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Geochronological implications of ^{210}Pb and ^{137}Cs mobility in cave guano deposits

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Abstract: Some recent publications on the paleo- and historical environmental interpretation of bat guano sequences have relied on ^{210}Pb and ^{137}Cs distribution to establish age-depth models, even when these are at odds with radiocarbon models in the lower parts of the sequence. Here, we present both field and laboratory evidence for the unpredictable mobility of lead and cesium in decomposing bat guano deposits. We suggest that ^{210}Pb - and ^{137}Cs -based chronologies of bat guano deposits should only be used when independently supported, for example, by a robust radiocarbon age-depth model.

Keywords: Pb-dating, guano, redox chemistry, ^{210}Pb , ^{137}Cs , Borneo

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INTRODUCTION

Cave dwelling insectivorous bats form the largest colonies of any mammals, often comprising $10^4 - 10^5$ individuals and occasionally reaching 10^6 individuals (McCracken, 2003; Betke et al., 2008; Fury et al., 2018). In Southeast Asia, cave roosting colonies of swiftlets (genus *Collocalia*) reach comparable numbers. Insectivorous bat and swiftlet guano is composed largely of chitin, a highly decomposition-resistant polysaccharide that can accumulate in caves over millennial timescales to depths of many meters and volumes of $10^2 - 10^3$ cubic meters (Briggs, 1974; Frank, 1998; Bird et al., 2007).

DesMarais (1980) was the first to recognize that bat guano carried a stable isotope record of the environments over which the bats fed. That work was followed up a decade later by Mizutani and McFarlane (1992), who extended the concept to the stable isotope paleoecological record of Jamaica. More recently, Wurster and colleagues reinvigorated the field by developing new preparation and analysis techniques, leading to the resolution of important records in Arizona (Wurster et al., 2008), and Borneo (Wurster et al., 2010). Additional recent studies followed, including Guadeloupe (Royer et al., 2015), Romania (Johnson et al., 2010; Ferenc et al., 2015) and Jamaica (Lauren et al., 2020).

A foundational requirement for extracting a paleoecological record from a guano sequence is a

reliable age-depth model, which can be complicated by non-linear factors such as compression and decomposition-related compaction. The former, a significant issue with guano samples recovered by coring, was addressed by McFarlane and Keeler (1991) but has not been widely recognized. Properly treated guano accumulations are very tractable to radiocarbon dating (Wurster et al., 2009) but a dense set of dates, at high cost, is required to establish a reliable non-linear age-depth model. An additional complication is that radiocarbon dates on very recent deposits have 1 sigma errors no better than ~40 years, making the technique of little value in young deposits. Thus, beginning with work by Utida et al. (2014), a few authors (e.g., Wirmann et al., 2017) have attempted to adapt the ^{210}Pb steady-accumulation model often used in peat studies to bat guano sequences. Nevertheless, the validity of the ^{210}Pb method for age-depth models in guano has not been explicitly demonstrated, and two recent studies (Gallant et al., 2020; Bogdanowicz et al., 2020) give us cause for concern. Smith (2001) offers a salutary reminder of the potential problems of ^{210}Pb dating, recommending that at least one independent tracer should be used to validate the ^{210}Pb chronology (by implication, for all studies, regardless of substrate).

Here, we review the biogeochemistry of guano decomposition and present evidence of unpredictable ^{210}Pb and ^{137}Cs mobility, which likely makes ^{210}Pb chronologies and ^{137}Cs stratigraphic marker dating

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that are unsupported by alternative independent dates, unreliable in most guano sequences. Although we worked with bat guano, these principles are also relevant for bird guano accumulations (such as those by Xu et al., 2010, 2016, 2018).

Overview of principles of Pb-210 and Cs-137 dating

Pb-210 is constantly being created in the atmosphere by decay of radon gas, and, being non-gaseous, the ^{210}Pb falls to the surface of the Earth (in 5–10 days), where it then gradually radioactively decays (to ^{206}Pb), with a half-life of 22.26 years, until it has essentially disappeared after about 200 years. The amount of fallout varies with geographic location but is generally constant at a given site. Therefore any site where sediment is accumulating will incorporate the fallout ^{210}Pb , burying each successive layer of sediment plus its gradually-decaying ^{210}Pb . After ~200 years the buried layer of sediment no longer has any detectable ^{210}Pb . Thus, a graph of ^{210}Pb activity should show the topmost layer, representing zero age, with the highest value and a simple exponential reduction with depth to the ~200 year old layer, beyond which the technique cannot be used (Fig. 1).

Lead and cesium are incorporated into cave guano by a three step route: plants absorb the elements from the soil, insects eat the plants, bats eat the insects out in the landscape and then defecate inside the cave.

Dating using ^{137}Cs also depends on deposition unto surfaces from atmospheric fallout. However, most of the atmospheric ^{137}Cs was created during the 20th century nuclear bomb tests, starting in the early 1950s with the main (sometimes detectable as double) peak in 1959–1963. Thus it acts as a marker or tracer rather than having a constant rate of fallout, and a graph of ^{137}Cs with depth should show an obvious peak marking the layers laid down around the year 1961. With a half-life of ~30.17 years, the bomb-test ^{137}Cs should still be detectable for about 300 years.

Fig. 1. Ideal activity:depth profiles for undisturbed sedimentary ^{210}Pb and ^{137}Cs .

Both ^{210}Pb and ^{137}Cs adsorb to sediments, and, in many environments, such as soil, are not further translocated after deposition. Thus both isotopes can be used as dating tools. If both ^{210}Pb and ^{137}Cs values are graphed, the curves should look something like Figure 1. However, if the isotopes do not remain in their original place of deposition (e.g., Drexler et al., 2018, note that, at least for wetlands, ^{137}Cs appears to be a lot more mobile than was formerly assumed), then they may lose their efficacy – which is the subject of the present manuscript.

Geochemistry of bat guano deposits in relation to Pb sequestration

A fundamental assumption of ^{210}Pb dating is that the atmospherically derived ^{210}Pb is immobilized in the stratigraphic column. In peat studies, it has been shown that the substrate has a high cation exchange capacity and that heavy metal cations (notably Pb, Cu and Zn) are preferentially bound (Wiedler, 1990). The relative affinity for heavy-metal binding in peat is in the order $\text{Pb} > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn}$ (Vile et al., 1999). The sorption capacity of peat at pH 5 is reported as around 80 mg/g Pb^{2+} (Logan et al., 1997). Peat is generally well preserved in cores, and thus organically-bound Pb is generally immobile. However, it has been shown that changing redox conditions associated with changes in local water table, and the tendency of Pb to bind to dissolved organic carbon can result in high degrees of Pb mobility (Van Dijk, 1971; Urban & Schurr, 1990).

Bat and swiftlet guano consists primarily of fragments of insect cuticle composed principally of chitin initially in the size range of 0.5–1.5 mm up to a maximum of 3 mm (Lundberg & McFarlane, 2021). The basis of ^{210}Pb dating of guano is that Pb^{2+} ions sorb to chitin. Biosorption of Pb^{2+} ions onto chitin and chitosan has been directly demonstrated for crustacean chitin under laboratory conditions (Muhaemin, 2005), and shown to be pH dependent. Similar studies by Dewage et al. (2018) reported binding rates of 5.8 mg/g Pb^{2+} at pH 5 on laboratory-prepared chitin+cellulose beads. Additional components of guano, including proteins, lipids and waxes (Breger, 1966; DesMerais et al., 1980), are quickly broken down by the guanophagous invertebrate and microbiological community of cave-guano ecosystems (Ferreira, 2019), and are therefore not relevant to Pb sequestration. In any case these are normally removed by chemical treatment in guano studies (e.g., Wurster et al., 2009).

Chitin, a long-chain N-acetylglucosamine polysaccharide (Cohen, 2009), may eventually be decomposed under suitable conditions by specialized chitinase-producing bacteria and fungi, via two pathways: direct cleavage to water-soluble monomers, and deacetylation to chitosan (Beier & Bertilsson, 2013), the latter being more important in soil (and guano?) communities (Gooday, 1990). Chitin degradation rates are known to be temperature sensitive (Metcalf et al., 2002) and the guano microbial communities are pH dependent (e.g., De Leo et al., 2018). However, because chitin is so resistant to degradation – the oldest known preserved

chitin is ~25 million years old (Briggs, 1999) – chitin degradation over the timeframe of ²¹⁰Pb dating is unlikely to compromise the technique in relatively dry accumulations. Nevertheless, anecdotal observations in moist, tropical environments suggest that chitin can be substantially decomposed over decadal timescales.

None of the published studies of biosorption of Pb²⁺ ions onto chitin has dealt with the chitin in natural guano, or in natural settings. In this paper, we present direct measurements of Pb²⁺ (and Cs²⁺) binding to insectivorous bat guano. Since the binding of Pb²⁺ is known to be sensitive to redox conditions, our research was divided into three stages: 1) in the field we recorded the in-situ geochemical environments of three guano accumulations in Borneo; 2) we measured ²¹⁰Pb on two of these profiles; and 3) in the lab we assessed potential Pb²⁺ and Cs²⁺ binding to insectivorous bat guano.

METHODS

1) Field redox conditions: Actively forming guano piles under roosts of the Wrinkle-lipped bat (*Chaerephon plicatus*) in Deer Cave (*Gua Rusa*), Gunung Mulu National Park, Sarawak (4.0242° N; 114.8260° E.), were rapidly excavated from surface to base. Measured vertical profiles were immediately tested for temperature with a horizontally inserted 10 cm thermistor probe, and pH was measured in a suspension of guano and deionized water using an Extech PH110 pH meter.

2) Measurement of ²¹⁰Pb: Two profiles were sampled (under permit). The deeper profile was sampled at 5, 30, and 60 cm from the surface, and the shallower profile at 5 and 40 cm from the surface. ²¹⁰Pb decays via beta emission to ²¹⁰Bi (half life ~5 days) and then to the alpha-emitter granddaughter isotope, ²¹⁰Po (half life 138 days). Samples from the first profile were measured for ²¹⁰Pb levels via ²¹⁰Po by alpha spectrometry at MyCore Scientific Inc., Ontario, Canada (and repeated to give two estimates for each sample), and from the second core at UQAM, Géotop, Montreal. Note that these few measures of ²¹⁰Pb were simply done to demonstrate that the profiles do not conform to the ideal decay curve (rather than as a genuine attempt to date the material) and therefore they need neither be many nor very precise.

3) Lab experiment on binding of Pb²⁺ and Cs²⁺ ions to guano: In order to test the potential for natural bat guano chitin to bind to Pb²⁺ and Cs²⁺ ions and the strength of binding under acid conditions, we exposed guano to a solution of known Pb and Cs concentration at different pHs. A sample of ~1.5 g of fresh insectivorous bat guano (collected under permit from Niah Cave, Sarawak) was cleaned, following standard preparation procedures (e.g., Wurster et al., 2009; Brock et al., 2010), in dilute HCl for 24 hrs at 20°C; triple-washed in deionized water, re-suspended in 5% NaOH for 48 hrs at 4°C; and triple-washed again in deionized water. Two of three splits were adjusted to pH 6 with HCl, and suspended for 4 hours in a solution of 36 ppm Pb²⁺ [lead acetate, Pb(C₂H₃O₂)₂] and 50 ppm Cs²⁺ (cesium carbonate, Cs₂CO₃), separated

by filtration, and washed 5 times with 10 volumes of ultrapure water per wash. One of these two splits was then suspended in pH 3.0 HCl for 24 hours, and again water washed. The third split served as a control (Fig. 2). Pb concentration was measured by ICP-MS at ACTLABS, Ontario, Canada.

Fig. 2. Experimental protocol for chelation and leaching tests.

RESULTS

1) Field redox conditions

Temperature and pH profiles for the three sites are shown in Figure 3. Guano Pile B is in the main chamber of Deer Cave, but well secluded from human activity. Pile C is at a high level close to the south-eastern wall near to the Garden of Eden entrance (and is the source of the phosphate-rich waters stimulating growth of stromatolites: see Lundberg & McFarlane, 2011). Air temperature was 23.5°C. The profiles all show temperatures above ambient (reaching a maximum of 28.1°C), with the highest temperatures generally about 10-30 cm from the top, the smaller pile reaching ~2°C above ambient, and the deeper pile ~4.5°C above ambient. With an average pH of 4.9, the guano piles are all on the acid side of neutrality (reaching a minimum pH of 2.8 in profile 1, and an average pH at a depth of ~12 cm of 4.4). While more variable than the temperature patterns, all of the profiles have a tendency towards greater acidity at about 10-30 cm depth. These data indicate that moist, decomposing guano accumulations generate significant metabolic warmth and increased acidity.

2) Pb-210 on two guano profiles

Data on ²¹⁰Pb activity (in Becquerels per gram) are shown in Table 1 and Figure 4. Overall the activity values are rather low and the error therefore rather high, but the general pattern is clear: in both cases,

Fig. 3. Results for pH and temperature conditions in the three guano profiles. Note the difference in scale for the y-axis in Profile 3.

^{210}Pb activity is greatest at the greatest depth, rather than at the surface – a clear departure from the ideal decay curve as shown in Figure 1.

Table 1. ^{210}Pb activity data.

Sample ID	^{210}Pb Bq/g	±%
Geotop, Profile 1 5 cm depth	0.010	8.3
Geotop, Profile 1 40 cm depth	0.038	6.2
*Mycore, Profile 3 5 cm depth	0.039	8.3
	0.043	8.0
Mycore, Profile 3 30 cm depth	0.021	8.1
	0.018	8.6
Mycore, Profile 3 60 cm depth	0.127	4.3
	0.134	4.6

*The detection limit for the MyCore lab was 0.013 ± 0.003 Bq/g

3) Pb and Cs binding and leaching test

The purpose of this leaching test was to simulate conditions in a guano profile where the uppermost layer is usually the least acidic, but the centers of decomposition at lower layers are more strongly acidic. At time of deposition ^{210}Pb will be retained on the chitin surfaces. However, as this layer gets buried by later accumulations, the ^{210}Pb decays away, but, more importantly, becomes subject to conditions of increasing temperatures and decreasing pH.

Pb^{2+} and Cs^{2+} retention and leaching values appear in Table 2. The results are straightforward and similar for both elements: pH 6 allows substantial binding to chitin; and subsequent leaching at pH of 3 substantially reduces the binding levels, especially noticeable for ^{137}Cs . The implication is that a significant proportion of chitin-bound Pb and Cs is likely to be mobilized at depth, and elute either out of the guano profile entirely or to be re-bound at depths below the decomposition strata.

It should be noted that our measurements of ^{210}Pb are based on the standard alpha-spectrometry technique,

which actually assays to granddaughter ^{210}Po (which reaches secular equilibrium with ^{210}Pb in a few weeks). These elements differ chemically and thus may be expected to behave differently in the environment. However, it is well established that ^{210}Pb and ^{210}Po are in secular equilibrium in most soils (Carvalho et al., 2017), and that the patterns of mobility demonstrated here for Pb and Cs (and observed in guanos for a wide range of heavy metals) can be expected to apply equally to ^{210}Po . The leaching experiments conducted by Barbero et al. (2014) for acid mine drainage studies indicate that mobility of Po is actually very low in acid conditions. Two implications can be drawn from this: firstly, in our profiles the ^{210}Pb had migrated downwards, but the ^{210}Po that is measured as a proxy for ^{210}Pb is very unlikely to have migrated any further; and, secondly, if the ^{210}Po in our guano were mobile, then the ^{210}Pb would be much more so.

Fig. 4. Changes in ^{210}Pb activity (in Bq/g) with depth, from two profiles.

Table 2. Metal chelation by guano at different pH.

	Pb^{2+} ppm	Cs^+ ppm
Control	2.4	0.03
Chelated (pH6)	851	>500
Chelated (pH6) and remobilized (pH3)	514	3.06

DISCUSSION

Redox conditions and Pb binding

The pH of guano is significant for consideration of Pb^{2+} binding. Keleşoğlu (2007) has shown that heavy metal binding to chitin and chitosan peaks at $\sim\text{pH } 6\text{--}7$, and then declines rapidly with falling pH (Fig. 5). Thus, whereas peat bogs support pH environments of ~ 4.0 (Clymo et al., 1984), decomposing guano accumulations can develop localized acidities an order of magnitude higher, which might be expected to mobilize $\sim 60\%$ of the Pb^{2+} load.

The pattern of change of temperature and pH in a guano pile (Wurster et al., 2015) relates logically to metabolic activities. Typically, the uppermost layer of very recently deposited guano is not yet acidic (surface guano is potentially even basic, due to released ammonia). Wurster et al. (2015) found the pH of fresh guano generally to be near neutral, but becoming strongly acidic with depth (e.g., from 7.3 at the surface to 2.7 at 66 cm depth, from 5.1 at surface to 2.7 at 123 cm depth). Acidity develops with depth as bacterial decomposition (and therefore production of CO_2 and organic acids) progresses, peaks, and then falls as the amount of decomposable organics remaining falls off.

Guano is generally well drained and well aerated, especially in the upper layers. Mobilization of Pb^{2+} ions might therefore be expected to increase with increased acidity and increased de-polymerization of the guano, the released ions freed to move down-profile by elution. In the lower layers of reduced decomposition, reduced heat, and reduced acidity, the Pb^{2+} ions may well be re-deposited. The final fate of the Pb will depend on substrate and moisture. In a wet, raised deposit of guano the Pb is probably washed

out completely in guano drainage. In other deposits it might bind to basal clays and/or re-bind to chitin. The pH changes we observed with depth, especially in our Profile 1, suggest that very little Pb could be retained in the uppermost layers, but there might be a tendency towards greater retention in the less acidic deeper layers – a pattern that is confirmed in our ^{210}Pb activity measures. While the three measurements of ^{210}Pb from Profile 3 certainly do not reveal the complete ^{210}Pb curve we can speculate that the higher sequestration of ^{210}Pb at 60 cm depth may represent the elution front (see also further discussion of guano decomposition processes and chelation below).

Chelation in guano deposits

Diagenesis rates for guano accumulations range from essentially zero for “mummified” deposits in extremely dry environments to complete degradation on apparent-decal timescales in warm, moist caves. For example, bat guano from Aden Crater, New Mexico, on which rested an extinct ground sloth dated at $9,840 \pm 160$ yr (Simons & Alexander, 1964), retains the original unaltered structure of the fecal pellets. In contrast, freshly-forming deposits in Deer Cave, Sarawak, may fully decompose to non-organic basal layers on apparently short timescales (i.e., prior to their removal by recurring large floods).

In moist deposits, decomposition adds significant quantities of sulphuric, phosphatic and nitric acids to the pore water, which may move freely through the guano profile. Heavy metals chelated to chitin and chitosan at modest pH (~ 6.0) in upper layers are subject to vigorous leaching in lower layers where pH may reach 3.0 or lower. In situations where the guano rests on limestone bedrock, these acids are neutralized and form a layer of calcium phosphate and/or calcium sulphate. Even within the main guano mass, percolating cave dripwater, carrying heavy loads of Ca^{2+} ions, locally react with the decomposition acids and form discrete masses of gypsum nodules or bands (Fig. 6) – a phenomenon which appears to result from the higher affinity of SO_4^{2-} to Ca^{2+} relative to PO_4^{3-} and Ca/P ratio (Onac & Veres, 2003; Queffelec et al., 2018).

The increasing pH associated with this neutralization will increase heavy metal chelation to any remaining organics, and have the effect of concentrating heavy metals in these locations. In caves with strong airflow, seasonal variations in humidity and drip water availability may reverse pore fluid movement, resulting in sulphate, phosphate and in low-humidity environments, nitrate minerals within the guano sequence or efflorescences on the guano surface (Hill, 1981; Onac et al., 2009).

In simpler cases, general downward movement of the pore water can result in increasing enrichment of mobile heavy metals, including Pb^{2+} , in lower strata (Fig. 7). This phenomenon was recognized as early as the late 19th Century in the form of extreme copper enrichment of bat guanos from Italy ($\sim 3,200$ ppm Cu; Hutchinson, 1950) and Batu Cave, Malaysia (2,900 ppm Cu; Dunstan, 1905). Recent data (Wurster et al., 2015) identified 7,932 ppm in guano from Batu

Fig. 5. Effect of pH on adsorption of Pb^{2+} ions by chitin (data from Keleşoğlu, 2007) and pH values from Deer Cave guano profiles.

Fig. 6. Ancient guano sequence in Niah Cave, Sarawak. Light-colored bands and nodules are autochthonous gypsum (Lundberg & McFarlane, 2021).

Cave, Malaysia, and 8,081 ppm from Gangub Cave, Palawan. Lead, which is present in unaltered bat guano from tropical forest environments at levels of $\sim <10$ ppm, reaches concentrations as high as 216 ppm in some decomposed/decomposing bat guano accumulations (Batu Cave, Wurster et al., 2015), an enrichment of more than 500%. However, it is notable that enrichment in Pb^{2+} and other heavy metals with depth is often reversed in the lowest levels of a guano deposit (Fig. 7), also observed in Romania by Onac et al. (2015). This reflects a process of release during early decomposition, followed by downward transport in percolating acidic drainage, chelation to chitin, and finally release and leaching as the chitin reaches an advanced stage of breakdown.

Pb-210 profiles

The most reliable profile for convincing ^{210}Pb dating is one showing the maximum at the top and a simple radioactive decay curve with depth (as shown in Figure 1). However, as is apparent in many of the published profiles, the pattern can be quite variable with peaks in odd places: for example, of the four cores of seabird guano tested by Xu et al. (2010), only one showed the classic pattern of exponential decay with depth and a single ^{137}Cs peak at the depth that correlates with the calculated ^{210}Pb date. The other cores show several peaks of both ^{210}Pb and ^{137}Cs . The authors offer the suggestions that the varying depths of peak values in some cores may be related to changes in deposition rates, but that the absence of correlation of the ^{137}Cs peak and ^{210}Pb dates are more likely caused by differential downward diffusion rates,

Fig. 7. Pb concentration (ppm) versus depth (cm) in two cave guanos, (Makangit and Niah). Data from Wurster et al. (2015).

^{137}Cs being more mobile than ^{210}Pb . Smith (2001) noted that a ^{210}Pb peak at depth may be indicative of post-depositional reworking (the discussion was of ocean and lake cores, but the principal applies to other materials). Further work on these ornithogenic sediments by Xu et al. (2016) used a combination of ^{210}Pb and C-14 dating and Xu et al. (2018) relied only on C-14 dating.

In another example, Stewart et al. (2015) used ^{210}Pb dating on four cores in bird-guano-rich lake sediments. Investigation of their supplementary material shows that of the four cores, only one shows the clear-cut, simple curve of ^{210}Pb exponential decay with depth and single ^{137}Cs peak. Another shows ^{210}Pb remaining constant over the first 12 cm, meeting the first ^{137}Cs peak at 15 cm, and then decaying to zero at 25 cm depth, where it meets the second ^{137}Cs peak. A third core shows ^{210}Pb decay with depth, but no identifiable peak in ^{137}Cs . The fourth (from which they were unable to obtain a date) shows ^{210}Pb remaining relatively constant with depth, the final drop towards the base of the core coinciding with the ^{137}Cs peak.

Of the very few examples of published ^{210}Pb dating on bat guano, the Utida et al. (2014) abstract unfortunately offers no details of their profile and we have found no subsequent in-depth publication on the study. Therefore we cannot judge the shape of the Pb curve. One of the few examples that shows the expected simple pattern of highest ^{210}Pb at the surface and exponential decay with depth is by Wirmann et al. (2017). The only other published data on ^{210}Pb in guano is the study reported by Gallant et al. (2020) and also used by Bogdanowicz et al. (2020). Their supplementary data shows the ^{210}Pb activity peaking

at a depth of 8.5 cm, suspiciously coincident with the ^{137}Cs peak – leading to an apprehension that both isotopes may have migrated under acidic leaching. A recent increase in accumulation rate may explain the ^{210}Pb at depth, but it would be rather surprising if the 1963 ^{137}Cs peak should happen to coincide with it. Smith (2001) recommended that at least one independent tracer should be used to validate every ^{210}Pb chronology, and, more recently, Sanchez-Cabeza and Ruiz-Fernández (2012) warn that most real situations are complex, such that the ^{210}Pb age model should be validated using some other time marker, especially where the profile deviates significantly from an exponential relation. However the Gallant study has done precisely the opposite: they suggest that the ^{14}C dating must be flawed because it does not correspond with the ^{210}Pb dating. The authors argue, on the basis that the carbon dates at one particular depth – 14.5 cm – are 580 years older than the ^{210}Pb date, that the carbon dates must therefore be “corrected” by removal of the “extra” 580 years. We note that the original carbon date and the ^{210}Pb date seem to be rather close at ~7 cm depth (~1988 for ^{14}C and ~1979 for ^{210}Pb , well within the 1 sigma error on the ^{14}C date). We also wonder, if the carbon dates at depths below 21.5 cm were considered to be falsely old from addition of rock-derived non-carbonate dead carbon (a very rare occurrence in guano dating that is substantiated in only one, geographically unique, case – Bird et al., 2007), why the two uppermost carbon dates would not also be similarly contaminated. However, the 580 year “correction” would bring these dates well into the future (these two carbon dates were replaced by the ^{210}Pb dates in Gallant et al., 2020 and Bogdanowicz et al., 2020).

CONCLUSIONS

Our research has led us to the conclusion that reported ^{210}Pb dating – and probably ^{137}Cs stratigraphic marker dating – from guano should be viewed with some caution. With the possible exception of extremely dry guano deposits in desert environments, the pattern of lead and cesium leaching, mobilization and chelation in bat guano is dependent on an unknowable history of pore water movement and saturation, as well as temperature-dependent microbial decomposition rate of the guano. These circumstances violate the basic assumptions of ^{210}Pb and ^{137}Cs dating techniques. Unless a ^{210}Pb age-depth model can be shown to be fully compatible with a supporting ^{14}C age-depth model, we suggest that ^{210}Pb guano chronologies are likely to be unreliable and misleading.

We did not measure clay contents of our profiles. However, as pointed out by Bassam Ghaleb (pers. comm.), Pb will also bind to high cation-exchange clays. This adds a further complication to the interpretation of ^{210}Pb profiles in guano, and we suggest that future studies should bear this in mind. We recommend that all future attempts to use ^{210}Pb dating or ^{137}Cs stratigraphic markers in guano should also include collection of data on pH changes with depth, as well as clay content with depth.

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