# $^{81}$Kr-dating is now available

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Due to its simple production and transport processes in the terrestrial environment, the long-lived noble-gas isotope $^{81}$Kr is the ideal tracer for old water and ice in the age range of $10^5$-$10^6$ years, a range beyond the reach of $^{14}$C. $^{81}$Kr-dating, a concept pursued over the past four decades by numerous laboratories employing a variety of techniques, is now available for the first time to the earth science community at large. This is made possible by the development of ATTA-3, an efficient and selective atom counter based on the Atom Trap Trace Analysis method and capable of measuring both $^{81}$Kr/Kr and $^{85}$Kr/Kr ratios of environmental samples in the range of $10^{-14}$-$10^{-10}$. The instrument was calibrated with 12 samples whose $^{85}$Kr/Kr ratios were independently measured using Low Level Decay Counting, including six samples that were measured in a blind arrangement. Compared to the previously reported ATTA-2 instrument, the counting rates of ATTA-3 are higher by two orders of magnitude and the required sample size lower by one order of magnitude. For $^{81}$Kr-dating in the age range of 200 – 1,500 kyr, the required sample size is 5 – 10 micro-L STP of krypton gas, which can be extracted from approximately 100 – 200 kg of water or 40 – 80 kg of ice. Moreover, a laser-induced quenching scheme was developed to enable measurements of both the rare $^{81,85}$Kr and the abundant $^{83}$Kr, whose isotopic abundances differ by 11 orders of magnitude. This scheme allows ATTA-3 to directly determine $^{81}$Kr/Kr and $^{85}$Kr/Kr ratios without other supplemental measurements. Combining the significant reduction in sample size with several advances in the measurement procedure, ATTA-3 represents the state-of-the-art instrument for routine analysis of these rare noble gas tracers for a wide range of earth science applications.

More information regarding ATTA-3 is posted at http://www.phy.anl.gov/mep/atta/. This work is supported by the U.S. DOE, Office of Nuclear Physics, under contract DE-AC02-06CH11357; and by NSF, Division of Earth Sciences, under Award No. EAR-0651161.

# Climate controls the fluctuations of fish mercury levels in Québec lakes

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## Data mining

The compilation of data bases of Québec Ministry of Environment, Hydro-Québec, COMERN strategic network as well as Environment Canada's CARA research program allowed us to reconstruct the history of total mercury levels (Hg) over the 1979-2011 period in two predatory fish species most consumed in mid-northern Québec (Canada): northern pike (*Esox lucius*) and walleye (*Sander vitreus*). We present results for a series of 82 large lakes frequently fished by sport fishers. In order to compare different years and lakes among each other, we calculated fish flesh Hg levels at standardized lengths using von Bertalanffy growth models. We also used fish growth rates data whenever available. We run our statistical analysis considering 20 GIS variables (lake order, watershed slopes, drainage density, mining sites, vegetation cover, geological substratum) and 15 climatic variables (monthly precipitations, temperatures, and sulfate deposition).

## Trends in mercury levels in walleye and pike over the last three decades

Climatic factors such as annual mean temperatures and winter precipitations could explain 60% of the variations of walleye Hg levels. In turn, these climatic variables appeared to strongly control walleye growth rates. In addition, logging activities equivalent to at least 20% of the watershed surface every 10 years could explain 15% of the variations of waleye Hg levels. The influence of mining activities in lakes watershed appeared to be masked by the dominant climatic conditions and eventual logging activities. In fact, walleyes caught in lakes heavily impacted by mining activities such as Chibougamau and Matagami lakes presented some of the lowest Hg levels at standardized length. 35% of the variations of pike Hg levels could be explained by the nature of the watershed, rather steep slopes having a positive influence on the bioaccumulation of the heavy metal in that fish species. Mining activities in the watershed also explained 15% of the variations of pike Hg levels. Watershed characteristics (10 to 20% slopes and higher fraction of the watershed covered by mixed forest) was in turn linked to fish growth rates, which by itself explained 45% of the variations of pike Hg levels.

## Climate conditions control fish mercury levels

Hg levels in walleyes and to some extent in pikes in large lakes of mid-northern Québec have been significantly increasing from the 1980's to the 1990's due to colder and dryer conditions prevailing at that time and sharply decreasing since then mainly because of average temperatures rises, in turn stimulating fish growth rates. The effect of measured decreased acid rain deposition could not be detected with our data set. In the absence of monitoring stations of wet and dry atmospheric Hg deposition in the region, the effects of decreased Hg atmospheric emissions at the continental scale could not be evidenced either.