WINDERMERE LAKE

WATER QUALITY CHANGES OVER THE PAST 300 YEARS AS DETERMINED FROM A BOTTOM SEDIMENT CORE

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Executive Summary

Windermere Lake is an important recreational feature in the East Kootenays. It is particularly so to the growing population around the lake who also rely on the lake as a source of drinking water. The question for residents and those involved in land and water management is whether past and present human activity (agriculture, industry and, in particular, residential development with on-site sewage disposal) has had any negative effects on lake water quality?

Various water quality monitoring efforts over the past 25 years have concluded the lake has reasonably good water quality, is not showing definite signs of eutrophication, nor is there serious bacterial contamination from the septic field disposal of sewage of the population on the east side of the lake. More subtle indications of concern, such as possible slight increases in lake-wide phosphorus and septic field leachate "hot spots" with associated high bacterial counts, have been offset by the knowledge that the lake has a high flushing rate.

It is difficult to rely on water quality sampling to determine subtle, long-term changes in lakes. Sampling seldom begins prior to human influence, which may extend into the last century. Years, if not decades, of sampling may be necessary to detect changes, which must be distinguished from seasonal and annual variation and unavoidable analytical error. Chemical and biological evidence from bottom sediment cores has become an invaluable tool in reconstructing the water quality history of lakes, often uncovering changes in flora and fauna that could never be detected through water sampling.

A sediment core from Windermere Lake, sampled in 1998, shows that water quality began to change around 1950, concurrent with population growth. There is some evidence of slight eutrophication (increasing nutrients causing more algal growth) coupled with a change in the composition of the phytoplankton community. Types of algae commonly associated with clean water and low nutrient levels, have been displaced by forms that may cause taste and odour problems in water supplies. Water users on systems with intakes drawing from the bottom of the lake may detect unpleasant odours or taste during the winter when the lake is covered with ice and snow.

The findings of this study do not mean that there is currently a serious problem in drinking water quality in Windermere Lake. A consumer's personal preferences and experience heavily influence the acceptability of drinking water. Windermere Lake water quality was probably better prior to 1950 than it is today, though it is not certain that a consumer would be able to distinguish the change.

The most important finding of this study is that there is a significant amount of evidence that Windermere Lake water quality is slowly deteriorating. The study has produced little hard evidence linking this change to increased human settlement in the basin but this is circumstantially the most logical cause.

Acknowledgements

The coring apparatus and skill to use it was kindly provided by Dr. Richard Nordin during his lake coring tour of southern B.C. in the summer of 1998. Dr. Gordon Kan of the Pacific Environmental Science Centre handled the management of the various university contracts. The report was reviewed by Ms. Julia Beatty, Dr. Richard Nordin, and Mr. Robert Wetham.

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Introduction and Methods

On July 23, 1998 a core of bottom sediment was taken from the deepest point in Windermere Lake, off the Akiskanook resort, by staff of the Ministry of Environment, Lands and Parks. Thin 5 mm sections of the core were stored in plastic cups and forwarded to Dr. Brian Cumming at Queen's University in Kingston, Ontario. Dr. Cumming's laboratory analyzed some of the sections for fossil algal remains. These single-celled algae are called diatoms and their cell walls, comprised of silica and called "frustules", remain after death like shells. These frustules are unique to each species and allow the make-up of the diatom community in each slice of the sediment core to be determined.

Changes to the diatom community occur when water quality, particularly the nutrient phosphorus, increase or decrease. The eutrophication of a lake (increase in algal growth) is usually caused by an increase in phosphorus and is often the result of human settlement (accelerated erosion, sewage, lawn fertilizer, etc.) or other human endeavours such as agriculture and industry. Lake eutrophication is often a slow process taking decades before effects can be perceived by other than sophisticated technical studies. By the time water use (drinking supplies, recreation, etc.) become noticeably impaired, the effort required to alter the human activity related cause can be substantial and expensive.

Sub-samples of the core were forwarded by Dr. Cumming to MYCORE Ltd. laboratories for Lead-210 (210 Pb) dating and to Dr. Peter Leavitt at the University of Regina for plant pigment analysis. Remaining sediment from these analyses was returned to MELP and analyzed by our contract laboratory for a number of metallic elements. Plant pigments, characteristic of certain types of algae, also change in relation to algal and larger aquatic plant community changes. Lead-210 dating allows sections of the core to be chronologically dated so changes in the algal community and water quality can be related to historical events in the lake basin such as forest fires, agriculture or human settlement.

Two technical reports by Drs. Cumming and Leavitt are appended; this brief cover report is an attempt to provide a less technical summary of these findings combined with the elemental analysis performed by MELP.

The intent of this work is to determine, to the extent possible, whether Windermere Lake water quality has changed over the recent past and, if so, how significant the change. There is some discussion about the reasons for down-core change and whether human settlement may be a cause. This information should be useful to local government in future land-use planning.

Field Observations

The core was taken in a depth of approximately 3.5 meters (maximum lake depth is about 6 meters, off Timber Ridge). The lake is 1.6 km across at the sample point so the core was about 800 meters from either shore. There was a small amount of *Chara sp.* or stonewort on the surface of the core but no other aquatic vegetation in the immediate vicinity. The core had no obvious banding, though the top 3 cm was light brown and the rest was a uniform dark grey. The

core had a strong sulphide odour indicating an absence of oxygen, a condition in which organic material, like plant pigments, are well preserved.

Core Dating and Diatom Community Changes

The following is a summary of Dr. Cumming's report *Paleolimnological analysis of Windermere Lake, B.C.—Final Report (March 1999)* (Appendix I) with some possible explanations for the findings as they relate to lake basin history.

The ²¹⁰Pb profile and percent organic matter suggest some mixing of surface sediments which is not surprising in a shallow lake with a large surface area like Windermere Lake. The mixing of surface sediments due to wind and currents is not a desirable feature for lake coring because older and newer sediments near the top or the core are mixed during randomly occurring wind events. The sulphide smell of the core, taken in mid-summer after considerable wind exposure, indicates little or no oxygen in the sediments suggesting that sediment mixing is confined to the upper few millimeters.

The fact that the bottom of the 35 cm core dates back to 1700 indicates a slow sedimentation rate, an average of 1.17 mm/year. Sediment deposited in the center of lakes is derived from erosion of the basin, transported in via inflowing streams, and from settling biological material that has grown in the lake. Windermere Lake has a relatively small volume compared to the amount of water flowing through, mostly via the Columbia River. This means the lake has a high flushing rate or short water residence (McKean and Nordin 1985, reported the lake volume replaced every 47 days). Rapid flushing means the internal production of sediment is relatively low, a condition less than ideal for sediment core analysis. The inflowing Columbia River passes through a series of wetlands (Mud Lake and Tatley Slough) before entering the lake, which may serve to reduce sediment loads.

The sedimentation rate and the percent organic matter began to increase around 1920, peaking in the late 1940s, then falling back to historic levels from 1960 to the present. This may have been due to land disturbance from logging or cattle ranching, which increase erosion and sediment transport to the lake. Forest fires may also have been a factor, though response to such events is usually more dramatic and short lived, and surface sediment mixing due to wind might obliterate the evidence of such events. Whatever the cause of the increased sedimentation rate, it does not appear related to settlement, which did see an increase from 1920 to 1960 but has greatly accelerated since 1970.

The diatom assemblages found in Windermere Lake sediments were dominated by benthic species (those living on the surface of the sediments) with some epiphytic forms (those living on aquatic plants). Planktonic species (those living in the water column), the most abundant forms in deeper lakes with smaller littoral zones, were relatively rare in Windermere Lake. In deeper lakes (>15 meters) benthic species would be a minor component, only living in the shallow margins because their is insufficient light penetration for photosynthesis. Windermere Lake is shallow enough throughout so that sufficient light reaches the bottom for algal growth and there is abundant large aquatic plant growth upon which epiphytic algae grow. The database used by Cumming to infer historical water quality is comprised of the over 200 B.C. lakes that are

generally deeper, with minor benthic components (Wilson et al. 1996). This means that diatom analysis is less useful in reconstructing historic water quality in Windermere Lake than other core methods employed.

Dr. Cumming's analysis does show some minor changes in the diatom community structure starting around 1950, with the loss of a few species and the appearance of others. Unfortunately the species involved are not well represented in the database from other B.C. lakes, which is used to infer changes in lake phosphorus. This means that predictions of the change in total phosphorus in Windermere Lake over time must be considered preliminary.

The observed changes in the diatom community do generally correspond with an increase in settlement around the lake. Of a total of 1290 lots subdivided on the east side of the lake from 1940 to 1986, 623 (48%) were established between 1947 and 1957 (Whetham, personal communication 1999). Although the diatom community change evidence from the core is not strong, it does suggest a subtle change in water quality, probably an increase in nutrients, and is circumstantially associated with accelerated settlement since 1950.

Fossil Plant Pigments

The following is a summary of Dr. Leavitt's report Analysis of Fossil Pigments from Windermere Lake (March 1999) (Appendix II).

Many algal photosynthetic pigments are unique to certain taxonomic groups and the various types of algae found can influence water quality. These pigments decompose in the presence of oxygen but are preserved in sediments when oxygen in the overlying water is low or when diffusion into the sediment is limited. Being shallow and wind-blown, the overlying water in Windermere Lake is rarely depleted of oxygen, save perhaps under ice and snow cover. The low sedimentation rate and compact nature of the bottom sediment would seem to be limiting the downward diffusion of oxygen to the upper most layer. The sulphide smell of the core, evidence of an absence of oxygen, confirms this.

Leavitt concludes, based on the increase in newer sediments of certain pigments common to all algae, that there has been a slight increase in algal production (eutrophication) since about 1960. Other changes in specific pigments indicate a shift in the algal community away from diatom dominance and toward green, blue-green and chrysophyte types over this period. Unlike diatoms, these other forms of algae do not leave behind fossil "shells", so photosynthetic pigments, preserved in sediments void of oxygen, are the only evidence of their historical representation in the phytoplankton community. Leavitt, who was given no prior information about Windermere Lake, describes these algae as "bloom-forming" types and states that the pigment evidence does not allow distinction between surface forms that people would see or deep-water forms that would occur unnoticed. Windermere Lake, of course, has no deep water and these algae have not yet reached bloom proportions. The lake water might appear less clear and greener in color today compared to pre-1960, if one could make such a visual comparison, but the difference would probably be subtle.

Sampling done by MELP in the lake in 1982 and 1983 indeed showed the dominance of two blue-green genera, *Gomphosphaeria* and *Chroococcus*, and the chrysophyte *Dinobyron* in the late-summer/fall and the diatoms *Synedra* and *Cyclotella glomerata* (McKean and Nordin 1985). Standard Methods for the Examination of Water and Wastewater (APHA 1975) identifies *Gomphosphaeria*, *Chroococcus*, *Dinobyron*, *and Synedra* as types of algae that can cause taste and odour problems in drinking water.

Algal pigment analysis also shows the presence of purple-sulphur bacteria in Windermere Lake. These photosynthetic bacteria are usually found in deeper lakes with permanent stratification and a bottom layer of water (hypolimnion) completely void of oxygen. The bacteria grow in the region at the top of this anoxic layer where there is low but sufficient light. Their photosynthetic pigments often give the water in this region a purple color, thus the name. The presence of these bacteria is not desirable in a lake because the permanent lower strata of the lake, in addition to being void of oxygen and thus uninhabitable to fish, accumulates odorous by-products of organic decay like methane, ammonia and hydrogen sulphide. Windermere Lake is too shallow to develop such stratification. These bacteria, which Leavitt states are at lower levels than strongly stratified lakes, probably grow on the surface of the sediments during winter ice and snow cover when oxygen depletion occurs in a small zone immediately above the sediments where low but sufficient light penetrates. Another requirement for the growth of these bacteria is sufficient quantities of sulphur, seldom in short supply in permanently stratified lakes. Windermere Lake receives large quantities of sulphate from the hot springs upstream and the gypsum (calcium sulphate) deposits in Windermere Creek.

Of particular concern is Leavitt's finding that the purple-sulphur bacterial pigment has increased 5 to 10 fold in the lake since about 1960. The consequence of such a change to drinking water supplies may be a deterioration in aesthetic water quality during the winter as quantities of sulphides, ammonia and methane increase, particularly in water intakes drawing from near the bottom. Leavitt states that the reasons for this increase are greater oxygen deficits in bottom waters due to stronger stratification or increased light penetration. Given the shallow depth of the lake neither of these causes seems likely. Because these increases in purple-sulphur bacteria occur at the same time as the shift in the phytoplankton community from diatoms to blue-green and chrysophytes, the causes are probably the same. This is also the period in the lake's recent history of the greatest human settlement. Though these associations seem reasonable cause-effect relationships the available evidence is purely circumstantial. Unfortunately conclusive evidence that human-settlement has caused a deterioration in water quality may only be forthcoming if the degradation becomes severe.

Elemental Analyses

The results of elemental analysis of selected sections of the sediment core are listed in Table 1 and summarized in Figures 1-4. Unfortunately there was no sediment left in the sections from the upper 3 cm of the core because it was all required for other analyses. Elemental analysis thus covers a time period from about 1700, at the core bottom, to 1983.

The alkaline-earth metals, (in order of abundance) calcium, magnesium, barium, strontium, and beryllium (Figure 1, beryllium not graphed, see Table 1), are among the most common cations in

the lakes and streams of the East Kootenays. Calcium and magnesium are by far the most abundant and are the main causes of water hardness leading to scaling problems in potable water. These elements are found throughout the watershed as carbonates such as limestone or chalk (calcium carbonate), magnesite (magnesium carbonate) or as sulphates, e.g. gypsum (calcium sulphate), barite (barium sulphate). Weathering and erosion release these minerals which are then transported via tributaries to the lake. Human activities such as agriculture, mining, logging, road construction and settlement can accelerate erosion leading to increases in the deposition of these elements in lake sediments (Wetzel 1983).

Why calcium and strontium show increasing trends, commencing around 1950, while magnesium and barium show decreasing trends over the same period (Figure 1) is unknown. Gypsum deposits (calcium sulphate) in the south fork of Windermere Creek are unlikely the source of increasing calcium because sulphur shows an opposite, decreasing trend (Figure 3).

A number of other elements exhibit similar patterns of change over time. Quantities of iron (Figure 2), potassium and sulphur (Figure 3), aluminium, and titanium (Figure 4) all begin to decline around 1950. The inputs of extremely inert elements such as titanium are used to determine erosion rates in lake basins (Wetzel 1983). Falling titanium concentrations in this core indicate that erosion rates are decreasing in the Windermere Lake drainage basin from 1950 to 1983, and this seems corroborated by Cumming's sedimentation rate estimates which also decline after 1950.

Boron (Figure 3) shows a different pattern than any other element. Core concentrations remained uniformly low at around 50 μ g/g from the bottom (1700) until around 1960 when they increased to over 200 μ g/g. This may be an indication of human related sources entering the lake as boron is found in detergents, water softeners, pesticides, and fertilizers. This increase in boron, an algal micronutrient, may be a contributing factor in the change in the phytoplankton community, observed at a similar level in the core, by providing a competitive advantage to certain species that did not previously exist (Wetzel 1983).

Phosphorus, the most critical nutrient controlling algal and weed growth, appears to have steadily increased since about 1800, almost doubling by 1983. Iron, and to a lesser extent manganese, are important in controlling phosphorus concentrations in lakes by chemically binding the phosphorus in insoluble forms in the sediments. Sulphur "competes" with phosphorus for iron and manganese and the addition of sulphate to lakes has been used as a means of "fertilizing" by increasing the availability of the phosphorus already present in the lake (Wetzel 1983). Windermere Lake has ample quantities of sulphate from its drainage basin so that iron complexing of phosphorus is probably less important than in a lake with lower sulphur levels. The close association between iron and sulphur in the sediments can be seen in the core graphs of each element (Figures 2 and 3) which are almost identical. The presence of large quantities of ferrous sulphide in the sediments was confirmed by the "rotten egg" smell of the core. The reason for the simultaneous decrease in iron and sulphur, commencing around 1950, is unknown.

Calcium, which has increased 87% in the core from 1950 to 1983, probably exists mainly as calcium carbonate, which can also bind phosphorus. While the cause of the increase is unknown, this may explain an accelerated increase in phosphorus over the same period. Unless the inflow

of phosphorus to the lake has also increased, the consequence of an increase in sediment phosphorus would be a decrease in available phosphorus in the water column. McKean and Nordin (1985) reported an apparent increase in phosphorus in the lake between 1973 and 1983, probably relating to human activities, but caution that differences may only be seasonal variation. Monitoring subtle changes to available phosphorus in lakes over decades is a difficult proposition because of annual and seasonal variation and technical challenges, though the effects on the phytoplankton community may be significant.

Conclusions

- Diatom community reconstruction from sediment core sectioning are a less useful tool for determining historic water quality in Windermere Lake than in deeper lakes. Light penetration to the bottom throughout the lake means that the benthic component is much larger compared to the phytoplankton component than in most of the B.C. lakes used to develop Cummings' total phosphorus inference model.
- Notwithstanding the above, there have been subtle changes in the diatom community in the lake starting around 1950 which are probably associated with a change in water quality.
- ➤ Algal pigment analysis indicates a slight eutrophication since 1960 and a shift from cleanwater diatom species to varieties of phytoplankton that are potentially bloom-forming and are associated with taste and odour problems in potable water supplies.
- There has been an increase in photosynthetic purple sulphur bacteria in the lake sediments since 1960. This means that dissolved oxygen is completely absent from the interstitial water in the uppermost sediments, probably during winter ice cover. A consequence of this condition could be the accumulation of undesirable anoxic by-products such as hydrogen sulphide, ammonia and methane in water near the bottom of the lake, under winter ice, where some water supplies draw from.
- > Chemical analysis of the core shows levels of a number of elements decreasing in abundance since 1950 and a small number increasing over the same period. This indicates a change in water quality in the lake since 1950, which corresponds with core observed changes in the algal communities and, circumstantially, with the sustained increase in human activity, mainly in the form of settlement.
- An increase in phosphorus in the sediments since 1950 may be an indication of eutrophication, caused by human activity. The increase matches a similar increase in calcium which, as calcium carbonate, probably serves as a phosphorus-binding agent. Were this latter process alone occurring, without an increase in phosphorus entering the lake, the result would be a more oligotrophic state (less nutrient, clearer water) which is the converse of the algal evidence.

Recommendations

Future lake monitoring programs should include some effort to confirm the findings of this sediment core study, including the following:

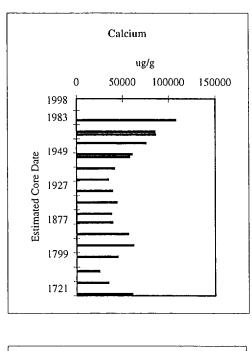
- Phytoplankton sampling over one year, including under various ice-cover conditions (i.e. heavy snow cover in January, clear ice in February/March) to confirm the dominance of colonial blue-green and green species in relation to diatoms and determine how the community structure changes over the seasons. This effort should be accompanied by nutrient sampling employing low-level detection analysis and should also include some analysis of trace elements in the water column and perhaps the major inflowing streams.
- Purple-sulphur bacteria should be sampled in surface sediments several times through the year, focusing on the ice-cover period. In addition to taxonomic identification and enumeration of species, group specific pigments may be analyzed as a means of determining the abundance of this group. Water just above the lake bottom should be sampled at the same time and analyzed for total sulphides, ammonia, and trace metals and a careful field survey of dissolved oxygen, pH and oxidation-reduction potential (ORP) done at various depths.

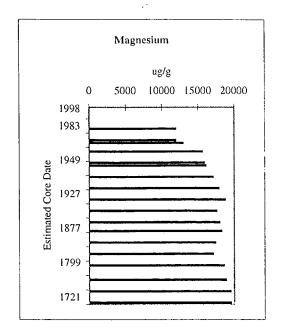
References

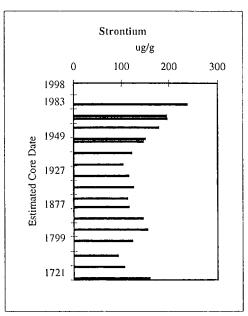
- APHA (American Public Health Association). Standard Methods for the Examination of Water and Wastewater. 14th ed. 1976.
- McKean, C.J.P. and R. N. Nordin. Upper Columbia River Area: Columbia and Windermere Lakes Sub-Basin Water Quality Assessment and Objectives Technical Appendix, Water Management Branch, B.C. Min. of Environment, 1985. 114p + map.
- Wetzel, R.G. Limnology. Second Edition. Saunders College Publishing. New York. 767p.
- Wilson, S.E., B.F. Cumming and J.P. Smol. 1996. Assessing the reliability of salinity inference models from diatom assemblages: An examination of a 219 lake dataset from western North America. Can. J. Fish. Aq. Sci. 53: 1580-1594.

Figure 1. Windermere Lake Sediment Core

Alkaline-Earth Elements







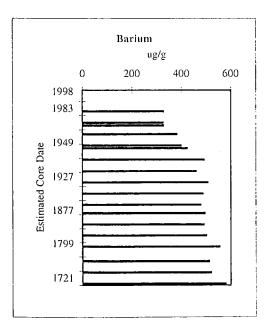


Figure 2. Windermere Lake Sediment Core

Nutrients and Binding Elements

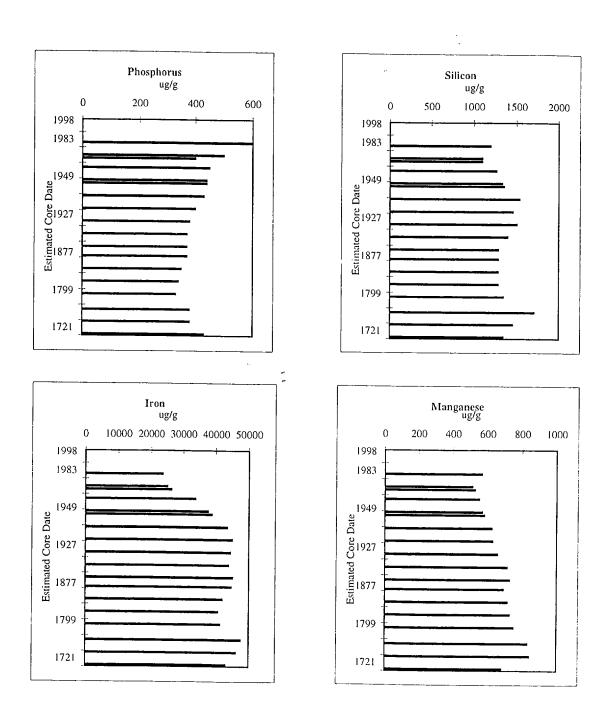


Figure 3. Windermere Lake Sediment Core

Alkali Metals, Sulphur and Boron

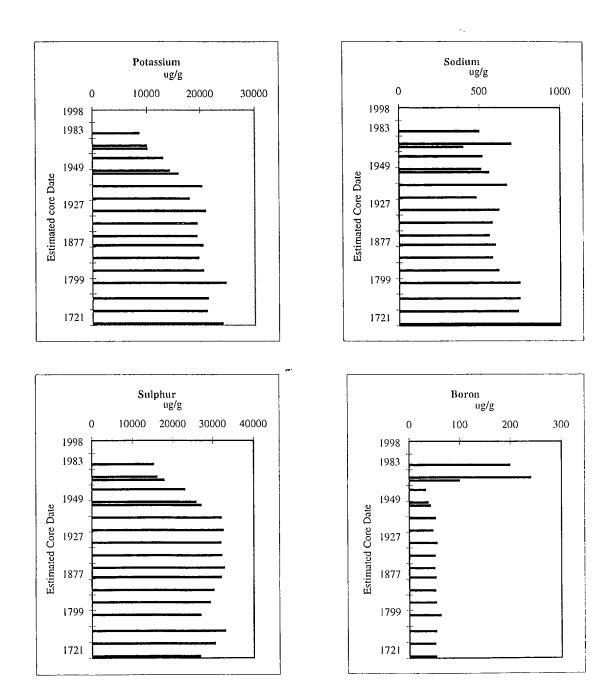


Figure 4. Windermere Lake Sediment Core

Metals

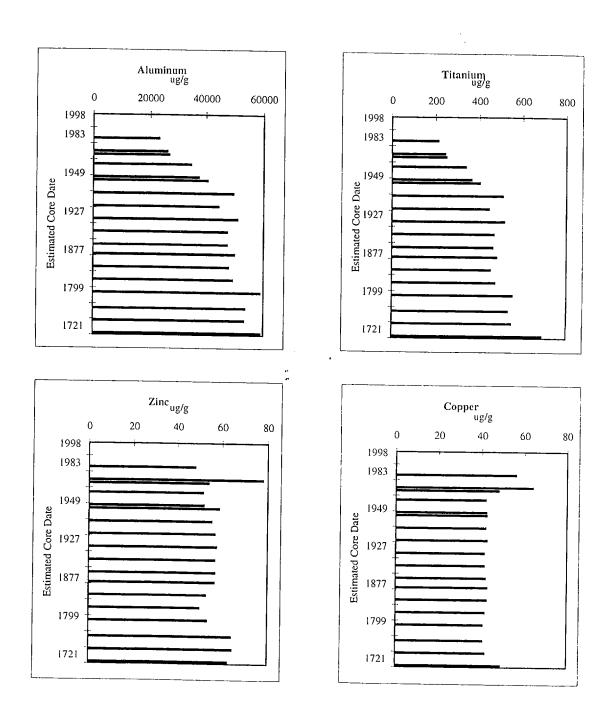


Table 1. Elemental Analysis of Windermere Lake Sediment Core

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Zinc		84	78	51.6	51.8	55.4	22	57.6	56.9	57	56.9	83	8	53.5	64.2	84.5	62.6
Vanadium		30	88	38	14 4	22	49	57	\$2	51	*		54	8	85	- 26	8
Titendum		213	243	339	366	510	446	517	469	463	481	452	474	554	532	248	689
Strontium		238	195	671	151	122	104	116	126	113	116	4	155	123	92.4	90	160
Silicon		1200	1100	1270	1340	1540	1460	1510	1400	1290	1290	1290	1290	1350	1710	1460	1350
Sulphur	<u> </u>	15200	16100	23000	25800	32100	32600	31900	32200	32800	32100	30200	29300	27000	33000	30500	26800
Phosphorus		009	800	650	440 440	430	400	380	370	370	370	350	340	330	380	380	430
Sodium	 	2009	400 700	520	510	029	480	920	280	280	009	280	920	750	750	740	1000
Potendum		8650	9980	13000	14300	20300	00621	21000	19400	19300	20500	19700	20600	24700	21400	21200	24100
Magnesium		12000	12000	15600	15900	17100	17900	00881	17600	18000	18300	17400	17100	18600	18900	19500	19600
Vanganese		268	513	552	571	627	631	999	716	730	694	716	729	750	832	843	682
Iron		23700	25100	33800	37700	43500	45000	44500	43900	45200	44800	42100	40700	41400	47600	46200	43100
Cupper		88	2 8	41.9	42.2	41.8	42.6	413	41.3	4	42.6	42.4	41.5	40.6	40.6	41.6	49
Chromium		78	10	38	39.5	48.5	44.1	- 21	49.6	45.4	47.6	45.4	45.5	55.1	53.6	995	53.9
Calcium		108000	85600	75800	60600	41600	34600	39100	44100	38100	39300	26100	62100	44700	25000	34700	00609
Rerylllum		70	2 2	2.6	2.5	2.7	2.5	5.8	2.7	2.7	2.8	5.9	3.1	3.2	27	2.8	3.5
Rariom		329	327	383	424	492	460	808	487	479	495	491	109	555	513	521	280
Boron		200	240	33	38	25	47	55	51	20	ß	22	23		83	51	53
Aluminum		23200	26200	34700	37400	49600	44600	51100	47600	47500	20100	48000	49400	29000	53800	53400	29100
	0 2 0 3	25 30 30 50 50 50 50 50 50 50 50 50 50 50 50 50	2 8 8 8 8	02 25 80 80	8 8 8 8 8	115	135	55 59 5	175 180 183	200 200 205	210 215 220	230 230 240	250	272 273 273 280	3 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	315 320 325	340
_1	1998	1989	1970	1958	1949	1942	1934	8161	<u> </u>	}	1877	1821	1825	1799	1773		

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APPENDIX I

Paleolimnological Analysis of Windermere Lake, B.C. Final Report (March 1999).

Dr. Brian Cumming, Assistant Professor Queen's University Kingston, Ontario

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Paleolimnological analysis of Windermere Lake, B.C -- Final Report (March 1999).

Contract Number - P.O. 812000

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Supplier: Queen's University, Contact person: Dr. Bruce Hutchinson, Office of Research Services, Ph.: (613) 533-6081; FAX: (613) 533-6853

List of Figures and Appendices:

Fig. 1 Summary of analyses for Windermere Lake.

Fig. 2 Stratigraphic distribution of diatom taxa in the Windermere Lake core.

Appendix A: Summary of ²¹⁰Pb and LOI data, and diatom analyses. Appendix B: Summary of data used in calculating ²¹⁰Pb dates and ²¹⁰Pb output.

Appendix C: Summary of relative abundances of diatom taxa in Windermere Lake.

BACKGROUND

Windermere Lake was cored on July 23, 1998 by Rick Nordin and Les MacDonald. The core was retrieved using a modified K-B corer (internal diameter ~ 6.35 cm) from the deep basin. On shore the core was sectioned into 0.5-cm intervals into 120-ml plastic containers. These samples were shipped on ice to Queen's University where they were stored in our coldroom at 4°C. Each container was weighed to determine the total wet weight of sediment then subsampled for 210Pb, diatom and pigment analyses. Twenty intervals (every 2 cm) were subsampled for diatom and pigment analyses, and sixteen intervals for 210Pb analysis. Subsamples for analysis of pigments were sent to Prof. Leavitt at University of Regina. Prepared samples for 210Pb analysis (see below) were sent to MYCORE Ltd.

METHODS

210-Pb Dating and Percent Organic Matter

The wet weight of the sediment was determined for all the subsections of the core. Sixteen subsamples of wet sediment from each core were weighed and oven-dried (24 hr at 105°C) and reweighed to determine percent water and dry weight of the sediment. Samples that were submitted for ²¹⁰Pb analysis were ground to a fine dust by use of a pestle and redried overnight at 105°C. The weight of this dried sediment was recorded to four

decimal places after it was put in a tared plastic digestion tube for determination of ²¹⁰Pb activity that was shipped to MYCORE Ltd.

Percent organic matter for each of the 16 210 Pb samples was determined using standard loss-on-ignition methods (Dean, 1974). A known quantity of dried sediment (recorded to four decimal places) was heated to 550°C for 2 hours. The difference between the original weight of the sediment and the weight of sediment remaining after ignition was used to estimate the percent of organic matter in each sediment sample.

²¹⁰Pb activities were estimated from determination of 209-Po and a tracer of known activity by alpha spectroscopy. Unsupported ²¹⁰Pb is calculated by subtracting supported ²¹⁰Pb (the baseline activity determined from bottom samples of the core) from the total activity at each level. The sediment chronology and sedimentation rates were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978) from the estimates of ²¹⁰Pb activities and estimates of cumulative dry mass (Binford, 1990). See Appendix B for summaries of ²¹⁰Pb analyses by MYCORE (B-1), summary of ²¹⁰Pb calculations (B-1,2), and output from the CRS model (B-3).

Diatom Preparation and Enumeration

Slides for diatom analysis were prepared using standard techniques (Cumming, Wilson, Smol and Hall, 1995). Briefly, a small amount of wet sediment was suspended in a 50:50 (molar) mixture of sulfuric and nitric acid in a 20-ml glass vial for 24 hr. prior to being submersed at 70°C in a hot water bath for 5 The remaining sediment material was settled for a period of 24 hr, at which time the acid above sample was removed. sample was rinsed with distilled water and allowed to settle once again for 24 hrs. The procedure was repeated approx. 10 times until the sample was acid free (litmus test). The samples were settled onto coverslips in a series of four 100% dilutions, which when dry, were mounted onto glass slides using a high-resolution mounting media called Naphrax®. For each sample, at least 400 diatom taxa were enumerated under oil immersion at 1000X magnification using an objective with a numerical aperture of These analyses were based on the references of Krammer and Lange-Bertalot (1986, 1988, 1991a,b), Patrick and Reimer (1966, 1975) and Cumming et al. (1995).

Cluster Analysis

Cluster analysis, which groups similar diatom assemblages, was run on the taxa represented in Fig. 2. Cluster analysis on the diatom assemblage composition was constrained to the depth of the core samples to provide an unbiased assessment of changes in diatom assemblages through time. A squared chord was used to determine similarity between samples in the cluster analysis (Fig.2). Zones were placed based on these analyses to represent distinct groups in diatom assemblages through time (dashed line on Fig. 2).

Environmental Reconstructions from diatom assemblages

Inferences of total phosphorus downcore were based on a total phosphorus model based on the 111 freshwater lakes from the 219 lakes sampled by Wilson, Cumming & Smol (1996). This model is based on estimates of taxa optima from weighted-averaging regression on non-transformed relative percentage data. The coefficient of determination (r²) of this model is 0.66, and the jackknifed r² is 0.47. This model is superior to the earlier models developed by Reavie, Hall & Smol (1995) for several reasons including its better predictive ability and the larger number of samples which provide more analogs for downcore reconstructions.

The total phosphorus inferences (Fig. 1E) were critically assessed to determine: 1) if they tracked the main direction of variation in the diatom species assemblages (Fig. 1D); and 2) to assess if the assemblages encountered downcore are well represented in the modern-day samples (Fig. 1F). If the diatom-based phosphorus reconstruction matches the main direction of variation in the diatom assemblages downcore, then we can be fairly confident that the diatoms are tracking changes correlated to phosphorus. If the directions of variation do not match, then the diatom-inferred phosphorus reconstructions do not fully represent the changes, if any occurred, in diatom species composition downcore. Presumably, other environmental variables, or interactions between environmental variables, are contributing to the changes in diatom assemblages.

The main direction of variation in the diatom assemblages downcore in Windermere Lake was determined from the first axis scores from a principal components analysis (PCA) ordination using a co-variance matrix and non-transformed species abundance data. A PCA was chosen to represent the main direction of variation in this core since only minor changes in diatom assemblages occurred and thus a linear ordination technique would more effectively capture changes in this core then an approach

based on unimodal techniques.

The reliability of the downcore total phosphorus inferences assumes that the diatom assemblages encountered downcore are well represented in our modern diatom assemblages. To determine if appropriate analogs existed for the core samples, we determined which samples in our present-day dataset of 111 lakes most resembled each of the downcore samples. This determination was based on a squared chord dissimilarity coefficient between all species found in the core samples. The best match between downcore and modern samples was compared with the distribution of best match between modern samples. Any downcore sample that was more dissimilar than 80% of the modern distribution were deemed to be a 'poor analog'. Similarly, any downcore sample that was more dissimilar than 95% of the modern distribution were deemed to have 'no analog' in our present-day dataset. If the downcore assemblages have good representation in modern samples, more confidence can be placed in the reconstruction. If modern analogs do not exist or are poor, then caution must be placed in

reconstructions from these downcore samples.

RESULTS AND DISCUSSION

²¹⁰Pb Profile, Sedimentation Rates and Organic Matter The 210Pb profile from Windermere Lake shows a slight flattening in activity in the top 2 cms of the core(Fig. 1A). The two most likely explanations for this pattern in the 210Pb profile are: 1) an increase in sedimentation rate that could cause a dilution of the 210Pb activity; or 2) slight sediment mixing. Small changes in the precent organic matter and diatom assemblages in the top few centimeters do not allow us to rule out slight mixing in the uppermost 2 cm of this core. Sedimentation rates in general are quite slow resulting in the short core representing a fairly long span of time, with estimated bottom dates of the early 1700s. The inferred increase in sedimentation rate from approximately 1920 to 1960(Fig. 1B) corresponds to a few percent increase in percent organic matter (Fig. 1C, * note the different time scales). Increases in organic matter can be attributed to several factors including increased in-lake production of organic matter, increased inwash of organic matter, or decreases in the load of inorganic sediment to the lake. Historical information on the development of Windermere Lake may provide insight to these patterns.

Diatom Assemblage Changes and Analyses

Approximately 85 diatom taxa were encountered in the sediment core from Windermere Lake (Appendix C-1). The assemblages are dominated by a diversity of benthic taxa, such as Fragilaria brevistriata, Fragilaria construens, Fragilaria pinnata, Navicula vitabunda, and Navicula cf. minuscula. The latter two Navicula taxa only occur in the modern-day B.C. dataset at low abundances (6% or less) and thus not a lot is known about the ecological preferences of these taxa. The rest of the assemblage consist primarily of other benthic taxa in the genera Amphora, Gomphonema, Navicula, Nitzschia, and the ephiphytic taxa (live attached to macrophytes) in the genera Achnanthes. Planktonic taxa are very rare, with Cyclotella gamma being the only taxon to reach greater than 2%.

Cluster analysis suggests the changes in diatom assemblages through time can be divided into two primary zones (Fig. 2). The difference in zones A and B is the loss of Nitzschia bacillum, Navicula diluviana, and Achnanthes rosenstockii in Zone A, and the increase or appearance of other taxa such as Navicula cf. minuscula, Cyclotella gamma, Navicula modica, and Navicula schaderi in Zone A. The latter three taxa are not in the modernday B.C. dataset, and thus little is known of their ecological requirements in this region.

The changes that have occurred in the diatom assemblages are quite minor and this is reflected in the small changes seen in the inferred total phosphorus (TP). TP has remained relatively stable since the 1700s, with a small increase in TP

since approximately 1950 (Fig. 1E). However, these latter changes are being largely driven by the increases in *Navicula* cf. *minuscula*, which we have poor analogs (Fig. 1F), and thus the TP estimates must be viewed as preliminary at this time.

PCA axis 1 scores (Fig. 1D) accounts for 66% of the variation in diatom taxa in this core. The correlation between the reconstructed TP and the main direction of variation in taxa(represented by PCA axis 1 scores) is 0.75 when all 20 points are considered, which suggests that the changes seen in the diatom assemblages may be related to changes in total phosphorus.

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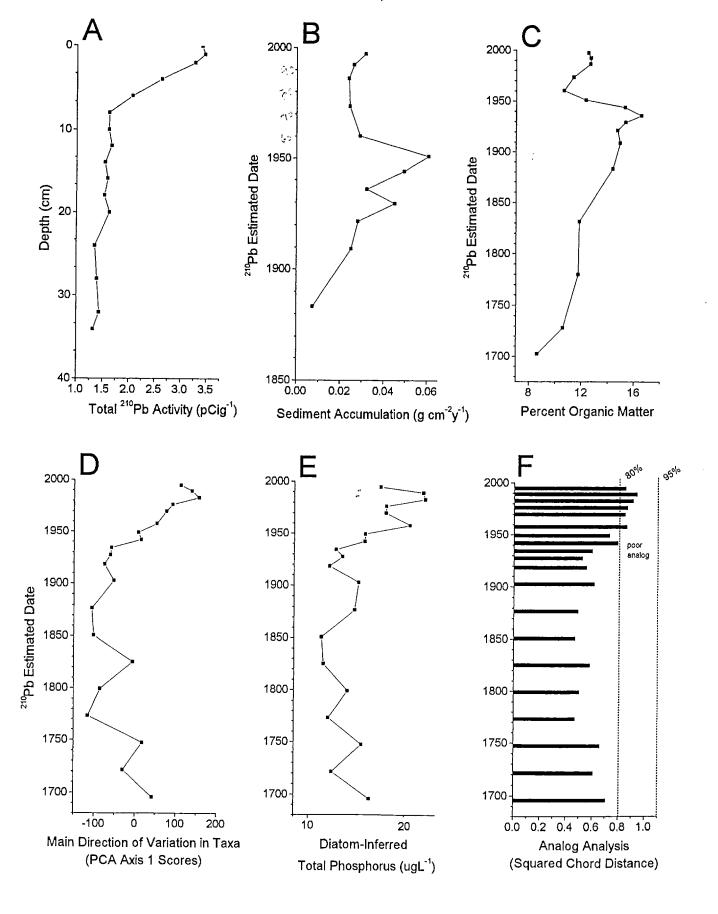
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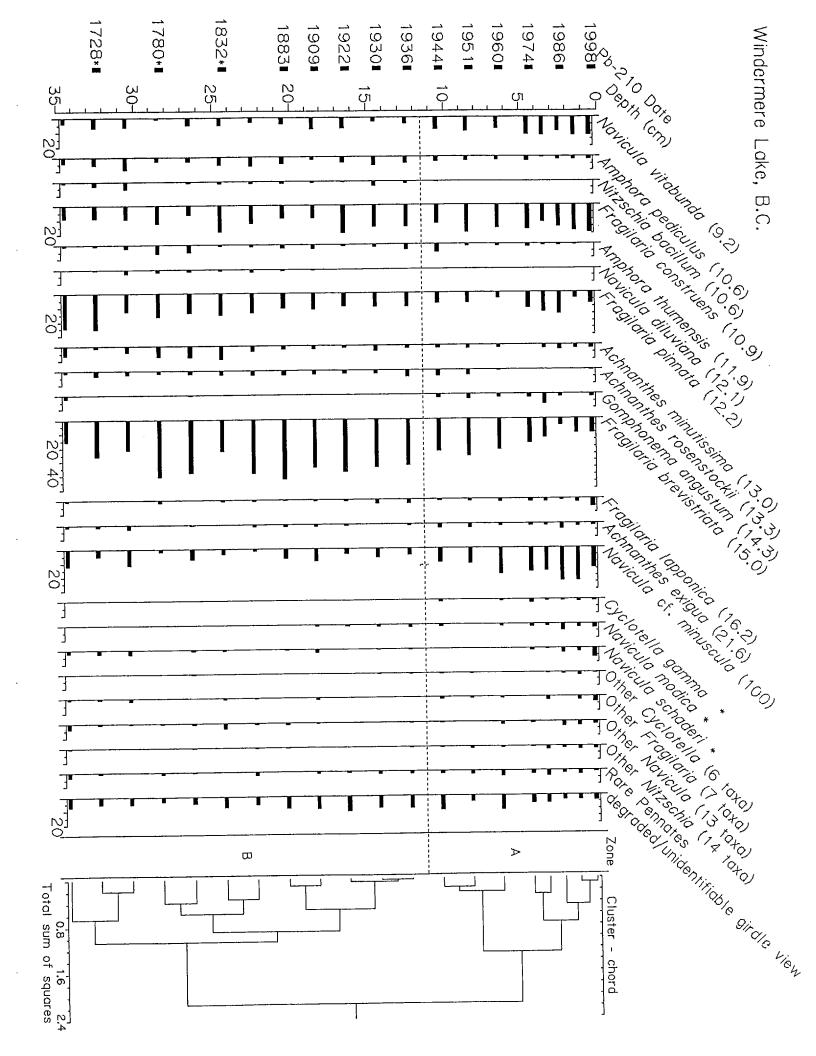
Figure Captions

Figure 1. Summary diagram for the sediment core from Windermere lake showing: A) total ²¹⁰Pb activity from which the chronology of the core is based; B) the sediment accumulation rate; C) the change in the percent of organic matter in the core; D) the main direction of variation in the diatom assemblage data; E) diatom-based estimated late-summer total phosphorus; and F) analog analysis showing the dissimilarity between present-day and downcore samples (any sample that has a squared chord distance > 0.8 was determined to be a poor analog, whereas any sample with a squared chord distance greater than 1.1 was determined to have no analog in the modern dataset).

Figure 2. Diatom stratigraphy of the diatom taxa that were present in at least ~2% relative abundance in the sediment core from Windermere Lake, B.C. (see Appendix C for a complete list of taxa and the relative percentage data). The diatom taxa are arranged in order of increasing late-summer total phosphorus (TP) optima which is indicated in parentheses for those taxa with known optima. Those taxa without known optima are marked with an asterisk. The dotted line separates the stratigraphy into two zones that were identified by a cluster analysis on the diatom assemblage composition that was constrained to the depth of the core samples. ²¹⁰Pb dates with an asterisk are based on extrapolation of the sedimentation rates of the bottom two dates with unsupported ²¹⁰Pb activity.

Windermere Lake, British Columbia





Diatom analyses summary

SEDRATE Depth (c _a) Depth (c _a) Estimated (g/cm2/yr) TOP BOTTOM AD-DATE log TP TP (u ₃ L ⁻¹) LogSalinit salinity AX
lated ATE log TP TP (ugL ⁻¹) LogSalini PATE log TP TP (ugL ⁻¹) LogSalini P5.1 1.223 16.71 1.949 1.954 1.358 22.80 1.945 1.96.8 1.242 17.46 1.965 1.970 1.965 1.970 1.965 1.970 1.965 1.971 1.044 12.71 1.972 1.972 1.972 1.974 1.974 1.975 1.974 1.975 1.9
LogSalinii 1.949 1.949 1.966 1.966 1.966 1.969 1.974 1.989 2.006 2.014 2.014 2.003 2.033 2.033 1.952 1.952

Windermere Lake 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32		SUMMARY PB210 ANALYSES BY MYCORE - Wi Sample Disk Section of Cor Sample Number # Top Bottom Weight Number used
791 792 793 794 795 796 797 797 797 797 798 800 800 800 800 800 800 800 800 800 8	<u>~</u>	O ANALYSES Disk Section Top
332822111111	(cm) (c	SES BY MYO tion of Cor Top Bottom
10.5 6.5 1.5 6.5 1.6 6.5 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.6	(cm) (MYCORE - W Cor Sample om Weight used
1255 1358 1304 1302 1298 1403 1403 1215 1321 1321 1321 1321 1321 1337 1345 1436 1436 1436 1436	(pm)	Ž
1836 3311 4928 6628 6628 7755 7751 5895 12653 5474 5129 6239 6239 6239 6239 6239 6239 6239 62		DERMERE 209 Po Counts
398 0. 807 0. 1113 0. 1318 0. 855 0. 907 0. 663 0. 1427 0. 651 0. 651 0. 650 0. 552 0. 553 0. 553 0.	(Đ	E 210 Po 210 Po Counts Meas
0.098 0.106 0.106 0.1084 0.052 0.052 0.052 0.053 0.053 0.053 0.054 0.054 0.045 0.045	(Bq/g)	
0.125 0.126 0.126 0.120 0.096 0.059 0.069 0.058 0.058 0.058 0.058 0.058 0.058 0.058	(Bq/g)	210 Po
4.6.6.4.4.4.2.2.3.3.3.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5	(%)	Precisn 1 STD
Windermere Lake 0 0.5 98 12 23 98 7 23 153 1 1.5 98 12 23 98 7 23 153 2 2.5 98 12 23 98 7 23 153 4 4.5 98 12 23 98 7 23 153 8 8.5 98 12 23 98 7 23 153 10 10.5 98 12 23 98 7 23 153 112 12.5 98 12 23 98 7 23 153 12 12.5 98 12 23 98 7 23 153 14 14.5 98 12 23 98 7 23 153 16 16.5 98 12 23 98 7 23 153 18 18.5 98 12 23 98 7 23 153 18 18.5 98 12 23 98 7 23 153 20 20.5 98 12 23 98 7 23 153 21 24.5 98 12 23 98 7 23 153 22 28.5 98 12 23 98 7 23 153 23 28.5 98 12 23 98 7 23 153 24 24.5 98 12 23 98 7 23 153 25 28.5 98 12 23 98 7 23 153 26 28.5 98 12 23 98 7 23 153 27 28.5 98 12 23 98 7 23 153 28 32.5 98 12 23 98 7 23 153 34 34.5 98 12 23 98 7 23 153	coring (cm) (year) (month) (day) (year) (month) (day) (days)	SUMMARY PB210 CALCULATIIONS FOR DETERMINING DATES - WINDERMERE Back calculate to coring (KRL) Section of Core Date Po Sample Extracte Date of coring Time Top Bottom
0.125 0.126 0.126 0.059 0.059 0.059 0.059 0.058 0.058 0.058 0.058 0.058 0.058 0.058 0.058 0.058	(Bq/g)	Decay Corr. to Extractn
5 0.1264 6 0.1281 6 0.0974 6 0.09765 9 0.0601 1 0.0618 1 0.0572 8 0.0572 8 0.0589 9 0.0501 1 0.05189 9 0.0501 1 0.0517	(Bg/g)	Decay Corr. to Coring
	<u>(a)</u>	Sample Weight
1.255 1.358 1.358 1.392 1.298 1.403 1.321 1.208 1.215 1.295 1.295 1.406 1.431 1.431 1.436 1.436	(B)	
0.0071 0.0053 0.0041 0.0032 0.0032 0.0027 0.0018 0.0027 0.0018 0.0027 0.0027 0.0027 0.0027 0.0025 0.0027 0.0025 0.0025	(Bg/g)	Std dev

Windermere-Pb210

INTTOP INTBOT

10 12 14 16 18 20 24 24 28 32

avg stds

1.375035 = supported Pb210 0.050898 1.476831

BINFORD FILE INPUTS FOR CALCULATION OF DATES AND SEDIMENTATION RATES

13171773 ひ

1

					8.5												ĭ					
0.0487	0.0530	0.0517	0.0501	0.0603	0.0570	0.0589	0.0572	0.0618	0.0600	0.0601	0.0765	0.0974	0.1212	0.1281	0.1264	activity	(Bq/g)	Pb-210	Back calcu			
0.0023	0.0040	0.0029	0.0025	0.0025	0.0027	0.0027	0.0025	0.0018	0.0027	0.0024	0.0030	0.0032	0.0041	0.0053	0.0071	Bg/g)		Std dev	Back calculated to coring			
1.3170	1.4338	1.3965	1.3529	1.6284	1.5404	1.5912	1.5467	1.6700	1.6210	1.6233	2.0683	2.6336	3.2746	3.4618	3.4156	(pCig-1)	activity	Pb210	ring			
0.0609	0.1073	0.0779	0.0665	0.0673	0.0729	0.0721	0.0677	0.0486	0.0724	0.0638	0.0806	0.0856	0.1121	0.1420	0.1918	(pCig-1)		Std dev				
0.3402	0.2424	0.2088	0.1951	0.1786	0.1685	0.1599	0.1207	0.1160	0.2187	0.1615	0.1957	0.1585	0.1456	0.1643	0.1256	(g cm-3)	Rho					
																(c	z			0.	16	Q
34.00	32.00	28.00	24.00	20.00	18.00	16.00	14.00	12.00	10.00	8.00	6.00	4.00	2.00	1.00	0.00	<u>m</u>	INTTOP I			0.0509	٠,	
34.50	32.50	28.50	24.50	20.50	18.50	16.50	14.50	12.50	10.50	8.50	6.50	4.50	2.50	1.50	0.50	(cm)	INTBOT					
1.3170	1.4338	1.396	1.3529	1.628	1.540	1.5912	1.546	1.670	1.621	1.623	2.068	2.633	3.274	3.461	3,415	(pCig-1)	Total	Pb210				
0.0000	3 0.000	0.000	0.000	1 0.253	0.165	2 0.216	7 0.171	0.295	0.246	3 0.248	3 0.693	3 1.258	5 1.899	3 2.086	5 2.040	(pCig-1)	Unsup.	Pb210				
0 0.3402	0.24	0 0.20	0 0.19	4 0.17	4 0.16	1 0.15	6 0.12	0 0.11	0.21	3 0.16	3 0.19	6 0.15	5 0.14	8 0.16	6 0.12	(g cm-3)	Rho					
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0.086	106	.118	118	144	.149	147	.154	166	.153	.123	106	.114	.127	.127	.125	tion (gc	2					
6.2944	5.5627	4.6394	3.8423	3.1241	2.8133	2.5130	2.2424	1.9876	1.6586	1.3374	0.9454	0.5894	0.3032	0.1455	0.0000	m-2) (MTOP (
6.4645	5.6839	4.7438	3.9399	3.2135	2.8976	2.5929	2.3028	2.0456	1.7680	1.4182	1.0432	0.6687	0.3760	0.2276	0.0628	cm-2)	UMBOT					
0.0609	0.1073	0.0779	0.0665	0.0673	0.0729	0.0721	0.0677	0.0486	0.0724	0.0638	0.0806	0.0856	0.1121	0.1420	0.1918	(pCig-1)	Pb210	std				

OU ARE ANALYZING CORE C1

FROM LAKE Windermere

THE DAT	A ARE:						CIDAL CCD	CD 3 CM
TNTTOP	INTBOT	PB210ACT	UNSUPACT	RHO	PERCORG	CUMMASST	CUMMASSB	SDACT
0.0	0.5	3.41560	2.04060	0.12560	0.120	0.0000	0.0628	0.1918
1.0	1.5	3.46180	2.08680	0.16430	0.120	0.1455	0.2276	0.1420
2.0	2.5	3.27460	1.89950	0.14560	0.120	0.3032	0.3760	0.1121
4.0	4.5	2.63360	1.25860	0.15850	0.110	0.5894	0.6687	0.0856
6.0	6.5	2.06830	0.69330	0.19570	0.100	0.9454	1.0432	0.0806
8.0	8.5	1.62330	0.24830	0.16150	0.120	1.3374	1.4182	0.0638
0.0	10.5	1.62100	0.24600	0.21870	0.150	1.6586	1.7680	0.0724
2.0	12.5	1.67000	0.29500	0.11600	0.160	1.9876	2.0456	0.0486
14.0	14.5	1.54670	0.17160	0.12070	0.150	2.2424	2.3028	0.0677
	16.5	1.59120	0.21610	0.15990	0.140	2.5130	2.5929	0.0721
16.0		1.54040	0.16540	0.16850	0.140	2.8133	2.8976	0.0729
8.0	18.5		0.10340	0.17860		3.1241	3.2135	0.0673
∠0.0	20.5	1.62840		0.19510	7 7 7 7 7	3.8423	3.9399	0.0665
24.0	24.5	1.35290	0.00000		_	4.6394	4.7438	0.0779
8.0	28.5	1.39650	0.00000	0.20880		• • •	• • • •	0.1073
_2.0	32.5	1.43380	0.00000	0.24240	0.100	5.5627	5.6839	
34.0	34.5	1.31700	0.00000	0.34020	0.080	6.2944	6.4645	0.0609

TANDARD DEVIATION OF SUPPORTED PB-210 = 0.0509

b-210 dates	for	Lake	Windermere
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core C1

INTTOP	INTBOT	MIDINT	TTOP	SDTTOP	TBOT	SDTBOT	SEDRATE	SDSEDRT	SUMTOP
0.0	0.5	0.2	0.00	1.05	2.00	1.07	0.0314	0.0100	2.1214
1.0	1.5	1.2	4.49	1.11	7.62	1.15	0.0262	0.0081	1.8445
2.0	2.5	2.2	10.73	1.22	13.80	1.28	0.0238	0.0074	1.5188
4.0	4.5	4.2	23.31	1.56	26.59	1.66	0.0242	0.0084	1.0266
•	6.5	6.2	36.60	2.12	39.99	2.28	0.0290	0.0120	0.6786
6.0		8.2	46.86	2.71	48.19	2.78	0.0606	0.0255	0.4931
8.0	8.5		53.33	3.15	55.54	3.26	0.0493	0.0243	0.4031
10.0	10.5	10.2		3.83	63.44	4.02	0.0320	0.0165	0.3113
L2.0	12.5	12.2	61.62		69.51	4.73	0.0320	0.0271	0.2539
14.0	14.5	14.2	68.18	4.59			0.0280	0.0201	0.2029
16.0	16.5	16.2	75.37	5.56	78.22	5.95	• • •		0.1390
18.0	18.5	18.2	87.51	7.72	90.91	8.35	0.0249	0.0219	
20.0	20.5	20.2	108.96	14.16	121.22	20.13	0.0074	0.0123	0.0713

Execution terminated: 0

C:\pb210>

WINDERMERE LAKE - DIATOM RELATIVE ABUNDANCES (%)

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APPENDIX II

Analyses of Fossil Pigments from Windermere Lake March 30, 1999

> Dr. Peter Leavitt, Associate Professor University of Regina Regina, Saskatchewan

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From:

Peter Leavitt

To:

Gordon Kan, Les McDonald

Subject:

Final Report for Fossil Pigment Analyses

Date:

30 March 1999

Title:

Analyses of fossil pigments from Windermere Lake

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LIST OF FIGURES AND APPENDICES

- Fig 1. Fossil pigment concentrations (nmoles g-1 organic matter) in short core from Windermere Lake. Pigment names and taxonomic affinities indicated for each profile.
- Appendix 1. Organic-matter specific concentrations (nmoles pigment/g organic matter) of fossil pigments from Windermere Lake.

BACKGROUND

Windermere Lake was cored in July 1998 by Rick Nordin and Les MacDonald using standard gravity corer procedures. The core was taken from the deepest point in the basin of Windermere Lake. At lakeside, cores were sectioned into 0.5-cm intervals into whirlpak bags. Samples were shipped on ice to Dr. Brian Cumming, Department of Biology, Queen's University, Kingston, Ontario. Samples were stored at 4°C until further analysis. In Fall 1998, Dr. Cumming forwarded subsamples of sediment to the University of Regina where they were stored at -12°C until analysis. Aliquots of each sample were obtained for analysis of organic content (as weight loss on ignition at 500°C for 1 hr) and phototrophic pigments (by liquid chromatography).

METHODS

Sediment Chronology

At the time of report preparation, no information was available concerning the procedures used for determination of sediment age. Consequently, all stratigraphic patterns are reported relative to burial depth (in cm). Normally, ²¹⁰Pb activity is used to estimate core chronology. Inquiries about sediment chronology should be forwarded to either: Dr. Gordon Kan, Environment Canada, Pacific Environmental Science Centre, 2645 Dollarton Hwy, North Vancouver, BC, V7H 1V2, or; Dr. Brian Cumming, Dept Biology, Queen's University, Kingston, ON, K7L 3N6.

Pigment Analyses

Sediments from each sample were freeze-dried under a hard vacuum (0.1 Pa) for 48 hrs using a VirTis model 24Dx48 lyophilizer to remove excess water prior to extraction of lipid-soluble carotenoids, chlorophylls (Chls) and their derivatives. Dried sediments were stored at -80°C in the dark under an inert nitrogen gas atmosphere following drying to

prevent pigment oxidation.

Carotenoids, chlorophylls (Chls) and their derivatives were extracted (18 h, 4°C, dark, under N_2) from freeze-dried sediments using a standard mixture of acetone:methanol:water (80:15:5, by vol.; Leavitt et al. 1989). Sediment residues were exhaustively extracted with three aliquots of solvent mixture, extracts filtered (0.22 μ m Acropore membrane), and solvents evaporated in the dark using N_2 gas. Dried extracts were stored at -20°C under N_2 in the dark until pigment analysis. Just prior to quantification, pigments were brought to room temperature in the dark and dissolved in a precisely known volume of injection solvent (acetone:ion-pairing reagent:methanol; 70:25:5, by volume) containing 3.2 mg litre⁻¹ Sudan II (Sigma Chemical Co.). This chromatographic dye is an internal standard that has carotenoid-like absorption characteristics ($\lambda_{max} = 485$, 442.5 nm in acetone), runs at a unique position on the chromatogram, and is used to correct for dilution, injection, and chromatographic errors (Leavitt and Findlay 1994). Ion-pairing regent (IPR) consists of 0.75 g tetrabutyl ammonium acetate and 7.7 g ammonium acetate in 100 ml distilled water.

Concentrations of fossil pigments are quantified using a Hewlett Packard (HP) model 1040 HPLC system with HP model 1040 photo-diode array detector and model 1046A fluorescence detector following the reversed-phase liquid chromatography procedure of Leavitt et al. (1989). Briefly, analytical separation was achieved by isocratic delivery (1.5 ml min⁻¹; 21,000 kPa) of a mobile phase A (10% IPR in methanol) for 1.5 min, a linear succession to 100% solution B (27% acetone in methanol) over 7 min, and isocratic hold for 12.5 min. Rainin C-18 columns (10 cm, 5 μ m particles) were re-equilibrated by continued isocratic delivery for 3 min, a linear return to 100% A over 3 min, and isocratic supply for a final 4 min.

Pigments isolated from sediments were compared to those from unialgal cultures of known pigment composition (Leavitt et al. 1989; Leavitt and Findlay 1994) and, for some compounds, with authentic standards provided by the US Environmental Protection Agency

(US-EPA). Spectral characteristics and chromatographic mobility were used to identify pigments from sediments (Leavitt et al. 1989). Analysis of fossil pigments was restricted to carotenoids characteristic of cryptophytes (alloxanthin), mainly diatoms (diatoxanthin), diatoms with chrysophytes and some dinoflagellates (fucoxanthin), diatoms and dinoflagellates (diadinoxanthin), chlorophytes and cyanobacteria (lutein-zeaxanthin), cyanobacteria (echinenone), colonial cyanobacteria (myxoxanthophyll), colonial cyanobacteria from the group Nostocales (canthaxanthin) and N2-fixing cyanobacteria (aphanizophyll), as well as the major \underline{a} , \underline{b} , and \underline{c} -phorbins. Chlorophyll (Chl) \underline{b} and pheopigment derivatives (mainly pheophytin b) were used to distinguish green algae from cyanobacteria, whose carotenoid zeaxanthin was not separated from the chlorophyte pigment lutein on our HPLC system. Similarly, chromatographic peaks from aphanizophyll (Aphanizomenon), oscillaxanthin (Oscillatoriaceae), and 4-keto-myxoxanthophyll (Anabaena) were incompletely resolved and were reported as aphanizophyll. Compounds tentatively identified as originating from purple sulphur phototrophic bacteria (okenone) were also noted in Windermere Lake sediments. Unfortunately, insufficient material was provided for more complete characterization, and interpretation of these compounds is regarded as tentative. Further details of pigment distribution among algal groups are provided by Davies (1976) and Goodwin (1980).

Pigment concentrations were expressed as nmoles pigment g⁻¹ organic matter, as recommended by Leavitt (1993) and Leavitt and Findlay (1994). Organic matter contents of freeze-dried sediments were determined as weight loss on ignition for 1 hr at 500°C (Leavitt and Findlay 1994). Comparison of 20 years of phytoplankton data with annual fossil records has demonstrated that organic matter-specific concentrations are linearly correlated to algal biomass for a wide variety of fossil carotenoids, particularly for algae that are abundant during the ice-free season (Leavitt and Findlay 1994).

All profiles were interpreted following recommendations by Leavitt (1993), Leavitt and Findlay (1994), and Leavitt et al. (1994). Copies of these publications are available on request. In brief, organic-matter specific pigment concentration are interpreted as indices of

the past biomass of the main algal groups in the lakes, including, but not limited to total algae, diatoms, cryptophytes, greens, cyanobacteria, and colonial (surface bloom-forming) cyanobacteria. Species-level information is not available from the analysis of fossil pigments. Instead, analyses summarized past algal community change and lake production in the functional units most important to lake managers (as above). Data are most useful for documenting historical changes in algal abundance within individual lakes, rather than differences in production among lakes (see Leavitt 1993 for further information).

In this report, we will provide brief analyses of organic-matter specific fossil concentration as a metric of lake production. However, as we have demonstrated elsewhere (Leavitt 1993, Leavitt and Findlay 1994), absolute concentrations of pigments can be strongly influenced by the morphometry of the lake (depth, light penetration, deepwater oxygen content). Consequently, stratigraphic changes are most reliably interpreted as changes in individual pigment abundance relative to the historical maximum or minimum exhibited for that compound, rather than as a function of other compounds (e.g., alloxanthin interpreted relative to the history of alloxanthin alone).

RESULTS and DISCUSSION

Windermere Lake

Sediments of Windermere Lake were characterized by relatively low organic matter content ($\sim 15\%$ of dry weight) throughout the 35 cm core (Fig. 1). Low organic matter content may reflect unproductive lake conditions (Leavitt 1993), or may result from dilution of autochthonous organic matter (i.e., originating from within the lake) by inorganic matter from the lake catchment (Rowan et al. 1992). In general, the organic matter content of Windermere Lake sediments increased steadily from a minimum of $\sim 12\%$ at the bottom of the core to a maximum of $\sim 20\%$ at 10 cm depth, before declining sharply to stable values of 13-14% in the uppermost 8 cm of sediments.

Organic-matter specific concentrations of most carotenoids were intermediate to minimum values recorded in unproductive alpine lakes and high concentrations characteristic of eutrophic systems (e.g., Leavitt and Findlay 1994, Vinebrooke et al. 1998). Pigment preservation was good throughout the core, with high molecular ratios of undegraded Chl a:pheophytin a (>2:1) at most depths, moderate concentrations of labile pigments (Chl a, fucoxanthin), and the presence of okenone from phototrophic bacteria, organisms characteristic of environments with low oxygen contents and optimal pigment preservation. However, unlike some lakes, extremely labile carotenoids and chlorophylls (e.g., Chl c from diatoms, chrysophytes, dinoflagellates) were not well preserved. Together, these observations suggest that while some pigment degradation occurred during deposition, fossil stratigraphies were reliable and could be used to infer historical changes in the production of Windermere Lake.

Analysis of fossil pigments suggested that total algal production has increased only modestly through the period of time encompassed by the Windermere sediment core (Fig. 1). Concentrations of ubiquitous pigments (β -carotene, Chl \underline{a} , pheophytin \underline{a}) were stable between 10 and 35 cm burial depth, increased slightly between 5 and 10 cm depth, and exhibited core-wide maxima in the uppermost 3 cm of sediments. The observation that both chemically-stable β -carotene and easily-degraded Chl \underline{a} exhibited similar stratigraphic patterns suggests that changes in fossil pigment concentrations reflected historical variations in algal abundance rather than artifacts of selective pigment preservation or deposition.

Fossil pigment analyses suggested that the original algal communities were composed of similar abundances of diatoms and chlorophytes (green algae), with lesser amounts of cryptophytes and bloom-forming cyanobacteria (Fig. 1). Although pigments from colonial cyanobacteria were present throughout the core (e.g., myxoxanthophyll, echinenone; canthaxanthin not shown), concentrations in deep sediments (>15 cm) were only 20% those recorded for eukaryotic algae such as diatoms (diatoxanthin) and chlorophytes (lutein-zeaxanthin).

Concentrations of most indicator pigments increased modestly over the course of the sediment core. For example, pigments from green algae (lutein-zeaxanthin, Chl b, pheophytin b), cyanobacteria (echinenone, myxoxanthphyll, canthaxanthin) and cryptophytes (alloxanthin) increased two-fold to maxima in the uppermost 3 cm of the Windermere Lake core. Similarly, fucoxanthin from diatoms, chrysophytes and dinoflagellates increased more than 500% above background levels in the uppermost 10 cm of the core, whereas diatoxanthin from diatoms was inferred to have declined ~25% over the same period. Because sedimentary fucoxanthin content increased, whereas that of diatoxanthin declined slightly, we interpret that recent algal communities have experienced a recent increase in the relative abundance of either chrysophytes or dinoflagellates at the expense of diatoms, possibly in the form of deepwater blooms (cf. Leavitt et al. 1989).

Concentrations of algal and bacterial pigments increased to peak values in the most recently deposited sediments (upper 3 cm; Fig. 1). In particular, pigments from colonial cyanobacteria (myxoxanthophyll, canthaxanthin) and green algae (lutein-zeaxanthin, Chl b, pheophytin b) increased two-fold in the surface 3 cm, whereas smaller increases were recorded for other indicator compounds. Because these pigments are among the most reliable of the algal indicators (Leavitt 1993, Leavitt and Findlay 1994), these patterns suggest a recent increase in the abundance of bloom-forming taxa. However, at this juncture it is uncertain whether inferred increases algal abundance have occurred in surface waters (where they are seen by the public) or at depth in the form of deepwater populations. Further, despite the relative stability of the indicator compounds, nonselective post-depositional degradation of pigments is common in many lakes and may have also contributed to the observed patterns in the most recently-deposited sediments (Leavitt 1993).

Analysis of fossil okenone from purple sulphur bacteria suggested that the stratification regime of Windermere Lake has varied in the recent past. For example, concentrations of okenone increased five- to 10-fold in the uppermost 10 cm of sediment. Because these phototrophic bacteria require light for photosynthesis, yet are fatally poisoned by molecular oxygen, the presence of their pigments throughout the core suggests that light

has always penetrated into anoxic bottom waters. Most commonly, this condition occurs when a lake is strongly or permanently stratified (meromictic), relatively transparent and when bottom waters are completely anoxic. However, sharp increases in the deposition of okenone in the most recent sediments suggest either that light penetration has recently improved, or that the lake has become more strongly stratified and that deepwater anoxia has become more profound. Presently, we cannot distinguish among these mechanisms.

Regardless of the cause, we note that concentrations of okeneone were always low when compared with values recorded from strongly stratified sites (e.g., Leavitt et al. 1989), suggesting that Windermere Lake exhibited only seasonal stratification.

In summary, analysis of sedimentary pigments from Windermere Lake suggested that original fossil assemblages were mainly composed of eukaryotic algae, particularly diatoms, cryptophytes, and green algae. Bloom-forming cyanobacteria were present, but relatively uncommon. Total algal production is inferred to have increased slightly from minimum values recorded deep in the core to maxima in the uppermost 3 cm of sediment. Concentrations of many indicator pigments, particularly those of colonial cyanobacteria, also increased ~two-fold to peaks in the uppermost sediments, although it is unclear whether this pattern arises from increased production of deepwater blooms, surface blooms or nonselective degradation of pigments following algal deposition to the lake bottom. Analysis of fossil carotenoids from anaerobic sulphur bacteria suggested that the stratification regime of Windermere Lake has changed recently, either due to improved light penetration into anoxic waters, or increased chemical stratification leading to more profound oxygen deficits in bottom waters.

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APPENDICES

Windermere Lake pigment concentrations.

All pigment concentrations in units of ninoles pigment/gram organic matter. Missing values (.) are distinguished from sample without pigment (0.000). Column headings represent:

Lake - character variable identifying site

Chlorophyll c - pigment from diatoms, chrysophytes and dinoflagellates (10x actual concentration)

Chlorophyll c isomer - pigment from diatoms, chrysophytes and dinoflagellates (10 x actual concentration)

Fucoxanthin - carotenoid derived from diatoms, chrysophytes and some dinoflagellates.

"Aphanizophyll"- groups of carotenoids produced by nitrogen-fixing cyanobacteria. Includes aphanizophyll, 4-keto-myxoxanthophyll, and oscillaxanthin

Diadinoxanthin - carotenoid from diatoms and some dinoflagellates.

Myxoxanthophyll - carotenoid from colonial cyanobacteria

Alloxanthin - carotenoid from cryptophytes

Diatoxanthin - carotenoids from diatoms and some chrysophytes

Lutein-zeaxanthin - carotenoids from green algae (Lutein) and cyanobacteria (zeaxanthin)

Canthaxanthin - carotenoid from colonial cyanobacteria, predominantly bloom-forming Nostocales.

Chlorophyll b - pigment from green algae

Carotenoid X - unknown origin, possibly phototrophic bacterial pigment

Okenone - carotenoid from phototrophic purple sulphur bacteria.

Chlorophyll a - pigment from all algae

Echinenone - carotenoid from all cyanobacteria

Isorenieratene - carotenoid from green sulphur bacteria (tentative)

Pheophytin <u>b</u> - derivative of Chl <u>b</u>

Pheophytin a - derivative of Chl a

3-carotene - carotenoid from all algae

Organic content - % weight loss on ignition at 550°C (1 hr)

Total Chl C - sum of Chl c isomers

36.784,	33.921,	35.931,	20.190,	27.710,
12.071,	5.338,	12.149,	7.873,	5.198,
11.384,	10.132,	11.366,	6.509,	8.832,
107.292,	95.660,	106.291,	56.872,	82.305,
36.217,	31.302,	35.184,	21.685,	32.582,
45.672, 0.000	40.740,	44.130,	23.044, 0.000	28.550,
27.525, 14.167,	24.520, 14.404,	27.734, 13.852,	14.909, 12.886,	16.359,
0.000, 42.208,	0.000,	0.000,	0.000,	11.871,
8.258, 18.911,	7.391, 17.022,	7.787, 20.845,	4.156, 10.159,	6.693,
121.118, 4.112,	123.476, 2.456,	120.199, 4.367,	43.737, 2.513,	40.864,
0.000,	0.000,	0.000,	0.000,	0.000,
0.000, 11.876,	0.000,	0.000,	0.000,	28.236,
"WIND ", 0.500, 0.000, 0.000, 27.575, 84.609, 11.876, 0.000,	", 1.500, 0.000, 0.000, 78.701, 10.044, 0.000,	"WIND ", 2.500, 0.000, 0.000, 31.356, 76.428, 11.813, 0.000.	WIND ", 3.500, 0.000, 0.000, 18.496, 38.664, 4.809, 0.000,	", 4.500, 28.236, 0.000,
"WIND 27.575,	"WIND",	"WIND 31.356,	"WIND 18.496,	"WIND

	31.830,	0.000,	17.301,	20.504,	7.106,	15.595,	14.537,	17.451,	16.986,	22.649,	9.930,	5.009,	11.459,	13.869,
	7.049,	6.283,	6.718,	8.690,	5.720,	5.680,	2.920,	4.266,	5.991,	5.772,	1.029,	3.335,	2.811,	2.126,
	8.234,	7.966,	5.114,	5.524,	3.612,	3.912,	4.755,	5.094,	4.611,	5.848,	2.403,	3.097,	4.669,	4.739,
	91.202,	116.161,	66.732,	91.586,	60.889,	66.500,	57.731,	70.084,	65.299,	93.110,	52.120,	57.724,	59.182,	44.098,
	37.298,	44.540,	32.475,	45.684,	32.154,	37.424,	42.851,	51.069,	49.647,	79.043,	36.628,	49.776,	44.288,	39.398,
28.236	34. <i>975</i> , 0.000	44.921,	25.286, 0.000	39.224, 0.000	22.138, 0.000	24.329, 0.000	23.483, 0.000	26.871, 0.000	22.590, 0.000	35.972, 0.000	18.543, 0.000	22.247, 0.000	20.689,	13.286,
13.682,	14.362, 13.385,	17.961, 13.860,	13.180, 19.113,	11.884, 19.257,	9.305, 18.375,	6.550, 17.478,	12.785, 18.007,	8.028, 16.944,	9.329, 16.123,	8.961, 12.616,	4.430, 15.459,	8.282, 14.745,	6.555, 14.233,	6.477,
20.948,	0.000, 28.134,	18.356, 31.400,	8.640, 16.919,	26.577, 18.813,	0.000, 21.261,	0.000, 25.990,	0.000, 29.622,	0.000, 21.999,	. 0.000, 27.393,	0.000, 40.818,	8.682, 15.400,	5.068, 20.355,	5.810, 20.907,	0.000,
8.600,	14.097, 13.591,	23.022, 10.543,	12.072, 7.033,	19.158, 6.114,	8.287, 8.435,	9.107, 8.198,	9.134, 8.840,	8.311, 8.502,	6.522, - 9.197,	10.240, 12.798,	5.271, 5.580,	6.144, 7.519,	5.935, 6.931,	2.039,
2.154,	26.409, 3.221,	13.749, 2.009,	9.882, 1.592,	8.449, 1.042,	4.125, 1.491,	6.007, 0.898,	9.375, 1.009,	9.097, 1.593,	5.900, 1.877,	8.018, 2.336,	5.082, 0.606,	4.267, 0.923,	6.131, 0.634,	7.525,
0.000,	0.000,	0.000,			0.000,	0.000,	0.000,	0.000, 00,	0.000,	0.000,	0.000, 5.08. 0.000, 0.606,	0.000,	30.500, 0.000, 0.000, 0.000, 0.076, 3.146, 0.000,	0.000, 0.000,
4.973,	0.000,	0.000, 6.138,	0.000, 3.126,	0.000, 4.091,	0.000, 3.528,	0.000, 3.526,	0.000,	0.000, 4.097,	0.000, 2.946,	0.000, 4.740,	0.000,	0.000, 2.293,	0.000, 3.146,	0.000,
33.838,	", 6.500, 33.062, 5	", 8.500, 0.000, 32.315, 6.138,	", 10.500, 0.000, 0.000, 17.739, 3.126, 0.000,	", 12.500, 0.000, 0.000, 22.806, 4.091, 0.000,	", 14.500, 0.000, 17.765, 3.528, 0.0	", 16.500, 0.000, 0.000, 6.00 20.493, 3.526, 0.000, 0.898,	", 18.500, 0.000, 0.000, 9.37 20.019, 4.253, 0.000, 1.009,	", 20.500, 0.000, 21.553, 4.097, 0.0	", 22.500, 0.000, 0.000, 17.974, 2.946, 0.000,	", 24.500, 0.000, 0.000, 29.820, 4.740, 0.000,	", 26.500, 0.000, 0.00 12.766, 2.137, 0.000,	", 28.500, 0.000, 0.000, 15.090, 2.293, 0.000,	", 30.500, 16.076,	", 32.500,
21.613,	"WIND 19.264,	"WIND 8.911,	"WIND 3.852,	"WIND 2.974,	"WIND 2.761,	"WIND 3.122,	"WIND 6.021,	"WIND 4.128,	"WIND 3.320,	"WIND 4.096,	"WIND 2.680,	"WIND 2.428,	"WIND 1.830,	"WIND

6.869, 14.050, 3.011, 0.000, 1.914, 7.904, 20.428, 13.357, 0.000

29.391, 50.886, 5.517, 4.750, 15.092, "WIND ", 34.500, 0.000, 0.000, 21.387, 1.369, 0.000, 6.865, 14.615, 16.034, 19.860, 3.993, 0.000, 2.185, 8.058, 20.974, 12.247, 0.000

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