A RECONNAISSANCE OF THE
HEAVY METAL CONTENT
OF
ASHUELOT RIVER SEDIMENTS

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Introduction

The Ashuelot River is an important hydrologic feature of south-western New Hampshire, draining the major portion of Cheshire County, a small portion of Sullivan County, and a small portion of north-central Massachusetts. Along its 64-mile course are several population centers and sites of historic and current industrial activity, including the city of Keene.

The release of heavy metals to the environment has long been associated with various industrial activities, but heavy metal contamination has also been correlated with population density in areas without significant industrial activity (e.g. Callender & Rice, 2000). Given the history and geography of the Ashuelot River, we undertook a reconnaissance assessment of the possibility that the river's sediments might be contaminated with heavy metals, presumably in and downstream from Keene. The metals assessed in this study include Chromium (Cr), Nickel (Ni), Copper (Cu), Zinc (Zn), or Lead (Pb)—all of concern because of their potential toxicity.

In this report, we present chemical analyses for total Cr, Ni, Cu, Zn, and Pb, determined by X-ray fluorescence (XRF) spectrometry, in selected sediment samples from the Ashuelot River. These data are compared with toxicological effect levels and thresholds compiled by the National Oceanic and Atmospheric Administration's Coastal Protection and Restoration Division for screening sediment quality (Buchman, 1999). We do not attempt to determine the sources of these metals in this report.

X-ray fluorescence spectrometry, a mature analytical technique well described elsewhere (e.g. Fitton, 1997; Bertin, 1978), determines directly the total concentration of each element in the sample, *not* it's bioavailability (as might be determined by acid leaching studies) *nor* the concentration of particular species of an element, such as the different oxidation states of Cr which may have different levels of toxicity. Buchman (1999) does not distinguish between total and bio-available concentrations, nor between different oxidation states, in establishing toxicological effect levels and thresholds for screening purposes.

Methods

Sample sites were selected for ease of access, geographic distribution, and suitability of the river bed for yielding a sample (convenience). Sample sites are shown in Figures 1 and 2. Sites were selected both upstream and downstream of Keene (Fig. 1), with additional detailed sampling conducted near the industrial heart of Keene (Fig. 2). At each of three sites (Culvert, Railroad Trestle, and A-Field Bridge), four samples were collected in a transect across the width of the river; an additional sample was collected at the Railroad Trestle. At one site (Bike Path), both the surficial sediment ("Muck") and the underlying stratum ("Clay") were sampled. No attempt was made at any of the sites to select samples based on flow or sedimentation regimes; rather these were "grab" samples collected for reconnaissance.

Samples were collected by wading in the river and pulling up sediment from the bottom with a hand-held bucket auger. Sediment in the bucket was transferred

to a plastic bag and sealed for transport back to the laboratory. No effort was made to characterize the particle size distribution, mineralogy, or other physical or chemical properties of the samples.

The collected samples were dried overnight in a convection drying oven at 60°C and then sieved through a 2 mm sieve to remove gravel and other large debris. Material that passed through the sieve was pulverized in a hardened steel planetary ball mill for seven minutes to produce a uniformly fine powder. Between samples, the sieve and mill was washed and scrubbed with soap and water, and then blow-dried with compressed air.

A 6.000 ± 0.001 gram aliquot of the sample powder was combined with 0.750 ± 0.001 gram of SPEX CertiPrep UltraBind, a proprietary binding agent (Obenauf, et al., 2002). These were mixed in a vial in a high-speed mixer/mill for 1 minute. The resulting mixture was pressed into a pellet, with an aluminum backing cup, in a 35 mm die assembly placed in an automated hydraulic press. The press applied 30 tons of force for 3 minutes, and slowly released the pressure over another three minutes. Once extracted from the die assembly, the resulting pellet is a dense compacted solid with a smooth flat surface ready for analysis by XRF.

To test the potential for contamination during sample processing, aliquots of laboratory-grade silica sand (~100% SiO_2; Fisher Scientific catalog #S151-10) were also pulverized, in both the hardened steel mill and a tungsten carbide mill, and pressed into pellets as above.
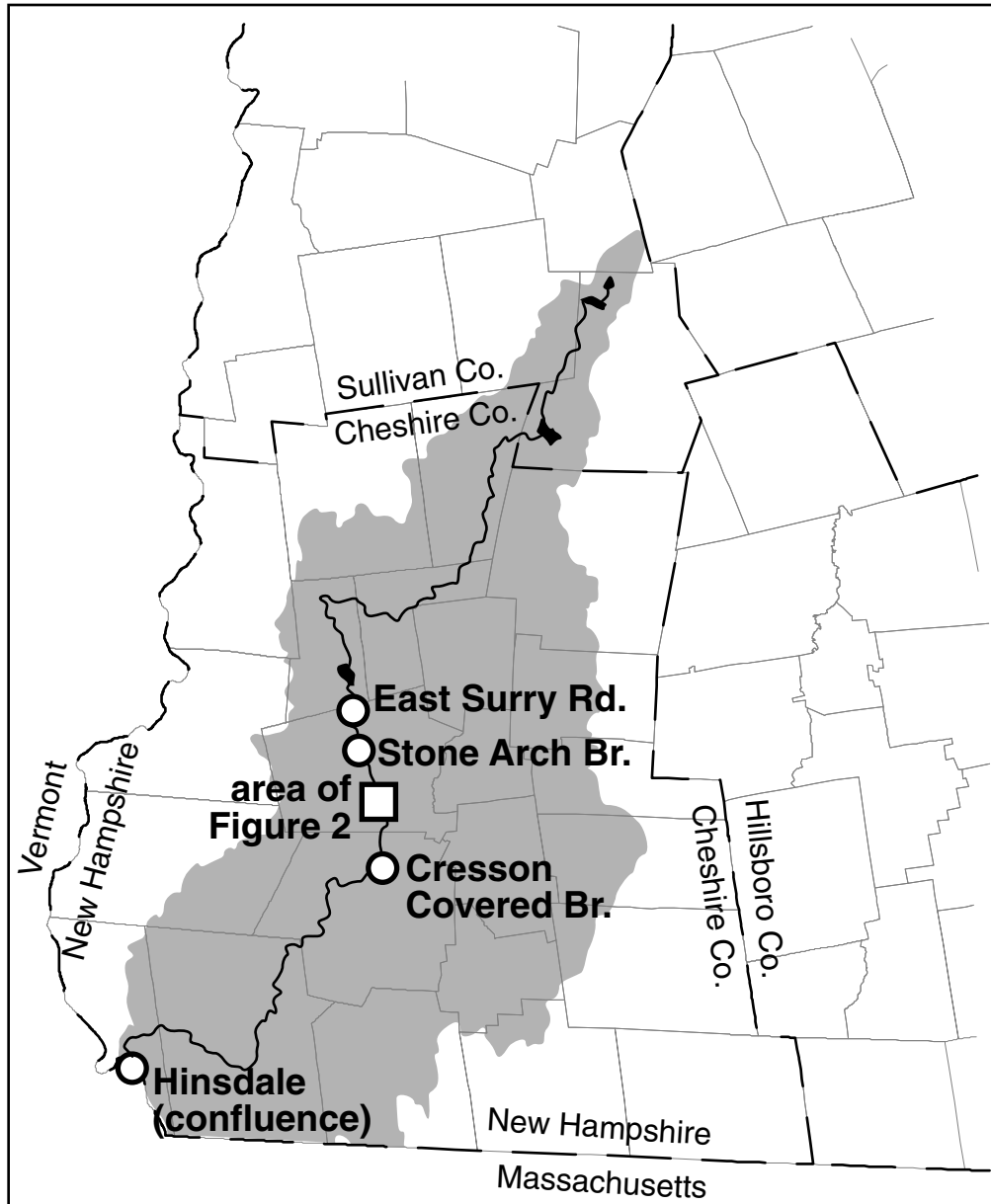
Figure 1: Watershed of the Ashuelot River in south-western New Hampshire, showing upstream and downstream sample locations, and the location of Figure 2. Base map from the *Atlas of the Ashuelot River and the Ashuelot River Watershed*, published by the Ashuelot River Local Advisory Committee, 2001.
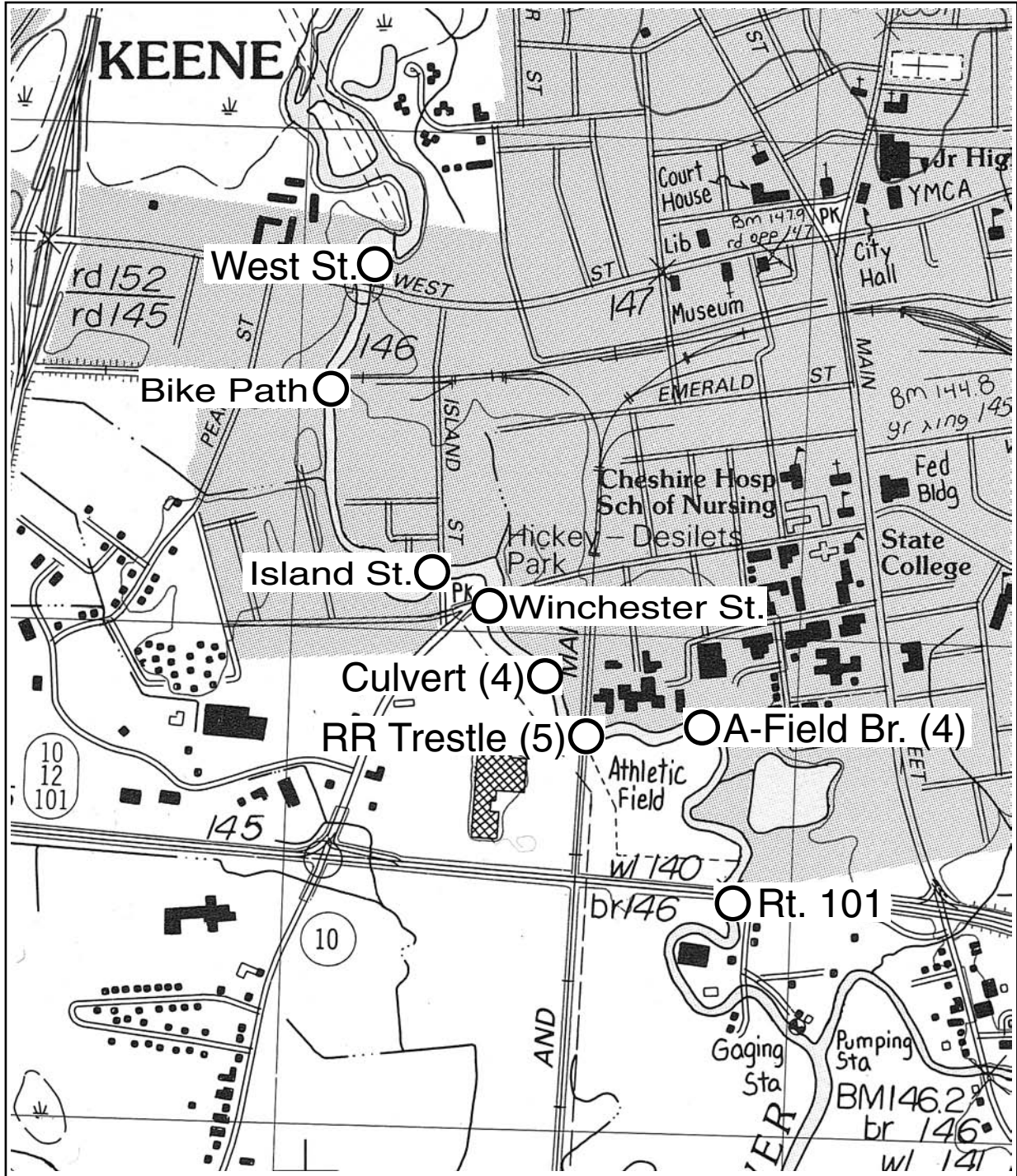
Figure 2: Detail of the Ashuelot River in downtown Keene, New Hampshire, showing sediment sample locations. Base map enlarged from the U.S. Geological Survey Keene New Hampshire-Vermont 1:25,000-scale 7.5 x 15 minute quadrangle.

The analyses were carried out on the Rigaku ZSX 100e wavelength dispersive sequential XRF spectrometer in the Keene State College Analytical Geochemistry Laboratory. Instrument settings and measuring conditions are listed in Table 1. The instrument was calibrated with pellets prepared from selected US Geological Survey Rock Reference Materials (http://minerals.cr.usgs.gov/geo_chem_stand/), whose bulk compositions were expected to be roughly similar to those of the sediment samples. Calibration graphs comparing measured x-ray intensity to recommended concentration for the each element of interest in the reference materials are shown in Figure 3. The uncertainty in the measurements obtained by these methods is discussed below, in the context of our results.

Table 1: Instrumental Settings

X-ray tube: Rh target, 50 kV, 72 mA
Filter: out
Diaphragm: 30 mm (30 mm sample mask)
Attenuator: 1/1
Collimator: Standard
Analyzing Crystal: LiF200
Detector: Scintillation Counter

Elem.	Line	Peak, °2θ	time, sec	BG1, °2θ	time, sec	BG2, °2θ	time, sec	PHA
Cr	KA	69.330	80	68.750	20	70.200	20	100-330
Ni	KA	48.645	80	48.000	20	49.500	20	100-320
Cu	KA	45.010	80	44.410	20	45.610	20	100-320
Zn	KA	41.780	70	41.000	25	42.500	25	100-300
Pb	LB1	28.240	90	27.880	60	28.840	30	100-300

Cr

R= 0.99996

W-2

SDC-1

GSP-2

AGV-2

X-ray Intensity (kcps)

Standard Value (ppm)

Ni

R= 0.99242

W-2

SDC-1

GSP-2

AGV-2

X-ray Intensity (kcps)

Standard Value (ppm)

Cu

R= 0.98994

W-2

GSP-2

AGV-2

SDC-1

X-ray Intensity (kcps)

Standard Value (ppm)

Zn

R = 0.96648

GSP-2

AGV-2

SDC-1

W-2

X-ray Intensity (kcps)

Standard Value (ppm)

Pb

R= 0.98603

GSP-2

SDC-1

AGV-2

W-2

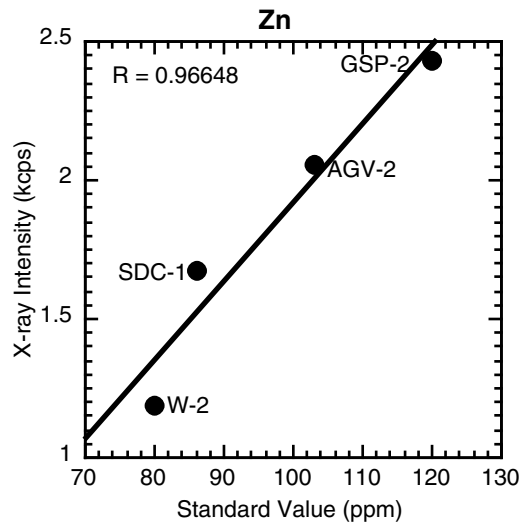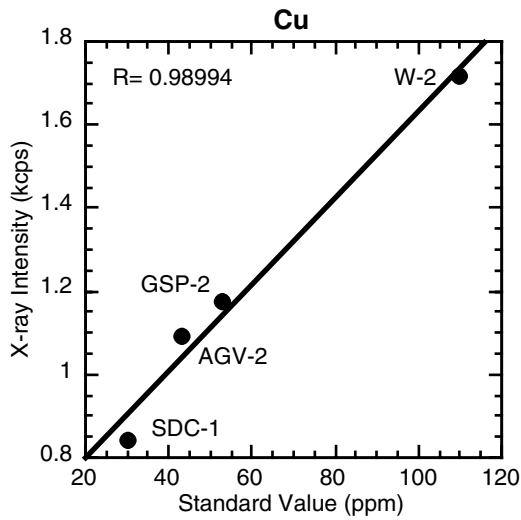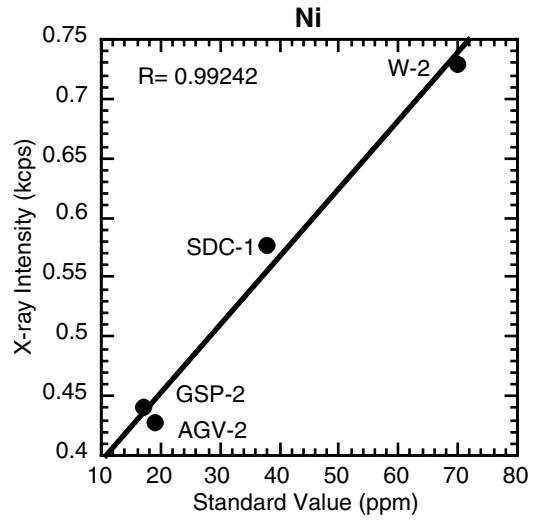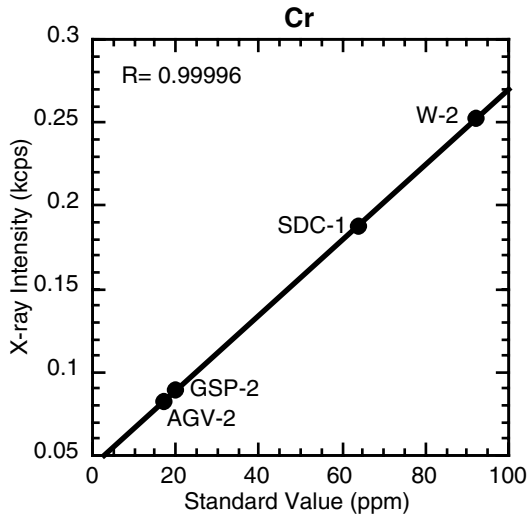X-ray Intensity (kcps)

Standard Value (ppm)
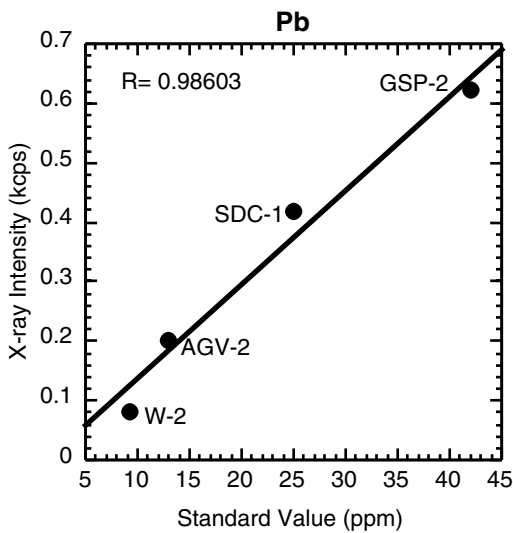
Figure 3: Calibration lines (X–ray intensity versus concentration) for Cr, Ni, Cu, Zn, and Pb, using four USGS Rock Reference Materials (AGV-2, GSP-2, SDC-1, and W-2) prepared as pressed powder pellets.

8

Results and Discussion

The results are presented in Table 2 and in Figures 4 through 8— graphs of concentration versus river kilometer, with the sampling sites identified. Included in Table 2 are three toxicological effect levels and thresholds for each of the 5 elements, in freshwater sediments, as compiled by Buchman (1999).

At concentrations below the "Threshold Effects Level" (TEL), adverse effects on benthic organisms are very rare. Above the "Probable Effects Level" (PEL), adverse effects on benthic organisms are frequently expected. At concentrations greater than the "Upper Effects Threshold" (UET), adverse impacts on the benthic community are *always* expected. The ranges of normal background levels, in soils and in freshwater sediments, are also indicated in Table 3 (Buchman, 1999).

The detection limit for XRF analysis of Cr in geological materials is approximately 5 to 10 ppm; for Ni, Cu, Zn, and Pb, the detection limit is in the range of 1 to 5 ppm (Fitton, 1997). A "check sample" (Monson Slate) was analyzed 28 times over the period of the study, to assess instrumental precision (Table 4). The standard deviations of these measurements varied from 0.7 to 1.7 ppm for the five elements; thus with greater than 99% confidence (3σ), the precision of these measurements is between ±2 and ±5 ppm (Table 4). One Ashuelot River sediment sample was prepared in duplicate ("Culvert 4," Table 2). The results show very good agreement, particularly for Ni, Zn, and Pb. The differences for Cr and Cu suggests that the variability (lack of homogeneity) of the original samples, and errors involved in sample preparation (see further discussion below), are the most

significant source of uncertainty in these measurements. Not only are the samples themselves possibly heterogeneous, but the sample sites are likely to be as well.

Accuracy can be assessed by measuring standard reference materials of known composition as unknowns (Table 5); our measured results are generally in agreement with the accepted values within the level of precision cited above. It should be noted that many of the values obtained in our measurements (Table 2) exceed the highest value in the range of concentrations of the reference materials used in calibrating the instrument (Fig. 3, Table 5). For example, the calibration range for Pb is from 9 to only 41 ppm (Fig. 3), yet we report values of over 1000 ppm among the samples (Table 2, Fig. 8). The further one extrapolates beyond the calibration range, the greater the uncertainty associated with the value obtained. None-the-less, it is clear that those samples *do* have significantly elevated Pb levels. Future analyses might be improved through calibration with additional reference materials having a greater range of concentrations. For screening purposes, the preparation and analytical methods seem sufficiently precise and accurate.

Pulverizing the samples in a hardened steel ball mill has caused significant contamination of the samples with Cr (Table 2, Fig. 4), but there may still be useful information in these results. The typical composition of hardened steel includes Fe as the major element, and Cr, Si, Mn, and C as minor elements (Obenauf, et al., 2002). Comparing the analyses of specimens of laboratory-grade silica sand prepared in the hardened steel ball mill and in a tungsten carbide ball mill (Table 2) shows that up to 300 ppm Cr may be attributable to contamination during processing of the samples.

Table 2: Analytical Results; values that exceed the TEL (from Table 3) are indicated with italics; values that exceed the PEL (from Table 3) are indicated in bold; and values that exceed the UET (from Table 3) are indicated in bold italics.

Sample	Cr ppm	Ni ppm	Cu ppm	Zn ppm	Pb ppm
East Surry Road	191	*26*	7	85	25
Stone Arch Bridge	117	*31*	10	96	35
West Street	122	**41**	22	*126*	*51*
Bike Path Clay	250	**40**	27	121	*65*
Bike Path Muck	121	***80***	*58*	134	29
Island Street	365	*27*	7	76	24
Winchester Street	613	*32*	29	*128*	*75*
Culvert 1	515	*23*	9	82	*46*
Culvert 2	437	*21*	4	78	*54*
Culvert 3	468	*24*	5	76	*59*
Culvert 4-1	353	*24*	***280***	78	***229***
Culvert 4-2	380	*25*	***335***	79	***230***
RR Trestle 1	503	*25*	19	110	*74*
RR Trestle 2	291	18	-3	78	*90*
RR Trestle 3	225	18	18	97	***237***
RR Trestle 4	404	*27*	12	102	***1033***
RR Trestle 5	746	*23*	23	89	***1152***
A-Field Bridge 1	465	*21*	24	92	*56*
A-Field Bridge 2	383	*32*	23	*132*	***176***
A-Field Bridge 3	460	*24*	0	73	*54*
A-Field Bridge 4	344	*22*	0	75	*44*
Route 101	172	**38**	*37*	*130*	*79*
Cresson Covered Bridge	116	*32*	*47*	*139*	**93**
Hinsdale (confluence)	267	*34*	*51*	112	*60*
Silica Sand in Hardened Steel	301	11	0	39	0
Silica Sand in Tungsten Carbide	11	5	-1	39	-2

Table 3: Normal background for soils and freshwater sediments, and toxicological effects levels and thresholds for freshwater sediments (see text for definitions), as compiled by the National Oceanic and Atmospheric Administration's Coastal Protection and Restoration Division, for screening sediment quality (Buchman, 1999).

|	Cr ppm	Ni ppm	Cu ppm	Zn ppm	Pb ppm
"Natural" Range in Soils	1–2000	0–700	0–700	0–2900	0–700
Geometric Mean for Soils	37	13	17	48	16
Normal Background Range in Freshwater Sediments	7–13	9.9	10–25	7–38	4–17
Threshold Effects Level (TEL)	37.3	18.0	35.7	123.1	35.0
Probable Effects Level (PEL)	90	35.9	197	315	91.3
Upper Effects Threshold (UET)	95	43	86	520	127

Table 4: Repeated analyses (28) of the Monson Slate check sample indicate instrumental precision of between ±2 and ±5 ppm at the greater than 99% confidence level (3σ).

Monson Slate	Cr ppm	Ni ppm	Cu ppm	Zn ppm	Pb ppm
Average of 28	114	76	29	106	31
Maximum	117	80	31	107	33
Minimum	111	73	28	105	25
Range	6	7	3	2	8
Standard Deviation (σ)	1.66	1.54	0.68	0.63	1.62

Table 5: Analysis of standard reference materials as unknowns indicates accuracy of analytical method. Accepted values for U. S. Geological Survey Rock Reference Materials taken from Certificates of Analysis provided with the materials (http://minerals.cr.usgs.gov/geo_chem_stand/).

		Cr ppm	Ni ppm	Cu ppm	Zn ppm	Pb ppm
AGV-2	*Accepted Values*	17	19	53	86	13
AGV-2	Measured	20	15	56	91	13
GSP-2	*Accepted Values*	20	17	43	120	42
GSP-2	Measured	19	18	47	117	40
SDC-1	*Accepted Values*	64	38	30	103	25
SDC-1	Measured	64	41	25	104	28
W-2	*Accepted Values*	92	70	110	80	9.3
W-2	Measured	95	67	108	76	6

It would be expected that the contamination in processing of the actual sediment samples should be less than that for the silica sand. The degree of contamination probably depends on the mineralogy of the sample—specifically the hardness of those minerals—as well as the grain size of the incoming sample and the grinding time. Quartz is likely to be the most abundant mineral in these samples, and is likely to be the hardest mineral (hardness 7 on the Mohs scale). The degree of contamination might be related to the quartz content, which will vary from site to site. Quartz content was not determined as part of this study. The laboratory-grade silica sand samples are, of course, 100% quartz, and thus may be the most abrasive
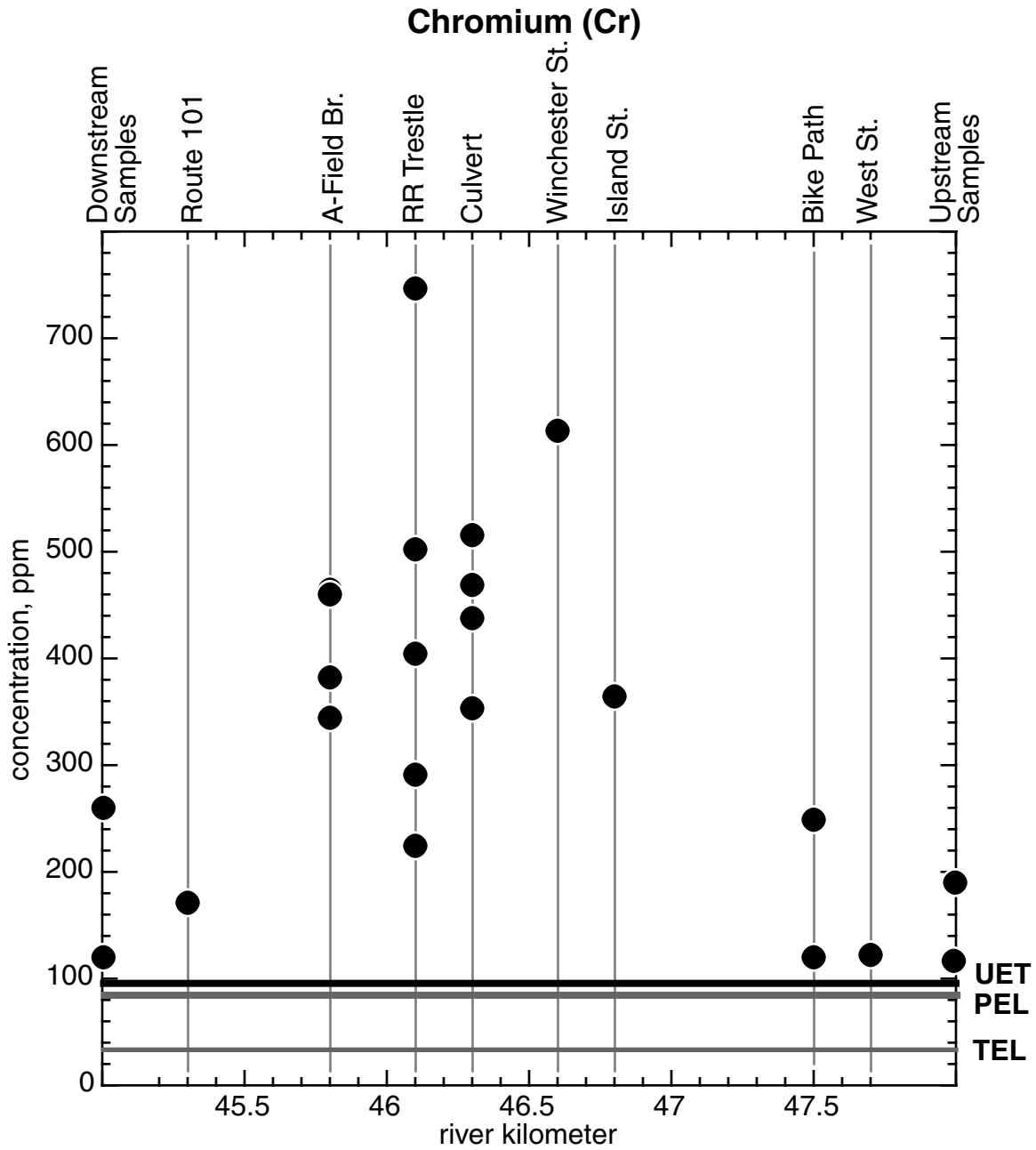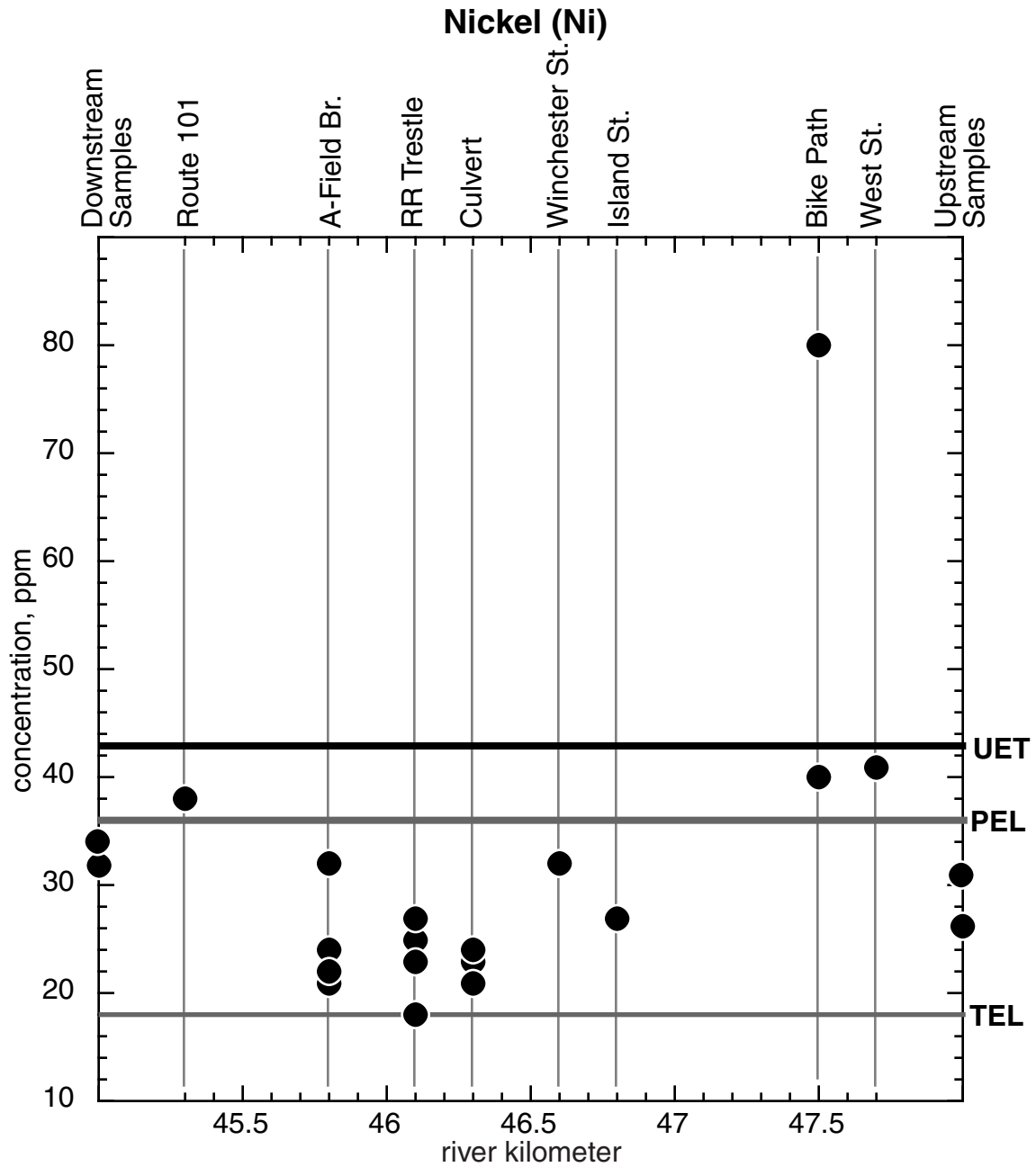
Chromium (Cr)

Figure 4: Results for Chromium, concentration versus river kilometer for samples in Keene (Fig. 2). Samples from downstream and upstream of Keene (Fig. 1) are also plotted, but not by river kilometer. Freshwater sediment UET, PEL and TEL values from Buchman (1999).

producing the most contamination. In the future, samples for which Cr

determinations are desired should be pulverized in a tungsten carbide or other mill

rather than in hardened steel, to avoid this problem.

None-the-less, many of the samples from the several locations in Keene have

Cr concentrations well above—up to 2.5 times—the maximum level that might be

attributable to contamination during processing based on the tests with silica sand.

Thus it is likely that some Ashuelot River sediments in Keene contain Cr at levels

exceeding the TEL, PEL and/or UET. Clearly a number of samples—particularly

those upstream and downstream of Keene—have Cr concentrations below that

found in the silica sand (Table 2, Fig. 4). It is possible that nearly *all* of the Cr found

in these samples was introduced during processing and thus it is likely that these

samples probably fall below the TEL, PEL and/or UET.

All of the samples we collected, including those upstream and downstream of

Keene, had Ni concentrations at or exceeding the TEL (Table 2, Fig. 5); several

exceed the PEL, and one—Bike Path Muck—exceeds the UET. Perhaps Ni is present

in elevated levels among the rocks or glacial tills of the watershed, or perhaps Ni

contamination was introduced upstream of our highest sample site and has since

been efficiently transported and evenly distributed downstream.

Obenauf and others (2002) do not mention Ni as a component of hardened

steel. None-the-less, comparison of the silica sand samples ground in the two

different mills (Table 2) suggests that it might be possible that a small amount of Ni

may have been introduced into the samples by pulverization in the hardened steel

15

Nickel (Ni)

Figure 5: Results for Nickel, , concentration versus river kilometer for samples in Keene (Fig. 2). Samples from downstream and upstream of Keene (Fig. 1) are also plotted, but not by river kilometer. Freshwater sediment UET, PEL and TEL values from Buchman (1999).

mill. However, the magnitude of this contamination—if any—is very small. The difference between the values for the two silica sands may not be significant, because the concentrations are low enough that they may be approaching the quantitation limits of the analytical technique.

Copper concentrations generally are at normal background levels (Table 2, Fig. 6), with the exception of the Culvert 4 sample which exceeds the UET (and the *higher* PEL), and samples downstream of Keene which exceed the TEL. Further work is needed to determine how unique the localized Cu "hot spot" at the Culvert 4 site is, and to understand the increasing Cu concentration in the sediments of the downstream reaches.

Zinc concentrations, while generally above normal background levels (Table 2, Fig. 7), are within the range typically found in rocks, such as the US Geological Survey Rock Reference Materials used in calibration (Fig. 3). While several samples have Zn values slightly exceeding the TEL, none even approach the PEL or UET—there were no extreme values. Zinc contamination, although it may be widespread—for example from tire wear (Callender & Rice, 2000)—has not reached concentrations that are of much concern.

Lead contamination of sediments in the Ashuelot River is of real concern (Table 2, Fig. 8). Most of the sample sites in Keene and downstream had Pb values exceeding the TEL, and several sites had samples with values exceeding the UET, to significantly high values well outside our calibration range.
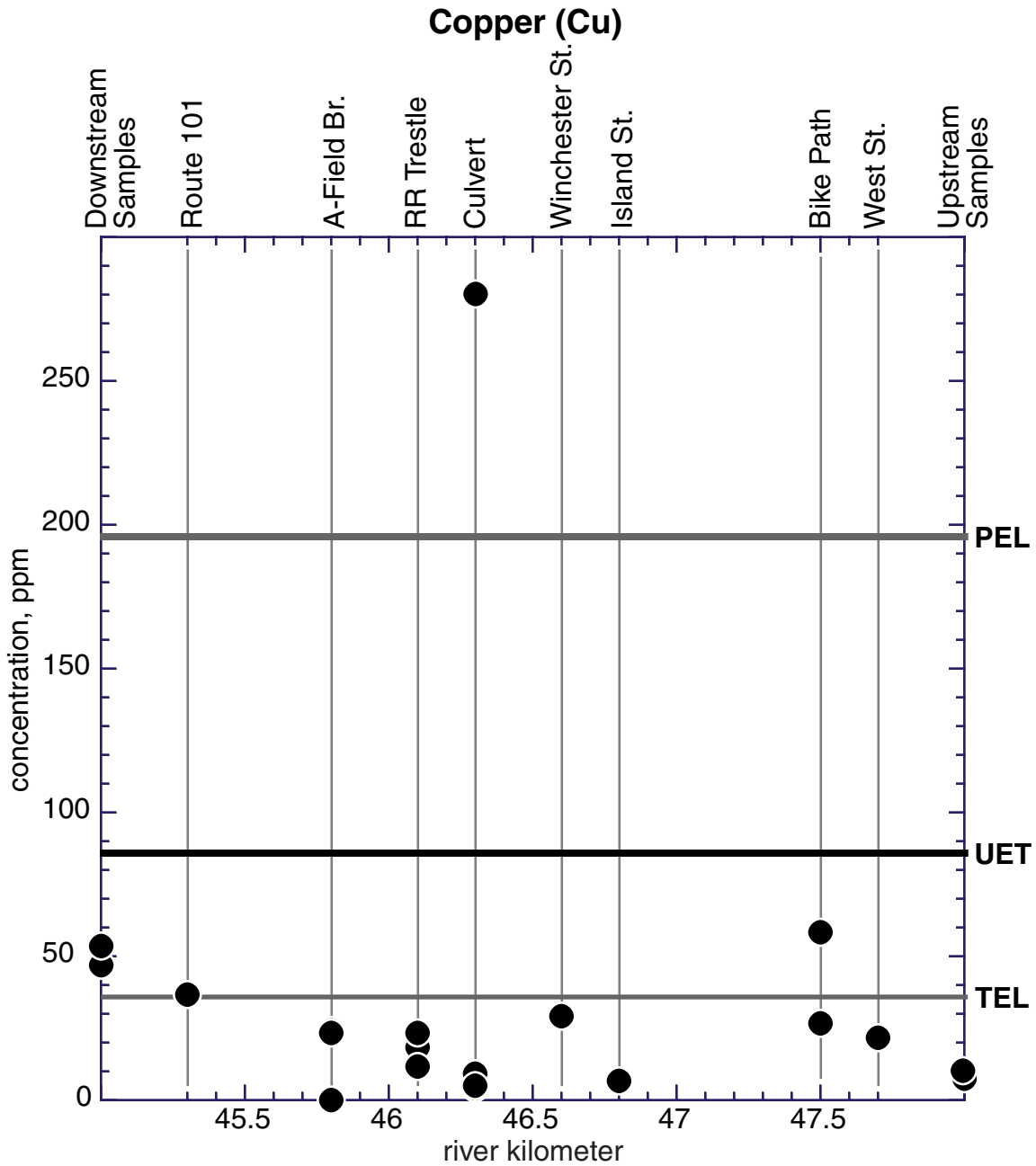
Figure 6: Results for Copper, , concentration versus river kilometer for samples in Keene (Fig. 2). Samples from downstream and upstream of Keene (Fig. 1) are also plotted, but not by river kilometer. Freshwater sediment UET, PEL and TEL values from Buchman (1999).
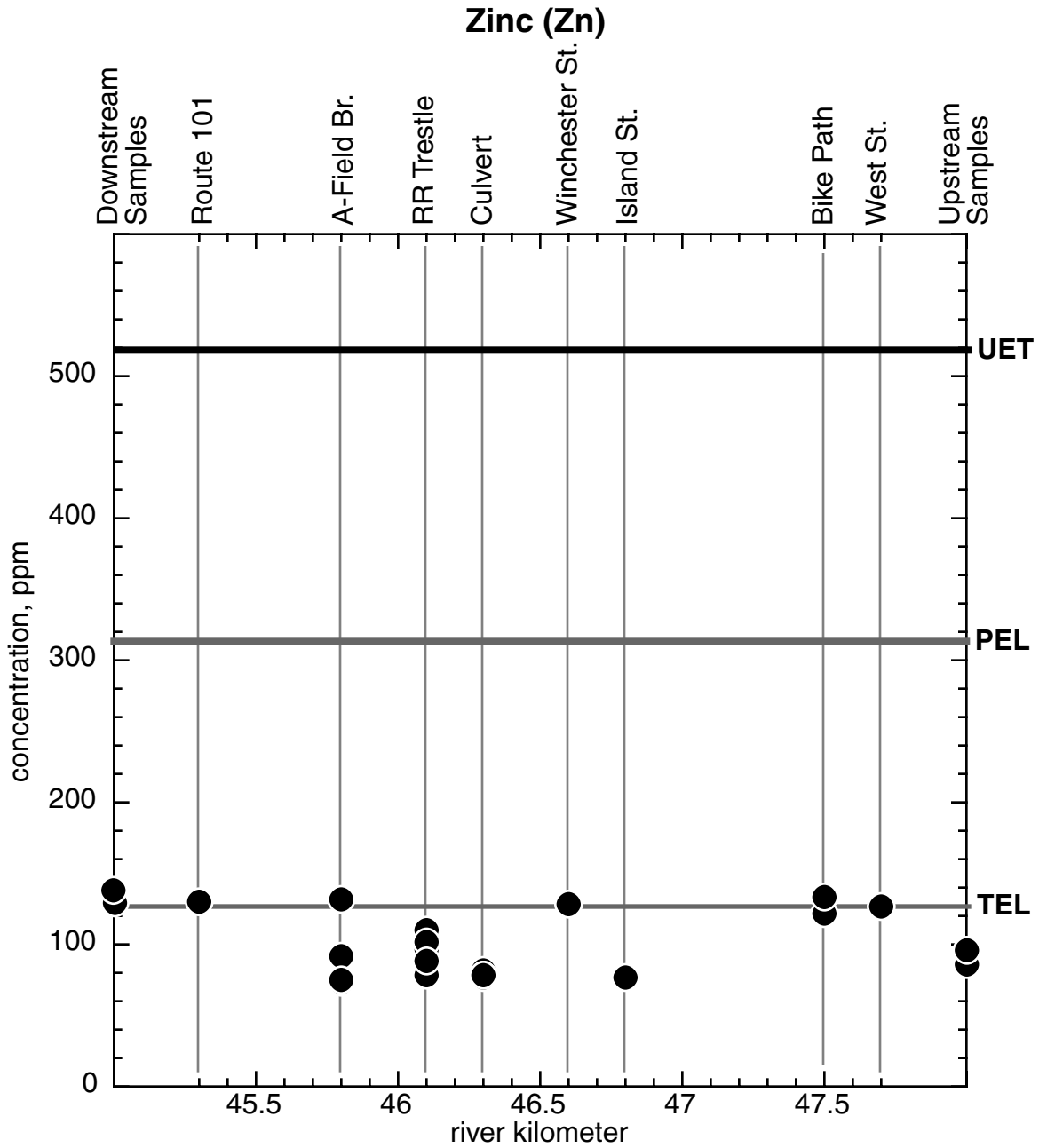
Figure 7: Results for Zinc, concentration versus river kilometer for samples in Keene (Fig. 2). Samples from downstream and upstream of Keene (Fig. 1) are also plotted, but not by river kilometer. Freshwater sediment UET, PEL and TEL values from Buchman (1999).

Lead (Pb)
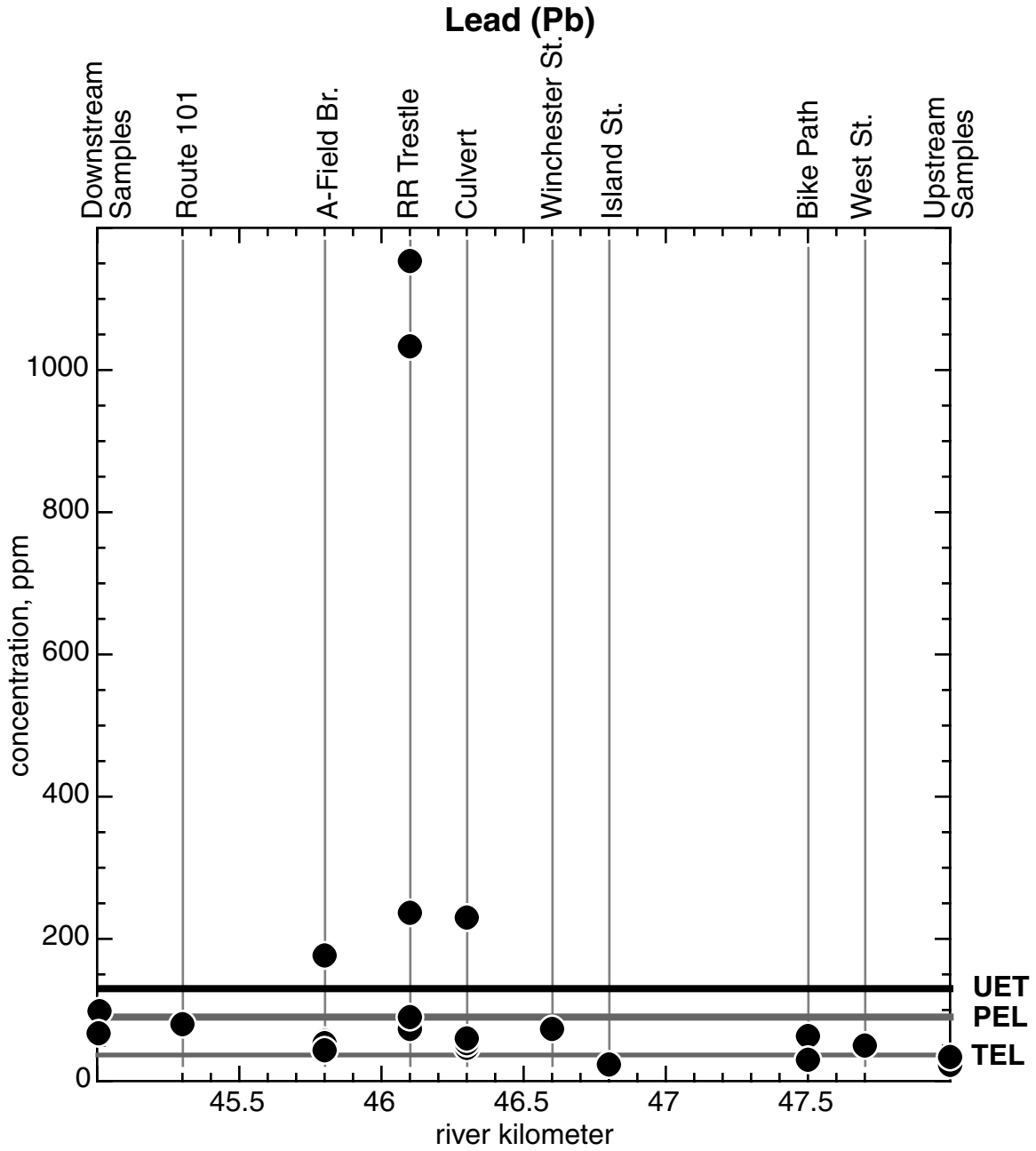
Figure 8: Results for Lead, , concentration versus river kilometer for samples in Keene (Fig. 2). Samples from downstream and upstream of Keene (Fig. 1) are also plotted, but not by river kilometer. Freshwater sediment UET, PEL and TEL values from Buchman (1999).

The site with the highest Pb values (two samples >1000 ppm) was at the Railroad Trestle on the Keene State College campus. There are many possible sources of Pb at this location, perhaps including leaded paint that might have been used on the bridge in the past (e.g., Zarcinas & Rogers, 2002).

Conclusions

Don't eat the mud from the bottom of the Ashuelot River in Keene! Lead, Copper, and Nickel are all found at relatively high total concentrations—exceeding the UET, in some cases significantly, at one or more sediment sampling sites in Keene. Several of these sites may also be significantly contaminated with Chromium. These sediments are presumably toxic to some organisms in the benthic community, which will in turn have an adverse impact on other aspects of the ecosystem.

Sediment quality is worse in Keene, compared to upstream or downstream locations, as expected due to the concentration of industrial and other anthropogenic sources of contamination in the city. Sediment quality is poorer at the downstream sample sites than at the upstream sample sites. This is consistent with downstream transport of contaminated sediment and/or the presence of more potential sources of contamination downstream than upstream.

Additional careful work may be warranted to further characterize the nature and extent of heavy metal contamination of sediments in the Ashuelot River, both to aid in risk assessment and to perhaps help identify likely sources of these metals, both historical and current. There may also be other heavy metal contaminants of

interest that were not assessed in this study, including Arsenic (As), Cadmium (Cd), and Mercury (Hg).

Acknowledgements

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