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Electrochemical properties of lanthanide metals in relation to their application as shark repellents

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ABSTRACT

Sharks comprise a large portion of unwanted bycatch in longline fisheries worldwide and various technologies have been proposed to reduce elasmobranch bycatch without impacting the catch of target species. Recently, the naturally electrogenic lanthanide metals have been introduced as an elasmobranch-specific repellent. We quantified the voltage produced by six lanthanide metals in seawater, compared their dissolution rates, and performed a behavioral assay to determine their efficacy against two coastal shark species. We found that there was no difference in the voltage produced by the six tested metals and the voltage decayed as a power function (approximately $x^{-1.5}$) with distance from the metal sample. We calculated that sharks should detect a sample of neodymium from a distance of 65–85 cm in seawater. Voltage was greatest in freshwater and decreased logarithmically with increasing salinity but did not differ above salinities greater than 10 ppt. The dissolution rate for the lanthanides varied from −1.6 to −0.2 g h^{-1} and 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 juvenile lemon sharks (*Negaprion brevirostris*) in groups.

1. Introduction

Sharks comprise the largest portion of non-targeted bycatch in most of the world's pelagic longline (PLL) fisheries (Gilman et al., 2008). In the US Atlantic longline fishing industry, shark bycatch comprised 24.78% of the total catch from 1992 to 2003, nearly equaling the catch rate of targeted species, tuna (24.93%) and swordfish (27.32%) (Abercrombie et al., 2005). Both tunas and sharks are top level predators in the pelagic realm, but sharks are more vulnerable to overfishing due to their low intrinsic rebound potential (Dulvy et al., 2008; Stevens et al., 2000; Frisk et al., 2005; Smith et al., 1998). Therefore, the removal of these slow reproducing, top level predators may present detrimental long-term ecological consequences (Friedlander and DeMartini, 2002; Myers et al., 2007). In addition to ecological concerns, shark bycatch also creates a handling concern due to their sharp teeth and powerful tails, and an economic burden to commercial longline fishermen due to gear damage and loss, time spent to repair gear and remove sharks, and depredation (Gilman et al., 2007, 2008). Therefore, shark specific deterrents have been proposed to reduce shark bycatch with minimal to no reduction in the catch rate of target species.

Unlike most marine organisms, elasmobranch fishes (sharks, skates, rays) possess an electrosensory system that is extremely sensitive to voltage gradients. This enables them to detect electric fields down to the nV cm^{-1} range (Kajiura, 2003; Kajiura and Holland, 2002; Kalmijn, 1982), well below the range of bioelectric fields produced by their prey (20–100 μV; Haine et al., 2001; Kalmijn, 1972; Bedore and Kajiura, 2013). 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-specific deterrent (Gilman et al., 2008; Wang et al., 2008). When submerged in a polar solution, such as water, lanthanide metals undergo hydrolysis, which produces a charge distribution in the surrounding medium. The voltage produced by the metals likely exceeds anything that sharks naturally encounter in the wild and it is thought that this voltage overwhelms their electrosensory system, or localized changes in pH may act as an irritant (Brill et al., 2009; Stoner and Kaimmer, 2008; Tallack and Mandelman, 2009).

To date, four lanthanide metals have been investigated as potential shark deterrents with varying results. For example, the catch rate of the piked dogfish [spiny dogfish], *Squalus acanthias*, was significantly reduced by the presence of CeLa mischmetal in a field-based longline fishing trial in the Pacific (Kaimmer and 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 and Mandelman, 2009). Similarly, Galapagos sharks,

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Table 1
Lanthanide metal, purity, and price for lanthanides used in this study. All of the metals reflect the prices from November 2009, except for the second lot of neodymium (Nd 2) which was ordered in August 2010 as sheets rather than unprocessed ingots.

Metal	Purity (content)	Price (per kg)
Nd	99.60%	$145
Nd 2	99.5%	$230
Pr	99.60%	$150
Ce	99.90%	$135
PrNdA	99.5% (76.49% Nd, 23.41% Pr)	$179
CeLa	99.5% (64.09% Ce, 35.89% La)	$105
PrNdM	99.7% (52.76% Ce, 27.79% La, 14.64% Nd, 4.81% Pr)	$120

Carcharhinus galapagensis, were not deterred by PrNdA or Nd using rod and reel fishing (Robbins et al., 2011). However, Galapagos sharks and sandbar sharks, *C. plumbeus*, removed significantly fewer baits adjacent to PrNdA than adjacent to a lead control (Wang et al., 2008). These inconsistent results illustrate that not all elasmobranch species respond similarly and the use of different metals and different experimental methodologies further confounds comparisons.

Knowledge of the relevant electrochemical properties of lanthanides could facilitate comparisons among studies. Therefore, we (1) measured the normalized voltage of various lanthanide metals, (2) compared the dissolution rate of each metal, and (3) identified the best candidate lanthanide metal for subsequent behavioral assays. From these results, we evaluated the efficacy of the candidate lanthanide metal as a potential shark repellent by conducting a behavioral, laboratory study using bonnethead (Sphyrnidae: *Sphyrna tiburo*) and juvenile lemon sharks (Carcharhinidae: *Negaprion brevirostris*).

2. Methods

2.1. 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 lot of 99.5% pure Nd was procured for use in the last set of behavioral trials and for the voltage over time experiment (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 thought to not be strongly electrogenic.

All metals were machined to 2.54 cm × 2.54 cm × 0.64 cm with a 0.64 cm diameter hole in the center of the face. Lanthanide metals readily oxidize so before every experiment each metal sample was polished with a stainless steel wire brush Dremel® tool attachment to remove surface oxidation. Metals were stored in a dessicator when not in use.

2.2. DC voltage measurement

The direct current (DC) voltage of the metals in seawater was measured at the Florida Atlantic University Marine Science Laboratory in Boca Raton, FL. All measurements were taken in an electrically grounded acrylic experimental tank (89 cm × 43 cm × 21 cm) equipped with flow-through seawater at ambient temperatures (22–24 °C) and salinity (34 ppt). Six replicates of each of the six lanthanide metals and two controls were individually tested. To measure the voltage produced by a sample when immersed in seawater, the sample was secured with a non-conductive nylon bolt 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 metal into the seawater (Fig. 1). 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) with a single axis stepper motion controller (NSC-1S, Newmark Systems, Inc.) that provided precise linear horizontal movement. This arrangement enabled us to dip a metal sample into the tank at a particular distance from the electrode, measure the voltage, remove the metal sample from the water, translate the actuator and metal sample to the next location, and dip again and repeat until the voltage was measured at ten distances from the recording electrode: 1, 2, 3, 4, 5, 10, 15, 20, 25, and 30 cm. The order of the ten 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 in the far corner of the tank, as far from the recording electrode and sample as possible. The output from the two electrodes was differentially amplified at 1000 or 10,000× (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 voltage, normalized 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 homoscedasticity. 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 *voltage gradients* that sharks detect, the first order derivative was calculated from the power function that best fit the decline of the voltage with increasing distance from the recording electrode. The derived voltage gradient was compared to the reported median detection sensitivity, 25–48 nV cm^{-1}, of six elasmobranch species (Jordan et al., 2009; Kajiura, 2003; Kajiura and Holland, 2002). From the intercept of the median detection values with the derived voltage gradient we could determine at what distance the lanthanide should be detectable by the elasmobranchs.

2.3. 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 a range of salinities naturally encountered by sharks in the wild (0, 10, 21, 34 ppt). The full-strength seawater was taken from the inflow seawater at the FAU Marine Science Laboratory, 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,

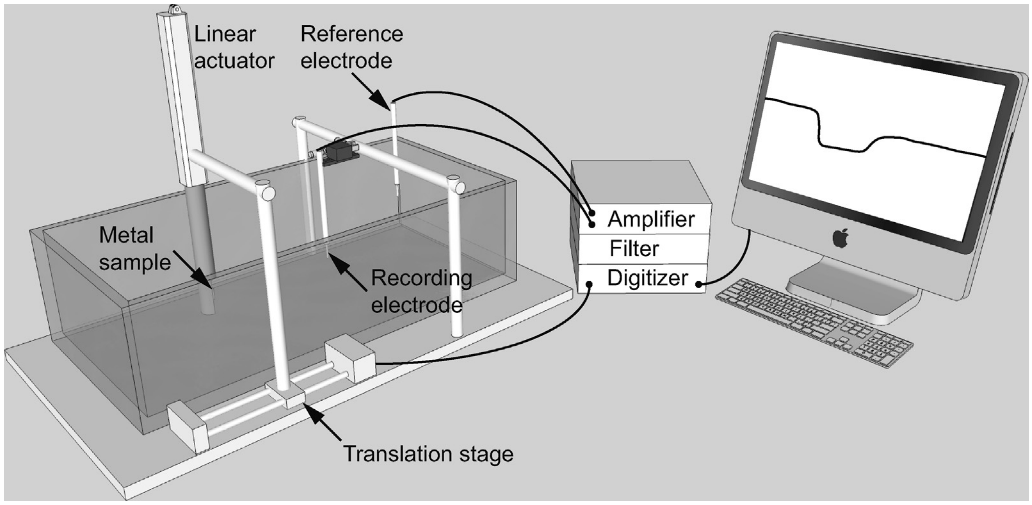

Fig. 1. Experimental apparatus for voltage measurements. A metal sample was affixed to an acrylic rod on a linear actuator that dipped the sample into the experimental tank. The actuator was mounted on a linear translation stage, which positioned the sample at a precise distance from a recording electrode.

pH, and salinity were monitored throughout the experiment using a Hanna HI9835 EC/TDS/NaCl/°C meter (Worthington, OH, USA). The voltage produced by the three lanthanide metals was measured at the pre-determined ten distances from the recording electrode. The normalized voltages at various salinities were log-transformed and tested in a two-way ANOVA with orthogonal a *priori* contrasts.

2.4. Dissolution

To determine how quickly the lanthanides dissolve in seawater, six samples of each of the six lanthanide metals and the two control metals were immersed in seawater and weighed periodically until each sample completely dissolved. The metals were suspended with monofilament fishing line in a 1.2 m × 2.4 m × 0.9 m fiberglass tank with flow-through seawater (22–24 °C, 34 ppt) that eliminated the potential for changes in pH that might have affected dissolution rate. To minimize any electrochemical interactions, samples were staggered both horizontally and vertically in the tank so that each metal was separated by a minimum of 30 cm (the distance at which there was no measurable voltage). Each metal was removed from the tank, dried, and weighed every four hours for the first 48 h and then every eight hours until they completely dissolved. Two samples of Pb and SS were tested for 96 h and showed no sign of dissolution; therefore the other four replicates were tested for only 40 h. 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.

2.5. Voltage over time

To determine the effect of dissolution on voltage production, six replicates of Nd were suspended with monofilament in an acrylic tank equipped with flow-through seawater. A single sample was affixed to the acrylic dipping rod assembly described in Section 2.2 and the voltage was measured at a distance of 1 cm from the face of the metal. 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.

2.6. Animal collection

Thirteen juvenile lemon sharks (*N. brevirostris*, 65.1–77.5 cm TL; five female and eight male) and six subadult to adult bonnethead sharks (*S. tiburo*, 77.3–86.9 cm TL; all female) were caught by gillnet and hook and line fishing from Long Key Bight, Layton, Florida between September 2010 and August 2011. Six additional bonnethead sharks (69.0–89.2 cm TL; all female) were captured by gillnet from Sarasota Bay and maintained at the Mote Marine Laboratory in September 2010. All sharks were provided at least two days to recover from the capture stress before being transported to the FAU Marine Science Laboratory. At FAU, the sharks were maintained in a 6.1 m diameter outdoor tank covered with a shade cloth and equipped with flow-through seawater at 22–24 °C and 34 ppt. Sharks were given at least one week to acclimate to their holding tank before behavioral tests commenced. During this time they were fed to satiation every other day. Animals were collected under FWC SAL 08SR-522 and behavioral trials were conducted in accordance with FAU IACUC protocol A10-07.

2.7. Experimental apparatus and protocol for behavioral trials

A behavioral assay was employed to assess whether Neodymium (Nd) deterred sharks from removing bait. Four equal-sized (2.54 cm × 2.54 cm × 0.64 cm) samples of acrylic (AC), lead (Pb), stainless steel (SS), and neodymium (Nd) were equidistantly spaced and affixed with non-conductive nylon bolts to a 1 m^2 acrylic plate. The position of the samples on the acrylic plate was randomized for every trial. Bait was attached to each treatment with monofilament fishing line. Bait was chosen specifically for each species based upon their natural diet, crustaceans (shrimp) for bonnetheads (Cortes et al., 1996) and teleosts (mullet or herring) for lemon sharks (Newman et al., 2010). In any given trial, the bait on each of the four targets was the same. To ensure that the sharks were sufficiently motivated to feed, they were starved for 48 h prior to a trial. Most of the experiments were conducted in an indoor 4.6 m diameter tank with a water depth of 0.9 m. Sharks were quickly transferred from the holding tank to the experimental tank and allowed to acclimate for 30 min. Once the sharks resumed 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 shark until the first bait was removed and the treatment from which the bait was removed was recorded. The plate was immediately removed

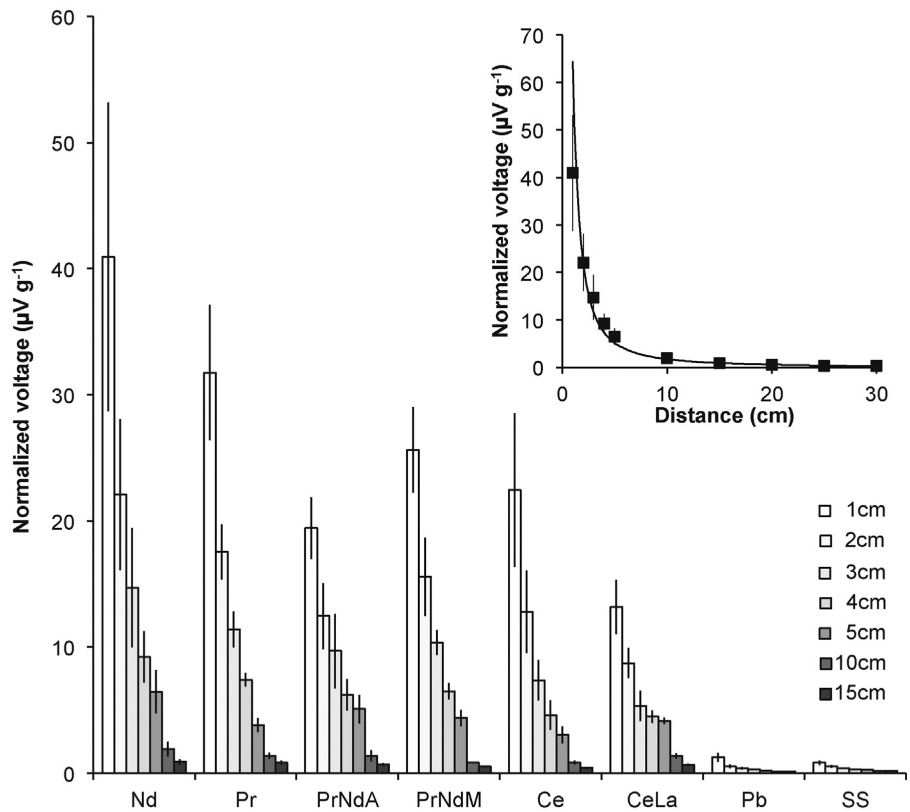

Fig. 2. The normalized voltage (mean ± s.e.m.) produced by the lanthanide and control metals at increasing distance from the recording electrode. The inset is the normalized voltage produced by Nd (mean ± s.e.m.), which decreased as a power function with increasing distance from the recording electrode.

from the tank, the position of the treatments randomized and the treatments re-baited with fresh baits. If no bait was removed in the first 3 min, the trial was concluded and the shark returned to the holding tank. To minimize habituation, only the first 10 baits removed by each individual were included in the analysis. In order to determine if repeated exposure affected bait preference a repeated-measures (R-M) ANOVA was applied to all of the sharks that were involved in more than one day of feeding. Bonnethead sharks were tested individually and in groups of 2–4 and lemon sharks were tested only in groups of 2–4. To evaluate whether the Nd sample had fewer bites, a chi-squared goodness-of-fit analysis was applied with the assumption that the bait would be removed from each of the four treatments equally, i.e. 25% of the time.

3. Results

3.1. Normalized voltage production in ambient seawater

The six lanthanide metals produced large voltages near the recording electrode that decreased dramatically with increasing distance (Fig. 2). The steep voltage decline was best modeled as a power function with an exponent of approximately −1.5. 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 ($\mu V g^{-1}$, Fig. 2) or surface area ($\mu V cm^{-2}$). For distances up to and including 10 cm, all of the lanthanide metals produced a significantly greater ($p < 0.05$) normalized voltage than the lead and stainless steel controls, which produced similar ($p > 0.05$) normalized voltages to one another. At distances of 15 cm and greater, the normalized voltage from some of the lanthanides became statistically indistinguishable from the control metals (the normalized voltages produced by Ce and PrNdM were not significantly different from SS) and at 20 cm the lanthanides' normalized voltage was indistinguishable from the low level background electrical noise in the tank.

The electric field was calculated from the equation describing normalized voltage with distance. At a distance of 1 cm from the recording electrode, the Nd squares produced a mean raw voltage of 888 ± 237s.e.m. μV, which resulted in an electric field of 2.15 $mV cm^{-1}$. The calculated electric field produced by Nd was compared to the median detection range of elasmobranchs from the literature and resulted in a median detection distance of approximately 73 cm (Fig. 3).

3.2. Normalized voltage of select lanthanides at various salinities

The three lanthanides that produced the greatest normalized voltage at 15 cm, Nd, Pr, and PrNdA, were tested at various salinities (0, 10, 21, 34 ppt). The normalized voltage was greatest in freshwater and decreased logarithmically with increasing salinity (Fig. 4). At all distances the lanthanides produced a significantly greater normalized voltage in freshwater than brackish water (10, 21 ppt) and full strength seawater ($p < 0.05$). For eight of the ten distances tested (1, 2, 3, 5, 10, 15, 20, 25 cm), there was no significant difference ($p > 0.05$) in normalized voltage when measured in brackish and full strength seawater. The only exceptions were at 4 cm and 30 cm where the voltage in brackish water exceeded the voltage in full strength seawater ($p < 0.05$). Lanthanide metal type had a significant effect on normalized voltage at all ten distances ($p < 0.05$). PrNdA produced significantly less normalized voltage than both Nd and Pr at all distances ($p < 0.05$). However, there was no significant difference between Nd and Pr at any of the distances ($p > 0.05$).

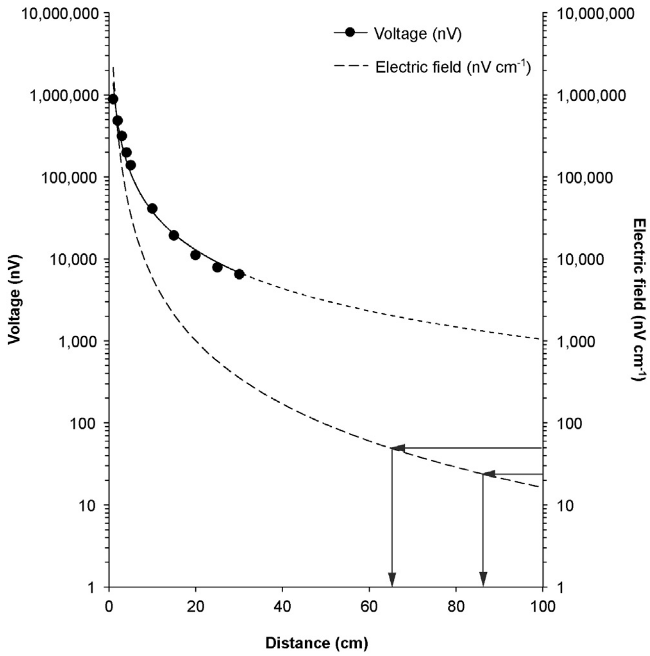

Fig. 3. The voltage (nV) produced by neodymium decreased inversely with distance from the recording electrode (solid line and extrapolated dotted line) as did the calculated electric field (nV cm^{-1}; dashed line). The horizontal arrows extend from the minimum and maximum reported median detection thresholds of six elasmobranch species, which provides an estimate of the effective detection distance of neodymium indicated by the vertical arrows.

3.3. Dissolution rate

The dissolution rates for all metals were best modeled with linear regression and the slopes varied greatly, ranging from $-1.64\,g\,h^{-1}$ for PrNdA to $-0.23\,g\,h^{-1}$ for CeLa mischmetal (Table 2). Each of the lanthanides had significantly different dissolution rates, with two exceptions; Nd1 and Pr did not differ from each other ($F=3.35$, $p=0.0695$) and neither did Nd2 and CeLa1 ($F=0.29$, $p=0.5900$). Neodymium was purchased in two lots at different times and the samples demonstrated significantly different dissolution rates (Nd1 = $-0.6882\,g\,h^{-1}$ and Nd2 = $-0.9074\,g\,h^{-1}$, $F=13.78$, $p=0.0003$). Similarly, the two lots of CeLa mischmetal demonstrated even greater differences in dissolution rate (CeLa1 = $-0.8728\,g\,h^{-1}$ and CeLa2 = $-0.2324\,g\,h^{-1}$; $F=215.05$, $p<.0001$).

Table 2
The dissolution rate in seawater for various lanthanide and control metals. Nd1 and Nd2 and CeLa1 and CeLa2 refer to two lots of neodymium and cerium lanthanum mischmetal respectively that were received at different times.

Metal	Equation	R^2	Time to dissolution (h)
Nd1	$y=-0.6882x+21.29$	0.9584	30.1
Nd2	$y=-0.9074x+27.118$	0.9892	29.9
Pr	$y=-0.5970x+21.467$	0.9877	36.0
PrNdA	$y=-1.6369x+25.492$	0.9869	15.6
CeLa1	$y=-0.8728x+25.285$	0.9904	29.0
CeLa2	$y=-0.2324x+25.017$	0.9907	107.6
PrNdM	$y=-0.3649x+29.339$	0.9564	80.4
Ce	$y=-0.2960x+26.208$	0.9872	88.5
SS	$y=0.0002x+31.886$	0.1733	–
Pb	$y=8x10^{-5}x+46.051$	0.0996	–

3.4. Voltage over time

To investigate how voltage changed over time, six replicates of Nd were suspended in flow through seawater and voltage measurements were taken over 28 h. The voltage (mV) of the Nd did not change over time ($F=0.92$, $p=0.5349$) despite the fact that the mass decreased linearly (Fig. 5).

3.5. Behavioral trials

To determine the best metal for use in behavioral trials, voltage, dissolution rate, cost, and ability to machine were all considered. The best candidate metals demonstrate both high voltage and low

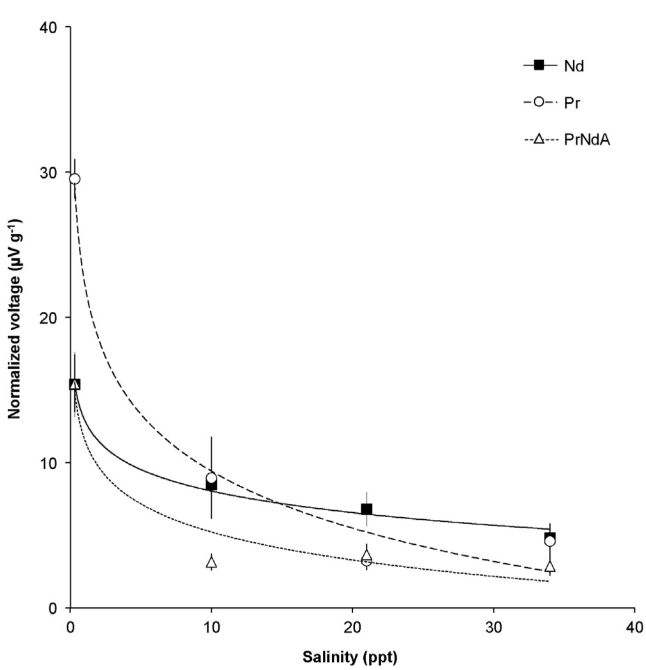

Fig. 4. Normalized voltage, measured at 5 cm from the recording electrode, for three lanthanide metals (mean ± s.e.m.) at four biologically relevant salinities: 0, 10, 21, and 34 ppt.

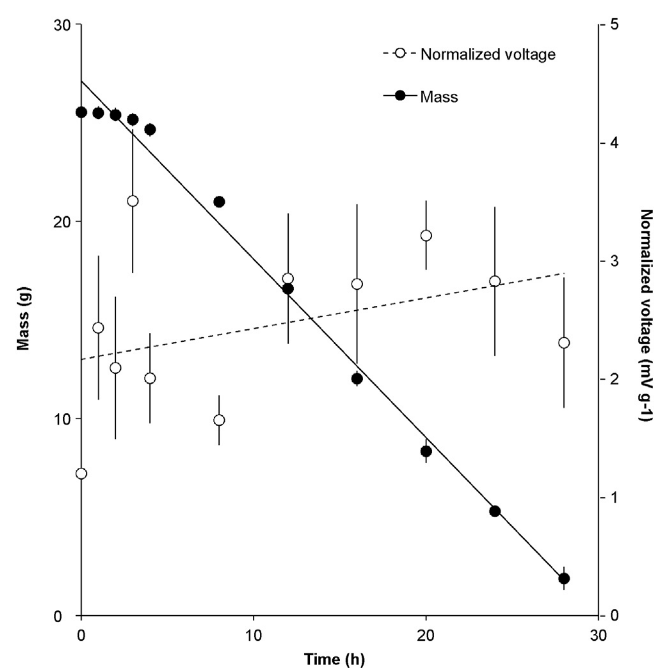

Fig. 5. Mass (g) and Voltage (mV) of neodymium (mean ± s.e.m.) at 1 cm from the recording electrode. Despite the decreasing mass of neodymium over time, the overall voltage remained constant.

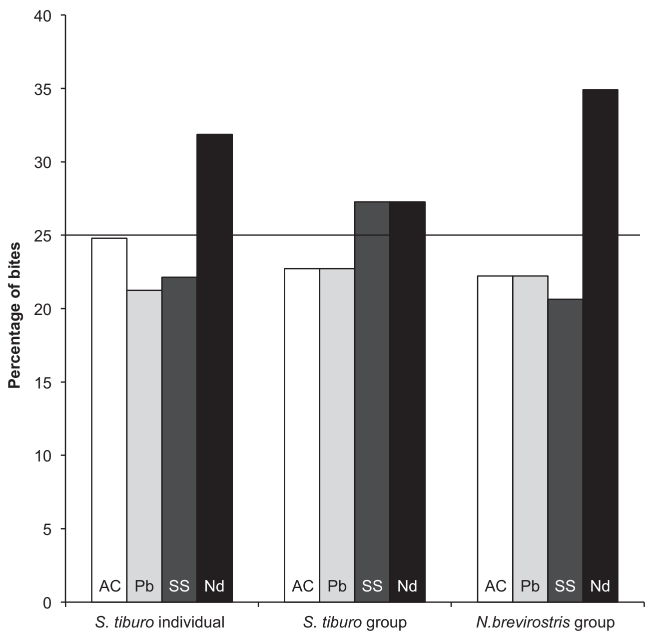

Fig. 6. The percentage of bait taken from each of four treatments. Each treatment had an equal chance of being removed (25%, as indicated by the horizontal line). There were no significant differences in bait removal from any treatment by any of the sharks. AC = acrylic, Pb = lead, SS = stainless steel, N = neodymium.

dissolution rates (i.e. are long-lasting). From these selection criteria, Nd was selected for shark behavioral trials.

We examined the material (AC, Pb, SS, Nd) from which 13 lemon sharks (*N. brevirostris*) and 12 bonnethead sharks (*S. tiburo*) removed baits in order to determine if Nd had a deterrent effect on the sharks. Over half of the sharks completed all 10 bait removals in the first day, and the remaining sharks were exposed to only one additional day of trials. Trials were typically very quick, with each individual trial lasting between 40 and 180 s, including time to remove the plate, rebait it, and return it to the water. The R-M ANOVA revealed that repeated exposure had no significant effect on bait preference (6 lemons with 2 trials $F < 0.001$, $p = 1.000$, and 6 bonnetheads with 2 trials $F < 0.001$, $p = 0.9988$). There was no significant difference in the material from which bait was removed for any of the experimental paradigms: *S. tiburo* tested individually ($\chi^2 = 3.1416$, p = 0.3703), S. tiburo in groups ($\chi^2 = 0.9091$, p = 0.8232), and N. brevirostris in groups ($\chi^2 = 6.6984$, p = 0.0822) (Fig. 6).

4. Discussion

4.1. Electrical and physical properties of lanthanides

The six lanthanide metals that we tested did not differ significantly in normalized voltage, which can be partly attributed to the large inter-sample variance, and also due to the identical electronegativity values (1.1) of their constituent elements. The electric field produced by Nd at 1 cm distance downstream of the recording electrode (2.15 mV cm^{-1}) was six orders of magnitude greater than electric fields elasmobranchs are able to detect (1 nV cm^{-1}). The median detection range reported for three tested ray species and three shark species is between 25 and 48 nV cm^{-1} (Jordan et al., 2009; Kajiura, 2003; Kajiura and Holland, 2002) and this range of electric field values was created by the Nd squares at distances of 65.5–84.5 cm (Fig. 3). The calculated detection distance is based on median electrosensitivity but sharks are able to detect electric fields of less than 1 nV cm^{-1} (Kajiura, 2003; Kajiura and Holland, 2002) which would be present at a greater distance from the metal and coincides with the reported ~100 cm effective range of deterrence of PrNdA for juvenile sandbar sharks (Brill et al., 2009). Because the voltage decay with distance was measured in a tank with a fixed volume, the charge distribution was more constrained, and the voltage consequently higher than it would be in the effectively infinite volume of the ocean. In the ocean, the charge distribution could freely dissipate and the voltage would decay more strongly with distance so a shark would need to be closer to a metal for it to be detected.

Lanthanides have the potential to be deployed in a wide variety of habitats so we measured the normalized voltage produced by the metals across a range of salinities from freshwater (0 ppt) to seawater (34 ppt). The normalized voltage decreased logarithmically with increasing salinity and did not differ among metals at most of the distances for salinities >10 ppt. Therefore, the lanthanides should behave comparably across saline environments and greater normalized voltage could be expected in freshwater. However, a greater normalized voltage in freshwater does not equate to a greater repulsion distance. Because elasmobranchs demonstrate reduced electrosensitivity in freshwater (McGowan and Kajiura, 2009) the greater voltage in freshwater would likely elicit a similar repulsion as a lower voltage in seawater.

The lanthanides achieve their electric field by hydrolyzing in water to produce hydrogen gas and a metallic precipitate. In the process the metals slowly dissolve. The dissolution rates of the lanthanide metals varied greatly, ranging from −1.64 g h^{-1} (PrNdA) to −0.23 g h^{-1} (CeLa) (Table 2). Because more than one sample was suspended in the large seawater tank, there was the potential for electrochemical interaction to have accelerated or retarded dissolution rates. However, the metals lasted between 16 to 100+ h, and these times are consistent with those previously reported: 69.5% CeLa mass loss in 40 h (Stoner and Kaimmer, 2008), 50% CeLa mass lost after 20 h (Kaimmer and Stoner, 2008), and an estimated 50% CeLa dissolved in 30 h and 100% dissolved in ~40 h (Tallack and Mandelman, 2009). Of interest is that CeLa mischmetal and Nd were both ordered in two separate lots and both lots produced significantly different dissolution rates despite having the same purity and normalized voltage. The type of impurities in the samples can differ from within the same mine by date, metal deposit, or site within the mine (Trout, 1990) and these impurities, although minute (<0.5%), are likely responsible for the observed differences in dissolution.

The dissolution rate of the metal dictates the length of time that baited hooks would be protected so the variable dissolution rates for the same metal with the same purity complicates the estimation of effective use time. In the Australian tuna and billfish fishery, more than 95% of the trips have longline soak times of 4–13 h, and in Japan, longlines soak for 9–10 h (Gilman et al., 2007), at which point many of the quick dissolving lanthanides (i.e. PrNdA) would have dissolved off the line leaving the hooks unprotected for several hours. Interestingly, as the lanthanides dissolve, the voltage (mV) remains unchanged despite the decreasing mass (Fig. 5). This is likely due to increased pitting, which creates a greater three-dimensional surface area in contact with the seawater, and thus allows a similar overall rate of reaction despite decreasing mass. This property suggests that the metals will remain effective as long as they remain in proximity to the hook.

4.2. Shark behavioral responses to lanthanides

Lanthanide metals have produced inconsistent results as shark repellents (Table 3). A given species may be deterred by a lanthanide in one study, but the same species tested with the same lanthanide may yield different results in another study (e.g. *S. acanthias*: Kaimmer and Stoner, 2008; Stoner and Kaimmer, 2008; Tallack and Mandelman, 2009). To determine the effectiveness of

Table 3
The efficacy of lanthanide metals from studies investigating the potential of using lanthanides as shark repellents. The general effectiveness is based on whether a statistically significant avoidance, or reduction in catch rate, was obtained.

Order	Family	Species	Lanthanide	Study	General Effectiveness	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	*Carcharhinus plumbeus*	PrNdA	Field	No	Hutchinson et al. (2012)
Carcharhiniformes	Carcharhinidae	*Prionace glauca*	PrNdA	Field	No	Hutchinson et al. (2012)
Carcharhiniformes	Carcharhinidae	*Prionace glauca*	PrNdA	Field	No	Godin et al. (2013)
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 lewini*	PrNdA	Field	Yes	Hutchinson et al. (2012)
Carcharhiniformes	Sphyrnidae	*Sphyrna tiburo* – group	Nd	Lab	No	This study
Carcharhiniformes	Sphyrnidae	*Sphyrna tiburo* – individual	Nd	Lab	No	This study
Lamniformes	Lamnidae	*Isurus oxyrhinchus*	PrNdA	Field	No	Hutchinson et al. (2012)
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Lab	Yes	Stoner and Kaimmer (2008)
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Field	Yes	Kaimmer and Stoner (2008)
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Lab	No	Tallack and Mandelman (2009)
Squaliformes	Squalidae	*Squalus acanthias*	CeLa	Field	No	Tallack and Mandelman (2009)
Squaliformes	Squalidae	*Squalus acanthias*	Nd	Lab	Yes	Jordan et al. (2011)

Nd as a shark repellent, a behavioral trial was conducted with bonnethead sharks (*S. tiburo*) and juvenile lemon sharks (*N. brevirostris*).

When isolated from their conspecific tank mates, the lemon sharks showed no interest in food but exhibited stressed swimming behavior, characterized by rapid circuits of the tank near the water surface. When a conspecific was added to the tank the stressed shark immediately resumed a normal swimming pattern and both sharks readily ate. As a result, lemon sharks were tested only in groups. Lemon sharks are known to be social animals, especially as juveniles (Guttridge et al., 2010, 2011) so providing only 30 min for them to acclimate to isolation prior to testing might have been insufficient. In contrast, bonnethead sharks would readily feed in isolation and in groups. Because the lemon sharks were tested in groups, there may have been strong competition for food. The lemon sharks would immediately swim toward the acrylic plate as it was being lowered into the water and typically removed the first bait encountered. The bonnethead sharks were tested individually and they also typically removed the first bait encountered even without competition for food.

In addition to shark density, elevated hunger level has been suggested to adversely impact the repellent abilities of lanthanide metals (Brill et al., 2009; Jordan et al., 2011; Kaimmer and Stoner, 2008; Robbins et al., 2011; Tallack and Mandelman, 2009). The sharks in this study were starved for 48 h prior to a trial, so their hunger level was presumably high and feeding selectivity resultantly low, which may partially account for the failure of Nd to act as an effective repellent. Elasmobranchs in the wild will presumably be similarly motivated, and thus non-discriminatory feeders. Therefore, the results from these lab trials are likely representative of responses to be expected when Nd is deployed in the field.

Although there were very few instances in which a shark exhibited avoidance to the Nd, they were clearly aware of its presence. 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 evidenced by 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 and indeed, may have stimulated them to bite.

It has been suggested that sharks can learn to tolerate lanthanide metals, and this can occur in as few as two days (Brill et al., 2009). The sharks in this study did not exhibit any aversion to Nd, even upon first exposure, which indicates that they were not repelled even when the stimulus was novel. Furthermore, repeated-measures ANOVA on the data from sharks that were exposed to the bait selection trial for more than one day revealed no difference in the percentages of bait removed from any treatment over time.

Although the results suggest that Nd does not repel bonnethead and juvenile lemon sharks, care must be taken to avoid extrapolating these results. Since the tested lemon sharks were juveniles, their electrosensory system and associated behaviors likely differs from the much larger adults. Electrosensory pore density decreases through ontogeny (Kajiura, 2001) but the concomitant lengthening of ampullary tubules confers greater sensitivity (Sisneros et al., 1998; Sisneros and Tricas, 2002). Therefore, adult sharks may react differently to the same stimulus. This study tested only small sharks, <1 m TL, which would be representative of sharks encountered in coastal fisheries. Results obtained with pelagic sharks may differ due to the relative reliance of different species on different sensory systems. Recent work has demonstrated that juvenile scalloped hammerhead sharks that inhabit turbid coastal water were effectively repelled by PrNdA but several pelagic shark species were not (Hutchinson et al., 2012). This might be attributable to the reliance of the juvenile hammerhead sharks on electroreception to locate their cryptic prey in contrast to the pelagic species, which are primarily visual predators (Hutchinson et al., 2012).

Currently, the efficacy of lanthanide elements has been tested on only nine shark species from five families (Table 3). This represents only about 2% of the named shark species and less than 1% of elasmobranch species. The high degree of variability among tested species suggests that a universal repellent may not exist, and different techniques may be needed for sharks that inhabit different environments, or from different phylogenetic branches. Lanthanides dissolve quickly in seawater, have a small effective range (less than 80 cm), are expensive, and hazardous to machine, all of which contribute to the challenge of deploying them in commercial longline fishing industries. Nonetheless, the principle of their mode of action is promising and future research should continue to investigate other electrogenic repellents that specifically stimulate the electrosensory system of elasmobranchs and remain undetectable by the target teleost fishes.

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