Report as of FY2006 for 2006OK67B: "Historical Ecological and Geochemical Analysis of Lakes Eucha and Spavinaw"

Publications

Project 2006OK67B has resulted in no reported publications as of FY2006.

Report Follows

Student Status	Number	Disciplines
Undergraduate	5	Biology, Geosciences
M.S.	1	Chemistry
Ph.D.		
Post Doc		
Total	6	

Title: Retrospective Ecosystem Analysis of the Eucha-Spavinaw Watershed

Start Date: 02/01/2005

End Date: 07/31/2007

Congressional District: University of Tulsa - Federal Congressional District 1; Eucha-Spavinaw Watershed Federal Congressional District 2

Focus Category: WQL, SED, M&P, GEOCHE, ECL, AG

Descriptors: Sediments, lake, reservoir, watershed, poultry, pollution, ecology, agriculture, phosphorous, arsenic, selenium

Principal Investigators: J. B. Fisher, University of Tulsa, Bryan Tapp, University of Tulsa, Ken Roberts, University of Tulsa, William Potter, University of Tulsa, Harrington Wells, University of Tulsa

Publications: Fisher, J. Berton. 2006. Secular Variation in Arsenic and Selenium Concentrations in Sediments from Lakes Eucha and Spavinaw and Spavinaw. Oral Presentation, Oklahoma Water 2006, October 5-6, Oklahoma City, OK.

Murdianti, Befrika, 2006. Eucha-Spavinaw Lake Sediments: A Poultry Production Fingerprint. Poster Presentation, Oklahoma Water 2006, October 5-6, Oklahoma City, OK.

Problem and Research Objectives: Just under than 50% of the drinking water used by approximately 500,000 persons in the City of Tulsa and surrounding communities comes from the Eucha-Spavinaw watershed, located in western Arkansas and eastern Oklahoma. This watershed covers roughly 415 mi^2 of largely agricultural land in Mayes County and Delaware County, Oklahoma, and Benton County, Arkansas. Lake Eucha and Lake Spavinaw impound water from Spavinaw Creek (the primary drainage channel). Water quality within the watershed has substantially changed from 1924 when the dam forming Lake Spavinaw was closed. The most notable biological change is the clear and profound increase in phytoplankton production in the lakes and an apparent change in the relative abundance of phytoplankton species. Water from the

Eucha-Spavinaw watershed could and was originally used by Tulsa with little or no treatment. In recent years, however, treatment costs have risen. Moreover, the frequency of taste and odor complaints has increased. Water quality monitoring data indicate that both Lake Eucha and Lake Spavinaw were originally oligotrophic, but are now both nutrient-enriched and display high or excessive levels of algal production. During much of the year, the phytoplankton community in both lakes is dominated by dominated by blue-green algae. Changes in composition and abundance of phytoplankton community in the lakes may be attributable to increases in nutrient levels in the lakes, and in the waters feeding the lakes. Unfortunately, detailed water quality studies of phosphorous loading to the watershed did not begin until 1997 when a Conservation Commission report indicated increasing phosphate content in Spavinaw Creek. It is reasonably probable that changes in land use and land cover (LULC) are likely the cause of increased nutrient loading to the watershed. In the 1930s, land usage within the watershed was focused on corn, wheat, and oat production in Oklahoma (Kesler, 1936), and on apple, peach and grape production in western Arkansas. Moreover, at that time, nearly 80% of the watershed was undeveloped scrub timber. Since the mid-1950s, and especially since about 1980, land usage within the watershed has changed to support ever-increasing levels of poultry (primarily broiler) production, and most agricultural land is now pastured for the production of beef cattle. At present, just over 50% of the land area of Delaware County, Oklahoma and Benton County, Arkansas is classified as “Land in Farms” (USDA, 1997). In particular, the shift to poultry production is likely highly significant in impacting nutrient loading to the Eucha-Spavinaw watershed. Historically, the phosphorus laden fecal wastes from poultry production have been spread as fertilizer on land within the watershed. In the recent past, the Eucha-Spavinaw watershed had the capacity to produce over 84 million chickens, along with some 1,500 tons of phosphorous rich waste per year (Tulsa Metropolitan Utility Authority, 2001). Phosphorous present in these wastes and excess phosphorous stored in soil may then be washed into streams as a non-point-source pollutant. Ultimately, this phosphorus reaches the water supply lakes and promotes excessive algal growth. Although poultry waste disposal on fields within the watershed is now largely governed by a court order (see Egan, 2004) that limits the land disposal of poultry wastes, some wastes continue to be spread, and soil levels of phosphorus remain high. As a consequence, agricultural runoff, and the resultant nutrient loading and eutrophication of Lake Eucha and Lake Spavinaw remains a source of significant controversy and friction between those who use water from the Eucha-Spavinaw Watershed and those who produce chickens within the watershed.

Methodology: This problem was address through review of historical records of poultry production, analysis of land use and land cover and geochronological and geochemical analysis of undisturbed sediment cores from Lake Eucha and Lake Spavinaw.

Principal Findings and Significance: Within the sediments of Lake Eucha and Lake Spavinaw, increases in the concentrations for arsenic, selenium, and molybdenum, beginning in the early 1980's, are coeval and consistent with the increased poultry production within the watershed.

ABSTRACT

Within the last twenty five years, the Eucha-Spavinaw drinking water watershed in Northeastern Oklahoma and Northwestern Arkansas has shown a large increase in commercial poultry production. Presently, the level of nutrients entering Lakes Eucha and Spavinaw has put both lakes under eutrophic and hypereutrophic conditions. This project evaluates the sedimentary history of the Lakes to evaluate if there is any correlation between the timing of the increased poultry production and any changes in sedimentary trace metals. The sedimentary chronology is determined by gamma spectrometry using standard ^{210}Pb and ^{137}Cs dating methods. The sediments are analyzed for metals using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The data show increases in the concentrations for arsenic, selenium, and molybdenum beginning in the early 1980's, concurrent and consistent with the increased poultry production within the watershed.

Introduction

The Eucha-Spavinaw watershed has been used by the City of Tulsa as a source of its water supply since the early 1920's. The watershed covers roughly 415 square miles of agricultural land in Mayes County and Delaware County, Oklahoma, and Benton County, Arkansas.

The Eucha-Spavinaw watershed has a long history of agricultural activity. At present, the watershed supports a high level of poultry production. Recent water quality data for Lakes Eucha and Spavinaw indicate that higher levels of nutrients are now entering the watershed (OWRB 2002). Both lakes are presently classified as eutrophic or hypereutrophic. The lakes now show higher levels of algae production and the related taste and odor problems have increased the costs for water treatment by the City of Tulsa. The City of Tulsa is presently in litigation with the Poultry Integrators over the role of poultry production and poultry waste disposal within the watershed.

The poultry industry in the United States is the world's largest producer and exporter of poultry meat. Since the year 1980, the Eucha-Spavinaw watershed has supported a rapid increase in the commercial poultry industry, especially broilers (Figure 1). It is estimated that the watershed has the capacity to produce over 8 million chickens, along with some 1,500 ton of phosphorous per year.

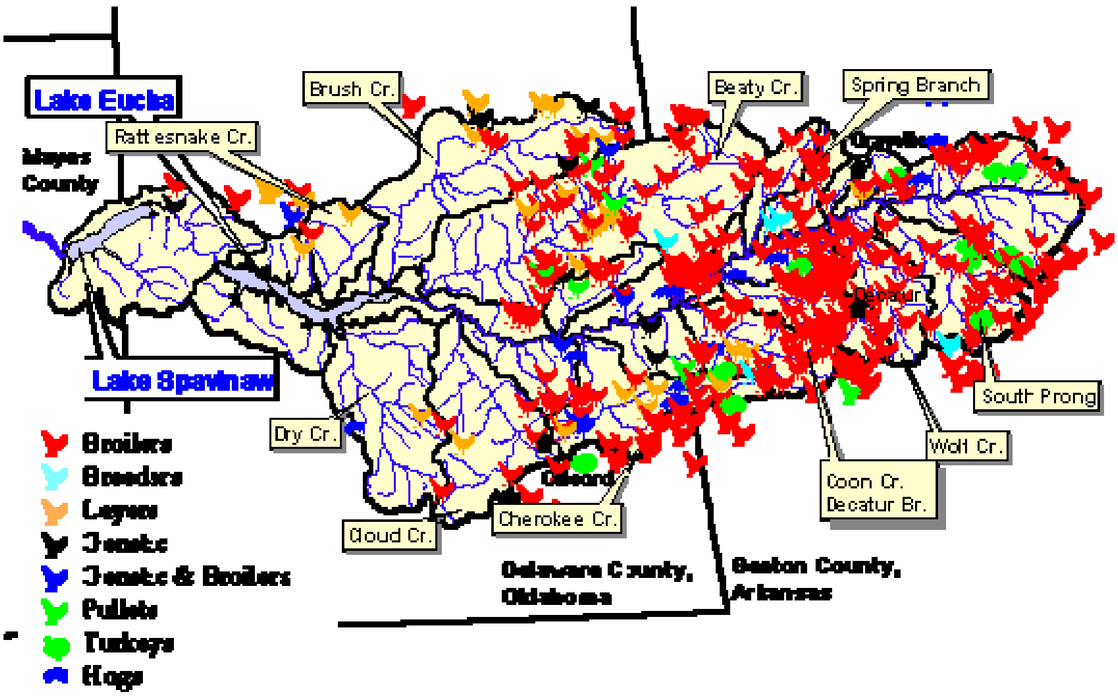

Figure 1. Map of Eucha-Spavinaw watershed with poultry farms, available online at http://www.tulsawater.com/eucha.html

According to the 2006 Poultry - Production and Value Report by the United States Department of Agriculture (USDA 2006), the total number of broilers produced in 2005 for Oklahoma and Arkansas were 0.25 billion and 1.21 billion, respectively (USDA 2006, 2002). The distribution of this poultry production within the Eucha-Spavinaw watershed for the last 50 years is presented in Table 1. As illustrated for yearly broiler sales in Figure 2, poultry production began to accelerate dramatically in the early 1980's.

In poultry feed, trace minerals are commonly used as additives. These feed additives can enhance immune function and disease resistance. In 1981, Underwood suggested that there were 22 minerals categorized as essential (Underwood and Suttle 1999) and include zinc, copper, manganese, molybdenum, selenium, and arsenic. As a result of these additions to poultry feeds, poultry waste normally contains higher concentrations of certain trace minerals.

Organoarsenicals, such as p-arsanilic acid and roxarsone (3-nitro-4-hydroxy-phenylarsonic acid), are commonly used as a growth stimulant antimicrobials to improve poultry production efficiency. Most of the arsenic fed to broilers is excreted (Laski, Sun et al. 2004).

The rapid growth of the poultry industry has produced a staggering amount of poultry waste. The most inexpensive way to treat poultry wastes with high nutrient content is through land disposal (Sims and Wolf 1994). Land disposal of poultry wastes may produce an accumulation of trace metals in soil and water system. Previous studies have raised concerns regarding application of poultry manure containing the organoarsenical feed additive roxarsone (Garbarino, Bednar et al. 2003; O'Connor, O'Connor et al. 2005; Cortinas, Field et al. 2006).

Table 1. Agricultural activity in the Eucha-Spavinaw watershed (estimated from USDA data)

Year	TOTAL Pasture (acres)	TOTAL Cropland (acres)	TOTAL Broiler Sales (birds)	TOTAL Cattle and Calves Sold (individuals)
2002	75,861	83,488	38,215,494	27,508
1997	80,970	87,360	34,003,897	24,701
1992	74,048	83,360	27,561,817	22,544
1987	85,299	82,953	18,928,529	23,255
1982	78,107	77,039	13,848,852	20,945
1978	87,082	77,856	10,049,832	25,678
1974	133,041	74,549	9,783,270	19,703
1969	134,188	85,962	10,344,923	21,601
1964	126,190	70,903	8,891,238	11,565
1959	156,503	79,871	5,788,672	13,230
1954	182,748	75,721	3,329,527	11,326

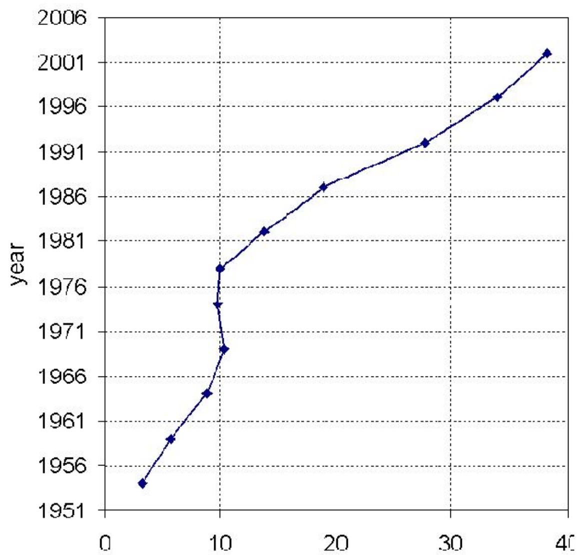

Fig. 2. Total broiler sales per year (in millions)

Nearly all the roxarsone used as an additive in chicken feed is excreted unchanged and is relatively stable in fresh dried poultry waste (Morrison 1969); however, during storage and land disposal (as fertilizer), arsenic species in poultry waste are degraded from roxarsone to arsenate, a more toxic inorganic species (Arai, Lanzirotti et al. 2003; Garbarino, Bednar et al. 2003; Jackson, Bertsch et al. 2003). Under anaerobic conditions, the degradation product of roxarsone and related N-substituted phenylarsenic acids is arsenite (Cortinas, Field et al. 2006).

This research examines the sedimentary history of Lakes Eucha and Spavinaw. The dates of sediment deposition were determined by using both ^{210}Pb and ^{137}Cs gamma spectrometric dating methods (Appleby and Oldfield 1992; Dabous 2002). Trace metals within the sediments were analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Materials and Methods

Sediment cores were collected by SCUBA divers on June 2005 from Lakes Eucha and Spavinaw. Lake Eucha is located approximately 6 miles south the city of Jay, Delaware County, Oklahoma, USA, off SH-10 and US-59. Lake Spavinaw is located approximately 4 miles downstream of Lake Eucha. The Eucha-Spavinaw watershed is located on the border of Northeastern Oklahoma and Northwestern Arkansas. Coring of the sediments was done using clear polycarbonate core tubes with a 3-mm wall thickness. The inside diameter of the tubes was 5 cm. The tubes were sealed with plastic caps on top and on the bottom, in situ, until ready to be sectioned off. The cores were maintained vertically to avoid disturbances. After arriving on land, the cores were prepared to be sectioned. The water inside the tubes was siphoned slowly so that no sediment was lost, and the bottom cap was released while the tube was placed

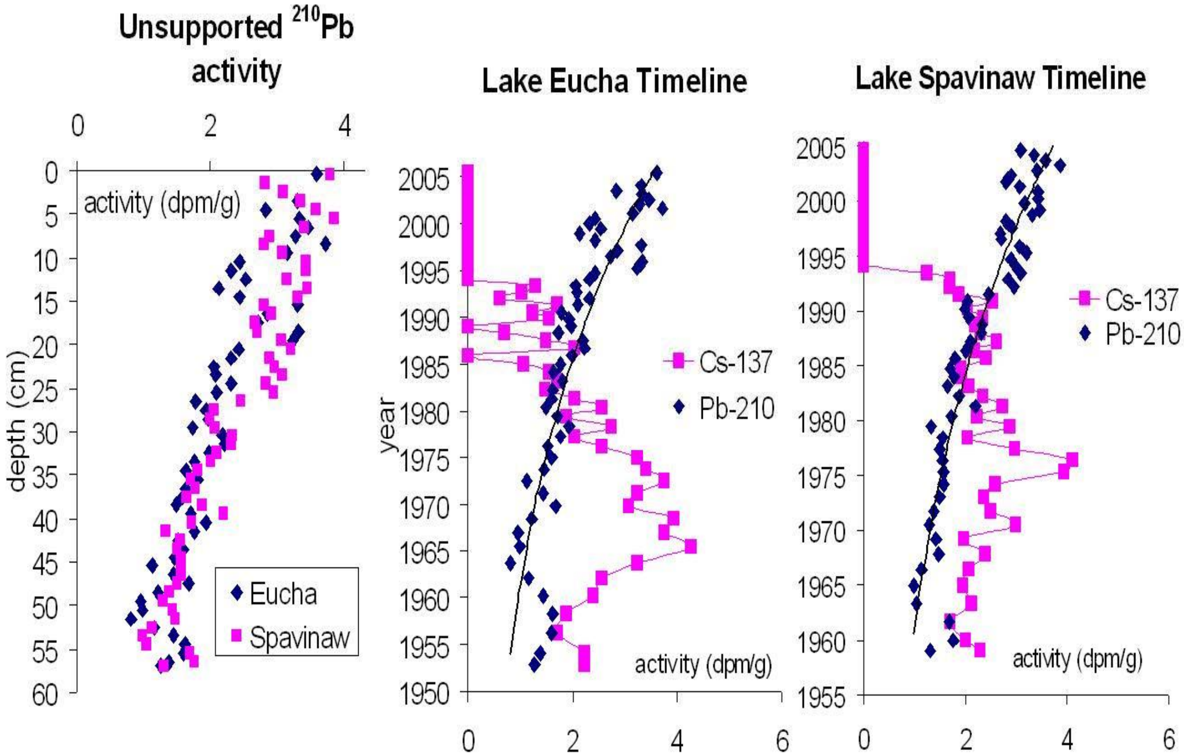

Fig. 3: Plot of unsupported ^{210}Pb with depth for Lakes Eucha and Spavinaw; ^{210}Pb and ^{137}Cs activity and time of deposition for Lakes Eucha and Spavinaw

onto a base plate with an incremental extrusion rod such that sections were sliced at 1 cm increments. The sectioned material was processed for water content by drying at 85^{o}C, and ground by hand using a mortar and pestle. Individual aliquots were taken for gamma spectrometry and trace metals analyses.

Gamma spectrometry was done using 4.0 gram samples in a sterile plastic petri dish (85mm x 15 mm) as a container. The petri dish was sealed by applying a thin layer of methylene chloride along the seam and samples were equilibrated for one month to allow for daughter product equilibration before gamma spectrometric analyses (24 hours, using a Low Energy Germanium (LEGe) detector model GL2020R from CANBERRA).

Acid digestion for trace metals analysis was performed using the EPA standard method 3050B which uses 1.0 gram of dry sample digested with repetitive addition of high purity nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). ICP-MS analyses were performed using the ELAN® 6100 DRC II ICP-MS from PerkinElmer Instruments which uses ammonia with its dynamic reaction cell to eliminate interference for As, Fe, Cr and Se analytes. Combo multi- elements standard and internal standard solutions used were provided by PerkinElmer with catalog #N9301721 in 5% HNO_3 and #N9301722 in 2% HNO_3 respectively. For metal analyses with ICP-MS, 15-mL plastic tubes were used as sample containers. External standards with concentration of 1, 10 and 50 ppb were used

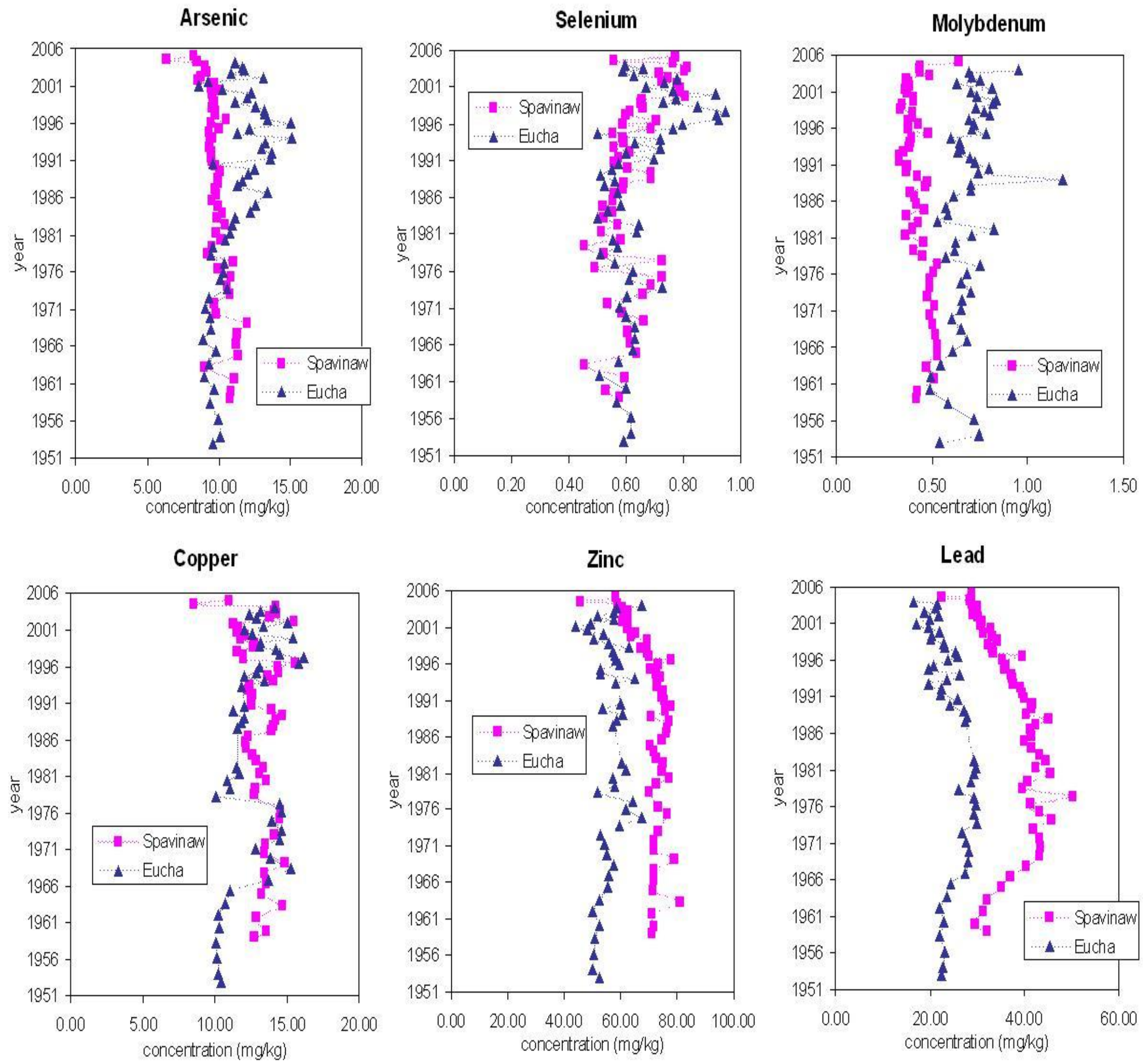

Figure 4. Plots of concentration of trace metals versus depositional year for Lakes Eucha and Spavinaw

for calibration. External standards were made of the multi-elements standard stock solution from PerkinElmer (catalog #N9301721 in 5% HNO_3). Nitric acid and water used for preparation of external standards were of high purity. Samples were diluted 10 times using 1% HNO_3 prior to analyses. Twenty ppb of internal standard (catalog #N9301722 in 2% HNO_3) were added to each external standards and samples prior to analyses. Calibrated micropipettes with sterile plastic tips were used for transferring internal standard solution to the samples and to the external standards.

Results and Discussion

Geochronology using ^{210}Pb and ^{137}Cs

The geochronology of the lakes sediments were determined using ^{137}Cs and ^{210}Pb dating (Figure 3). The year of deposition was calculated using a constant initial concentration model, which assumes that the initial activity of unsupported ^{210}Pb is the same at all depths. ^{210}Pb is a naturally occurring radioisotope in the ^{238}U decay series. Unsupported ^{210}Pb, that is the isotope derived from atmospheric deposition, was determined by difference between the total ^{210}Pb and supported ^{210}Pb (derived from decay of *in situ* ^{238}U). The sediment cores date to the 1950's.

The maximal ^{137}Cs activity, derived from atmospheric nuclear testing, is generally considered to have occurred in mid-1960. Sediments in Lakes Eucha and Spavinaw show maximal ^{137}Ca activity which corroborates the ^{210}Pb dating to the mid-1960's (Figure 3).

Trace metals analyses

Trace metal concentrations in Eucha and Spavinaw sediments are presented in Figure 4. Plots of arsenic, selenium, and molybdenum show increases beginning in the early - to mid-1980's, predominantly in Lake Eucha.

The increase of arsenic and selenium concentration in Lake Eucha began in the early 1980's. There is no significant change for arsenic concentration throughout the sediment profile in Lake Spavinaw. The increase of arsenic and selenium concentrations in Lake Eucha is time- correlative with the growth of poultry industry within the watershed.

Both arsenic and selenium are commonly used as additives in poultry feed. The changes of arsenic and selenium concentration in Lake Eucha suggest that Lake Eucha sediments are acting as a sink for arsenic and selenium released to the environment as a result of poultry waste application within the watershed.

Copper, zinc and lead concentrations show minor variability between Eucha and Spavinaw. The decreasing concentration of lead in both lakes shows a correlation with the ban of leaded gasoline usage in the United States beginning in 1970's. Copper increases slightly in the more recent sediments for both lakes, whereas zinc decreases showing a consistently higher level in Spavinaw.

Conclusions

Lake Eucha and Spavinaw sediments display changes over the last 50 years that are time-correlated with increased poultry production in the watershed.

Arsenic and selenium are commonly used additives in poultry feed. Both of these contaminants have increased in Lake Eucha beginning in the early to mid 1980's. At present, we do not know if molybdenum is added to poultry feed, but our data suggests that is has been. Independent studies on the trace metal contents in poultry feed are underway.

Finally, differences in arsenic concentration in Lake Eucha and Spavinaw sediments suggest selective bio-trapping in Lake Eucha.

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