Assessing the contribution of combustion-derived contaminants to a remote subarctic environment from traffic on the Tibbitt to Contwoyto winter road (Northwest Territories, Canada)

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Abstract

Remote mining operations in Canada's Northwest Territories and Nunavut are supported by a 600 km winter road, which spans the transition from subarctic boreal forest in Yellowknife to low Arctic tundra. Each year, thousands of truckloads of fuel, large equipment, and other heavy loads are hauled up the winter road. We investigated whether diesel emissions from commercial truck traffic is a major source of metals and polycyclic aromatic compounds (PACs) to aquatic ecosystems along the winter road. In March 2014, at the end of the hauling season, we collected integrated snow samples, water, and sediment from nine lakes located along the winter road, as well as from six lakes located within the city of Yellowknife. We did not observe any evidence of metal contamination in snow collected along the winter road, and metal concentrations in snow from winter road sites were consistently lower than Yellowknife sites. Concentrations of PACs, including those associated with diesel emissions, were variable in snow, water, and sediment across all sites. The highest concentrations of PACs in snow were reported in winter road lakes located in the subarctic boreal forest. Examination of PAC composition and diagnostic ratios in snow samples showed that wildfires are an important source of PACs to lakes along the winter road, while anthropogenic sources are more prevalent in snow from Yellowknife lakes. No compositional differences were observed for PACs in sediment and water samples between Yellowknife and winter road lakes. Our results show that a high contribution of PACs from natural sources can obscure potential contributions from diesel traffic emissions along the winter road.

Keywords: polycyclic aromatic compounds; boreal forest; tundra; diesel emissions; wildfire; lakes

Introduction

Since the initial discovery of kimberlite deposits in 1991, the remote tundra wilderness of the Northwest Territories and Nunavut (Canada) known colloquially as the barrenlands has undergone considerable development to support the growing diamond mining industry. This industry is an important driver of economic growth in the Northwest Territories, with the three operating diamond mines (Ekati Diamond Mine, Diavik Diamond Mine, and Snap Lake Mine) collectively generating an estimated $1.96 billion in revenue in 2013 (Natural Resources Canada, 2014). Polar regions with extreme cold climates may be particularly susceptible to environmental degradation from resource extraction (McDonald and Knox 2014), and consequently mining companies spend millions of dollars per year monitoring the lakes and landscapes around their respective mine sites. There has, however, been limited monitoring of aquatic systems along the main route of access to these operations, the Tibbitt to Contwoyto winter road. With additional mining projects under development, and exploration ongoing, understanding and mitigating the potential environmental stressors of mining and infrastructure development will be crucial for maintaining ecological integrity in this sensitive ecosystem.

Considerable infrastructure and logistical support is required to support year-round mining activities in remote polar regions. The Tibbitt to Contwoyto winter road, constructed of ice and snow, has typically operated in February and March each year since 1982 at an estimated cost of $10M USD annually (Prowse et al. 2009). The winter road begins at Tibbitt Lake, located at the end of the Ingraham Trail outside of the city of Yellowknife, and has run as far as the now abandoned Lupin Gold Mine near Contwoyto Lake in Nunavut. It is the major re-supply route for fuel, heavy loads, and large equipment, and is vital to mining operations. Due to extreme cold temperatures, transport trucks are kept idling when not in use, contributing a continuous output

of diesel exhaust, and raising concerns about the potential for accumulation of traffic-derived contaminants in this otherwise pristine environment. Vehicular traffic is often considered to be the dominant source of metals and polycyclic aromatic compounds (PACs) in urban areas (Arellano et al. 2014; Kuoppamaki et al. 2014), many of which are known mutagens and carcinogens (Hawkins et al. 1990; Lafleur et al. 1993; Lemieux et al. 2008). Snow is an efficient scavenger of both gas- and particulate-phase metals and PACs, and therefore contaminants emitted by winter road traffic and associated operations can accumulate in the snowpack. At spring freshet, these compounds would subsequently enter lakes and rivers in pulses and could pose a potential risk to aquatic biota. This includes culturally/economically important fish species like lake trout (*Salvelinus namaycush*), lake whitefish (*Coregonus clupeaformis*), northern pike (*Esox lucius*), walleye (*Stizostedion vitreum*) and burbot (*Lota lota*) that are harvested for subsistence or recreational purposes from the larger lakes traversed by the winter road. As well, the winter road runs through the migratory route of the barren-ground Bathurst caribou herd, whose population has been in decline since 2006 due to unknown causes (Boulanger et al. 2011). Caribou are a vital component of the traditional lifestyle of Dene, Metis, and Inuit communities residing in the Northwest Territories and Nunavut (Case et al. 1996).

In this study, we investigate whether vehicular diesel emissions along the Tibbitt to Contwoyto winter road are a significant contributor of metals and PACs to the environment. At the end of the hauling season (March 2014), integrated snow samples, water, and surface sediments were collected from nine lakes along the winter road, including one heavily-used lake where the primary maintenance camp for the road is located and trucks idle almost continuously, and another lake off the main artery of the winter road that has less traffic. Snow, water and sediment samples were also collected from lakes located alongside roads in the city of

Yellowknife, to determine how the quantity and composition of metals and PACs in snow and lakes along the winter road compare to a subarctic urban centre.

Methods

Study Site Description

Winter Road Sites

The Tibbitt to Contwoyto winter road is constructed each year, extending over 600 km from the Ingraham Trail outside of the city of Yellowknife to the Lupin Gold Mine on Contwoyto Lake in Nunavut (Figure 1). Over the last two decades, the road has serviced the Northwest Territories three operating diamond mines. More than 87% of the Tibbitt to Contwoyto winter road is constructed over frozen lakes and rivers. The road crosses a treeline ecotone, from the northern boreal forest region to the tundra (Figure 1). The climate can be characterized generally as polar continental, with long cold winters and short cool summers, and daily temperatures in the winter often below -30°C. We sampled nine lakes along the winter road, including three lakes (Ross, Dome, and Waite) within the Taiga Shield ecozone (boreal forest), approximately 60-70 km northeast of Yellowknife (Figure 1). The dominant vegetation in the region is trembling aspen (*Populus tremuloides*), balsam poplar (*Populus balsamifera*), Alaskan paper birch (*Betula papyrifera*) jack pine (*Pinus banksiana*), white spruce (*Picea glauca*), and black spruce (*Picea mariana*). The remaining six lakes (Pat's, Brown, Drybones, Lockhart, Lake 13, and "Portage Junction" (unofficial name)) are within the Coppermine River Upland Ecoregion, part of the forest-tundra transition zone (Figure 1). The dominant vegetation

types in this zone include stunted black spruce, dwarf birch (*Betula glandulosa*), willow (*Salix* spp.), ericaceous shrubs, sedges (*Carex* spp.), lichens, and *Sphagnum* moss. Forested areas along the road have an active forest fire history, and recent burn scars were evident at many of our sampling sites. The main winter road maintenance camp is located at Lockhart Lake, which houses approximately 50 people for the duration of winter. The heavy machinery used to maintain and construct the winter road operates out of the camp. Vehicles are left running overnight, and the camp is also used as a re-fueling station for helicopter traffic in the region. Lake 13 is located on a side road off the main winter road, towards the Snap Lake diamond mine. The side road also receives an appreciable volume of vehicle traffic.

Yellowknife sites

Yellowknife is the center of economic activity in the Northwest Territories of Canada, and with a population of approximately 19,000 people, accounts for almost half the total population of the Northwest Territories. We sampled six lakes within or just outside the city limits of Yellowknife, including Range Lake, Kam Lake, Frame Lake, Niven Lake, and Long Lake (located near the Yellowknife airport), as well as Pocket Lake, located just outside Yellowknife (Figure 1). Each of these lakes are located along well-traversed paved roads, and would be receiving metals and PACs from multiple urban sources including road, air, and snowmobile traffic, residential development, and industry. Similar to Ross, Dome, and Waite Lake along the winter road, Yellowknife is within the Taiga Shield ecozone of the boreal forest. In winter, the prevailing winds are northwest and southeast (Pinard et al. 2008), while our sampling sites along the Tibbit to Contwoyto winter road are located northeast of Yellowknife. Consequently, we do not expect long-range transport of airborne emissions from urban activities

125 in Yellowknife to be a major source of contaminants along the southern portions of the winter
126 road.
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128 Field Methods
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130 Field sites were road-accessible, and samples were collected over a three-week period
131 from late March to early April, 2014. Integrated snow samples were taken from just off the road,
132 and care was taken to avoid snowmobile tracks. Snow was collected using a cleaned stainless
133 steel shovel, packed into a double layer of polyethylene bags, placed in a sealed pail, and kept
134 frozen until analysis. Measurements of snow depth and density were recorded at 5-10 sites
135 around the primary snow sampling site using an Eastern Conference Snow Sampler, to determine
136 snow-water equivalents in order to estimate total contaminant load to the snow pack. Two sites
137 were sampled at Lockhart Lake (maintenance camp where trucks idle) and Lake 13 (a less
138 travelled portion of the winter road located on a side spur), from the north and south side of the
139 winter road.
140 Once snow sampling was complete, a hole was drilled through the ice, and surface water
141 and sediment samples were collected. Water and sediment samples could not be obtained from
142 Lake 13 or Portage Junction due to the thickness of the lake ice, or Niven Lake and Range Lake,
143 which were frozen to the bottom. Water and sediment were sampled at only one site in Lockhart
144 Lake (the south site). For the surface water samples, water was collected into 1L HDPE bottles,
145 which were rinsed three times with lake water prior to filling. Lake sediments were sampled
146 using an Eckman grab sampler, with only the top few centimeters of sediment retained.
147 Sediments were placed in individual Ziploc bags and frozen until analyzed.

148

149 Laboratory Methods

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151 Upon return from the field, snow samples were weighed, allowed to melt at room
152 temperature, and processed within an hour of melting in clean laboratory facilities provided by
153 the Taiga Environmental Laboratory, Yellowknife, NT. Reference blanks (n = 3) of 1 L of Milli-
154 Q water were put in polyethylene bags, sealed in pails, and kept at 4°C for 24 hours to simulate
155 time for snow to melt. Subsamples of snowmelt were submitted to the Taiga Environmental
156 Laboratory, an ISO/IEC 17025 accredited laboratory and a member of the Canadian Association
157 for Laboratory Accreditation (CALA) for analysis of total metals by inductively coupled plasma-
158 mass spectrometry.

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160 *Processing of water and snow samples for PAC analysis*

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162 Reference blanks, lake water, and snow melt samples (1 L volume for each) were filtered
163 through pre-ashed and pre-weighed 0.4 µm 47 mm GF Advantec filters, and the GF filters were
164 refrigerated for later analysis of particle-bound PACs at the University of Ottawa Laboratory for
165 the Analysis of Natural and Synthetic Toxicants (LANSET). Sample filtrate was spiked with a
166 known concentration of ^{13}C-labeled PACs from the Cambridge Isotope Laboratories
167 (Tewksbury, MA) and mixed thoroughly. Dissolved PACs were then extracted from the filtrate
168 on Empore^{TM} C-18 SPE disks, following US EPA Method 550.1, with the following
169 modifications: methanol was not added during the extraction process, and the SPE disks were

refrigerated after the sample was loaded, for transport back to the University of Ottawa for analysis at LANSET.

At LANSET, SPE disks were eluted without acetonitrile and filtered through anhydrous sodium sulfate columns to remove residual water. The GF filters were dried at room temperature and weighed, then spiked with ^{13}C-labeled PACs and extracted with US EPA Method 3540C, adapted for accelerated solvent extraction using Hydromatrix as method blanks (n = 4). For both the SPE disks and GF filters, 2 mL of 2,2',4-trimethylpentane (TMP) was added to the sample, and evaporated to 1 mL for analysis using gas chromatography-mass spectrometry as outlined in Korosi et al. (2013). Analytes were quantified using isotopic dilution of ^{13}C-labelled PACs, then recovery and blank corrected. The full suite of US EPA priority PACs and alkylated PACs analyzed are listed in Table 1. Mean recovery rates (low molecular weight – high molecular weight) ranged from 25.9 – 122.0 % for dissolved PACs and 21.7 – 116.8 % for particulate PACs.

Processing of sediment samples for PAC analysis

Analysis of total organic carbon (TOC) was conducted at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa) following the procedure described in Korosi et al. (2013), to estimate the weight of sediment required for PAC extractions. Sediment PACs were analyzed using the methods outlined in Korosi et al. (2013) with minor modifications and using Hydromatrix as method blanks (n = 3). Wet sediments were mixed with elemental copper prior to extraction to remove sulfur in lieu of using US EPA Method 3640A. Clean up with US EPA Method 3630C was adapted for use on 6ml (1g) Supelclean™ LC-Si solid-phase extraction cartridges. Analytes were recovery corrected and quantified using isotopic dilution of ^{13}C-

193 labelled PACs and method blank corrected. Mean sediment PAC recovery rates ranged from
194 10.7 – 178.3 %. Triplicates of sediment from Brown Lake and Frame Lake produced relative
195 standard deviation of 13.3 %.
196
197 *Data Analysis*
198 Three separate principal components analyses (PCA) were conducted on the relative
199 abundance (% of the total PACs present in the sample) of PACs in snow (dissolved +
200 particulate), water (dissolved + particulate), and sediment, to visualize spatial trends in PAC
201 variability among sites. Relative abundances were square-root transformed prior to running the
202 PCAs, to normalize the data, and PACs not present in at least two samples with relative
203 abundances greater than 5% were removed (Leps and Šmilauer 2003). PCAs were conducted
204 using the vegan package (Oksanen et al. 2010) for the R software environment (R Development
205 Core Team 2010). In order to ascertain the sources of PACs in environmental samples,
206 diagnostic ratios of common PACs across our dataset were calculated following methods
207 outlined in Yunker et al. (2002) and Tobiszewski & Namieśnik (2012).
208
209 **Results and Discussion**
210
211 *Are vehicle emissions on the Tibbitt to Contwoyto winter road a significant source of*
212 *combustion-derived contaminants in snow?*
213
214 Yellowknife snow samples contained a higher mass of particulate matter relative to lakes
215 along the winter road (mean = 0.26 g versus 0.02 g; Table 2). We investigated trends in several

metals, including six that are indicative of diesel exhaust emission (Hjortenkrans et al. 2006; Carrero et al. 2013): antimony (Sb), barium (Ba), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn). Sb was below detection limit in all winter road sites. Concentrations of Cu and Cr, metals that are strongly associated with heavy duty traffic sources like transport trucks (Gunawardena et al. 2012), were low in snow samples from both Yellowknife sites and sites collected along the winter road (Figure 2). Barium, which is often considered an elemental tracer for diesel emissions from heavy duty trucks (Chellam et al. 2011), was elevated in Yellowknife sites relative to the low concentrations reported along the winter road (typically 0.1-0.4 µg/L), including near the maintenance camp at Lockhart Lake. The metal present in highest concentrations in both Yellowknife and winter road sites was Zn, which averaged ~8.0 µg/L in Yellowknife, and ~2.5 µg/L along the winter road (Figure 2). Nickel (Ni) was below detection limit (0.1 µg/L) in Yellowknife lakes, but present at concentrations ranging from 0.1-1.6 µg/L along the winter road (Figure 2). In contrast, arsenic (As) was below detection limit in winter road lakes, and present at 0.2-0.8 µg/L in Yellowknife lakes, with the exception of Pocket Lake, which had a concentration over an order magnitude higher (7.0 µg/L) compared to the other Yellowknife sites (Figure 2). Pocket Lake is located on the lease territory for Giant Mine, an abandoned gold mine that was a large point source of arsenic during its operation (Hutchinson et al. 1982). Recent construction of a bypass road beside Pocket Lake may have remobilized arsenic stored in soils as dust, accounting for the high As burden in Pocket Lake snow over a decade following the closure of Giant Mine. Beryllium, cadmium, cobalt, molybdenum, selenium, and vanadium were below detection limit (0.1 µg/L) in both Yellowknife and winter road sites.

238 Surprisingly, despite a greater number of potential anthropogenic sources (e.g. residential
239 heating, asphalt, higher traffic density), snow collected from lakes in Yellowknife did not have
240 higher concentrations of unsubstituted or alkyl PACs compared to snow collected from remote
241 lakes along the winter road, and PACs exhibited substantial variability among sites for all
242 environmental samples (snow, water, sediment) (Figure 3). Lockhart Lake, predicted to be the
243 most impacted of the winter road sites, had among the lowest concentrations of PACs in the
244 particulate fraction of snow, but a high concentration of C4 phenanthrene/anthracene in the
245 dissolved snow fraction at the north sampling location. The highest concentrations of PACs in
246 snow across all sites (Yellowknife and winter road sites) were recorded in the three lakes (Dome,
247 Ross, Waite) along the southern portion of the winter road that passes through boreal forest, 60-
248 70 km northeast of Yellowknife (Figure 3). The highest concentrations of PACs in water samples
249 were also recorded in Ross and Waite lakes (Figure 3). Prevailing winds reported in winter at the
250 Yellowknife airport are northwest and southeast (Pinard et al. 2008); therefore, we do not expect
251 that long-range transport of atmospheric emissions from Yellowknife is a contributing factor to
252 higher concentrations of PACs in snow at these lakes. The sediment of Drybones Lake, located
253 along the northern portion of the winter road, had notably elevated concentrations of both alkyl
254 and unsubstituted PACs when reported as ng/g organic carbon (Figure 3). This is likely due to
255 the exceptionally low TOC (0.2%) content of Drybones sediment, which was predominantly
256 sandy. When reported as ng/g dry weight, the PAC concentration in Drybones is low (data not
257 shown).
258 PACs originate from diverse sources (both natural and anthropogenic), contributing to the
259 variability observed in PAC concentrations across all sites, and obscuring potential contributions
260 from diesel traffic emissions along the winter road. In an attempt to tease apart the contribution

261 from diesel emissions, we grouped together select PAC compounds that are often associated with
262 emissions from diesel trucks, including naphthalene, phenanthrene, pyrene, fluoranthene, and
263 alkyl naphthalenes and phenanthrenes (Correa and Arbilla 2006; Dobbins et al. 2006; Casal et al.
264 2014). Alkyl PACs are not typically associated with fossil fuel emissions, but in diesel trucks,
265 alkyl phenanthrenes and naphthalenes have been shown to survive the engine combustion
266 process to be released as gaseous or particulate emissions from the tail pipe (Dobbins et al. 2006;
267 Kuo et al. 2013). Concentrations of diesel-indicator PACs in the snowpack of Yellowknife lakes
268 were comparable to lakes along the winter road (Figure 3). The snowpack of Lockhart Lake had
269 lower concentrations of diesel-indicator PACs than Lake 13, an opposite pattern to what we
270 would expect if these compounds were predominantly tracking diesel emissions (Figure 3). The
271 composition of PACs emitted from diesel exhaust is variable depending on the type of traffic
272 (heavy duty versus light duty trucks), fuel source, and driving conditions (Riddle et al. 2007;
273 Borrás et al 2009), and this variability creates additional challenges for identifying potential
274 contributions of PACs from traffic along the winter road.
275 Winter road operations do not appear to be a significant source of metals to snow, but the
276 results for PACs are inconclusive. High concentration of C4 phenanthrene/anthracene in the
277 dissolved fraction of snow at Lockhart Lake North may originate from a fuel source related to
278 winter road use, perhaps a spill, although this is speculative. Yellowknife lakes receive a higher
279 loading of PACs from diverse anthropogenic sources, compared to the winter road where the
280 primary anthropogenic source of PACs is related to winter traffic limited to a few months of the
281 year. Despite this, winter road sites display PAC concentrations in snow, water, and sediment
282 that are comparable to or higher than Yellowknife lakes, indicating a high contribution of PACs
283 from natural sources. Wildfires are likely the predominant natural source of PACs along the

284 winter road, and burn scars from recent fires were evident at many winter road sites. This
285 includes Dome, Ross, and Waite lakes, which are located within the subarctic boreal forest
286 (compared to northern lakes, which are near the northern limit of trees), and had the highest
287 concentrations of PACs in snow and lake water. We examined spatial patterns in PAC
288 composition in snow, water, and sediment from urban Yellowknife lakes to remote lakes across
289 the boreal forest and forest-tundra transition zone to further resolve the influence of multiple
290 sources on PAC burdens in the environment.
291
292 *Composition of PACs in environmental samples from Yellowknife to the forest-tundra transition*
293 *zone*
294
295 A clear indication of the importance of wildfires on PAC loading to winter road lakes is
296 seen in the ratio of retene to retene+chrysene (RET/RET+CHR) in snow samples (Figure 4).
297 Retene is an alkyl phenanthrene that is an indicator of combustion of coniferous plants (Ramdahl
298 1983), and a ratio of RET/RET+CHR between 0.8-1.0 is highly indicative of wildfires
299 (Tobiszewski & Namieśnik 2012). Only one sample (Pocket Lake) from Yellowknife had a
300 RET/RET+CHR value within this range, compared to all snow samples collected along the
301 winter road. The remaining Yellowknife sites had values <0.6, indicating contribution from non-
302 wood burning sources (Figure 4). Fly ash produced during forest fires is easily transported by
303 wind, and our results suggest that fly ash produced during summer forest fires provides a source
304 of wildfire-derived PACs to snowpack throughout the winter. C4 phenanthrene concentrations
305 were elevated in Dome, Ross, and Waite Lake, where forest fires are generally more common
306 compared to the northern lakes along the winter road (Figure 1). River sediments from recently

burned regions of northern Alberta were found to have high concentrations of retene and C4 phenanthrenes (Gabos et al. 2001), suggesting that C4 phenanthrene in our boreal winter road sites may similarly be associated with recent forest fires. Snow samples from both Yellowknife and winter road sites have a signature of fluoranthene to fluoranthene plus pyrene (FL/(FL+PY) that indicates grass/wood/coal combustion sources (Figure 4). Based on the diagnostic ratio of benz[a]anthracene (BaA) (preferred IUPAC name: tetraphene; Table 1) to BaA plus chrysene (BaA/228), four out of six snow samples from Yellowknife sites are from mixed sources, while all of the winter road snow samples, and two Yellowknife snow samples, have a dominant petroleum source (Figure 4).

The presence of high molecular weight unsubstituted PACs in snow samples is often a strong signal of anthropogenic impacts. Snow samples taken from Yellowknife lakes contained a relatively high proportion of high molecular weight (>4 aromatic rings) unsubstituted PACs in the particulate phase, which were absent or in low proportions along the winter road (Figure 5). The 4-6 ring PACs are strongly associated with high-temperature combustion from anthropogenic sources, including gasoline-fueled vehicles (Zelinska et al. 2004; Riddle et al. 2007), and decreases in concentration with distance from heavily-travelled urban roads have been reported for benz[a]anthracene, fluoranthene, chrysene, and benzo[b]/benzo[k[fluoranthene (Nascimbene et al. 2014). These compounds were absent in the dissolved snow phase for all sites (Figure 5), reflecting the high affinity of these compounds for binding to particulates. Snow samples from Yellowknife lakes also contained a higher proportion of the high molecular weight alkyl PACs relative to the winter road (Figure 5). Low molecular weight alkyl PACs were dominant in snow collected from Yellowknife lakes and winter road lakes (Figure 5), despite different predominant sources.

330 Based on a principal components analysis (PCA) of PACs in snow samples, variation in
331 snow PAC composition among sites was driven by C4 phenanthrene/anthracene on axis 1 (66%
332 of variation explained), and C4 dibenzothiophene, C2 fluoranthene/pyrene, and C3 fluorene
333 along axis 2 (16%) (Figure 6). No clear separation of Yellowknife lakes from winter road lakes
334 was evident on the PCA biplot, despite geographical differences and differences in the
335 predominant sources of PACs. However, Dome, Waite, and Ross lakes, in the boreal forest
336 region of the winter road, clustered together along axis 1, and were characterized by a high
337 proportion of C4 phenanthrene/anthracene (Figure 6). As discussed above, this may be a marker
338 for PACs derived from forest fires. Lockhart Lake north also plots along this PCA axis, due to a
339 high concentration of C4 phenanthrene/anthracene in the dissolved phase (versus the particulate
340 phase of Dome, Ross, and Waite). Range, Niven, and Kam Lake, three urban lakes in
341 Yellowknife, cluster together based on relatively high levels of C2 fluoranthene/pyrene, and C3
342 fluorene (Figure 6).
343 The composition of PACs in water collected from under the winter ice was similar across
344 all sites, being heavily dominated by low molecular weight alkyl PACs, followed by
345 dibenzothiophenes, and low molecular weight unsubstituted PACs (Figure 5), consistent with
346 Rabodonirina et al. (2015). High molecular weight compounds were uncommon (Figure 5).
347 There was no evidence of clustering based on region or dominant PAC sources in the principal
348 components analysis, including Dome, Ross, and Waite Lake (Figure 6). Variation in water PAC
349 composition (PCA axis 1 = 48%; PCA axis 2 = 26%) was driven by naphthalene, C1 and C2
350 naphthalene, C3 fluorene, C3 phenanthrene/anthracene, and C4 dibenzothiophene (Figure 6).
351 Our water samples were collected from under the ice at the end of the winter season, and had
352 been sealed off from new inputs of PACs for several months. Consequently, the PAC

353 composition of water samples likely reflects the partitioning of PACs in the environment based
354 on their physicochemical properties, and is not providing diagnostic information on the
355 predominant sources of PACs to the lake. Our study lakes along the winter road are relatively
356 large, and any contaminant input from the snowmelt would be diluted. Collection of surface
357 water after spring freshet may potentially reveal trends more reflective of what was observed in
358 snow.

359 Similar to water samples, PAC composition in sediment samples do not clearly reflect
360 differences in predominant sources of PACs to the aquatic environment between urban
361 Yellowknife lakes and remote lakes along the winter road. No clear separation of PAC sources
362 between Yellowknife and winter road sites was evident from diagnostic ratios analyzed for
363 sediment samples, and each region showed a contribution from mixed combustion and petroleum
364 sources based on different ratios (Figure 7). However, sediment samples were only available for
365 4 out of 6 Yellowknife lakes, as Niven and Range Lake were frozen to the bottom at the time of
366 sampling. The composition of PACs in sediments was similar between Yellowknife and winter
367 road sites (Figure 7). Alkyl PACs, especially low molecular weight compounds, were most
368 abundant, but unsubstituted PACs were recorded in higher relative proportions in sediment than
369 was observed for snow or water samples (Figure 5). Dibenzothiophenes were detected in most
370 Yellowknife and winter road lake sediments, in relatively small proportions (Figure 5). Variation
371 in sediment PAC composition among sites (PCA axis 1 = 44%; PCA axis 2 = 24%) was
372 predominantly driven by C1 and C2 naphthalene, C3 fluorene, and C4 fluoranthene/pyrene, with
373 smaller contributions from benzo[b]fluoranthene, fluoranthene, C3 dibenzothiophene, and C3
374 phenanthrene/anthracene (Figure 6).

375 Lake sediment samples are incorporating material deposited over multiple years. The
376 time period included in sediment samples is likely highly variable among our study lakes, due to
377 unquantified differences in lake sedimentation rates. In contrast, snow samples, which showed
378 clear compositional differences between Yellowknife and winter road lakes, are incorporating
379 material deposited during the winter months between November and March. The PAC
380 composition in lake sediments is also the net result of complex processes involved in the
381 transport and deposition of PACs from their source to the sediments, which is influenced by
382 factors such as catchment size and surface run-off, among others. Despite the many potential
383 confounding factors, PACs in river sediments from the Fraser River Basin (British Columbia,
384 Canada) clearly reflected their predominant sources, with PAC composition in sediments shifting
385 from a predominant wood burning source in remote environments, to vehicle emissions in urban
386 environments (Yunker et al. 2002). Yellowknife is a small urban centre, with a population of less
387 than 20,000, and no major industrial developments, which may explain why sediments do not
388 record a clear signal of anthropogenic development similar to that observed in Yunker et al.
389 (2002). A lack of detection of differences in PAC composition and concentration in sediments
390 may also be partially attributed to the low sediment sample size (4) from Yellowknife lakes.
391 Analysis of a larger sample size of urban lakes from Yellowknife may reveal PAC compositional
392 differences in sediments between Yellowknife and remote winter road sites not detected in this
393 study. Similarly, the reconstruction of historical trends in PAC composition from lake sediment
394 cores (e.g. Eide et al. 2011; Guan et al. 2012; Korosi et al. 2013) would provide further insights
395 on the role anthropogenic activities play in altering PAC transport and accumulation in aquatic
396 environments in Yellowknife and along the winter road.
397

Conclusions

We did not detect any evidence of metal contamination in snow samples collected from lakes along the Tibbitt to Contwoyto winter road that would indicate a contribution from commercial diesel traffic supporting diamond mining operations in the Northwest Territories. Metal concentrations in snow from the winter road were consistently lower than snow collected from lakes in the urban centre of Yellowknife. Wildfires are likely a more important source of polycyclic aromatic compounds (PACs) to lakes along the winter road than traffic. Snow samples from Yellowknife lakes contained high molecular weight unsubstituted PACs that were not present in lakes along the winter road. This reflects the greater density and diversity of anthropogenic sources of PACs in Yellowknife relative to more remote lakes along the winter road, where the primary anthropogenic input is winter traffic emissions. While snow samples showed clear differences in PAC composition between Yellowknife lakes and winter road lakes indicative of predominant sources, water and sediment samples were similar between the two regions. Our results highlight the importance of natural, background sources of PACs (especially wildfires) as a confounding factor in investigations of anthropogenic PAC inputs in regions with minor or moderate anthropogenic activities. Our work also highlights the value of measuring contaminant loads to the seasonal snow pack for remote regions where the magnitude of loading may be minor, and the detection of contaminants may be missed if sampling is focused on sediment or other environmental media influenced by confounding factors.

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427 and Environment Department about the impact of 30+ years of vehicle traffic on the water
428 quality of lakes along the winter road.
429

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Figure Captions

Figure 1 – Map showing the location of the Tibbitt to Contwoyto winter road, Northwest Territories, with the study lakes sampled along the road indicated. Also shown is the location of the Yellowknife study lakes (square box, magnified in the inset), the ecoregions traversed by the winter road, and the locations of recent (1990-2013) and old (pre-1990) forest fire events.

Figure 2 - Mean concentration of antimony (Sb), barium (Ba), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), and arsenic (As) measured in snow (dissolved + particulate) samples from Yellowknife (n=6) and along the winter road (n=11). Error bars represent standard deviation. Method detection limit (MDL) = 0.1 µg/L for Sb, Ba, Cr, Pb, and Ni; MDL = 0.2 µg/L for Cu and As; MDL = 5 µg/L for Zn.

Figure 3 – Total concentration of unsubstituted PACs, alkyl PACs, and diesel emission indicator PACs (naphthalene, phenanthrene, pyrene, fluoranthene, alkyl phenanthrenes) in snow (dissolved + particulate), water (dissolved + particulate), and sediment collected from lakes along the winter road (left panel) and in Yellowknife (right panel). N.D. = no available data.

Figure 4 – Diagnostic ratio plots and cross plots for PACs in snow samples. Top: benz[a]anthracene (BaA) to BaA plus chrysene (228) and fluoranthene (FL) to fluoranthene plus pyrene (PY); Bottom: retene (RET) to RET plus chrysene (CHR). Lakes along the winter road are represented by black circles; Yellowknife lakes are represented by white circles. Source apportionment based on these diagnostic ratios are from Yunker et al. (2002) and Tobiszewski &

617 Namieśnik (2012). Note: PAC nomenclature follows common names used by the US EPA.
618 Where differences exist, the preferred IUPAC names are listed in Table 1.
619
620 **Figure 5** – Composition of PACs in the dissolved and particulate phases of snow and water (in
621 ng/L), and in sediment (in ng/g organic carbon) collected from lakes along the winter road and in
622 Yellowknife. LMW = low molecular weight (3 or fewer aromatic rings), HMW = high molecular
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626 **Figure 6 -** Principal components analysis biplots showing the variation in PAC composition
627 measured in snow (dissolved + particulate), water (dissolved + particulate) and sediment samples
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630 Table 2 for corresponding lake names. DB = dibenzothiophene, P/A = phenanthrene/anthracene,
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635 (BaA) to BaA plus chrysene (228) and fluoranthene (FL) to fluoranthene plus pyrene (PY);
636 Middle: indeno[1,2,3-cd]pyrene (IP) to IP plus benzo[ghi]perylene (IP+Bghi) vs. 1,7-
637 dimethylphenanthrene (DMP) to 2,6-DMP plus 1,7-DMP (1,7/2,6+1,7-DMP); Bottom:
638 anthracene (ANT) to anthracene plus phenanthrene (178) vs. C0/C0+C1 for
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Yellowknife lakes are represented by white circles. Source apportionment based on these diagnostic ratios are from Yunker et al. (2002). Note: PAC nomenclature follows common names used by the US EPA. Where differences exist, the preferred IUPAC names are listed in Table 1.

Table 1 – List of the polycyclic aromatic compounds (PACs) analyzed in this study. Where differences between common nomenclature and preferred IUPAC nomenclature exist, common nomenclature is used and preferred IUPAC nomenclature is shown italicized in brackets, following recommendations in Ehrenhauser (2015).

Individual Compound	CAS#	Alkyl PAC Group
Naphthalene	91-20-3	C1-Naphthalene
Acenaphthylene	208-96-8	C2-Naphthalene
Acenaphthene	83-32-9	C3-Naphthalene
Fluorene	86-73-7	C4-Naphthalene
Phenanthrene	85-01-8	C1-Fluorene
Anthracene	120-12-7	C2-Fluorene
Fluoranthene	206-44-0	C3-Fluorene
Pyrene	129-00-0	C1-Phenanthrene/Anthracene
Benz[a]anthracene (*Tetraphene*)	56-55-3	C2-Phenanthrene/Anthracene
Chrysene	218-01-9	C3-Phenanthrene/Anthracene
Benzo[b]fluoranthene (*Benzo(e)acephenanthrylene*)	205-99-2	C4-Phenanthrene/Anthracene
Benzo[k]fluoranthene	207-08-9	C1-Dibenzothiophene
Benzo[a]pyrene (*benzo(pqr)tetraphene*)	50-32-8	C2-Dibenzothiophene
Indeno[1,2,3-cd]pyrene	193-39-5	C3-Dibenzothiophene
Dibenz[a,h]anthracene (*benzo(k)tetraphene*)	53-70-3	C4-Dibenzothiophene
Benzo[g,h,i]perylene	191-24-2	C1-Fluoranthene/Pyrene
Dibenzothiophene	132-65-0	C2-Fluoranthene/Pyrene
2-Methylnaphthalene	91-57-6	C3-Fluoranthene/Pyrene
1-Methylnaphthalene	90-12-0	C4-Fluoranthene/Pyrene
3-Methylphenanthrene	832-71-3	C1-Benz[a]anthracene/Chrysene
2-Methylphenanthrene	2531-84-2	C2-Benz[a]anthracene/Chrysene
1-Methylphenanthrene	832-69-9	C3-Benz[a]anthracene/Chrysene
3,6-Dimethylphenanthrene	1576-67-6	C4-Benz[a]anthracene/Chrysene
2,6-Dimethylphenanthrene	17980-16-4	C1-Benzofluoranthene/Benzopyrene
1,7-Dimethylphenanthrene	483-87-4	C2-Benzofluoranthene/Benzopyrene
1,8-Dimethylphenanthrene	7372-87-4	
Retene	483-65-8	

651 **Table 2 –** Physical characteristics of snow samples (density, kg/L; mass of particulate matter, g)
652 collected from lakes along the winter road and in Yellowknife. Lockhart Lake and Lake 13 were
653 sampled at two sites, on opposite sides of the winter road (north, N; south, S).
654

Lake	Location	Density	Particulates
1. Ross	Winter Road	0.16	0.006
2. Dome	Winter Road	0.24	0.34
3. Waite	Winter Road	0.35	0.003
4. Pat's	Winter Road	0.35	0.004
5. Brown	Winter Road	0.26	0.002
6. Drybones	Winter Road	0.27	0.002
7. Lockhart N	Winter Road	0.21	0.002
Lockhart S	Winter Road	0.27	0.003
8. Lake 13 N	Winter Road	0.51	0.002
Lake 13 S	Winter Road	0.78	0.002
9. Portage Junction	Winter Road	0.78	0.002
Mean		0.41	0.02
Max		0.78	0.34
Min		0.16	0.002
10. Pocket	Yellowknife	0.31	0.59
11. Long	Yellowknife	0.33	0.53
12. Frame	Yellowknife	0.34	0.36
13. Niven	Yellowknife	0.34	0.05
14. Kam	Yellowknife	0.33	0.02
15. Range	Yellowknife	0.34	0.01
Min		0.31	0.01
Max		0.34	0.26
Mean		0.33	0.59

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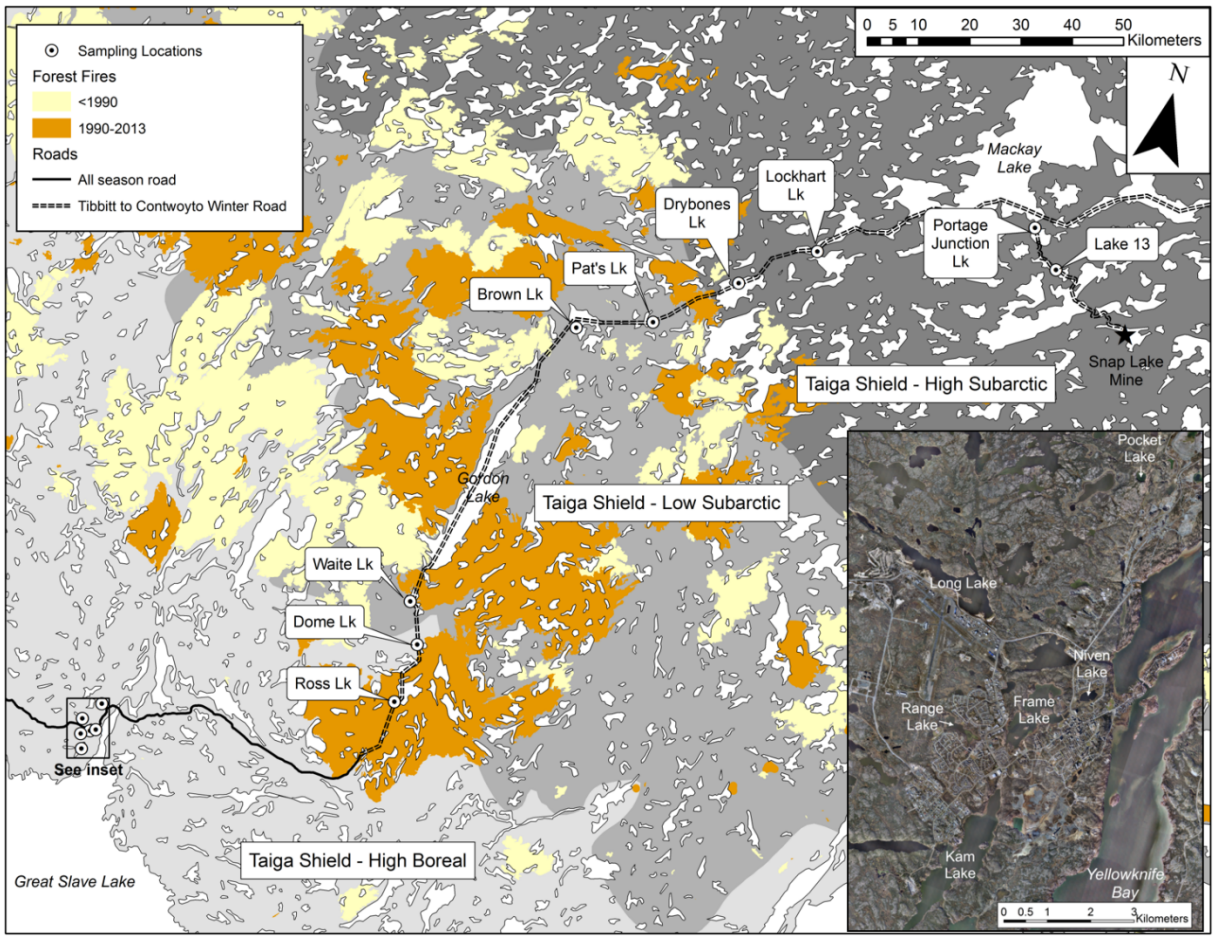

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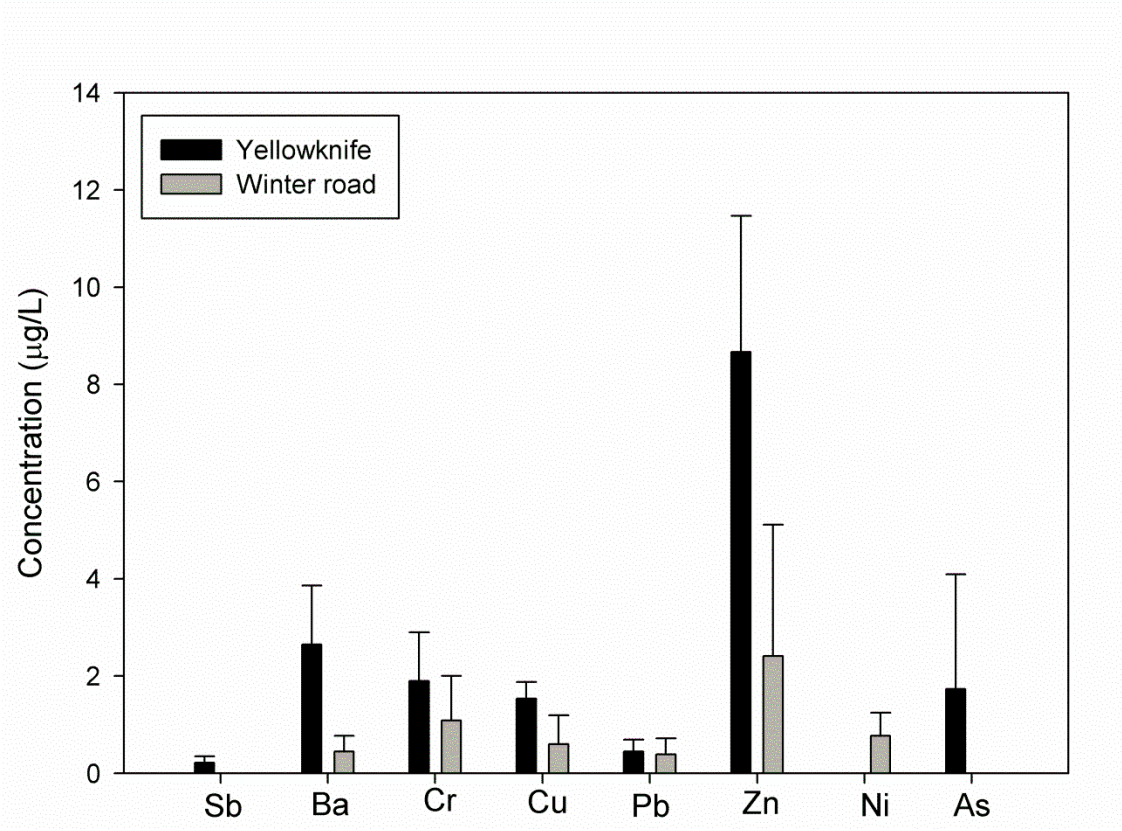

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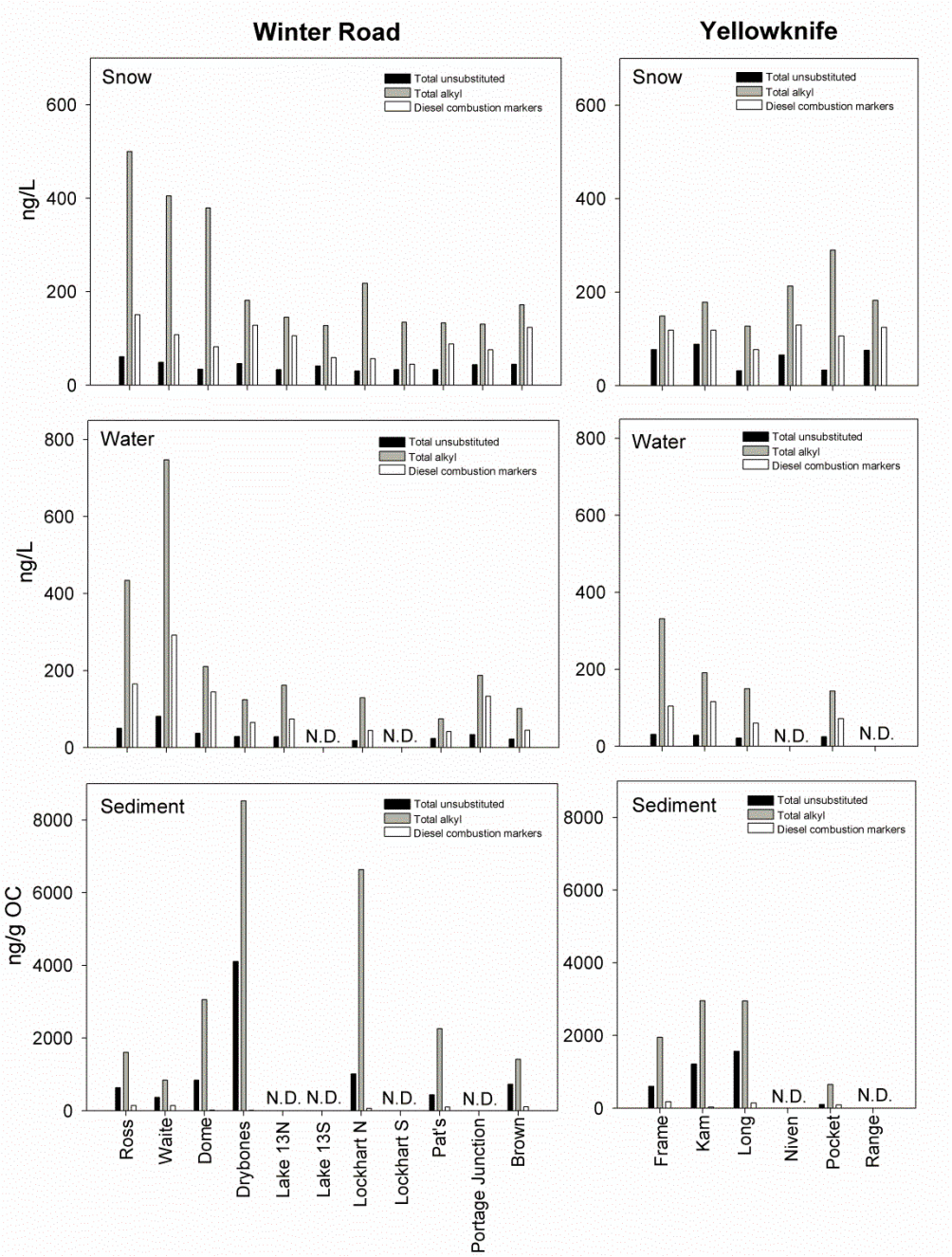

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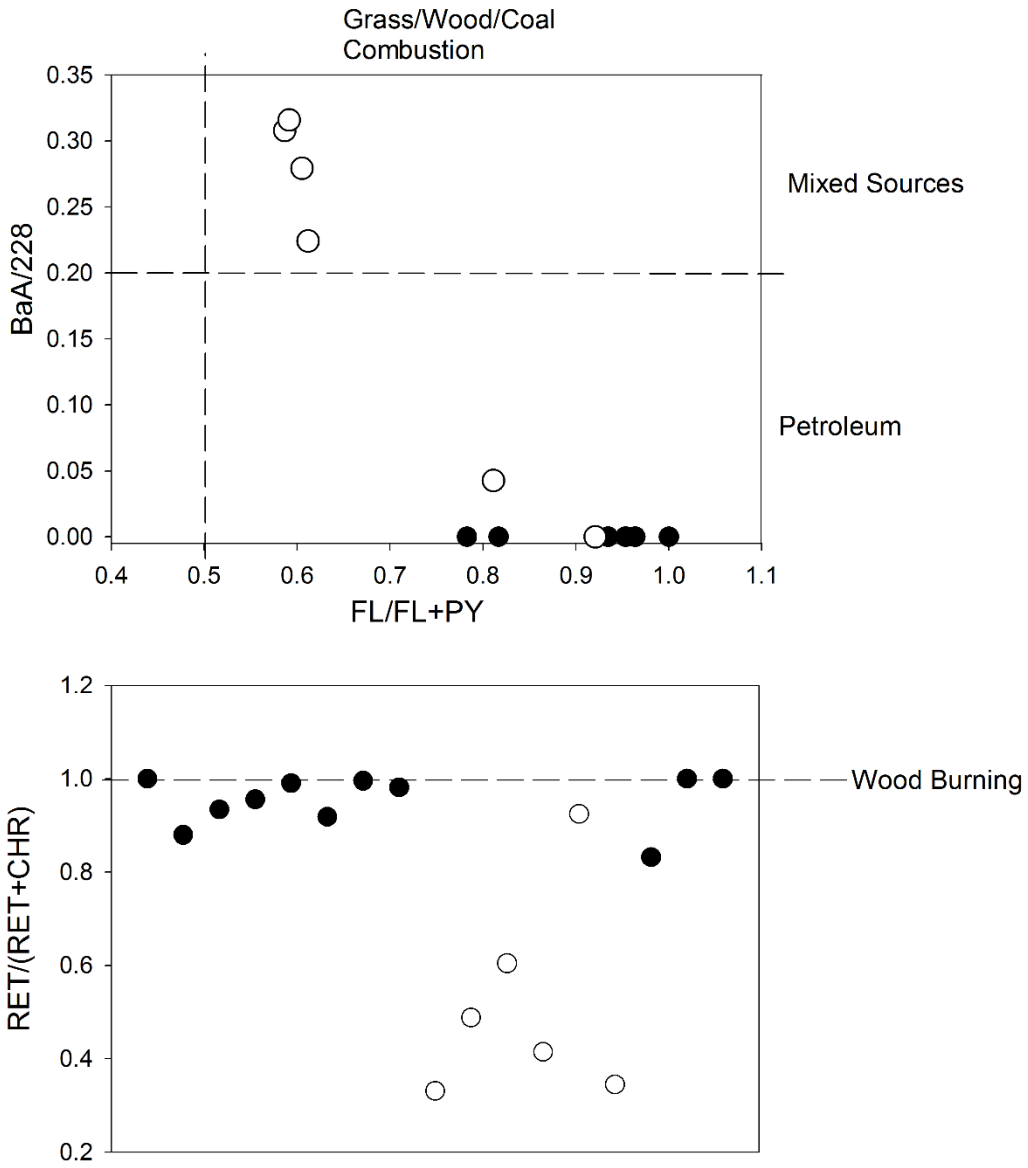

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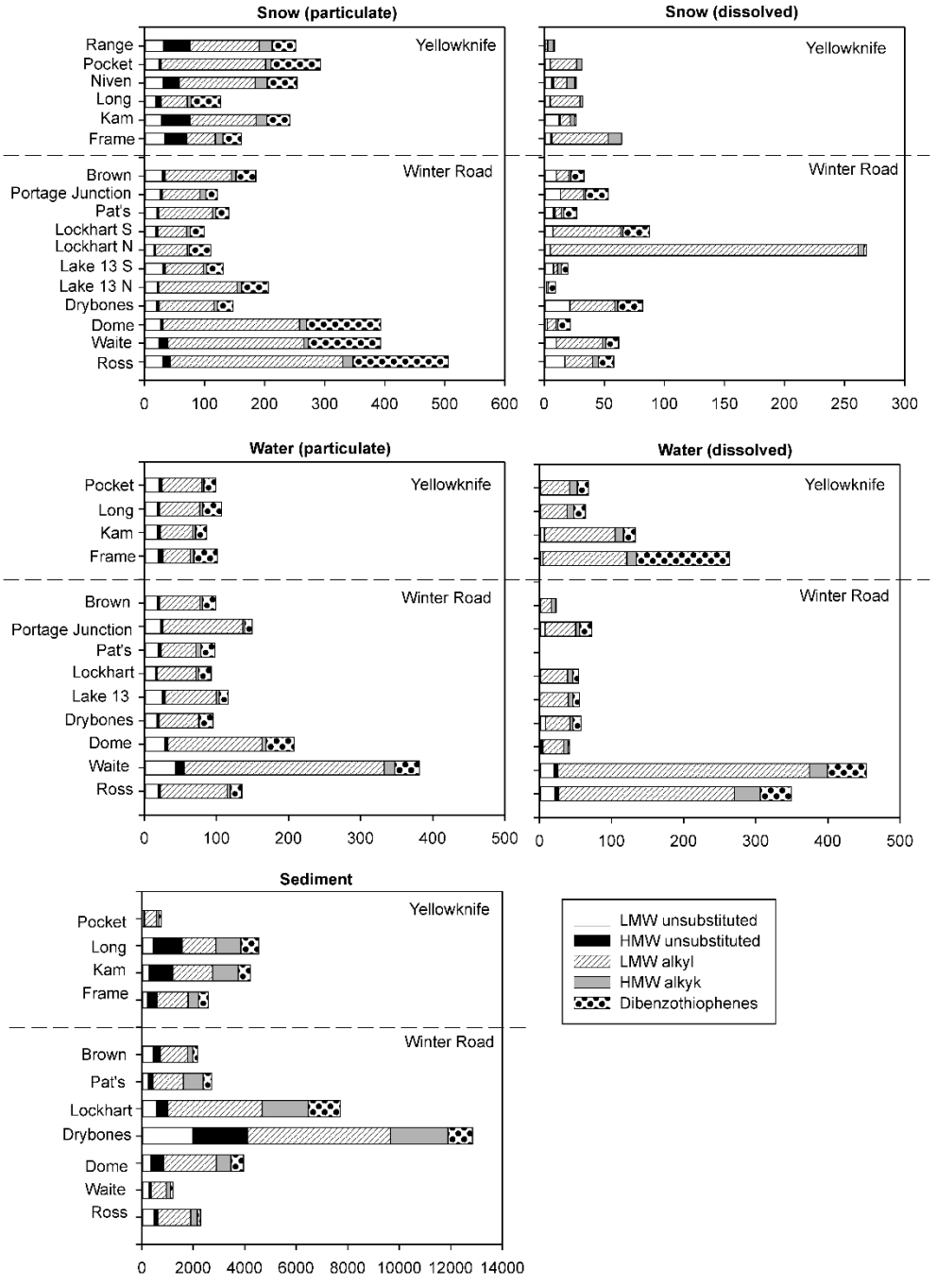

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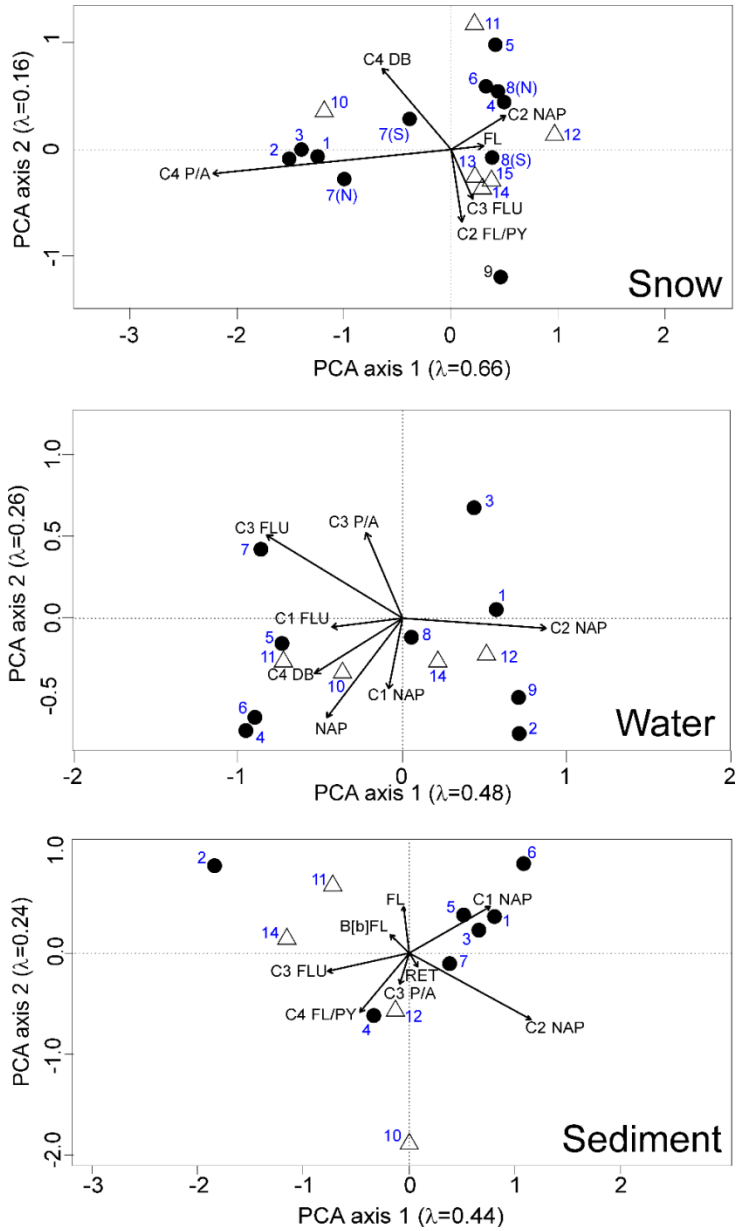

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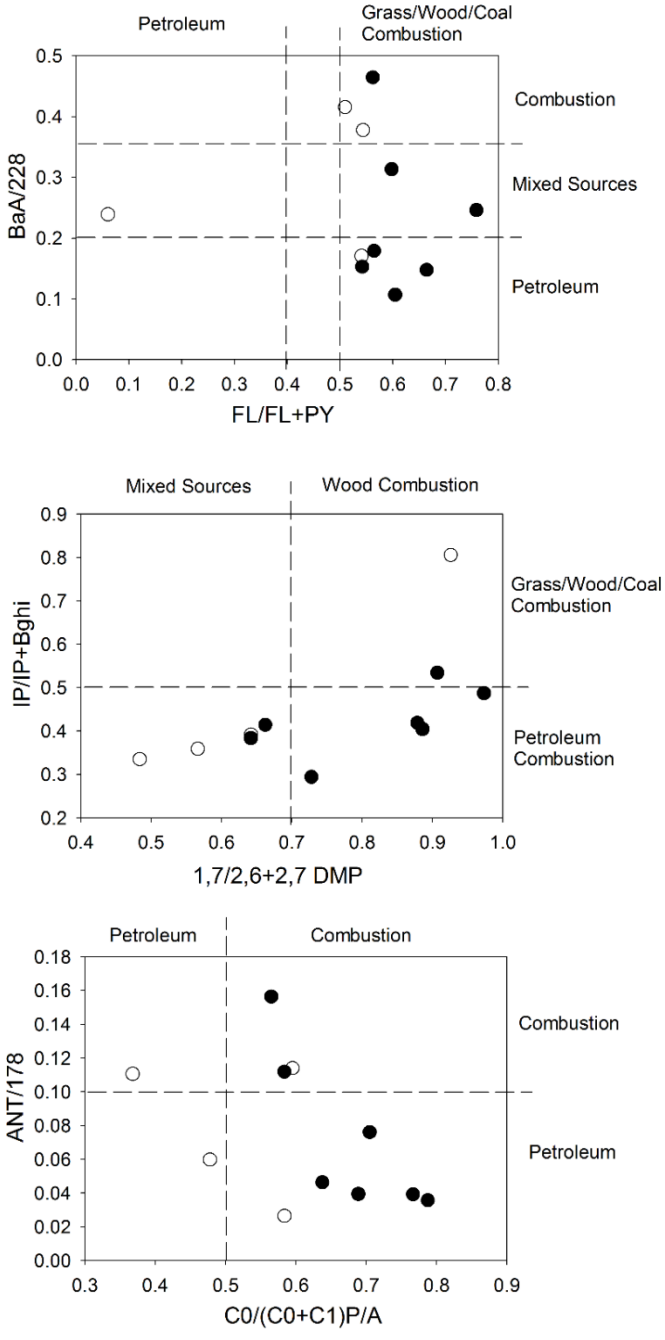

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