

MARINE RADIOCARBON RESERVOIR VALUES IN SOUTHERN CALIFORNIA ESTUARIES: INTERSPECIES, LATITUDINAL, AND INTERANNUAL VARIABILITY

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ABSTRACT. Many studies use radiocarbon dates on estuarine shell material to build age-depth models of sediment accumulation in estuaries in California, USA. Marine ¹⁴C ages are typically older than dates from contemporaneous terrestrial carbon and local offsets (ΔR) from the global average marine offset need to be calculated to ensure the accuracy of calibrated dates. We used accelerator mass spectrometry (AMS) ¹⁴C dating on 40 pre-1950 salt marsh snail and clam shells previously collected from four California estuaries. The average ΔR and standard deviation of 217 ± 129 ¹⁴C yr is consistent with previous calculations using mixed estuarine and marine samples, although the standard deviation and resulting age uncertainty was higher for our estuarine calculations than previous studies. There was a slight but significant difference ($p = 0.024$) in ΔR between epifaunal snails ($\Delta R = 171 \pm 154$ ¹⁴C yr) and infaunal clams ($\Delta R = 263 \pm 77$ ¹⁴C yr), as well as between samples from individual estuaries. However, a closer examination of the data shows that even for the same species, at the same estuary, ΔR can vary as much as ~ 500 ¹⁴C yr. In some cases, the bulk of this variation occurs between samples collected by different collectors at different times, potentially indicating time dependence in carbon sources and ΔR variation. These variations could also be attributed to differences in collection location within a single estuary and resulting spatial differences in carbon sources. Intertidal specimens located in the high marsh may have lower ΔR than fully marine counterparts because of increased terrestrial ¹⁴C input. The large variations in ΔR here highlight the need for conservative chronological interpretations, as well as the assumption of wide uncertainties, when dating samples from estuarine sources.

INTRODUCTION

Radiocarbon dating of carbonate material from marine shells is a vital tool for paleoenvironmental studies (Cole and Liu 1994; Malamud-Roam et al. 2006; Hassan et al. 2009; Enkin et al. 2013; Nolte et al. 2013; Ouyang and Lee 2013). However, these types of dates are subject to the marine ¹⁴C offset effect. The ¹⁴C ages measured from marine organisms tend to be older than terrestrial material of the same age because of the lag in ocean-atmosphere equilibration and the upwelling of ¹⁴C-depleted dissolved inorganic carbon (DIC) into the ocean mixed layer. Marine calibration curves have been developed to address this problem using dating of known-age carbonates and a random-walk statistical design (Reimer et al. 2013). Marine13, the oceanic calibration curve, is offset from IntCal13, the terrestrial calibration curve, by an average of 350 yr from 0 to 10,500 yr BP (Reimer et al. 2013). However, there is substantial local variation in the marine offset due to differences in water mass sources and degrees of upwelling, among other factors. Calculating the difference between local marine ¹⁴C ages and the marine ¹⁴C calibration curve (ΔR) is vital to accurately address this variability.

Surface waters off of North America's Pacific coast tend to have higher ΔR values than the standard marine calibration because of strong upwelling caused by the western deflection of the California Current as it moves south from British Columbia to Baja California. Latitudinal variation in upwelling strength causes a tendency for poleward waters to have higher ΔR than equatorial waters (Bard 1998). Temporal variation in upwelling strength has been used to explain the large range in ΔR observed throughout the Holocene from studies of paired marine and terrestrial material along the California coast (Kennett et al. 1997; Ingram 1998; Hendy et al. 2013).

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Previous studies have calculated ΔR in southern California by either dating known material from museum collections (Berger et al. 1966; Robinson et al. 1981; Ingram and Southon 1996), or comparing marine and terrestrial ^{14}C dates in stratigraphic cores (Ingram and Southon 1996; Culleton et al. 2006; Hendy et al. 2013). Ingram and Southon (1996) synthesized existing data with original data and calculated a ΔR of 220 ± 40 ^{14}C yr for southern California, a slightly higher ΔR for northern California and the San Francisco Bay ($\Delta R = 290 \pm 35$ and 365 ± 35 ^{14}C yr, respectively), and a much higher ΔR for the Gulf of California ($\Delta R = 410 \pm 40$ ^{14}C yr).

Known-age studies of ΔR in southern California include both marine and estuarine specimens (Berger et al. 1966; Robinson and Thompson 1981; Ingram and Southon 1996; Figure 1). However, ^{14}C uptake by organisms in estuarine environments may be fundamentally different from that in open marine systems because estuarine systems include carbon from marine, terrestrial, and freshwater inputs. Ingram and Southon (1996) observed a range in ΔR of 300 ^{14}C yr for the San Francisco Estuary due to differences in marine versus freshwater input. Additionally, the shallow water of tidal marshes may reach equilibrium with the atmosphere much faster than deep marine systems.

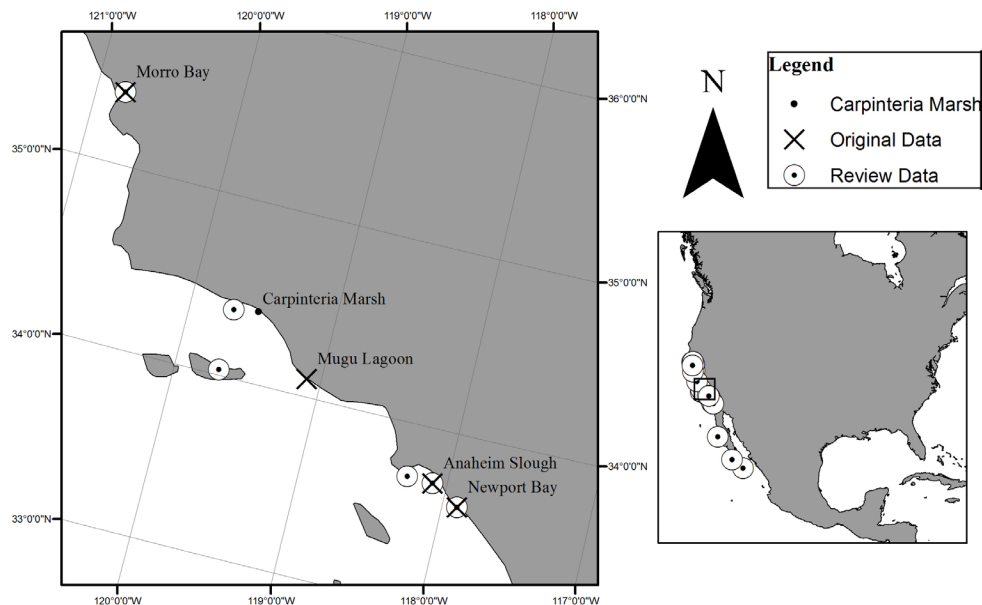


Figure 1 Map of study sites, review data (<http://calib.qub.ac.uk/marine/>), and other locations mentioned in the text

Studies on the behavior and lifecycles of gastropods and bivalves living in estuaries indicate that these organisms may incorporate carbon into their shells from multiple sources. In a study of ΔR of gastropods in Caution Bay, Papua New Guinea, members of the Strombidae family accumulated more ^{14}C -depleted carbonate because they burrowed in carbonate-rich mud, while *Cerithidea largillierti* had the most variation in ΔR because they absorbed ^{14}C from both enriched and depleted sources (Petchev et al. 2012). Ingram and Southon (1996) noted ΔR differences between species and hypothesized that preferential feeding could influence shell isotopic ratio. However, in the majority of marine mollusks, localized differences in DIC account for more variability in ΔR than diet because of high replacement of respired CO_2 by environmental CO_2 (McConnaughey and Gillikin 2008). A study from Carpinteria Marsh concluded that ^{13}C depletion in estuarine invertebrates was much more similar to offshore plankton values than to terrestrial invertebrates (Page 1997).

Marine shells are present in many marsh sediment cores, have been used historically in age-depth models, and continue to serve as an important chronological control in estuarine system studies (Mudie and Byrne 1980; Brevik and Homburg 2004). Due to the current paucity of ΔR values for marsh species in southern Californian estuaries, we designed a 40-sample multispecies, multi-location study to address the following questions: (1) What is the ΔR and the standard deviation for estuaries in southern California, and how does it compare to previously published values from mixed marine and estuarine data? (2) Is there a significant difference in ΔR between largely epifaunal *Cerithidea californica* and largely infaunal marsh bivalves (*Tagelus californianus* and *Clinocardium nuttallii*)? (3) Are local differences in ΔR based on differences in latitude or terrestrial carbon sources?

MATERIALS AND METHODS

Dating specimens of a known age is a common method for calculating ΔR (Ingram and Southon 1996; Ascough et al. 2005a). This method has advantages over dating paired plant and carbonate samples in a sediment core. Less uncertainty is introduced in known-age studies because, at least in principle, collection dates provide an accurate age with which to compare the measured ¹⁴C ages and their inherent uncertainty, rather than combining two sets of associated ¹⁴C age uncertainties (Ascough et al. 2005a; Petchey et al. 2009). Unfortunately, limited material is available for such analysis because samples need to be from the mid-1950s or earlier to avoid the confounding effects of ¹⁴C fallout from nuclear weapons testing (Druffel 2002; Scourse et al. 2012).

A preliminary examination of marsh species from the Los Angeles Natural History Museum (LACM) and the Santa Barbara Natural History Museum (SBNHM) indicated that *Cerithidea californica* and *Tagelus californianus* were commonly collected marsh species for which a number of samples were available for analysis (Appendix). *Tagelus* spp. and *C. californica* have been used in ¹⁴C studies requiring ΔR estimates (Hassan et al. 2009; Scott et al. 2011). Common estuarine sampling locations included Newport Bay, Anaheim Slough, Mugu Lagoon, and Morro Bay (Figure 1). In order to test the effect of location and species on ΔR , we designed a four-site, two-species, and five-replicate sampling strategy, for a total of 40 separate calculations of ΔR . Ideally, we would have only compared two species across four sites; however, we were not able to find any pre-1950 specimens of *Tagelus* spp. for Morro Bay. Therefore, we substituted an ecologically similar clam species (*Clinocardium nuttallii*) and refer to the comparison as two “functional types.” *C. californica* are epifaunal benthic algae feeders, and *T. californianus* and *C. nuttallii* are infaunal suspension feeders.

Similar to Ingram and Southon (1996), we assume that shells from museum collections are representative of living material, at least within the 5-yr uncertainty inherent in ¹⁴C calibration curves (Reimer et al. 2013). However, details regarding the collection of these samples are very limited and there is no confirmation that specimens were collected live (Appendix).

Prior estimates of ΔR are available for Newport Bay (Ingram and Southon 1996), Seal Beach near Anaheim Slough (Berger et al. 1966), and Morro Bay (Robinson and Thompson 1981), but these estimates are based on few measurements and not from the marsh species that we studied (Figure 1). We used ¹⁴C ages and collection years from review data (<http://calib.qub.ac.uk/marine/>) to recalculate reservoir effect (R) and local reservoir effect (ΔR) with Equations 1 and 2 to ensure a consistent comparison using the most current calibration curves (Reimer et al. 2013):

$$R = {}^{14}\text{C age} - \text{IntCal13}[\text{collection year}] \quad (1)$$

$$\Delta R = {}^{14}\text{C age} - \text{Marine13}[\text{collection year}] \quad (2)$$

We used a Dremel® saw to subsample the youngest portion of each sample while minimizing the amount of destructive sampling. For *Cerithidea californica*, we subsampled a ~0.5 cm² section of the inner lip near the shell's aperture. For the *Tagelus californianus* and *Clinocardium nuttallii* shells, we subsampled a ~0.5-cm² section from the ventral side of one of the two valves.

All samples were prepared, and AMS ¹⁴C measurements were performed, at the University of California Irvine's Keck AMS facility. Shell subsamples were crushed into a coarse powder and leached of 50% of their mass using HCl, resulting in a sample of ~8 mg of carbonate. Carbonate was converted into CO₂ in evacuated Vacutainer® blood collection vials using phosphoric acid. CO₂ was graphitized on Fe powder with hydrogen gas at 525°C. AMS measurements of Δ¹⁴C were normalized to results on multiple aliquots of the NBS oxalic acid I standard; known-age coral secondary standards and ¹⁴C-free calcite blanks were prepared and run with the unknowns.

We removed two outlier samples from the initial data set that were much older than could be explained by differences in surface water age and were most likely reworked material (Table 1). We replaced the outliers with two additional specimens from the same site and species, but from different collections.

Table 1 Specimen information, AMS ¹⁴C results for specimens used in this study, as well as R and ΔR calculated from IntCal13 and Marine13 (Reimer et al. 2013) according to Equations 1 and 2: ^(a) Refers to samples that were removed as outliers, because they were likely from reworked material and ^(b) refers to replacements for those outliers.

Collection ID	Species	Location	Collect- ed year	UCIAMS #	Δ ¹⁴ C (‰)	¹⁴ C age BP	R	ΔR
LACM 113265	<i>Cerithidea</i>	Anaheim Slough	1948	138737	-74.50 ± 1.78	620 ± 20	421	151
LACM 113265	<i>Cerithidea</i>	Anaheim Slough	1948	138738	-75.96 ± 1.58	635 ± 15	436	166
LACM 113265	<i>Cerithidea</i>	Anaheim Slough	1948	138739	-75.39 ± 1.58	630 ± 15	431	161
LACM 42-3.2	<i>Cerithidea</i>	Anaheim Slough	1942	138735	-95.72 ± 1.51	810 ± 15	638	350
LACM 42-3.2	<i>Cerithidea</i>	Anaheim Slough	1942	138736	-82.91 ± 1.53	695 ± 15	523	235
LACM 33895	<i>Cerithidea</i>	Morro Bay	1949	138740	-61.14 ± 1.60	505 ± 15	306	36
LACM 33895	<i>Cerithidea</i>	Morro Bay	1949	138741	-64.08 ± 1.65	530 ± 15	331	61
SBNHM 131271	<i>Cerithidea</i>	Morro Bay	1943	138742	-60.64 ± 1.83	500 ± 20	312	36
SBNHM 131271	<i>Cerithidea</i>	Morro Bay	1943	138743	-57.66 ± 1.74	475 ± 15	287	11
SBNHM 131271	<i>Cerithidea</i>	Morro Bay	1943	138744	-63.58 ± 1.60	530 ± 15	342	66
LACM 19654	<i>Cerithidea</i>	Mugu Lagoon	1923	138747	-57.67 ± 1.67	475 ± 15	343	24
LACM 19654	<i>Cerithidea</i>	Mugu Lagoon	1923	138748	-64.18 ± 1.86	535 ± 20	403	84
LACM 19654	<i>Cerithidea</i>	Mugu Lagoon	1923	138749	-61.90 ± 1.60	515 ± 15	383	64
LACM 64037	<i>Cerithidea</i>	Mugu Lagoon	1937	138745	-113.80 ± 1.52	970 ± 15	816	513
LACM 64037	<i>Cerithidea</i>	Mugu Lagoon	1937	138746	-109.13 ± 1.53	930 ± 15	776	473
LACM 41-222.1	<i>Cerithidea</i>	Newport Bay	1941	138751	-51.25 ± 1.62	425 ± 15	253	-35
LACM 41-222.1	<i>Cerithidea</i>	Newport Bay	1941	138750 ^(a)	-195.46 ± 1.39	1745 ± 15	—	—
LACM 54135	<i>Cerithidea</i>	Newport Bay	1948	138647 ^(b)	-77.60 ± 2.04	650 ± 20	451	181
LACM 54135	<i>Cerithidea</i>	Newport Bay	1948	138752	-90.80 ± 1.71	765 ± 20	566	296
LACM 54135	<i>Cerithidea</i>	Newport Bay	1948	138753	-88.55 ± 1.56	745 ± 15	546	276
LACM 54135	<i>Cerithidea</i>	Newport Bay	1948	138754	-88.64 ± 1.56	745 ± 15	546	276
LACM 19062	<i>Clinocardium</i>	Morro Bay	1940	138755	-78.21 ± 2.04	655 ± 20	483	195
SBNHM 235531	<i>Clinocardium</i>	Morro Bay	1944	138756	-93.87 ± 1.55	785 ± 15	597	321
SBNHM 235531	<i>Clinocardium</i>	Morro Bay	1944	138757	-87.01 ± 1.56	550 ± 15	362	86
SBNHM 235531	<i>Clinocardium</i>	Morro Bay	1944	138758	-86.44 ± 1.60	625 ± 15	437	161
SBNHM 235531	<i>Clinocardium</i>	Morro Bay	1944	138759	-87.09 ± 1.71	605 ± 20	417	141
LACM 38-174	<i>Tagelus</i>	Anaheim Slough	1938	138760 ^(a)	-518.95 ± 1.29	5880 ± 25	—	—

Table 1 (Continued).

Collection ID	Species	Location	Collect- ed year	UCIAMS #	Δ ¹⁴ C (‰)	¹⁴ C age BP	R	ΔR
LACM 116692	Tagelus	Anaheim Slough	1926	138761	-93.87 ± 1.55	790 ± 15	658	339
SBNHM 103958	Tagelus	Anaheim Slough	1918	138648 ^(b)	-78.21 ± 2.04	655 ± 20	526	207
SBNHM 103958	Tagelus	Anaheim Slough	1918	138762	-87.01 ± 1.56	730 ± 15	601	282
SBNHM 103958	Tagelus	Anaheim Slough	1918	138763	-86.44 ± 1.60	725 ± 15	596	277
SBNHM 103958	Tagelus	Anaheim Slough	1918	138764	-87.09 ± 1.71	730 ± 20	601	282
LACM 18865	Tagelus	Mugu Lagoon	1923	138765	-101.55 ± 1.67	860 ± 15	728	409
LACM 18865	Tagelus	Mugu Lagoon	1923	138766	-90.79 ± 1.55	765 ± 15	633	314
LACM 64593	Tagelus	Mugu Lagoon	1935	138767	-86.45 ± 1.63	725 ± 15	571	268
LACM 64593	Tagelus	Mugu Lagoon	1935	138768	-96.65 ± 1.73	815 ± 20	661	358
LACM 64593	Tagelus	Mugu Lagoon	1935	138769	-92.00 ± 1.58	775 ± 15	621	318
LACM 64591	Tagelus	Newport Bay	1936	138649	-87.05 ± 2.15	730 ± 20	576	273
LACM 64591	Tagelus	Newport Bay	1936	138650	-84.86 ± 2.02	710 ± 20	556	253
LACM 64591	Tagelus	Newport Bay	1936	138651	-82.59 ± 2.03	690 ± 20	536	233
SBNHM 115574	Tagelus	Newport Bay	1948	138652	-87.81 ± 2.07	740 ± 20	541	271
SBNHM 115574	Tagelus	Newport Bay	1948	138653	-87.95 ± 1.95	740 ± 20	541	271

We used a two-tailed, unpaired *t* test to determine the significance of functional type (epifaunal versus infaunal) on ΔR. We also used analysis of variance (ANOVA) with site as the independent variable and ΔR as the dependent variable to determine if location contributed significantly to ΔR variability. All statistics were calculated using “R” software (R Core Development Team 2014).

RESULTS AND DISCUSSIONS

In 39 out of 40 measurements, ΔR was positive, indicating that more shell carbonate originates from ¹⁴C-depleted sources than predicted by global averages (Table 1; Figure 2). ΔR ranged from -35 to 513 ¹⁴C yr (Table 2). The average ΔR of 217 ± 129 ¹⁴C yr measured in our 40 specimens (Table 2) is within error of previous estimates for both estuarine and marine shells (220 ± 40 ¹⁴C yr; Ingram and Southon 1996). The range of ΔR that we calculated fits within the pattern and variability observed previously along the California coast and is lower than estimates from San Francisco Bay (Figure 3).

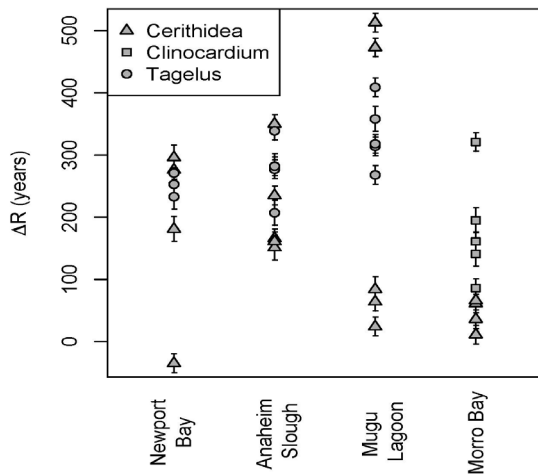


Figure 2 ΔR by site and species along with associated ¹⁴C age error bars.

Table 2 Summary of ΔR means, standard deviation, minimum and maximum by site, species, and functional type for original data presented in this study.

Category	<i>n</i>	Average ΔR	\pm stand. dev.	Min	Max
<i>Cerithidea californica</i>	20	171	154	-35	513
<i>Clinocardium nuttallii</i>	5	181	88	86	321
<i>Tagelus californianus</i>	15	290	51	207	409
Total bivalve	20	263	77	86	409
Anaheim Slough	10	245	72	151	350
Morro Bay	10	111	95	11	321
Point Mugu	10	283	172	24	513
Upper Newport Bay	10	230	98	-35	296
Total	40	217	129	-35	513

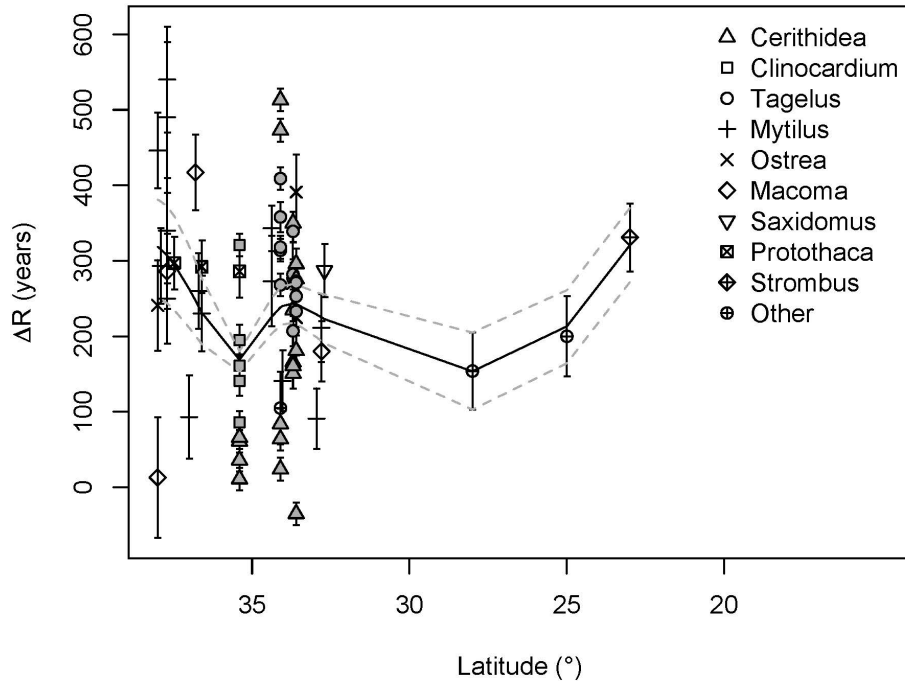


Figure 3 ΔR values from this study by latitude, with associated ^{14}C age error, compared to previous data from the Pacific coasts of California and Baja California (Berger et al. 1966; Robinson et al. 1981; Ingram and Southon 1996). The black line is a spline of the ΔR means and the gray lines are splines of the minimum and maximum of the measurements. An online database (<http://calib.qub.ac.uk/marine>) was used as a resource to compile this review.

We observe a slight but significant difference between *Cerithidea californica* and marsh clams ($p = 0.024$; Table 3). *C. californica* has a lower average ΔR , but a much larger standard deviation (Table 2). DIC is the dominant determinate of isotopic ratios in marine shells (McConnaughey and Gillikin 2008), and the differences in the mean and variance of ΔR may reflect differing ambient DIC conditions experienced by epifaunal snails (*C. californica*) and infaunal clams (*Tagelus californianus* and *Clinocardium nuttallii*). Some previous studies have shown that deposit feeders can have greater deviations of ΔR in comparison to suspension feeders possibly because of preferential consumption habits (Petchey et al. 2012), while other researchers report no significant differences in ΔR between species and position in the intertidal zone (Ascough et al. 2005b).

Table 3 Summary of statistics for an unpaired t test with functional type as the independent variable, as well as an ANOVA with site as the independent variable, and ΔR as the dependent variable.

Test	Model	df	p value
t test	$\Delta\text{R}\sim\text{Functional Type}$	27.9	0.024
ANOVA	$\Delta\text{R}\sim\text{Location}$	3	0.014

There was also a slight but significant difference in ΔR based on location ($p = 0.014$; Table 3). Mugu Lagoon had the highest standard deviation and the highest maximum ΔR (Figure 2; Table 2). The locations all have similar bedrock characteristics and none contain prominent limestone outcrops directly upland in their catchments (Jennings et al. 2010), although the Western Transverse Ranges, which source Mugu Lagoon, are known to contain tufa and travertine deposits suggesting the presence of older carbon in the surface waters (Boles 2004; Ibarra et al. 2014).

A closer inspection of the data shows that some of the variability in ΔR may be due to the fact that individuals collected at different times, or from slightly different places within an estuary, were combined to form a set of five replicates. In four cases, the maximum variation in ΔR measured in a single species from a single marsh resulted from samples from different collections. Three of these cases occur in *C. californica* samples. At Anaheim Slough, the average ΔR for two specimens from 1942 is 130 ^{14}C yr higher than three from 1948. At Mugu Lagoon, the average ΔR for two specimens from 1937 is 440 ^{14}C yr higher than three from 1923. At Newport Bay, the average ΔR from four specimens from 1948 is 290 ^{14}C yr higher than a single specimen from 1941. At Anaheim Slough, the ΔR for a single *T. californianus* sample from 1926 is much higher than the average of four collected from 1918.

Many studies indicate that ΔR for a particular location is time dependent (Heier-Nielsen et al. 1997). Extreme cases in the Pacific indicate Holocene shifts in ΔR of up to 800 ^{14}C yr between 10,000 and 300 yr BP in the Gulf of California (Taylor et al. 2007), and 400 ^{14}C yr between 500 and 0 yr BP in Puget Sound and the Gulf of Georgia (Deo et al. 2004). In Jutland, Denmark, estuarine ΔR ranges from -130 to 300 ^{14}C yr from 7300 to 1300 yr BP, and was highly variable from 7300 to 5400 yr BP, indicating variability in the influence of marine water and “hardwater” effects from surface runoff (Philippesen et al. 2013). In California, the temporal dependence of ΔR may be due to annual or seasonal changes in upwelling (Culleton et al. 2006). In the Santa Barbara Basin, comparisons of terrestrial and planktonic foraminifera ^{14}C dates indicate that ΔR varied from 80 to 350 ^{14}C yr since ~ 2000 yr BP (Hendy et al. 2013).

Along the California coast, extreme upwelling is tied to La Niña events; however, none of the collection years from anomalously old specimens coincide with extreme La Niña years (Wolter et al. 2011; Ferguson et al. 2013). Changes in ΔR can also occur over time because of changes in lagoon barriers and sediment transfer dynamics (Sabatier et al. 2010), or input of ^{14}C -depleted runoff (Culleton et al. 2006).

Some of the collection-specific variation in ΔR may be explained by differences between intertidal and fully marine specimens. Although we do not have specific location descriptions for all samples, two sets of samples indicate material was collected from specific subenvironments within an estuary. For the Newport Bay *Cerithidea californica* samples, LACM 41.222.1 was collected from “intertidal sand flats along shore” while the other four samples from LACM 54135 simply list “Newport Bay” in the collection notes (Appendix). For the Anaheim Slough *Tagelus californianus*

samples, LACM 38-175 was collected from “intertidal on sand and mud” while LACM 116692 simple lists “Anaheim Landing” under collection notes ([Appendix](#)). Both sets of specimens specifying intertidal collection have much lower ΔR than their companions, which do not specify collection zone. If intertidal shells have lower ΔR compared to fully marine shells because of increased atmospheric carbon input through ambient DIC, then the ^{14}C reservoir effect could vary by hundreds of years, even within the same estuary (Rick et al. 2012).

These findings reinforce the need to assume a broad range in error when calibrating estuarine ^{14}C dates. This study also reinforces the current consensus, that it is difficult to determine an appropriate ΔR for species that tolerate a range of salinities (Reimer 2014). Future studies could specifically determine ΔR spanning the intertidal zone of a single marsh for a single species to test if ΔR is lower in the intertidal zone, and how much variability is potentially introduced by tidal exchange.

CONCLUSION

We used 40 pre-1950 shell samples from California estuaries to calculate local marine ^{14}C offsets, and determine the effects of species and site on the variability in ΔR . Our ΔR estimates of 217 ^{14}C yr on average replicated previous measurements using marine and estuarine samples. However, we did find a wider standard deviation than previously reported. ΔR fluctuated based on species and site with slight statistical significance. However, it is hard to have confidence in these trends given the uncertainty introduced by variation between specimens of the same species, and from the same site, but from different collections. This variability may result from temporal variability, or may be due to spatial variability of reservoir effects between subenvironments. Although our average value of ΔR in four Californian estuaries does not vary from previous estimates calculated for shells, the intraspecies and intrasite variations of up to 300 ^{14}C yr highlight the need for caution in dating estuarine samples.

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