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# Phase I Final Rule and Technical Development Document of Uniform National Discharge Standards (UNDS)

**Appendix A** 

 **Cathodic Protection: Nature of Discharge** 

April 1999

### **NATURE OF DISCHARGE REPORT**

### *Cathodic Protection*

### **1.0 INTRODUCTION**

The National Defense Authorization Act of 1996 amended Section 312 of the Federal Water Pollution Control Act (also known as the Clean Water Act (CWA)) to require that the Secretary of Defense and the Administrator of the Environmental Protection Agency (EPA) develop uniform national discharge standards (UNDS) for vessels of the Armed Forces for "...discharges, other than sewage, incidental to normal operation of a vessel of the Armed Forces, ..." [Section  $312(n)(1)$ ]. UNDS is being developed in three phases. The first phase (which this report supports), will determine which discharges will be required to be controlled by marine pollution control devices (MPCDs)—either equipment or management practices. The second phase will develop MPCD performance standards. The final phase will determine the design, construction, installation, and use of MPCDs.

A nature of discharge (NOD) report has been prepared for each of the discharges that has been identified as a candidate for regulation under UNDS. The NOD reports were developed based on information obtained from the technical community within the Navy and other branches of the Armed Forces with vessels potentially subject to UNDS, from information available in existing technical reports and documentation, and, when required, from data obtained from discharge samples that were collected under the UNDS program.

The purpose of the NOD report is to describe the discharge in detail, including the system that produces the discharge, the equipment involved, the constituents released to the environment, and the current practice, if any, to prevent or minimize environmental effects. Where existing process information is insufficient to characterize the discharge, the NOD report provides the results of additional sampling or other data gathered on the discharge. Based on the above information, the NOD report describes how the estimated constituent concentrations and mass loading to the environment were determined. Finally, the NOD report assesses the potential for environmental effect. The NOD report contains sections on: Discharge Description, Discharge Characteristics, Nature of Discharge Analysis, Conclusions, and Data Sources and References.

### **2.0 DISCHARGE DESCRIPTION**

This section describes the discharge associated with cathodic protection and includes information on: the equipment that is used and its operation (Section 2.1), general description of the constituents of the discharge (Section 2.2), and the vessels that produce this discharge (Section 2.3).

### **2.1 Equipment Description and Operation**

Nearly all vessels use some form of cathodic protection to prevent metal hulls and underwater structures from corroding. The Armed Forces (Navy, Air Force, Army, Military Sealift Command (MSC)) and the U.S. Coast Guard (USCG) use cathodic protection, in conjunction with corrosion-resistant coatings, to protect their vessels. This combination provides an optimal corrosion control system which utilizes the advantages of each individual system. While coatings are the primary means of controlling corrosion, nearly all coatings have some defects (whether from wear or damage) and some components are uncoated by design (e.g., propellers). Cathodic protection could, in theory, be used alone to protect a hull and other external underwater structures, but the number of anodes for sacrificial-anode-based systems or power requirements for Impressed Current Cathodic Protection (ICCP)-based systems would increase greatly. When used in conjunction with coatings, cathodic protection reduces the effects of wear and failure of the paint systems and reduces the associated required repairs and maintenance. Without cathodic protection systems, vessels would be subject to severe corrosion (i.e., dissolution and discharge of hull material) of the underwater hull and appendages resulting in either increased underwater repairs and maintenance or more frequent dry-docking of the vessels for renewal of underwater hull paint systems.

The two types of cathodic protection used by the Armed Forces -- sacrificial anodes and ICCP systems -- are illustrated schematically in Figure 1. Small boats and craft which have wood, aluminum, fiberglass or rubber (inflatable) hulls do not require cathodic protection to protect these materials from corrosion (but may have small anodes located near the propellers for their protection). Also, many of the small boats and craft with steel hulls that utilize sacrificial anodes are stored out of the water on trailers or blocks.

### **2.1.1 Sacrificial Anodes**

When sacrificial anodes are used, the anodes are physically connected (e.g., by bolts or welding) to ship components and structures. As shown in Figure 2, an electrochemical cell is formed between the anode and the cathode (the structure to which the anode is connected) through the surrounding electrolyte (usually seawater). The anode is preferentially corroded or "sacrificed", producing a flow of electrons to the cathode which results in a reduction or elimination of corrosion at the cathode. Large ships with mandatory dry-dock inspection and overhaul intervals of less than three years, as well as the most boats and small craft, use sacrificial anodes to protect the underwater hull. The numbers and sizes of the anodes are determined by the wetted surface area of the hull, the planned replacement cycle of the anodes, and the corrosion history of the vessel.

Sacrificial anodes continually corrode when immersed and require routine replacement to maintain sufficient mass and surface area for adequate cathodic protection. On average, zinc anodes are estimated to be completely consumed every six years.<sup>1,2,3,4</sup> The consumption rate depends on the service environment, the condition of the hull coating, and the location of the anode on the hull.

Zinc anodes are used almost exclusively by DoD and USCG vessels for sacrificial cathodic protection of hulls,<sup>5</sup> with aluminum anode usage limited to a few (less than 5) Navy submarines. Naval Sea Systems Command (NAVSEA) continues to evaluate aluminum anodes for use on other Navy ships and their use requires prior NAVSEA authorization and design review.5

Aluminum anodes have 3.4 times the current capacity<sup>i</sup> of zinc anodes due primarily to differences in valence (3 for aluminum vice 2 for zinc) and density.<sup>5</sup> The lower density of aluminum anodes also results in aluminum anodes occupying more volume than zinc anodes of the same weight. Development of the military specification  $\delta$  for aluminum anodes has only recently been completed although commercial aluminum anodes have been available for many years. Aluminum anodes are not as readily available as zinc anodes and are more prone to passivate (become inactive) than zinc anodes, but may be considered for use where the benefits of increased current capacity and reduced weight offset the disadvantages of increased volume.

Sacrificial anodes used to prevent corrosion of heat exchangers, condensers, evaporators, sewage collection, holding and transfer tanks, ballast tanks, bilges, sea chests, sonar domes, or other non-hull areas or components are not addressed in this NOD report, but in NOD reports describing these discharges (e.g. Seawater Cooling Discharge and Clean Ballast).

### **2.1.2 ICCP Systems**

The Armed Forces also use ICCP systems (see Figure 3) to protect hulls in lieu of sacrificial anodes. ICCP systems are employed when the wetted surface of the hull and other underwater components requiring cathodic protection is large or a controllable system is required.<sup>5</sup> ICCP systems protect against corrosion using direct current (DC) from a source within the ship in lieu of current provided by a sacrificial anode. Except for the source of current, the mechanism of protection is identical for sacrificial anode cathodic protection and ICCP (see Figure 1). The current is passed through platinum-plated tantalum anodes designed for a 20-year service life. A silver/silver chloride (Ag/AgCl) reference electrode (control reference cell) measures the electrical potential of the hull and is used to determine how much current is required from the ICCP system to provide adequate cathodic protection.

<sup>&</sup>lt;sup>i</sup> Current capacity, a sacrificial anode material property, is the total current available per unit mass over the life of the anode, commonly expressed as (amp-hr/kg) or (amp-yr/lb). The current capacity for zinc and aluminum anodes is 812 amp-hr/kg and 2759 amp-hr/kg, respectively. Current capacity should not be confused with the *maximum output current* of an anode, which is a function of the anode material, anode surface area, system resistance, and driving potential. For most common types of zinc anodes used on underwater hulls, the maximum output current is approximately 0.4 amps per anode.<sup>5</sup>

### **2.2 Releases to the Environment**

#### **2.2.1 Sacrificial Anodes**

As the zinc or aluminum anode is consumed (oxidized), ionized zinc or aluminum is released into the receiving waters. Water at the cathode (such as the steel hull) is reduced forming hydroxyl (OH) ions which combine with the zinc or aluminum ions to form zinc or aluminum hydroxide if excess oxygen is present. Another possible reaction produces hydrogen at the cathode, especially in deaerated seawater.

In addition, oxidants (primarily chlorine and bromine) could also be produced in secondary reactions because of the electrical potential of the anode. Precise reactions and probabilities will vary with conditions in the seawater environment. However, the relatively low electrical potential of the sacrificial anode (-1.05 volts average) compared with ICCP systems ( 15volts Ag/AgCl reference electrode) will result in less oxidant being formed. Those oxidants which are formed will rapidly react with the surface of the sacrificial anode to form zinc or aluminum chloride, or react with oxidant-demanding substances in the water. Due to the relatively low electrical potential of sacrificial anodes and the rapid reactive nature of the anode surface, the possible generation of oxidants by sacrificial anodes will not be considered further.

#### **2.2.2 ICCP Systems**

ICCP systems operate at higher electrical potentials than sacrificial anodes and consequently can generate more oxidants. Precise primary and secondary reactions of oxidants will vary with seawater conditions such as salinity, temperature, ammonia content, pH, etc., but will primarily consist of various chlorinated and brominated substances. These substances include: hypochlorous and hypobromous acids, hypochlorite and hypobromite, chloro- and bromo-organics, chloride, bromide, chloramines, and bromamines. These substances are commonly called Chlorine-Produced Oxidants (CPO) when associated with brackish or seawater.<sup>7</sup>

The general reactions related to CPO are initiated when chlorine  $(Cl<sub>2</sub>)$  is generated by the reduction of chloride ions (CI) in seawater. The chlorine reacts to form hypochlorous acid (HOCl) and the hypochlorite ion (OCl<sup>-</sup>) in the water. These two compounds, along with the chlorine, are referred to as free chlorine. Free chlorine, the standard disinfection agent used in water treatment facilities, undergoes four important types of reactions in natural waters: (1) oxidation of reduced substances and subsequent conversion to chloride; (2) reaction with ammonia and organic amines to form chloramines, collectively called combined chlorine; (3) reaction with bromide to form hypobromous acid (HOBr) and hypobromite (OBr), called free bromine; and (4) reaction with organics to form chloro-organics. Free bromine reacts in a manner similar to free chlorine, oxidizing reduced substances or forming bromamines (combined bromine) or bromo-organics. Most common analytical methods for quantifying CPO measure the sum of all free and combined chlorine and bromine in solution, but do not measure the chloro- and bromo-organics.

Human health issues are a concern for some of these chlorinated hydrocarbons, which are suspected carcinogens and pose a concern when found in significant quantities in drinking water. However, these small quantities of chloro- and bromo-organics are produced only in brackish or seawater. These materials are not generated by ICCP systems in freshwater ports due to the low concentrations of chlorides and bromides. Most drinking water is drawn from groundwater or freshwater sources. Armed Forces vessels that are homeported in seawater or brackish water ports are not docked near drinking water intakes. Given the limited quantity and the location of discharge, exposure to drinking water intakes is unlikely. These chlorinated hydrocarbons are not separately addressed further in this NOD report.

#### **2.3 Vessels Producing the Discharge**

Table 1 shows the vessels that produce this discharge.<sup>1,8,9,10</sup> The table identifies whether vessels use sacrificial anodes or ICCP systems. Boats and craft of the Navy, Naval Auxiliary, USCG, MSC, Army, and Air Force use sacrificial anodes for cathodic protection. Of the approximately 5000 miscellaneous small boats and craft, approximately 30% are expected to have steel hulls and therefore cathodic protection. The remaining 70% are assumed to have hulls constructed of fiberglass, wood, aluminum, or other non-ferrous materials which do not require cathodic protection.

### **3.0 DISCHARGE CHARACTERISTICS**

This section contains qualitative and quantitative information that characterizes the discharge. Section 3.1 describes where the discharge occurs with respect to harbors and nearshore areas, Section 3.2 describes the rate of the discharge, Section 3.3 lists the constituents in the discharge, and Section 3.4 gives the concentrations of the constituents in the discharge.

### **3.1 Locality**

Discharge from cathodic protection systems associated with a vessel's hull occurs continuously whenever the vessel is waterborne. This discharge occurs both within and beyond 12 nautical miles (n.m.).

### **3.2 Rate**

### **3.2.1 Sacrificial Anodes**

The discharge from sacrificial anodes is characterized by a mass flux instead of a volumetric flow rate because the "constituents" enter the receiving water directly (via corrosion and dissolution). The following factors were used to calculate the average mass flux (also called corrosion/dissolution) of sacrificial anodes while pierside and underway:

1. Based on underwater hull inspections and maintenance records one-half of an

anode is consumed after three years.<sup>4</sup>

- 2. The corrosion/dissolution rate while underway is approximately three- to fivetimes the pierside rate based on field studies.<sup>3,11</sup> A factor of four is used for calculations. Probable explanations for this phenomenon are: (1) the fully aerated seawater produced by a moving hull increases reaction rates; and (2) more corrosion products and other deposits and surface films are removed due to the erosion forces of the seawater.
- 3. Based on the actual vessel movement data available, the average Navy vessel spends approximately 176 days in port (pierside) and transits to or from port (underway) approximately 11 times each year.<sup>12</sup> The average MSC vessel spends approximately 94 days in port and performs approximately six transits. Vessel movement estimates for the Air Force, Army, and USCG vessels were made based on operational knowledge (see Table 2). The vessel movement data for the Navy was used in dissolution calculations since it results in the highest period of time that vessels are in port.

Using the above factors, the corrosion/dissolution rates were calculated for zinc anodes as shown in Calculation Sheet 1. At pierside, the rate was calculated to be 7.4 x  $10^{-6}$  (lb zinc/lb anode)/hr, and underway, it was  $3.0 \times 10^{-5}$  (lb zinc/lb anode)/hr. These rates can also be expressed as a function of wetted hull area using a conversion factor based on information presented in Table 2 which lists the vessels incorporating sacrificial anode cathodic protection. This relationship is stated as follows:

Average density of zinc anodes  $=$  (total amount of anodes) / (total wetted surface area)

 $= (1,860,000 \text{ lb}) / (10,826,000 \text{ ft}^2) = 0.17 \text{ lb/ft}^2$ 

This results in average pierside and underway zinc generation rates of 1.3 x  $10^{-6}$  and 5.1 x  $10^{-6}$  (lb zinc/square foot of underwater surface area)/hr.

Shipboard experience with aluminum anodes is limited, but as with zinc anodes the corrosion/dissolution rate of the anode is primarily determined by factors such as the area of bare metal requiring protection. Rates for aluminum anodes can therefore be calculated based on process knowledge and the previously calculated generation rates for zinc anodes. Using the ratio of current capacity of aluminum to zinc anodes, generation rates for aluminum anodes are 2.2 x  $10^{-6}$  (lb aluminum/lb anode)/hr pierside, and 8.8 x  $10^{-6}$  (lb aluminum/lb anode)/hr underway.

Current capacity ratio = (aluminum anode current capacity) / (zinc anode current capacity)

 $= (2759 \text{ amp-hr/kg}) / (812 \text{ amp-hr/kg}) = 3.4$ 

### **3.2.2 ICCP Systems**

Oxidant discharges from operating ICCP systems are also characterized by mass flux instead of flow rate because the constituents are created from the surrounding water due to electrolysis. Precise reactions and probabilities depend on a variety of conditions as described in Section 2.2.2.

In order to estimate the rate that CPOs are formed from ICCP systems, a sample of ICCP system logs was reviewed and the average current output for Navy vessels in port was found to be approximately 35 amperes (amps).<sup>13</sup> Using the assumption that 100% of ICCP system current goes into producing chlorine, an hourly pierside chlorine generation rate of 46.3 grams (g) per vessel was calculated using Faraday's Law:

(35 amps) (1 coulomb/amp-sec) (3,600 sec/hr) (35.45 g chlorine/mole) (mole/96,484 coulomb)

 $= 46.3$  g chlorine/hr

Since ICCP systems are designed (i.e., anode design and system operating voltage) to maximize cathodic protection provided to the hull, and generation of chlorine or CPO is a secondary reaction, actual CPO generation rates are expected to be significantly lower.

ICCP anode deterioration rates have been measured at 4.4 to 6.1 milligrams/ampere per year by the manufacturer.<sup>14</sup> For a vessel operating an ICCP system at 35 amps in port for  $176$ days per year, the resulting dissolution rate of platinum using 6.1 milligrams/ampere per year is:

 $(6.1 \text{ mg/amp-year})$   $(35 \text{amps/ship}) = 214 \text{ mg/(ship-year)}$ 

### **3.3 Constituents**

### **3.3.1 Sacrificial Anodes**

Zinc anodes are approximately 99.3% zinc and contain small amounts of cadmium and aluminum (for activation).<sup>15</sup> Table 3a lists the chemical composition of zinc anodes according to military specifications.<sup>15</sup> Zinc and cadmium are priority pollutants. None of the materials in zinc anodes are bioaccumulators.

Aluminum anodes are approximately 95% aluminum, 5% zinc, and contain small amounts of silicon and indium (for activation). $6\degree$  Table 3b lists the chemical composition of aluminum anodes according to military specifications.<sup>6</sup> Zinc is a priority pollutant in aluminum anodes. Aluminum anodes could possibly contain up to 0.001% mercury as an impurity; mercury is a known bioaccumulator.

### **3.3.2 ICCP Systems**

The deterioration of ICCP anodes (see Section 3.2.2) produces 214 mg/yr per ship of platinum. ICCP systems also produce by-products (oxidants) when they operate. In addition to the reduction reactions at the hull, ICCP systems can also produce chlorine, bromine and other oxidants (CPO) through secondary reactions at the anode because of the electrical potential (voltage) of the anode (see Section 2.2). These constituents are the primary concern for the ICCP portion of this discharge. Chlorine or CPOs are neither priority pollutants nor bioaccumulators, though EPA has developed water quality criteria for chlorine/CPO.

### **3.4 Concentrations**

The discharge due to cathodic protection is a mass flux rather than a flow. The resultant concentration of constituents in the environment are discussed in Section 4.2.

### **4.0 NATURE OF DISCHARGE ANALYSIS**

Based on the discharge characteristics presented in Section 3.0, the nature of the discharge and its potential impact on the environment can be evaluated. The estimated mass loadings are presented in Section 4.1. In Section 4.2, the concentrations of discharge constituents after release to the environment are estimated and compared with the water quality criteria. In Section 4.3, the potential for the transfer of non-indigenous species is discussed.

### **4.1 Mass Loadings**

### **4.1.1 Sacrificial Anodes**

The number of sacrificial anodes installed on a vessel is related to the area of wetted surface needing protection and the area that is available for placing the anodes. The discharge from sacrificial anodes is therefore proportional to vessel size (except for submarines because the anodes only protect the propeller and stern appendages and not the hull). The amount of anodes installed is based on:

- 1. One 23-pound zinc anode per 115 ft<sup>2</sup> of total wetted area for large vessels (with more than 3,000  $\text{ft}^2$  of wetted area).<sup>3,5</sup>
- 2. One 23-pound anode per 400 ft<sup>2</sup> of total wetted area for smaller vessels, boats, and craft.3
- 3. 2,024 pounds (88 anodes) of zinc anodes per submarine.3

Using the large vessel criteria for all vessels with over  $3,000$  ft<sup>2</sup> of wetted surface is a conservative assumption because this criteria was written for large, high value vessels that have long periods between drydockings (and thus, less opportunity for anode replacement). Vessels

with wetted surface areas between 3,000 ft<sup>2</sup> and 10,000 ft<sup>2</sup> are drydocked more frequently, increasing the opportunity for repainting and anode replacement, and therefore could use fewer zinc anodes than the large vessel criteria. If the actual wetted surface area of a vessel was unavailable, it was approximated using a formula in the Naval Ships' Technical Manual  $(NSTM)$ , Chapter 633:<sup>5</sup>



Where available, data on actual vessel movements were used to determine the number of days in port, number of transits, and days underway operating within 12 n.m. for Navy, MSC, USCG, and Army vessels. Where actual vessel movement data were not available, movement data for vessels with similar missions were used. This information is shown in Table 2 and Table 4. Using these data, the numbers of anodes installed on vessels, and anode corrosion/dissolution rates, the mass flow rate of this discharge was calculated.<sup>ii</sup> When vessels are in port, the pierside dissolution rate is used to calculate the constituent mass flow rate. When vessels are operating within 12 n.m. of shore, the applicable dissolution rate is derived by summing 66.7% of the pierside dissolution rate and 33.3% of the underway dissolution rate. This applicable dissolution rate is then used to calculate the constituent mass flow rate. Total constituent-specific mass flow rates are calculated by summing the pierside constituent mass flow rate and the constituent mass flow rate when the vessel is operating within 12 n.m. An example of the calculation for determining total constituent-specific mass loading is provided below.

(305 days in port/yr) (24 hrs/day) (417 lb anode/class) (7.4x10<sup>-6</sup> lb zinc/lb anode/hr) + (60 days operating within 12 n.m./yr) (24 hrs/day) (417 lb anode/class) [(0.667) (7.4x10<sup>-6</sup> lb  $\text{zinc/lb}$  anode/hr) + (0.333) (3.0x10<sup>-5</sup> lb zinc/lb anode/hr)] =  $(22.59$  lb zinc/yr/class) +  $(8.96$  lb zinc/yr/class) = 31.55 lb zinc/yr/class

For the 89 submarines in the Navy fleet that use sacrificial anodes, the total estimated annual loading of zinc within 12 n.m. is 6,360 pounds. Zinc anodes on submarines are required to protect propellers and stern appendages, which are similar in surface area for all submarine classes. Fifty-six of the Fleet's 89 submarines are Los Angeles Class submarines. A Los Angeles Class submarine has eighty-eight 23-pound zinc anodes (2,024 pounds total) to protect propellers and stern appendages.<sup>3</sup> The number of anodes on a Los Angeles Class submarine (88) was used for all submarine classes because the surface areas of the propellers and stern appendages are similar among submarine classes.

 $\frac{1}{10}$  Most DOD vessels will be at anchor or otherwise stationary 2/3 of the time and conducting transits or otherwise moving 1/3 of the the time when operating within 12 n.m. of shore. For mass loading calculation purposes, a combination of the pierside and underway dissolution rates was used, weighted 66.7% and 33.3% respectively. These percentages are based on fleet provided information.

For surface vessels, an estimated 113,201 pounds of zinc is discharged annually within 12 n.m. The wetted surface areas and total amount of anodes used to calculate the zinc discharged by vessels within 12 n.m. are presented in Table 2. The estimated mass loading was based on 1,805 surface vessels with a total wetted surface area of approximately 11 million square feet.

Mass loading for the approximately 5,000 small boats and craft of the Armed Forces was estimated using the following information:

- 1. 30% have steel hulls, and therefore sacrificial anodes (the remaining have wood, fiberglass, or aluminum hulls which do not require cathodic protection);
- 2. The average wetted surface area is  $1,000$  ft<sup>2</sup> (the approximate wetted surface area of a 65 ft tug boat), which is protected by approximately 58 pounds of zinc anodes  $(23$  pounds per 400 square feet);<sup>iii</sup>
- 3. Each vessel spends 100% of the time in the water (a conservative estimate since many spend considerable time out of the water on trailers or blocks);

The resulting zinc discharged was then calculated using the static dissolution rate.

 $(5,000 \text{ vessels})$  (30%) (58 lb anodes/vessel) (100%) (7.4 x 10<sup>-6</sup> lb zinc/lb anode/hr) (365 days/yr)  $(24 \text{ hr/day}) = 5,640 \text{ lb zinc/yr}$ 

Based on conservative assumptions, this calculation presents the maximum magnitude of the discharge from small boats and craft, which represents approximately only 5% of the previously estimated total annual discharge of 119,561 pounds of zinc (surface ships and submarines combined) for a maximum combined total of 125,201 pounds of zinc per year. This discharge could contain up to 626 pounds per year of aluminum and up to 88 pounds per year of cadmium, based on the potential concentration of minor constituents in zinc anodes.

Aluminum anodes are currently used on no more than 5 submarines.<sup>16</sup> Using the information in Table 4, each submarine with zinc anodes discharges approximately 71.5 pounds zinc/year within 12 n.m. This zinc loading was scaled for aluminum anodes using the current capacity ratio derived in Section 3.2.1 and the maximum number of vessels with aluminum anodes, resulting in a total fleetwide annual consumption (discharge) of 105 pounds of aluminum anodes as shown below.

iii Small boats and craft are non-standard vessels with wetted surface areas ranging from under one hundred square feet to one thousand square feet. Because adequate information is not available to characterize the surface area of specific small boats and craft, the upper bound of this range, one thousand square feet, is used as a conservative estimate of the average wetted surface area.

(71.5 lb zinc anode/submarine) /  $(3.4) = 21.0$  lb aluminum anode/submarine  $(21.0$  lb aluminum anode/submarine)  $(5 \text{ submarines}) = 105$  lb aluminum anodes consumed, fleetwide

Based on the composition of aluminum anodes, this discharge is comprised of 100 pounds aluminum, 5 pounds zinc, and could contain up to 0.21 pound per year of silicon and 0.02 pound per year of indium. The maximum potential loading of mercury from aluminum anodes was estimated to be 0.001 pound fleetwide, assuming that all aluminum anodes contain the highest allowable amount of mercury.

#### **4.1.2 ICCP Systems**

The mass loading due to deterioration of ICCP anodes was calculated using the previously discussed anode deterioration rate and the number of vessels with ICCP systems. For the 267 vessels with ICCP systems, this results in a total fleet-wide platinum loading of:

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(214 \text{ mg/yr}) (273 \text{ vessels}) = 57,138 \text{ mg/yr} = 57 \text{ g/yr} \approx 2 \text{ ounces/yr}
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Annual CPO loadings were calculated using the estimated CPO generation rate of 46.3 g/hr per vessel (see Section 3.2). This rate was applied to the 273 vessels with ICCP systems (see Table 1) and time spent in port for each class to calculate the mass loadings presented in Table 5. The estimated annual loading of CPO based on the 273 vessels with ICCP systems is 98,000 pounds.

#### **4.2 Environmental Concentrations**

Two approaches were used to estimate the concentration of zinc and CPO in receiving waters from cathodic protection systems. The first uses a simplified dilution model, based on tidal flow in three major Armed Forces ports and is hereafter referred to as the "tidal prism" approach. The second approach was based on a mixing zone proximate to the hull of a typical Navy vessel. Each approach used the hourly zinc corrosion/dissolution rates and CPO production rate developed in Section 3.2 (i.e., for zinc: a pierside rate of 1.3 x  $10^{-6}$  (lb zinc/ft<sup>2</sup>)/hr and an underway rate of 5.1 x  $10^{-6}$  (lb zinc/ft<sup>2</sup>)/hr, and for CPO: 46.3 (g/vessel)/hr).

**Tidal Prism.** The tidal prism approach uses the mass of the constituent generated by vessels and mixes this mass with a volume of water. The mass is calculated by determining the number of vessels in a particular homeport, the type of cathodic protection system utilized, and the number of hours each vessel spends in port (both pierside and in transit) along with the aforementioned zinc and CPO generation rates. Together, these factors are used to calculate an annual loading to the harbor. The water volume used is the sum of all outgoing tides over a year times the surface area of the harbor. The sum of outgoing tides is called the "annual tidal excursion" which is defined as the difference between mean high water and mean low water over the course of a year. Annual tidal excursion data is readily available from the National Oceanographic and Atmospheric Agency (NOAA), and the 1996 data $17$  was used for these calculations.

The tidal prism model assumes steady-state conditions, where zinc and CPO are completely mixed with the harbor water and are removed solely by discharge from the port during ebb tides. The outgoing tidal volumes are assumed to be carried away by long-shore currents (i.e., those moving parallel to shore) and do not re-enter the harbor. The tidal prism model also does not assume removal or concentration by other factors such as river flow, precipitation, evaporation, sediment exchange, or natural decay. By not accounting for removal or dilution due to river flow, precipitation, sediment exchange, and natural decay, the calculations result in a higher constituent concentration. The effect of evaporation could be to increase concentration due to water loss, or the effect could be neutral since water loss by evaporation is replaced by (additional) water inflow from the sea. While the model assumes complete mixing, there will be areas in the harbors with higher concentrations, primarily near the source vessels, along with areas of lower concentration.

The three ports that are used for the tidal prism model shown in Tables 6a, 6b, and 6c include Mayport, FL, San Diego, CA, and Pearl Harbor, HI. These ports were selected because they have minimal river inflow, small but well-defined harbor areas, and a high number of vessels of the armed forces. Each of these factors will tend to overestimate concentrations of zinc and CPO, either due to less volume of water or high numbers of potential sources. Other major ports, such as Norfolk (VA) and Bremerton (WA), were considered, but not included because of large river effects and very large harbor areas. The 1996 annual tidal volumes (annual tidal excursion times the harbor surface area) for the three ports (calculations provided in Calculation Sheet 2) are shown below:

- San Diego, CA:  $3.77 \times 10^{13}$  liters;
- Mayport, FL:  $6.67 \times 10^{11}$  liters; and
- Pearl Harbor HI:  $3.41 \times 10^{12}$  liters.

**Mixing Zone:** For the mixing zone approach, the previously calculated zinc and CPO generation rates were used for each discharge, but the resultant environmental concentrations were calculated based on various volumes of water around a typical Armed Forces vessel (i.e., a "mixing zone") instead of the entire port, as above. A vessel with 19,850 ft<sup>2</sup> of wetted surface area (i.e., a FFG 7 Class frigate size vessel) was selected for modeling the environmental concentration from sacrificial anodes since precise information was available for the number of zinc anodes installed on that ship class. A vessel with  $37,840$  ft<sup>2</sup> of wetted surface area (i.e., a CG 47 Class cruiser size vessel) was selected for modeling ICCP system discharges because of the large number of vessels in this ship class and it's hull size is typical of most vessels with ICCP systems.

The model assumes the hull to be a half immersed cylinder (see Calculation Sheets 3 and 4). The zinc and CPO generation rates were then applied to various sizes of mixing zones (volumes of water surrounding the vessel), ranging from 0.1 to 100 feet from the hull, and mixing rates (the time required for the mixing zone contents to be exchanged with a new volume of clean seawater), ranging from 0.1 to 1 hour, to calculate resultant incremental zinc and CPO concentration increases shown in Table 7. The maximum time of exchange of 1 hour

corresponds to a realistic duration of slack tide, and is also the time required for a volume of water flowing at 0.1 knots to flow past a 600 foot long vessel longitudinally. Actual exchange times will usually be much less. For example, water flowing at 2 knots (typical for tidal flow) past the same 600 foot long vessel results in a time of exchange of 3 minutes.

### **4.2.1 Sacrificial Anodes**

The in-port (static) and transient (dynamic) zinc corrosion/dissolution rates of 7.4 x  $10^{-6}$ and 3.0 x  $10^{-5}$  pounds of zinc per pound of anode per hour, respectively, (see Calculation Sheet 1) were used for the tidal prism model. Only the static rate was used for the mixing zone model since the highest potential concentrations would occur while the vessel is pierside.

**Tidal prism.** Based on the number and types of ships located in each of the three harbors<sup>18</sup> and the type of cathodic protection, the numbers of sacrificial anodes installed on each of the vessels in each ship class were estimated, based on the information in Section 3.2.1. The number and types of vessels using zinc sacrificial anodes at each port are listed in Table 6a. Using the annual zinc loadings and annual tidal excursion volumes, the average zinc concentrations caused by these vessels were calculated for each port (also shown in Table 6a). The average zinc concentration estimated by the tidal prism model and the ambient zinc  $concentrations<sup>19</sup>$  are summarized below.



As shown above, the contribution of zinc from sacrificial anodes makes up only a small portion of the ambient concentration, except for Mayport, where almost 30 percent of the ambient concentration can be attributed to the dissolution of zinc anodes. In each case, the ambient concentrations are well below the Federal and most stringent state water quality criteria (between 76 and 85  $\mu$ g/L) as shown in Table 8. Resultant incremental concentration increases of minor constituents (aluminum and cadmium) are shown in Table 6a and are at least 40,000 times lower than the most stringent Federal or state WQC.

A similar tidal prism analysis can be performed for aluminum anode usage on submarines. Assuming that Pearl Harbor and San Diego each have the maximum five submarines with aluminum anodes, Table 6b shows the concentrations resulting from aluminum sacrificial anodes to be 0.02 µg/L of aluminum and  $2x10^{-7}$  µg/L of mercury for Pearl Harbor, and much less for San Diego. These concentrations are significantly less than the most stringent state WQC of 1,500  $\mu$ g/L of aluminum (FL) and 0.025  $\mu$ g/L of mercury (CT, FL, WA, and VA). Incremental concentration increases for other minor constituents (zinc, silicon, and indium) are also shown in Table 6b and are nearly 1,000,000 times lower than the most stringent Federal or state WQC.

**Mixing zone.** The mixing zone model calculated zinc concentrations within "envelopes" or mixing zones of uniform size and shape around a vessel's hull, assuming various exchange rates. For calculation purposes, the mixing zones ranged from 0.1 foot to 100 feet from the hull, and the exchange rates ranged from 0.1 hour to 1 hour. Actual exchange rates are rarely more than one hour as discussed previously. Tabulated mixing zone calculations are presented in Table 7 and do not include ambient concentrations of zinc in the water. Ambient zinc concentrations for each port were then added to the mixing zone concentrations and compared to ambient WQC.

Federal and state WQC exist for zinc (see Table 8). The Federal WQC is 81  $\mu$ g/L for chronic exposure. Washington state's WQC of  $76.6 \mu g/L$  for chronic exposure is the most stringent state criteria.<sup>19</sup> For exchange rates of one hour or less, any mixing zone of six inches or more results in zinc concentrations (including the contribution of zinc from ambient water in each port) less than the most stringent state WQC of 76.6  $\mu$ g/L for chronic exposure. Ambient zinc concentrations for Mayport, FL and Pearl Harbor, HI were obtained from EPA's STORET system. The Navy had more recent data on San Diego Bay and used this data rather than the data from the STORET system.<sup>9,19</sup> These concentrations are assumed to include any contributions of zinc from sacrificial anodes.

The results of the mixing zone analysis developed for sacrificial zinc anodes (Table 7) can be scaled to provide similar results for aluminum anodes using the current capacity ratio (3.4) developed in Section 3.2.1 and the maximum allowable concentration of mercury (0.001%). The sample calculation below was performed for the scenario from Table 7 that would produce the highest estimated concentrations of aluminum and mercury (a time of exchange of one hour, and a mixing zone of 0.1 foot):

Zinc concentration at radius of 0.1 ft =  $236 \mu g/L$ 

Aluminum concentration at same radius:  $= (236 \,\mu g/L)/(3.4) = 69.4 \,\mu g/L$ 

Maximum potential mercury concentration at same radius  $= (69.4 \text{ µg/L})/(100,000)$ 

The estimated concentration for aluminum  $(69.4 \mu g/L)$  is twenty times less than the most stringent state chronic WQC of 1,500  $\mu$ g/L (Fl), and there are no federal WQC for aluminum. The estimated concentration for mercury (0.0007  $\mu$ g/L) is 35 times less than Federal and most stringent state chronic WQC (0.025 µg/L). Similar calculations can be performed for other minor constituents of sacrificial anodes. In all cases, the resultant concentration increase is at least 50 times less than the most stringent Federal and state WQC at a distance 0.1 feet from the hull.

### **4.2.2 ICCP Systems**

This discharge consists of various chlorinated and brominated substances (CPOs). As discussed in Section 3.2.2, these generation rates assume that 100% of the current passed by the ICCP system creates CPOs, while in actuality, the current also produces metal complexes, oxygen, hydrogen, and other compounds in addition to CPOs with each collateral reaction consuming a portion of the total current. Seawater conditions have a strong influence on the type and magnitude of secondary reactions at the hull and sacrificial anodes. Because seawater conditions vary with geographic location, the extent of secondary chemical reactions cannot be accurately predicted. Therefore, a conservative assumption that 100% of the current produces CPOs is used.

In order to estimate the amount of CPOs generated by ICCP systems, ships' logs for a variety of vessels were reviewed to determine the average current produced by ICCP systems in port (35 amps).<sup>13</sup> From this information and Faraday's Law, an hourly, pierside CPO generation rate of 46.3 g/hr was calculated (see Section 3.2.2). This rate was used for both the tidal prism and the mixing zone models.

**Tidal prism.** Using the same approach as described in Section 4.2.1 and CPO generation rates, annual CPO loading due to the Armed Forces vessels in each of the three ports were calculated as shown in Table 6c. The chronic criteria and concentrations estimated from the tidal prism model are summarized below:



\* San Diego discharge limits are set on a case-by-case basis

This model assumes complete mixing and does not consider any decay or secondary reactions. However, CPO is known to rapidly decay in seawater. In the first stage of CPO decay, a portion of the CPO disappears within one minute, consumed by the instantaneous oxidant demand. The rate of this first-stage reaction is related to temperature. One study, for example, found that the percentage of CPO that disappeared within one minute varied from 4% at  $0^{\circ}$ C to

 $20$  Other factors that influence the initial rate of decay include ammonia concentration and the nature of the oxidant demand. In the second stage of CPO decay, the CPO remaining after the first stage is reduced more slowly. Second stage decay half-lives of between 1 and 100 minutes have been observed.<sup>20</sup> In most cases, however, the majority of CPO will disappear within an hour of being added to seawater.<sup>20,21</sup>

If these decay rates were incorporated into the tidal prism model, the average CPO concentrations shown above for the three ports would be lower. For example, the average CPO concentration of 3.43 µg/L in Mayport, FL was calculated assuming zero CPO decay for the duration of a tidal excursion. Using average decay estimates (i.e., 25% first stage decay after one minute, 50% second stage decay per hour) provides a 98.8% reduction in CPO for the 12 hour duration of a tidal excursion, resulting in CPO concentrations orders of magnitude below WQC.

**Mixing zone.** Using the mixing zone approach described for sacrificial anodes, CPO concentrations within "envelopes" or mixing zones around a vessel's hull were calculated. For calculation purposes the mixing zones ranged from 0.1 foot to 100 feet from the hull, and the mixing rates ranged from 0.1 hour to 1 hour. As stated previously, actual exchange rates are rarely more than 1 hour, and may be as low as a few minutes.

Tabulated calculations of CPO mixing zone calculations are included in Table 7. For exchange rates of 1 hour or less, any mixing zone of 5.5 feet or more results in CPO concentrations below the most stringent state chronic WQC of 7.5  $\mu$ g/L. EPA's STORET system does not contain monitoring data for chlorine; therefore, ambient conditions can not be determined.

As for the tidal prism model calculations, these figures assume no decay of CPO. Using the CPO decay rates discussed above, a 47.0% reduction in the CPO concentrations listed in Table 6b for a 1 hour mixing zone exchange rate would be expected. Applying this decay rate to the mixing zone model and assuming a time of exchange of one hour, any mixing zone with a radius of 3 feet or more results in CPO concentrations caused by ICCP systems less than the most stringent state chronic WQC of 7.5 µg/L.

### **4.3 Potential for Introducing Non-Indigenous Species**

There is insignificant potential for transport of non-indigenous species by this discharge because no water is retained nor transported.

### **5.0 CONCLUSIONS**

### **5.1 Sacrificial Anodes**

Cathodic protection discharges from sacrificial anodes have a low potential for causing adverse environmental effects for the following reasons:

- the loadings from sacrificial zinc and aluminum anodes do not result in zinc or aluminum concentrations, or concentrations of minor constituents, above ambient water quality criteria in any of the harbors based on the results of the tidal prism model;
- zinc, aluminum, and mercury concentrations are below WQC within a distance of 0.5, 0.1, and 0.1 feet, respectively, during periods of slack water (little water movement in the harbor); and
- loadings of mercury are small (less than 0.001 pound per year fleetwide).

This conclusion is based on corrosion/dissolution rates estimated from the average anode replacement intervals for Navy vessels. The number of anodes per vessel class was based on actual numbers or, in lieu of such data, estimated using the vessel's wetted surface area. This

approach was also applied to other Armed Forces vessels.

### **5.2 ICCP Systems**

Cathodic protection discharges from Impressed Current Cathodic Protection (ICCP) systems have a low potential for causing adverse environmental effects for the following reasons:

- the loadings from ICCP systems do not result in CPO concentrations above ambient water quality criteria in any of the harbors based on the results of the tidal prism model; and
- CPO concentrations drop below WQC within a distance of 5.5 feet during periods of slack water without considering CPO decay (which would reduce concentrations even lower).

This conclusion is based on a review of ICCP system logs and the assumption that 100% of the current passed from the ICCP system anodes generates CPO.

### **6.0 DATA SOURCES AND REFERENCES**

To characterize this discharge, information from various sources was obtained. Table 9 shows the sources of data used to develop this NOD report.

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# **Table 1. Listing of Vessels, Navy, MSC, Army, and USCG using Cathodic Protection**



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Notes:

(a) Denotes an estimate of amount of anodes on ship class based on a calculated wetted surface area.

(b) Denotes an estimate of days in port and number of transits.

(c) Denotes actual amount of anodes installed on ship class.

(d) Denotes an estimate of amount of anodes on ship class based on a known wetted surface area.

(e) Denotes round-trip transits

Vessels with a wetted surface area greater than 3,000 sq ft are assumed to have 23 pound of zinc anodes for each 115 sq ft of wetted surface area. Vessels with a wetted surface area less than 3,000 sq ft are assumed to have 23 pounds of zinc anodes for each 400 sq ft of wetted surface area.



### **Table 3a. Chemical Composition, Zinc Anodes (Galvanic Protectors)**

### **Table 3b. Chemical Composition, Aluminum Anodes (Galvanic Protectors)**









### **Table 5. Vessels Estimated Annual ICCP Discharges**



### **Table 6a. Tidal Prism Model - Zinc From Sacrificial Cathodic Protection Anodes**



# **Table 6b. Tidal Prism Model - Aluminum and Mercury From Sacrificial Cathodic Protection Anodes**







<b>Constituent</b>	<b>Tidal Prism Concentrations: San</b> Diego; Mayport; Pearl Harbor	<b>Federal Chronic</b> <b>WQC</b>	<b>Most Stringent State Chronic</b> <b>WQC</b>
<b>CPO</b>	0.17; 3.43; 0.75	$\overline{\phantom{a}}$	7.5 (CT, HI, MS, NJ, VA, WA)
Zinc	0.09; 1.35; 0.31	81	76.6 (WA)
Aluminum	0.000005; 0; 0.049	None	$1,500$ (FL)
Mercury*	0.00000004; 0; 0005	0.025	0.025 (CT, FL, GA, MS, VA, WA)
$CT =$ Connecticut			
$FL = Florida$			
$GA = Georgia$			
$HI = Hawaii$			
$NJ = New Jersey$			
$MS = Mississippi$			
$VA = Virginia$			
$WA = Washington$			
Notes:			
Refer to federal criteria promulgated by EPA in its National Toxics Rule, 40 CFR 131.36 (57 FR 60848; Dec. 22,			
1992 and 60 FR 22230; May 4, 1995)			
Where historical data were not reported as dissolved or total, the metals concentrations were compared to the			
most stringent (dissolved or total) state water quality criteria.			
* Bioaccumulator			

Table 8. Comparison of Constituent Environmental Concentrations and Water Quality Criteria ( $\mu$ g/L)

### **Table 9. Data Sources**





**Figure 1. Sacrificial Anode and Impressed Current Cathodic Protection** 



ANODE:

- CONSUMED IN THE<br>ELECTROCHEMICAL REATION
- SITE OF OXIDATION<br>REATION(S)

CATHODE:

- PROTECTED SURFACE

- SITE OF REDUCTION REACTION(S)

- OTHER REDUCTION REATIONS ARE POSSIBLE.

**Figure 2. Electrochemical Cell** 



**Figure 3. Impressed Current Cathodic Protection System** 



### **Calculation Sheet 1. Calculation of Corrosion/Dissolution Rates from Sacrificial Anodes**

Vertical tidal excursions for 1996 is based on the summation of the daily outgoing tides ( i.e., high-high water to low-low water and high water to low water).

#### **San Diego**

- Surface Area = (10,532 acres) (4046.2 m<sup>2</sup>/acre) = 4.26 x 10<sup>7</sup> m<sup>2</sup>
- Total annual vertical tidal excursion for  $1996 = 884.5$  m Average tidal excursion =  $(884.5 \text{ m/yr})/( (365 \text{ days/yr}) (2 \text{ tides/day}) = 1.2 \text{ m}$
- Tidal prism volume for 1996 =  $(4.26 \times 10^7 \text{ m}^2)$  (884.5 m) = 3.77 x 10<sup>10</sup> m<sup>3</sup>  $= 3.77 \times 10^{3}$  L

#### **Mayport**

- Surface Area = (169.8 acres) (4046.2 m<sup>2</sup>/acre) = 6.87 x 10<sup>5</sup> m<sup>2</sup>
- Total annual vertical tidal excursion for  $1996 = 970.3$  m Average tidal excursion =  $(970.3 \text{ m/yr})/( (365 \text{ days/yr}) (2 \text{ tides/day}) = 1.3 \text{ m}$
- Tidal prism volume for 1996 =  $(6.87 \times 10^5 \text{ m}^2) (970.3 \text{ m}) = 6.67 \times 10^8 \text{ m}^3$  $= 6.67 \times 10^{11}$  L

#### **Pearl Harbor**

- Surface Area = (3,031 acres) (4046.2 m<sup>2</sup>/acre) = 1.23 x 10<sup>7</sup> m<sup>2</sup>
- Total annual vertical tidal excursion for  $1996 = 278.2$  m Average tidal excursion =  $(278.2 \text{ m/yr})/( (365 \text{ days/yr}) (2 \text{ tides/day}) = 0.38 \text{ m}$
- Tidal prism volume for  $1996 = (1.23 \times 10^7 \text{ m}^2) (278.2 \text{ m}) = 3.41 \times 10^9 \text{ m}^3$  $= 3.41 \times 10^{12}$  L

#### **Calculation Sheet 2. Calculation of Tidal Prism Volumes for San Diego, CA; Mayport, FL; and Pearl Harbor, HI**



**Calculation Sheet 3. Zinc Concentration (Mixing Zone Model) Sample Calculations** 



**Calculation Sheet 4. CPO Concentration (Mixing Zone Model) Sample Calculations**