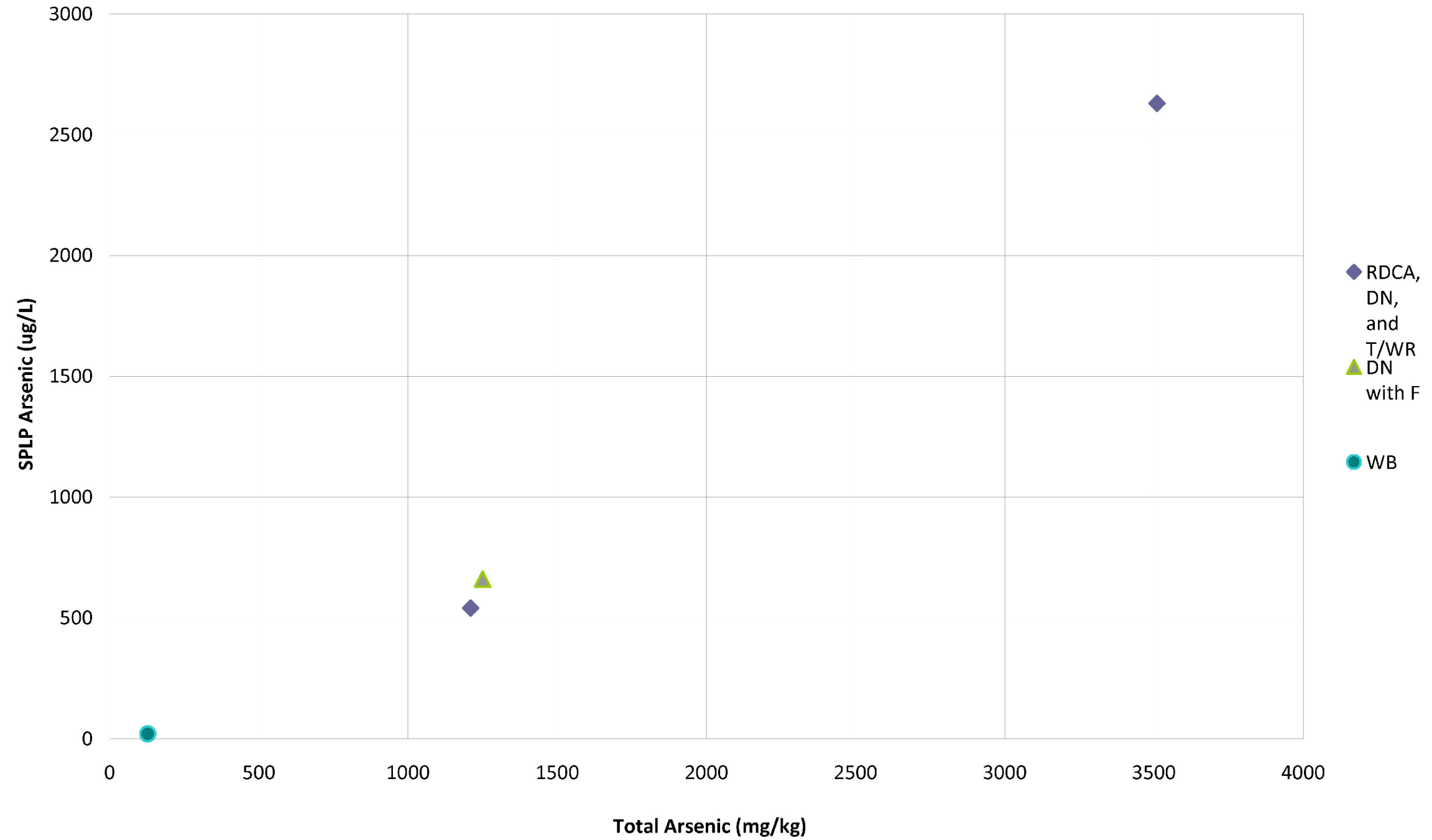Post-1955 Main Processing Area

Figure 5-3 Antimony - SPLP vs. Total
Surface Mined Area, Dolly Sluice, and Rice Sluice
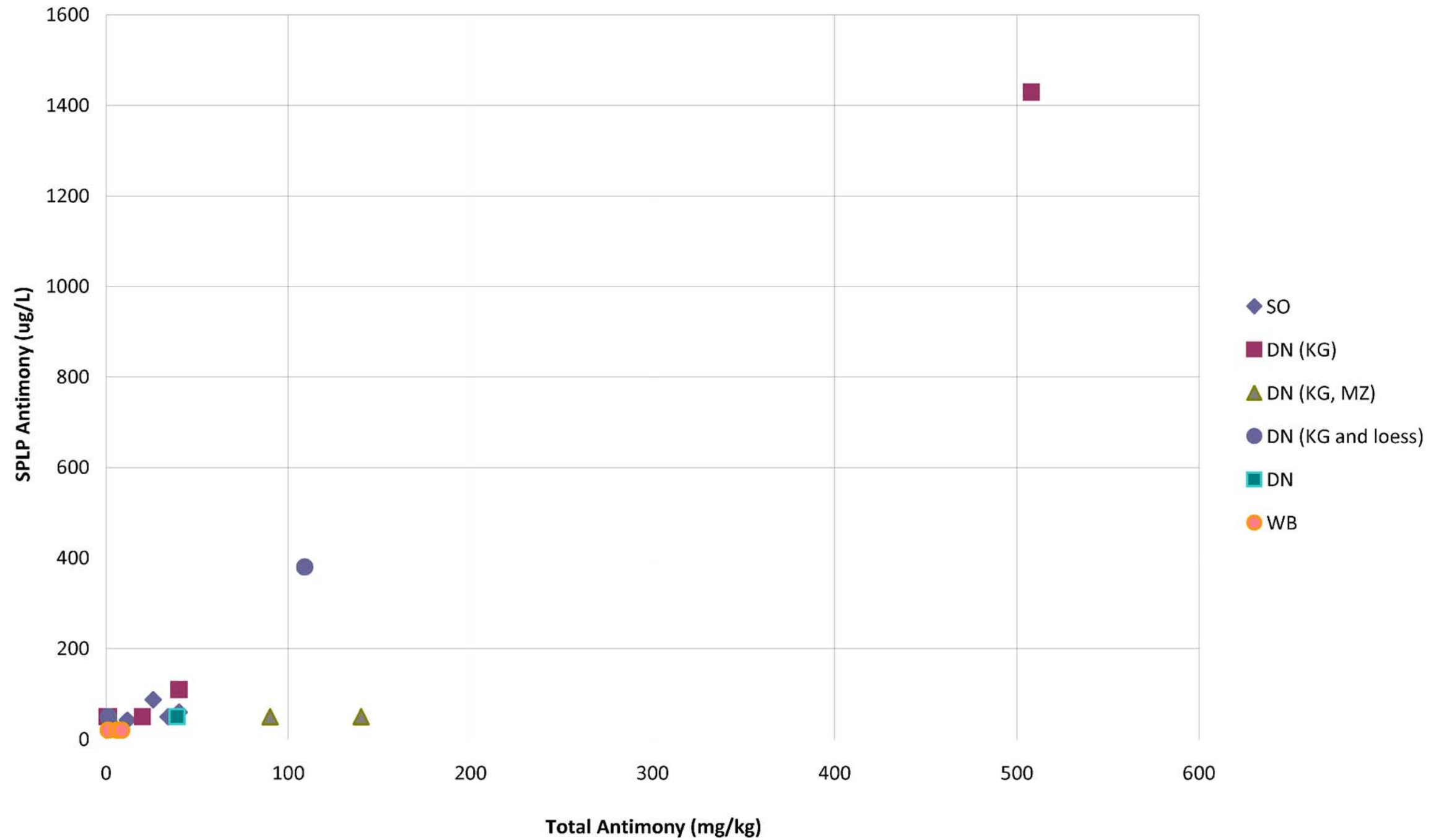
RED DEVIL MINE

Red Devil, Alaska

Figure 5-3
Antimony - SPLP vs. Total
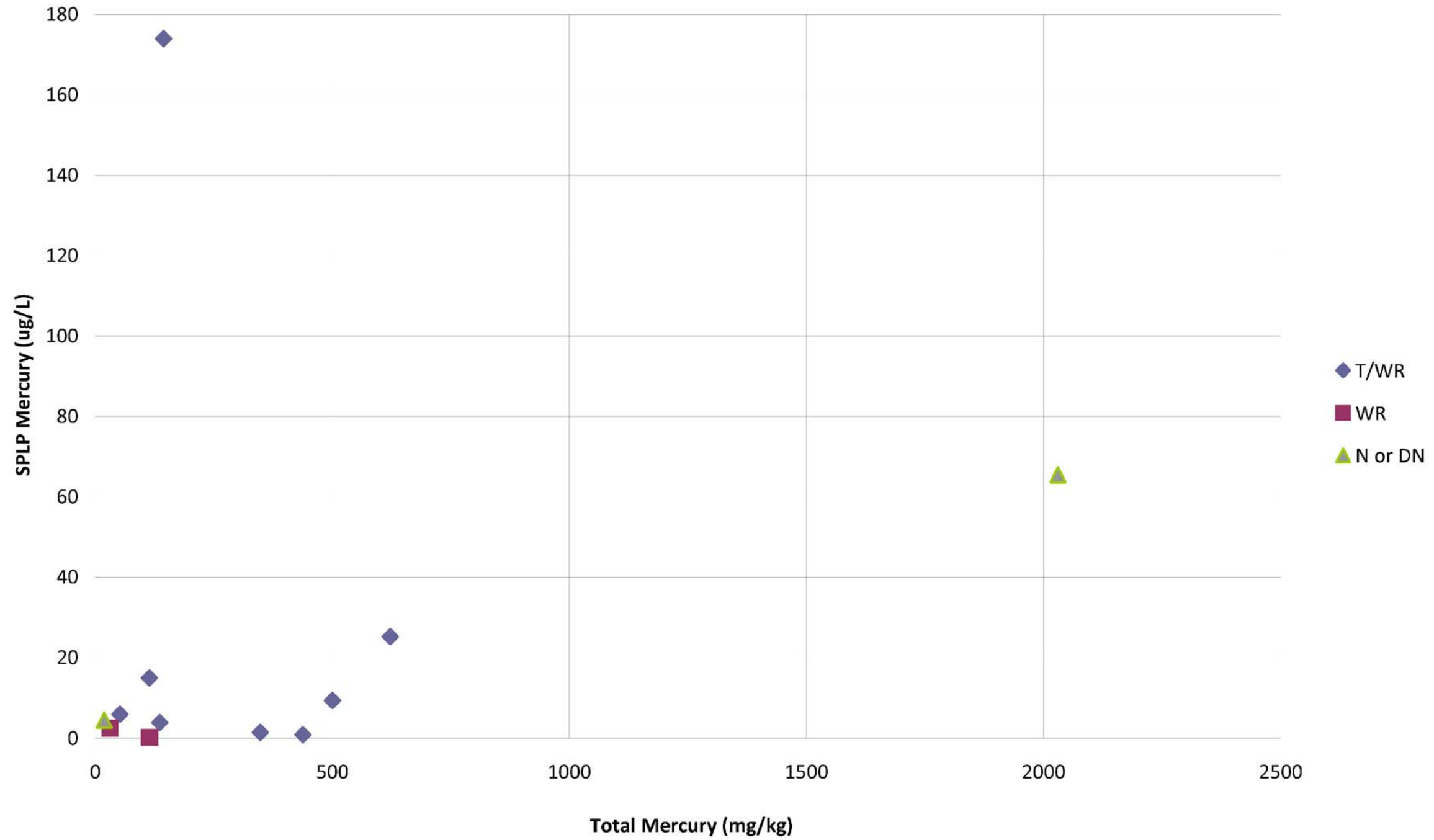Surface Mined Area, Dolly Sluice,
and Rice Sluice

Figure 5-4 Antimony - SPLP vs. Total
Red Devil Creek Downstream Alluvial Area and Delta
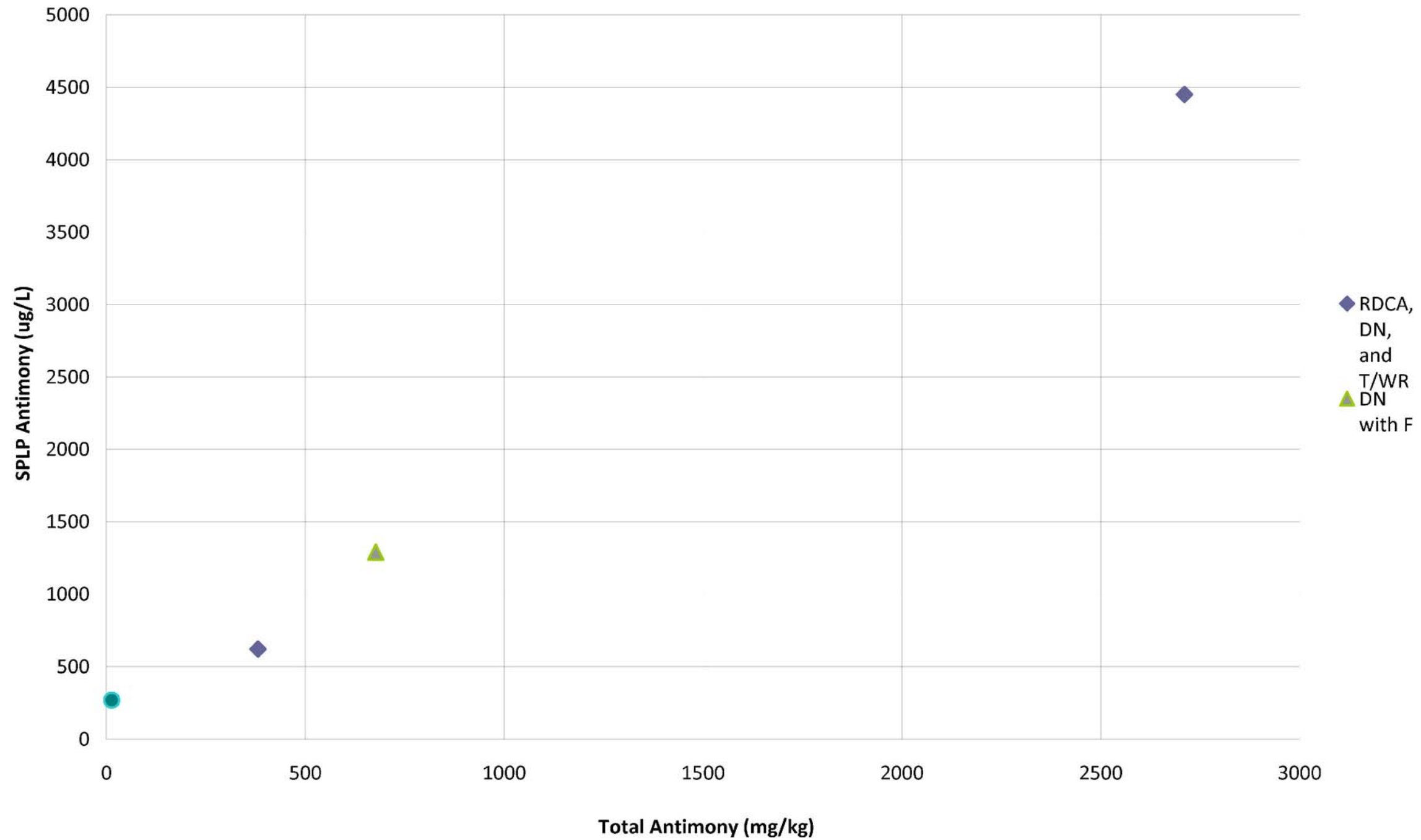
RED DEVIL MINE

Red Devil, Alaska

Figure 5-4
Antimony - SPLP vs. Total
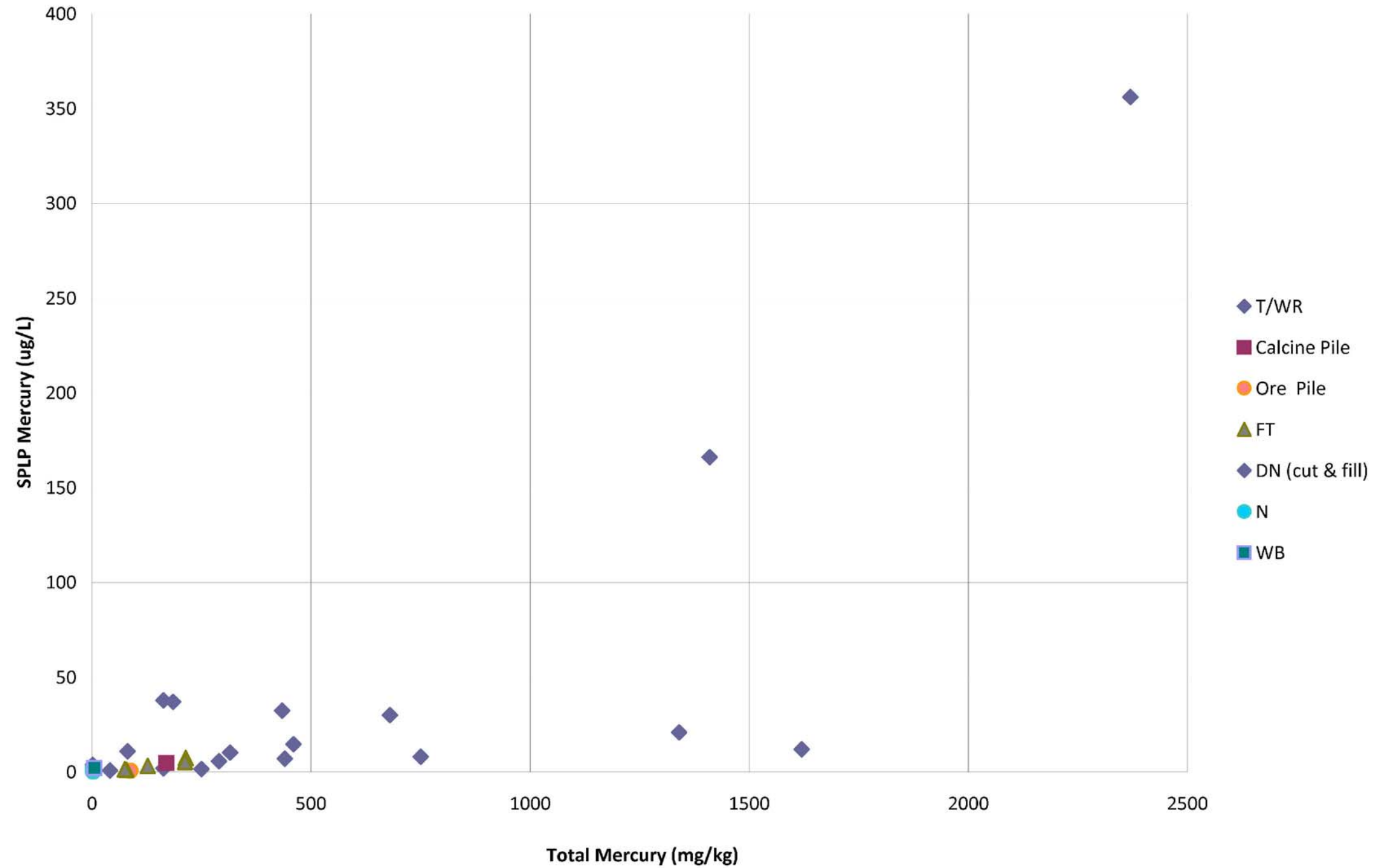Red Devil Creek Downstream
Alluvial Area and Delta

Figure 5-5 Arsenic - SPLP vs. Total
Pre-1955 Main Processing Area
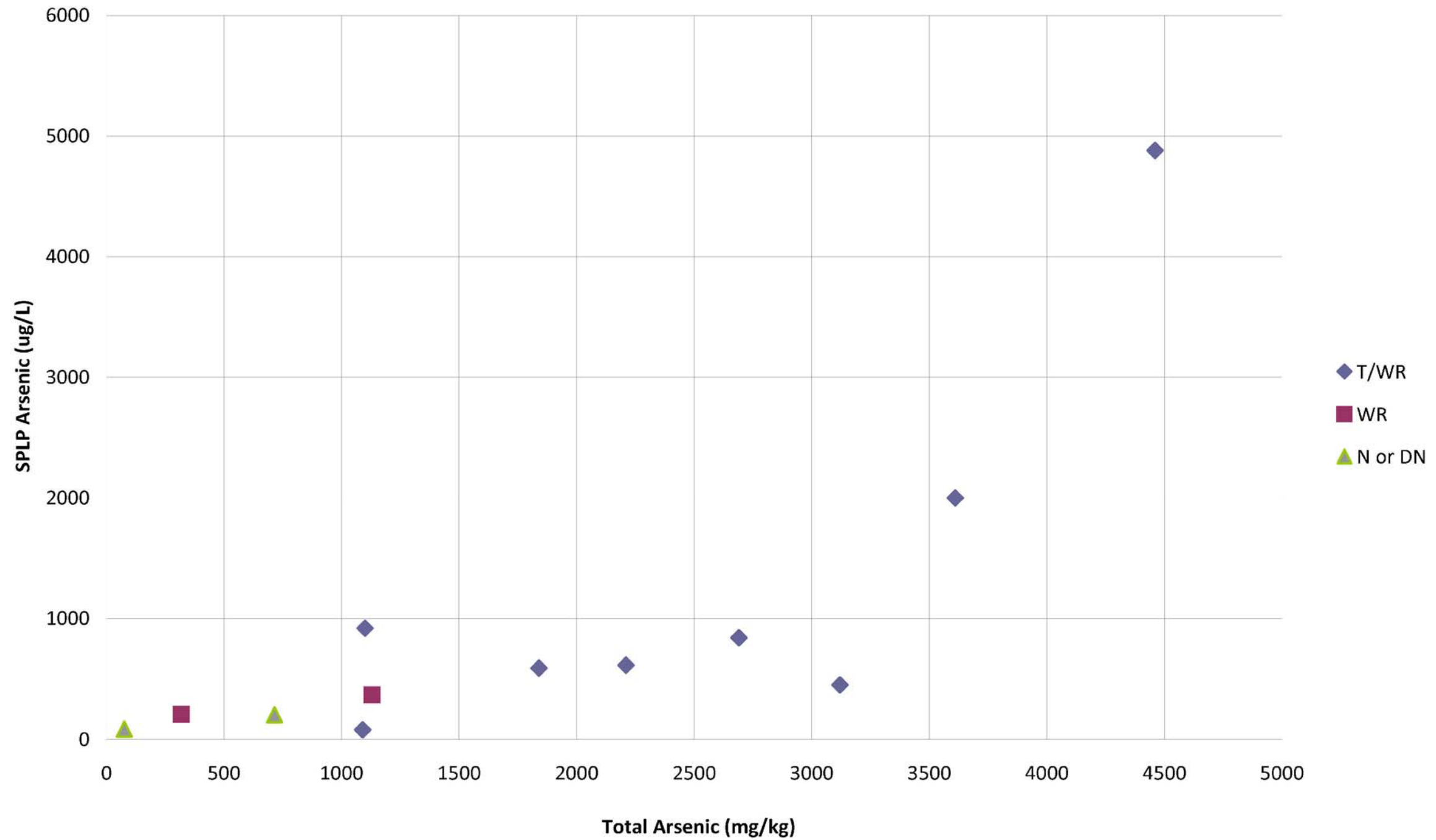
RED DEVIL MINE

Red Devil, Alaska

Figure 5-5
Arsenic - SPLP vs. Total
Pre-1955 Main Processing Area

Figure 5-6 Arsenic - SPLP vs. Total
Post-1955 Main Processing Area

Legend:
- T/WR
- Calcine Pile
- Ore Pile
- FT
- DN (cut & fill)
- N
- WB

X-axis: Total Arsenic (mg/kg)
Y-axis: SPLP Arsenic (ug/L)
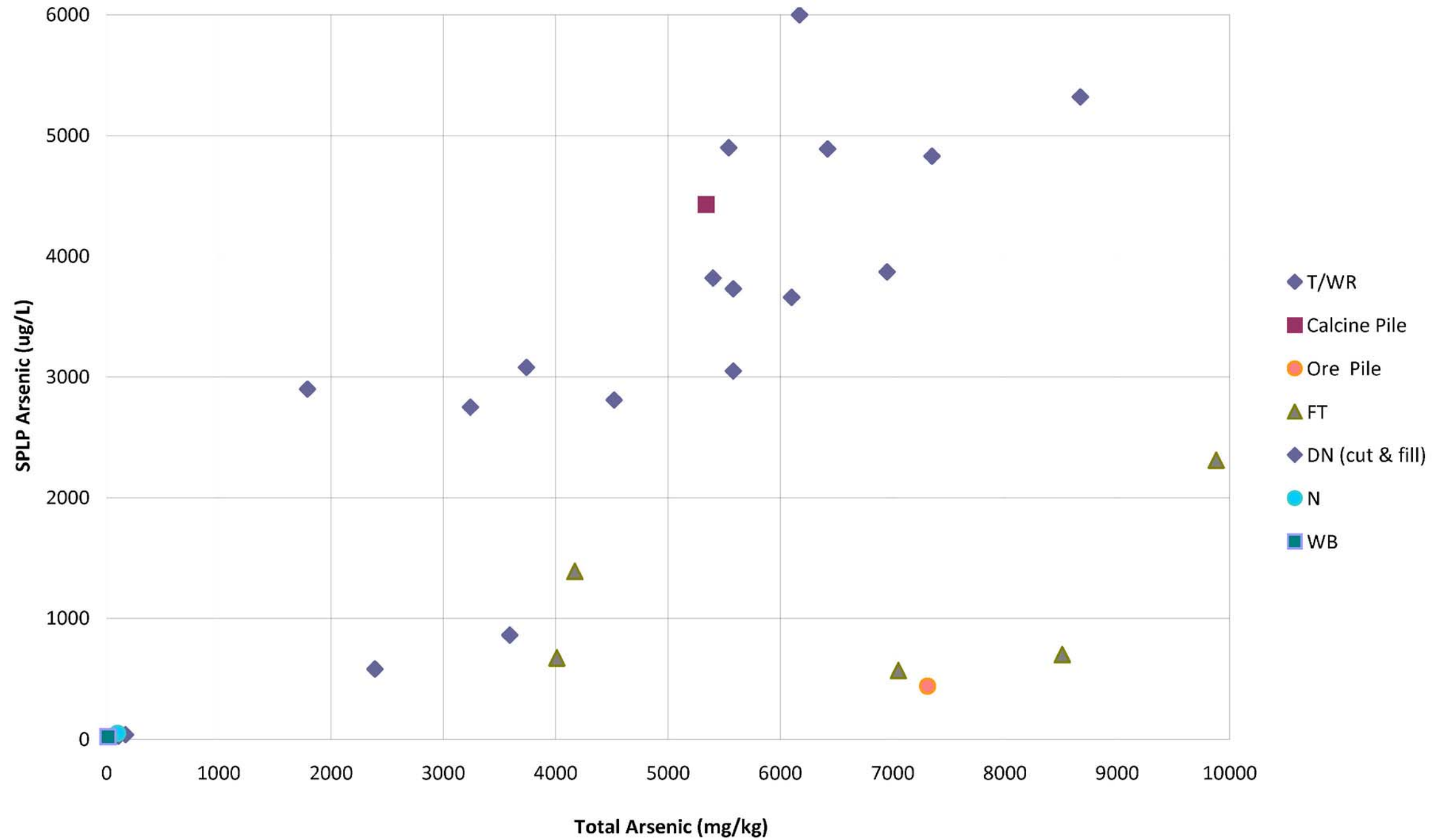
RED DEVIL MINE

Red Devil, Alaska

Figure 5-6
Arsenic - SPLP vs. Total
Post-1955 Main Processing Area

**Figure 5-7 Arsenic - SPLP vs. Total
Surface Mined Area, Dolly Sluice, and Rice Sluice**

RED DEVIL MINE

Red Devil, Alaska

Figure 5-7
Arsenic - SPLP vs. Total
Surface Mined Area, Dolly Sluice,
and Rice Sluice

Figure 5-8 Arsenic - SPLP vs. Total
Red Devil Creek Downstream Alluvial Area and Delta

RED DEVIL MINE

Red Devil, Alaska

Figure 5-8
Arsenic - SPLP vs. Total
Red Devil Creek Downstream
Alluvial Area and Delta

Figure 5-9 Mercury - SPLP vs. Total
Pre-1955 Main Processing Area

RED DEVIL MINE

Red Devil, Alaska

Figure 5-9
Mercury - SPLP vs. Total
Pre-1955 Main Processing Area

Figure 5-10 Mercury - SPLP vs. Total
Post-1955 Main Processing Area

RED DEVIL MINE

Red Devil, Alaska

Figure 5-10
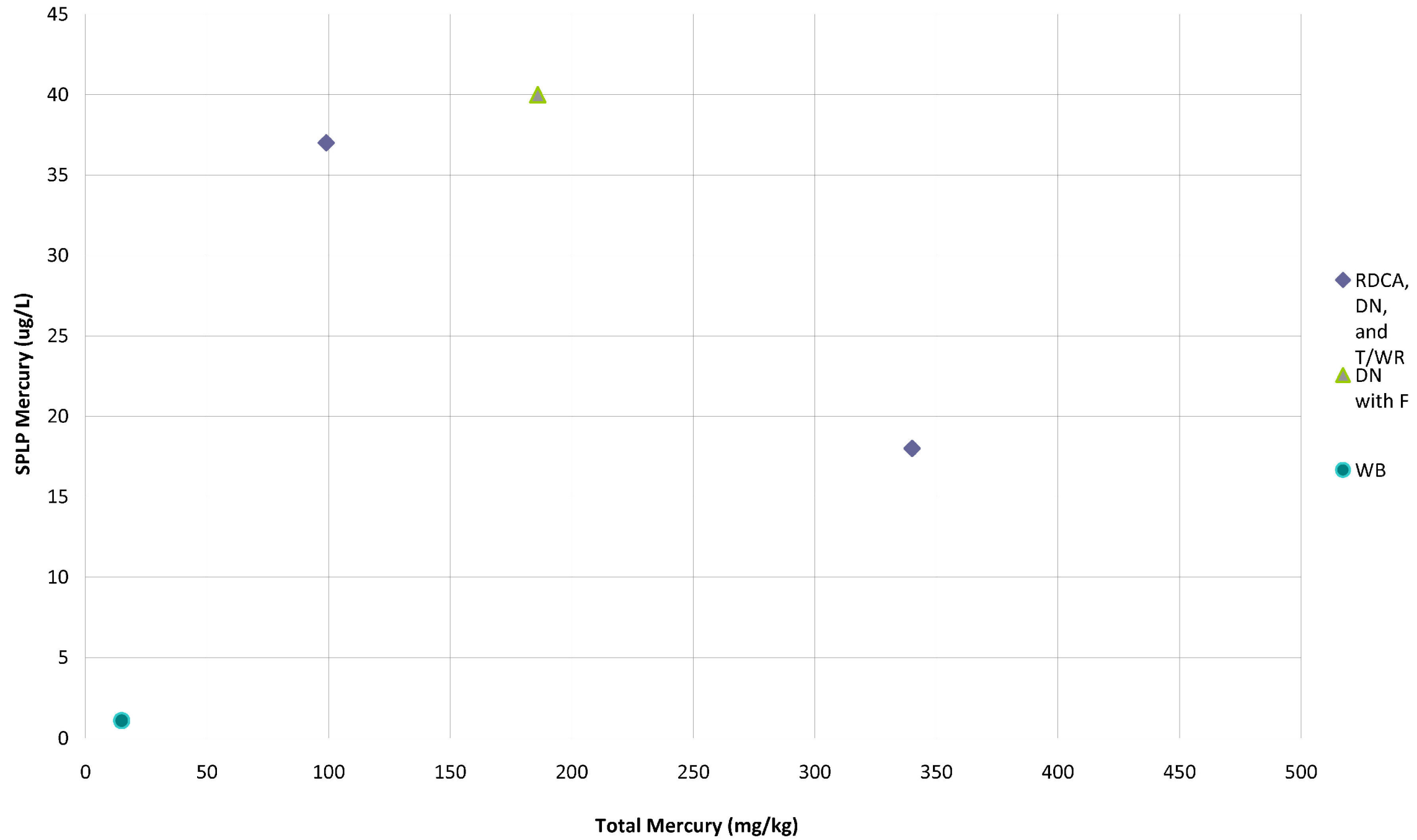Mercury - SPLP vs. Total
Post-1955 Main Processing Area

Figure 5-11 Mercury - SPLP vs. Total
Surface Mined Area, Dolly Sluice, and Rice Sluice
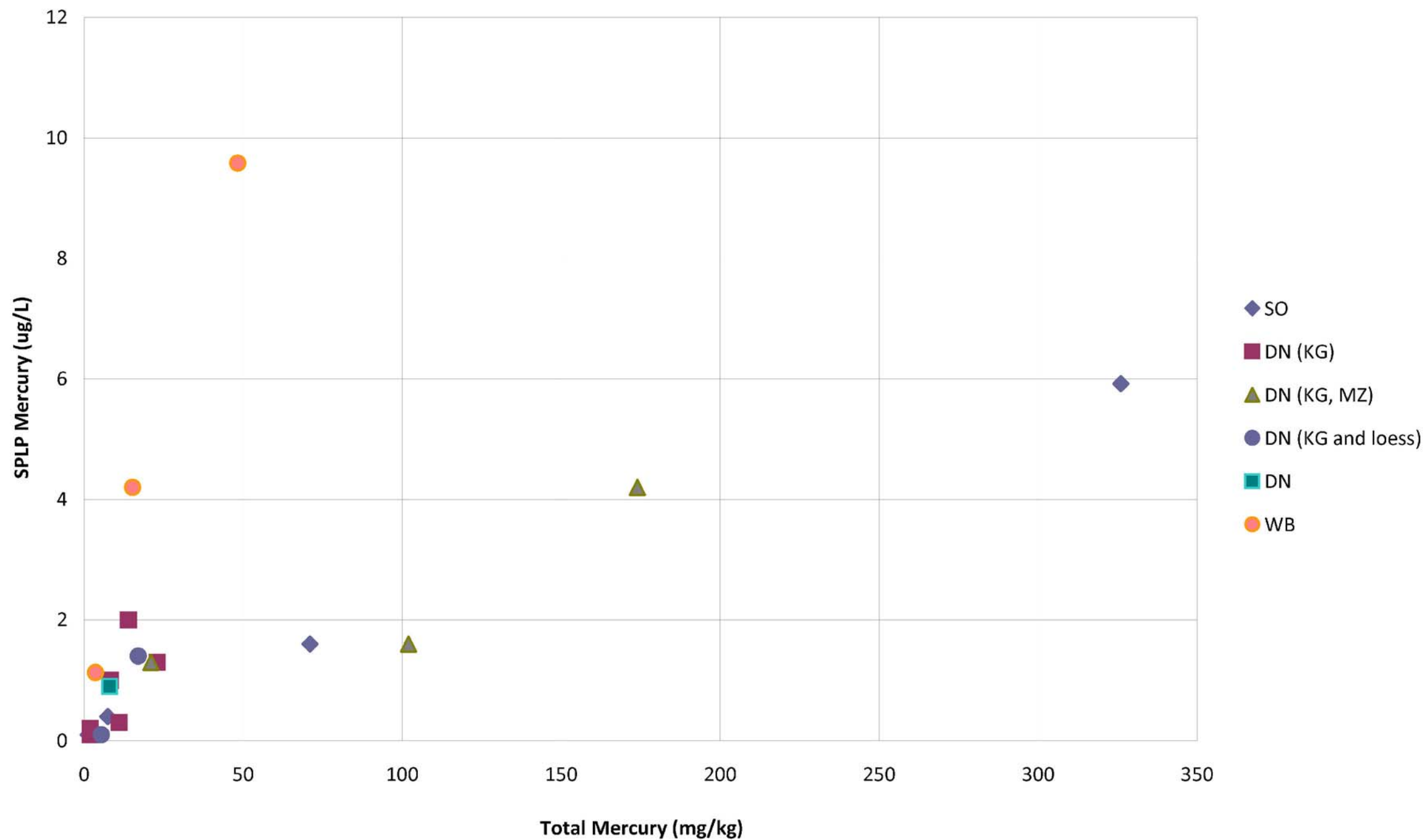
RED DEVIL MINE

Red Devil, Alaska

Figure 5-11
Mercury - SPLP vs. Total
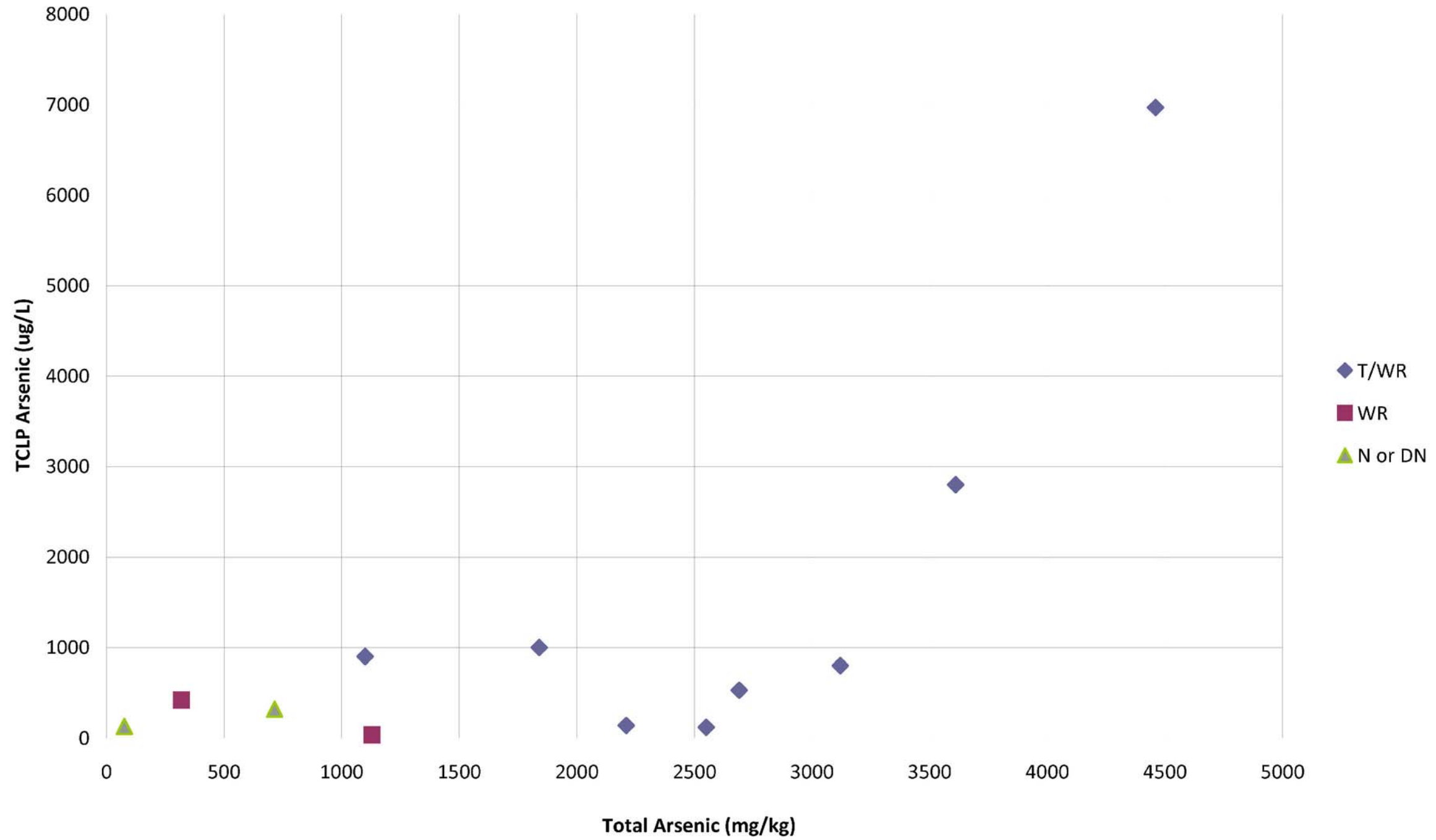Surface Mined Area, Dolly Sluice,
and Rice Sluice

Figure 5-12 Mercury - SPLP vs. Total
Red Devil Creek Downstream Alluvial Area and Delta

RED DEVIL MINE

Red Devil, Alaska

Figure 5-12
Mercury - SPLP vs. Total
Red Devil Creek Downstream
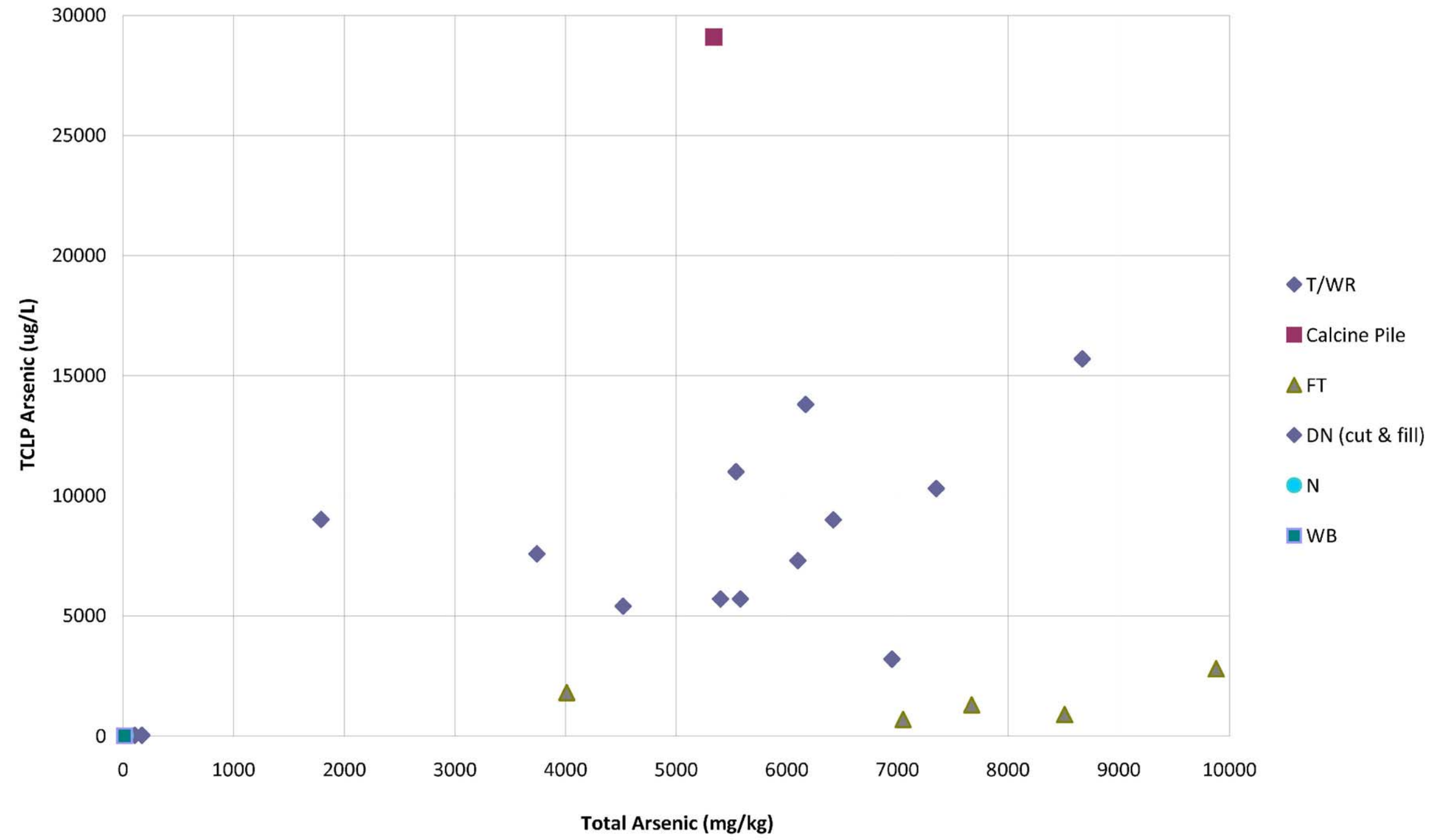Alluvial Area and Delta

Figure 5-13 Arsenic - TCLP vs. Total
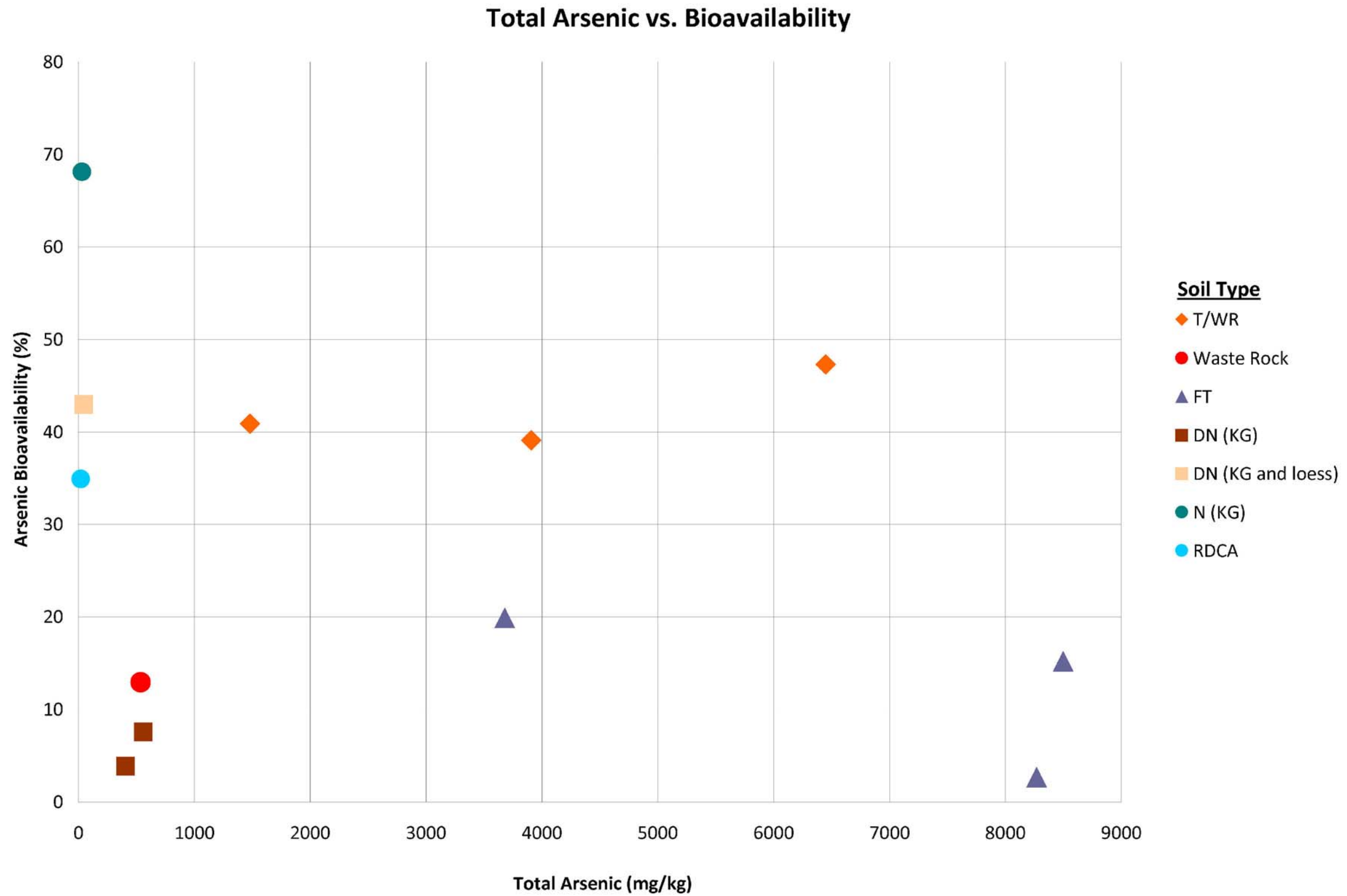Pre-1955 Main Processing Area

RED DEVIL MINE

Red Devil, Alaska

Figure 5-13
Arsenic TCLP vs. Total
Pre-1955 Main Processing Area

Figure 5-14 Arsenic - TCLP vs. Total
Post-1955 Main Processing Area

RED DEVIL MINE

Red Devil, Alaska

Figure 5-14
Arsenic TCLP vs. Total
Post-1955 Main Processing Area

Total Arsenic vs. Bioavailability

RED DEVIL MINE

Red Devil, Alaska

Figure 5-15
Total Arsenic vs. Bioavailability