Institution: University of Liverpool

Unit of Assessment: 10 – Mathematical Sciences

Title of case study: Radiometric dating of environmental records in natural archives

1. Summary of the impact (indicative maximum 100 words)

Environmental management decisions are frequently based on records of environmental change recovered from natural archives such as lake sediments. Key to deciphering these records is a reliable technique for dating sediment sequences. Researchers in the Liverpool University Mathematical Sciences Department have played a major role in the development of dating techniques using natural (^{210}Pb) and artificial (^{137}Cs) fallout radionuclides. Working with environmental scientists they have been responsible for the implementation of these techniques in research programs that have resulted in national and international controls on e.g. emissions from power stations, the use of persistent organic pollutants and climate change. In particular, the US National Parks Service (NPS) is using their research to monitor pollution levels at sensitive locations in their National Parks and this research has also been a key factor in the UN decision in 2011 to ban the widely-used insecticide Endosulfan. Their research also enabled the NPS in 2012 to identify the most effective solution for marsh restoration off Long Island, New York, resulting in a considerable financial saving to the NPS; and finally their research on pollutants in the Norfolk Broads has led to the current campaign by the Broads Authority to promote environmentally friendly anti-fouling paints.

2. Underpinning research (indicative maximum 500 words)

Note: All superscript references within this section refer to research listed in Section 3

The ^{210}Pb dating methodology is underpinned by research carried out by Professor P G Appleby and Dr G T Piliposyan (University of Liverpool Department of Mathematical Sciences) on the ^{210}Pb cycle[1,2,3]. ^{210}Pb is a naturally occurring fallout radionuclide created in the atmosphere by the decay of ^{222}Rn gas, a daughter product of ^{226}Ra that enters the atmosphere by diffusion from land surfaces. The ^{210}Pb atoms are then quickly attached to atmosphere particulates and deposited on the landscape principally during rain. A fraction of this fallout ^{210}Pb deposited on a lake and its catchment is transported through the water column and incorporated in sediments forming on the bed of the lake. Each layer so formed is in time buried by subsequent deposits, and the initial concentration reduced by radioactive decay. By measuring the present day concentrations it is then possible to calculate the age of each layer provided accurate estimates can be made of the original concentrations.

Although the general nature of this cycle has been reasonably well known at a qualitative level, mathematical models in recent papers by Piliposyan and Appleby[1,2,3] have led to a much better quantitative understanding of these processes, and in a more reliable dating methodology in which the ^{210}Pb calculations for each site can be calibrated against chronostratigraphic dates determined from sediment records of ^{137}Cs[4], an artificial radionuclide fallout of which originated from the atmospheric testing of thermo-nuclear weapons, and nuclear accidents such as Chernobyl. The method has been used in numerous environmental studies, e.g. climate change in Tibet[5]

Key to the widespread use of these methods was the development of non-destructive methods for determining ^{210}Pb, ^{226}Ra and ^{137}Cs in environmental samples by gamma assay using hyper-pure germanium well-type gamma spectrometers, pioneered at Liverpool. One of the inherent problems with this technique, particularly when analysing low energy gamma photons such as those emitted by ^{210}Pb, is the effect of self-absorption within the sample. Appleby and Piliposyan have developed models for making corrections for such losses in samples of varying size, mass and composition[6]. These models have been incorporated into a software suite used to analyse data from the University of Liverpool Environmental Radiometric Laboratory operated jointly with colleagues in the Department of Physics and recognised as internationally one of the leading facilities of its kind in the world.

Because of their expertise both with the modelling and radio-analytical techniques, research groups from all around the world continue to seek the advice of, and collaborate with

Appleby and Piliposyan on the implementation of the ^{210}Pb dating methodology in the context of a wide range of projects concerned with recovering records of environmental change stored in lake sediments, salt-marshes and peat bogs. Recent projects in which they have been partners include

- US EPA (2003-6) Western Airborne Contaminants Assessment Project studying trans-pacific transport of pollutants from the Asian land mass.
- US EPA (2005-8) Study of salt marsh sedimentation on Long Island and its impact on landscape structures.
- Spanish Ministry of the Environment (2006-9) Study of reservoir sedimentation rates in Spain
- Alfred-Wegener-Institute, Potsdam, Germany (2009-12) Studies of recent environmental change in Tibet and Arctic Russia.

3. References to the research (indicative maximum of six references)

1. Piliposyan G & P G Appleby, 2003. A simple model of the origin and transport of ^{222}Rn and ^{210}Pb in the atmosphere. Continuum Mech. Thermodyn. 15: 503-518. (Impact factor 1.091). DOI:10.1007/s00161-003-0129-1
2. Appleby P G, E Y Haworth, H Michel, D B Short, G Laptev & G T Piliposyan, 2003. The transport and mass balance of fallout radionuclides in Blelham Tarn, Cumbria (UK). J Paleolimnology 29: 459-473. (Impact factor 2.209). DOI: 10.1023/A:1024437426878
3. Piliposyan G & P G Appleby, 2003. A model of the impact of winter ice cover on pollutant concentrations and fluxes in mountain lakes. Water, Air & Soil Pollution 44: 101-115. (Impact factor 1.748). DOI: 10.1023/A:1022994812659
4. Klaminder J, Appleby P, Crook P & Renberg I (2012). Post-deposition diffusion of ^{137}Cs in lake sediment: implications for radiocesium dating. Sedimentology, 59:2259-2267. (Impact factor 2.601). DOI:10.1111/j.1365-3091.2012.01343.x
5. Wischnewski J, Mackay AW, Appleby PG, Mischke S & Herzschuh U, 2011. Modest diatom response to regional warming on the southeast Tibetan Plateau during the last two centuries, J Paleolimnology, 46:215-227. (Impact factor 2.209). DOI 10.1007/s10933-011-9533-x
6. Appleby P G & G T Piliposyan, 2004. Efficiency corrections for variable sample height in well-type germanium detectors. NIMB 225: 423-433. (Impact factor 1.266). DOI:10.1016/j.nimb.2004.05.020

4. Details of the impact (indicative maximum 750 words)

Note: All superscript references within this section refer to corroborating sources listed in Section 5

Most projects studying recent environmental change as recorded in natural archives such as lake sediments involve teams of scientists working on a range of environmental indicators. Decisions on environmental issues are generally based on findings from many different sources, and may have long-term impacts. Ongoing work with colleagues studying sediment records in Siberia is one of many investigations informing the debate on climate change in the Arctic. Below are brief accounts, supported by letters from lead contacts, of three recent projects with more limited objectives and readily identifiable impacts.

Western Airborne Contaminants Assessment Project (WACAP)[1]

The lead contact for this USEPA funded project, carried out during 2002-7, was Dr Dixon H. Landers, Senior Research Environmental Scientist at the U.S. Environmental Protection Agency.

The main results were reported in 2008[1] and a summary (including initial impacts and actions) in 2009[2]. According to a letter from Dr Landers[3], the project has had wide ranging impacts on chemical registration decisions, new research, conservation actions and decisions relating to regulation of pollution sources. The knowledge framework has been used to inform various regulatory bodies[3] concerned with the impact of emissions from industrial sources and agricultural uses of pesticides. The Liverpool role in providing dated profiles made a major contribution to two main elements of the project. First, to compare current contaminant deposition rates with those from historic, pre-industrial times. Second, to explicitly link the sediment records to increases in airborne contaminants from "regional" sources. Dr Landers describes Appleby and Piliposyan's

contribution as "*authoritative*" and confirms that their "*careful and thorough work was a key component in the high level of success that WACAP has enjoyed*".
To be precise, according to Dr Landers[3], the sediment work by Appleby and Piliposyan "*provided strong evidence on the extent to which recent increases in Hg contamination ... were due to emissions from local or regional sources, as opposed to higher global background concentrations*". There are presently a number of research efforts funded by the NPS (National Parks Service) and other government and non-government organizations building on these results. As Dr Landers states[3], "*the WACAP data has been used to help select which parks to target for this research*" by identifying the sites most at risk from local Hg emissions.
Moreover the sediment records resulting from Appleby and Piliposyan's work for WACAP "*have been most useful in helping NPS understand which Historic Use Pesticides continue to persist in park ecosystems often well after they have been banned, and which Current Use Pesticides are beginning to increase in park ecosystems over time."* In particular, data supplied by Appleby and Piliposyan on the residual incidence of the pesticide Endosulfan in the natural environment was a major part of the evidence base which resulted in the UN decision to ban it. As Dr Landers states*, "Data on the temporal record of the presence of the widely-used insecticide Endosulfan obtained from WACAP sediment records was entered as evidence of the long term persistence and widespread occurrence of this substance in hearings that preceded the [United Nations] decision to ban it*". In 2011, Endosulfan was added to the UN list of persistent organic pollutants to be eliminated worldwide[4].

Restoration of mosquito control ditches on Fire Island, New York
This US National Park Service funded project, led by Dr Roman (NPS) and Professor John King (University of Rhode Island), was designed to provide evidence concerning plans to restore marshes on the Fire Island National Seashore that decades earlier had been ditched for mosquito abatement. In a letter[5], Prof King says that the work of Appleby and Piliposyan "*provided important information for environmental managers at the National Park Service*" and "*supported a management option that will save considerable money*". Specifically, the NPS needed to make a decision whether to actively fill in the ditches, "*a costly and major undertaking*" according to Professor King[5], or leave them alone to fill in naturally. Dr Roman confirmed in an e-mail[6] that Appleby and Piliposyan's research was "*instrumental in the NPS decision to allow human made ditches at Fire Island National Seashore to fill naturally*". The Liverpool role was to analyse and date sediment cores from various locations on Fire Island. ^{210}Pb records in salt-marsh sediment cores were used to determine the rate of sea level rise[7]. ^{210}Pb records in sediment cores from the ditches were used to determine current natural sediment accumulation rates[8]. The results (published in 2012[8]) suggested that natural inundation would best achieve the desired goal. In consequence management has subsequently decided on the non-intervention option; Professor King states in his letter[5] that "the paper which resulted from this work [Ref. 8 below] is being applied now". This has resulted in a considerable financial saving to the NPS.

Use of antifoulant paints in UK inland waters
The lead contact for this English Nature, DEFRA and NERC funded project, carried out during 2000-3, was Dr Carl Sayer of University College London (UCL). The main purpose was to determine the cause of the ecological degradation of the Norfolk Broads shallow lake system, one of the suspects being the use of toxic tributyltin (TBT) in boat antifouling paints. The Liverpool role was to date sediment cores from the Broads. The resulting chronology was used by UCL to reconstruct the historical record of TBTs in the lake waters. The results, widely reported in the media, demonstrated not only that TBT was a key contributory factor but also that previously contaminated sediments acted as a long-term reservoir for pollution in spite of the world-wide ban on the use of TBTs that came into force in 2008. The Senior Ecologist at the Broads Authority, Dr Andrea Kelly, confirms in a letter[9] that "*as a consequence of this work and subsequent media coverage the Broads Authority initiated a campaign to promote environmentally friendly antifoulant use in the Broads system*". This ongoing campaign informs their current advice to boat users[10], and as Dr Kelly states[9], "*this research… has been influential in informing the authorities policy and strategic conservation direction in regard to policy on ecoboating and anti-foulant paint use on the Broads*" and developing literature for the 2013 Green Boat Show on the Broads[10].

5. Sources to corroborate the impact (indicative maximum of 10 references)

1. A summary of the findings of the WACAP project can be found at http://www.nature.nps.gov/air/studies/air_toxics/docs/2008FinalReport/08_FactSheet_HiRes_letter.pdf
2. Bulletin issued by NPS to summarise study findings and impacts, corroborating the use of Liverpool research.
3. Senior Research Environmental Scientist, U.S. Environmental Protection Agency, can corroborate, in a statement of support, the impact of the Liverpool contribution on chemical registration and regulation of pollution sources policy.
4. An announcement of the ban on Endosulfan may be found at http://cep.unep.org/repcar/prohibicion-del-uso-de-endosulfan-en?set_language=en
5. Professor of Oceanography at Paleomagnetics and Coastal Mapping Laboratory, University of Rhode Island, has provided a letter of support to corroborate the impact on Environmental Management in the United States.
6. Coastal Ecologist at National Park Service, University of Rhode Island, USA, can corroborate, in a letter of support, that the manuscript 'Journal of Coastal Research', co-authored by Appleby, has been instrumental in the National Parks decision making on human-made mosquito ditches
7. A National Park Service report on which the mosquito ditch management decision was based may be found at http://www.nps.gov/nero/science/FINAL/FIIS_marsh/FIIS_marsh_sealevel_final_July07_v2.pdf
8. The second report on which the mosquito ditch management decision was based was Corman SS, Roman CT, John W. King JW and Appleby PG, 2012. Salt Marsh Mosquito-Control Ditches: Sedimentation, Landscape Change, and Restoration Implications, J Coastal Research **28**:874-880. DOI: 10.2112/JCOASTRES-D-11-00012.1.
9. Senior Ecologist, Broads Authority can corroborate the role research played in informing the Authorities policy on ecoboating and anti-foulant paint use on the Broads.
10. Broads factsheet on cleaner and greener boating, citing "recent research on past use of antifouling paints".