LANTHANIDE METALS AS POTENTIAL SHARK DETERRENTS

by

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ABSTRACT

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Sharks comprise a large portion of bycatch in pelagic longline fisheries worldwide. Lanthanide metals have been proposed as shark repellents. This study quantified the normalized voltage of lanthanide metals in seawater and found that there was no difference in normalized voltage among the six tested metals. Temperature and salinity had a significant effect on lanthanide normalized voltage. The output at 18ºC was significantly greater than at both 12 and 24ºC. The normalized voltage was significantly greater in freshwater than brackish or seawater. The dissolution rate for the lanthanides varied from -1.6 to -0.2g/h. As the metals dissolved the voltage remained constant. In a behavioral assay, neodymium was ineffective at repelling bonnethead sharks (*Sphyrna* *tiburo*) tested individually and in groups, and lemon sharks (*Negaprion brevirostris*) in groups. Due to high cost, fast dissolution rates, and lack of deterrent effects, lanthanide metals are not recommended for use in mitigating shark bycatch.

LANTHANIDE METALS AS POTENTIAL SHARK DETERRENTS

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INTRODUCTION

Sharks comprise the largest portion of non-targeted bycatch in most of the world's pelagic longline (PLL) fisheries (Gilman *et al*., 2008), and shark bycatch is especially high in the United States where the PLL fishing industry targets large pelagic fishes such as tuna (*Thunnus spp.)* and swordfish (*Xiphias gladius*) (Gilman *et al.*, 2008). In the US Atlantic longline fishing industry, shark bycatch comprised 24.78% of the total catch from 1992-2003, nearly equaling the targeted species catch of tuna (24.93%) and swordfish (27.32%) (Abercrombie *et al.*, 2005). The high bycatch rate indicates that current fishing practices are inefficient.

Tunas and sharks are apex predators in the pelagic realm, but due to differences in life history characteristics, longline fishing will have exceptionally different effects on the population structure of these two groups (Schindler *et al.*, 2002). Due to the slow growth rates, longevity, late-onset sexual maturity, and low fecundity of elasmobranchs, sharks are more vulnerable to overfishing than PLL targeted teleost fishes (Dulvy *et al*., 2008; Stevens *et al.*, 2000). Whereas population doubling times of targeted species are relatively fast, 1.4-4.4 years for tuna, 4.5-14 years for swordfish (Musick, 1999), the population doubling time for the highly fecund blue shark is 11.4 years and large coastal sharks have population doubling times of more than 20 years without fishing mortality (Smith *et al.*, 1998).

The loss of large numbers of apex predators may have detrimental long-term ecological consequences (Friedlander & DeMartini, 2002; Myers *et al.*, 2007). Decreasing shark abundance can alter food web dynamics through direct effects, such as predator-prey interactions (e.g. Stevens *et al*., 2000). In addition to direct effects, the threat of predation can also change the behavior of prey species and these behavioral changes can have large effects on the structure of the ecosystem (Heithaus *et al.*, 2008; Heithaus *et al*., 2007). Despite the fact that yellowfin tuna have a 4-5 times greater predation rate per capita than blue sharks, the removal of sharks from an environment will have greater impacts on food web dynamics than the removal of tunas (Schindler *et al*., 2002). Therefore, there are unquantifiable ecological benefits for maintaining shark populations.

In addition to ecological consequences, shark bycatch also creates an economic burden to commercial longline fishermen due to gear damage and loss, time spent to repair gear and remove sharks, and depredation (the partial or complete removal of bait or hooked fish from fishing gear) (Gilman *et al*., 2007). Sharks occupying hooks, and depredation, represent hooks that are no longer able to catch targeted fish. The greatest source of revenue loss to commercial fishermen while fishing is damage to target species that have been caught on the line and are preyed upon by sharks (Gilman *et al*., 2007). There are also risks for the fishermen attributed to shark bycatch due to the sharks' erratic behavior during handling making sharks unsafe to dehook because a line may snap and send tackle flying towards the crew (Gilman *et al*., 2008).

To mitigate their interactions with sharks, fishermen change fishing gear, fishing depth, switch to different bait, or move to alternate fishing sites when catch rates of sharks are high and targeted species are relatively low (Gilman *et al.*, 2007). However, these adjustments may also adversely affect the catch rates of the targeted species (Gilman *et al*., 2007). An alternative method to reduce shark bycatch, and consequently increase catch rates of target species, is to use a shark-specific deterrent on longlines. This would allow fishermen to continue to target the most productive waters while minimizing shark interactions.

Shark sensory biology and lanthanide metals

Unlike most marine teleosts, elasmobranchs (sharks, rays, and skates) possess an electrosensory system that is extremely sensitive to voltage gradients. This enables them to detect electric fields down to the nV/cm range (Haine ,*et al*., 2001; Kajiura, 2003; Kajiura & Holland, 2002; Kalmijn, 1982; McGowan & Kajiura, 2009) well below the range of bioelectric fields produced by their prey (20-100 μV; Haine *et al*., 2001; Kalmijn, 1972). Targeting the electrosensory system of elasmobranchs may provide a mechanism to differentially dissuade sharks without impacting the non-electrosensitive target species.

Lanthanide metals have been proposed as a potential shark deterrent for use in longline fisheries. When submerged in a polar solution, such as water, lanthanide metals undergo a hydrolytic reaction and release electrons, which produces a charge distribution in the water. The voltage produced by the metals is likely greater than anything that sharks naturally encounter in the wild and will presumably overwhelm their electrosensory system.

To date, four lanthanide metals have been investigated as potential shark deterrents: cerium-lanthanum mischmetal (CeLa; Kaimmer & Stoner, 2008; Stoner & Kaimmer, 2008; Tallack & Mandelman, 2009), praseodymium-neodymium metal alloy (PrNdA; Brill *et al*., 2009; Robbins *et al.*, 2011; Wang *et al.*, 2008), praseodymium-neodymium mischmetal (PrNdM; Brill *et al*., 2009), and neodymium metal (Nd; Jordan *et al.*, 2011; Robbins *et al.*, 2011) (Figure 1). Lanthanide metals have produced varying results as shark repellents. In a lab study, CeLa mischmetal caused a 70% reduction in the number of baits attacked by the Pacific piked dogfish, *Squalus acanthias* (Stoner & Kaimmer, 2008). In a later field study, CeLa mischmetal significantly reduced the amount of piked dogfish caught on longline gear by 19% (Kaimmer & Stoner, 2008). However, using the same metal and shark species in the Atlantic, CeLa failed to reduce piked dogfish catch rates in the field (Tallack & Mandelman, 2009). In yet another lab study with the Atlantic piked dogfish, Nd successfully deterred them from removing bait (Jordan *et al.*, 2011). Nd was also used in a lab study with the dusky smoothhound, *Mustelus canis*; Nd deterred the smoothhounds that were tested individually but not in groups (Jordan *et al.*, 2011). Galapagos sharks, *Carcharhinus galapagensis*, were not deterred from PrNdA or Nd in a field study using rod and reel fishing (Robbins *et al.*, 2011). In a field study, Galapagos sharks and sandbar sharks, *C. plumbeus*, removed significantly fewer baits next to PrNdA than next to a lead control (Wang *et al.*, 2008) . PrNdM also significantly reduced the catch of juvenile sandbar sharks on longlines but did not significantly reduce the number of rays or skates, species which also possess electrosensory capabilities (Brill *et al*., 2009). These variable results illustrate that not all elasmobranch species respond similarly which may reflect the use of different metals and different experimental methodologies that further confound comparisons.

Despite the importance of these landmark studies, there remain several caveats to their results. First, four different types of lanthanide metals have been used: CeLa mischmetal, PrNd mischmetal, PrNd metal alloy, and Nd metal. To date, no studies have investigated the electrochemical properties of the metals themselves so it remains unknown whether all lanthanides produce equivalent voltages. Knowledge of the electrochemical properties of lanthanides could facilitate comparisons among studies. Second, only four shark species have been studied, the Galapagos shark, *C. galapagensis*, the sandbar shark, *C. plumbeus*, the piked dogfish, *S. acanthias*, and the dusky smoothhound, *M. canis*, which is problematic because it is unknown if all elasmobranchs will react in a similar manner to the presence of a lanthanide metal. Finally, the methodologies varied considerably across the experiments which complicate direct comparisons among the studies.

The objective of this study was to evaluate the efficacy of lanthanide metals as a shark repellent with Carcharhinid and Sphyrinid sharks that represent commonly encountered families in commercial pelagic longline fisheries (Hoey & Moore, 1999). To accomplish this I 1) measured the normalized voltage of various lanthanide metals, 2) compared the dissolution rate of each metal, 3) identified the best candidate lanthanide metal for subsequent behavioral assays, and 4) conducted a behavioral, lab-based study using bonnethead (Sphyrnidae: *Sphyrna tiburo*) and lemon sharks (Carcharhinidae: *Negaprion brevirostris*) to evaluate the effectiveness of the candidate lanthanide metal as a potential shark repellent.

METHODS

Material acquisition

Six lanthanide metals were tested, all minimally 99.5% pure: cerium (Ce), neodymium (Nd), praseodymium (Pr), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium metal alloy (PrNdA), and praseodymium-neodymium mischmetal (PrNdM) (from Hefa Rare Earth Canada Co. Ltd., Richmond, BC, Canada) (Table 1). A second shipment of 99.5% pure Nd was procured for use in the last batch of behavioral trials and for the voltage over time experiment; these metals were shipped in oil to prevent oxidation (CSTARM Advanced Materials Co., Shanghai, China). Lead (Pb) (Pure Lead Products, Lake Placid, Florida) and stainless steel (SS) (MetalsDepot, Winchester, Kentucky) were used as controls since these metals are commonly employed in fishing gear and are not thought to be strongly electrogenic.

All metals were machined to 2.54 x 2.54 x 0.64 cm with a 0.64 cm-diameter hole in the middle. Lanthanide metals are highly oxidative; therefore before every experiment each metal sample was polished with a stainless steel wire brush Dremel® tool attachment to remove surface oxidation.

DC voltage testing

The normalized voltage of the metals in seawater was measured at Florida Atlantic University's Marine Science Facility at Gumbo Limbo Environmental Complex, Boca Raton, Florida in an electrically grounded acrylic experimental tank (89 x 43 x 21 cm) equipped with flow-through seawater at ambient temperatures (22-24ºC).

To measure the voltage produced by a sample when immersed in seawater, six replicates of each of the lanthanide metals were attached with a non-conductive nylon screw to a flat face acrylic dipping rod via the 0.64 cm diameter hole in the middle of the metal. The rod was affixed to a linear actuator (4" stroke mini-style linear actuator, Firgelli Automations, Surrey, BC, Canada), which vertically dipped the metals into the seawater at a repeatable velocity. The linear actuator was mounted over the tank on an arm that connected it to a linear translation stage (eTrack-300 Linear Stage, Newmark Systems, Inc., Rancho Santa Margarita, CA, USA). The linear translation stage was controlled by a single axis stepper motion controller (NSC-1S, Newmark Systems, Inc.) that provided precise linear horizontal movement (Figure 2). The metals were tested at 10 distances from the recording electrode: 1, 2, 3, 4, 5, 10, 15, 20, 25, and 30 cm. This arrangement enabled me to dip a sample into the tank at a particular distance from the electrode, measure the voltage, remove, translate the actuator and metal sample to the next distance, and dip again until the voltage produced at all distances was measured. The order of the 10 distances at which the metal was dipped was randomized for every trial.

The voltage was measured with non-polarizable Ag-AgCl electrodes (E45P-M15NH, Warner Instruments, Hamden, CT, USA) fitted with a seawater/0.5%agar-filled glass capillary tube. The recording electrode was positioned in the middle of the tank and the reference electrode was positioned along the far side of the tank, as far upstream from the recording electrode and sample as possible. The output from the two electrodes was differentially amplified at 1,000 or 10,000x (DP-304, Warner Instruments), filtered (0.1 Hz - 0.1 kHz, 50/60 Hz) (DP-304, Warner Instruments and Hum Bug, Quest Scientific, North Vancouver, BC, CA), digitized at 1 kHz using a Power Lab® 16/30 model ML 880 (AD Instruments, Colorado Springs, CO, USA) and recorded using Chart™ Software (AD Instruments, Colorado Springs, CO, USA).

To facilitate comparisons, the voltage measurements were normalized by mass to 1 g and by surface area to 1 cm^2. As the metals dissolved and became pitted, the surface area continually changed in three dimensions, so mass was chosen as a more reliable measure for subsequent comparisons. The voltage produced at 5 cm from the recording electrode, normalized by mass, is used for figures. The 5 cm distance was chosen because this was the farthest distance from the metal where the mean voltage exceeded the variance.

The normalized voltage, by mass and surface area, was analyzed using SAS® v9.2. The data were tested using Shapiro-Wilk's test for normality and

Levene's test for homogeneity of variance. The data were log-transformed to meet the assumptions required for ANOVA and *a posteriori* Tukey's pairwise comparisons were performed.

To relate the voltage produced by the lanthanides to electric fields that sharks detect, the electric field was calculated. This was done by taking the derivative of the power function that best fit the decline of the raw voltage with increasing distance downstream of the recording electrode. Once the electric field produced by the lanthanide was calculated it was compared to the reported median detection range, 25-48 nV/cm, of six elasmobranch species (Jordan *et al.*, 2009; Kajiura, 2003; Kajiura & Holland, 2002). The points within the area where the median detection range intercepted the lanthanide electric field correspond to the distance where elasmobranchs should be able to detect the lanthanide.

Temperature and Salinity

The three metals that produced the greatest normalized voltage at a distance of 15 cm from the electrode (Nd, Pr, and PrNdA) were tested at various temperatures (12ºC, 18ºC, 22-24ºC) and salinities (0, 10, 21, 34 ppt).

To achieve the desired temperature, Styrofoam panels were secured around the outside of the acrylic tank to provide insulation and plastic bags filled with ice were floated in the experimental tank. The flow-through seawater system was turned off and a submersible pump recirculated the water in the tank to create a uniform temperature throughout the tank. The pump was turned off during recordings to reduce electrical noise in the tank. Water temperature and pH were monitored throughout the experiment using a Hanna HI9835 EC/TDS/NaCl/ºC meter (Worthington, OH, USA), and if the temperature raised 0.5ºC the ice bags were replaced until the temperature returned to the desired temperature. The voltage produced by the three lanthanide metals was measured at the same 10 pre-determined distances from the recording electrode. The normalized voltages at various temperatures were log-transformed and tested in a two-way ANOVA with orthogonal *a priori* contrasts.

To determine the effect of salinity on lanthanide voltage production, I examined the normalized voltage produced at four salinities which cover the range of salinities naturally encountered by sharks in the wild. The full-strength seawater was taken from the inflow seawater at the Gumbo Limbo Environmental Complex, which is pumped directly from the Atlantic Ocean. To adjust the salinity to 21 and 10 ppt, freshwater was added to the tank until the desired salinity was reached using a recirculating pump to create a uniform salinity distribution throughout the tank. Temperature, pH, and salinity were monitored throughout the experiment. The voltage produced by the three lanthanide metals was measured at the pre-determined 10 distances from the recording electrode. The salinity data were analyzed in the same manner as previously described for the temperature trials.

Dissolution Trials

To determine how quickly the lanthanides dissolve in seawater, six samples of the six lanthanide metals and the two control metals were immersed in seawater and weighed periodically to determine the amount of time required for each sample to completely dissolve. The metals were suspended with monofilament fishing line in a 1.2x2.4x0.9 m fiberglass tank with flow-through seawater. Up to 15 randomly selected metals were suspended in the tank at a time. Each metal was separated by a minimum of 30 cm (the distance at which there was no measurable voltage) to minimize any electrochemical interactions between adjacent metals. Each metal was removed from the tank, dried, and weighed every 4 hours for the first 48 hours and then every 8 hours until they completely dissolved. Two samples of Pb and SS were tested for 96 hours and showed no sign of dissolution; therefore the other 4 replicates were only tested for 40 hours. The interaction of mass and time (i.e. slope) from a two-way ANOVA was compared to determine if the dissolution rates differed among samples and *a priori* contrasts were designed to examine those differences.

Voltage over time

To determine the effect of dissolution on voltage production, six replicates of Nd were kept suspended in the acrylic experimental tank equipped with flow-through seawater. The samples were suspended with monofilament and all but one sample was removed from the tank for individual voltage measurements.

The other samples were placed in glass dishes with seawater during the individual measurements. The voltage was measured every hour for the first four hours and then every four hours until the samples completely dissolved. A repeated-measures ANOVA was applied to the raw voltage (mV) to determine if the voltage changed over time.

Animal Collection

Six bonnethead sharks (*Sphyrna tiburo* ranging from 77.3-86.9 cm TL; all female) and thirteen lemon sharks (*Negaprion brevirostris* ranging from 65.1-77.5 cm TL; five female and eight male) were caught by gillnet and hook and line fishing from Long Key Bight, Layton, Florida between September 2010 and August 2011. Six bonnethead sharks (*S. tiburo* ranging from 69.0-89.2 cm TL; all female) were captured by gillnet from Sarasota Bay and maintained at Mote Marine Laboratory in September 2010. All sharks were provided at least two days to recover from the capture stress before being transported to Florida Atlantic University's Marine Science Facility at Gumbo Limbo Environmental Complex, Boca Raton, Florida. At FAU, the sharks were acclimated to local conditions and were then maintained in a 6.1 m diameter outdoor tank covered with a shade cloth and equipped with flow-through seawater. Sharks were fed to satiation every other day and given at least one week to acclimate to their holding tank before behavioral feeding trials ensued according to IACUC protocol A10-07. Striped burrfish, *Chilomycterus schoepfi*, that were captured during routine sampling were provided by Florida Fish and Wildlife.

Experimental apparatus and protocol for behavioral trials

A behavioral assay was employed to assess whether the lanthanide metal deterred sharks from removing bait. A 1 m^2 acrylic plate was fitted with four equal-sized (2.54 x 2.54 x 0.64 cm) samples: acrylic, lead, stainless steel, and a test lanthanide metal. Each treatment was attached to the plate with a non-conductive nylon bolt. The position of the test materials was randomized for every trial. Bait was attached to each treatment with monofilament fishing line. Shrimp were used as bait for the bonnethead sharks and burrfish and either mullet or herring were used for the lemon sharks. Food was chosen specifically for each species based on their natural diet, crustaceans for bonnetheads (Cortes *et al.*, 1996) and burrfish (Motta *et al.*, 1995) and teleosts for lemon sharks (Newman *et al.*, 2010). Most of the experiments were conducted in an indoor 4.6 m diameter experimental tank at a depth of 0.9 m. Sharks were quickly transferred from the holding tank to the indoor tank and allowed to acclimate to their surroundings for 30 minutes. Once the sharks returned to a typical swimming behavior, the baited plate was placed on the bottom of the tank and the feeding trial began. The acrylic plate remained in the water with the sharks until the first bait was removed and the treatment from which the bait was removed was recorded. The plate was immediately removed from the tank, the position of the treatments randomized and the treatments rebaited with fresh baits. This process was repeated until a minimum of 10 baits had been removed by each shark. In 2011, the indoor tank was unavailable and the behavioral trials were conducted in the outdoor holding tank. A non-conductive plastic divider was used to separate the test subject from the other animals, and the experiments were conducted using the same protocol as described for the indoor tank. To preclude any individual biases, only the first 10 baits removed by each individual were included in the analysis.

Bonnethead sharks, *S. tiburo*, were tested individually and in groups of 2-4 and lemon sharks, *N. brevirostris* were tested only in groups of 2-4 because lemon sharks would not feed in isolation.

A repeated-measures ANOVA was applied to sharks that had more than one feeding trial to determine if time exhibited an effect on their feeding behavior. Since time did not have a significant effect, the data were pooled and a chi-squared goodness-of-fit analysis was used to evaluate the effect of the lanthanide element. For the chi-squared analysis, the null hypothesis was that the bait would be removed from each of the four treatments equally, i.e. 25% of the time.

Teleost control

Striped burrfish (*Chilomycterus schoepfi*, N=3) were tested as a teleost positive control. They were subjected to the same behavioral feeding trials as the bonnethead and lemon sharks. The burrfish were held and tested in a 1.2x2.4x0.5 m tank using the same baited acrylic plate.

RESULTS

Normalized voltage production in ambient seawater conditions

The six lanthanide metals in ambient seawater conditions (22-24°C, 34 ppt) produced large voltages near the recording electrode that decreased dramatically with increasing distance (Figure 3). The steep voltage decline was best modeled as a power function (Table 2). To facilitate comparisons among the lanthanide metals, it was necessary to normalize the voltage by either mass or surface area. For any given distance, the normalized voltage did not differ among any of the lanthanide metals for either mass (μV/g, Figure 4) or surface area ($\mu V/cm^2$, Figure 5). For distances up to and including 10 cm, all of the lanthanide metals produced a significantly greater normalized voltage than the lead and stainless steel controls, which produced similar normalized voltages to one another (Table 3). At distances of 15 cm and greater, the normalized voltage from some of the lanthanides became statistically indistinguishable from the control metals (the normalized voltage produced by Ce and PrNdM were not significantly different from SS) and at 20 cm the lanthanides' normalized voltage was indistinguishable from the electrical background noise in the system.

To relate the voltage produced by the lanthanides to electric fields that sharks detect, the electric field was calculated. The downstream electric field of neodymium reached the detection median of elasmobranchs at about 73 cm (Figure 6).

Normalized voltage of select lanthanides at various temperatures and salinities

The three lanthanides that produced the greatest normalized voltage at 15 cm, Nd, Pr, and PrNdA, were tested at various temperatures and salinities. At any given temperature (12, 18, 24°C) the normalized voltage of the three metals did not differ (Table 4). This held true at all distances except 30 cm where the normalized voltage was very small and indistinguishable from background noise.

In contrast, for any given metal (Nd, Pr, PrNdA), the normalized voltage differed significantly among the temperatures. For any given distance, the normalized voltage at 12°C and 24°C was not significantly different. However, at some of the distances (1, 2, 3, 4, 10 cm), the normalized voltage produced at 18°C was significantly greater than at the other two temperatures (Figure 7).

I tested lanthanide voltages at several salinities (0, 10, 21, 34 ppt) and found that normalized voltage was greatest in freshwater and decreased logarithmically with increasing salinity (Figure 8). Lanthanides produced a significantly greater normalized voltage in freshwater than brackish water (13, 25 ppt) and full strength seawater at all distances (Table 5). For eight of the 10 distances tested (1, 2, 3, 5, 10, 15, 20, 25 cm), there was no significant difference in lanthanide normalized voltage between brackish and full strength seawater.

Lanthanide metal type had a significant effect on normalized voltage at all 10 distances (Table 5). There was no significant difference between Nd and Pr at any of the distances, but PrNdA was usually significantly less than both Nd and Pr at all distances (Table 5).

Dissolution rate

The metals varied greatly in their dissolution rates, ranging from -1.64 g/h for PrNdA to -0.23 g/h for CeLa mischmetal (Figure 9). Each of the lanthanides had significantly different dissolution rates (Table 6), except for Nd1 and Pr which did not differ from each other ($F=3.35$, $p=0.0695$) and Nd2 and CeLa1 ($F=0.29$, $p=0.5900$). The dissolution rates for all metals were best modeled with linear regression (Figure 9; Table 7). The metals were grouped by their dissolution rates: those that did not dissolve (Pb and SS), the best lanthanides (CeLa2, Ce, PrNdM), and the intermediate group (Pr, Nd2, CeLa1, Nd1, PrNdA) (Figure 9). Of particular interest is cerium-lanthanum mischmetal. It was purchased in two batches which dissolved at very different rates (CeLa1 = -0.8728 g/h and CeLa2 = -0.2324 g/h; $F=215.05$, $p<.0001$). Nd was also procured in two batches that had significantly different dissolution rates (Nd1 = -0.6882 g/h and Nd2 = -0.9074 g/h, $F=13.78$, $p=0.0003$), although not as dramatically dissimilar as the CeLa.

Voltage over time

To investigate how voltage changed over time, six replicates of Nd were suspended in seawater and voltage measurements were taken over time. The raw voltage (mV) of the neodymium did not change over time ($F=0.92$, $p=0.5349$) despite the fact that the mass decreased linearly (Figure 10).

Behavioral trials

To determine the best metal for use in behavioral trials, voltage, dissolution rate, cost, and machineability were all considered. Voltage (from ambient seawater and 5 cm distance) and dissolution slope for each lanthanide and control were plotted on a Cartesian plane (Figure 11). The metals in quadrant I are the best candidates; they demonstrate both high voltage and low dissolution rates (i.e. are long-lasting). Quadrant II was not considered due to the fast dissolution, quadrant III was not considered due to both fast dissolution and low voltage production, and quadrant IV was disqualified due to low voltage production. From these selection criteria, neodymium was selected for shark behavioral trials.

I examined the material (AC, Pb, SS, Nd) from which 12 bonnethead (*S. tiburo*) and 13 lemon (*N. brevirostris*) sharks removed baits in order to determine if lanthanides have a deterrent effect on sharks. Because it sometimes took multiple days for the less voracious feeders to reach 10 bites, there were multiple feeding trials for the gluttonous eaters. Therefore, a repeated-measures (R-M)

ANOVA was applied to all of the sharks which were involved in more than one day of feeding in order to determine if the sharks' preference changed over time. The R-M ANOVA revealed that time had no significant effect on treatment selection (3 lemons with 4 feeding trials $F<0.001$, $p=1.000$; 3 lemons with 3 trials $F<0.001$, $p=1.000$; 6 lemons with 2 trials $F<0.001$, $p=1.000$, and 6 bonnetheads with 2 trials $F<0.001$, $p=.9988$). Also, there was no effect of group size (individual vs. group) for bonnethead sharks ($F<0.001$, $p=1.000$). Therefore, the data were pooled for each species by group size and used in a chi-squared goodness-of-fit test.

There was no significant difference in the material from which bait was removed: *S. tiburo* tested individually ($X^2=3.1416$, $p=0.3703$), *S. tiburo* in groups ($X^2=0.9091$, $p=0.8232$), and *N. brevirostris* in groups ($X^2=6.6984$, $p=0.0822$) (Figure 12). Therefore, the neodymium did not elicit a deterrent effect.

Striped burrfish (*Chilomycterus schoepfi*, N=3) would feed off the acrylic plate. However, due to the small sample size, a chi-squared goodness-of-fit test is not valid and therefore I was unable to draw any conclusions.

DISCUSSION

The goal of this study was to evaluate the efficacy of lanthanide metals as potential shark repellents. Sharks are the prevalent bycatch component in pelagic longline fisheries worldwide (Gilman *et al*., 2008) and recent work has investigated whether lanthanide elements are effective as potential shark deterrents (Brill *et al*., 2009; Jordan *et al.*, 2011; Kaimmer & Stoner, 2008; Robbins *et al.*, 2011; Stoner & Kaimmer, 2008; Tallack & Mandelman, 2009; Wang *et al.*, 2008). To determine their potential deterrent effect on sharks, I measured the voltage produced by lanthanide metals, dissolution rates in seawater, and examined sharks' performance in a behavioral experiment. My data indicate that lanthanide metals are not effective shark repellents.

The six lanthanide metals that I tested did not differ significantly in normalized voltage (Table 3), which is likely due to the identical electronegativity values (1.1) of the elements. The Nd squares that were used in the experiments produced a raw voltage of 888 μV and an electric field of 2.15 mV/cm, at a distance of 1 cm downstream from the recording electrode while immersed in seawater. The electric field produced by the metal at this distance was nine orders of magnitude greater than electric fields elasmobranchs are able to detect.

Euryhaline stingrays are able to detect electric fields as low as 6 nV/cm (McGowan & Kajiura, 2009), while three shark species can detect <1 nV/cm (Kajiura, 2003; Kajiura & Holland, 2002). The median detection range reported for three ray species and three shark species is between 25-48 nV/cm (Jordan *et al.*, 2009; Kajiura, 2003; Kajiura & Holland, 2002) and these electric field values were created by the neodymium at distances of 65.5-84.5 cm. This coincides with the reported ~100 cm effective range of deterrence for juvenile sandbar sharks in the absence of food (Brill *et al*., 2009). This literature supports the working hypothesis (Brill *et al*., 2009; Stoner & Kaimmer, 2008; Tallack & Mandelman, 2009) that the high voltage produced by lanthanide metals overwhelms the electrosensory system of the sharks at close range.

The normalized voltage was also examined at various biologically relevant temperatures, 12, 18, and 24ºC. There was no difference in lanthanide normalized voltage between 12 and 24°C; however, the normalized voltage was significantly greater at 18°C. Temperature should not have had an effect on voltage over the narrow range of biologically relevant temperatures that were tested. If temperature had any effect, it would be expected to be consistent across the temperature gradient (i.e. continuously increasing or decreasing). The measurements for the 18 and 12°C temperature trials were conducted on the same day and the electrodes were not moved between experiments. The experiments at 24°C were conducted two months prior to the 18 and 12°C trials. To achieve the cooler water temperatures, Styrofoam had to be added to the sides and the bottom of the acrylic tank, which resulted in a lower water level so that the linear actuator, whose height was not adjustable, would have enough clearance to avoid submerging the test metals. These inconsistencies in the methodology preclude comparing the 24°C treatment. While the 18°C treatment produced significantly greater normalized voltage than the 12°C treatment, no general trends can be drawn from these two points.

Although pelagic longlining is strictly marine, lanthanides have the potential to be used by recreational fishermen who fish in a wide variety of habitats; therefore, I measured the normalized voltage produced by the metals across a range of salinities from freshwater (0 ppt) to seawater (34 ppt). The lanthanide metals produced significantly greater normalized voltage in freshwater (0 ppt) than in brackish water (10 and 21 ppt) or full strength seawater (34 ppt). The normalized voltage decreased as a power function with increasing salinity and did not differ at most of the distances for salinities >10 ppt (Table 5). Therefore, as long as the fisher was fishing in a saline environment the lanthanides should behave comparably and even greater normalized voltage could be expected in freshwater. The ions found in seawater cause brackish and full strength seawater to be highly conductive which rapidly grounds out any electric charge distribution. This results in a steep decline in the electric field produced by a given voltage, which is much steeper than the electric field decay that is exhibited by the same voltage in freshwater (McGowan & Kajiura, 2009). Euryhaline stingrays may be sensitive to the rate at which voltage declines rather than a minimum electric field threshold (McGowan & Kajiura, 2009). Due to the much lower rate at which the electric field decreases for a given voltage in freshwater, the elasmobranchs' sensitivity to the electric field is reduced in freshwater (McGowan & Kajiura, 2009). A larger voltage is needed in freshwater to induce the same behavioral response in the elasmobranch.

The dissolution rates of the lanthanide metals varied greatly, ranging from -1.64 g/h (PrNdA) to -0.23 g/h (CeLa) (Figure 9, Table 7). The metals lasted between 16-100+ hours, these times are consistent with those reported by Stoner and Kaimmer (69.5% weight loss by CeLa in 40 hours) (Stoner & Kaimmer, 2008), Kaimmer and Stoner (50% CeLa mass lost after 20 h of fishing over three days) (Kaimmer & Stoner, 2008), and Tallack and Mandelman (estimated 50% CeLa dissolved in 30 h and 100% dissolved in ~40 h) (Tallack & Mandelman, 2009). Of interest is that CeLa mischmetal and Nd were both ordered in two separate batches and both batches produced significantly different dissolution rates. Samples from the first batch of CeLa had a dissolution rate of -0.87 g/h compared to -0.23 g/h for samples from the second batch despite there being no difference in the purity or the normalized voltage between the two batches. The two batches of Nd from different suppliers also exhibited significantly different dissolution rates (Nd1 -0.69 g/h and Nd2 -0.91 g/h). The type of impurities in the samples can differ from within the same mine by date, metal deposit, or site within the mine and these impurities, although minute (<0.5%), can cause very different results (Trout, 1990).

The variable dissolution rates for the same metal with the same purity makes estimating effective use time problematic. If these metals were to be deployed in commercial longline fishing operations this could cause severe miscalculations due to the inconsistency between batches of metals. The amount of time that a lanthanide will last directly influences the amount of time that the baited hooks are protected by the lanthanide metals. In the Australian tuna and billfish fishery, more than 95% of the trips have longline soak times of 4-13 hours and in Japan, longlines soak for 9-10 hours (Gilman *et al*., 2007), at which point many of the quick dissolving lanthanides (i.e. PrNdA) would have dissolved to the point that they would fall off the line. If the lanthanides dissolve more quickly than anticipated, this may lead to several hours where the hooks are not protected. Interestingly, as the lanthanide metals dissolve, the voltage (mV) remains unchanged despite the decreasing mass (Figure 10). This is likely due to the increased pitting which creates a larger three-dimensional surface area despite the decreasing mass. This suggests that the metals will remain effective for the duration of a longline soak.

Neodymium was chosen for use in behavioral experiments because it produced a high voltage, had a moderately slow dissolution rate, and was relatively easy to machine. Of the metals examined, CeLa and PrNdA were the most dangerous and difficult metals to machine. CeLa produced more sparks than the other lanthanides and PrNdA was very dense and had to be machined under a running lubricant to reduce the heat and sparks. Lanthanide metals are already fairly expensive and the price has almost tripled over the last two years (from $145/kg for Nd in November 2009 to $445/kg in November 2011, HEFA, personal communication) and the difficulty of machining them to size will impose additional costs if they are to be considered for longline fishing. Since lanthanides' effective detection distance extends to only 70 cm, each hook would need to be protected by a metal. A typical Hawaiian swordfish vessel deploys 800 hooks per set for a total of 163,200 hooks per year whereas a tuna longline vessel deploys 2,000 hooks per set and a total of 300,000 hooks per year (Gilman *et al*., 2007). Based on 2010 prices for Nd sheet metal, after a 12"x2"x1/4" sheet of Nd was cut into 1" squares, each square cost $14.50. Assuming that each piece of Nd could be used for 2 sets before it dissolves, it would cost a Hawaiian swordfishermen approximately $1,183,200/yr, and tuna fishermen $2,175,000/yr to purchase enough Nd to protect their hooks from shark depredation. Those prices would double if the squares could be used for just one set. Although the same fishermen typically lose $688,500/yr in swordfish and $393,750/yr in tuna due to shark damage, the total cost of adding Nd would still exceed the savings by protecting the catch of the target fish. The cost of lanthanide metals would need to be reduced by 170-550% before they could be commercially implemented into the commercial PLL industry.

To determine the effectiveness of neodymium as a shark repellent, a behavioral trial was conducted with lemon sharks (*Negaprion brevirostris*) and bonnethead sharks (*Sphyrna tiburo*). The lemon sharks would not feed in isolation; therefore all of their feeding trials were conducted in groups. They would immediately swim toward the acrylic plate as it was being lowered into the water and typically removed the first bait encountered. Because the lemon sharks were tested in groups, there may have been strong competition for food which may account for why the bait was removed equally from all treatments. The bonnethead sharks were tested individually and in groups and they also typically removed the first bait encountered even without competition for food. There were very few instances where a shark exhibited avoidance to the Nd but they were clearly aware of it. Sharks would often continue to bite at the Nd even after the bait was removed, a behavior not exhibited with any of the other treatments. Also, the sharks appeared to have difficulty locating the bait affixed to the Nd as evident from repeated bites and longer time spent trying to remove the bait from the Nd. This suggests that even though the sharks seemed to detect the voltage produced by Nd, it was ineffective as a deterrent.

Lanthanide metals have produced inconsistent results as shark repellents (Table 8). Currently, six shark species have been investigated from four families. Whereas a certain species may be deterred by one lanthanide in one study, the same species tested with the same lanthanide may behave differently in another study. In some studies lanthanides have been shown to effectively deter shark bait depredation (Brill *et al*., 2009; Jordan *et al.*, 2011; Kaimmer & Stoner, 2008; Stoner & Kaimmer, 2008; Wang *et al.*, 2008) but in others sharks have not been deterred (Brill *et al.*, 2009; Jordan *et al.*, 2011; Robbins *et al.*, 2011; Tallack &

Mandelman, 2009). In this study, Nd did not deter bonnethead sharks, *S. tiburo*, from removing baits when tested either individually or in groups nor did it repel lemon sharks, *N. brevirostris*, when tested in groups.

When there was no food present, juvenile sandbar sharks, *C. plumbeus*, would not pass within 100 cm of PrNdA (Brill *et al*., 2009), however hunger level and shark density have been suggested to adversely affect lanthanide metals' repellent abilities (Brill *et al*., 2009; Jordan *et al.*, 2011; Kaimmer & Stoner, 2008; Robbins *et al.*, 2011; Tallack & Mandelman, 2009). The sharks in this study were fed to satiation every other day, so even despite the fact that their hunger level was relatively low and they could afford to be picky eaters, Nd still failed to act as a repellent. Elasmobranchs in the wild will not be as well fed and should therefore be less discriminatory feeders, so the lanthanides should be even less effective. Also, it has been suggested that a tolerance to lanthanide metals can be learned (Brill *et al*., 2009). To account for this, a repeated-measure ANOVA was performed for the sharks that had more than one experimental day and over this short period, there was no difference in the percentages of bait removed from any treatment which suggests that over a short time frame sharks will not learn to tolerate lanthanides. Due to the large spatial extent of pelagic species and fishermen, repeated encounters between sharks and longlines should be sufficiently infrequent to prevent a learned tolerance to the lanthanides.

Teleosts are the targeted species in PLL fishing, therefore a positive teleost control was used to determine if Nd affects bait removal. Striped burrfish, *Chilomycterus schoepfi*, were the only teleosts that would feed off the acrylic plate. Sailor's choice grunts (*Haemulon parra*), gray snappers (*Lutjanus griseus*), and lookdowns (*Selene vomer*) were acquired but did not feed in the behavioral trials. Burrfish did not appear to exhibit bait preference or avoidance to the Nd; however due to the small sample size (n = 3) these results could not be tested statistically. Since the Nd did not deter the electroreceptive elasmobranchs, it is unlikely that the Nd would have had any effect on the burrfish.

There has been extensive work done examining different types of shark repellents, including: chemical (sodium lauryl sulfate, Smith, 1991; dodecyl sulfate, Sisneros & Nelson, 2001), magnetic (O'Connell *et al.*, 2011; O'Connell *et al.*, 2010; Rigg *et al.*, 2009; Robbins *et al.*, 2011; Stoner & Kaimmer, 2008), and lanthanide metals (Brill *et al*., 2009; Jordan *et al.*, 2011; Kaimmer & Stoner, 2008; Robbins *et al.*, 2011; Stoner & Kaimmer, 2008; Tallack & Mandelman, 2009; Wang *et al.*, 2008). Chemical repellents have the problem of being short-lived, may adversely affect target catch, and may be toxic to sharks. Magnetic repellents are relatively permanent so dissolution is not a concern, but the magnets become easily tangled and can attach to other hardware including the boat itself. In addition, the mass of the magnets may weigh down the hooks, which is especially undesirable in demersal longlines. Lanthanide repellents have produced widely variable results. Due to the high cost of lanthanides (which have increased over twenty-fold in the past five years, from $20/kg in

2008 to $440/kg in 2011 for CeLa mischmetal), the hazards of machining these metals (they give off sparks and cause fires), the fast dissolution, the small effective range (less than 80 cm), and most importantly, the lack of a consistent deterrent effect, lanthanides do not appear to be suitable for use in the commercial longline fishing industry. Future research should continue to investigate electrogenic repellents that specifically stimulate the electrosensory system of elasmobranchs and remain undetectable by the target teleost fishes.

APPENDIX

Table 1

Purity and Cost of Lanthanide Metals

Lanthanide metal, purity, and cost information for lanthanides used in this study. All of the metals were procured from Hefa Rare Earth Canada Co. Ltd. and reflect the prices from November, 2009, except for the second batch of neodymium which was obtained from CSTRAM Advanced Materials Co., China and was packed in oil to prevent oxidation. The cost was elevated because the metal was ordered as sheets rather than unprocessed ingots and the price was set in August, 2010. The metals tested were neodymium (Nd), praseodymium (Pr), praseodymium-neodymium metal alloy (PrNdA), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium mischmetal (PrNdM), cerium metal (Ce), stainless steel (SS), and lead (Pb).

Metal	**Purity (content)**	**Cost (per kg)**
Nd	99.60%	$145.00
Nd 2	99.5%	$230.30
Pr	99.60%	$150.00
Ce	99.90%	$135.00
PrNdA	99.5% (76.49% Nd, 23.41% Pr)	$179.00
CeLa	99.5% (64.09% Ce, 35.89% La)	$105.00
PrNdM	99.7% (52.76% Ce, 27.79% La, 14.64% Nd, 4.81% Pr)	$120.00

Table 2

Equations and R^2 Power Trendline Values from the Lanthanide Normalized Voltage Production in Ambient Seawater

The normalized voltage of the lanthanide metals declined with increasing distance from the recording electrode, and is best modeled by a power function. The metal, equation, and R^2 values are listed. The metals tested were neodymium (Nd), praseodymium (Pr), praseodymium-neodymium metal alloy (PrNdA), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium mischmetal (PrNdM), cerium metal (Ce), stainless steel (SS), and lead (Pb).

Metal	**Equation**	**R^2**
Nd	$y = 64.349x^{-1.572}$	0.9856
Pr	$y = 44.105x^{-1.470}$	0.9871
PrNdA	$y = 35.397x^{-1.465}$	0.9686
CeLa	$y = 21.523x^{-1.309}$	0.9663
PrNdM	$y = 42.359x^{-1.584}$	0.9776
Ce	$y = 30.707x^{-1.496}$	0.9870
SS	$y = 0.6441x^{-0.434}$	0.8877
Pb	$y = 0.8462x^{-0.650}$	0.9020

Table 3

Statistical Output for all Metals in Ambient Seawater

The statistical results of the normalized voltage produced by the metals in ambient seawater. Significant differences are in bold. The metals tested were neodymium (Nd), praseodymium (Pr), praseodymium-neodymium metal alloy (PrNdA), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium mischmetal (PrNdM), cerium metal (Ce), stainless steel (SS), and lead (Pb).

Distance	**ANOVA**		**Tukey pairwise comparisons**							
(cm)	F	p	Ce vs. Nd	Ce vs. Pr	Ce vs. PrNdM	Ce vs. CeLa	Ce vs. PrNdA	Ce vs. Pb	Ce vs. SS	Nd vs. Pr
1	30.19	<0.001	0.9378	0.9304	0.9950	0.9409	1.0000	**<.0001**	**<.0001**	1.0000
2	35.32	<0.001	0.9084	0.8935	0.9943	0.9954	1.0000	**<.0001**	**<.0001**	1.0000
3	29.60	<0.001	0.9176	0.8481	0.9207	0.9637	0.9989	**<.0001**	**<.0001**	1.0000
4	38.26	<0.001	0.4141	0.3668	0.6513	0.9988	0.8589	**<.0001**	**<.0001**	1.0000
5	28.25	<0.001	0.7208	0.9803	0.8495	0.8593	0.7997	**<.0001**	**<.0001**	0.9963
10	16.20	<0.001	0.6260	0.8691	1.0000	0.7554	0.9620	**<.0001**	**<.0001**	0.9998
15	9.69	<0.001	0.3888	0.2798	0.9679	0.5881	0.6838	**0.0184**	0.3940	1.0000
20	6.70	<0.001	0.5171	0.3610	1.0000	0.9548	1.0000	0.0911	0.3903	1.0000
25	3.71	0.0035	0.9801	0.9999	0.9984	0.9998	1.0000	0.0327	0.6939	0.9994
30	8.50	<.0001	0.6942	0.2863	1.0000	1.0000	0.9860	0.0016	0.9106	0.9972

Table 3 cont.

Distance	**Tukey pairwise comparisons**									
(cm)	Nd vs. PrNdM	Nd vs. CeLa	Nd vs. PrNdA	Nd vs. Pb	Nd vs. SS	Pr vs. PrNdM	Pr vs CeLa	Pr vs. PrNdA	Pr vs. Pb	Pr vs. SS
1	0.9999	0.3131	0.9701	**<.0001**	**<.0001**	0.9998	0.2995	0.9658	**<.0001**	**<.0001**
2	0.9996	0.5000	0.9381	**<.0001**	**<.0001**	0.9993	0.4783	0.9193	**<.0001**	**<.0001**
3	1.0000	0.3299	0.9979	**<.0001**	**<.0001**	1.0000	0.2436	0.9907	**<.0001**	**<.0001**
4	0.9999	0.7805	0.9949	**<.0001**	**<.0001**	0.9998	0.7339	0.9904	**<.0001**	**<.0001**
5	1.0000	1.0000	1.0000	**<.0001**	**<.0001**	0.9997	0.9998	0.9991	**<.0001**	**<.0001**
10	0.7761	1.0000	0.9951	**<.0001**	**<.0001**	0.9499	1.0000	1.0000	**<.0001**	**<.0001**
15	0.9413	1.0000	0.9997	**<.0001**	**0.0022**	0.8722	0.9995	0.9973	**<.0001**	**0.0012**
20	0.6660	0.9869	0.7390	**0.0004**	**0.0040**	0.5004	0.9462	0.5773	**0.0002**	**0.0019**
25	0.7696	0.8515	0.9821	**0.0054**	0.1759	0.9668	0.9871	0.9999	**0.0111**	0.4337
30	0.7289	0.4816	0.1967	**<.0001**	0.0909	0.3150	0.1536	0.0442	**<.0001**	**0.0171**

Table 3 cont.

Distance (cm)	Tukey pairwise comparisons PrNdM vs.CeLa	PrNdM vs. PrNdA	PrNdM vs. Pb	PrNdM vs. SS	CeLa vs. PrNdA	CeLa vs. Pb	CeLa vs. SS	PrNdA vs. Pb	PrNdA vs. SS	Pb vs. SS
1	0.5636	0.9985	**<.0001**	**<.0001**	0.9287	**<.0001**	**<.0001**	**<.0001**	**<.0001**	0.9931
2	0.8069	0.9970	**<.0001**	**<.0001**	0.9917	**<.0001**	**<.0001**	**<.0001**	**<.0001**	1.0000
3	0.3351	0.9981	**<.0001**	**<.0001**	0.7284	**<.0001**	**<.0001**	**<.0001**	**<.0001**	1.0000
4	0.9362	0.9999	**<.0001**	**<.0001**	0.9924	**<.0001**	**<.0001**	**<.0001**	**<.0001**	1.0000
5	1.0000	1.0000	**<.0001**	**<.0001**	1.0000	**<.0001**	**<.0001**	**<.0001**	**<.0001**	0.9908
10	0.8780	0.9916	**<.0001**	**<.0001**	0.9994	**<.0001**	**<.0001**	**<.0001**	**<.0001**	0.9025
15	0.9902	0.9971	**0.0010**	0.0510	1.0000	**<.0001**	**0.0056**	**0.0001**	**0.0085**	0.5407
20	0.9879	1.0000	0.0532	0.2684	0.9950	0.0054	0.0425	0.0397	0.2164	0.9938
25	1.0000	0.9980	0.1386	0.9600	0.9997	0.0982	0.9187	0.0312	0.6830	0.7003
30	0.9999	0.9800	**0.0013**	0.8900	0.9992	0.0042	0.9822	0.0193	0.9999	0.0495

Table 4

Statistical Output for Temperature Trials between Metals

The statistical results for the normalized voltage produced by select lanthanide metals (Nd, Pr, PrNdA) at various temperatures (12, 18, 24ºC) at all 10 distances. Significant differences are in bold.

Distance	**ANOVA**				**Contrasts**					
(cm)	**metal**		**temp**		**12 vs. 18**		**18 vs. 24**		**12 vs. 24**	
	F	p	F	p	F	p	F	p	F	p
1	2.20	0.1221	6.84	**0.0026**	9.40	**0.0037**	11.04	**0.0018**	0.07	0.7981
2	0.17	0.8474	8.88	**0.0006**	8.82	**0.0048**	16.60	**0.0002**	1.22	0.2752
3	0.06	0.9387	9.22	**0.0004**	11.50	**0.0015**	15.83	**0.0002**	0.34	0.5605
4	0.20	0.8196	7.21	**0.0019**	6.96	**0.0114**	13.58	**0.0006**	1.09	0.3012
5	0.19	0.8248	3.70	**0.0324**	3.19	0.0808	7.14	**0.0105**	0.78	0.3806
10	0.31	0.7326	12.79	**<.0001**	12.23	**<.0001**	13.96	**0.0005**	1.17	0.2846
15	0.72	0.4940	7.36	**0.0017**	14.69	**0.0004**	3.07	0.0867	4.33	**0.0432**
20	0.61	0.5458	3.71	**0.0323**	7.06	**0.0109**	0.66	0.4209	3.40	0.0717
25	0.03	0.9688	4.72	**0.0138**	7.14	**0.0104**	0.00	0.9807	7.01	**0.0111**
30	6.57	**0.0031**	4.60	**0.0152**	2.20	0.1386	2.33	0.1338	9.21	**0.0040**

Table 4 cont.

Distance (cm)	Contrasts Nd vs. Pr		Nd vs. PrNdA		Pr vs. PrNdA	
	F	p	F	p	F	p
1	0.38	0.5421	4.19	**0.0466**	2.05	0.1592
2	0.06	0.8102	0.33	0.5687	0.11	0.7410
3	0.01	0.9128	0.06	0.8130	0.12	0.7294
4	0.32	0.5739	0.28	0.6013	0.00	0.9680
5	0.30	0.5894	0.00	0.9922	0.28	0.5961
10	0.61	0.4388	0.08	0.7810	0.25	0.6185
15	1.42	0.2403	0.50	0.4835	0.23	0.6311
20	0.64	0.4285	0.07	0.7920	1.13	0.2929
25	0.06	0.8066	0.03	0.8667	0.01	0.9387
30	1.35	0.2521	5.73	**0.0209**	12.64	**0.0009**

Table 5

Statistical Output for Salinity Trials between Metals

The statistical results for the normalized voltage produced by select lanthanide metals (Nd, Pr, PrNdA) at various salinities, freshwater (FW = 0 ppt), brackish seawater (BW = 10 and 21 ppt) and full strength seawater (SW = 34 ppt), at all 10 distances tested. Significant differences are in bold.

Distance	**ANOVA**				**Contrasts**							
(cm)	**metal**		**salinity**		**0 vs. 10**		**10 vs. 21**		**21 vs. 34**		**FW vs. BW**	
	F	p	F	p	F	p	F	p	F	p	F	p
1	6.43	**0.0029**	29.19	**<.0001**	30.30	**<.0001**	6.58	**0.0128**	0.00	0.9484	64.43	**<.0001**
2	5.83	**0.0048**	42.94	**<.0001**	54.89	**<.0001**	4.18	**0.0453**	0.40	0.5320	94.78	**<.0001**
3	4.61	**0.0137**	36.83	**<.0001**	42.57	**<.0001**	5.88	**0.0183**	0.07	0.7856	79.81	**<.0001**
4	4.61	**0.0137**	44.50	**<.0001**	53.40	**<.0001**	2.39	0.1277	3.82	0.0552	87.04	**<.0001**
5	7.32	**0.0014**	39.86	**<.0001**	52.97	**<.0001**	2.86	0.0961	0.68	0.4137	87.98	**<.0001**
10	4.42	**0.0163**	54.72	**<.0001**	94.33	**<.0001**	0.93	0.3377	0.03	0.8643	138.60	**<.0001**
15	5.28	**0.0077**	39.41	**<.0001**	75.43	**<.0001**	0.24	0.6235	0.20	0.6602	106.37	**<.0001**
20	3.87	**0.0262**	60.91	**<.0001**	107.50	**<.0001**	2.05	0.1571	1.12	0.2937	163.83	**<.0001**
25	4.59	**0.0140**	50.23	**<.0001**	98.40	**<.0001**	0.33	0.5695	0.85	0.3613	138.88	**<.0001**
30	3.21	**0.0473**	64.78	**<.0001**	167.04	**<.0001**	5.72	**0.0199**	0.72	0.3987	183.41	**<.0001**

Table 5 cont.

Distance (cm)	**Contrasts**									
	BW vs. SW		**FW vs. SW**		**Nd vs. Pr**		**Nd vs. PrNdA**		**Pr vs. PrNdA**	
	F	p	F	p	F	p	F	p	F	p
1	2.42	0.1249	66.18	**<.0001**	1.84	0.1795	12.63	**0.0007**	4.82	**0.0319**
2	3.63	0.0614	101.64	**<.0001**	1.45	0.2327	11.36	**0.0013**	4.69	**0.0344**
3	2.94	0.0914	85.06	**<.0001**	0.18	0.6712	5.72	**0.0199**	7.94	**0.0065**
4	9.92	**0.0025**	116.81	**<.0001**	0.81	0.3713	8.78	**0.0044**	4.25	**0.0436**
5	3.71	0.0588	95.88	**<.0001**	0.12	0.7260	12.07	**0.0010**	9.75	**0.0028**
10	0.57	0.4525	117.73	**<.0001**	1.75	0.1909	8.80	**0.0043**	2.7	**0.1056**
15	0.05	0.8226	76.33	**<.0001**	0.04	0.8408	8.47	**0.0051**	7.34	**0.0088**
20	0.16	0.6939	115.39	**<.0001**	0.00	0.9924	5.78	**0.0193**	5.83	**0.0188**
25	0.54	0.4671	91.62	**<.0001**	0.07	0.7977	7.52	**0.0080**	6.17	**0.0158**
30	5.58	**0.0214**	93.75	**<.0001**	0.11	0.7462	4.06	**0.0485**	5.47	**0.0227**

Table 6

Dissolution Comparisons between Metals

The interaction of mass and time (i.e. dissolution slope) from a two-way ANOVA was compared to determine if the dissolution rates differed among samples and *a priori* contrasts were designed to examine those differences; significant differences are in bold.

Contrast	F	p	Contrast	F	p
Ce vs. Nd1	101.81	**<.0001**	Nd2 vs. SS	333.99	**<.0001**
Ce vs. Nd2	175.82	**<.0001**	Pr vs. PrNdM	46.12	**<.0001**
Ce vs. Pr	80.95	**<.0001**	Pr vs. CeLa1	24.58	**<.0001**
Ce vs. PrNdM	23.64	**<.0001**	Pr vs. CeLa2	143.93	**<.0001**
Ce vs. CeLa1	156.49	**<.0001**	Pr vs. PrNdA	111.97	**<.0001**
Ce vs. CeLa2	80.40	**<.0001**	Pr vs. Pb	246.32	**<.0001**
Ce vs. PrNdA	206.95	**<.0001**	Pr vs. SS	244.37	**<.0001**
Ce vs. Pb	181.40	**<.0001**	PrNdM vs. CeLa1	118.60	**<.0001**
Ce vs. SS	178.53	**<.0001**	PrNdM vs. CeLa2	167.73	**<.0001**
Nd1 vs. Nd2	13.78	**0.0003**	PrNdM vs. PrNdA	185.18	**<.0001**
Nd1 vs. Pr	3.35	0.0695	PrNdM vs. Pb	249.87	**<.0001**
Nd1 vs. PrNdM	67.00	**<.0001**	PrNdM vs. SS	246.64	**<.0001**
Nd1 vs. CeLa1	9.78	**0.0022**	CeLa1 vs. CeLa2	215.05	**<.0001**
Nd1 vs. CeLa2	160.06	**<.0001**	CeLa1 vs. PrNdA	54.75	**<.0001**
Nd1 vs. PrNdA	89.57	**<.0001**	CeLa1 vs. Pb	310.70	**<.0001**
Nd1 vs. Pb	257.76	**<.0001**	CeLa1 vs. SS	309.01	**<.0001**
Nd1 vs. SS	255.99	**<.0001**	CeLa2 vs. PrNdA	237.58	**<.0001**
Nd2 vs. Pr	31.13	**<.0001**	CeLa2 vs. Pb	95.94	**<.0001**
Nd2 vs. PrNdM	135.30	**<.0001**	CeLa2 vs. SS	93.75	**<.0001**
Nd2 vs. CeLa1	0.29	0.5900	PrNdA vs. Pb	297.68	**<.0001**
Nd2 vs. CeLa2	237.88	**<.0001**	PrNdA vs. SS	296.82	**<.0001**
Nd2 vs. PrNdA	49.90	**<.0001**	Pb vs. SS	0.01	0.9344
Nd2 vs. Pb	335.74	**<.0001**			

Table 7

Dissolution Rate Equations

The dissolution rate was best modeled with linear regression; the metal, linear regression equation, and R^2 values are listed.

Metal	Equation	R^2
Nd1	y = -0.6882x + 21.29	0.9584
Nd2	y = -0.9074x + 27.118	0.9892
Pr	y = -0.597x + 21.467	0.9877
PrNdA	y = -1.6369x + 25.492	0.9869
CeLa1	y = -0.8728x + 25.285	0.9904
CeLa2	y = -0.2324x + 25.017	0.9907
PrNdM	y = -0.3649x + 29.339	0.9564
Ce	y = -0.296x + 26.208	0.9872
SS	y = 0.0002x + 31.886	0.1733
Pb	$y = 8x10^{-5}x + 46.051$	0.0996

Table 8

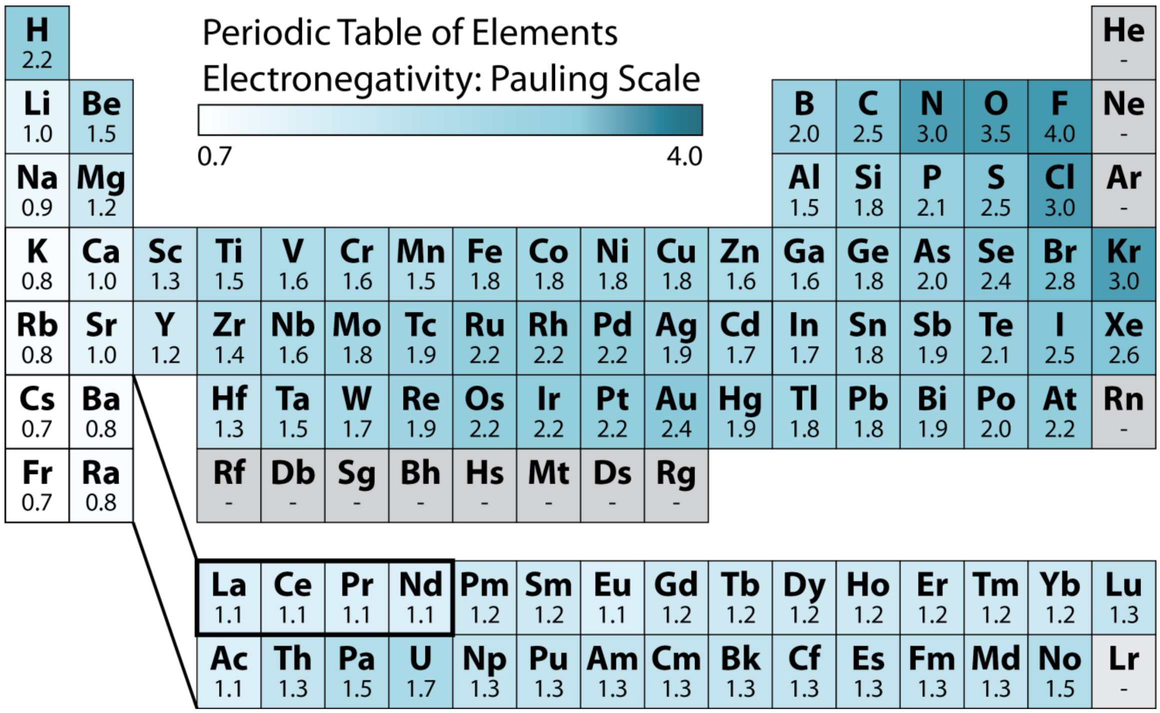
Summary of Lanthanide Effectiveness

The efficacy of lanthanide metals from studies investigating the potential of using lanthanides as shark repellents. The order, family, and species of each shark that has been used in these studies are provided. The lanthanide in the study, the study type (lab vs. field), the effectiveness of the lanthanide as a shark repellent (yes or no), and the authors of the study are listed.

Order	**Family**	**Species**	**Lanthanide**	**Study**	**Effective**	**Reference**
Carcharhiniformes	Carcharhinidae	*Carcharhinus galapagensis*	PrNdA	Field	Yes	Wang *et al.*, 2008
Carcharhiniformes	Carcharhinidae	*Carcharhinus galapagensis*	PrNdA	Field	No	Robbins *et al.*, 2011
Carcharhiniformes	Carcharhinidae	*Carcharhinus galapagensis*	Nd	Field	No	Robbins *et al.*, 2011
Carcharhiniformes	Carcharhinidae	*Carcharhinus plumbeus*	PrNdA	Field	Yes	Wang *et al.*, 2008
Carcharhiniformes	Carcharhinidae	*Carcharhinus plumbeus*	PrNdA	Lab	No	Brill *et al.*, 2009
Carcharhiniformes	Carcharhinidae	*Carcharhinus plumbeus*	PrNdM	Field	Yes	Brill *et al.*, 2009
Carcharhiniformes	Carcharhinidae	*Negaprion brevirostris*	Nd	Lab	No	This study
Carcharhiniformes	Triakidae	*Mustelus canis* – group	Nd	Lab	No	Jordan *et al.*, 2011
Carcharhiniformes	Triakidae	*Mustelus canis* – individual	Nd	Lab	Yes	Jordan *et al.*, 2011
Carcharhiniformes	Sphyrnidae	*Sphyrna tiburo* – group	Nd	Lab	No	This study
Carcharhiniformes	Sphyrnidae	*Sphyrna tiburo* – individual	Nd	Lab	No	This study
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Lab	Yes	Stoner & Kaimmer, 2008
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Field	Yes	Kaimmer & Stoner, 2008
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Lab	No	Tallack & Mandelman, 2009
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Field	No	Tallack & Mandelman, 2009
Squaliformes	Squalidae	*Squalus acanthias*	Nd	Lab	Yes	Jordan *et al.*, 2011

Figure 1

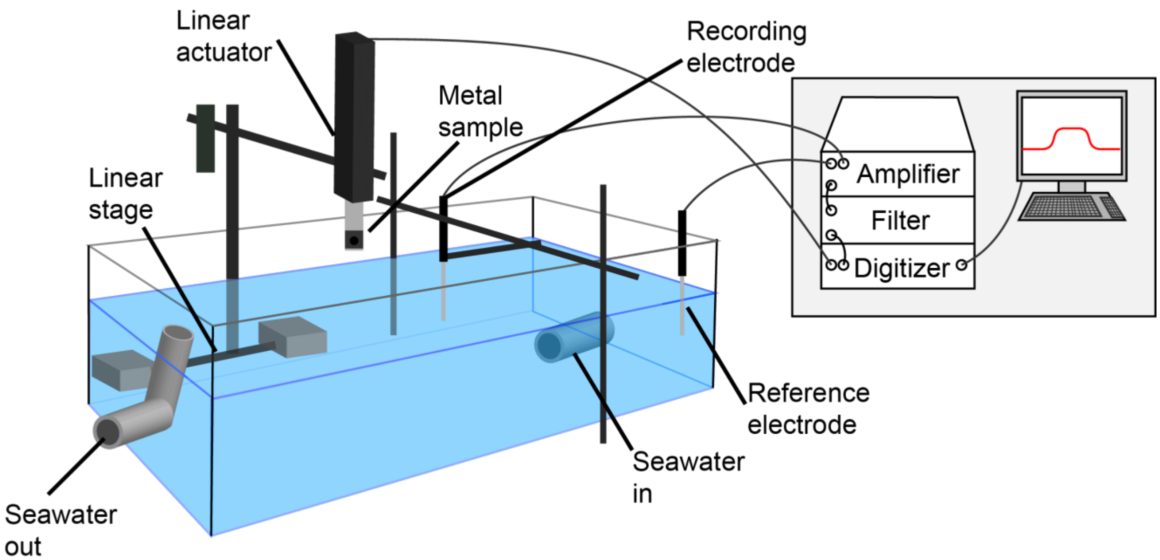
Periodic Table of the Elements with Electronegativity Values



The periodic table of elements colored according to Pauling scale electronegativity; the lanthanides used in this study are enclosed in the bold box. Materials tested include: cerium (Ce), neodymium (Nd), praseodymium (Pr), praseodymium-neodymium mischmetal (PrNdM), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium metal alloy (PrNdA), lead (Pb), stainless steel (SS), and acrylic (AC, a nonmetallic control). The lanthanide elements all have identical electronegativity values (1.1).

Figure 2

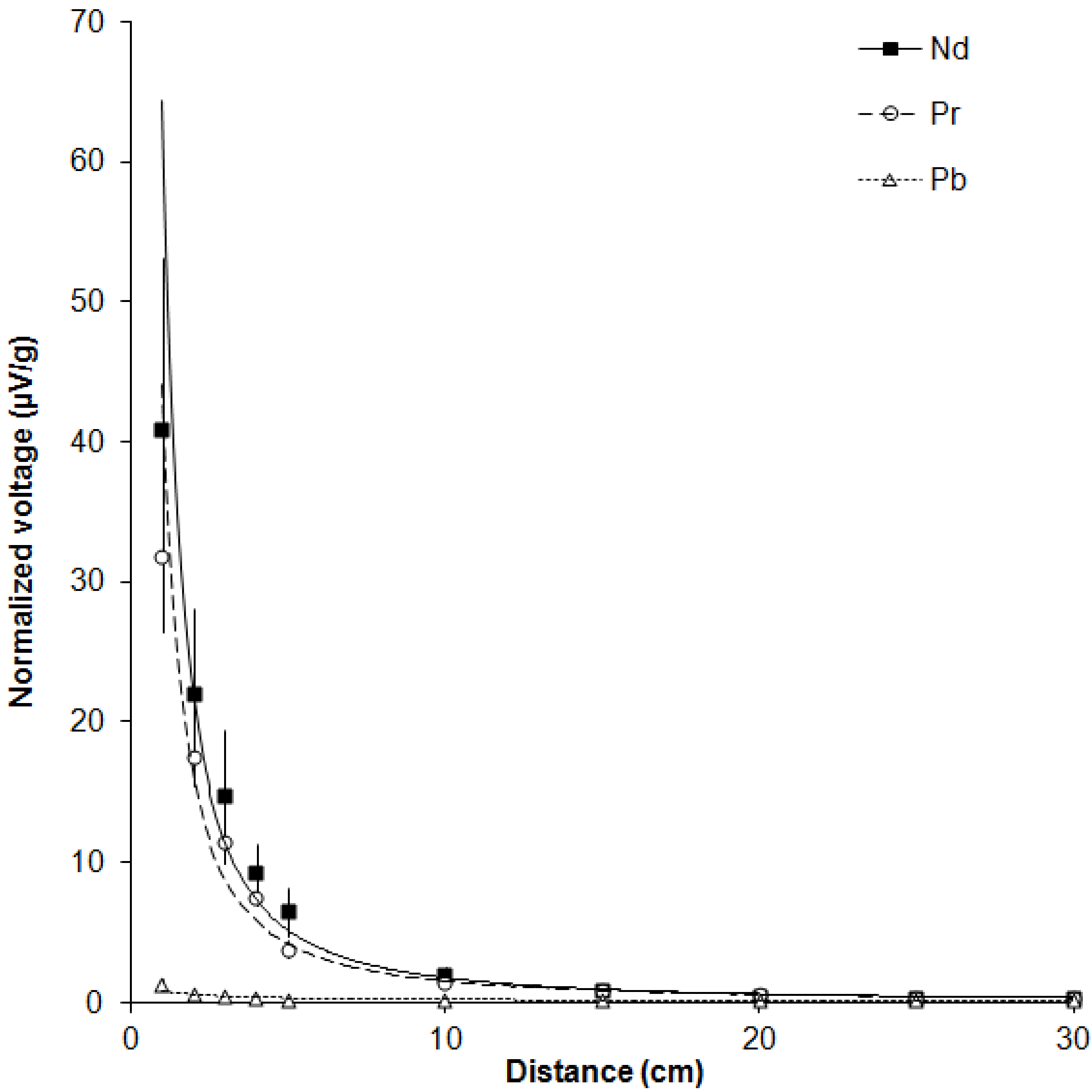
Apparatus for Voltage Experiments



Experimental apparatus for voltage measurements. A metal sample (n = 6 each) was affixed to an acrylic rod on a linear actuator that dipped the sample into the experimental tank. The actuator was attached to a linear translation stage, which positioned the sample at a precise distance from a recording electrode. The differential output from the recording and reference electrodes was amplified, filtered, and digitized. The voltage of each metal was measured at 10 distances in random order from the recording electrode.

Figure 3

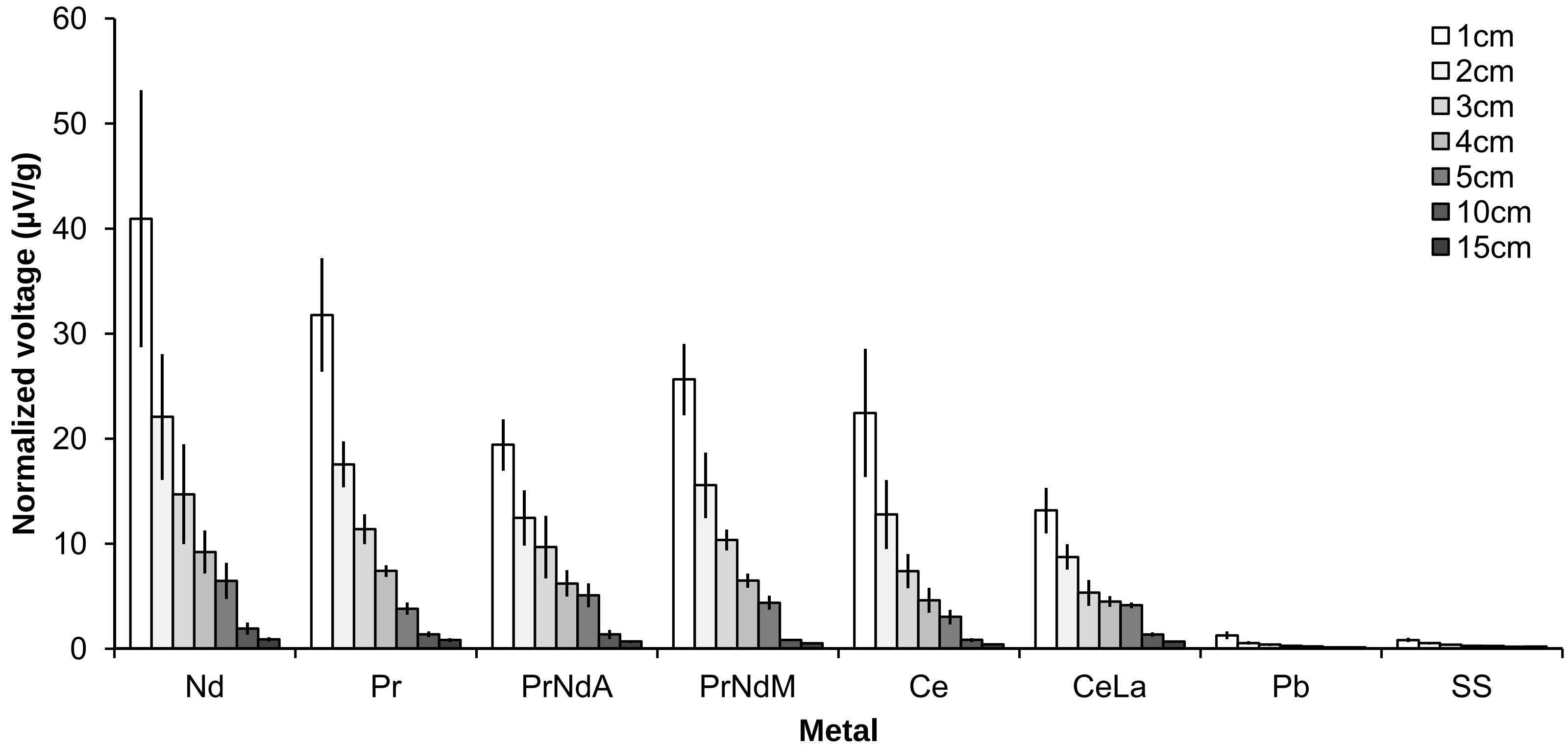
Normalized Voltage over Distance



The voltage produced by a subset of the metals (Nd = neodymium, Pr = praseodymium, Pb = lead; n = 6 each, mean ± s.e.m.), normalized to 1 g mass, decreased with increasing distance from the recording electrode. Normalized voltage curves of the lanthanide metals are best fit with a power function. I recorded almost no voltage from the lead control.

Figure 4

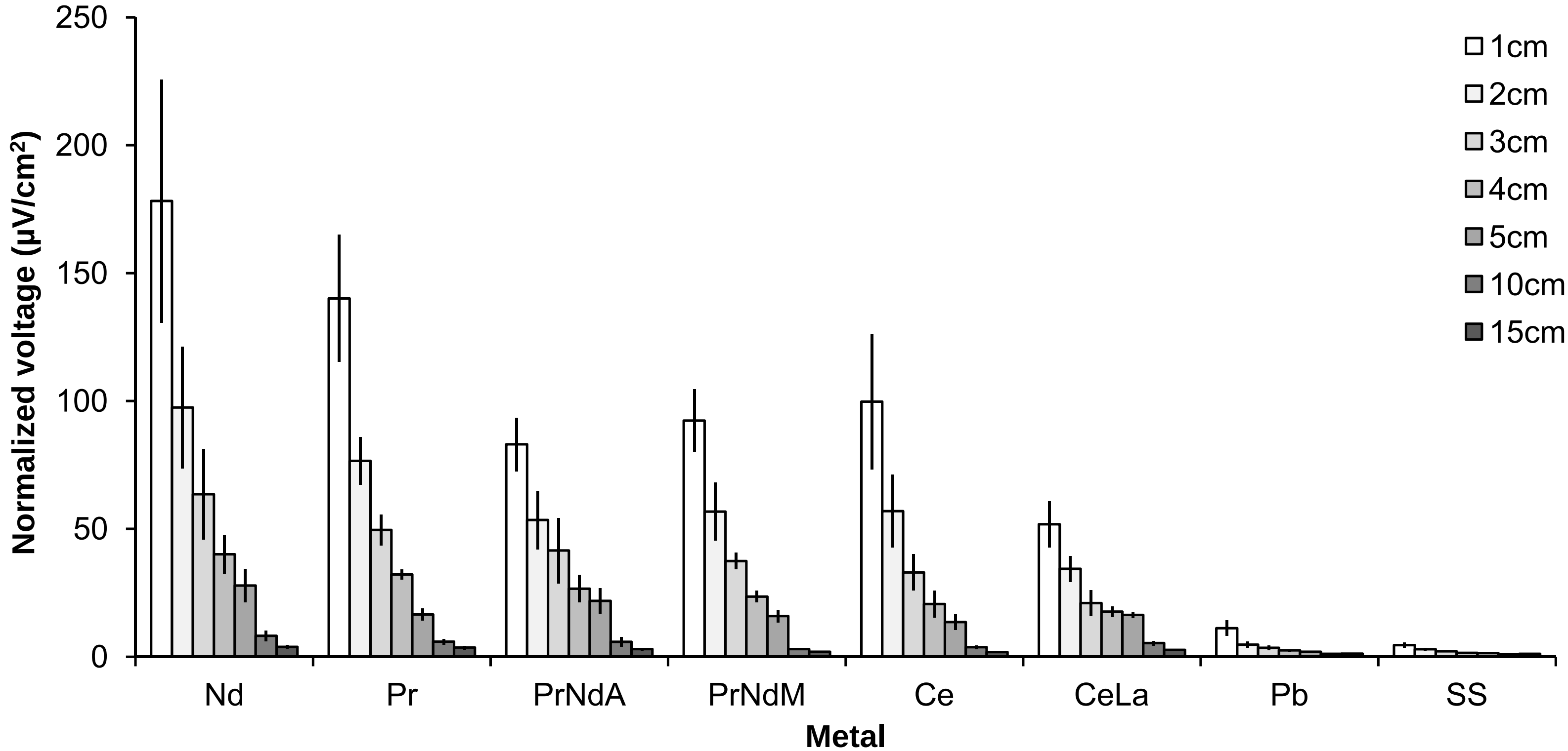
Normalized Voltage of all Metal by Mass



The voltage (mean ± s.e.m.), normalized to 1 g mass, produced by the lanthanide and control metals with increasing distance from the recording electrode. For each distance the lanthanides are not significantly different from one another nor are the control metals. The lanthanides produce a consistently greater voltage than the control metals at all distances except 15 cm where Ce and PrNdM do not differ from SS. Metals tested include: cerium (Ce), neodymium (Nd), praseodymium (Pr), praseodymium-neodymium mischmetal (PrNdM), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium metal alloy (PrNdA), lead (Pb), and stainless steel (SS).

Figure 5

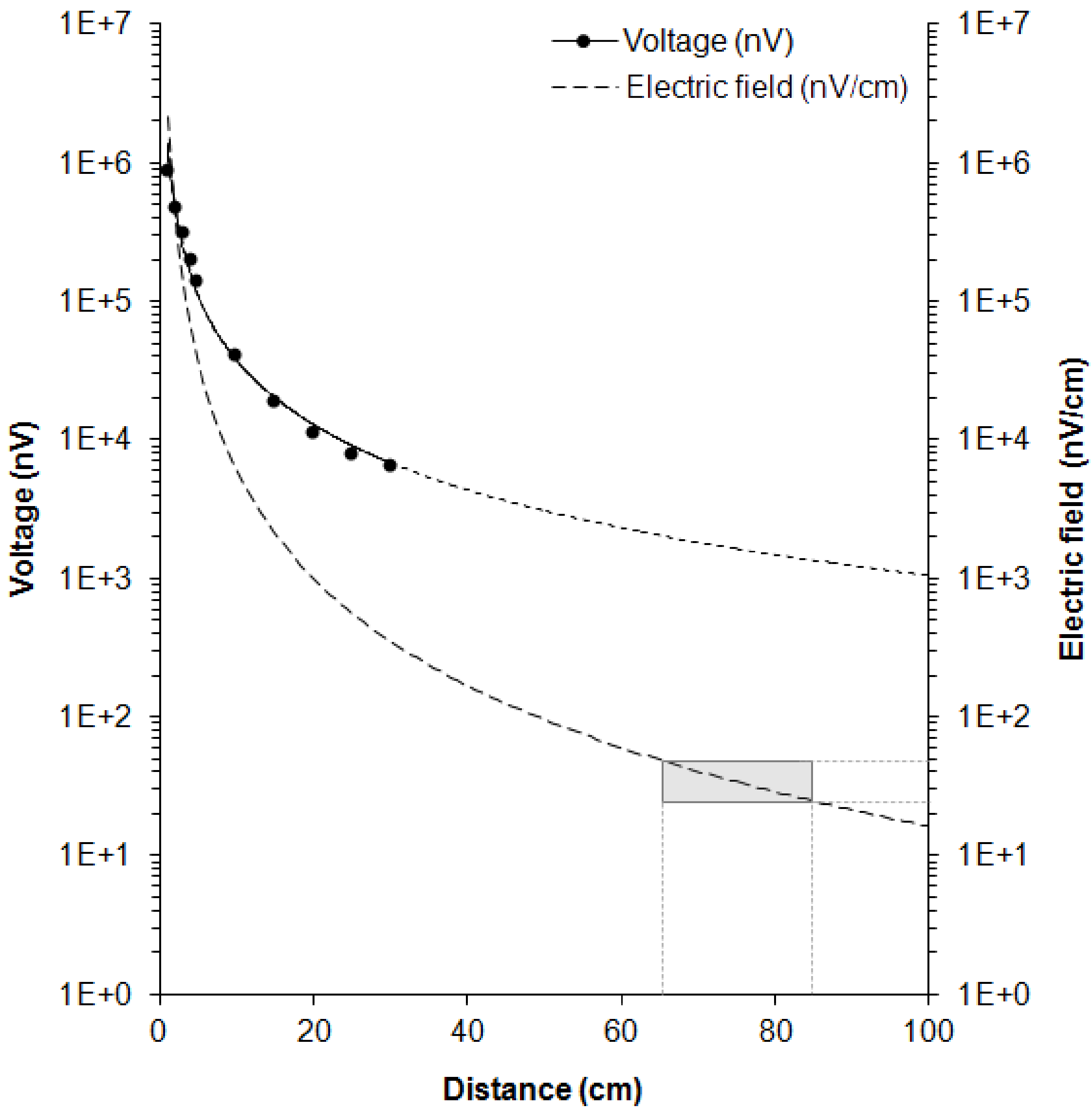
Normalized Voltage of all Metals by Surface Area



The voltage (mean ± s.e.m.), normalized to 1 cm^2, produced by the lanthanide and control metals with increasing distance from the recording electrode. For each distance the lanthanides are not significantly different from one another nor are the control metals. The lanthanides produce a consistently greater voltage than the control metals. Metals tested include: cerium (Ce), neodymium (Nd), praseodymium (Pr), praseodymium-neodymium mischmetal (PrNdM), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium metal alloy (PrNdA), lead (Pb), and stainless steel (SS).

Figure 6

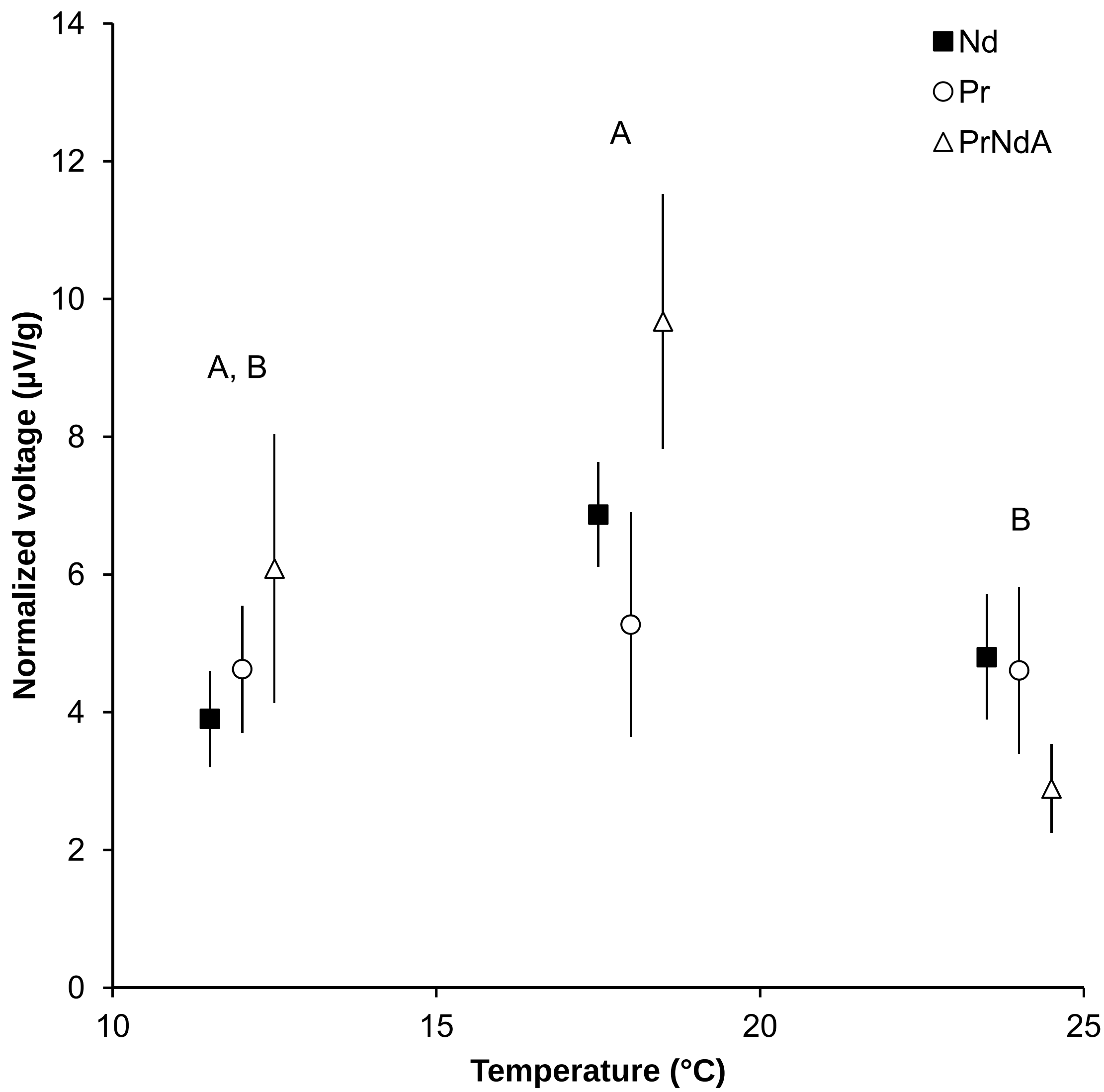
Voltage and Electric Field of Neodymium



The voltage (nV) produced by neodymium decreased with increasing distance from the recording electrode (solid line). The electric field (nV/cm; dashed line) was calculated in the downstream direction by taking the derivative of the best fit power function curve for the voltage. The gray box encloses the minimum and maximum reported median detection thresholds of six elasmobranch species, which provides an estimate for the effective detection distance of neodymium indicated by the dashed light gray lines.

Figure 7

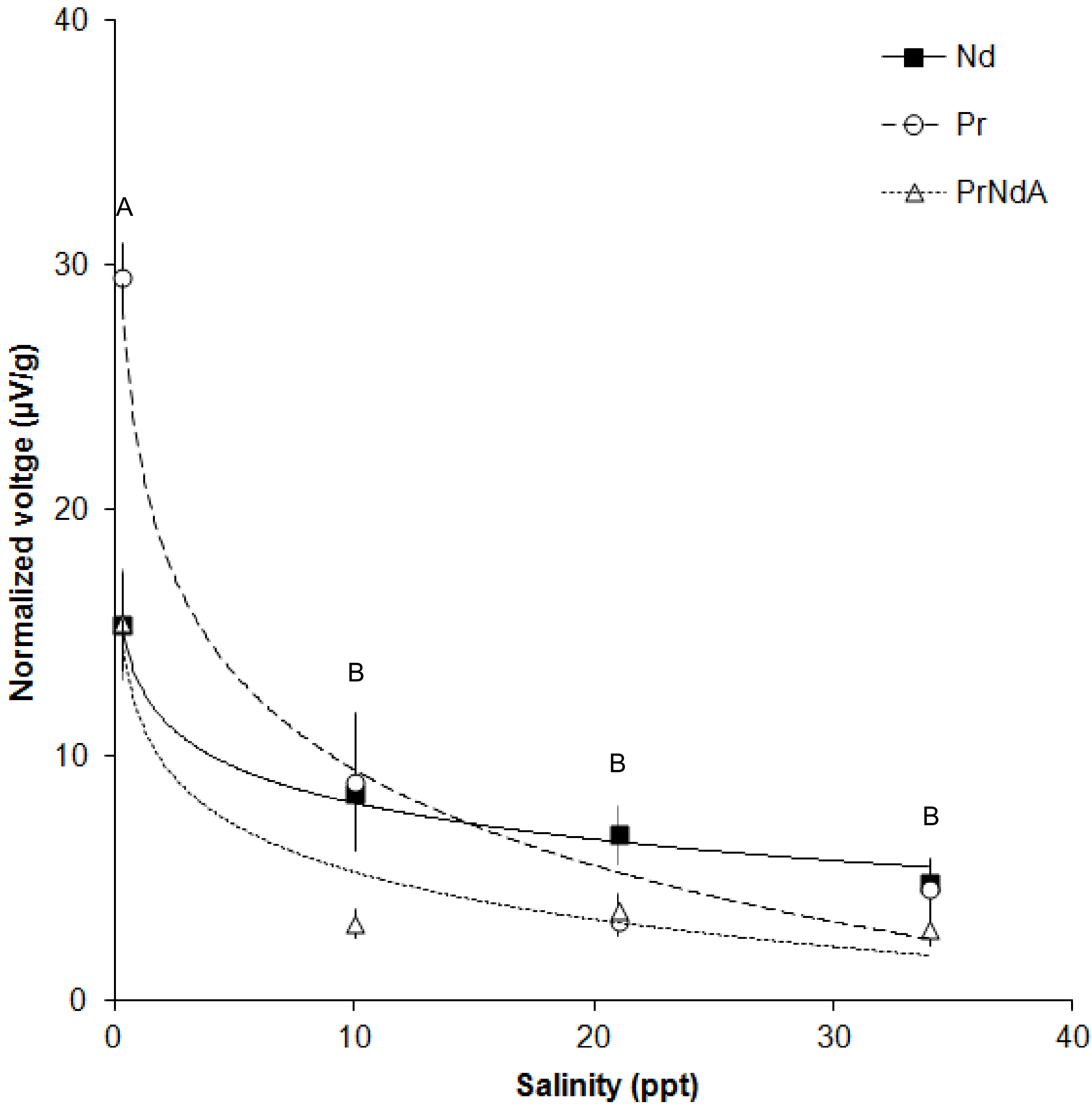
Temperature as a Variable for Normalized Voltage



The normalized voltage produced by three lanthanide metals (Nd = neodymium, Pr = praseodymium, PrNdA = praseodymium-neodymium metal alloy; n=6 mean ± s.e.m.) at 5 cm from the recording electrode. The metals were sampled at three biologically relevant temperatures: 12, 18, and 24°C. Although all metals were sampled at the same temperatures, the data are plotted with a 0.5°C offset to facilitate comparisons. The different metals did not produce significantly different voltages at any of the three temperatures. Temperature had a significant effect; temperatures that are not significantly different from one another share the same letter.

Figure 8

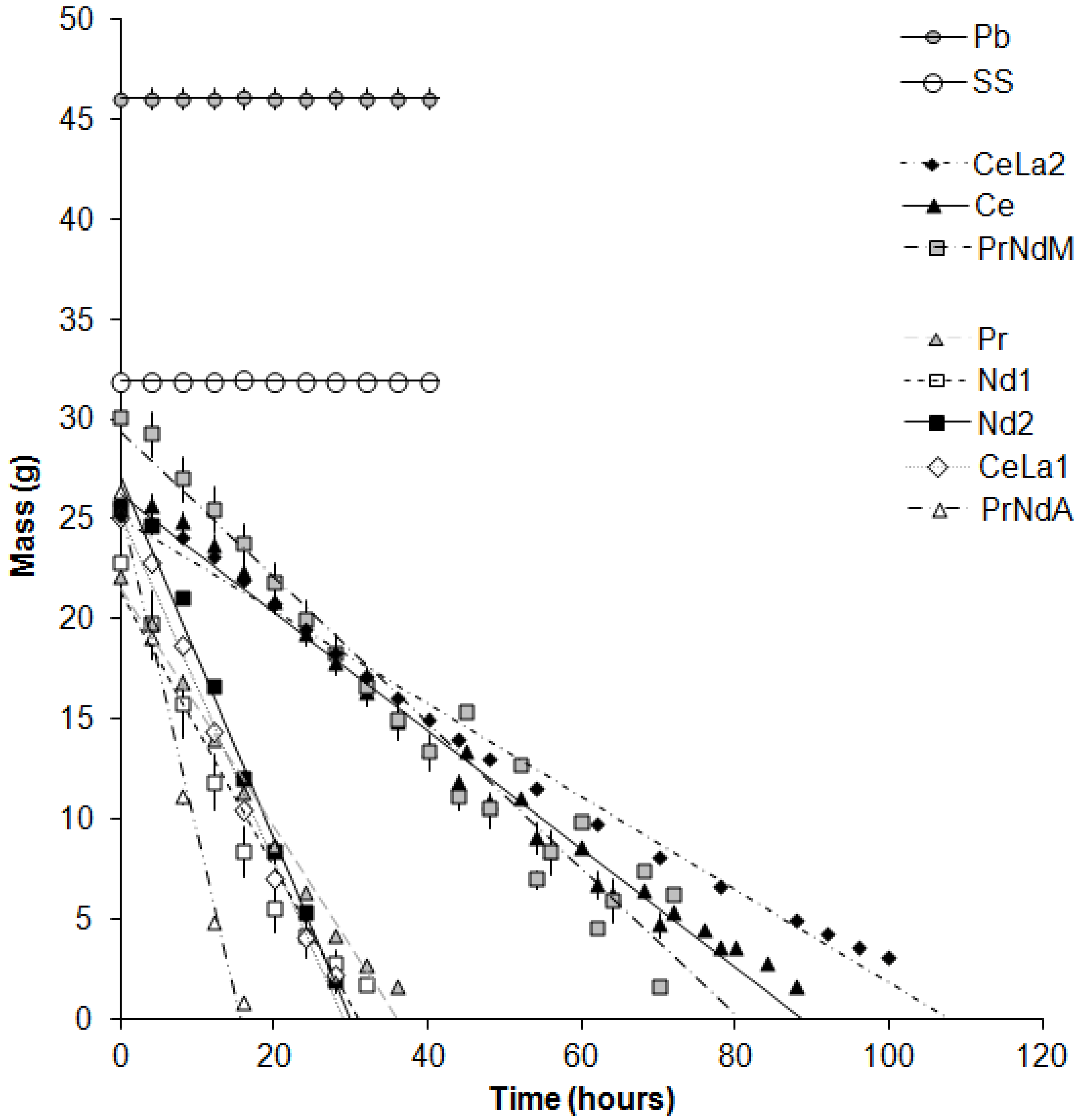
Salinity as a Variable for Normalized Voltage



Normalized voltage by a subset of lanthanide metals (Nd=neodymium, Pr=praseodymium, PrNdA=praseodymium-neodymium metal alloy; n=6 each, mean ± s.e.m.) at 5 cm from the recording electrode. Normalized voltage decreases with increasing salinity and is best modeled with a logarithmic function. The metals were sampled at four biologically relevant salinities: 0, 10, 21, and 34 ppt. Salinity had a significant effect on lanthanide voltage production as indicated by different letters. There was no significant difference between the normalized voltage produced by Nd and Pr; however, there was a significant difference between PrNdA and both Nd and Pr at all distances.

Figure 9

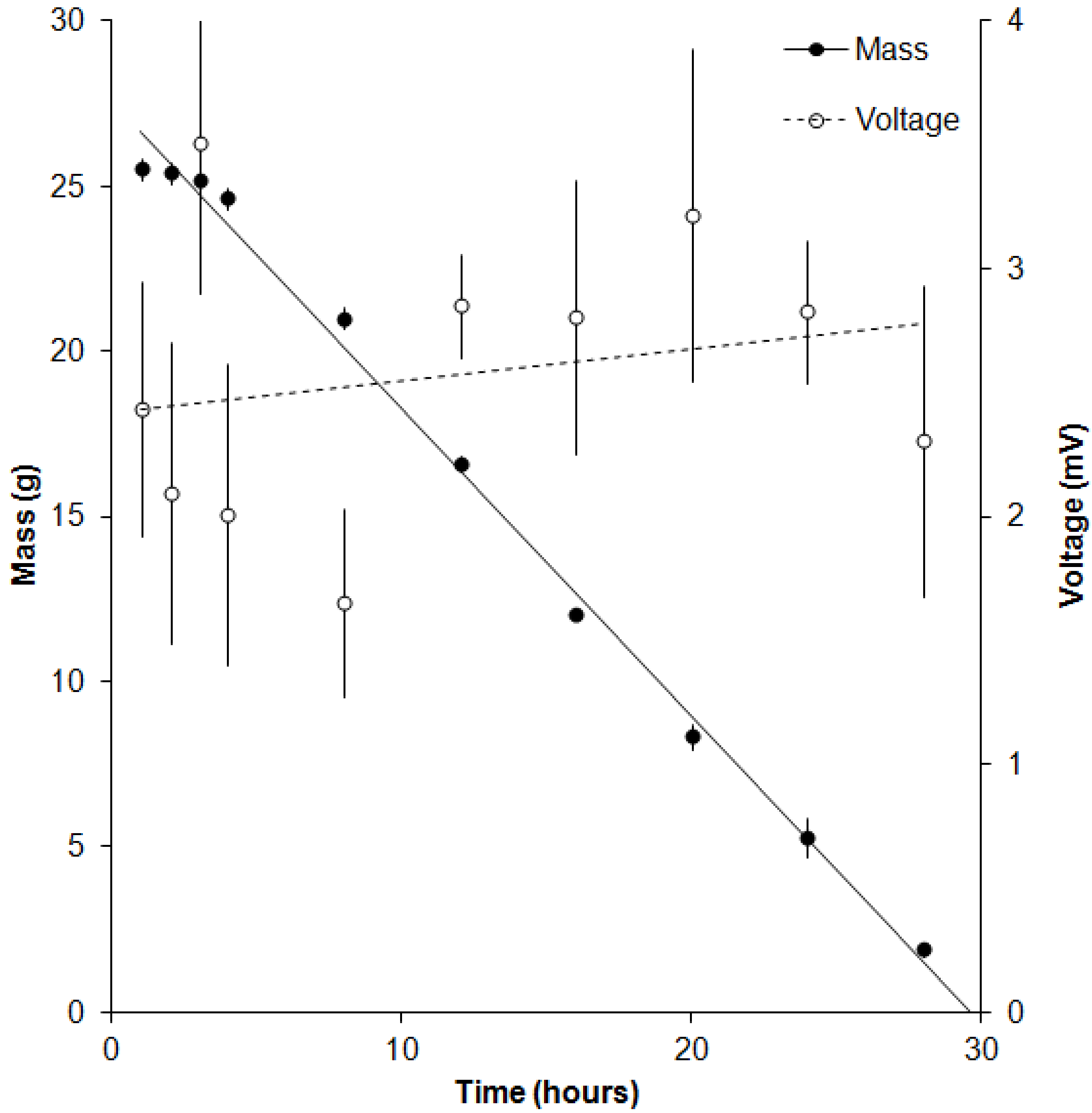
Dissolution Rates of Lanthanide Metals



Dissolution rate for the metals (n = 6 each, mean ± s.e.m.) during a 110 hr trial period at ambient seawater conditions (22-24°C, 34 ppt). The dissolution rate is best modeled with linear regression. The two controls, Pb and SS, showed no dissolution. CeLa and Nd were ordered in two batches which exhibited very different dissolution rates. Of the samples examined, PrNdA dissolved the fastest (-1.64 g/h) and CeLa2 dissolved the slowest (-0.23 g/h). Metals tested include: cerium (Ce), neodymium (Nd), praseodymium (Pr), praseodymium-neodymium mischmetal (PrNdM), cerium-lanthanum mischmetal (CeLa), praseodymium-neodymium metal alloy (PrNdA), lead (Pb), and stainless steel (SS).

Figure 10

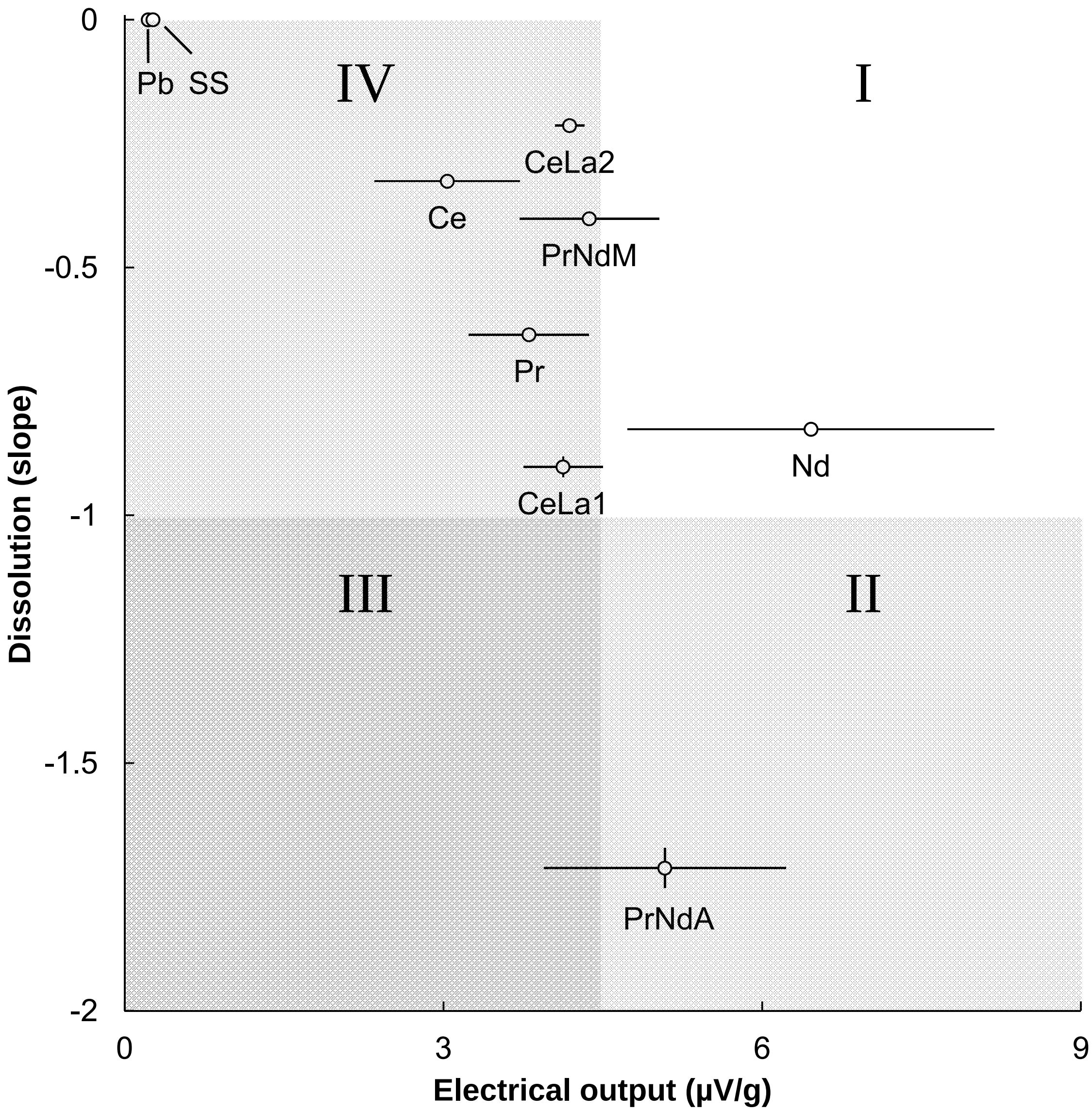
Voltage and Mass over Time



Voltage (mV) of neodymium (n = 6, mean ± s.e.m.) at 1 cm from the recording electrode over time. There was no significant difference in voltage over time (F=0.92, p=0.5349). Despite the decreasing mass of neodymium over time, the overall voltage remains constant.

Figure 11

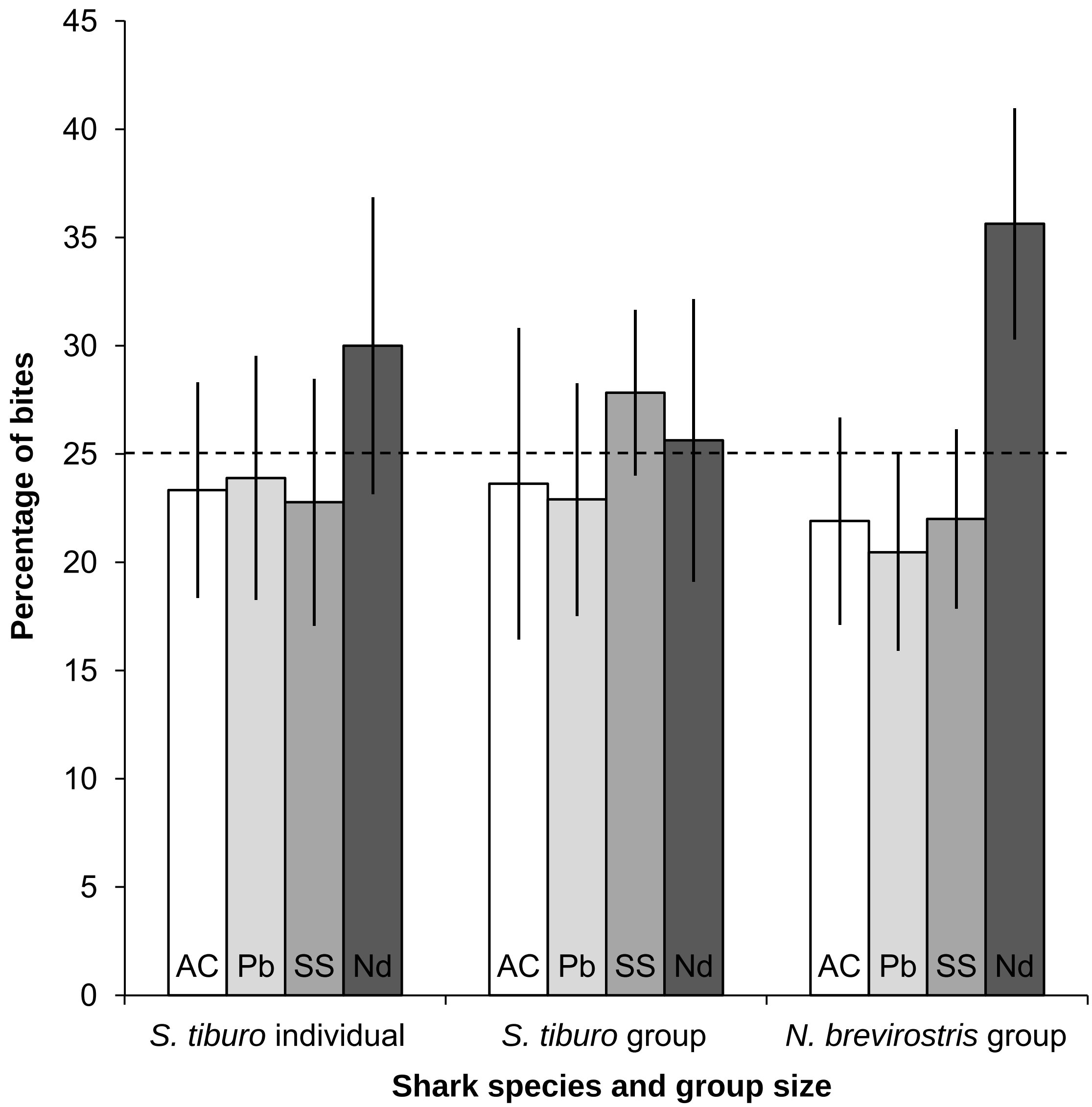
Voltage vs. Dissolution



To determine the best candidate metal for shark behavioral trials, voltage (mean ± s.e.m.) was plotted against dissolution rate (mean ± s.e.m.). The dissolution rate values were taken from the linear regression of each of the six samples from the dissolution experiment. The best candidate metals produce the greatest voltage and possess the greatest dissolution slope (i.e. slowest dissolution time) and occur in quadrant I. Quadrant II demonstrated high voltage, but also high dissolution. Quadrant III demonstrated both low voltage and high dissolution and quadrant IV was long lasting but had low voltage production. As a result, neodymium (Nd) was chosen for the shark behavioral trials.

Figure 12

Bite Ratio Analysis



An acrylic array with each of the treatments (AC = acrylic, Pb = lead, SS = stainless steel, and Nd = neodymium) was placed into the tank with the sharks and the percentage of bait taken from each treatment was recorded. The sharks were tested individually and in groups: *Sphyrna tiburo* individually (N = 12 sharks, n = 113 bites), *S. tiburo* in groups (N = 12 sharks, n = 110 bites), and *Negaprion brevirostris* in groups (N=13 sharks, n=126 bites). *N. brevirostris* were tested individually, but would not feed in isolation. Each treatment has an equal chance of being removed (25%, as indicated by the dashed line). There were no significant differences in bait removal from any treatment by any of the sharks (*S. tiburo* individually X^2 = 3.1416, p = 0.3703; *S. tiburo* group X^2 = 0.9091, p = 0.8232; *N. brevirostris* group X^2 = 6.6984, p = 0.0822).

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