



HAL
open science

Characterization of the submarine disposal of a Bayer effluent (Gardanne alumina plant, southern France): I. Size distribution, chemical composition and settling rate of particles forming at the outfall

Stéphanie Jacquet, Christophe Monnin, Olivier Herlory, Deborah Mille, Aurélie Dufour, Benjamin Oursel, Lars-Eric Heimbürger-Boavida, Sébastien d'Onofrio, Nicolas Layglon, Cédric Garnier

► To cite this version:

Stéphanie Jacquet, Christophe Monnin, Olivier Herlory, Deborah Mille, Aurélie Dufour, et al.. Characterization of the submarine disposal of a Bayer effluent (Gardanne alumina plant, southern France): I. Size distribution, chemical composition and settling rate of particles forming at the outfall. *Chemosphere*, 2021, 263, pp.127695. 10.1016/j.chemosphere.2020.127695 . hal-02935238

HAL Id: hal-02935238

<https://hal.science/hal-02935238>

Submitted on 13 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Characterization of the submarine disposal of a Bayer effluent (Gardanne alumina**
2 **plant, southern France): I. Size distribution, chemical composition and settling rate of**
3 **particles forming at the outfall**

4
5 Stéphanie Jacquet^{1,*}, Christophe Monnin², Olivier Herlory³, Deborah Mille³, Aurélie Dufour¹,
6 Benjamin Oursel¹, Lars-Eric Heimbürger-Boavida¹, Sébastien Donofrio¹, Nicolas Layglon¹,
7 Cédric Garnier¹

8
9 ¹ Aix Marseille Université, CNRS/INSU, Université de Toulon, IRD, Mediterranean Institute
10 of Oceanography (MIO), UM 110, 13288 Marseille, France

11 ² Geosciences Environnement Toulouse, CNRS - Université Paul Sabatier – IRD
12 (Observatoire Midi-Pyrénées), 14 avenue Edouard Belin, 31400 Toulouse, France

13 ³ CREOCEAN, Valparc – Bât B, 230 avenue de Rome, 83500 La Seyne sur Mer, France

14
15 * Corresponding author: stephanie.jacquet@mio.osupytheas.fr

16
17
18
19 Chemosphere

20

21 ABSTRACT

22 The submarine discharge of the high pH clarified Bayer effluent of the Gardanne
23 alumina plant (Marseille region, France) leads to the formation of concretions at the outfall
24 324 meters underwater and to a plume of white particles. Calibration of turbidity using
25 effluent/seawater mixing experiments and in situ measurements shows that 1 turbidity unit
26 (NTU) represents about 4.7 mg L^{-1} of suspended particles, allowing to trace the effluent
27 plume in the mixing zone. The bulk chemical composition of the concretions has been
28 determined by SF-ICP-MS. Mg and Al are the major elements measured in concretions with
29 concentrations of a few hundred mg g^{-1} . Ca and S are also found at concentrations in the range
30 of mg g^{-1} . Among the measured trace elements there is a specific interest in As and V because
31 of environmental concerns pointed out by regulation authorities. Their concentrations are of
32 tens to thousands $\mu\text{g g}^{-1}$, respectively. The concentrations of the following elements are in the
33 range of a few hundreds $\mu\text{g g}^{-1}$: Si, V, K, Sr, P, As, B, Mo, Fe, Ti, Cu, Zn, Sn. The
34 concentrations of the other elements are below $1 \mu\text{g g}^{-1}$ down to a few ng g^{-1} : Rb, U, Ba, Cr,
35 Ni, Co, Sb, Mn, Ag, Cd, Pb, Hg, Th. In order to constrain the dispersion of particles in the
36 environment and to understand how chemical elements can be scavenged from or released to
37 seawater, the size distribution of particles composing the concretions has been measured by
38 settling rate experiments and, for each size class of particles, their chemical composition has
39 been determined. For example, As and V are mainly associated to particles with mean
40 diameters between 15.6 and 63 μm and settling rates around 96 m d^{-1} . Overall, all the main
41 elements (Mg, Al, Ca, S) composing concretions are associated to this size class of particles
42 which represents 53 to 60 % of the total concretion mass.

43

44 **KEYWORDS:** Bayer effluent, trace metals, settling rate, size distribution, Gardanne alumina
45 plant, Cassidaigne Canyon, Mediterranean Sea.

46 1. Introduction

47 The alumina production plant located in Gardanne (about 30 km North of Marseille in
48 Southern France) was created more than 120 years ago. It is the place where the Bayer
49 process was first implemented in 1893 at an industrial scale. It is nowadays operated by the
50 Alteo Company, which is today one of the first world producers of specialty aluminas.
51 Specialty (or chemical-grade) alumina is dedicated to technological uses at the difference with
52 metallurgical (or smelter-grade) alumina mainly used to produce aluminum by electrolysis.
53 The Bayer process is based on the dissolution of the ore (bauxites) in NaOH solutions at about
54 250°C and on the precipitation of aluminum hydroxides separated from impurities by
55 decantation and filtration. Al-hydroxides are precipitated with no addition of chemicals (that
56 for example would alter the pH), but by changing the temperature to lower their solubilities
57 and favour nucleation and growth. Oxalate produced during the alkaline degradation of the
58 organic matter contained in bauxites is removed from solution by addition of lime that leads
59 to the precipitation of calcium oxalate. Flocculating agents such as starch may be added in the
60 decanters to increase the settling rate of the particles (Hill and Sehnke, 2006). This industrial
61 process generates a residue generally called "red mud", a slurry also named Bayer residue or
62 Bayer precipitate. One also finds the ambiguous denomination Bayer liquor that can be used
63 to designate either a slurry or a clarified effluent (the liquid part of the red muds). The
64 production of one ton of alumina generates between 1 and 1.5 tons of red muds (Hill and
65 Sehnke, 2006).

66 From 1967 to the end of 2015, the Gardanne alumina plant has disposed its residues
67 (red muds) in the Mediterranean Sea through a 55 km-long pipe, 7 km of which being under
68 water. The outfall of this pipe is at a depth of 324 m at the top of the Cassidaigne Canyon
69 which cuts the continental shelf off the coast of the Calanques National Park (Figure 1). New
70 regulations in force since January 1, 2016 do not allow any longer the disposal at sea of a

71 slurry, but only that of a high pH (12.5) -high metals content clarified liquid effluent obtained
72 by filtration of the Bayer residue (Bru et al., 2014). The solid part of the waste is now stored
73 in on-land tailing ponds at the Mangegarri site close to the plant. The authorization for these
74 new operational conditions has been in place since 2016 and will expire in 2021. During this
75 5-year authorization period the company is committed to studying the environmental aspects
76 of the effluent disposal at sea. It is also committed to proposing alternative solutions to the
77 present Bayer process that would minimize, and ultimately stop the effluent disposal. The
78 long-term concern of the environmental impacts of this disposal (Dauvin, 2010) had been
79 enhanced after the Ajka (Hungary) red mud spill in 2010 (Mayes et al., 2016). Furthermore, in
80 the case of the Gardanne plant regulation authorities have pointed out particular marine
81 environmental concerns such as the formation of concretions with an important plume of
82 white suspended particles when the Bayer effluent mixes with seawater (Figure 2). According
83 to previous studies on red mud neutralization using seawater (Hanahan, 2004; Palmer et al.,
84 2009), such concretions are made up of hydrotalcite, an Mg-Al Double Layered Hydroxide
85 (Mills et al., 2012). Because of the high capacity of hydrotalcite to scavenge metals from the
86 solution (Cavani et al., 1991), concretions and particles that would form at sea in the
87 Cassidaigne Canyon may play a major role as a sink collection point for metals, or on the
88 contrary in releasing metals to the coastal zone of the Calanques National Park.

89 In this context, the aims of the present study were (1) to collect concretions and
90 suspended particles formed at the outfall of the effluent at sea for the first time, (2) to
91 determine their chemical composition with a specific focus on trace metals, and (3) to
92 measure their settling rate and determine the distribution of chemical elements as a function
93 of particle size. The chemical composition of the source effluent and the mineralogical
94 composition of the concretions are reported in a companion paper (Monnin et al., submitted).
95 This study was part of a broader survey aiming at determining the impact of the discharge of

96 the Bayer effluent of the Gardanne plant in the Mediterranean Sea, as requested by the French
97 State. Results from the present work will serve as the basis for further studies on the
98 behaviour of trace metals in the context of concretions stability field destabilization due to
99 particle dispersion in seawater or to the effluent discharge suppression or composition
100 changes as it is planned in 2021. Data presented here are the first of their kind and very
101 relevant in the need for a detailed characterization and understanding of industrial waste
102 disposals at sea as well as for an accurate assessment of their consequences (Morello et al.,
103 2016; Ramirez-Llodra et al., 2015).

104 2. Material and methods

105 The Bayer effluent of the Gardanne alumina plant is discharged into the sea at a rate of
106 around $270 \text{ m}^3 \text{ h}^{-1}$. The discharge leads to the formation of concretions at the submarine pipe
107 outfall and to a plume of white suspended particles (Figure 2). Two sampling cruises took
108 place on August 24, 2016 and from December 6th to 8th, 2016 on board the *RV Janus*
109 (COMEX company) using the ROV Super Achille (also from the COMEX company). These
110 cruises targeted the zone of the effluent discharge a few kilometres offshore. The effluent
111 plume was observed up to 100 m above the outfall. These cruises allowed to collect for the
112 first time concretions and particles created by the residue discharge.

113 a) Measurements in samples collected in the effluent plume

114 Water samples were collected from December 6th to 8th 2016 within the plume and
115 then processed on board. The ROV was equipped with a clean Teflon seawater sampling
116 system. Water samples were taken at 5 depths between 310 and 324 m directly above the
117 outfall of the effluent. An aliquot of about 330 mL of these water samples was filtered on 0.22
118 μm Durapore® PVDF filters and another one (about 100 ml) on 0.7 μm Whatman® GF/F

119 glass filters. These filters were dried at 65°C and weighted before and after filtering to
120 determine the mass of particles.

121 The turbidity of the water samples was measured on board using a Seapoint
122 turbidimeter (Seapoint Sensors Inc., Exeter, USA) installed on a RBR-MAESTRO probe
123 (RBR Ltd, Ottawa, Canada). Turbidity is expressed in NTU (Nephelometric Turbidity Unit).
124 The turbidimeter has been calibrated using data collected during the measurements in the lab
125 of the particle size distribution and their settling rate (see below).

126 b) Effluent/seawater mixing experiments in the laboratory

127 The goal of these experiments was to reproduce in the laboratory the conditions of the
128 underwater effluent/seawater mixing. The source effluent used for the experiments was
129 provided by the Gardanne plant. It was collected during the same period as the effluent plume
130 sampling at sea, i.e. every day at 4 pm between December 4th and 9th, 2016. The variation in
131 the effluent composition is negligible during this sampling period (i.e. about a week, see the
132 companion paper Monnin et al., submitted). For the sake of the laboratory experiments, an
133 averaged effluent was obtained by mixing the effluent samples collected at these various
134 dates.

135 The seawater used for the experiments was sampled at a depth of 50 m in the
136 Mediterranean Sea in the vicinity of the Cassidaigne Canyon but away from the zone of the
137 effluent discharge. Seawater and effluent aliquots were mixed by volume using five different
138 effluent/seawater ratios: 1/5, 1/10, 1/20, 1/200 and 1/2000. Turbidity was measured before
139 filtration using the same Seapoint turbidimeter as described above. The mixture was then
140 filtered on pre-weighted 0.22 µm Durapore® PVDF filters. Filters were dried at 65°C and
141 weighted to determine the mass of formed particles.

142 c) Submarine concretions

143 Concretions were collected on August 24 2016 (*RV Janus II*, COMEX) at the direct outfall
144 of the effluent. Because concretions are very crumbly, a sampling system especially designed
145 by the COMEX company was installed on the ROV next to the monitoring devices. All
146 previous attempts to sample concretions by using direct ROV collection (manipulator arm)
147 were unsuccessful. Briefly, the sampling system designed by COMEX is a cylindrical
148 structure that can be reversed allowing to smoothly collect the concretions avoiding any
149 shaking or brutal movement.

150 Concretions were sampled at three locations in the close area of the outfall, respectively
151 named H1, H2 and H3. H1 was not venting at the time of the cruise (Figure 3A) in contrast to
152 H2 and H3 as revealed by the presence of a white plume of particles above the concretion
153 massif (Figures 2 and 3C). Concretions are composed of a soft middle white core crossed by
154 orange veins, and an external crumbly crust. H1 was subsampled in 2 cm slices from the core
155 to the external crust (Figure 3B). H2 corresponds to a fragment of the external crust. H3 was
156 subsampled in the core and in the orange veins of the concretion (Figure 3D). All samples
157 were then freeze-dried and kept at 4°C until analyses. On average the water content of the
158 concretions is about 80%. We sorted the samples into three groups (Table 1): samples from
159 the core (group 1), group 2 represents intermediate samples between the core and the external
160 crust (group 2) and groups 3 is the samples taken in the external crust. The mineralogical
161 composition of these concretions is given in a companion paper (Monnin et al., submitted).
162 Briefly, results of this paper showed that H1, H2 and H3 concretions are mainly dominated by
163 hydrotalcite, with white core samples containing pure hydrotalcite and samples from other
164 slices containing assemblage of minerals (hydrotalcite plus calcium carbonate or brucite).

165 d) Measurement of the settling rate and size distribution of particles

166 Due to their high friability particles collected in the effluent plume could not be used for
167 the settling rate and size distribution measurements. As these particles form in the concretions
168 before being transferred in seawater through the effluent plume, subsamples taken from the
169 core of concretions have thus been considered analogous to the white particles in the effluent
170 plume. Hence subsamples H1 and H3 “soft core” samples (group 1; Table 1) were used in the
171 experiments.

172 We followed the same experimental procedure as reported in Oursel et al. (2014). Briefly,
173 the experimental device was composed of a vertical Plexiglas tube (1m long and 10 cm
174 diameter), open at the top and equipped with a valve on the bottom to collect water samples.
175 The tube was filled with 7.5 L of seawater sampled at a depth of 50 m in the area of the
176 Cassidaigne Canyon away from the influence of the discharge. Experiments were performed
177 with 1.3 g and 2.3 g of the freeze-dried concretion samples H1 and H3, respectively. Particles
178 were injected at the top of the vertical tube. Water samples have been collected at the bottom
179 14 times in two weeks. The first sample was taken 2 minutes after the particle injection and
180 the last one after 15.5 days of experiment, in order to cover a large range of settling rates and
181 particle diameters. The 14 samples were immediately filtered (150 to 350 mL) after collection
182 on pre-weighted 0.22 μm Nucleopore PC filters and 0.7 μm Whatman® GF/F glass filters,
183 dried at 65°C and weighted to determine the mass of particles. Nucleopore PC and GF/F
184 filters have been used for trace metal and Hg analyses, respectively.

185 Measured settling velocities and particle diameters were then grouped in 4 main size
186 classes of particles based on the Udden-Wentworth sediment grain size scale, according to
187 Leeder (1982) and Bainbridge et al. (2012). The recovery of the injected particles was 93%
188 for H1 and 98% for H3 by weight. This shows that particles did not significantly dissolve
189 during the time of the experiment.

190 e) Chemical analyses

191 We dissolved H1, H2 and H3 concretion samples and H1 and H3 “soft core” size classes
192 filters (from settling rate experiments) in a mixture of two acids (HCl/ HNO₃; all Suprapur
193 grade). The solutions were then analyzed for major and trace elements using a Sector Field
194 Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS; ELEMENT XR,
195 ThermoElement). The instrument was calibrated using standard solutions, and we used an
196 external calibration method with In as an internal standard. The efficiency of the dissolution
197 procedure and the quality of the SF-ICP-MS measurements were controlled by the
198 determination of element concentrations on Certified Reference Materials (MESS-4, SLRS-5,
199 SLEW-3 and CASS-5). Particulate Hg was analyzed by cold vapor atomic absorption
200 spectrometry (CV-AAS, LECO AMA-254).

201 3. Results and discussion

202 As revealed by ROV images of the effluent outfall at sea the pipe is nowadays covered
203 with historical red muds (i.e. disposed before January 2015) and debris of concretions (Figure
204 2). After passing through this cover the effluent mixes with seawater and forms concretions
205 and a plume of white particles. The concretions may form chimneys 3 to 4 m high,
206 surrounded by debris of these chimneys and covering an area of about 170 m². These
207 chimneys look like pinnacles observed at the Lost City (mid-Atlantic ocean) or Prony (New
208 Caledonia) that are natural hyperalkaline hydrothermal vents (Kelley et al., 2001; Monnin et
209 al., 2014). ROV observations in the Cassidaigne Canyon show that particles from the effluent
210 plume extend up to 100 m above the outfall (i.e. to a depth of about 200 meters below sea
211 level).

213 a) Particles concentration, size distribution and settling rate

214 The concentration of particles in the clarified liquid effluent produced by the Gardanne
215 plant is around 25 mg L^{-1} . The suspended particle concentration measured in the water
216 column within the effluent plume at sea ranges from 20 to 274 mg L^{-1} (Figure 4). The relation
217 between the concentration of suspended particles and turbidity has been established by the
218 effluent/seawater mixing experiments and is similar to the one obtained from measurements
219 of the samples collected at sea by the ROV. The two datasets display a unique trend with a
220 slope of 4.7, which indicates that 1 NTU corresponds to 4.7 mg L^{-1} of suspended particles. An
221 estimate of the mixing ratios of the samples collected at sea can be obtained from the
222 measured turbidity and from the curve calibrated by the laboratory data. The turbidity of these
223 samples is between 4.9 and 64.6 NTU. As such, samples collected at sea would correspond to
224 mixing ratios from 1/8 at the direct outfall to 1/190 10 m above the outfall.

225 The distribution of particles as a function of their settling rate is given in Figure 5. H1
226 and H3 “soft core” samples present a similar distribution of particle sizes. As reported above,
227 settling velocities and particle diameters were then grouped in the 4 main size classes of
228 particles according to the Udden-Wentworth scale (Table 2). Settling rate values range from
229 less than 1 m d^{-1} (fine fraction) to more than 500 m d^{-1} (sand). The larger fraction of the
230 particles lies in the “coarse silt” category, which corresponds to particle diameters between 15
231 and $63 \text{ }\mu\text{m}$ and a settling rate of about 1 mm s^{-1} , i.e. 86 m d^{-1} . The second largest fraction, 22
232 and 23 % of the sample weight respectively, corresponds to particles whose settling rate is
233 about 500 m d^{-1} , and an estimated diameter larger than $63 \text{ }\mu\text{m}$ (sand). The remaining fractions
234 (fine silt and fine fraction) correspond to particles which settling rate is lower than 10 m d^{-1} .
235 Overall, the main particle fractions of concretions have relatively high settling rates.
236 Compared to natural marine particles, these would correspond to particles generally called
237 fast-sinking particles. The major part of the particles formed by the mixing of the effluent and

238 seawater will thus rapidly sink and in the vicinity of the outfall, at the difference with the
239 slurry (red muds) that has been discharged at the top of the Cassidaigne Canyon until 2015
240 and expanded far away from the outfall by gravity flow.

241 b) Chemical composition of the concretions

242 The major elements of the concretions are Mg, Al, Ca and S (Figure 6A).
243 Concentrations range from 316 to 626 mg g⁻¹ for Mg, 84 to 340 mg g⁻¹ for Al, 7.6 to 52.1 mg g⁻¹
244 for Ca and 2.2 to 12.8 mg g⁻¹ for S (Table 1). The average concentrations are reported in
245 Figure 6B-C for the three groups of concretions. Among the minor and trace elements, As and
246 Co present trends similar to that for Al, with lower concentrations in the core compared to the
247 crustal layer of the concretion (Figure 7A-A'). Higher V concentrations also appear associated
248 with the central/intermediate part of the concretion while Fe is mainly concentrated in the
249 external parts (Figure 7B-B'). Similarly to Fe, Mo and Ti (Figure 7C-C') and Pb and Cd
250 (Figure 7D-D') are also enriched in the crust, as Mg and Ca. Other elements presenting the
251 same trend as Al are Cu, Ag, Sn, Hg, Si, P and Rb, while B, Th, Sr, K, U, Ba, Cr, Mn, Ni and
252 Zn present the same trend as Ca and Mg (not shown). Minimum, maximum and average
253 values for all the elements analysed are reported in Table 3 next to upper and lower
254 continental crust values (Wedepohl, 1991) which are generally used to trace material from
255 continental origin. On average Mg, As and Mo concentrations in the concretions are 23-25
256 times higher than continental crust values. V and S are 12 times higher and Al is 3 times
257 higher. Ca (group 3) and Cd concentrations are of the same order as continental crust values.
258 All the other elements present on average concentrations from 10 to 10³ times lower than
259 continental crust values.

260 As reported above, H1 and H3 “soft core” samples (group 1) can be considered
261 analogous to the white particles found in suspension in the effluent plume at sea. With regards
262 to concentration levels, these are composed on average by: (1) of Mg, Ca, Al and S at

263 concentrations between a few tens to hundreds of mg g^{-1} , (2) few to ten of mg g^{-1} of V and Si,
264 (3) hundreds of $\mu\text{g g}^{-1}$ of K, Sr, P and As, (4) tens of $\mu\text{g g}^{-1}$ of B, Mo and Fe, (5) few $\mu\text{g g}^{-1}$ of
265 Ti, Cu, Zn and Sn, (6) hundreds of ng g^{-1} of Rb, U, Ba, Cr, Ni, Co, Sb, Mn, and (7) tens of ng
266 g^{-1} of Ag, Cd, Pb, Hg and Th (Table 3) .

267 The chemical composition of particles of the different size classes was also
268 determined. Figure 8 reports the distribution of the chemical elements between the 4 main size
269 classes of particles, in an order determined by their content in the coarse silt fraction, which is
270 the larger fraction of particles in H1 and H3 (Table 3). 50 to 70 % in weight of Al, Mg, Ca, S,
271 V and As are concentrated in this fraction. In contrast, elements found in lower concentrations
272 are associated to fine silt or sand fractions. Overall, these results outline the importance of for
273 the size of the particles on the transfer of metals in seawater. A recent study on the levels of
274 fish contamination in the Cassidaigne Canyon area has shown that fish would especially be
275 contaminated by Al and to a lesser extent by Ti and V (Bouchoucha et al., 2019). These
276 elements are indeed among the main elements found in the concretions and particles. The
277 direct impact of the actual effluent discharge is not easy to assess because element
278 bioaccumulation in fish is blurred by interaction with biological effects (trophic level and
279 size). The evolution of the historical red mud deposited on the seafloor can also play a role in
280 releasing metals to seawater. A better understanding of the different sources of metals
281 (historical red mud, actual effluent, concretion particles and impacted seawater) and the
282 trophic structure in the Cassidaigne Canyon will provide greater evaluation of the health risk
283 for humans consuming fish from the area.

284 4. Conclusion

285 Submarine concretions and white particles plume form when the high pH clarified Bayer
286 effluent of the Gardanne alumina plant mixes with seawater in the Cassidaigne Canyon (NW-
287 Mediterranean Sea). We estimated effluent/seawater mixing ratios of around 1/8 at the direct

288 outfall to 1/190 10 m above the outfall. We estimated that 1 NTU (turbidity) would represent
289 4.7 mg L⁻¹ of particles, allowing to trace the effluent plume in the mixing zone. Next to the
290 major elements Mg, Al, Ca and S, As and V are the main trace metals found in the
291 concretions. Concretions are mainly composed by aggregated particles falling in the category
292 of coarse silt, according to the Udden-Wentworth scale, thus corresponding to diameters
293 between 15.6 and 63 µm. When suspended in the water column these particles would settle at
294 a sinking velocity of around 96 m d⁻¹. Particles transferred by the plume will probably rapidly
295 reach the sediment. However, investigating the fate of the particles formed by the discharge of
296 the clarified effluent will also require to take into account the dispersion of the particles at the
297 same time as their dissolution during their transport in the water column. This would allow a
298 better evaluation of the potential impact of the effluent in the coastal zone.

299

300 *Acknowledgements*

301 This work has been carried out within the framework of a contract between the Alteo
302 company and the Mediterranean Institute of Oceanography- MIO (Université Aix-Marseille
303 and CNRS), with the Geosciences Environnement Toulouse- GET laboratory as a sub-
304 contractor. We gratefully acknowledge the logistical and financial support and the incentive to
305 publish the present results, provided by ALTEO and the CREOCEAN consulting firm. The
306 work was co-funded by the Labex OT-MED (CONTALT project) (ANR-11-LABEX-0061)
307 and by the Labex DRIIHM (CONTAMIN project) (ANR-11-LABEX-0010), French
308 programme “Investissements d’Avenir” which are managed by French ANR. We are thankful
309 to the captain and crew of the *R/V Janus* from COMEX Company. The HR-ICP-MS at MIO is
310 part of the PACEM analytical platform of the MIO- Chemistry Team dedicated to marine
311 trace elements and metals. The instrument (ELEMENT XR, Thermo) was supported in 2012
312 by European Regional Development Fund (ERDF). This work is a contribution to the

313 transverse research axe « AT-CONTAM » of the MIO and to the MISTRALS (Mediterranean
314 Integrated Studies at the regional And Local Scales) INSU programme (transverse Action
315 « Transfer of contaminants in the Mediterranean”).

316 Our colleague Cédric Garnier, who had played key roles in the elaboration and
317 advancement of this project has passed away during this work. May he rest in peace.

318 [Figure captions](#)

319 Figure 1: Location of the effluent outfall at 324 m depth at the top of the Cassidaigne Canyon
320 (south of France; north-western Mediterranean Sea).

321
322 Figure 2: View of the outfall of the effluent at sea (ROV images). The mixing between the
323 effluent and seawater leads to the formation of massive concretions, with an important plume
324 of white particles.

325
326 Figure 3: Concretions sampled in the Cassidaigne Canyon: (A) column H1 at sea (ROV
327 image), (B) column H1 subsampled in 2 cm slices from the core to the external crust of the
328 concretion, (C) column H2 and particles plume at sea (ROV image) and (D) fragment of
329 column H3 presenting orange veins.

330

331 Figure 4: Relationship between the concentration in suspended particles (mg L^{-1}) and turbidity
332 (NTU) using in situ measurements with the ROV and laboratory mixing experiments.

333

334 Figure 5: Variation of the percentage of particles for each class as a function of their settling
335 rate and calculated diameter for H1- and H3- “soft core” samples.

336

337 Figure 6: Concentrations (log scale) of the major elements (Mg, Al, Ca and S) of concretions
338 in $\mu\text{g g}^{-1}$ (A). Average concentrations (mg g^{-1}) of same elements for the three groups of
339 concretions: (B) Mg and Al and (C) Ca and S. Group 1: core samples, Group 2: intermediate
340 samples and Group 3: crustal samples.

341

342 Figure 7: (A-D) Concentrations in Co (ng g^{-1}) and As ($\mu\text{g g}^{-1}$), Fe and V ($\mu\text{g g}^{-1}$), Ti and Mo
343 ($\mu\text{g g}^{-1}$) and Pb and Cd (ng g^{-1}) for all the samples. (A'D') Concentrations of the same
344 elements for the three groups of concretions. Groups: same as reported in Figure 7.

345

346 Figure 8: Element distributions between each of the 4 main size classes of particles, ordered
347 by increasing content of coarse silt (15-63 μm ; settling rate between 2.0×10^{-2} and 3.3×10^{-1}
348 cm s^{-1}), the major fraction of particles composing H1 and H3 soft core concretions.

349

350

351 **Tables**

352 **Table 1:** Concentrations of the major elements in the concretions: Mg, Al, Ca and S (mg g^{-1}).

353 On average water content of the concretions is about 80%. Group 1: core samples, Group 2:

354 intermediate samples and Group 3: crustal samples.

355

356 **Table 2:** Characteristics and chemical composition of the 4 main size classes of particles

357 composing H1 and H3 “soft core” concretion samples. Measured settling velocities and

358 particle diameters are grouped in 4 main size classes of particles based on the Udden-

359 Wentworth sediment grain size scale, according to Leeder (1982) and Bainbridge et al.

360 (2012): sand ($> 63 \mu\text{m}$; settling rate $> 3.3 \times 10^{-1} \text{ cm s}^{-1}$), coarse silt ($15\text{-}63 \mu\text{m}$; settling rate

361 between 2.0×10^{-2} and $3.3 \times 10^{-1} \text{ cm s}^{-1}$), fine silt ($3.9\text{-}15 \mu\text{m}$; settling rate between 1.3×10^{-3}

362 and $2.0 \times 10^{-2} \text{ cm s}^{-1}$), and fine fraction ($< 3.9 \mu\text{m}$; settling rate low $< 1.3 \times 10^{-3} \text{ cm s}^{-1}$).

363

364 **Table 3:** Minimum, maximum and average concentrations of all the elements analysed in the

365 concretions, next to UCC and LC reference values (Wedepohl, 1991). UCC: continental crust,

366 LC: lower crust. Elements are ordered by decreasing mean concentrations for group 1 (from

367 mg g^{-1} to ng g^{-1}).

368

369

370

371

372

373

374

375

377 References

- 378 Bru, K., d'Hugues, P., Michel, P., Save, M., 2014. Usine d'alumines de spécialités d'ALTEO
379 Gardanne (13). Tierce expertise sur le Dossier de Demande d'Autorisation d'Exploiter
380 (DDAE) visant à supprimer les rejets de boues rouges en maintenant un rejet
381 d'effluent liquide résiduel. Rapport final. . BRGM/RP-64161-FR.
- 382 Bainbridge, Zoe T., Eric Wolanski, Jorge G. Álvarez-Romero, Stephen E. Lewis, and Jon E.
383 Brodie. "Fine Sediment and Nutrient Dynamics Related to Particle Size and Floc Formation
384 in a Burdekin River Flood Plume, Australia." *Marine Pollution Bulletin* 65, no. 4 (2012):
385 236–48. doi:<https://doi.org/10.1016/j.marpolbul.2012.01.043>.
- 386 Bouchoucha, M., R. Chekri, A. Leufroy, P. Jitaru, S. Millour, N. Marchond, C. Chafey, et al.
387 "Trace Element Contamination in Fish Impacted by Bauxite Red Mud Disposal in the
388 Cassidaigne Canyon (NW French Mediterranean)." *Science of The Total Environment* 690
389 (2019): 16–26. doi:<https://doi.org/10.1016/j.scitotenv.2019.06.474>.
- 390 Cavani, F., Trifiro, F. and Vaccari, A. (1991) Hydrotalcite-Type Anionic Clays: Preparation,
391 Properties and Applications. *Catalysis Today*, 11, 173-301.
- 392 Dauvin, J.C., 2010. Towards an impact assessment of bauxite red mud waste on the
393 knowledge of the structure and functions of bathyal ecosystems: The example of the
394 Cassidaigne canyon (north-western Mediterranean Sea). *Marine Pollution Bulletin*, 60(2):
395 197-206.
- 396 Hanahan, C. et al., 2004. Chemistry of seawater neutralization of bauxite refinery residues
397 (red mud). *Environmental Engineering Science*, 21(2): 125-138.

398 Hill, V.G., Sehnke, E.D., 2006. Bauxite In: J. E. Kogel, N.C.T. (Ed.), *Industrial Minerals &*
399 *Rocks: Commodities, Markets, and Uses*. Society for Mining, Metallurgy and Exploitation
400 Inc. - Ingelwood, pp. 227-261.

401 Kelley, Deborah, JA Karson, Donna Blackman, G Früh-Green, David Butterfield, Marvin
402 Lilley, Eric Olson, et al. “An off-Axis Hydrothermal Vent Field near the Mid-Atlantic Ridge
403 at 30 Degrees N.” *Nature* 412 (2001): 145–49. doi:10.1038/35084000.

404 Leeder, M.R., 1982. *Sedimentology; Process and Product*. Chapman and Hall, London.

405 Mayes, W.M. et al., 2016. Advances in Understanding Environmental Risks of Red Mud
406 After the Ajka Spill, Hungary. *Journal of Sustainable Metallurgy*, 2(4): 332-343.

407 Mills, S.J., Christy, A.G., Genin, J.M.R., Kameda, T., Colombo, F., 2012. Nomenclature of
408 the hydrotalcite supergroup: natural layered double hydroxides. *Mineralogical Magazine*,
409 76(5): 1289-1336.

410 Monnin, Christophe, Valérie Chavagnac, Cedric Boulart, Bénédicte Ménez, Martine Gérard,
411 Emmanuelle Gérard, Marianne Quéméneur, et al. (2014). The Low Temperature
412 Hyperalkaline Hydrothermal System of the Prony Bay (New Caledonia). *Biogeosciences*
413 *Discussions* 11: 6221–67. doi:10.5194/bgd-11-6221-2014.

414 Morello, E.B. et al., 2016. THE ECOLOGICAL IMPACTS OF SUBMARINE TAILINGS
415 PLACEMENT. In: Hughes, R.N., Hughes, D.J., Smith, I.P., Dale, A.C. (Eds.), *Oceanography*
416 *and Marine Biology: An Annual Review*, Vol 54. *Oceanography and Marine Biology*. Crc
417 Press-Taylor & Francis Group, Boca Raton, pp. 315-366.

418 Oursel B. et al. (2014). Behaviour and fate of urban particles in coastal waters: Settling rate,
419 size distribution and metals contamination characterization. *Estuarine, Coastal and Shelf*
420 *Science*, 138: 14-26.

421 Palmer, Sara J., Ray L. Frost, and Tai Nguyen. "Hydrotalcites and Their Role in Coordination
422 of Anions in Bayer Liquors: Anion Binding in Layered Double Hydroxides." *Coordination*
423 *Chemistry Reviews* 253, no. 1 (January 1, 2009): 250–67. doi:10.1016/j.ccr.2008.01.012.

424 Ramirez-Llodra, E. et al., 2015. Submarine and deep-sea mine tailing placements: A review
425 of current practices, environmental issues, natural analogs and knowledge gaps in Norway
426 and internationally. *Marine Pollution Bulletin*, 97(1–2): 13-35.

427 Wedepohl K.H. (1991). Chemical Composition and Fractionation of the Continental Crust.
428 *geologischce Rundschau* 80, No2: 207-23. doi: 10007/BF01829361.

429

430

431

432