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Distribution and geochemical behaviour of anionic surfactants determined as ethyl violet active substances in Lake Biwa, Japan

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Distribution and Geochemical Behavior of Anionic Surfactants Determined as Ethyl Violet
Active Substances in Lake Biwa, Japan
Hiroo Yoshida, Shunsuke Kudari, Toshitaka Hori, Masahito Sugiyama

1 **Distribution and geochemical behavior of anionic surfactants determined**

2 **as ethyl violet active substances in Lake Biwa, Japan**

3

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13 **Abstract**

14 The distribution and geochemical behavior of anionic surfactants (AS)
15 determined as ethyl violet active substances (EVAS) were studied in Lake Biwa,
16 Japan. We determined the vertical distributions of dissolved EVAS (DEVAS),
17 suspended particulate EVAS (PEVAS), particulate organic carbon (POC), and
18 the PEVAS/POC ratio. Statistical analyses conducted using plots of PEVAS vs.
19 POC and PEVAS/ Chlorophyll-a (Chl-a) vs. POC/Chl-a revealed that the
20 distributions of DEVAS and PEVAS were affected by the concentrations of
21 freshly produced POC and aged POC and by the pH of the lake water.
22 Adsorption and desorption of EVAS onto the POC phase were found to be
23 important mechanisms regulating the distribution and
24 environmental/geochemical behavior of EVAS in the lake. The organic
25 carbon-normalized particle–water partitioning coefficient, K_{OC} , for EVAS was also
26 estimated and compared to that for nonylphenol.

27 **Keywords**

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28 anionic surfactants; ethyl violet; distribution, geochemical behavior, Lake Biwa

29

30 **Introduction**

31 Linear alkylbenzene sulfonate (LAS) is the primary anionic surfactant found in
32 Japan. This compound is listed as Class I in the Pollutant Release and Transfer
33 Register Law of Japan. A Class I Designated Chemical Substance is defined as
34 continuously occurring throughout much of the environment based on its
35 physical and chemical properties, manufactured volume, and importation and
36 usage, and having risks to human health and the ecosystem (Japan Ministry of
37 the Environment 2013). Production of LAS was 72 kt in 2002 and the amount of
38 LAS discharged to the sewage in Japan was 64 kt in 2001 (National Institute of
39 Technology and Evaluation 2005). The degree of discharge is related to the
40 environmental risk.

41 Research on anionic surfactants (AS) in the aquatic environment has been
42 carried out globally. In Japan, AS concentrations have been reported to range

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43 between 50–8500 $\mu\text{g/L}$ in river water (Kobayashii and Yamauchi 1979; Kobuke
44 1981; Yoshimura *et al.* 1984; Hirayama *et al.* 2006), 0–264 $\mu\text{g/g}$ in river
45 sediments (Ambe 1972; Uchiyama 1982; Yoshimura *et al.* 1984), and 10–50
46 $\mu\text{g/g}$ in lake sediments (Ambe 1972). LAS concentrations ranged between
47 0.6–79 $\mu\text{g/L}$ in river water in Japan (Kobuke 2004; Miura *et al.* 2008), 0–342 $\mu\text{g/L}$
48 in South Africa (Gordon *et al.* 2009), and 2–126 $\mu\text{g/L}$ in the Philippines (Dyer *et*
49 *al.* 2003). LAS concentrations also ranged between 60–2300 $\mu\text{g/g}$ in suspended
50 particles in rivers in Japan (Takada and Ishiwatari 1987) and between
51 0.03–17.76 $\mu\text{g/g}$ and 0.101–0.186 $\mu\text{g/g}$ in river sediments in Portugal (Hampel *et*
52 *al.* 2009) and South Africa (Gordon *et al.* 2009), respectively.

53 As noted above, most limnological and environmental studies of AS have been
54 focused on rivers, but few studies have been conducted of AS in lakes. The
55 distribution of AS in rivers is important in determining anthropogenic pollution
56 levels and discharges to the natural environment of AS by human activities.
57 However, these studies alone are not sufficient to fully delineate the

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58 environmental and geochemical processes of AS, because water masses are
59 constantly renewed by flows from upstream. On the other hand, water masses
60 may stagnate in lakes and thus, studies on partitioning of AS between lake water
61 and suspended and sediment particles are more feasible.

62 Several authors have studied removal processes for AS in laboratory
63 experiments (Ou *et al.* 1996; Perales *et al.* 1999; Doi *et al.* 2002; Garcia *et al.*
64 2002). These compounds are generally known to be degraded by
65 microorganisms (Perales *et al.* 1999) and adsorbed by solid phases (Ou *et al.*
66 1996; Doi *et al.* 2002; Garcia *et al.* 2002). The former depends on the water
67 temperature, while the latter is related to the organic carbon content of the solid
68 phase, known as the particulate organic carbon (POC) content. To date, there
69 have been few studies of adsorption and partitioning of AS to POC in lakes.
70 Although some authors have addressed POC, they treated it as a homogeneous
71 material despite being a mixture of various organic materials (Yoshida *et al.*
72 2009). In our previous study (Yoshida *et al.* 2009), we clarified that POC in lakes

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73 could be classified into two fractions, freshly produced POC (f-POC) and aged
74 POC (a-POC), based on differences in the affinity of nonylphenol (NP) to POC;
75 its affinity to a-POC was approximately 4 times higher than that to f-POC. A
76 similar evaluation is also needed for AS.

77 Colorimetric methods have often been used for analysis of AS. Among these
78 methods, methylene blue, which offers the advantage of being an easy-to-use
79 and convenient technique, is widely used. In recent years, the methylene blue
80 reagent has been replaced by an ethyl violet reagent (Soejima 1982). The ethyl
81 violet colorimetric method is more useful than methylene blue as it has: (1) high
82 sensitivity, (2) a very simple and less time-consuming procedure, (3) little
83 interference by coexisting ions, and (4) good reproducibility and quantification of
84 trace amounts of anionic surfactants (Motomizu *et al.* 1982). It is also used as a
85 standard method in Japan (Japan Standards Association 1998). Therefore, we
86 quantified AS as ethyl violet active substances (EVAS).

87 In this study, we determined the distribution and geochemical behavior of AS in

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88 Lake Biwa as EVAS. Using plots of suspended particulate EVAS (PEVAS) vs.
89 POC and PEVAS/Chlorophyll-*a* (Chl-*a*) vs. POC/Chl-*a*, we evaluated adsorption
90 and partitioning of EVAS to POC in Lake Biwa. The average PEVAS/POC ratio
91 and organic carbon-normalized particle–water partitioning coefficient (K_{oc}) of
92 EVAS to f-POC and a-POC were estimated and compared to those of NP.

93

94 **Materials and methods**

95 **Solvents and standards**

96 Sodium sulfate and sodium hydroxide were purchased from Nacalai Tesque
97 (Kyoto, Japan). Acetic acid, toluene, disodium ethylenediaminetetraacetate
98 (EDTA), and sodium dodecyl sulfate (SDS) were obtained from Wako Chemicals
99 (Osaka, Japan). Ethyl violet was obtained from Tokyo Chemical Industry (Tokyo,
100 Japan).

101

102 **Sampling site and sample collection**

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103 The sampling sites for this study were located in Lake Biwa (35°15' N, 136°05' E)
104 and the Yasu River. Lake Biwa, which is the largest lake in Japan, is divided into
105 two parts, the northern and southern basins. The former has a volume of 27.3
106 km³ with an average depth of 44 m. Thermal stratification typically occurs from
107 May to January and vertical convection of the entire water column in the lake
108 occurs regularly from February to April. The southern basin of the lake has a
109 volume of 0.2 km³ with an average depth of 3.5 m. The water in this basin is not
110 thermally stratified and is more or less saturated with atmospheric oxygen
111 throughout the year (Sugiyama *et al.* 2005). Field surveys were conducted at
112 Station Ie-1 (35°12.58' N, 135°59.55' E) between September 2000 and August
113 2001.

114 The Yasu River is a large river that flows near Station Ie-1 in Lake Biwa. It has
115 the largest drainage area and the second highest water discharge among the
116 more than 110 rivers flowing into Lake Biwa (Lake Biwa Environmental
117 Research Institute 1986; Kanimatsu 1988). Several towns are located along this

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river with a total population of 220,000. The river water is generally used for industrial water, domestic supply, and irrigation, and then the discharge is released to the river (Kimaro *et al.* 2002). Field surveys of the river were conducted at Stations YS-1 (35°09.70' N, 135°99.30' E) and YS-2 (35°02.37' N, 136°01.12' E) on 5 September 2000 and 9 March 2001.

Lake water samples were collected vertically with a Van Dorn water sampler and river water samples were collected with a glass bottle. The samples were filtered through a Whatman GF/F filter (diameter 47 mm, pore size 0.7 μ m) to separate suspended particles from the water. The water samples were analyzed within 3 days of sampling. Suspended particle samples collected on the filter were kept frozen until they were analyzed.

Analytical procedures

Sample treatment for AS determination was carried out as follows. Forty milliliters of a water sample was transferred into a glass centrifuge tube. Two

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133 milliliters 1 mol/L sodium sulfate solution, 2 mL acetic acid–EDTA buffer (pH 5.0),
134 0.8 mL 1 mmol/L ethyl violet solution, and 2 mL toluene were added to the tube.
135 The tube was shaken for 60 min and then centrifuged for 5 min. After phase
136 separation, the absorbance of the toluene phase was measured at 611 nm
137 (UV-1600; Shimadzu, Kyoto, Japan) and calibrated against an SDS solution.
138 Suspended particle and sediment samples were dried at 60 °C and
139 ultrasonicated twice with 10 mL methanol for 45 min at room temperature. The
140 obtained extracts were evaporated until they were dry using a centrifugal
141 vaporizer (Model CVE 2wd; Tokyo Rika Kikai, Tokyo, Japan). The residue was
142 redissolved in 40 mL water and the solution was then treated as a water sample.
143 POC was quantified with a CHN analyzer (Model 2400; Perkin Elmer, Tokyo,
144 Japan). The temperatures of the combustion and reduction chambers were set
145 to 925 °C and 640 °C, respectively.
146 Chl-*a* was quantified spectrophotometrically according to the methods of
147 UNESCO and Lorenzen (Lorenzen 1967).

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148

149 **Results and discussion**

150 **Method validation**

151 In the analyses using the ethyl violet colorimetric method, sodium sulfate was
152 used to accelerate phase separation and EDTA was used to reduce
153 interferences from multivalent metal ions. AS were determined as EVAS.
154 Method validation was carried out to evaluate the suitability of this method. SDS
155 was used as a standard material for analysis of AS. The linearity of its calibration
156 curve was evaluated by taking measurements at four different concentrations of
157 SDS. The correlation coefficient r of the curve was >0.999 from 0 to $38 \mu\text{g/L}$ SDS.
158 The detection limit was determined as the concentration of SDS that gave a
159 signal three times the background noise, which was $0.27 \mu\text{g/L}$.

160 Accuracy and precision were calculated based on recovery of SDS from
161 sediments, since sediments have a more complex matrix. For this evaluation,
162 $101 \mu\text{g/g}$ SDS was spiked into a sediment sample containing $235 \mu\text{g/g}$ of EVAS.

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The recovery rate and precision were 115% and 3.3% ($n = 3$). Thus, this method was found to be suitable for analysis of AS in environmental and geochemical studies.

Distribution and geochemical behavior of EVAS in Lake Biwa

Figure 1 shows the vertical distributions for water temperature, pH, and EVAS concentration in Lake Biwa. During the circulation period (2 April 2001), the vertical distribution of dissolved EVAS (DEVAS) was relatively constant, because the lake water was well mixed due to the vertical convection that occurs in early spring. Conversely, the DEVAS concentration during the stagnation period (12 September and 5 October 2000, 11 April 2001) had higher values at the surface and decreased at the thermocline. The concentration in the hypolimnion was nearly constant except near the bottom and was similar to that during the circulation period. The high DEVAS concentrations in the epilimnion are believed to be due to river water with high DEVAS concentrations flowing

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only into the epilimnion and/or to desorption of AS from the POC phase due to the increase in pH in the surface water during the stagnation period. Average DEVAS concentrations in the Yasu River were 18.2 $\mu\text{g/L}$ on 5 September 2000 and 55.7 $\mu\text{g/L}$ on 9 March 2001. These values were higher than those in the epilimnion during the stagnation period and in the entire water column during the circulation period. Weighted average concentrations in the epilimnion were 12.2 $\mu\text{g/L}$ on 12 September 2000, 14.6 $\mu\text{g/L}$ on 5 October 2000, and 12.2 $\mu\text{g/L}$ on 11 April 2001. During the circulation period (2 April 2001), the weighted average concentration over the entire water column was 10.5 $\mu\text{g/L}$. These results indicate that the DEVAS concentration in the surface water is increased by the Yasu and other rivers flowing into the epilimnion during the stagnation period.

In addition, the pH in the epilimnion increases with active biological productivity in the summer in many lakes, including Lake Biwa (Lake Biwa Research Institute and National Institute for Research Advancement 1984; Sugiyama *et al.* 2005). It has been reported that AS desorb from the suspended

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193 POC phase when the pH of the aqueous phase increases (Yoshimura and
194 Nakae 1982). Therefore, the DEVAS concentration in the surface water may
195 have increased by desorption of AS from the POC phase in the suspended
196 particulate matter and the sediments in shallow and littoral area of the lake when
197 the pH of the water increased. This hypothesis was supported by the results for
198 PEVAS vs. POC (see below).

199 The concentration of PEVAS decreased from the surface to the thermocline or
200 the middle layer. However, at any given sampling time in Fig. 1, the vertical
201 distribution of PEVAS/POC, which represents the organic carbon-normalized
202 concentration of EVAS in the suspended particles, was neither uniform nor
203 similar to those of PEVAS or POC. Figure 2 plots PEVAS vs. POC. The
204 correlation coefficient r was relatively low at 0.619. There are believed to be two
205 reasons for this result. The first is the treatment of POC as a homogeneous
206 material despite actually being a mixture of various organic materials. The
207 second is not considering changes in the pH of the lake water, although AS is

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208 known to desorb from the suspended POC phase when the pH of the aqueous
209 phase increases.

210 The first issue can be explained further based on the results of our previous
211 environmental and geochemical study on NP in Lake Biwa (Yoshida *et al.* 2009).

212 In that study, POC was mathematically classified into two fractions, f-POC and
213 a-POC, based on the affinity of NP to these fractions. The differences between
214 f-POC and a-POC are likely associated with their chemical structure and the
215 nature of the organic matter. Therefore, in the present study, we examined the
216 distribution of PEVAS and POC in a similar manner. The total concentration of
217 POC, [POC], can be expressed as:

218
$$[\text{POC}] = [\text{POC}]_f + [\text{POC}]_a$$

219 where $[\text{POC}]_f$ and $[\text{POC}]_a$ are the concentrations of f-POC and a-POC,
220 respectively. If the EVAS concentration accumulated by f-POC and a-POC are
221 defined as $[\text{PEVAS}]_f$, and $[\text{PEVAS}]_a$, respectively, then the total PEVAS
222 concentration, [PEVAS], can be expressed as:

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$$[PEVAS] = [PEVAS]_f + [PEVAS]_a$$

$$= R_f[POC]_f + R_a[POC]_a$$

$$= R_f[POC]_f + R_a([POC] - [POC]_f)$$

where R_f and R_a are the average PEVAS/POC ratios for f-POC and a-POC,

respectively.

Phytoplankton is typical of freshly produced organic matter in a lake and the

Chl-a concentration is an index of phytoplankton abundance. Therefore, if Chl-a

is regarded as an index of the f-POC concentration, $[POC]_f$ can be expressed as:

$$[POC]_f = \alpha[Chl-a]$$

where α is the average f-POC/Chl-a ratio. The following relationship can be

obtained from the above equations:

$$[PEVAS] = R_f\alpha[Chl-a] + R_a([POC] - \alpha[Chl-a])$$

$$= R_a[POC] + \alpha(R_f - R_a)[Chl-a]$$

$$[PEVAS]/[Chl-a] = R_a[POC]/[Chl-a] + \alpha(R_f - R_a)$$

The obtained equation can be interpreted as follows. The plot of PEVAS/Chl-a

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vs. POC/Chl-*a* is predicted to be linear, with a slope and intercept of R_a and $\alpha(R_f$
– R_a), respectively. If AS accumulates in a-POC more than in f-POC (i.e., $R_a >$
 R_f), the intercept will be negative. Figure 3 plots PEVAS/Chl-*a* vs. POC/Chl-*a*.
The plot showed good linearity and its correlation coefficient ($r = 0.916$) was
higher than that of the PEVAS vs. POC plot ($r = 0.619$). These results suggest
that classification of POC into f-POC and a-POC is possible through this method
and is important for understanding the behavior of AS in the lake. As expected,
the intercept $\alpha(R_f - R_a)$ of the plot was negative (-1.27×10^{-2} g/g). Therefore, the
affinity of AS to a-POC was higher than to f-POC. These results are consistent
with our previous study showing that NP also has stronger affinity to a-POC than
to f-POC (Yoshida *et al.* 2009).
The slope R_a and intercept $\alpha(R_f - R_a)$ of the linear regression line in Fig. 3 were
 5.5×10^{-3} g/g and -1.27×10^{-2} g/g, respectively. Using 87.8 g/g as the average α
value (Yoshida *et al.* 2009) based on the average POC/Chl-*a* value in culture
experiments of phytoplankton from Lake Biwa (Tezuka 1985), R_f can be

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estimated as 5.4×10^{-3} g/g. According to the definition given above, R_f and R_a are the average EVAS/POC ratios for f-POC and a-POC, respectively. Therefore, these values indicate that the affinity of AS to a-POC is somewhat higher than that to f-POC.

The second reason for the poor correlation coefficient ($r = 0.619$) between PEVAS and POC in Fig. 2 can be explained by the PEVAS vs. POC plots shown in Fig. 4. Based on the pH of the lake water, the data can be classified into 3 groups: Group A, samples of the epilimnion in September and October 2000 (pH 7.6–7.8; 0–13 m in September and 0–17 m in October); Group B, samples of the hypolimnion in September and October 2000 (pH 6.9–7.1; 20–72 m); and Group C, samples at all depths on 2 and 11 April 2001 (pH 7.1–7.4). The correlation coefficients for the three groups were 0.690, 0.926, and 0.908, respectively. The PEVAS/POC value (3.38) for the epilimnion with high pH values was smaller than those (5.57 and 7.84) for the hypolimnion and at all depths with low pH values. These results are consistent with the increase in the DEVAS

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concentration in the epilimnion with high pH values during the stagnation period,
and also indicates that PEVAS concentrations in the POC decreased with an
increase in the pH of the lake water. In other words, EVAS is desorbed from the
suspended POC phase when the pH of the aqueous phase increases.

We previously reported that some oxyanions are also released from solid
phases such as sediments and suspended particulate matter with an increase in
the pH of lake water (Harita *et al.* 2005), similar to the present results. Therefore,
adsorption and desorption of chemical components onto solid phases with
changes in the pH of lake water are considered to be important mechanisms
regulating their distribution and environmental/geochemical behavior in lakes.
However, such a trend was not observed in our previous study of NP. This is
likely because NP, as a non-ionic compound, is not affected by changes in pH.

As shown in Fig. 4, the PEVAS/POC value (5.57) in the hypolimnion in
September and October was smaller than that (7.84) at all depths in April. This is
believed to be due to degradation of PEVAS in the hypolimnion during the

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283 stagnation period.

284

285 **Comparison of K_{oc} values for EVAS and NP**

286 The partition coefficient K_{oc} is calculated using the following equation, which

287 uses the DEVAS concentration and the PEVAS/POC ratio (R_f and R_a):

288
$$K_{oc}(\text{mL/g} - \text{POC}) = [\text{PEVAS/POC}(\text{g/g} - \text{POC})]/[\text{DEVAS}(\text{g/mL})]$$

289 The average DEVAS concentrations were 15.9×10^{-9} g/mL and 9.1×10^{-9} g/mL in

290 the epilimnion and hypolimnion, respectively. Using these concentrations, log

291 K_{oc} was determined to be 5.5 and 5.8 for R_f and R_a , respectively. These values

292 are within those (2.5–5.9) obtained in a previous study (Vincent and Glenwood

293 1987).

294 The log K_{oc} values for EVAS (5.5–5.8) were higher than those for NP (4.8 and

295 5.4). The high K_{oc} values for EVAS are likely due to formation of a bulky ionic

296 pair with cationic organic compounds such as quaternary ammonium ions as

297 well as its high affinity to POC. Cationic surfactants, which typically contain

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298 quaternary ammonium ions, are widely used in industrial and household
299 detergents and are discharged into lake and river waters. Their production in
300 Japan was 70 kt in 1997 (Japan Surfactant Industry Association 1997). Cationic
301 surfactants easily form a stable ion pair with coexisting anionic surfactants in
302 environmental waters (Utsunomiya *et al.* 1998) and this ion pair is quickly
303 absorbed onto sewage sludge and sediments with a high partitioning coefficient
304 (Sun *et al.* 2003; Sütterlin *et al.* 2008).

305

306 **Conclusions**

307 We studied the distribution and geochemical behavior of EVAS in Lake Biwa,
308 Japan. The distributions of DEVAS and PEVAS were clearly affected by the
309 concentrations of the two POC fractions, f-POC and a-POC, and by the pH of the
310 lake water. Thus, adsorption and desorption of EVAS onto the POC phase were
311 found to be important mechanisms regulating their distribution and
312 environmental/geochemical behavior in lakes.

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319 with collection of samples in Lake Biwa.

320

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Figure captions

Fig. 1. Vertical distributions of WT, pH, DEVAS, PEVAS, POC, PEVAS/POC, and Chl-*a* at Station Ie-1 in Lake Biwa. WT: water temperature.

Fig. 2. Plot of PEVAS vs. POC. The regression line for the plot of PEVAS vs. POC was constrained to pass through the origin to estimate an average PEVAS/POC ratio. The correlation coefficient r was estimated from the PEVAS and POC data.

Fig. 3. Plot of PEVAS/Chl-*a* vs. POC/Chl-*a*. The correlation coefficient r was estimated from the PEVAS/Chl-*a* and POC/Chl-*a* data.

Fig. 4. Plot of PEVAS vs. POC. The data were classified into 3 groups: Group A, samples of the epilimnion (squares) in September and October 2000 (pH

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443 7.6–7.8; 0–13 m in September and 0–17 m in October); Group B, samples of the
444 hypolimnion (triangles) in September and October 2000 (pH 6.9–7.1; 20–72 m);
445 and Group C, samples from all depths (circles) on 2 and 11 April 2001 (pH
446 7.1–7.4). The regression line for the plot of PEVAS vs. POC was constrained to
447 pass through the origin to estimate an average PEVAS/POC ratio. The
448 correlation coefficient r was estimated from the PEVAS and POC data.

449

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Fig. 1.

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452

453 **Fig. 2.**

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Fig. 3.

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Fig. 4.