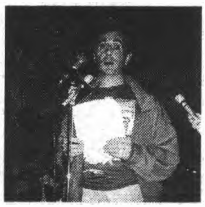
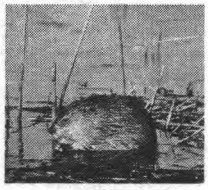
Canada Alberta Northwest Territories

Northern River Basins Study

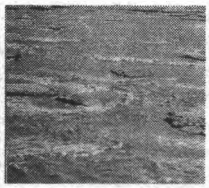


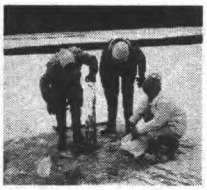




NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 97

ASSESSMENT OF TROPHIC POSITION AND FOOD SOURCES USING STABLE ISOTOPES OF SULFUR, CARBON AND NITROGEN, PEACE AND ATHABASCA RIVERS, 1992 AND 1993



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by

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PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

NORTHERN RIVER BASINS STUDY
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Whereas the above publication is the result of a project conducted under the Northern River Basins Study and the terms of reference for that project are deemed to be fulfilled,
IT IS THEREFORE REQUESTED BY THE STUDY OFFICE THAT;
this publication be subjected to proper and responsible review and be considered for release to the public.

(Dr. Fred J. Wrona, Science Director) — (Date) 14 Feb 96

Whereas it is an explicit term of reference of the Science Advisory Committee "to review, for scientific content, material for publication by the Board",
IT IS HERE ADVISED BY THE SCIENCE ADVISORY COMMITTEE THAT;
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SUPPLEMENTAL COMMENTARY HAS BEEN ADDED TO THIS PUBLICATION: [ ] Yes [ ] No

(Dr. P. A. Larkin, Ph.D., Chair) — (Date) 14 Feb 1996

Whereas the Study Board is satisfied that this publication has been reviewed for scientific content and for immediate health implications,
IT IS HERE APPROVED BY THE BOARD OF DIRECTORS THAT;
this publication be released to the public, and that this publication be designated for: **[ ] STANDARD AVAILABILITY [ ] EXPANDED AVAILABILITY**

(Lucille Partington, Co-chair) — (Date) 23 Feb. 96

(Robert McLeod, Co-chair) — (Date) 23 Feb 96

ASSESSMENT OF TROPHIC POSITION AND FOOD SOURCES USING STABLE ISOTOPES OF SULFUR, CARBON AND NITROGEN, PEACE AND ATHABASCA RIVERS, 1992 AND 1993

STUDY PERSPECTIVE

Contaminant transfer through the aquatic food chain (biomagnification) is common knowledge. Not as well understood are the transfer processes which can vary with location, biota and contaminant compound. A key step in the identification of contaminant transfer within the aquatic environment is definition of the aquatic food chain. Due to human use, fish became a principal focus of investigation under the Northern River Basins Study. Earlier work in other river systems have shown that carbon, nitrogen and sulphur isotope analyses can be used successfully to define food chain relationships and food sources.

This project report describes results of a follow-up investigation to an earlier Northern River Basins Study project (NRBS Report # 22). Fish, water and biofilm obtained from other NRBS collections were the source of material used for analysis. Carbon and sulphur results from this project have extended our understanding of the feeding and movement of fish in the middle and lower Athabasca River, and the upper and lower Peace River. As well, the nitrogen analyses has assisted in the definition of the food chain relationship of various aquatic biota.

Related Study Questions

6) What is the distribution and movement of fish species in the watersheds of the Peace, Athabasca and Slave rivers? Where and when are they most likely to be exposed to changes in water quality and where are their important habitats?

14) What long term monitoring programs and predictive models are required to provide an ongoing assessment of the state of the aquatic ecosystems. These programs must ensure that all stakeholders have the opportunity for input.

While researchers determined that the food chain relationship within fish is quite consistent, they noted that the base of the food chain leading to fish caught in the Athabasca River does not originate from plant material grown in the mainstem river. The sulphur isotope signature suggests that the principal source of organic material consumed by aquatic invertebrates in the mainstem river arises from the tributaries or terrestrial material in the tributary basins. Consequently, contaminants that **adsorb** to organic material could be picked up in either the tributary or mainstem river. However, for those contaminants that must be **incorporated** into organic material for them to bioaccumulate, they would have a much lower probability of transfer up the food chain if only the water is contaminated in the mainstem river.

As a result of better defining food chain relationships, there is a potential that nutrients could play an important role in modifying contaminant transfer. With improved light penetration of the mainstem water column and a more stable river substrate, nutrients would enhance the development of organic material within the mainstem river. Generation of mainstem organic material would permit the incorporation of water column contaminants (bioaccumulation) and transfer up the food chain (biomagnification).

Results from this project will be used by the contaminants component to interpret results on the distribution of contaminants with observed concentration and effects in biota.

REPORT SUMMARY

A study was carried out of the stable isotope composition of sulfur, carbon, and nitrogen in the tissues of fish from two locations in the Athabasca River, 630km, near the town of Athabasca, and 300km, near the town of Fort McMurray, and two locations in the Peace River, site IS1 near Many Islands, about 950km from the mouth, and IS11 just upstream from the confluence with the Slave River. Fish species analyzed consisted of burbot, walleye, mountain whitefish, northern pike, goldeye, longnose sucker, trout perch, emerald shiner, flathead chub, and lake chub. A set of samples (Sample Set #1) provided by the Northern River Basins Study consisting of biofilm, invertebrates, and fish from the upper Athabasca River was also analyzed.
Water samples from the winter oxygen survey of the Athabasca River and its tributaries carried out by Alberta Environment were analyzed for sulfur isotopes in dissolved sulfate and carbon isotopes in dissolved organic carbon.

The purpose of the study was to extend the data base on feeding and movement of the fish which could be derived from the sulfur and carbon isotope data, and to use the nitrogen isotope data to define the trophic positions of the organisms. The isotope analyses of the water samples was carried out to establish the isotope signals of the source of organic matter produced in or carried into the Athabasca River by its tributaries so that the dependence of the food chain on those sources could be assessed.

Sulfur isotopes of the Athabasca River fish from both sites were in the range -8 to 4‰, distinct from the range identified by Hesslein and Ramlal (1993) as characteristic of the mainstem populations in the upper Athabasca River. Variance in sulfur and carbon isotopes was lower at the 300km site possibly due to a more uniform food source from greater influence of the mixed material in the mainstem relative to tributaries. Nitrogen isotopes showed walleye clearly at the top of the trophic structure followed by northern pike, goldeye, emerald shiner, and trout perch with longnose sucker, flathead chub, and lake chub at the bottom.

The sulfur and carbon isotopes in the water of the Athabasca and its tributaries strongly suggest that the main food source for the food chain leading to fish is from terrestrial detrital material from the tributary watersheds. Particularly at the 300km and 630km sites reported on, fish do not have isotope signatures consistent with a food chain based on material photosynthesised in the Athabasca River.

Sulfur and carbon isotopes from the Peace River fish clearly discriminated three separate food sources for: 1.burbot, 2. mountain whitefish and longnose sucker, and 3. flathead chub. Burbot was at the top of the food chain. Mountain whitefish, flathead chub and longnose sucker share the lower level. Near the mouth of the Peace River flathead chub and goldeye food sources are clearly separated by sulfur. Other distinctions are not as clear. Walleye were again at the top of the food chain with burbot and northern pike. These were followed by goldeye, longnose sucker, and flathead chub.

Sulfur isotopes in the Sample Set #1 were characteristic of the upper Athabasca River as defined by Hesslein and Ramlal (1993). Nitrogen isotopes defined two trophic levels, the upper one with fish and the lower with the invertebrates.

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Figure 17. Sulfur isotopes in fish at three sites and dissolved sulfate of the tributaries and mainstem along the length of the Athabasca River. Labels are the same as in Table 1 and Figures 2-16.

1.0 INTRODUCTION

The purpose of analyzing fish tissues and other components of the food chains for the stable isotopes of sulfur, carbon, and nitrogen is twofold: 1. to determine the trophic position of the organism in the food chain and 2. to determine the food sources, ie. allocthonous (transported from the terrestrial watershed) versus autochthonous (produced within the aquatic system), and feeding locations ie. tributary or mainstem. For instance, if feeding in tributaries can be established, some inferences can also be made about fish movements.

The principle in using sulfur and carbon isotopes to determine food sources is "you are what you eat" or at least the aquatic organism is in this case. Sulfur and carbon isotopes are essentially unaffected by trophic transfers and therefore indicate the signal of the base of the food chain in which they are found. In contrast to analyses of gut contents which give an indication of material *ingested* in the previous hours to days, isotope analyses of muscle tissue in fish give information about food *assimilated* over a period of weeks to years. The period of integration represented by the isotope measurement varies depending on the growth rate and the metabolic rate of the organism or organ (Hesslein et al. 1993). Nitrogen isotopes are fractionated by a consistent amount at each trophic step and therefore can be used to indicate trophic level. Peterson and Fry (1986) have reviewed the general applications of these stable isotopes to food chain research. An application closer to that being used for the Northern River Basins Study (NRBS) has been published by Hesslein et al. (1991). It describes aquatic food chains in the lower Mackenzie River Basin.

Hesslein and Ramlal (1993) described the stable isotopes of carbon, nitrogen, and sulfur in fish and some other organisms in the Hinton Reach Specific Study Area of the Northern River Basins Study. The purpose of that study was to define the food source indicators and the trophic positions of the fish within that reach. This study (Figure 1) extends that investigation to fish caught in the spring of 1992 at two Athabasca River locations (630km and 300km, Site 6 and Site 9, R.L. & L. Environmental Services 1994) downstream of the Hinton RSS and two locations sampled in the spring of 1992 (IS1, near 950km and IS11, near the mouth, D.A. Westworth & Assoc. 1994) in the Peace River. A sample set consisting of biofilm, invertebrates and fish from the Athabasca River, winter 1993 (Sample Set #1), was also analyzed for stable isotopes. In addition, water samples obtained through the winter oxygen survey of 1994, (L. Noton, Alberta Environment) were analyzed to determine the isotope composition of sulfur in dissolved sulfate and carbon in dissolved inorganic carbon (DIC). These samples were taken in 11 tributaries of and 3 mainstem locations in the Athabasca River. Organisms dependant on food derived from the tributary basins are expected to have the same as isotope signals as that in dissolved sulfate.

2.0 METHODS

Samples of fish were supplied frozen by the NRBS either as homogenized muscle tissue or whole muscle tissue form. Samples for analyses reported here were chosen with the intention of getting a representative look at the variety of species and locations in the Athabasca and Peace Rivers. Toward this purpose, samples were chosen with the widest range of parameters of sex and size. Previous studies have shown that this best guess at maximizing the variance has given the most information on the population in

general. Samples other than fish were selected and supplied by the Northern River Basins Study in either a dried or frozen state. The methods used for stable isotope analyses have been described in detail by Hesslein et al. (1989) and will be briefly described here. For carbon and nitrogen analyses of non-fish samples, an aliquot of approximately 20 mg was oven dried in air, placed in a Vycor glass tube (9mm OD x 25mm long) with 1 g copper wire and 1 g copper oxide (both high purity) and a small piece of silver foil (2 mm x 2 mm). The tube was then evacuated overnight to a pressure of <10 um Hg and sealed with a torch using natural gas and oxygen. The sealed tube was then combusted at 850 °C for 2 hours and cooled slowly. The tube was attached to an evacuated glass extraction system and broken to release the H_20, CO_2, and N_2 to which the sample has been converted. The gases are then cryogenically purified. Water was removed at -55 °C, CO_2 at -293 °C, and N_2 at -293 °C on 5Å molecular sieve. The purified gases are transferred to the mass spectrometer in sealed glass vessels. A high precision dual inlet isotope ratio mass spectrometer was used (VG Micromass 602E) for the analyses. The principle of operation is that the ratio of the isotopes in the sample gas is compared to a reference gas in the same system by switching the analyses back and forth from reference to sample many times. We have used the same reference gases in our system over many years. The working reference gases have been calibrated to the internationally accepted standards for the stable isotopes of sulfur, carbon, and nitrogen.

The long term repeatability of analyses in our lab has had a standard deviation of 0.2 ‰ for $\delta^{34}S$, 0.1 ‰ for $\delta^{13}C$, and 0.3 ‰ for $\delta^{15}N$. For a single set of similar samples, as in this study, the precision is better than these values.

All fish samples were analyzed using the automated method for the analyses of carbon isotopes. In this method the tissue sample was burned at high temperature in an automated elemental analyzer (Carlo Erba NA1500). The resultant CO_2 was cryogenically cleaned of water at -75 °C and frozen at -293 °C. The purified gas was then automatically introduced to a dual inlet isotope ratio mass spectrometer (VG Optima) and analyzed as above. The precision of this method is better than the manual one (<0.1 ‰) but we don't have enough experience to say how much better in the long term. A comparison of analyses of the same 30 tissue samples by both methods gave a standard deviation of the difference of 0.07 ‰, better than our long term manual results would have predicted.

All fish samples were analyzed using the automated elemental analyzer system for nitrogen isotope analyses. As with carbon, the sample was oxidized at high temperature. The oxides of nitrogen were reduced to N_2 over copper at 600 °C and trapped on silica gel at -293 °C. The gas was then introduced to the mass spectrometer as above for isotope analyses. The precision of the automated method is <0.1 ‰, and was standardised to the results of our manual methods.

For sulfur isotope analysis of fish, an aliquot of muscle tissue (approx. 2 g fresh weight) was digested in concentrated nitric acid at gradually elevated temperature until a clear solution was attained (7-10 days). Approximately 0.2 g $NaNO_3$ was added and the excess liquid evaporated. The sample was then heated in a furnace at 400°C for 14 hours to complete oxidation and remove excess nitrate. After cooling, the sample was dissolved in 80 ml of distilled, deionized water and 1 mL saturated $BaCl_2$ solution added to precipitate the sulfate as $BaSO_4$ while the solution was held at 80°C overnight.

Water samples were filtered (Whatman GFC) and put through a chloride saturated ion exchange column to remove sulfate. The sulfate was eluted with HCl, titrated to pH near 5 and $BaSO_4$ precipitated as above.

The barium sulfate precipitate was filtered (Whatman 42, ashless) and combusted at 800°C for 2 hours in platinum crucibles. The required amount of $BaSO_4$ (about 20 mg) was weighed into a Vycor test tube mixed with 60-80 mg $NaPO_3$. Two to three cm of chopped copper wire was put in the tube just above the mixture and SO_2 was evolved by thermal decomposition at 850°C and frozen into an evacuated sample vessel at -196°C for mass spectrometric analysis as in the manual method for carbon and nitrogen.

The DIC was removed from water samples by a flow of CO_2-free nitrogen gas (100 mL min^{-1}) after the sealed sample bottles had been acidified and transferred to a gas stripping tower. The gas stream was dried (-50°C) and the CO_2 frozen from the gas stream (-196°C) and transferred to vessels for analysis on the mass spectrometer.

3.0 RESULTS AND DISCUSSION

The stable isotope data for the fish tissue are presented in Appendix A. The stable isotope data for Sample Set #1 are presented in Appendix B. Carbon to nitrogen ratios were too large to allow nitrogen isotope analyses for the biofilm samples. The stable isotope data for the water samples are presented in Table 1.

Figures 2-7 show the two component plots of the isotope data from the two locations in the Athabasca River. At both locations sulfur isotopes are, with one exception, in the range of -8 to 4‰. Most fish in the Hinton RSS (Hesslein and Ramlal, 1993) were in the range of 7 to 11‰. Some mountain whitefish identified as probable tributary feeders by Hesslein and Ramlal (1993), $\delta^{34}S$ of -3 to 2‰, may be fish which had migrated from these lower reaches. Both sulfur and carbon isotopes have a smaller range at the downstream location possibly due to the increased dominance of the food carried by the cumulative mainstem flow relative to the tributaries of the lower reaches. The carbon isotope data are in the same range as that of the Hinton RSS (Hesslein and Ramlal, 1993). The nitrogen isotopes delineate the trophic structure similarly at both locations. Walleye are at the top of the food chain followed by northern pike, goldeye, emerald shiner and trout perch and with longnose sucker, flathead chub, and lake chub at the lowest level.

Figures 8-13 show the two component plots of the isotope data from the two locations in the Peace River. The range of $\delta^{34}S$ is -8 to 3‰, very similar to that in the Athabasca River sites. The fish are more distinctly grouped by species than in the Athabasca River. The goldeye at site IS11 are very similar to those in the Athabasca, but the flathead chub are consistently more negative at both sites ($\delta^{34}S$ -8 to -4‰). Burbot at the IS11 site have $\delta^{34}S$ in the range -4 to -2 while those at site IS1 have $\delta^{34}S$ in the range -1 to 2‰, similar to that of the mountain whitefish from IS1. The separate ranges between species at both sites suggest different food sources. Carbon isotopes are generally in the same range found at other sites, however at site IS1 they suggest that mountain whitefish and longnose sucker have a different food

source than flathead chub and burbot. This presents a complex picture as the sulfur isotopes suggest a different food source for the flathead chub versus other species. Nitrogen isotopes show the burbot, northern pike, and walleye in the upper trophic level and goldeye, longnose sucker, and flathead chub at a lower level. A single burbot at site IS11 had very unusual combination of isotope values. It is very likely a migrant from a tributary or lake system.

The samples from Sample Set #1 (Figures 14-16) generally show $\delta^{34}S$ typical of the range (7 to 11‰) assigned to mainstem fish in the Hinton RSS by Hesslein and Ramlal (1993). The "blank tissue" samples are tightly grouped at 2 to 3‰. The nitrogen isotopes show the trophic separation between the fish samples, at the lower trophic level for fish found by Hesslein and Ramlal (1993) and invertebrates in one or two levels below. The ephemeroptera are on average slightly lower than the plecoptera and tricoptera. Unfortunately, because of the problems with the biofilm samples their trophic level could not be assigned on the basis of nitrogen isotopes.

The sulfur isotopes in dissolved sulfate compare generally well with analyses carried out by Hitchon and Krouse (1972) with the exception of the sites near at the Athabasca townsite Table 1). Their samples were taken in the summer of 1969 while our samples were taken in February and March, 1994. The different relative proportions of tributary waters constituting the mainstem Athabasca could explain the discrepancy. We find it surprising, however, that the $\delta^{34}S$ of Hitchon and Krouse (1972) rises considerably (about 10 ‰) between the Athabasca townsite and the Suncor location, since, according to our data, the intervening tributaries other than the Clearwater River have lower values and the SO_4 concentration delivered by the Clearwater is very low and unlikely to influence the SO_4 in the Athabasca. We can only postulate that the sample of Hitchon and Krouse (1972) was heavily influence by water flowing in from the Lesser Slave River ($\delta^{34}S$ = - 0.5‰).

We expect that the organic matter produced by photosynthesis in the rivers will have the $\delta^{34}S$ of that in the dissolved sulfate. With two exceptions (one which also has a very unusual $\delta^{13}C$) the biofilm and invertebrates show $\delta^{34}S$ consistent with $\delta^{34}S$ in the dissolved sulfate of the Athabasca River. However none of the fish caught at either the 630 km or the 300 km positions in the Athabasca River have $\delta^{34}S$ near these values. Figure 17 shows the all of the $\delta^{34}S$ data from the fish reported here as well as those from the Hinton RSS from Hesslein and Ramal (1993) and the $\delta^{34}S$ data for the dissolved sulfate from all of the tributaries. It is clear that the general pattern of $\delta^{34}S$ in the fish follows closely the $\delta^{34}S$ in the tributary sulfate not the rather constant value in the mainstem of the Athabasca. This is very strong evidence that the organic matter which supports the food chain in Athabasca River is not photosynthesised within the river itself. The organic matter supporting the food chain could be produced in the aquatic habitats of the tributaries or washed in from the terrestrial habitats of the tributary basins.

The $\delta^{13}C$ in DIC is generally more variable over time than $\delta^{34}S$ of sulfate because, though it is strongly influence by dissolution of carbonates in a watershed, it is also influenced by respiration of organic matter in surface and groundwater sources as well as by gas exchange with the atmosphere. The $\delta^{13}C$ in this study is remarkably constant in the Athabasca River and its tributaries Table 1). In general the Athabasca River is slightly more positive than the tributaries with the exception of the Lesser Slave River and the Pelican River. In their investigation of $\delta^{13}C$ in the Mackenzie Basin, Hitchon and Krouse

(1972) interpreted a factor analysis of 14 chemical variables and $\delta^{13}C$ as "confirming that the contribution of stable carbon isotopic composition from carbonate rocks to $\delta^{13}C$ in the bicarbonate is significant, but that the dominant contribution is clearly independent of the 14 chemical variables factored". The biogenic production of carbon dioxide in soils was suggested as the independent but unmeasured factor. Carbon dioxide produced by decomposition of terrestrial organic matter in the Athabasca River watershed would be expected to have $\delta^{13}C$ of ~-25 to -29‰. Carbonate minerals in the Mackenzie basin fall in the range of +1 to -5‰ (Hitchon and Krouse 1972). It is interesting that the Lesser Slave River and the Pelican River show the least "biogenic" influence in our late winter results and the greatest "biogenic" influence in the summer data of Hitchon and Krouse (1972).

Since it is the purpose of this study to interpret the food source using the stable isotope data it is necessary to consider what aquatic plants growing in the waters of the basin should have as their $\delta^{13}C$. Aquatic plants growing in turbulent waters, (an exception to this could be sessile plants growing in quiet backwaters) except in cases of very high growth rates or low DIC waters are, due to the enzymatic fractionation of photosynthesis, -20 to -27‰ relative to the $\delta^{13}C$ of the DIC of the water in which they grow. This would result in $\delta^{13}C$ of -30 to -38‰ in organic matter produced in the river waters (assuming $\delta^{13}C$ of -10‰ in DIC). Some of the biofilm and invertebrate sample values do fall in this range. Even allowing for a small shift in $\delta^{13}C$, perhaps as much as 1.5‰ due to trophic enrichment, very few of the fish from the Athabasca River fall in the range expected for autochthonous material. Most of the fish fall in the range expected if the food chain were supported by terrestrial organic matter.

4.0 CONCLUSIONS

The study of the food sources and trophic relationships of fish by stable isotope analyses has now been extended to the middle and lower Athabasca River and the upper and lower Peace River. Clear distinctions are possible in many cases. The trophic structure within fish is quite consistent throughout. A study of stable isotopes in invertebrates in the locations reported on here would allow completion of isotope definition of the trophic structure. Stable isotope analyses of suspended or bedload material would help resolve the issue of the source of organic matter to the base of the food chain.

The base of the food chain leading to fish caught in the Athabasca River does not originate through photosynthesis in the river itself. The sulfur isotopes strongly support a source in the tributaries or terrestrial material in the tributary basins. The stable isotopes of carbon support the terrestrial origin of the material. This conclusion is perhaps not surprising in that large amounts of organic matter are transported from these watersheds and in much of the river conditions of light and substrate are not ideal for plant growth. This conclusion is however important in the interpretation of potential contaminant pathways and the potential impact of nutrient additions. Just because the organic matter is not derived from the river does not mean that the invertebrates or fish do not feed on it in the river. Feeding could occur on materials of the same source in the tributary or in the mainstem. Also, contaminants which are adsorbed to the organic matter could be picked up in the tributary or the mainstem, but contaminants which are accumulated in organic matter by incorporation in tissue would have a much lower probability of transfer up the food chain if only the water of the mainstem was contaminated.

Stimulation of the production of autochthonous organic matter through the addition of nutrients, stabilisation of substrate, or improved light penetration could enhance this minor food chain pathway. This could produce locally higher contaminant transfers than those of the food chain supported by autochthonous materials.

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APPENDICES

Appendix A. Northern River Basins stable isotope data for fish.

NRBSID	RIVER	LOCATION	SPECIES	SEX	LENGTH	$\delta^{34}S$	$\delta^{13}C$	$\delta^{15}N$	ISOLAB
1702	ATHABASCA R.	633.8	GOLD	M	36.4	-3.33	-26.46	9.06	5432.0
1703	ATHABASCA R.	633.8	WALL	M	32.5	-2.35	-26.17	9.38	5433.0
1704	ATHABASCA R.	633.8	GOLD	F	37.3	0.89	-25.63	7.91	5434.0
1705	ATHABASCA R.	632.5	LNSC	UN	41.5	-1.43	-25.60	7.54	5435.0
1706	ATHABASCA R.	632.5	LNSC	UN	34.1	-1.18	-26.25	7.41	5436.0
1710	ATHABASCA R.	627.0	WALL	UN	33.8	0.54	-26.09	9.44	5438.0
1711	ATHABASCA R.	627.0	WALL	GM	39.1	-4.58	-26.32	9.48	5439.0
1713	ATHABASCA R.	627.0	LNSC	UN	31.7	-2.66	-23.45	8.52	5440.0
1714	ATHABASCA R.	627.0	LNSC	UN	25.0	-6.36	-29.42	6.17	5441.0
1715	ATHABASCA R.	627.0	GOLD	UN	31.0	1.22	-26.53	7.72	5442.0
1718	ATHABASCA R.	627.0	FLCH	UN	25.1	0.37	-24.65	7.24	5444.0
1719	ATHABASCA R.	627.0	FLCH	UN	24.7	-0.32	-27.49	7.30	5445.0
1723	ATHABASCA R.	627.0	FLCH	UN	23.1	-1.30	-24.44	7.42	5446.0
1722	ATHABASCA R.	627.0	FLCH	UN	17.5	-1.67	-25.41	6.54	5447.0
1724	ATHABASCA R.	627.0	FLCH	UN	17.6	-0.27	-25.60	7.30	5448.0
1726	ATHABASCA R.	627.0	FLCH	UN	15.6	0.98	-24.14	6.88	5449.0
1777	ATHABASCA R.	630.0	LNSC	UN	37.5	0.22	-27.03	7.34	5450.0
1778	ATHABASCA R.	630.0	LNSC	UN	43.6	-1.95	-24.97	7.87	5451.0
1780	ATHABASCA R.	630.0	LNSC	UN	27.7	-4.87	-24.21	8.13	5452.0
1781	ATHABASCA R.	630.0	LNSC	UN	27.1	-4.70	-28.70	7.02	5453.0
1782	ATHABASCA R.	630.0	WALL	RM	40.8	-2.48	-25.40	9.67	5454.0
1783	ATHABASCA R.	630.0	WALL	UN	32.8	-0.47	-24.64	10.13	5455.0
1784	ATHABASCA R.	630.0	NRPK	UN	42.8	-7.36	-27.95	7.56	5456.0
1789	ATHABASCA R.	630.0	EMSH	UN	8.9	1.47	-26.47	8.08	5459.0
1790	ATHABASCA R.	630.0	EMSH	UN	9.0	0.55	-25.41	7.76	5460.0
1791	ATHABASCA R.	630.0	EMSH	UN	6.6	-0.62	-26.60	7.27	5461.0
1792	ATHABASCA R.	630.0	EMSH	UN	6.9	-3.91	-26.71	8.52	5462.0
1793	ATHABASCA R.	630.0	EMSH	UN	7.2	2.23	-25.83	7.07	5463.0
1794	ATHABASCA R.	630.0	EMSH	UN	6.1	0.07	-25.71	7.70	5464.0
1796	ATHABASCA R.	630.0	LKCH	UN	8.6	0.38	-25.18	6.31	5465.0
1797	ATHABASCA R.	630.0	LKCH	UN	8.2	-3.60	-25.93	5.83	5466.0
1798	ATHABASCA R.	630.0	TRPR	UN	6.8	2.03	-27.07	7.84	5467.0
1799	ATHABASCA R.	630.0	TRPR	UN	4.6	-1.92	-25.86	6.92	5468.0
2661	ATHABASCA R.	299.8	GOLD	F	36.7	-0.26	-27.54	7.53	5469.0
2662	ATHABASCA R.	299.8	GOLD	M	33.2	1.02	-26.98	7.28	5470.0
2663	ATHABASCA R.	299.8	GOLD	M	31.0	0.16	-27.51	7.59	5471.0
2665	ATHABASCA R.	299.8	GOLD	F	29.9	0.36	-27.69	8.08	5472.0
2666	ATHABASCA R.	299.8	GOLD	M	31.7	1.41	-27.85	8.34	5473.0
2668	ATHABASCA R.	299.8	NRPK	SF	56.4	-3.72	-25.71	8.45	5475.0
2669	ATHABASCA R.	299.8	NRPK	SF	53.5	-0.90	-26.46	8.15	5476.0
2671	ATHABASCA R.	299.8	WALL	UN	43.3	-2.16	-26.95	8.91	5477.0
2673	ATHABASCA R.	299.8	WALL	SF	40.8	0.38	-27.58	8.37	5478.0
2676	ATHABASCA R.	299.8	WALL	UN	37.5	-0.33	-26.71	8.98	5479.0
2677	ATHABASCA R.	299.8	WALL	SF	35.6	8.10	-26.44	7.93	5480.0
2678	ATHABASCA R.	299.8	WALL	UN	33.2	2.59	-26.47	9.13	5481.0
2679	ATHABASCA R.	299.8	WALL	UN	32.5	-0.83	-26.24	8.58	5482.0
2680	ATHABASCA R.	299.8	LNSC	SM	45.1	1.61	-27.86	6.20	5483.0
2681	ATHABASCA R.	299.8	LNSC	M	44.4	1.85	-27.24	5.83	5484.0
2682	ATHABASCA R.	299.8	LNSC	UN	35.0	-0.40	-27.95	6.39	5485.0
2683	ATHABASCA R.	299.8	LNSC	UN	38.5	0.92	-26.16	5.63	5486.0
2684	ATHABASCA R.	299.8	LNSC	UN	30.9	1.13	-28.26	7.01	5487.0
2685	ATHABASCA R.	299.8	LNSC	UN	26.1	0.11	-26.87	6.56	5488.0
2686	ATHABASCA R.	299.8	FLCH	UN	24.4	0.89	-26.48	6.13	5489.0
2695	ATHABASCA R.	299.8	FLCH	UN	24.0	-2.10	-26.85	5.78	5490.0
2690	ATHABASCA R.	299.8	FLCH	UN	22.6	0.86	-28.23	6.87	5491.0
2688	ATHABASCA R.	299.8	FLCH	UN	18.8	1.78	-26.92	6.54	5492.0
2694	ATHABASCA R.	299.8	FLCH	UN	10.8	-1.81	-26.37	6.17	5493.0
2693	ATHABASCA R.	299.8	FLCH	UN	12.6	-3.63	-26.55	6.99	5494.0
2700	ATHABASCA R.	299.8	TRPR	UN	6.0	3.07	-27.23	5.95	5495.0
2699	ATHABASCA R.	299.8	TRPR	UN	8.1	1.41	-27.04	7.94	5496.0
2701	ATHABASCA R.	299.8	TRPR	UN	5.2	3.68	-26.94	6.88	5497.0
2702	ATHABASCA R.	299.8	TRPR	UN	3.6	0.79	-26.58	6.64	5498.0
2703	ATHABASCA R.	299.8	TRPR	UN	7.1	1.93	-26.55	7.55	5499.0
2704	ATHABASCA R.	299.8	TRPR	UN	4.4	2.27	-26.99	5.95	5500.0
104	ATHABASCA R.		BLTR	UN	31.2	6.26	-26.10	7.27	5501.0
105	ATHABASCA R.		BLTR	UN	38.8	-0.75	-27.39	9.14	5502.0
106	ATHABASCA R.		BLTR	UN	51.7	8.36	-26.48	8.44	5503.0
5	PEACE R.	IS1	MNWH	UN	37.8	2.05	-29.39	6.19	5504.0
6	PEACE R.	IS1	MNWH	UN	45.8	-1.94	-27.78	5.90	5505.0
7	PEACE R.	IS1	MNWH	UN	34.1	0.73	-28.01	6.56	5506.0

8	PEACE R.	IS1	MNWH	UN	29.9	1.40	-28.44	5.60	5507.0
11	PEACE R.	IS1	MNWH	UN	31.2	1.71	-28.63	6.70	5508.0
22	PEACE R.	IS1	MNWH	UN	44.5	0.73	-27.48	6.38	5509.0
29	PEACE R.	IS1	BURB	UN	49.3	-1.09	-26.64	7.55	5510.0
34	PEACE R.	IS1	BURB	UN	42.6	-0.54	-26.47	7.97	5511.0
80	PEACE R.	IS1	LNSC	UN	37.0	-1.56	-28.87	5.20	5512.0
81	PEACE R.	IS1	BURB	UN	48.3	1.06	-26.27	8.39	5513.0
164	PEACE R.	IS1	LNSC	UN	44.6	-3.90	-28.68	5.43	5514.0
170	PEACE R.	IS1	LNSC	UN	40.7	-0.30	-28.74	6.41	5515.0
173	PEACE R.	IS1	LNSC	UN	28.5	-0.01	-28.43	6.58	5516.0
174	PEACE R.	IS1	FLCH	UN	14.9	-5.88	-26.32	6.04	5517.0
175	PEACE R.	IS1	FLCH	UN	20.5	-5.70	-26.27	7.03	5518.0
185	PEACE R.	IS1	FLCH	UN	15.3	-5.35	-26.61	6.44	5519.0
186	PEACE R.	IS1	FLCH	UN	27.2	-4.62	-26.35	6.47	5520.0
188	PEACE R.	IS1	FLCH	UN	23.0	-4.15	-26.47	5.10	5521.0
191	PEACE R.	IS1	LNSC	UN	34.0	0.57	-27.94	5.25	5522.0
192	PEACE R.	IS1	LNSC	UN	46.1	-3.84	-29.52	5.21	5523.0
194	PEACE R.	IS1	FLCH	UN	27.6	-5.92	-26.72	7.10	5524.0
195	PEACE R.	IS1	BURB	UN	66.7	0.96	-26.78	9.47	5525.0
196	PEACE R.	IS1	BURB	UN	43.2	-1.10	-25.74	9.96	5526.0
2709	PEACE R.	IS11	LNSC	UN	22.1	-4.20	-27.85	8.62	5527.0
2711	PEACE R.	IS11	LNSC	UN	42.9	2.36	-28.03	7.41	5528.0
2712	PEACE R.	IS11	GOLD	UN	17.2	-0.48	-28.28	7.78	5529.0
2713	PEACE R.	IS11	GOLD	UN	17.4	0.74	-27.77	7.32	5530.0
2715	PEACE R.	IS11	GOLD	GF	36.7	0.58	-26.35	8.43	5531.0
2716	PEACE R.	IS11	GOLD	UN	27.6	0.24	-27.27	8.28	5532.0
2722	PEACE R.	IS11	WALL	UN	55.8	-2.89		10.00	5533.0
2726	PEACE R.	IS11	WALL	UN	45.4	-0.41	-25.87	10.16	5534.0
2727	PEACE R.	IS11	WALL	UN	30.4	-3.27	-27.04	10.08	5535.0
2732	PEACE R.	IS11	BURB	UN	62.8	-2.88	-26.71	11.21	5536.0
2734	PEACE R.	IS11	BURB	UN	31.9	-7.24	-30.98	7.02	5537.0
2735	PEACE R.	IS11	BURB	UN	43.0	-4.62	-28.41	9.44	5538.0
2736	PEACE R.	IS11	BURB	UN	24.5	-3.49	-28.53	8.94	5539.0
2741	PEACE R.	IS11	NRPK	UN	80.6	-3.52	-26.84	10.34	5540.0
2743	PEACE R.	IS11	NRPK	UN	34.7	-3.64	-27.25	9.67	5541.0
2747	PEACE R.	IS11	NRPK	UN	62.4	-1.46	-27.59	9.08	5542.0
2751	PEACE R.	IS11	FLCH	UN	29.6	-4.55	-27.31	6.57	5543.0
2753	PEACE R.	IS11	FLCH	UN	25.5	-7.97	-26.44	6.34	5544.0
2754	PEACE R.	IS11	FLCH	UN	14.7	-5.08	-27.37	8.65	5545.0

Appendix B. Northern River Basins Study sample set #1.

ISOLAB	NRBSID	IDENTITY	SPECIES	DATE	$\delta^{34}S$	$\delta^{13}C$	$\delta^{15}N$
5352.0		ATHAB.R. ARC	BIOFILM	03-Mar-93	-31.47	-39.99	
5353.0		ATHAB.R. ARWHB	BIOFILM	23-Feb-93	12.32	-22.07	
5354.0		ATHAB.R. AROB	BIOFILM	27-Feb-93	6.57	-26.77	
5355.0		ATHAB.R. AREL	BIOFILM	06-Mar-93	11.40	-25.06	
5356.0		ATHAB.R. ARBR	BIOFILM	12-Mar-93	8.55	-29.55	
5357.0		ATHAB.R. ARDSATHA	BIOFILM	17-Mar-93	8.05	-29.44	
5358.0		ATHAB.R. ARATHAB	BIOFILM	19-Mar-93	9.05	-30.17	
5359.0		ATHAB.R. ARALPAC	BIOFILM	22-Mar-93	-0.82	-31.87	
5360.0		ATHAB.R. ARFM	BIOFILM	25-Mar-93	9.08	-32.05	
5361.0		ATHAB.R. ARC	PLECOPTERA	03-Mar-93	8.68	-29.12	3.61
5362.0		ATHAB.R. ARC	TRICHOPTER	03-Mar-93	7.82	-30.38	3.70
5363.0		ATHAB.R. ARC	EPHEMEROPT	03-Mar-93	7.80	-33.71	1.57
5364.0		ATHAB.R. ARWHB	PLECOPTERA	23-Feb-93	7.73	-29.25	0.92
5365.0		ATHAB.R. ARWHB	TRICHOPTER	23-Feb-93	9.70	-28.55	1.46
5366.0		ATHAB.R. ARWHB	EPHEMEROPT	23-Feb-93	8.59	-29.18	-1.24
5367.0		ATHAB.R. AROB	PLECOPTERA	27-Feb-93	4.40	-25.84	2.98
5368.0		ATHAB.R. AROB	TRICHOPTER	27-Feb-93	10.04	-26.34	3.35
5369.0		ATHAB.R. AROB	EPHEMEROPT	27-Feb-93	9.74	-26.28	2.10
5370.0		ATHAB.R. AREL	PLECOPTERA	06-Mar-93	7.88	-25.68	4.01
5371.0		ATHAB.R. AREL	TRICHOPTER	06-Mar-93	10.45	-26.94	3.85
5372.0		ATHAB.R. AREL	EPHEMEROPT	06-Mar-93	11.66	-27.19	3.27
5373.0		ATHAB.R. ARBR	PLECOPTERA	12-Mar-93	10.16	-29.40	4.21
5374.0		ATHAB.R. ARBR	EPHEMEROPT	12-Mar-93	7.40	-29.71	3.75
5375.0		ATHAB.R. ARFM	PLECOPTERA	25-Mar-93	7.09	-26.42	4.01
5376.0		ATHAB.R. ARFM	TRICHOPTER	25-Mar-93	4.72	-28.35	2.72
5377.0	202123	ATHAB.R. ARC	FISH	03-Mar-93	9.73	-25.89	5.83
5378.0	1	ATHAB.R. ARWHB	FISH	23-Feb-93	9.30	-26.93	6.52
5379.0	2-9	ATHAB.R. ARWHB	FISH	23-Feb-93	8.76	-25.57	6.27
5380.0	12	ATHAB.R. AROB	FISH	27-Feb-93	9.50	-25.80	6.93
5381.0	45	ATHAB.R. AREL	FISH	06-Mar-93	10.13	-26.05	6.80
5382.0		ATHAB.R. U/S HINTON	BLANK TISS	03-Mar-93	2.38	-30.74	7.31
5383.0		ATHAB.R. ARWHB	BLANK TISS	23-Feb-93	3.20	-30.05	6.92
5384.0		ATHAB.R. AREL	BLANK TISS	07-Mar-93	2.07	-30.75	7.35
5385.0		ATHAB.R. ARFM	BLANK TISS	26-Mar-93	1.99	-30.97	6.64

NORTHERN RIVER BASINS STUDY

APPENDIX C - TERMS OF REFERENCE

STABLE ISOTOPE ASSESSMENT OF TROPHIC POSITION AND FOOD SOURCE

Project: 3131-C1 Food Webs and Stable Isotopes

I. PROJECT DESCRIPTION

The Northern River Basins Study requires the contract laboratory to analyze 150 samples of fish tissue, gut contents and benthic invertebrates for the stable isotopic composition of sulfur, carbon, and nitrogen. These results must be interpreted with respect to fish food sources, fish movements, and trophic status.

II. TERMS OF REFERENCE

1. The contract laboratory is required to analyze each fish tissue, gut contents, or benthic invertebrate sample for $\delta^{34}S$.

    a. The values shall be give relative to Canyon Diablo sulfur.

    b. Precision of the analyses must be ±0.3 ‰ or better.

    c. The influence of oxygen isotopic variation is to eliminated through laboratory methods or corrected for using the mass 48/50 peak.

    d. Digestion of fish to yield sulfate must not produce any isotopic fractionation.

2. The contract laboratory is required to analyze each fish tissue, gut contents, or benthic invertebrate sample for $\delta^{13}C$.

    a. The values shall be give relative to PDB carbon.

    b. Precision of the analyses must be ±0.2 ‰ or better.

    c. Acid treatment should be used to remove carbonate materials in the analyses of gut contents.

3. The contract laboratory is required to analyze each fish tissue, gut contents, or benthic invertebrate sample for $\delta^{15}N$.

   a. The values shall be give relative to nitrogen in air.

   b. Precision of the analyses must be ±0.3 ‰ or better.

   c. Argon measurement on the mass spectrometer is to be used for the assessment of air contamination.

III. REPORTING REQUIREMENTS

1. Submit draft report to the Project Liaison Officer by March 31, 1994. The Draft report is to follow the Northern River Basin Style Guide. The report is to include all the results. In addition to generally accepted scientific reporting standards the draft report will include:

   a. Specimen handling, processing and analytical methods, quality assurance/quality control measures.

   b. The values of $\delta^{34}S$, $\delta^{13}C$, $\delta^{15}N$ for each sample are to be reported.

   c. Difficulties encountered with any samples are to be noted.

   d. A brief interpretation of the meaning of the values with respect to the implications for food sources, fish migration and trophic levels.

   e. An assessment of the utility of the method in achieving the goals of improving the understanding of fish trophic structure, feeding sources, and fish movements between feeding areas.

2. Three weeks after the receipt of review comments, submit ten cerlox bound copies and two unbound, camera-ready copies of the final report to Project Liaison Officer. The final report is to conform with the requirements of the Northern River Basin Style Guide, unless otherwise approved by the Project Liaison Officer. In particular the report will:

   a. include a Project Summary, Acknowledgements section, table of contents, list of tables, list of figures, a table of the community residents from the Northern River Basin Study area who assisted in some meaningful way with the project (include name and location), and an appendix containing the Terms of Reference for this project.

3. One electronic copy of the final report, in Word Perfect 5.1 format (Times Roman - 12 pitch) is to be submitted to the Project Liaison Officer along with ten hard copies of the final report.

4. Data presented in tables, figures and appendices of the final report is to be placed in dBase IV files and submitted to the Project Liaison Officer along with the final report.

IV. INTELLECTUAL PROPERTY

Upon completion or termination of this project, all data, documents and materials which are acquired or produced under this project shall become the sole property of the Northern River Basins Study.

V. PROJECT MANAGEMENT PLAN

Freshwater Institute Winnipeg/Stable Isotope Laboratory

1. Frozen samples will be provided to the contract laboratory by the NRBS Project Liaison Officer.

2. Based on the distribution of the sample collections and the composition of the catches the project manager (Dr. R.H. Hesslein) will, in consultation with members of the Food Chain Group and the Contaminants Group of the NRBS, stratify the sample in order of priority for analyses.

3. The samples will be analyzed in order of priority for the stable isotopes of sulfur, carbon, and nitrogen. The priority will be periodically reviewed in light of results to date.

TABLES AND FIGURES

Table 1. Key to sample location labels of Figure 1 and isotope and chemical analyses of water samples from this study as well as previous studies.

Label[1]	Site	$\delta^{13}C$	$\delta^{13}C$ H&K[2]	$\delta^{34}S$	$\delta^{34}S$ H&K[2]	SO_4 mg L^{-1}
Water sample sites						
A1	Athabasca River upstream of Hinton	-6.2	-12.4[3], -6.6[4]	13.9	16.9, 11.8	99
A2	Berland River	-10.2		5.4		23
A3	Marshland River	-11.8		9.3		5
A4	Sakwataman River	-11.6		2.9		5
A5	McCleod River	-11.2	-9.8, -10.2	2.4	1.2	15
A6	Pembina River	-12.1	-9.1, -11.0	1.4		13
A7	Lesser Slave River	-5.0	-22.2	-0.5		9
A8	Athabasca River, Athabasca townsite	-9.0	-13.8, -11.3	11.7	-2.0, -0.6	45
A9	LaBiche River	-9.9		-0.6		40
A10	Calling River	-11.9		-3.4		53
A11	Pelican River	-5.5	-24.4	-0.5		13
A12	House River	-11.9	-14.9	-6.9		51
A13	Clearwater River	-11.7		15.2		8
A14	Athabasca River, near Suncor	-9.9	-10.7	8.2	8.2, 9.4	47
A15	Muskeg River	-10.9		12.5		3
A16	Ells River	-11.5		-2.4		24
Sites of Hitchon and Krouse (1972)						
P1	Peace River,				1.8	
P2	Simonette River				1.1	
P3	Peace River, confluence of Smoky River		-9.8		5.8	
P4	Wabasca River		-8.6		-16.0	
P5	Peace River, Peace Point		-10.3		3.2	
Fish collection sites						
S1	Intensive Site 1, (IS1), Clear River/Many Islands					
S2	Intensive Site 11, (IS11), Rocky Point					
S3	Hinton Reach Specific Site study area					
S4	Site 6, approximately 630 Km upstream of Lake Athabasca					
S5	Site 8, approximately 300 Km upstream of Lake Athabasca					

[1] This column refers to the label on the map in Figure 1.
[2] Hitchon, B, and H.R. Krouse. 1972. Geochim. Cosmochim. Acta. 36:1337-1357, closest sites.
[3] Site on Athabasca River far upstream of Hinton
[4] Sunwapta River near Athabasca River site
Dissolved sulfate data is from Alberta Environment, L. Noton, Technical Services and Monitoring Division.

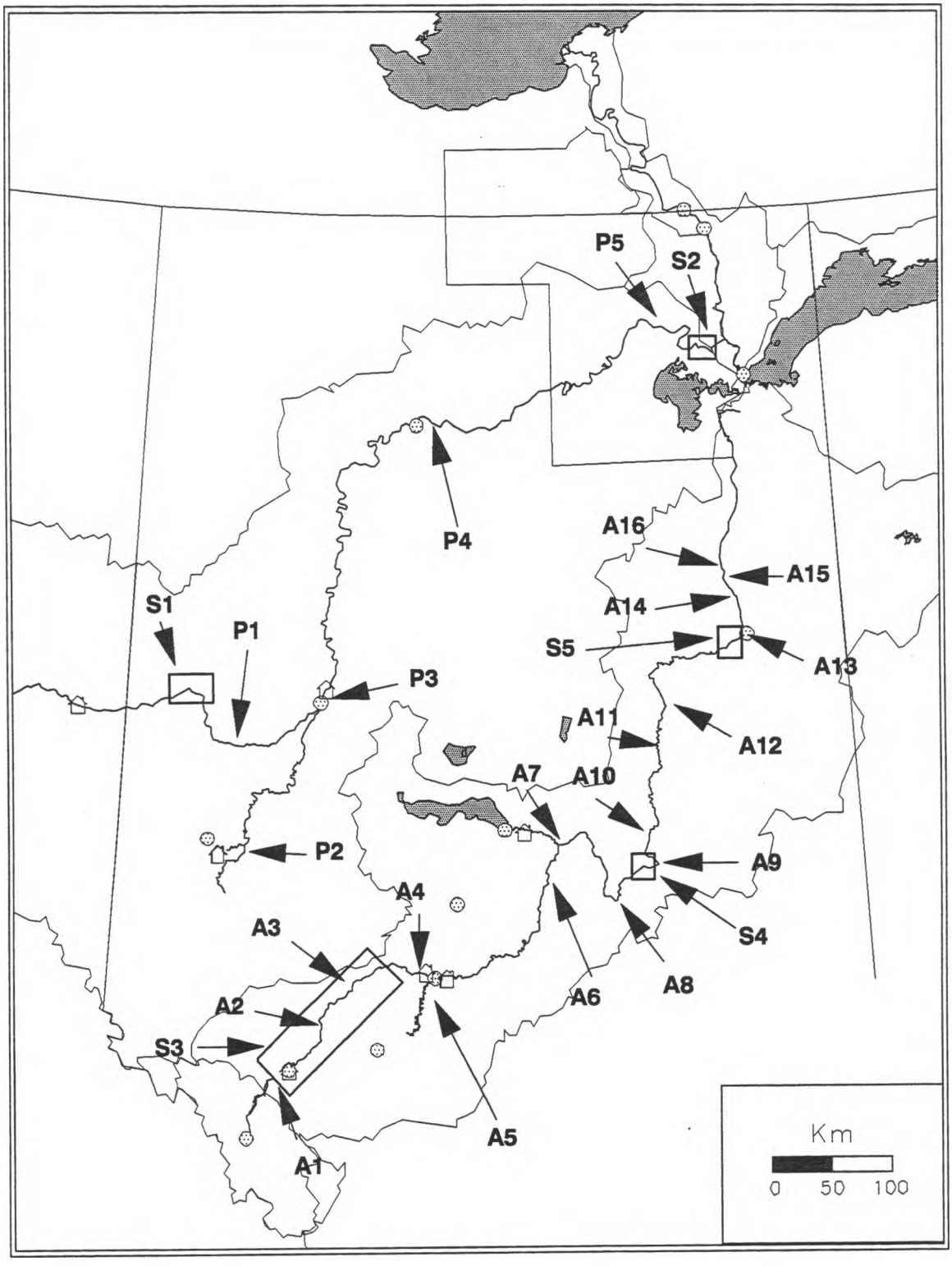

Figure 1. Sample collection sites in the Athabasca River and Peace River basins. A key to the site labels appears in Table 1.

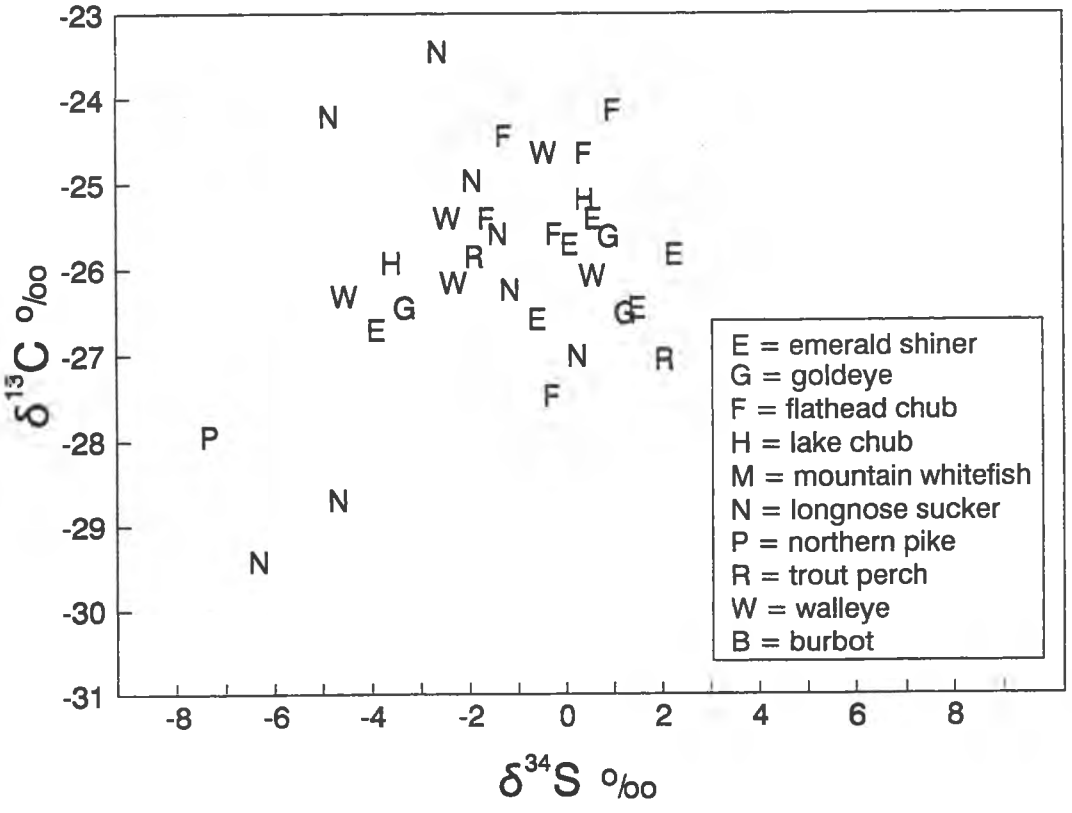

Figure 2. Sulfur and carbon isotopes in fish samples near the 630 km location in the Athabasca River.

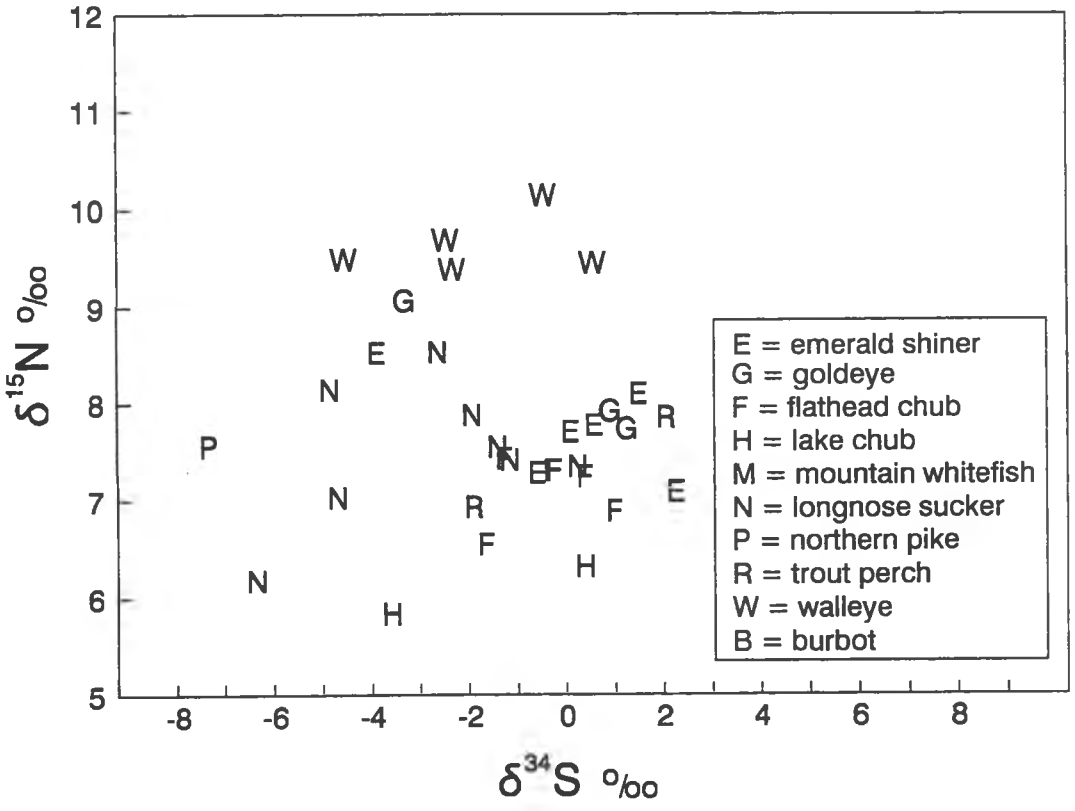

Figure 3. Sulfur and nitrogen isotopes in fish samples near the 630 km location in the Athabasca River.

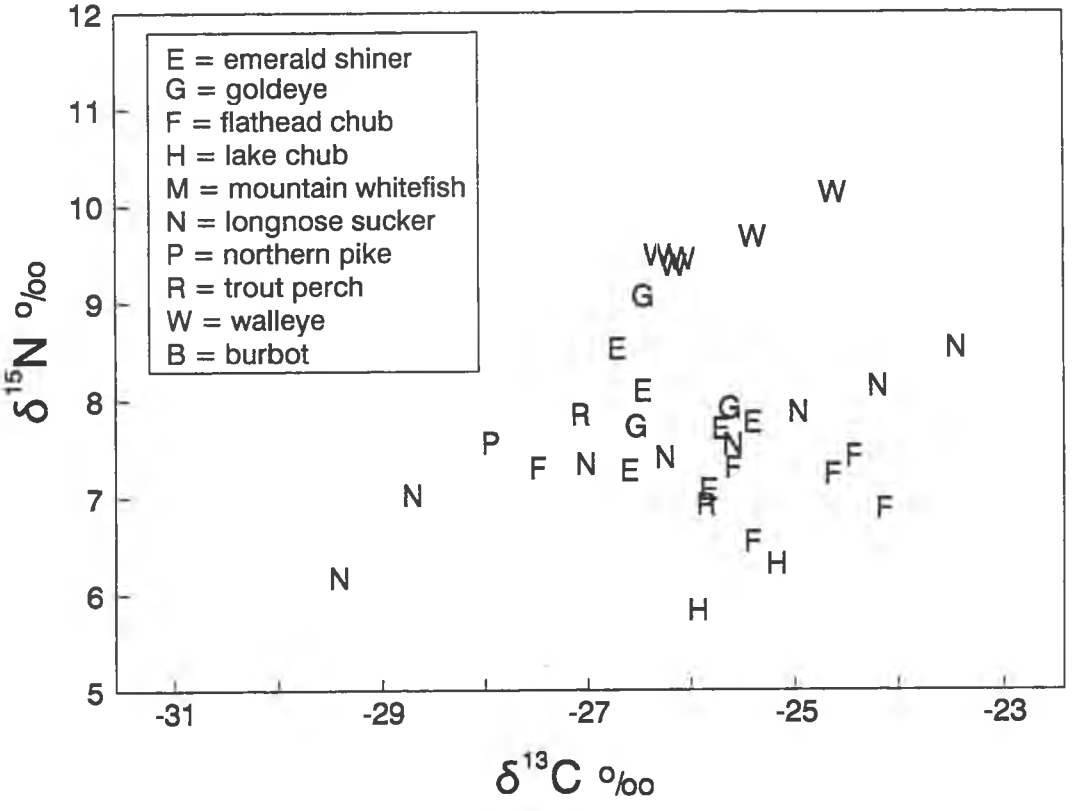

Figure 4. Carbon and nitrogen isotopes in fish samples near the 630 km location in the Athabasca River.

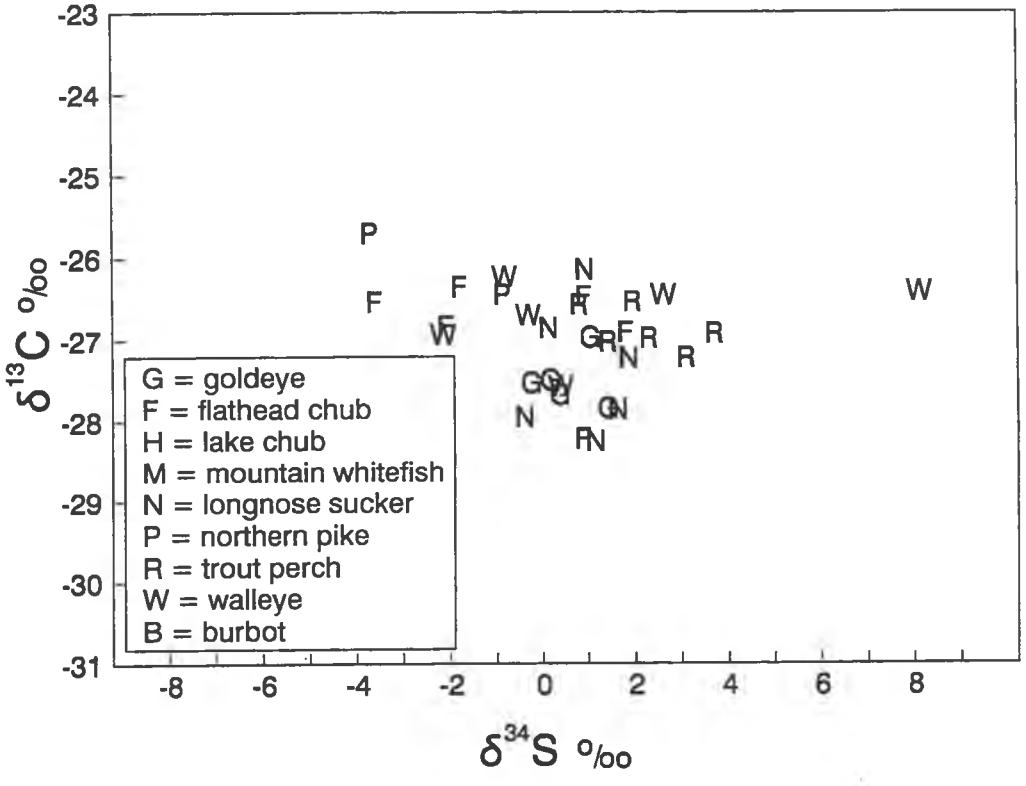

Figure 5. Sulfur and carbon isotopes in fish samples near the 300 km location in the Athabasca River.

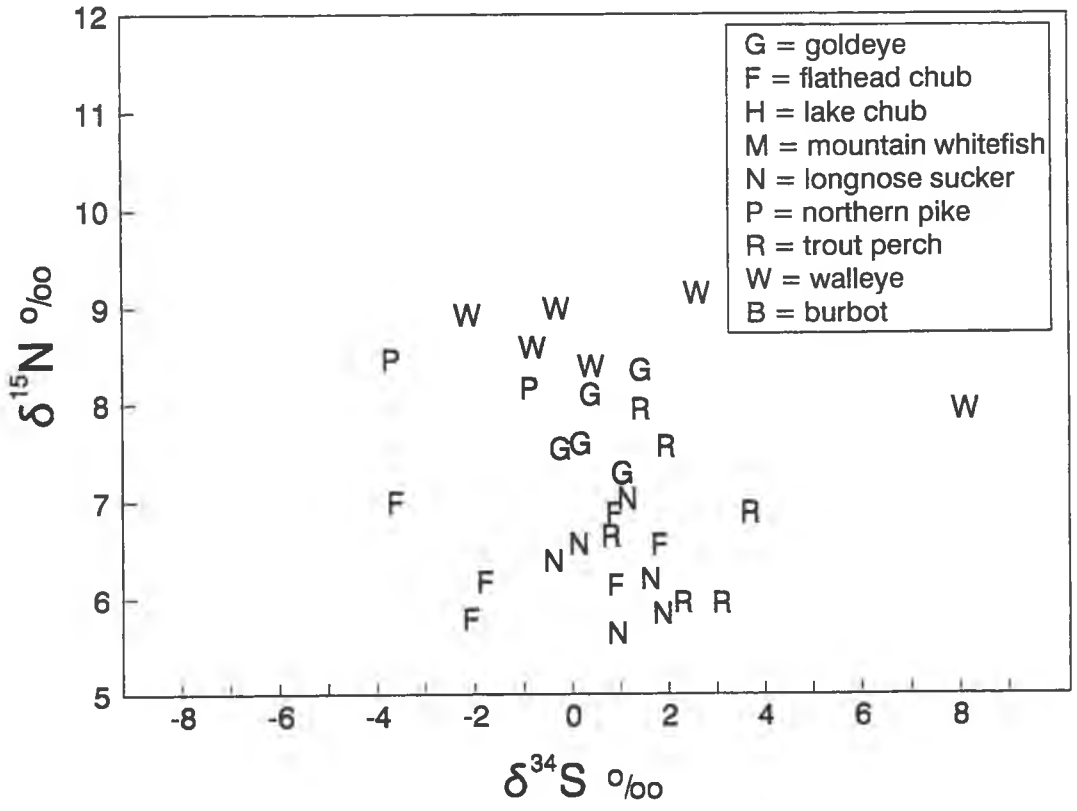

Figure 6. Sulfur and nitrogen isotopes in fish samples near the 300 km location in the Athabasca River.

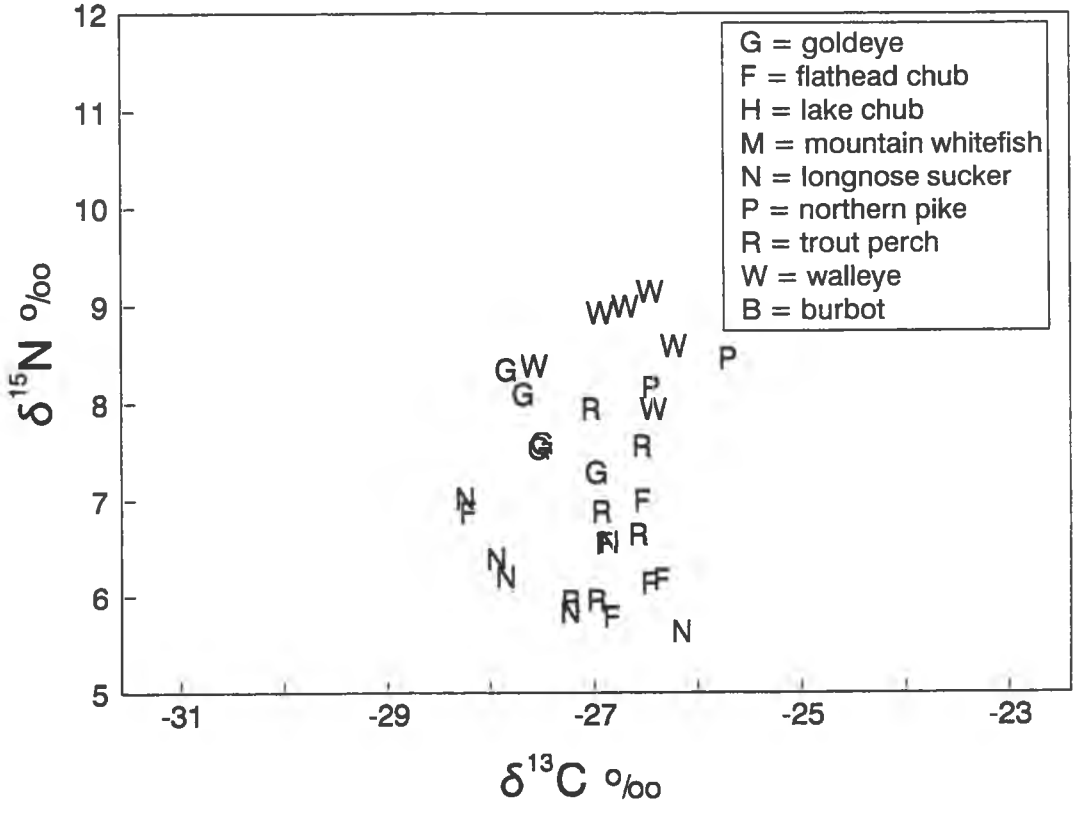

Figure 7. Carbon and nitrogen isotopes in fish samples near the 300 km location in the Athabasca River.

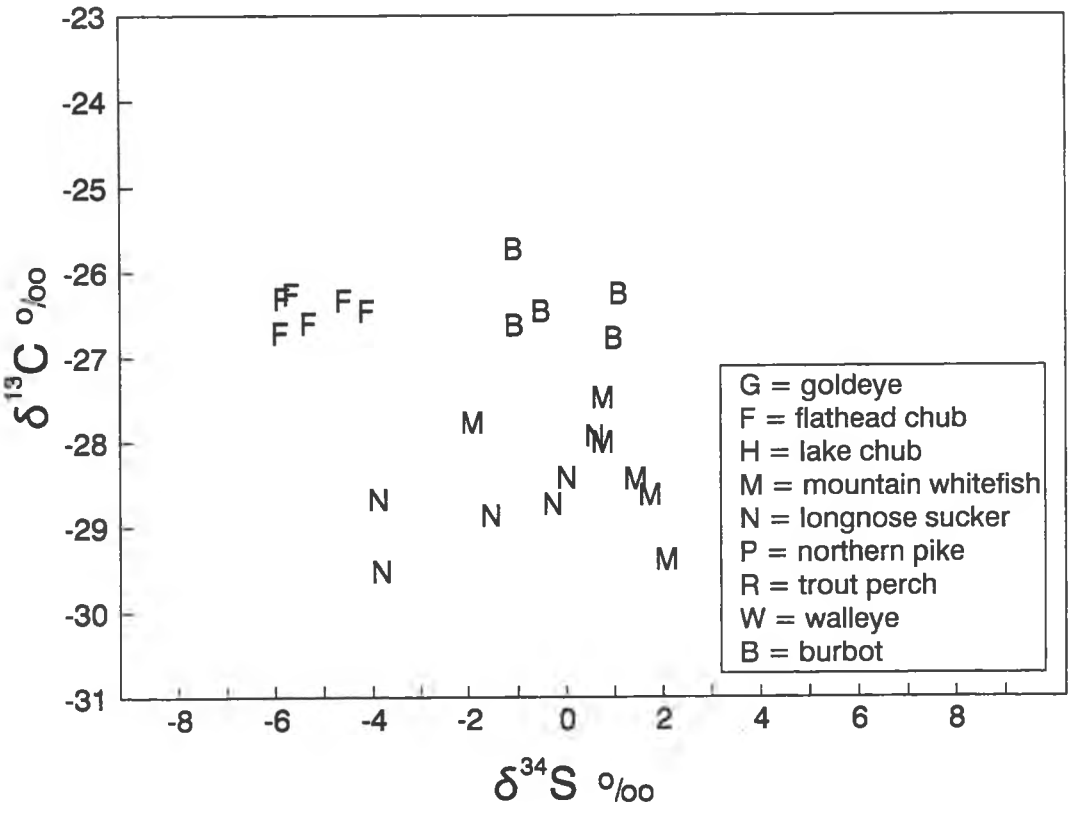

Figure 8. Sulfur and carbon isotopes in fish samples near the IS1 location in the Peace River.

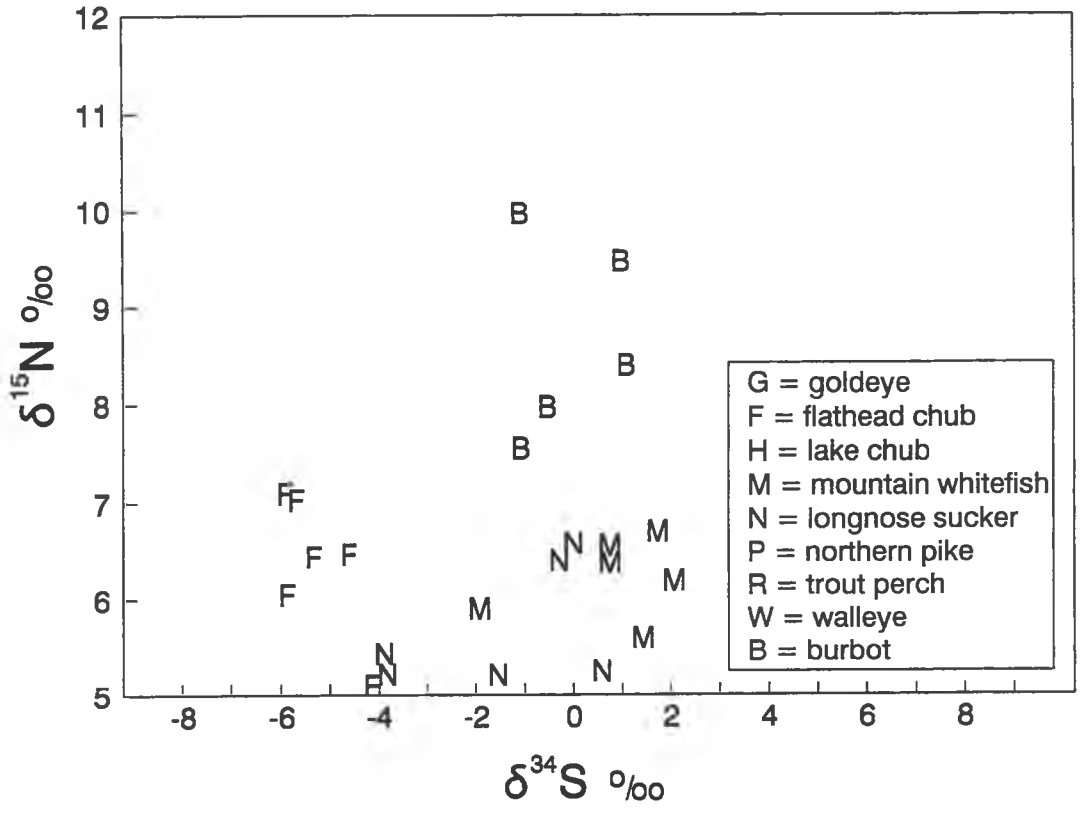

Figure 9. Sulfur and nitrogen isotopes in fish samples near the IS1 location in the Peace River.

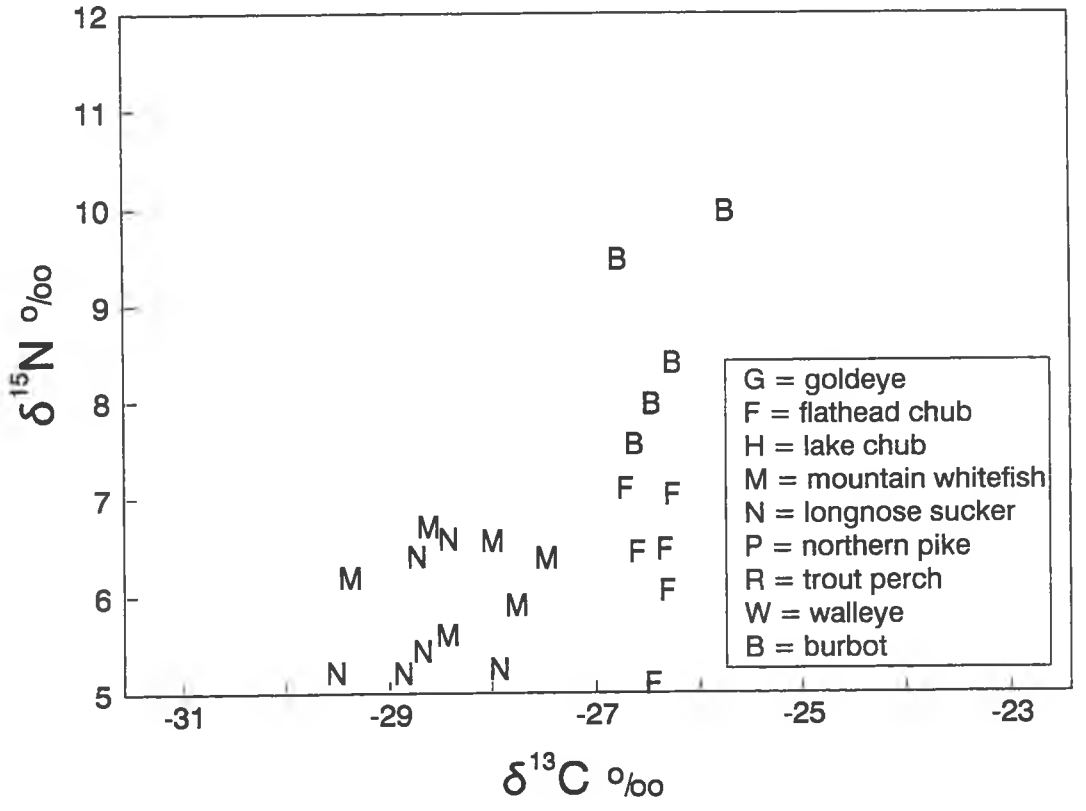

Figure 10. Carbon and nitrogen isotopes in fish samples near the IS1 location in the Peace River.

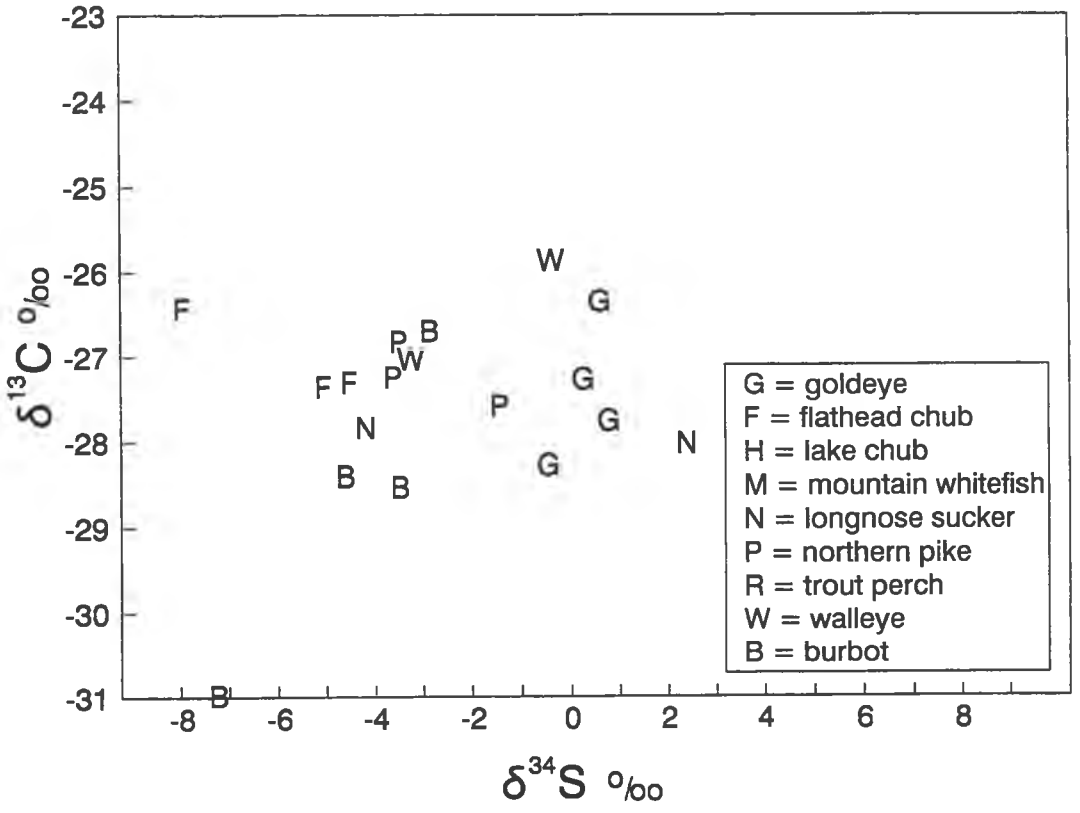

Figure 11. Sulfur and carbon isotopes in fish samples near the IS11 location in the Peace River.

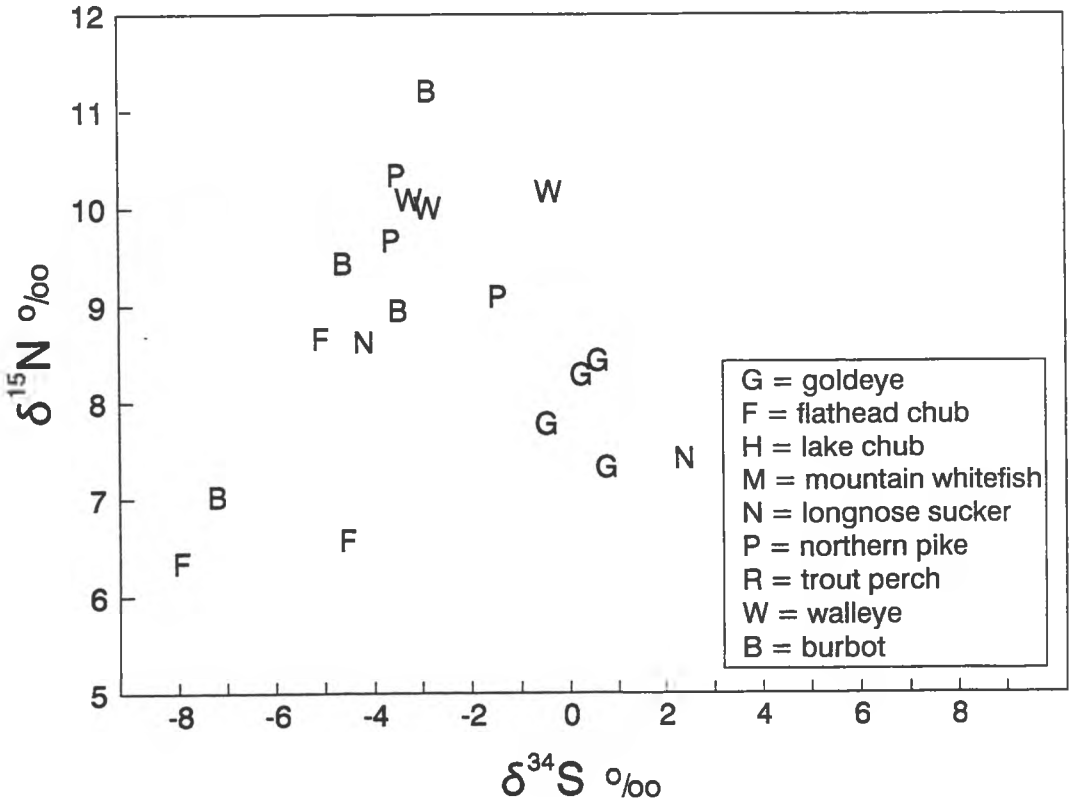

Figure 12. Sulfur and nitrogen isotopes in fish samples near the IS11 location in the Peace River.

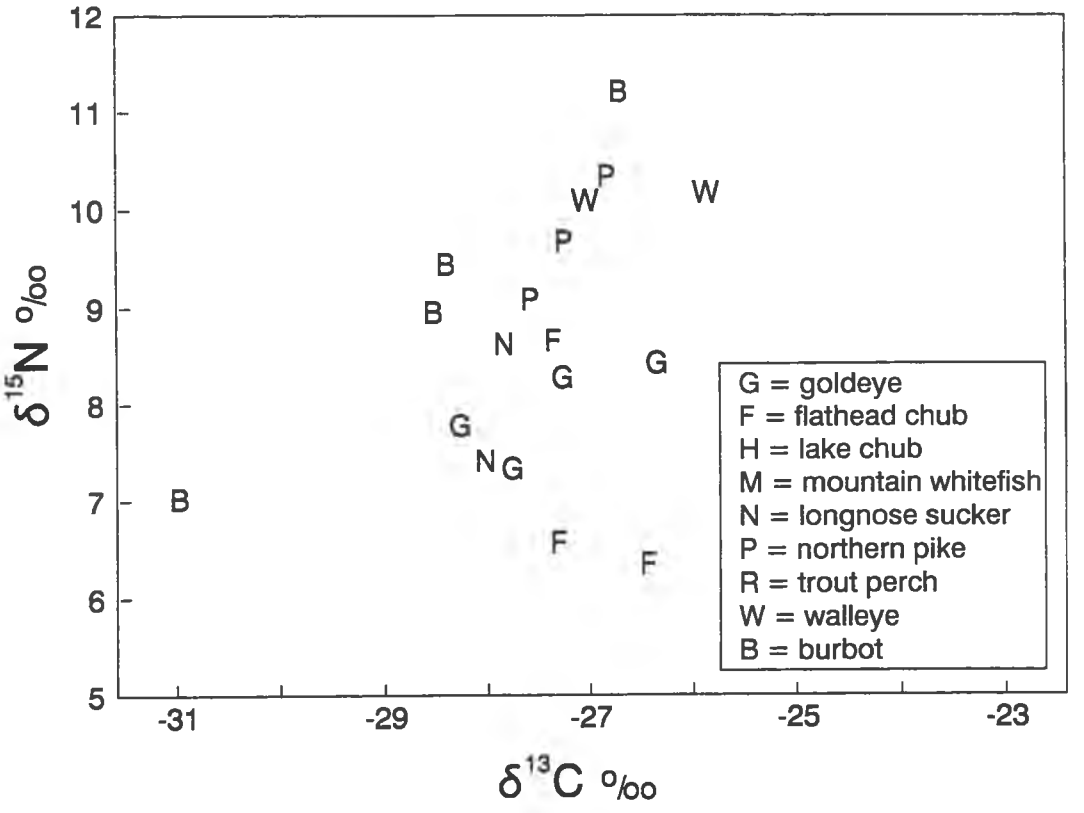

Figure 13. Carbon and nitrogen isotopes in fish samples near the IS11 location in the Peace River.

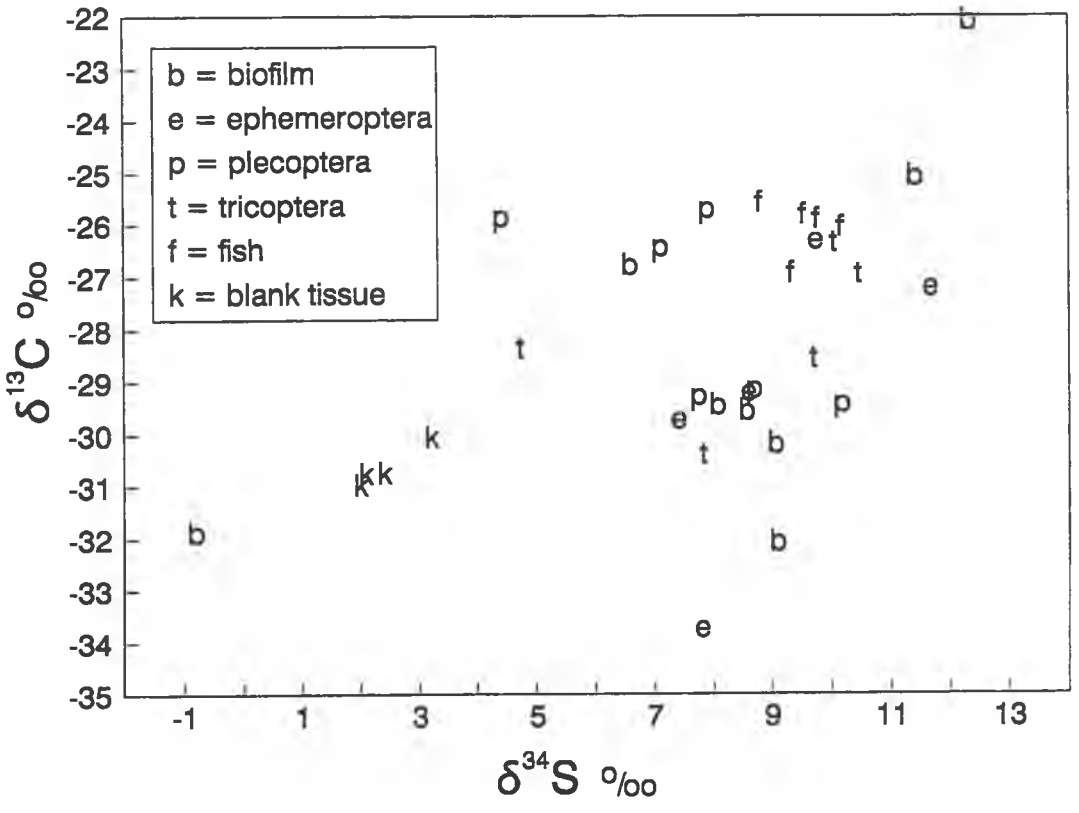

Figure 14. Sulfur and carbon isotopes in samples from sample set #1, Athabasca River.

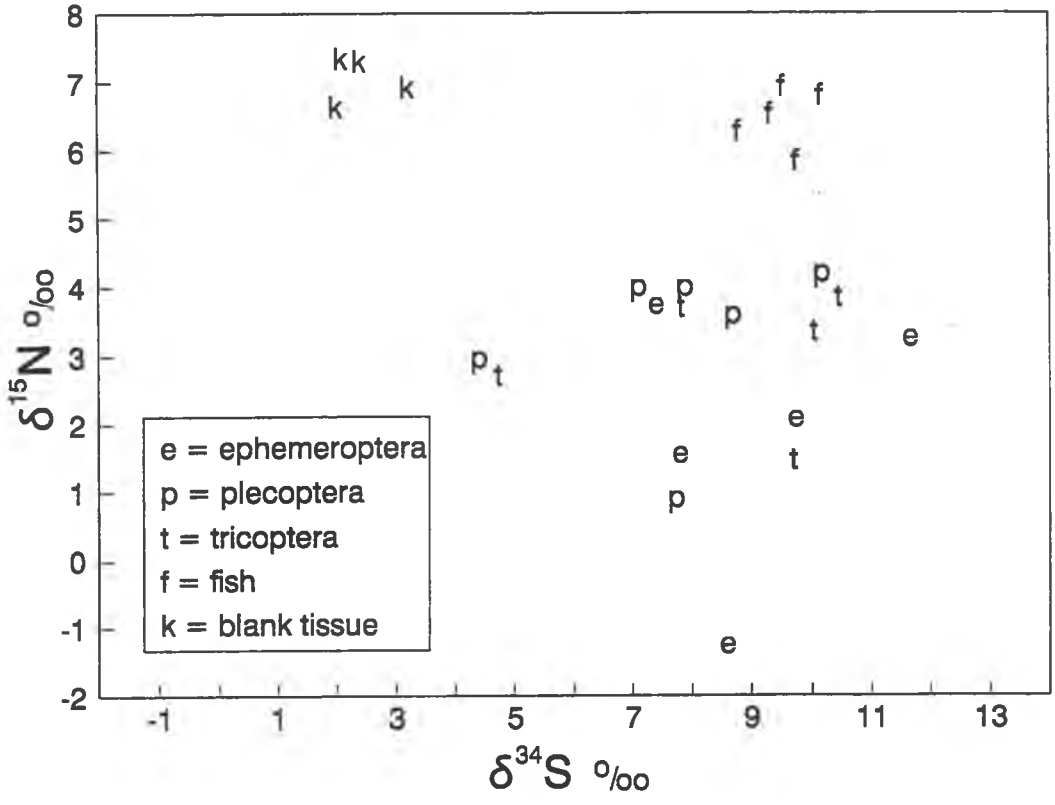

Figure 15. Sulfur and nitrogen isotopes in samples from sample set #1, Athabasca River.

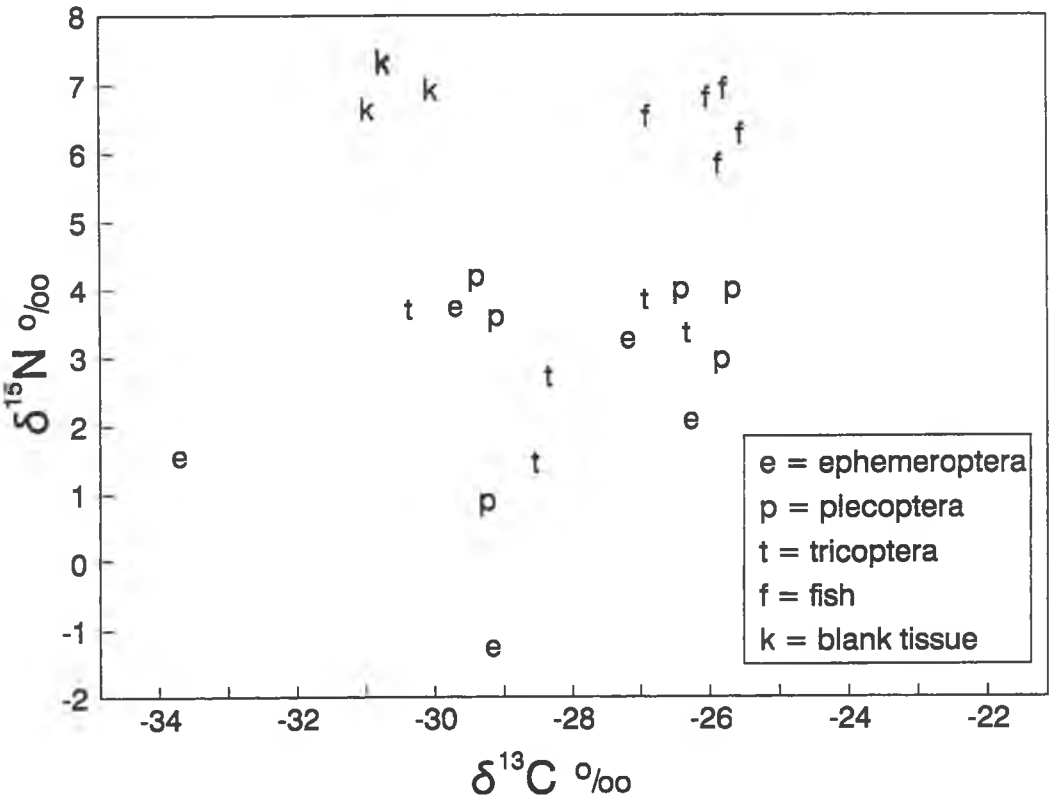

Figure 16. Carbon and nitrogen isotopes in samples from sample set #1, Athabasca River.

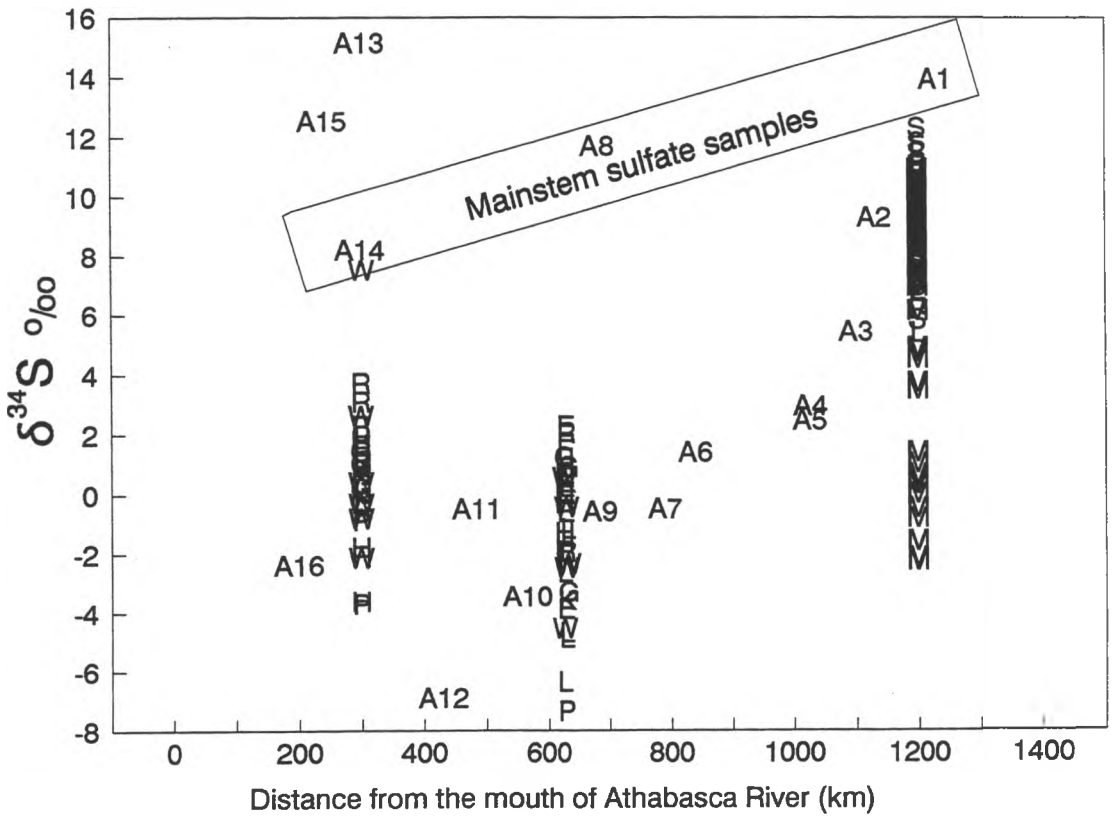

Figure 17. Sulfur isotopes in fish at three sites and in dissolved sulfate of the tributaries and mainstem along the length of the Athabasca River. Labels are the same as in Table 1 and Figures 2-16.