

Hydrocarbon pollution monitoring of the Kenai River has been very limited. Beginning in the summer of 1998, programmatic steps have been taken to quantify and better understand the concentration of hydrocarbons in the Kenai River Watershed. The Kenai Watershed Forum (KWF) along with numerous partners have developed three distinct components of monitoring to help characterize the concern of hydrocarbons in the Kenai River.

- Agency Baseline Monitoring coordinates and uses both non-governmental and government agency staff to collect grab samples from 20 index sites across the Kenai River Watershed
- Citizens' Monitoring Program utilizes citizen volunteers to visit Kenai River Tributaries year round on a monthly basis
- Passive Monitoring cooperatively with NOAA's Auke Bay Laboratory, passive hydrocarbon collectors are used to compare spatial and temporal hydrocarbon patterns in the Kenai River Watershed.

Each of these three components have different objectives that help increase our understanding of hydrocarbon pollution, yet many questions remain. Outlining these components, this fact sheet is intended to inform the reader of our understanding of hydrocarbon pollution within the Kenai River Watershed.



Figure 1. Sample location of 20 sites selected for sampling as part of the Agency Baseline Monitoring program. Red indicate sample location in Kenai River mainstem, yellow indicate sample location in tributary near confluence. Sample site density increases downstream near the more urbanized areas of Soldotna and Kenai.



Figure 2. Initial screening results from 65 samples - 13 sites; 5 sampling events. Levels exceeding state standards for aquatic life have been documented each July for the past three years in the Kenai River. No BTEX detected in either of the April sampling events.



Citizens' monitoring program in action. Responding to citizen monitors, Soldotna Officer and KWF staff remove 10 gallons of waste oil from Soldotna Creek

The Agency Baseline Monitoring program was established to determine current ambient water quality conditions across the Kenai River Watershed and to track those conditions over time, allowing for future trend analysis. The protocols in this effort are based on grab samples taken twice per year at 20 index sites across the Kenai River Watershed (Fig 1.). In addition to hydrocarbon monitoring, this effort also collects grab samples for nutrients, fecal coliform and metals (both total and dissolved). Specific to hydrocarbon monitoring, EPA 8021 is the standard method by which grab samples are analyzed for Benzene, Toluene, Ethylbenzene, and Xylene (BTEX).

Citizens' Monitoring trains interested citizens to monitor tributaries to the Kenai River and collect basic physical and chemical data. Monitors are asked to visit a designated site once a month on a year round basis. While this program does not conduct any hydrocarbon testing, on two occasions it has resulted in volunteers finding waste oil and fuel spills as pictured above. The program has also been a valuable tool, providing a mechanism for outreach and education at the neighborhood level.

The Passive Hydrocarbon Monitoring effort in conjunction with NOAA is designed to complement our Agency Baseline Monitoring. In contrast to twice per year grab samples, this protocol involves placing samplers in the water column at various locations throughout the year. The sampling devices remain in the water for up to 30 days, accumulating a wide array of large hydrocarbon molecules. Compared to the "snapshot" grab sample results, this methodology gives a better sense of the long-term presence of hydrocarbons in the water column. Unlike the agency baseline monitoring effort, this data cannot be used for comparison to state or federal guidelines and standards. The **Agency Baseline Monitoring** for hydrocarbons began in the summer of 2000. Twenty index sample stations were established during the development of the "Framework for Water Quality Monitoring of the Kenai River Watershed - 1998" as shown on the front page in figure 1. Dozens of participants helped chose the 20 locations that would best represent the ambient water quality conditions of the Kenai River Watershed.

All samples are collected following protocols established in a Quality Assurance Project Plan (QAPP) approved by the Alaska Department of Environmental Conservation in December of 2001. Staff from several agencies participate in a half-day training session the day prior to collecting samples. Samplers are instructed to collect water at elbow depth, avoiding surface water collection. To minimize the potential for collecting Cook Inlet water, sampling is timed such that all collection is done on an outgoing tide, near low tide.

Initial Baseline Hydrocarbon samples from 7/2000 to 7/2002

Hydrocarbon sample results from the five sampling dates are consistent and good for screening purposes, providing insights and pointing to areas of concern in the lower river as shown in figure 2. It is important to recognize that these data are limited and must be considered in context with all data collected. It is also important to note that only one tributary, the Moose River, has had any detection of hydrocarbons in the Agency Baseline monitoring program. For reference, the Moose River sample from 7/ 16/02 was 6.65 parts per billion.

Results from 2000 and 2001 were shown to each of the partners and numerous times in the communities of Kenai and Soldotna throughout the fall and winter of 2001. The total aromatic hydrocarbon (TAH) values are determined by summing the individual concentrations of Benzene, Toluene, Ethylbenzene, m,p-Xylene, o-Xylene in parts per billion. Sampling under this protocol has been completed five times, three times in July of '00, '01 and '02; twice in April, '01 and '02.

Concentrations exceeded state standards for fish and aquatic life in the lower river on each of the



Figure 3 Lower River Sample locations, samples were collected from the Kenai River at the three red, numbered locations

Lower River BTEX observations



Aerial Survey boat counts below Soldotna Bridge



Figure 4 - Comparison of Total Aromatic Hydrocarbon (BTEX) concentrations with boat traffic in the lower Kenai River. Zero detections of BTEX on 8/1 and 8/3 should be interpreted as below detection limits. Top figure shows BTEX concentrations for 5 days at 3 Lower River Sites. Bottom figure is the number of boats below the Soldotna Bridge (mile 21) observed during the same 5 days and just prior to sampling events.

three summer sampling occasions. No hydrocarbons were detected in either of the two spring sampling dates.

Summer 2002 Follow-up sampling

Questions from the partners and at community presentations helped guide additional sampling in the late summer of 2002.

In an attempt to isolate potential sources for the observed hydrocarbon concentrations, KWF took an additional 12 samples from three index sampling stations in the lower 10.1 miles of the Kenai River (figure 3).

This follow-up sampling strategy was designed to understand the contribution of hydrocarbons from one potential source, outboard boat motors. Four days were chosen to take samples from the three sites over an eight-day period. The eightday period was selected to coincide with sharp changes in boat traffic associated with the seasonal closure of the in-river Chinook and Coho fishery. There was no precipitation during the eight-day period.

The samples were correlated with boat traffic by flying over the river and counting the number of boats present immediately prior to the sampling event. Similar boat count data is available from

Normalized BTEX ratios - local refinery - regular unleaded gas





Figure 5 - Comparison of one representative sample (bottom) of the observed ratios of the constituent components that comprise Total Aromatic Hydrocarbons to that of refined gas from Alaska (top)

the Alaska Department of Fish and Game which we used for verification, but do not present here. Results from the end-of-season sampling are summarized in figure 4, which also includes the data from the regularly scheduled baseline monitoring sampling that occurred on July 16th, 2002.

A second measure was taken to characterize the hydrocarbon source by comparing the normalized ratios of BTEX collected in the water column to that of refined gas, figure 5. While this data does not serve as a source fingerprint, it does suggest that the majority of the hydrocarbon contamination observed in the agency grab samples comes from unburned refined gasoline product. This data combined with the observations in figure four suggests the most likely source being outboard motors. This data does not rule any other potential sources out. The observed ratio of the BTEX components may also be of use to help determine the volatilization rate of fuel out of the water column. Numerical models could be used to help determine the amount of fuel input into the river. A number of models could be used to estimate an amount of fuel entering the river. Sophisticated equations used in such calculations would require calibration. Since each of the constituent components of BTEX have differing volatilization rates, the relative percentages of BTEX may be used for future calibration of pollution load modeling.

Modeling Estimates of Observed Pollution

The simplest such model would be to use the U.S. Geological Survey's flow data as an estimate of the number of gallons of water

flowing past the Soldotna Bridge over a given time. Typical July flows are 10^5 gallons per second. To reach the 10ppb standard (a concentration of 10^{-8}) requires 10^{-3} gallons per second of BTEX input. This rate of pollution loading can be integrated in time to determine a load in gallons per unit of time. Using a 24 hour day as the time interval, our very simple model suggests 200 to 300 gallons of fuel per day entering the river.

These initial attempts to numerically model the load or volume of the observed hydrocarbon concentrations are enlightening for several reasons:

 Rather than expressing the concentrations in parts per billion, the model yields a more tangible concept of the concern by expressing the pollution in gallons per day.

2) It gives us a starting point in an accounting process to determine where such volume of pollution might come from.

3) It points out the lack of robust data necessary to accurately estimate the amount of hydrocarbon pollution that may be in our waters.

While we discuss our simple calculation here, we clearly recognize this is premature because of the following assumptions one needs to put into the model. Change these assumptions and the estimate can move in either direction.

Model assumptions

- complete mixing of contaminates in the water column
- no volatilization or hydrocarbon losses to any sink
- a concentration of 40% BTEX in Alaska's refined gas (a rather high percentage compared to other states refined product)
- 13,000 cubic feet per second of water flow equals 10⁵ gallons per second
- average concentration of 10 ppb of BTEX over a 24 hour period

Is the model reasonable?

Some agency partners have pointed to a known source of pollution in the inefficiency of 2strokes engines. During operation, both the intake and exhaust ports are open at the same time, this allows fuel to pass directly through the engine. As much as 25 percent of the consumed fuel passes directly to the air or water, releasing toxic and carcinogenic materials, such as hydrocarbons, to the environment. A more comprehensive discussion of two-stroke engines can be found on the internet at http://www.trpa.org/Boating/ boattahoe.html (Environmental Assessment for the prohibition of certain two-stroke powered watercraft 1999). The pollution generated by this motor type has led to restrictions in other parts of the country, as in the referenced Lake Tahoe example, and is a potential source of pollution in the Kenai River. However, there is no known prior documentation on the relative use of 2stroke engines in Alaskan waters.

Following this potential source, and at the request of the National Marine Fisheries Service, KWF conducted reconnaissance work in an attempt to determine the ratio of 2-stroke engines to 4stroke engines in use on the river during the month of July and Early August. Based on 775 observations, we found 34% of the motors were 2-stroke, and 66% 4-stroke. However, we also noted that there are distinct and dramatic differences within specific user group populations. Our data indicated that more than 90% of guided motor boats are using 4-stroke engines compared to less than 50% of the private boaters using 4-stroke motors.

Taking 34% from a total of 500 boats on the river during a peak use day (170 two-strokes), an estimate of 10 gallons of daily fuel consumption per boat, it is reasonable to assume that 400 to 500 gallons/day of raw fuel could be entering the river from this motor type. With the amount of data we have we can only speculate and it would be prudent to have these hypotheses independently tested.

The methodology of using grab samples works well for observing and correlating contaminates with known and predictable events, such as boat traffic; however, is very limiting in any attempt to characterize Non-point source pollution from unpredictable events such as road runoff or contamination resulting from spills. A better indicator of the latter potential sources is the passive hydrocarbon sampling techniques.

Passive Hydrocarbon Sampling - with NOAA's Auke Bay Laboratory.

To this point, we have been discussing the concentrations of five molecules that when combined, their sum is used for comparison to an established water quality standard set by the State of Alaska. These five molecules are single-ringed hydrocarbons that are known to harm life when present in sufficient concentrations. This is in contrast to the method the Auke Bay Laboratory uses where the hydrocarbons collected in the passive samplers are multi-ringed (larger) molecules. Recently published data suggest that some of these larger molecules can be equally or even more harmful to aquatic life than the singleringed BTEX suite.

The techniques used to collect and analyze grab samples for BTEX are relatively well established and straightforward. As discussed earlier, our protocols to date for the Agency Baseline Monitoring program call for the sampler to locate the index sampling site, and collect water into a sample bottle which is then shipped to a lab for analysis. Limitations of this component of our monitoring program are best described using a hypothetical scenario of a major fuel spill. In our sampling strategy, we have had funding to collect samples at 20 sites, twice per year. One sampling occurs in mid-July and one near breakup in mid-April. If a major spill, say several thousand gallons were to occur in early June the agency monitoring protocols are not likely to detect any evidence of the spill. Obviously or hopefully, such a large spill would be visually noticed and

Polynuclear Aromatic Hydrocarbons



Figure 6 - relative concentrations of multi-ringed aromatic hydrocarbons detected using passive hydrocarbon sampling techniques over a 1 year period. The four colors indicate four sampling sites, two from the Kenai River Mainstem and two from tributaries to the Kenai River

addressed.

The Kenai River is a large system that flushes relatively quickly. A more realistic concern that the Agency Baseline Monitoring data is unlikely to accurately characterize is pollution from runoff. It is almost impossible to predict where and when urban runoff is going to reach a given waterbody. As such it is difficult for a sampler to collect a grab sample that would document the contribution of hydrocarbons from sources such as runoff or small spills. Passive Hydrocarbon samplers help address this concern.

The technique used in Passive Hydrocarbon sampling is not currently used for comparison to legally defined standards. Nor is it possible to express the results in a concentration of a particular contaminate in parts per billion. It is very useful to compare the results from this technique to the Agency Baseline results to gain insight into what we may be missing with our limited number of grab samples.

Plastic strips of Low Density Poly Ethylene (LDPE) are placed in a perforated aluminum "puck" about the size of large doughnut. The "puck" is place in the water at the sample location for up to 30 days. Water flows through the "puck" and comes in contact with the plastic strip. The plastic strip absorbs these large-ringed hydrocarbons continuously throughout the period it is deployed in the water. The "pucks" are retrieved from the sample location and shipped to the Auke Bay Laboratory for analysis.

Since the device is left in the water for up to 30 days, the plastic strip accumulates contaminates continuously over the exposure period. This helps capture and integrate small runoff events, spills or any other mechanism by which contaminates

may be entering the waterbody. KWF has been assisting the Auke Bay Laboratory with this sampling protocol on a monthly basis since September 2000 and we continue to do so to date.

With the permission of Auke Bay Laboratory, we present some early findings that may be of use to the reading audience (fig. 6). This raw data needs to be interpreted by those that understand it best -The research staff at the Auke Bay Laboratory should be called upon to help decipher any conclusions. Three curious points worth calling out: 1) The highest values of Polynuclear Aromatic Hydrocarbons (PAHs) occur in a small tributary that drains a developed area similar in magnitude to Soldotna Creek, yet the PAH values are dramatically higher than any other location. 2) There is no possibility of either of the tributary creeks being impacted by outboard motor boat use. 3) Similar to the grab sample data, the highest values in the Kenai River are in the lower river and are much higher than observed at mile 44.5 (just upstream of the Kenai Keys). However, the highest values in the lower river do not occur in July as our grab samples suggest, but rather in May, again when very low boat traffic is present.

Summary

Hydrocarbon values have been observed to exceed state standards for fish and aquatic life in the Kenai River. These observations are not likely documenting a new source of pollution, rather one that has not been previously evaluated. The data presented herein has not been peer reviewed, and is limited in scope. All potential sources have not been identified, nor addressed equally. Additional and more frequent sampling is required to verify and better characterize the issue of hydrocarbon pollution in the Kenai River Watershed.