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Transfer of elements released by aluminum galvanic anodes in a marine sedimentary compartment after long-term monitoring in harbor and laboratory environments

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Abstract

Cathodic protection by galvanic anodes (GACP) is often used to protect immerged metallic structures in harbor environments, especially GACP employing aluminum-based anodes. To follow a previous study that was performed in a laboratory on Al-anode, two monitoring periods were performed in parallel, one in an in situ environment (in the Port of Calais) for 42 months and the other in a laboratory for 18 months, to evaluate the transfer of metals constituting the Al-anode towards the sedimentary compartment. During each monitoring, two conditions of agitation of water (weak and strong) were compared, and different factors of sediment quality were used to assess the enrichment and potential toxic effects of these released metals. The results showed that the dissolution of Al-anode-induced a greater Zn enrichment of sediment than an Al enrichment. This is in contrast with the abundance of these elements present in the composition of the anode and suggested a potential toxic effect for marine organisms with regards to the discovered Zn level, especially in confined areas.

Keywords: galvanic anode, aluminum, zinc, marine sediments, harbor, quality index

1. Introduction

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Numerous maritime structures are constituted by metallic components (sheet piles in harbor environment, monopiles foundation of offshore wind turbines and platforms or pipelines). This type of structure undergoes a normal process of corrosion when exposed in the marine environment (Kaesche, 2003). A study by NACE International (2002) estimates that the total cost of marine corrosion in the world ranges from $ 50 billion to $ 80 billion a year. The corrosion process of a metallic material can be limited by different methods of protection such as coatings, corrosion inhibitors, corrosion allowance (increasing the thickness of material) or anodic and cathodic protections (Kruger and Begum, 2016; Kirchgeorg et al., 2018).

The methods of "cathodic protection" (CP) are provided by two mainly used electrochemical devices: cathodic protection by galvanic anodes (GACP) and cathodic protection by impressed current (ICCP) (DNV-RP-B401, 2017). In marine environments, the ICCP is rarely used, while CP by galvanic anodes is preferred for several reasons such as easy installation and less maintenance (Roy et al., 1968). The GACP consists of coupling two metallic materials that have a free and distinct potential. Then, the coupling of both materials induces an electrochemical cell and decreases the potential of the noblest material. Reactions of oxidation occur with the consumption of these anodes and induce the liberation in waters of the elements that compose the anodes.

Different metals, such as zinc (Zn), magnesium (Mg) or aluminum (Al), are principal compounds of galvanic anodes. In a marine harbor environment, the use of Al anodes (at least 93.2% given by supplier) has been well known since the 1960s as a protectant for piles and sheet piles (Roy et al., 1968; Barbucci et al., 1997; Shibli and George, 2007). One of the principal reasons is the theoretical efficiency of this element in relation to its high electrochemical capacity (2000 Ah kg^{-1}) in seawater compared to Zn which usually composes the galvanic anode used in marine environment (DNV-RP-B401, 2017; Kirchgeorg et al., 2018). Al is one of the most abundant elements on Earth after oxygen and silicon and the first metal composing the Earth's crust (7.5% in mass). This metal is widely distributed in soils and rocks where it naturally exists under different chemical forms, such as oxides or aluminosilicates in feldspars (major constituents of granite and silicon-rich rocks), in mica or in clays (ATSDR, 2008). Al inputs to the surface waters are largely associated with mineral particulate

58 matter (Driscoll and Schecher, 1990), which quickly accumulate in sediments in which the anthropic
59 part appears to be difficult to assess. In seawater (pH 8.2), dissolved inorganic aluminum is principally
60 met in aluminate ($Al(OH)_4^-$, 68%) and non-colloidal neutral hydroxide species ($Al(OH)_3^0$, 32%)
61 (Millero et al., 2009). Another important factor that increases the solubility of Al is the concentration
62 of organic matter. In the presence of highly dissolved organic matter, Al solubility grows in relation to
63 complexation with organic ligands (Driscoll and Schecher, 1990; Ščančar and Milačič, 2006; ATSDR,
64 2008; Hagvall et al., 2015).
65 The speciation of Al is complex and determines its toxicity to organisms. A number of works have
66 been carried out on Al toxicity in marine environment but were mostly associated with the inputs of
67 acidic rivers into the coastal waters (Wilson and Hyne, 1997; Kroglund and Finstad, 2003; Golding et
68 al., 2015; Angel et al., 2016; Gillmore et al., 2016). The first studies about the impact of elements
69 released from galvanic anodes were performed on anodes principally composed by Zn (at least 99%
70 given by supplier) (Bird et al., 1996; Rousseau et al., 2009; Mottin et al., 2012). Zinc is present in
71 seawaters under ionic (including labile species), inorganic complexes and colloids as well as weak
72 organic complexes (Fukai and Huynh-Ngoc, 1975). This is an essential trace metal in living organisms
73 (Dušanka, 1970) which tends to be bioaccumulated (Pempkowiak et al., 1999; Baudrimont et al.,
74 2005). Its chronic exposure effects in the coastal marine environment have been previously
75 investigated by several authors (Watling, 1982; Sunda et al., 1987; Geffard al, 2001, 2007; Devos et
76 al., 2012). In the same period and more recently, some works focused on the Al released from anodes
77 into the different compartments of marine environment (Mao et al., 2011; Gabelle et al., 2012;
78 Deborde et al., 2015). But, no works were yet involved on the bioaccumulation potential of aluminum
79 released from anodes.
80 This study followed up on the works of Deborde et al. (2015), which were conducted to optimize the
81 simulation in the laboratory of the Al anodes degradation and to characterize the deposits of corrosion
82 formed on anode's surface. Here, investigations were focused on in situ monitoring of sediments
83 exposed for a long period to Al GACP anodes in natural and laboratory conditions. The sedimentary
84 compartment was chosen because is considered as an indicator of contamination, since it is recognized

as being able to store many contaminants such as metals (Xia et al., 2011; Li et al., 2012; Pan and Wang, 2012).

The metal concentrations recorded in sediments were first compared to guidelines (Long et al., 1995; Macdonald et al., 1996; Long et al., 1998; McCauley et al., 2000; Zahra et al., 2014). They were used to determine sediment quality indices in the aim to evaluate the degree of contamination of the exposed sediments and their potential ecological risk (Pourabadehei and Mulligan, 2016; Ranjbar Jafarabadi et al., 2017; Jahan and Strezov, 2018; Gargouri et al., 2018; Kim et al., 2018; Tunca et al., 2018). And a chemical speciation was investigated to provide information on mobility and potential bioavailability of the considered elements (Morillo et al., 2004; Gabelle et al., 2012).

2. Materials and methods

2.1. Al galvanic anodes (Al GACP)

All the Al galvanic anodes (Al Bera15, Bac Corrosion® Control) settled in situ in the harbor or that were used during the laboratory experiment were in the same Al alloy, which was mainly composed of seven elements (Al, Zn, Fe, Si, In, Mn and Cu). The mass percentages of each metal were given by the supplier as following: 93.2% to 97.1% of Al, 2.5% to 6.5% of Zn, 0.13% max of Fe, 0.1% max of Si, 0.01% à 0.03% of In, 0.01% max of Mn and 0.006% max of Cu. Depending of the supplier, the Al galvanic anodes can present impurities such as Cd, whose the mass percentage is less than 0.002% (DNV-RP-B401, 2017).

2.2. In situ sampling

The in situ study was conducted between September 2012 and June 2017 (42 months) in the Port of Calais located in northern France. As the great majority of harbor contracting authorities worldwide, the Port of Calais chose the method of CP by galvanic anodes to protect its immerged structures.

112 Approximately 615 tons of galvanic anodes were installed in 2014 in the harbor to protect the metallic
113 structures for a duration of at least 15 years. Fig. 1 shows the location of the three sampling points
114 monitored throughout the port: point 1 (at the entrance of the port) was considered to be the reference
115 point; point 2 was in agitated area with important sediment resuspension in relation to the comings and
116 goings of ferries (every 45 min, 350 to 400 boats per month); point 3 was located in the closed basin
117 of a marina, which was under non-agitated area characterized by weak hydrodynamic condition and
118 weak renewal of seawater. Point 2 is the only studied point that was subjected to soft dredging
119 operations (water injections) performed two times per year.
120 In the port, all along the quays, one anode (approximately 700 kg) was fixed in the immersed zone at
121 every one meter directly in contact with the steel sheet pile wall, in each hollow part. The pose of the
122 anodes was distributed with time and the monitoring of harbor sediments was divided into two
123 periods: first period corresponding to one year study carried out before the pose of the anodes,
124 between September 2012 and September 2013; and the second period was developed over 30 months
125 (January 2015 to end of June 2017) after the pose of the anodes, which ended in November 2014 for
126 point 2 and in August 2014 for point 3.
127 Sediment samples were collected at proximity and below the anode (0 m) and 15 m away from the
128 anode (15 m) for points 2 and 3. Two samples of undisturbed surface sediment samples were collected
129 every 2 months by boat with a Van-Veen Surficial (top 2 cm) grab. Each sample was constituted by
130 one kilogram of sediment obtained after mixing of three homogeneous grabs taken from an area of
131 approximately 1 m^2. Sediments were transferred in polyethylene bottles and placed in an ice-cooled
132 box until their return in the laboratory. At same time, natural populations of mussels were collected, as
133 well as caged mussels (*Mytilus edulis*) and marine sponges (*Hymeniacidon perlevis*) that were
134 previously collected in an uncontaminated area of Normandy. However, the results of in situ organism
135 monitoring will be published in a second part of this work.
136

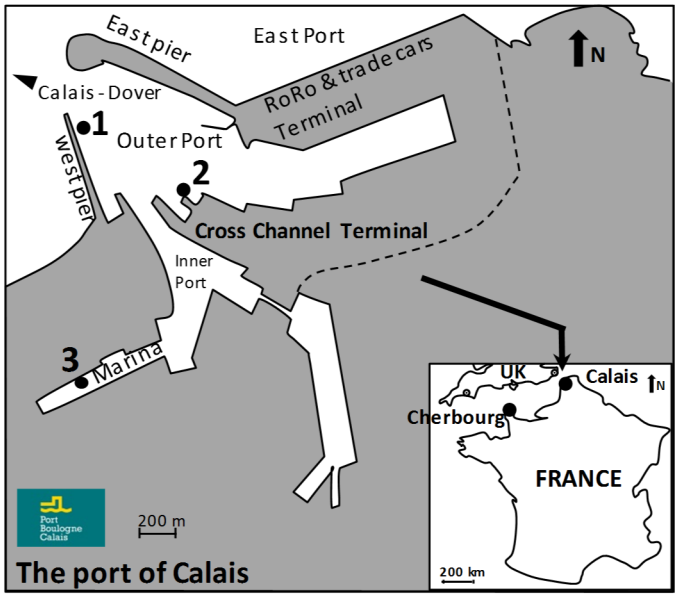


Fig. 1: Location of the sampling points monitored in port of Calais.

2.3. Laboratory experimental design

The laboratory experiment was conducted to reproduce the in situ degradation of galvanic anode. This experiment was intended to monitor the elements released from the anode in the different compartments of marine environment, in agitated and non-agitated conditions, such as in an in situ environment (harbor). Sediments and marine organisms (the mussel *M. edulis* and the sponge *H. perlevis*) were exposed to the release of these elements in two different tanks (60 L) connected to one to another by the dumping of seawater (Fig. 2). The results of organism monitoring will be published in a second part of this work.

A laboratory experiment was performed between September 2014 and March 2016 (18 months) in NAVAL GROUP Research buildings located at Cherbourg. For this experiment, natural sediments were collected near Port of Calais (free of contamination) to respect similar size distribution and physical-chemistry proprieties in comparison to in situ harbor sediments.

Sediments were placed in the bottom of 3 tanks of 15-cm thickness covered with 30 cm of water that was renewed with a water flow of 80 L h^{-1}. The 3 conditions of the experiment were the following: a tank without anode, which was considered to be the reference tank (tank 1); 2 tanks with one anode

positioned in suspension below the surface of the water, one in an agitated condition through a water pump brewing 3.33 L min^{-1} (tank 2) and one in non-agitated condition only with water renewal (tank 3). Three small cores (3 cm of thickness, approximately 60 mL) of undisturbed surface sediment samples were collected every 2 months in each tank. Sediments were transferred in polyethylene bottles and were placed in an ice-cooled box until their return to the laboratory.

Ten days after the supplying of sediments in the tanks, the anodes were connected to metallic plates (in carbon steel) to reproduce cathodic protection of the metal as in the in situ condition of the port. For that, the steel sample was proportioned to allow the coupled galvanic anode to discharge an average current of approximately 100 mA, following the first laboratory tests that were performed in the previous study (Deborde et al., 2015).

Electrochemical measurements (intensity and potential) of anodes were raised every two months. The results gave a mean current intensity of 93 ± 19 mA and a mean potential of -1063 ± 29 mV for the anode placed under the agitated condition (tank 2) and a mean current intensity of 82 ± 28 mA and a mean potential of -1058 ± 21 mV for the anode positioned under the non-agitated condition (tank 3).

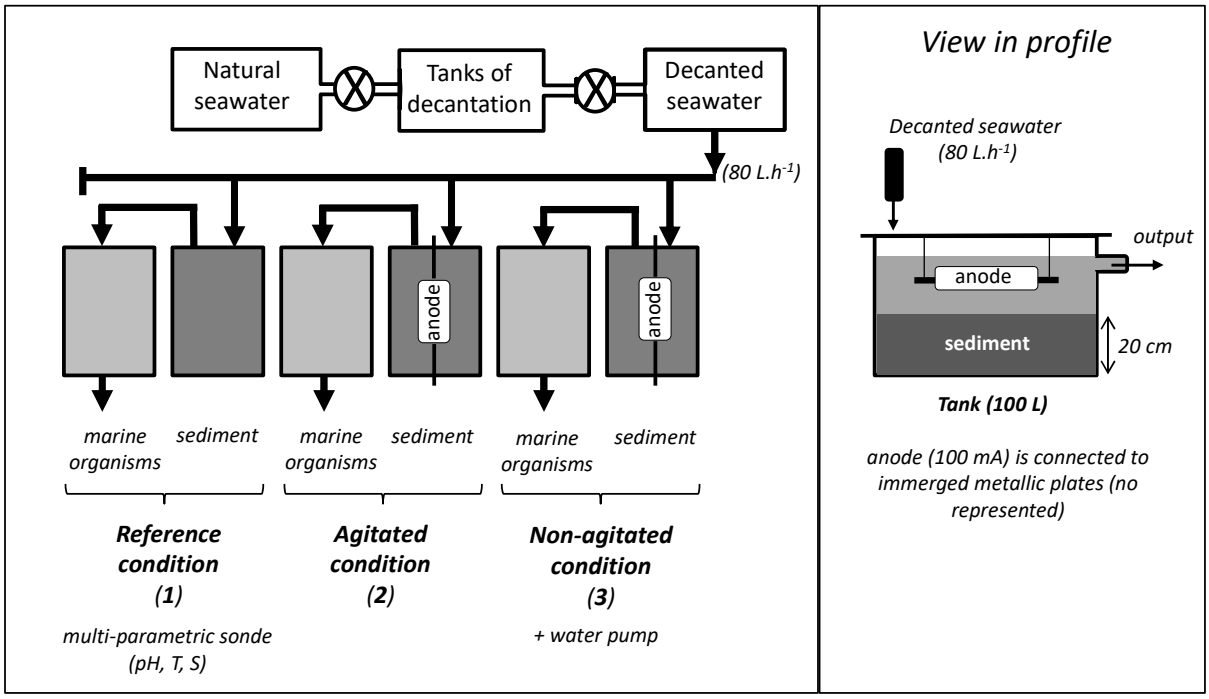


Fig. 2: Experimental devices with or without a galvanic anode to reproduce anode degradation under laboratory conditions.

172

173 *2.4. Sediment characterizations*

174

175 Once they reached the laboratory, sediment samples were immediately transferred to a cold chamber
176 (4 °C) before the analyses of the particle size distribution and the total organic matter (TOC). These
177 physical characteristics were performed for three periods of both in situ harbor monitoring and
178 laboratory experiment, at the beginning, the middle and the end of each experiment. A laser method
179 was applied to characterize the distribution of the particle size of sediments in accordance to the ISO
180 standard 13320. The ISO standard 14235 was used to obtain the TOC.
181 The second kilogram of sediment samples was frozen at -20 °C immediately upon returning to the
182 laboratory to be freeze-dried in a Labconco Freezone 2.5-L system with the aim to carry out the
183 element analyses. Total concentrations of elements constituting galvanic anode (Al, Cu, Fe, In, Mn, Si
184 and Zn) were analysed every two months for each experiment (harbor and laboratory monitoring).
185 To determine the total metal concentrations, sediment samples were digested by the alkaline fusion
186 method following the ISO standard 14869-2.

187

188 *2.5. Sequential extraction method*

189

190 The chemical distribution in different fractions of sediment (acid-soluble, reducible, oxidizable and
191 residual) of elements constituting the galvanic anode was determined by a sequential extraction
192 method that was proposed by the European Union's Standards, Measurements and testing program
193 (SM&T, formerly BCR). A detailed description of the method is found in Rauret et al. (1999) and
194 consisted of three steps of successive extractions that allow for the part of the elements that are
195 associated with one of the following fractions to be known:
196 *Acid-soluble fraction (fraction F1):* The metals associated with this fraction are specifically non-
197 adsorbed to solid particles (exchangeable metals) or are precipitated with natural carbonated forms,

198 which are sensitive to pH variation. This fraction is the most labile linked to the sediment and is
199 considered to be the most dangerous for the environment.
200 *Reducible fraction (fraction F2):* This fraction contains metals bound to iron and manganese oxides
201 that may be released if the sediment changes from the oxic to the anoxic state.
202 *Oxidizable fraction (fraction F3):* This fraction includes metals linked to organic matter and
203 sulfides that can be released under oxidizing conditions.
204 A fourth fraction, called *residual fraction*, was determined for each metal by the difference
205 between their total concentration and the sum of the concentrations that were obtained in the three
206 previous fractions (F1+F2+F3). The residual fraction represents the parts of metal that are associated
207 with minerals contained in the crystalline structure of solid particles (natural fraction) and are not
208 being removed from the sediment.
209
210 *2.6. Analytical method*
211
212 The analyses of elements (Al, Cu, Fe, In, Mn, Si, Zn) were carried out by ICP-AES (Vista MPX,
213 Agilent Technologies® Santa Clara, USA).
214 The accuracy of the analytical procedure for total metal determinations was checked using CRM
215 PACS-3 (Marine Sediment Reference Material for Trace Metals) available from INMS (Institute for
216 National Measurement Standards) of the NRC (National Research Council Canada). The relative
217 errors that were calculated between the experimental and certified concentrations were satisfactory for
218 environmental analysis with values lower than 9% for all concentrations. Another certified reference
219 material (BCR®-483, extractable trace elements in sewage sludge amended soil) was used to check the
220 accuracy of the sequential extraction procedure. For this last evaluation, only 2 metals (Cu and Zn)
221 could have been checked, since the other metals were not certified by CRM. Good results were
222 obtained for the first step with less than 1% relative errors and less than 20% relative errors were
223 calculated in steps 2 and 3.
224

225 *2.7. Sediment quality guidelines*

226

227 The total concentrations of elements recorded in sediments were compared to French
228 recommendations (GEODE, 2012; RECORD, 2017) relative to dredged sediment dumping operations,
229 which were established taken under the guidelines of the international OSPAR Convention of 1992.
230 Two levels (N1 and N2) were determined by the GEODE for 8 elements: As, Cd, Cr, Cu, Hg, Ni, Pb
231 and Zn. Level N1 gives the concentrations with no or an insignificant potential impact, for which the
232 dumping maybe authorized but a follow-up study is required from the overtaking of this threshold.
233 Level N2 gives the concentrations above which the dumping not maybe authorized, only if proof is
234 brought that it is the least harmful solution for the aquatic and ground environment.

235 The total concentrations of elements were also compared to the sediment quality guidelines (SQGs)
236 for marine ecosystems, such as ERL (effects range-low) and ERM (effects range-median) values
237 (Long et al., 1995) and TEL (threshold effect level) and PEL (probable effect level) values
238 (Macdonald et al., 1996). These SQGs were assessed from statistical analyses of data collected in the
239 sediments of North America and provide classifications of sediments in relation to their contamination
240 state to prioritize concerning areas (Macdonald et al., 1996; Long et al., 1998). ERL and ERM were
241 determined based on the chemical concentrations that are linked to adverse effects on organisms and
242 delineate 3 concentration ranges (Byrkit, 1975 in Long et al., 1995): concentration below the ERL
243 value representing the minimal-effects range of the sediment associated with the chemical on
244 organisms (< 10% of biota); the concentrations equal to and above the ERL value and below the ERM
245 value representing a possible-effects range; the concentration above the ERM value representing a
246 probable-effects range (≥ 50% of biota). TEL and PEL represent the concentrations that are associated
247 with the observed and non observed effects and give adverse effects that are expected to occur rarely
248 or frequently, respectively (Macdonald et al., 1996; Rahman et al., 2014a).

249

250 *2.8. Sediment quality assessment*

251

252 To assess the level of anthropogenic pollution of the sediments, the enrichment factors (EF_i) were
253 calculated after normalization of the total element concentrations C_i (Salati and Moore, 2010; Zahra et
254 al., 2014) and selection of a reference area. Normalization is defined as a procedure to correct
255 contaminant concentrations for the influence of the natural variability in sediment composition (grain
256 size, organic matter or mineralogy) and is recommended by the OSPAR Convention (OSPAR
257 Commission, 2014). An abundant element of the fine fraction (rich in aluminosilicates), such as Al,
258 Fe, Mn or Sc, is currently chosen to normalize the metal concentration (C_i) of sediment (Zahra et al.,
259 2014; Pourabadehei and Mulligan, 2016; Ranjbar Jafarabadi et al., 2017; Gargouri et al., 2018; Jahan
260 and Strezov, 2018; Kim et al., 2018; Savitha et al., 2018; Tunca et al., 2018). Here, the percentage of
261 the 63 µm fraction (%63) that was considered to represent the fine fraction was preferred to normalize
262 the metal concentrations. Point 1 (for harbor monitoring) and tank 1 (for laboratory experiment) were
263 chosen as reference areas to calculate the enrichment factor as in Eq. (1).
264

265 $$EF_i = \frac{(C_i / \%63)_{sample}}{(C_i / \%63)_{reference}} \qquad \text{Eq. (1)}$$

266

267 Based on EF_i values, Hasan et al. (2013) suggested seven categories of sediment metal enrichment: no
268 enrichment of sediment presenting EF < 1, minor enrichment with EF from 1 to 3, moderate
269 enrichment with EF from 3 to 5, moderately severe enrichment with EF from 5 to 10, severe
270 enrichment with EF from 10 to 25, very severe enrichment with EF from 25 to 50 and extremely
271 severe enrichment with EF ≥ 50.
272

273 *2.9. Ecological risk assessment*
274

275 To assess the ecological risk of the sediments in relation to their metal concentrations, different indices
276 are often used, such as individual potential ecological risk factor E_r^i, the toxic unit (TU) and the mean
277 effect range-median quotient (m-ERMq).

Hakanson (1980) was the first to develop an individual potential ecological risk factor (E_r^i) by using Eq. (2), as follows:

$$E_r^i = T_i . Cf_i \qquad \text{Eq. (2)}$$

where T_i is the toxic response factor associated with the element i and Cf_i is the contamination factor for the same element. But, as Brady et al. (2015) who proposed a modified pollution index based on using the enrichment factor instead of the contamination factor Cf_i to take consider the non-conservative behavior of sediments, Gargouri et al. (2018) proposed a modified ecological risk factor. Then, in this paper, the authors used the modified individual potential ecological risk factor mE_r^i, as the following Eq. (3):

$$mE_r^i = T_i . EF_i \qquad \text{Eq. (3)}$$

where EF_i is the enrichment factor of the element i based on its normalized concentrations to percentage of fine fraction < 63 µm (Eq. (1)). Then, the risk factor was described by the original classification of Hakanson (1980): < 40, 40 to 80, 80 to 160, 160 to 320 and ≥ 320, which involved low potential ecological risk, moderate potential ecological risk, considerable potential ecological risk, high potential ecological risk and very high potential ecological risk. In this work, only Cu and Zn could have been associated with T_i, since these factors were only established for the following metals: As = 10, Cd = 30, Cr = 2, Cu = Pb = 5, Hg = 40 and Zn = 1 (Hakanson, 1980).

The toxic unit (TU) is related to the toxic effects of elements on living organisms and was proposed by Long et al. (1998) as following Eq. (4):

$$TU = C_i / PEL_i \qquad \text{Eq. (4)}$$

According to the method, TU < 0.1 is a 10% probability of being toxic, 0.11 < TU < 1.5 is a 25% probability of being toxic, 1.51 < TU < 2.3 is a 50% probability of being toxic, and TU > 2.3 is a 76% probability of being toxic.

The mean effect range-median quotient (m-ERMq) was suggested by Long et al. (2000) as a method to understand the toxic effects on living organisms by taking account all the elements in the studied environment (Tunca et al., 2018). This index value is determined by the following Eq. (5):

$$\text{m-ERMq} = \frac{\Sigma C_i / ERM_i}{n} \qquad \text{Eq. (5)}$$

with n, the number of considered elements.

According to the method, m-ERMq < 0.1 is a 9% probability of being toxic, 0.11 < m-ERMq < 0.5 is a 21% probability of being toxic, 0.51 < m-ERMq < 1.5 is a 49% probability of being toxic, and m-ERMq > 1.50 is a 76% probability of being toxic (Long et al. 2000).

2.10. Statistical analyses

The analyses were conducted for each experiment (annual in situ monitoring, with experiments performed by caging and in the laboratory) using the software Statview 5.0 (SAS). To assess differences in the biochemical responses between sites and between dates of sampling, data were analyzed with a one-factor analysis of variance (ANOVAs) followed by Student's Newman-Keuls post hoc tests (SNK). Pairwise comparisons were then achieved between the groups. Levels of statistical significance were set at $p < 0.05$.

3. Results and discussion

3.1. Physical chemical characterizations of sediments in both studied areas

331 The results of the structural parameters (TOC and fine fraction < 63 µm) indicated significantly ($p < 0.001$) higher levels of TOC (37.4 ± 2.6%) in harbor sediments submitted to a weaker condition of agitation (point 3) than in sediments located at points 2 (23.1 ± 6.1%) and 1 (27.5 ± 5.1%), which were under stronger agitation. No significant differences were calculated between the fine fraction levels of harbor sediments collected at point 3 (71.2 ± 20.0%), point 2 (78.6 ± 10.6%) and point 1 (80.0 ± 9.4%). In sediments monitored in all tanks of the laboratory experiment, reproducing the anode degradation, TOC and fine fraction levels were similar under all conditions of agitation, and these levels were close to those measured in harbor sediments exposed to agitation (point 2). No significant differences in the TOC and fine fraction levels were recorded during the time of both monitoring (in harbor and in laboratory).

341 All these results were similar to those monitored in harbor areas (Stronkhorst and Hattum, 2003). They showed that the characterizations of sediments exposed in laboratory experiments reproduced the in situ harbor conditions well enough, with the exception of lower TOC levels recorded in the sediments of tank 3 under weak agitation.

345

346 *2.1 Total concentrations in sediments*

347

348 Table 1 relates the concentrations of elements measured in sediments collected in the harbor near (0 m) or distant from anodes (15 m), at point 1 (reference area), point 2 (agitated area) and point 3 (non-agitated area), during 42 months of monitoring. The first year of monitoring (Sept. 2012 to Sept. 2013) corresponding to the period prior to anode implantation, sediments were considered as homogeneous near and at 15 m away from the docks. Thus, analyses were performed only on sediments at proximity of the docks (0 m). These concentrations were compared to SQGs and GEODE levels (N1 and N2) that were only reported for Cu and Zn, since the other elements were not documented.

356 No significant differences in concentrations were observed in the harbor sediments of points 1 and 2. At these points, the Cu and Zn concentrations were relatively stable during the 42 months of

358 monitoring in sediments located at proximity of the anodes. These concentrations were 2 to 3 times
359 lower than those measured in the sediments of point 3 (non-agitated area), in which higher significant
360 ($p < 0.0001$) concentrations of Al and Fe were recorded. Then, Cu and Zn concentrations increased
361 with time (+86% for Cu and +137% for Zn) to respectively reach 51.4 mg kg^{-1} and 347 mg kg^{-1} during
362 the last months of monitoring. Despite its increase, Cu concentrations remained inferior to the N1
363 level of the French guidelines GEODE. This was not the case for Zn concentrations in the same
364 sediments that exceeded the N1 level (276 mg kg^{-1}) during the last year of monitoring (2016-2017).
365 The evaluation of the sediment quality was also discussed based on the comparison of the monitored
366 sediment concentrations with the two sets of SQGs guidelines, the ERLs/ERMs and TELs/PELs (Long
367 et al., 1998). Cu concentrations sometimes exceeded the TEL in the sediments of points 1, 2 and 3 and
368 were regularly over the ERL in the sediments of point 3 during the 42 months of monitoring. The Zn
369 concentrations that were recorded in the sediments of point 3 were over TEL, regularly close to the
370 ERL, and during the last year (2016 - 2017) of monitoring, exceeded the PEL and were close to the
371 ERM.
372
373
374 Table 1: Concentrations of elements (constituting galvanic anodes) researched in sediments collected in situ
375 harbor monitoring in the reference area (point 1), near anodes (0 m) or distant from anodes (15 m) under agitated
376 (point 2) and non-agitated (point 3) conditions of the harbor between September 2012 and September 2013
377 (before anode implementation) and between January 2015 and June 2017 (after anode implementation).
378 Concentrations are compared to the national N1/N2 guidelines (GEODE levels) and SQGs.

Reference condition in harbor (point 1)														
	Al		Cu		Fe		In		Mn		Si		Zn	
mg kg^{-1} dw	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m
Sep-12	11478	-	24.2	-	5754	-	nd	-	89	-	290651	-	242	-
Jan-13	23133	-	25.2	-	12934	-	< 4	-	210	-	179537	-	69	-
May-13	24185	-	23.0	-	13991	-	< 4	-	214	-	-	-	100	-
Sep-13	26259	-	30.3	-	14927	-	-	-	212	-	176144	-	87	-
Jan-15	26618	-	11.7	-	13122	-	-	-	193	-	207403	-	70	-
Jul-15	36519	-	27.5	-	20804	-	10.2	-	228	-	140405	-	108	-
Feb-2016	29765	-	11.4	-	15735	-	12.0	-	221	-	172049	-	69	-
Jul-16	32351	-	13.5	-	16486	-	10.3	-	214	-	155996	-	76	-
Feb-2017	32906	-	10.3	-	17176	-	12.6	-	280	-	163232	-	78	-
Jun-17	31419	-	12.3	-	16806	-	11.1	-	222	-	172385	-	73	-
Agitated condition in harbor (point 2)														
	Al		Cu		Fe		In		Mn		Si		Zn	
mg kg^{-1} dw	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m
Sep-12	19035	-	14.9	-	11046	-	nd	-	171	-	161203	-	70	-
Jan-13	17595	-	17.2	-	10215	-	nd	-	152	-	287124	-	47	-
May-13	25436	-	25.2	-	15436	-	< 4	-	248	-	-	-	109	-
Sep-13	26251	-	25.5	-	15451	-	< 4	-	211	-	200618	-	97	-
Jan-15	30884	20524	12.1	8.0	17016	9967	14.9	6.1	296	151	148202	264075	72	43
Jul-15	29056	15167	11.9	4.6	15471	6500	6.7	< 4	203	100	176487	326341	77	25
Feb-2016	26187	25074	10.6	8.0	13880	13166	10.3	< 4	222	213	202979	219363	54	49
Jul-16	27839	28508	11.5	14.1	14020	14309	7.0	9.9	188	187	194631	196485	68	73
Feb-2017	29782	18545	10.5	8.5	15982	8485	10.6	6.6	232	139	188219	300333	67	33
Jun-17	23887	13959	14.9	1.7	12293	5558	8.6	< 4	174	84	242662	345844	49	16
Non-agitated condition in harbor (point 3)														
	Al		Cu		Fe		In		Mn		Si		Zn	
mg kg^{-1} dw	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m
Sep-12	32063	-	27.6	-	17092	-	< 4	-	214	-	158290	-	146	-
Jan-13	33078	-	40.7	-	19870	-	nd	-	256	-	148529	-	142	-
May-13	31314	-	47.5	-	20458	-	< 4	-	278	-	-	-	186	-
Sep-13	36452	-	31.7	-	19739	-	< 4	-	244	-	159760	-	122	-
Jan-15	36299	37733	35.7	23.0	21667	21612	11.5	11.1	227	242	136244	137435	152	108
Jul-15	36631	27136	39.6	12.2	21873	13745	11.8	< 4	222	191	138336	179190	144	65
Feb-2016	40833	35961	42.9	37.5	21997	20685	10.9	10.9	217	215	133126	137663	225	136
Jul-16	45758	35985	43.0	48.2	19345	21450	14.7	10.7	205	217	109697	131955	357	153
Feb-2017	49501	37106	56.0	41.6	22565	21095	15.4	12.6	226	225	111007	135358	371	147
Jun-17	47379	36542	51.4	59.0	20620	21131	16.0	8.5	211	206	120954	136805	347	196
GEODE (N1)	-		45		-		-		-		-		276	
GEODE (N2)	-		90		-		-		-		-		552	
TEL[(a)]	-		18.7		-		-		-		-		124	
PEL[(b)]	-		108		-		-		-		-		271	
ERL[(c)]	-		34		-		-		-		-		150	
ERM[(d)]	-		270		-		-		-		-		410	

[(a)]Threshold effect level, [(b)]probable effect level, [(c)]effet range-low, [(d)]effect range-median nd: not detected

Table 2 reported concentrations of elements researched in sediments exposed in the laboratory to anodes in agitated (tank 2) and non-agitated conditions (tank 3). Tank 1 referred to uncontaminated sediment by anodes (reference). For the harbor sediments, only the Cu and Zn concentrations could have been compared to the GEODE levels, and the SQGs guidelines which were reported in the same Table.

In the sediments that were monitored in all tanks during the 18 months of experiment, the concentrations of In, Mn, Fe and Si were stable, and the Cu concentrations presented a small increase ($p < 0{,}008$). At the same time, concentrations of Al increased in tank 3 ($p < 0.0001$) and in tank 2 ($p < 0.001$), and the higher rises were given for Zn concentrations in the sediments of tank 3, with +1130% ($p < 0.0001$), and tank 2 with +337% ($p < 0.0005$). A few increases of Zn were simultaneously

390 observed in the sediments of tank 1 (control) with +187% ($p < 0.002$), which suggested small inputs
391 with natural seawater. In the controlled sediments (tank 1) and sediments of tank 2, no concentrations
392 exceeded the GEODE levels and the SQGs guidelines, except the TEL of Zn for sediments collected
393 in November 2015. Then, natural contributions of Zn (referred by the levels measured in the control
394 tank) were considered in all tanks during the laboratory experiment. Taking account this hypothesis,
395 sediments of tank 3 collected after 6 months of experiment presented Zn concentrations that exceeded
396 all sets of guidelines, including ERM and the N2 level of GEODE, especially in July 2015 and March
397 2016. Although Zn concentrations were more important at the end of the experiment, the highest level
398 was recorded in July 2015. The thickness of corrosion product formed on anode surface is not
399 homogeneous and not adherent (Deborde et al, 2015), which may explain the non-continuous release
400 of elements in the water and pics of concentration in sediment before the end of monitoring.
401 Based on these concentrations, sediments located near the anodes in the non-agitated harbor area, may
402 represent a possible risk of toxic effect on organisms linked to Zn concentrations (Rahman et al.,
403 2014a; Tunca et al., 2018). These results therefore justify the following analyses conducted to assess
404 the quality of harbor sediments.
405

406 Table 2: Concentrations of elements constituting galvanic anodes researched in sediments exposed to anodes
407 under agitated and non-agitated conditions during a laboratory experiment. Concentrations are compared to the
408 national N1/N2 guidelines (GEODE levels) and SQGs.

Reference condition in laboratory experiment (tank 1)							
mg kg^{-1} dw	**Al**	**Cu**	**Fe**	**In**	**Mn**	**Si**	**Zn**
Sep-14	15864	7.7	10210	5.5	174	203777	39
Nov-14	17332	7.2	10770	5.2	171	192295	52
Jan-15	18322	10.1	11170	4.2	175	194288	60
Mar-15	20900	10.7	12749	3.8	181	181751	78
May-15	18924	9.2	11529	3.8	171	196545	68
Jul-15	20040	10.0	12118	3.1	171	193072	86
Sep-15	19368	9.7	11633	1.5	169	193318	82
Nov-15	24795	20.2	14574	3.4	184	172167	139
Jan-16	21885	16.6	12837	2.9	176	194215	117
Mar-16	21840	15.9	12911	3.8	178	191534	112
Agitated condition in laboratory experiment (Tank 2)							
mg kg^{-1} dw	**Al**	**Cu**	**Fe**	**In**	**Mn**	**Si**	**Zn**
Sep-14	16727	8.7	10057	4.5	171	187908	48
Nov-14	18951	10.1	10652	4.1	172	195071	90
Jan-15	23087	14.4	12507	5.6	178	186675	125
Mar-15	20733	12.2	11710	5.0	174	186197	103
May-15	23835	11.7	12240	4.3	178	195620	124
Jul-15	32685	20.5	14715	5.6	176	174767	226
Sep-15	26268	15.5	14650	3.9	188	185661	170
Nov-15	46829	24.3	15523	8.6	172	160495	291
Jan-16	42743	16.9	14100	7.5	178	172588	239
Mar-16	32957	17.0	13808	3.3	173	191058	210
Non-agitated conditionin laboratory experiment (Tank 3)							
mg kg^{-1} dw	**Al**	**Cu**	**Fe**	**In**	**Mn**	**Si**	**Zn**
Sep-14	16423	8.8	10354	5.3	176	199151	45
Nov-14	18584	7.1	10767	3.9	179	192421	71
Jan-15	21256	9.5	11192	4.5	174	187505	89
Mar-15	27521	11.0	10105	4.4	158	184918	229
May-15	33940	11.0	11562	5.3	166	176257	324
Jul-15	47057	13.7	11349	8.1	154	160650	872
Sep-15	36022	19.0	12769	5.7	168	178370	448
Nov-15	35472	14.3	12497	5.0	175	174403	339
Jan-16	33832	13.2	11837	4.1	171	177982	331
Mar-16	36521	18.3	12857	5.0	177	174338	553
GEODE (N1)	-	45	-	-	-	-	276
GEODE (N2)	-	90	-	-	-	-	552
TEL[(a)]	-	18.7	-	-	-	-	124
PEL[(b)]	-	108	-	-	-	-	271
ERL[(c)]	-	34	-	-	-	-	150
ERM[(d)]	-	270	-	-	-	-	410

[(a)]Threshold effect level, [(b)]probable effect level, [(c)]effet range-low, [(d)]effect range-median nd: not detected

409

410

411 *2.2 Sediment quality assessment*

412

413 *2.2.1 Enrichment factors*

414

415 Table 3 reported enrichment factors (EF) calculated for sediments monitored in the harbor (point 2 and
416 point 3) and in the tanks exposed to one anode during the laboratory experiment (tank 2 and tank 3). In
417 the harbor, EFs were also calculated for sediment located at 15 m from the anodes. The EF values
418 helped us to identify the elements in sediments, which present an anthropogenic origin. According to
419 the Hasan et al. (2013), sediments of the harbor that were collected in proximity of the anodes in non-
420 agitated condition (point 3) can be classified as moderate to moderately severely enriched by Cu and
421 Zn, with respectively maximal values of EF = 10 and EF = 9 recorded at the end of monitoring. For
422 the same period, these sediments presented minor enrichments in Al and In, which did not exceed EF
423 of 3. At 15 m from point 3, minor to moderate Cu and Zn enrichments of sediments were calculated,
424 which suggested widespread contamination. The results achieved for sediments that are exposed to
425 anodes in non-agitated condition during the laboratory experiment (tank 3) showed the same levels of
426 Zn enrichment factors compared to in situ enrichment. The highest Zn EF were measured earlier, in
427 July (EF = 11) and September 2015 (EF = 6). The sediments that were collected during the months
428 following this operation were less impacted and presented moderate enrichment in Zn (EF values of 3
429 to 5), which suggested a dispersion of Zn in seawaters. However, if minor Al and In enrichment
430 factors (EF inferior of 4) were observed in the same sediments that were exposed to anodes in
431 laboratory conditions, these sediments were not or were slightly affected by a Cu enrichment ($EF < 2$).
432 In their study, Gabelle et al. (2012) related minor to moderate Al enrichment factors of harbor
433 sediments collected near or at 20 m from anodes with a maximal average value given for the Al EF of
434 2.8 ± 0.2. During our work, the same Al enrichment factors were recorded in sediments that were
435 monitored either in a harbor environment or under laboratory exposition conditions. Al is the major
436 component of the anode with 93.2%, and because of its mainly non soluble form, we might think that
437 the Al dissolved from galvanic anodes would have been induced quickly to accumulate into sediments.

Indeed, Al is known for its colloidal behavior, which conducts it to form rapid aggregates during the flocculation process. Al is integrated to sediment when the forming precipitates (called flocs) settled according to their weight. However, Al enrichment factors recorded in all sediments of both experiments (in situ and in laboratory), remained inferior to 3 and were considered to be minor. One explanation could be linked to the low kinetic of aggregation, which would conduct to the continuous dispersion of Al in the water even under weak agitation of the middle. The highest levels of metallic enrichment in harbor sediments were associated with Zn and Cu, while these elements are, respectively, the second (with 2.5 to 6.5%) and one of the last elements (with 0.006%) composing the anode. Such levels of enrichment were already given for harbor sediments but were often associated with other sources of contamination, such as antifouling paints (Singh and Turner, 2009; Pourabadehei and Mulligan, 2016; Amara et al., 2018) or urban runoff (Macdonald et al., 1996; Nabizadeh et al., 2005; Reddy et al., 2014). If the results of our laboratory experiment confirmed the same enrichment of Zn in sediments exposed to the anode (without ruling out the hypothesis of another source of contamination), they clearly did not attribute the Cu enrichment of sediment to the anode dissolution. The high levels of Cu recorded in the sediments harbor probably is associated with the other sources of contamination linked to the harbor environment cited previously. Our attention was retained by the In results. This element represents 0.01% of the anode composition but minor enrichments of harbor sediments were also observed, and it was confirmed or enhanced during the simulation of anode dissolution performed during our laboratory experiment. This element is not usually met in the harbor environment, which was confirmed at the beginning of our monitoring by very low values of EF. The origin of this element in the marine environment may be associated to e-waste generated by electronic manufacturing (Chen et al., 2015; Jensen et al., 2018). In our study, we demonstrated that this element might be considered to be a tracer of the anode dissolution, especially for sediments that are monitored in non-agitated environments.

Table 3: Enrichment factors calculated from concentrations of elements researched in sediments collected in situ (harbor monitoring) near anodes (0 m) or distant from anodes (15 m) under agitated (point 2) and non-agitated (point 3) conditions, between September 2012 and September 2013 (before anode implementation) and between January 2015 and June 2017 (after anode implementation in November 2014 for agitated condition and August 2014 for non-agitated condition). Enrichment factors calculated in sediments exposed to anodes in the laboratory experiment were also reported for agitated (tank 2) and non-agitated (tank 3) conditions.

HARBOR MONITORING

$EF_i = (C/\%63\mu m)_i / (C/\%63\mu m)_{pt1}$

	Al		Cu		Fe		In		Mn		Si		Zn	
	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m
Agitated condition (point 2)														
Sep-12	0.7	-	0.3	-	0.8	-	-	-	0.8	-	0.2	-	0.1	-
Jan-13	0.9	-	0.8	-	0.9	-	-	-	0.8	-	1.9	-	0.8	-
May-13	1.1	-	1.1	-	1.1	-	-	-	1.2	-	-	-	1.1	-
Sep-13	1.0	-	0.8	-	1.0	-	-	-	1.0	-	1.1	-	1.1	-
Jan-15	1.0	0.9	0.9	0.8	1.1	0.9	-	-	1.3	1.0	0.6	1.6	0.9	0.7
Jul-15	0.8	1.1	0.5	0.4	0.8	0.8	0.7	-	0.9	1.2	1.3	6.3	0.7	0.6
Feb-16	0.8	0.9	0.9	0.7	0.8	0.9	0.8	-	0.9	1.0	1.1	1.3	0.7	0.7
Jul-16	0.8	0.9	0.8	1.0	0.8	0.9	0.7	0.9	0.8	0.9	1.2	1.2	0.9	1.0
Feb-17	1.0	0.6	1.1	0.9	1.0	0.5	0.9	0.6	0.9	0.6	1.2	2.0	0.9	0.5
Jun-17	0.8	0.7	1.4	0.2	0.8	0.5	0.9	-	0.9	0.6	1.6	3.1	0.8	0.3
Non-agitated condition (point 3)														
Sep-12	1.0	-	0.4	-	1.1	-	-	-	0.9	-	0.2	-	0.2	-
Jan-13	1.2	-	1.4	-	1.3	-	-	-	1.0	-	0.7	-	1.7	-
May-13	1.2	-	1.9	-	1.4	-	-	-	1.2	-	-	-	1.7	-
Sep-13	1.3	-	0.9	-	1.2	-	-	-	1.0	-	0.8	-	1.3	-
Jan-15	1.2	1.2	2.6	1.6	1.4	1.4	-	-	1.0	1.0	0.6	0.5	1.9	1.3
Jul-15	1.0	0.7	1.4	0.4	1.0	0.6	1.1	-	0.9	0.8	0.9	1.2	1.3	0.6
Feb-16	1.3	1.0	3.5	2.6	1.3	1.1	0.8	0.7	0.9	0.8	0.7	0.6	3.0	1.6
Jul-16	1.5	1.1	3.4	3.4	1.3	1.3	1.5	1.0	1.0	1.0	0.8	0.8	5.1	2.0
Feb-17	2.7	1.1	9.7	4.0	2.4	1.2	2.2	1.0	1.4	0.8	1.2	0.8	8.6	1.9
Jun-17	1.8	1.0	5.1	4.1	1.5	1.1	1.7	0.6	1.2	0.8	0.9	0.7	5.8	2.3

LABORATORY EXPERIMENT

$EF_i = (C/\%63\mu m)_i / (C/\%63\mu m)_{tank1}$

	Al		Cu		Fe		In		Mn		Si		Zn	
	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m
Agitated condition (tank 2)														
Sep-14	1.1	-	1.2	-	1.0	-	0.8	-	1.0	-	1.0	-	1.2	-
Nov-14	1.1	-	1.4	-	1.0	-	0.8	-	1.0	-	1.0	-	1.8	-
Jan-15	1,3	-	1.5	-	1.2	-	1.4	-	1.0	-	1.0	-	2.2	-
Mar-15	1.0	-	1.2	-	0.9	-	1.3	-	1.0	-	1.1	-	1.4	-
May-15	1.3	-	1.3	-	1.1	-	1.2	-	1.1	-	1.0	-	1.9	-
Jul-15	1.7	-	2.1	-	1.3	-	1.8	-	1.1	-	0.9	-	2.7	-
Sep-15	1.4	-	1.7	-	1.3	-	2.6	-	1.1	-	1.0	-	2.1	-
Nov-15	1.9	-	1.2	-	1.1	-	2.6	-	1.0	-	1.0	-	2.1	-
Jan-16	2.0	-	1.0	-	1.1	-	2.7	-	1.0	-	0.9	-	2.1	-
Mar-16	1.6	-	1.1	-	1.1	-	0.9	-	1.0	-	1.0	-	1.9	-
Non-agitated condition (tank 3)														
Sep-14	1.1	-	1.2	-	1.1	-	1.0	-	1.1	-	1.1	-	1.2	-
Nov-14	1.2	-	1.1	-	1.1	-	0.8	-	1.1	-	1.1	-	1.5	-
Jan-15	1.3	-	1.0	-	1.1	-	1.2	-	1.1	-	1.0	-	1.6	-
Mar-15	1.4	-	1.1	-	0.9	-	1.2	-	0.9	-	1.1	-	3.2	-
May-15	1.9	-	1.3	-	1.1	-	1.5	-	1.0	-	1.0	-	5.1	-
Jul-15	2.5	-	1.5	-	1.0	-	2.8	-	1.0	-	0.9	-	11.0	-
Sep-15	2.0	-	2.1	-	1.2	-	4.0	-	1.1	-	1.0	-	5.9	-
Nov-15	1.5	-	0.8	-	0.9	-	1.6	-	1.0	-	1.1	-	2.6	-
Jan-16	1.7	-	0.9	-	1.0	-	1.5	-	1.1	-	1.0	-	3.0	-
Mar-16	1.8	-	1.2	-	1.1	-	1.4	-	1.1	-	1.0	-	5.3	-

Enrichment Factor classification according Hasan et al. (2013) :

< 1	no enrichment	1 - 3	minor enrichment	3 - 5	moderate enrichment	5 - 10	moderately severe enrichment

2.3 Ecological risk assessment

To assess the effects of elements on the living organisms in the different sediments, we selected three indicators that are usually used to assess the effect of sediment pollution on the ecosystem: the modified ecological risk assessment (E_R^i), the toxic unit (TU) and the mean effect range-median quotient (m-ERMq) (Table 4). The results associated with sediments collected in the harbor and during the laboratory experiment were reported in Table 4, but only for Zn and Cu since no references were given for the other elements constituting the anode, such as Al and In. In this study, sediments exposed to the condition of agitation (point 2 and tank 2) presented low ecological risk ($mE_i < 40$). The same observation was given for sediments under non-agitation conditions, except for one sediment collected at the end of the monitoring period (February 2017), which presented a moderate risk with mE_i of 49. The sediments in majority showed a TU < 1.5 except for those exposed to the anode after July 2015 for which the probability of being toxic increased to 50% with a maximum of 76%. The results of m-ERMq indicated the global toxic effect of Cu and Zn. The majority of sediments (whatever the condition of agitation) were classified on the second grade of the 4-level scale with a 21% toxicity level. However, this level of toxicity increased to 49% for sediments exposed to non-agitated conditions after one year of anode implementation in the harbor or after 9 months (July 2015) for the laboratory experiment. These results confirmed that the condition of agitation considerately influenced the potential effect of sediments to organisms, especially when these sediments were collected near the anodes. For Al and In, which were found to uncontaminate to moderately contaminate the sediment, it is difficult to assess their possible effect on organisms on the basis of the previous indicators. Previous works demonstrated the biological effects of Al in the aquatic environment but only in low pH conditions of the environment (pH < 4.5 where Al^{3+} form of Al is dominant), which was not the environmental condition of these works (Gostomski, 1990; Rosseland et al., 1990, Wilson, 2012).

Table 4: Modified ecological risk assessment (E_R^i), toxic unit (TU) and mean effect range-median quotient (m-ERMq) calculated from concentrations of Cu and Zn researched in sediments collected in situ harbor monitoring near anodes (0 m) or distant from anodes (15 m) under agitated (point 2) and non-agitated (point 3) conditions, between September 2012 and September 2013 (before anode implementation) and between January 2015 and June 2017 (after anode implementation in November 2014 for agitated condition and August 2014 for non-agitated condition). The same factors calculated in sediments exposed to anodes in laboratory experiments, were also reported for agitated (tank 2) and non-agitated (tank 3) conditions.

HARBOR MONITORING

	$mE_r^i = T_i \times EF_i$ [(a)]				$TU = C_i / PEL_i$ [(b)]				m-ERMq = $[\Sigma C_i/ERM]/n$ [(c)]	
	Cu		Zn		Cu		Zn		ΣM_i	
	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m
Agitated condition (point 2)										
Sep-12	1	-	0	-	0.14	-	0.26	-	0.11	-
Jan-13	4	-	1	-	0.16	-	0.17	-	0.09	-
May-13	6	-	1	-	0.23	-	0.40	-	0.19	-
Sep-13	4	-	1	-	0.24	-	0.36	-	0.17	-
Jan-15	4	4	1	1	0.11	0.07	0.27	0.16	0.11	0.07
Jul-15	2	2	1	1	0.11	0.04	0.28	0.09	0.12	0.04
Feb-16	4	4	1	1	0.10	0.07	0.20	0.18	0.09	0.07
Jul-16	4	5	1	1	0.11	0.13	0.25	0.27	0.10	0.12
Feb-17	5	5	1	1	0.10	0.08	0.25	0.12	0.10	0.06
Jun-17	7	1	1	0	0.14	0.02	0.18	0.06	0.09	0.02
Non-agitated condition (point 3)										
Sep-12	2	-	0	-	0.26	-	0.54	-	0.23	-
Jan-13	7	-	2	-	0.38	-	0.52	-	0.25	-
May-13	10	-	2	-	0.44	-	0.69	-	0.31	-
Sep-13	5	-	1	-	0.29	-	0.45	-	0.21	-
Jan-15	13	8	2	1	0.33	0.21	0.56	0.40	0.25	0.17
Jul-15	7	2	1	1	0.37	0.11	0.53	0.24	0.25	0.10
Feb-16	17	13	3	2	0.40	0.35	0.83	0.50	0.35	0.24
Jul-16	17	17	5	2	0.40	0.45	1.32	0.57	0.52	0.28
Feb-17	49	20	9	2	0.52	0.39	1.37	0.54	0.56	0.26
Jun-17	25	20	6	2	0.48	0.55	1.28	0.72	0.52	0.35

LABORATORY EXPERIMENT

	Cu		Zn		Cu		Zn		ΣM_i	
	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m	0 m	15 m
Agitated condition (tank 2)										
Sep-14	6	-	1	-	0.08	-	0.18	-	0.07	-
Nov-14	7	-	2	-	0.09	-	0.33	-	0.13	-
Jan-15	7	-	2	-	0.13	-	0.46	-	0.18	-
Mar-15	6	-	1	-	0.11	-	0.38	-	0.15	-
May-15	7	-	2	-	0.11	-	0.46	-	0.17	-
Jul-15	11	-	3	-	0.19	-	0.83	-	0.31	-
Sep-15	8	-	2	-	0.14	-	0.63	-	0.24	-
Nov-15	6	-	2	-	0.22	-	1.07	-	0.40	-
Jan-16	5	-	2	-	0.16	-	0.88	-	0.32	-
Mar-16	6	-	2	-	0.16	-	0.78	-	0.29	-
Non-agitated condition (tank 3)										
Sep-14	6	-	1	-	0.08	-	0.17	-	0.07	-
Nov-14	5	-	1	-	0.09	-	0.26	-	0.10	-
Jan-15	5	-	2	-	0.13	-	0.33	-	0.13	-
Mar-15	6	-	3	-	0.11	-	0.84	-	0.30	-
May-15	6	-	5	-	0.11	-	1.19	-	0.42	-
Jul-15	7	-	11	-	0.19	-	3.22	-	1.09	-
Sep-15	11	-	6	-	0.14	-	1.65	-	0.58	-
Nov-15	4	-	3	-	0.22	-	1.25	-	0.44	-
Jan-16	4	-	3	-	0.16	-	1.22	-	0.43	-
Mar-16	6	-	5	-	0.16	-	2.04	-	0.71	-

[(a)] Modified individual potential ecological risk factor (mE_r^i) classification according Hakanson et al. (1980):
< 40 Low toxic | 40 - 80 moderate risk | 80 - 160 higher risk | 160 - 320 much higher risk

[(b)] Toxic Unit (TU) or mean PEL quotient according Tunca et al (2018) and Long et al. (1998):
< 0.1 10% | 0.11 - 1.5 25% | 1.51 - 2.3 50% | ≥ 2.3 76% probability of being toxic

[(c)] Mean ERM quotient (m-ERMq) classification according Long et al. (2000):
< 0,1 9% | 0.11 - 0.5 21% | 0.51 - 1.5 49% | ≥ 1.5 76% probability of being toxic

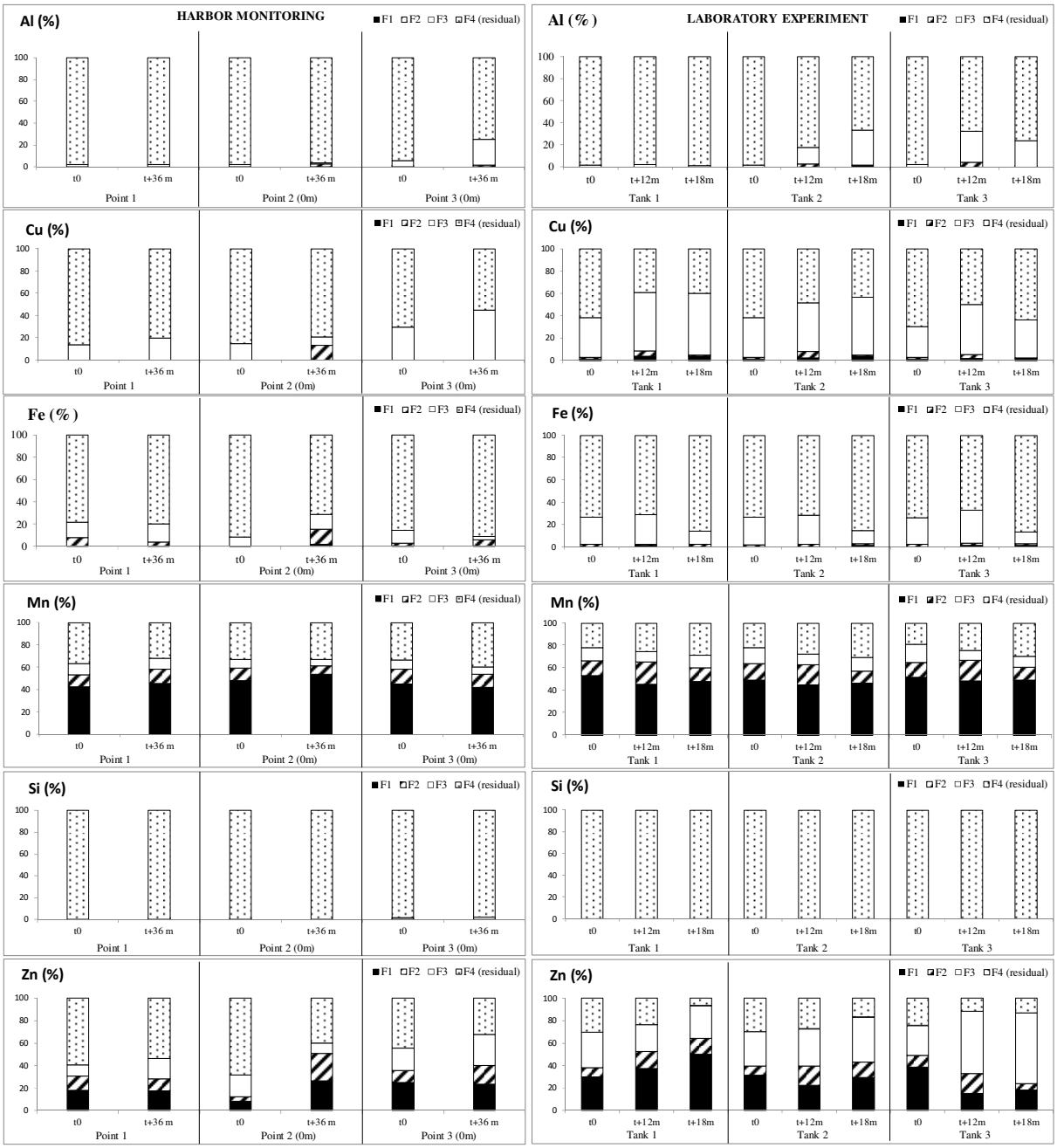
505 *2.4 Results of sequential extractions*

506

507 Although the SQGs guidelines and the previous quality indices helped us to identify the elements and
508 sites linked to a potential risk to organisms, they did not identify the chemical form of the element that
509 may be responsible for causing toxicity. Therefore, a study on the speciation of each element that was
510 released from the anode and eventually transferred to the sediments was conducted during both studies
511 (in the harbor and in the laboratory). Then, sequential extractions were performed to assess the
512 bioavailability of the elements by exploring their concentration in four fractions of the sediments:
513 acid-soluble fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4).
514 Fig. 3 shows the concentrations of elements (Al, Cu, Fe, Mn, Si and Zn) that were extracted from the
515 F1, F2, F3 and F4 fractions of sediments exposed to anodes in agitated and non-agitated conditions
516 during harbor monitoring (left graph) and the laboratory experiment (right graph). The sequential
517 extraction of In was not conclusive due to the low concentrations detected in each fraction (inferior to
518 the detection limits).
519 In harbor sediments, Al, Cu, Fe and Si were principally present in the F4 (residual, 78 to 98%)
520 fraction, Mn was mostly scavenged in the F1 (acido-soluble, 45%) fraction and Zn was distributed
521 between the F4 (residual, 60%) fraction and equally in fractions F1, F2 and F3 (10 to 17%). After 42
522 months of monitoring, Mn and Si distributions remained stable in all sediments. During the same
523 period, the oxidizable fraction (F3) of sediment collected at point 3 (under non-agitation conditions)
524 was enriched by Al, Cu and Zn while Fe was decreased in this fraction. Regarding the results of the
525 extractions performed in sediments exposed to anodes for 18 months in tank 3 (which reproduced the
526 harbor conditions of point 3), Al and Zn were similarly enriched by the F3 fraction and, at the same
527 time, a decrease in Fe occurred. The previous results showed higher organic matter, minor Al and
528 moderately severe Zn enrichment of sediments located at the proximity of the anode under non-
529 agitated conditions (point 3 and tank 3). We could suppose that Al was mobilized with time in an
530 oxidizable fraction of the sediment when organic matter increased. Humic substances dissolved in
531 seawater may represent important ligands for trace metals and stability of the complexes as functions

of the metal, such as the following decreasing scale proposed by Yang and van den Berg (2009): Cu > Zn > Fe > Al. The authors demonstrated the existence of competition between the metals for the same binding sites of humic substances and a decrease of Fe linked to humic substances with the addition of other metals. Mobilized in organic matter and the sulfides fraction (F3) of harbor sediments, Al, Cu and Zn, could be released under oxidizing conditions, which can occur if the sediment is resuspended, such as by dredging, currents, etc. (Morillo et al., 2004). In point 2 of the harbor, the evolution of the element distribution was different than in point 3, since enrichments of the F2 fraction by Zn, Fe and Cu as well as an enrichment of the F1 fraction by Zn were observed. Fraction F2 is representative of the potential element mobility under changing conditions. These differences of element mobilization were certainly linked to the difference of agitation conditions between point 3 and point 2. Actually, in the area of point 2, sediments are submitted to a resuspension technique two times per year. Pourabadehei and Mulligan (2016) showed that the effect of the resuspension technique reduced the concentration of metals in sediment and suspended matter by 24%. However, these enrichments were not significantly reproduced in tank 2 during the laboratory experiment, although, we noticed that Zn in control tank (tank 1) tended to enrich the F1 fraction with time instead of the F3 fraction as in tanks 2 and 3 exposed to the anode. This could suggest different sources of Zn in tank 1 (Zn associated with a natural origin) and Zn distribution in the sediments of tanks 2 and 3 (which would be linked to anode dissolution).

559



560

561 Fig. 3: Concentrations of elements constituting galvanic anodes researched in different fractions of sediments
562 (acid-soluble fraction F1, oxidizable fraction F2, reducible fraction F3 and residual fraction F4) exposed to
563 anodes under agitated and non-agitated conditions during in situ harbor monitoring and laboratory experiments.

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565

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4 Conclusions

These results are the first to be obtained from a long-term sediment monitoring achieved during both natural and laboratory experiments to study release of metals from Al galvanic anode dissolution in harbor applications. They demonstrated that metal enrichments in sediment were depending to the agitation condition and the metal species, but were not reliant to the metal proportion (% in mass) composing the anode. Indeed, at the end of the both experiments, high concentrations of Cu and Zn and moderate to low concentrations of Al and In were measured in sediments exposed to non-agitated conditions. If Cu and Zn levels were associated to a potential toxic effect of sediments, the experiment conducted in laboratory demonstrated that only Zn could be associated to the anode dissolution. Enrichments of Al (and In) did not present an ecological risk to the marine environment, while this element is the principal component of the anode (> 96%). The results obtained in our present study confirmed the hypothesis suggested by Deborde et al. (2015) that the corrosion product induced continuous metal diffusion towards the water column and the sediment. They added that once released, metals exhibit different behaviors related to their interaction with the environment (difference of chemical forms). Over time, the distribution study of the metals into the different fractions of sediments showed that released Zn and Al were transferred to the oxidizable fraction. These results supposed a potential mobilization of these elements from the sediment if physical-chemical changes would occur (for example during dredging operations).

On the other hand, these results suggested that In could be a good tracer of anode dissolution in harbor sediment monitored in non-agitated areas, under long-term monitoring condition (more than one year). All these results needed to be completed by further and sediment bioassays performed on living organisms to assess the potential toxic effects of Zn, Al and In that were released from the galvanic anode and that accumulated in sediments. They will be followed by the results obtained on organisms (mussels and sponges) that were exposed during the same experiments.

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