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1 **Influence of marine phytoplankton, transition metals and sunlight on the**
2 **species distribution of chromium in surface seawater**

3 **Running head:** Photo-induced reduction of Cr(VI) in sunlit seawater

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9 **Abstract**

10 The photo-reduction of Cr(VI) to Cr(III) by marine phytoplankton (diatoms, red and green algae), with or
11 without the presence of transition metals (Fe(III), Cu(II) and Mn(II)) was studied. The direct influence of
12 marine phytoplankton on the photochemical reduction of Cr(VI) was confirmed for the first time, and two
13 kinds of mechanism were suggested to be responsible for the species transformation: (a) Cr(VI) in excited
14 state could be reduced by the electron donor in its ground state via photo produced electrons; and (b) the
15 solvated electrons reduce the CrO_4^{2-} anions in their ground state. The conversion ratio of Cr(VI) to Cr(III)
16 increased with increasing algae concentration and irradiation time. Different species of marine
17 phytoplankton were found to have different photo-reducing abilities. The photochemical redox of transition
18 metals could induce the species transformation of chromium. After photo-reduction by marine
19 phytoplankton and transition metals, the ratio of Cr(VI) to Cr(III) was in the range of 1.45~2.16 for five
20 green algae (*Tetraselmis levis*, *Chlorella autotrophica*, *Dunaliella salina*, *Nannochloropsis sp.*, and
21 *Tetraselmis subcordiformis*), and only 0.48 for *Phaeodactylum tricorutum* (diatom) and 0.71 for
22 *Porphyridium purpureum* (red alga). The species distribution of chromium in the sunlit surface seawater
23 was greatly affected by combined effects of marine phytoplankton (main contributor) and transition metals;
24 both synergistic and antagonistic effects were observed. The results provided further insights into the
25 species distribution and the biogeochemical cycle of chromium, and have significant implications for the
26 risk assessment of chromium in the sunlit surface seawater.

27 **Keywords:** Chromium, Photoreduction, Marine phytoplankton, Species transformation

28 1. Introduction

29 Developing a full understanding of the distribution and biogeochemical behavior of trace elements in seawater
30 has the potential to provide: (a) unique insights into a wide range of oceanic processes and (b) the mechanisms
31 controlling the fate of contaminants added to the ocean by human activities. Both the Joint Global Ocean Flux
32 Study (JGOFS) and the Land-Ocean Interactions in the Coastal Zone Project (LOICZ), the core projects of the
33 International Geosphere-Biosphere Program (IGBP), are focused on the distribution, transport, transform, cycle,
34 end-result, production and consumption of trace metals.

35 In seawater, chromium exists in two different oxidation states, Cr(VI) and Cr(III). Similar to many other
36 elements, the toxicological and physiological behavior of chromium depends on its oxidation state, binding
37 partners, potential ligands and solubility. Chromium(III) shows a high affinity for particles at neutral pH (7-8),
38 and is a micronutrient for higher mammals (Mertz, 1993). In contrast, Cr(VI) is toxic and mobile, and can be
39 easily absorbed by living organisms (Richard and Bourg, 1991; Standeven and Wetterhahn, 1991).
40 Chromium(VI) is an important industrial metal that is considered a priority pollutant by many countries
41 including the USA, UK and Canada. Reduction of Cr(VI) to Cr(III) will not only reduce the toxicity of
42 chromium to living organisms, but also help to precipitate chromium out at pH 8.1 (mainly as insoluble
43 $\text{Cr}(\text{OH})_3$ and soluble coordination compounds). The species transformation of chromium would thus greatly
44 affect its toxicity or bioavailability and its biogeochemical cycle in the ocean.

45 Thermodynamic calculations predict that in oxygenated seawater (pH 8.1 and pE 12.5) the ratio of Cr (VI)
46 to Cr (III) is 10^{21} (Elderfield, 1970), i.e., chromium should exist almost exclusively as Cr(VI), but
47 thermodynamically unstable Cr(III) has also been detected, the ratio of Cr(VI) to Cr(III) was in the range of
48 1.6~3.1 (Hirata et al., 2000). It is important to provide valid explanations for the distribution of Cr (VI)/Cr (III)
49 in order to understand the species transformation and biogeochemical behavior of chromium, and to assess its
50 toxicity in seawater. The mechanistic investigations on the reduction of chromium have caused much attention

51 (Kieber and Helz, 1992; Buerge and Hug, 1997; Hug et al., 1997; Abu-Saba et al., 2000). Until now, the studies
52 of species transformation of chromium, especially the mechanism of reduction, were focused on single
53 environmental factor such as marine bacteria (Smillie et al., 1981; Yang et al., 1994), hydrogen peroxide (Pettine
54 and Millero, 1990; Pettine et al., 1991), iron (Deng et al., 1996; Buerge and Hug, 1997; Hug et al., 1997) and
55 copper (Abu-Saba et al., 2000), which could not provide conclusive reasons for the species transformation and
56 the distribution of chromium in the sunlit surface seawater.

57 The kinetic effects of biological uptake (Roitz et al., 2002; Li et al., 2007), redox and photochemical
58 reaction from biological activity on the species transformation and biogeochemical cycle of trace elements in
59 natural waters were very important, in fact may dominate (Costa and Liss, 2000; Powell and Wilson-Finelli,
60 2003; Rose and Waite, 2003). As the effects on the formation and decay of hydrogen peroxide and hydroxyl
61 radicals by some green and blue algae in freshwater were detected (Zepp and Schlotzhauer, 1983; Zuo and
62 Hoigné, 1992; Zuo and Hoigné, 1993; Liu et al., 2004; Wu et al., 2004), the species transformation of trace
63 elements might be affected by photochemical behavior that is driven by marine phytoplankton. In our previous
64 study, the photo-oxidation of Sb(III) in seawater was observed for the first time and could be accelerated by
65 marine phytoplankton (Li et al., 2006a). Dissolved organic matter (DOM) derived from phytoplankton could
66 facilitate Cr reduction in the presence of light (Sanders and Riedel, 1987). A field experiment implies that Cr(III)
67 concentrations were greatest during periods of high biological activity, as indicated by strong correlations
68 between the ratio of Cr(III):Cr(VI) and primary productivity (Connelly et al., 2006). Both the influence of
69 marine phytoplankton itself (excluding its exudates such as DOM) on the photo-reduction of trace metals and
70 the information on species specific differences in how different phytoplankton might facilitate this reaction have
71 not yet been published.

72 Transition metals in seawater, including iron, manganese and copper, are usually complexed with organic
73 ligands, forming coordinated complexes (Deng et al., 1997; Powell and Wilson-Finelli, 2003). Since the

74 electrons in these coordinated metal complexes and their organic ligands are easy to transport, they could
75 readily absorb ultraviolet and visible light and have remarkable photochemical activities. Reaction could affect
76 the redox potential of seawater in the euphotic layer and the speciation of trace elements (Zhang, 2000; Zhang
77 and Yang, 2000). For example, photo-induced reduction of Fe(III)-multi-hydroxyl-acid complex and
78 Fe(III)-hydroxy complexes was the significant source of Fe(II), active oxygen species and hydroxyl radicals
79 (Deng et al., 1997; Zhang et al, 2001; White et al., 2003). In sunlit oxygenated seawater, the dissolved manganese
80 present can be found in the reduced Mn (II) form. (Zhang and Yang, 2000). The photo-reduction of Cr(VI) could
81 be similarly driven by photo-redox from transition metals with light, e.g., the photocatalytic cycle of iron
82 contributed to reduction of Cr(VI) (Kocot et al., 2007). The non-living substances in seawater facilitate the
83 photoreduction of Cr(VI), including inorganic substances such as iron(II) (Buerge and Hug, 1997; Zhang et al.,
84 1995), Cu(I) (Millero, 1989), hydrogen sulfide (Pettine et al., 1994), superoxide (O_2^-) (Abu-Saba et al., 2000),
85 and organic compounds such as oxalate and citrate (Hug et al., 1997). The presence of Mn(II) affects the
86 oxidation of Cr(III) (Zhang, 2000), but the presence of manganese on the influence of photoreduction of Cr(VI)
87 in seawater is still not understood. Furthermore, multifactor mechanisms of photo-induced species
88 transformation of chromium have not been discussed to date.

89 The key parameters affecting the species transformation of trace elements in sunlit surface seawater should
90 include sunlight, marine phytoplankton due to their bioactivity and photo-reactivity and non-living substances
91 such as transition metals due to photochemical activity. Here we report our study on the photo-induced
92 reduction of Cr(VI) in the presence of marine phytoplankton with light, transition metals with light, and the
93 combination of both. Our objectives were to (a) study the influence of marine phytoplankton itself and Mn(II)
94 on the photochemical reduction of Cr(VI) for the first time; (b) exploit the combined effects from the
95 coexistence of bi- and tri- valent transition metals or the co-presence of marine phytoplankton and transition
96 metals on the photochemical reduction; (c) provide mechanistic explanations for the distribution of Cr(VI) and

97 Cr(III); (d) offer new insights into chromium biogeochemical behavior; and (e) assist in risk or bioavailability
98 assessment of Cr(VI)/Cr(III) in the sunlit surface seawater.

99 **2. Materials and methods**

100 *2.1. Apparatus*

101 A Model GBC 932AA atomic absorption spectrometer (GBC Co., Australia) with a chromium hollow-cathode
102 lamp operated at 6.0 mA was used for all the determinations of chromium. A slit of 1.3 nm was selected in order
103 to isolate 357.9 nm chromium absorption line. A UV-1200 PC spectrophotometer (Pekin Ruili Co., China) was
104 used for the determination of the optical density of algal suspensions. The irradiation experiments were
105 performed with a high-pressure mercury lamp (125 W, its photoemission spectrum was illustrated in Fig. 1) that
106 was covered by glass tube as a filter in order to keep the wavelength of the transmitted light over 300nm. The
107 illuminating intensity was $10000 \mu\text{mol}\cdot\text{photons}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, which was detected with a Digit Lux meter (TES 1332,
108 Taiwan, China).

109 *2.2. Reagents*

110 All other chemicals were of analytical grade from Shanghai Experiment Reagent Co., China. Double
111 de-ionized water of $18 \text{ M ohms cm}^{-1}$ specific resistivity, obtained in a Milli-Q plus Millipore system, was used
112 to prepare all the solutions and to rinse the previously cleaned laboratory material. Standard stock solutions of
113 Cr(III) and Cr(VI) were prepared, respectively, by dissolving an appropriate amount of CrCl_3 and $\text{K}_2\text{Cr}_2\text{O}_7$
114 (Merk Co.) in 0.5 mol L^{-1} HCl solution. All stock solutions were stored in the dark at $4 \text{ }^\circ\text{C}$. Working standard
115 solutions of lower concentrations were prepared daily by appropriate dilution. In order to avoid the adsorption
116 of chromium and contamination, Teflon vessels and $0.45 \mu\text{m}$ Nuclepore membrane filter (Teflon) were used,
117 which were precleaned in concentrated hydrochloric acid for 24 h. All solutions were sterilized in an autoclave
118 for 20 min at 121°C and 2 bar, and prepared in a dark chamber.

119 2.3. Marine phytoplankton cultures

120 Seven species of marine phytoplankton, including the diatom *Phaeodactylum tricornutum* (A), red alga
121 *Porphyridium purpureum* (B), and the green algae *Tetraselmis levi* (C), *Chlorella autotrophic* (D), *Dunaliella*
122 *salina* (E), *Nannochloropsis sp.* (F), and *Tetraselmis subcordiformis* (G), were obtained from the Microbial
123 Culture Laboratory, Ocean University of Qingdao, China. Marine phytoplankton were cultivated in f/2 media
124 prepared with sterile-filtered (Whatman GF/F glass fiber filter) artificial seawater prepared with the formula of
125 Keller (pH 8.1), with a cultivation temperature of $18\pm 0.5^\circ\text{C}$, and at a photon flux density of 140
126 $\mu\text{mol}\cdot\text{photons}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ with a day-night cycle of 12:12 h.

127 2.4. Determination of the biomass

128 The size of different microalgal genera was different. If the cells were from the same algal specie and cultivated
129 at the same time, the dry weight of the cells was linearly correlated with the optical density of the alga
130 suspension (Schmitt et al., 2001; Wang et al., 1997). The dry weight of the biomass was determined
131 gravimetrically at several optical densities of 500 ml alga suspension after being dried at 105°C for 24 h. The
132 optical density was determined with a UV-Vis spectrophotometer at specific wavelengths for A (750 nm), B
133 (750 nm), C (545 nm), D (486 nm), E (545 nm), F (475 nm), G (443 nm). Calibration of the dry weight of the
134 biomass against the optical density was carried out respectively. With the help of these calibrations, a fast
135 determination of marine phytoplankton concentration was feasible.

136 2.5. Verification of the bioactivity

137 Because the chromium concentration in ocean water is in a range of 0.2 to $50\ \mu\text{g L}^{-1}$ (U.S.EPA, 2006) and the
138 content of total chromium in coastal seawater was found to be $4\ \mu\text{g L}^{-1}$ (Nicolai et al., 1999), the initial
139 concentration of chromium in artificial seawater was $5\ \mu\text{g L}^{-1}$ in the irradiation experiments and dark controls
140 throughout this study. Tests were carried out to ensure that marine phytoplankton could survive and keep normal

141 bioactivity under the experimental conditions. Marine phytoplankton with concentrations ranging from 5 to 20
142 ng ml^{-1} were transferred to artificial seawater containing $5 \mu\text{g L}^{-1}$ Cr(VI) or Cr(III) and kept 24 h under
143 irradiation. The cells from the filters were resuspended into fresh medium under normal growth conditions. The
144 specific growth rates over the next 5 days and the cell shapes were recorded in triplicate cultures, and compared
145 with the normal growth rates and cell shapes. Abnormal phenomena were not observed, so it could be
146 concluded that $5 \mu\text{g L}^{-1}$ of Cr(VI) and Cr(III) were not toxic to the marine phytoplankton, i.e. living algal cells
147 were used in our photochemical experiments.

148 *2.6. Determination of Cr(VI) and Cr(III)*

149 Speciation analysis of chromium was performed following the procedures of Zhu and Li (2001). The detection
150 limit (3σ , $n = 11$) was $0.03 \mu\text{g L}^{-1}$ for Cr(VI) and $0.01 \mu\text{g L}^{-1}$ for Cr(III), respectively, at the level of $0.1 \mu\text{g L}^{-1}$,
151 the precision (relative standard deviation) was 3.3% for Cr(VI) and 2.8% for Cr(III), respectively. For samples
152 spiked with both Cr(III) and Cr(VI), the recovery varied from 97 to 102% for Cr(III) and from 96 to 103% for
153 Cr(VI).

154 To study the accuracy of this method, a synthetic artificial seawater sample with $0.1 \mu\text{g L}^{-1}$ Cr(VI), $0.1 \mu\text{g}$
155 L^{-1} Cr(III), and interfering substances (55 ng L^{-1} Fe(III), 250 ng L^{-1} Cu(II), 14 ng L^{-1} Mn(II), the exudates of 20
156 ng ml^{-1} marine phytoplankton), was analyzed. The concentration measured in synthetic water sample was
157 $0.10 \pm 0.01 \mu\text{g L}^{-1}$ for Cr(III), $0.10 \pm 0.01 \mu\text{g L}^{-1}$ for Cr(VI). The results demonstrated that: (a) the concentrations of
158 Cr(III) and Cr(VI) in synthetic artificial seawater sample agreed well with the added concentrations; (b) this
159 method avoided the reduction of Cr(VI) during the preliminary concentration and analysis process; (c) no
160 interference from the components of photochemical experimental system was observed.

161 Precautions were also taken to minimize the adsorption of Cr(III) and Cr(VI) during the experiments. These
162 included: (a) Teflon flasks were employed as the reactors for their good transparency and weak adsorptive

163 property; (b) the solutions or algal suspensions were stirred at 100 rpm during the irradiation experiments and
164 dark controls to simulate the current of seawater; (c) marine phytoplankton which have reached adsorption
165 equilibrium with $5 \mu\text{g L}^{-1}$ Cr(VI) in artificial seawater were used to reduce the adsorption from marine
166 phytoplankton in photochemical experiments; our preliminary study showed that the adsorption behaviors of
167 Cr(VI) and Cr(III) by marine phytoplankton were similar; (d) A relatively larger volume (500 ml) solution or
168 marine phytoplankton suspension was used to enhance the absolute mass of Cr(VI) in it, to weaken the relative
169 effects from the adsorptions.

170 Accumulation of anionic Cr(VI) (as chromate) in marine phytoplankton is generally slow (Wang, et al.,
171 2001). The preliminary study showed that the total concentration of chromium in solution or filtrate of marine
172 phytoplankton suspension could be kept at $5 \pm 0.06 \mu\text{g L}^{-1}$. In other words, the interferences of adsorption, the
173 deviation of adsorptive property between Cr(VI) and Cr(III), and the algae exudates on the determination could
174 be avoided through above-mentioned methods, and the influence from bio-absorption and biological
175 transformation on the distribution of chromium could be ignored.

176 *2.7. Photochemical experiments*

177 The cultures in the log phase were chosen to start photochemical experiments. Prior to the illumination
178 experiment, the procedure described by Tovar-Sanchez et al.(2003) was used to remove trace metals that might
179 have adsorbed on the algae cells, and it was harmless to live alga cells, and used in experiments. This procedure
180 involved washing the cells by gentle agitation with trace metal clean reagent (Tovar-Sanchez et al., 2003) for 5
181 min, filtering with $0.45 \mu\text{m}$ membrane filter. The filters were rinsed three times with 5 ml of artificial seawater.

182 Photo-induced reduction of $5 \mu\text{g L}^{-1}$ Cr(VI) in 500 ml artificial seawater (pH 8.1, $18 \pm 0.5 \text{ }^\circ\text{C}$) in the
183 presence of marine phytoplankton, transition metals, and the combination of both was studied. The vessel
184 temperature was controlled as $18 \pm 0.5 \text{ }^\circ\text{C}$. Because phytoplankton densities in subsurface water and at 20 m
185 depth were $870.9 \times 10^3 \text{ L}^{-1}$ and $327.8 \times 10^3 \text{ L}^{-1}$, respectively (Tengku-Rozaina and Ibrahim, 2001), the

186 concentration of marine phytoplankton was 5, 8, 10, 15, 20 ng ml⁻¹ for marine phytoplankton-light system and
187 10 ng ml⁻¹ for marine phytoplankton-transition metals-light system respectively. The concentration of transition
188 metals was 55 ng L⁻¹ for Fe(III), 250 ng L⁻¹ for Cu(II), and 14 ng L⁻¹ for Mn(II), i.e., the average concentration
189 of trace elements in actual seawater (Feng et al., 1999). The suspension or solution was agitated in an orbital
190 shaker at 100 rpm. The suspension or solution was sampled 50 ml after irradiation for 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7,
191 and 8 h.

192 These samples were filtered with 0.45 µm membrane filter and the concentration of Cr(VI) and Cr(III) in
193 the filtrates was determined respectively by FI-HG-AAS. The suspension or solution was covered with
194 aluminum foil and kept in the dark before and after irradiation. Dark controls were carried out in parallel. The
195 conversion percent was the concentration ratio between Cr(III) and total chromium at steady state.

196 **3. Results and discussion**

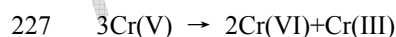
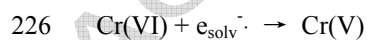
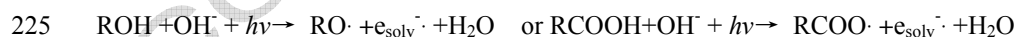
197 *3.1. Effect of marine phytoplankton on the reduction of Cr(VI)*

198 Light irradiation of 5 µg L⁻¹ Cr(VI) in artificial seawater with marine phytoplankton resulted in the formation of
199 Cr(III), but Cr(III) could not be detected in the dark control experiments. Its conversion ratio under different
200 species and concentrations of marine phytoplankton and different irradiation times was shown in Fig. 2. The
201 redox equilibrium between Cr (VI) and Cr (III) was also observed from Fig. 2.

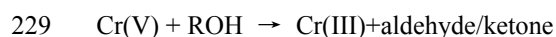
202 Light irradiation was essential to drive the reduction of Cr(VI) by marine phytoplankton, because Cr(VI) is
203 thermodynamically stable in the presence of oxygen, its reduction in aerobic environment is an endergonic
204 process, requiring investment of energy from an external source. To our knowledge, this was the first time that
205 marine phytoplankton itself could achieve the photoreduction of Cr(VI) was confirmed, because that: (a)
206 although DOM derived from phytoplankton has been proved to facilitate Cr reduction in the presence of light,
207 DOM is just the exudate from marine phytoplankton, not marine phytoplankton itself; (b) prior to our

208 photochemical experiments, the marine phytoplankton were rinsed three times with 5 ml of artificial seawater to
 209 remove exudates such as DOM; and (c) after light irradiation 30 min, Cr(III) could be detected, at the same time,
 210 the concentration of total organic carbon in seawater at this time is less than the detection limit of $4 \mu\text{g L}^{-1}$
 211 detected with to use a TOC-Vcph (Shimadzu Co.) analyzer.

212 In alkaline oxygenated solutions such as sunlit surface seawater, the CrO_4^{2-} anions are predominant
 213 (Mytych et al., 2004). Two kinds of mechanism were suggested to be responsible for the transformation of
 214 Cr(VI) to Cr(III): (a) Cr(VI) in excited state could be reduced by the electron donor in its ground state via
 215 photoinduced electron transfer; and (b) solvated electrons reduce the CrO_4^{2-} anions in their ground state by
 216 means of thermal reduction. The above mechanisms were based on: (a) the photoreduction of CrO_4^{2-} mediated
 217 by the electron donor (e.g. phenol and 2,3-butanediol) can proceed in alkaline oxygenated solutions (Mytych et
 218 al., 2003; Cieřła et al., 2004); (b) Cr(VI) could be thermal reduced by hydrated electrons photogenerated by
 219 phenol (Mytych et al., 2004); (c) the hydrated electron can be produced by the photolysis of the aromatic
 220 carboxyl acids (Calza and Pelizzetti, 2004); and (d) the surface acid groups such as phenolic hydroxyl and
 221 carboxylic acids are on the surface of marine phytoplankton cells (Garden-Torresdey et al., 1990; Wang et al.,
 222 1997; Li et al., 2006b). The possible mechanism of the influence of marine phytoplankton itself on the
 223 photochemical reduction of Cr(VI) was proposed as follows:



228 and/or



230 The concentration of the coloured dissolved organic matter (CDOM) derived from phytoplankton

231 increased with increasing the light irradiation time from 0.5 h to 8 h. The hydrated electron could be produced
232 by the photolysis of CDOM, then could facilitate Cr(VI) reduction (Thomas-Smith and Blough, 2001). The
233 photo-production of hydroxyl radical in seawater with marine phytoplankton under high-pressure mercury lamp
234 was observed by us (Li et al., 2008). The photo-production of hydroxyl radical enhances the concentration of
235 Fe(II), Cu(I) and Mn(II) in the sunlit surface seawater, induced the Cr(VI) reduction. At the same time, marine
236 phytoplankton could adsorb and complex chromium by their surface acid groups, which could change the redox
237 potential of chromium.

238 Fig. 2. indicated that the conversion ratio of Cr(VI) of Cr(III) was greatly affected by the species of
239 marine phytoplankton, its concentrations and the irradiation time. The conversion ratio increased and the
240 oxidation-reduction equilibrium time shortened with increasing algae concentration. As the influence factors of
241 marine phytoplankton on the photochemical reduction of Cr(VI), the surface acid amount on the surface of
242 marine phytoplankton cells (Wang et al., 1997), the components and contents of CDOM, and the interaction
243 between marine phytoplankton (or CDOM) and trace metals (chromium, iron, copper and manganese), were
244 different for different species of marine phytoplankton.

245 *3.2. Effect of transition metals on the reduction of Cr(VI)*

246 Our experiments proved remarkable but different photochemical activity on the species transformation of
247 chromium from transition metals (Fe(III), Cu(II), and Mn(II)). Cr(III) could not be detected in the dark control
248 experiments, so irradiation must also be essential for photochemical activity for transition metals. In seawater,
249 Fe(III), Cu(II), and Mn(II) could be chelated by organic substances such as citrate and gluconate (Zhang and
250 Yang, 2000), and electronic transition from such coordinated transition metals complexes could be induced
251 easily by light.

252 Through photo-induction, Fe(III) and Cu(II) were reduced into Fe(II) and Cu(I), and Mn(II) was oxidized
253 into Mn(III) and Mn(IV) oxide (MnO_x); at the same time, Fe(II) and Cu(I) were oxidized by oxidants such as

254 hydroxyl and superoxide radicals, H_2O_2 , and MnO_x was reduced to Mn(II) by photo-activation (Zuo and Hoigné,
255 1992; Zuo and Hoigné, 1993; Zhang et al., 1995; Voelker and Sedlak, 1995; Zuo and Jones, 1997; Zhang and
256 Yang, 2000; Voelker et al., 2000; Thomas-Smith and Blough, 2001; Deng et al., 2006). Photolysis of the
257 monohydroxyl complex of $\text{Fe}(\text{OH})^{2+}$ and oxidation reaction between transition metals (Fe(II), Cu(I), Mn(II)) and
258 oxidants (O_2 , H_2O_2) have been proposed as major sources of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ in sunlit surface waters (Zuo and
259 Hoigné, 1992; Zuo and Hoigné, 1993; Zuo and Jones, 1997; Wang and Yang, 2004). Superoxide and its
260 conjugate acid, hydroperoxyl radical (HO_2 , Zafriou, 1990), are produced in sunlit natural waters through
261 photochemical reactions. The bimolecular dismutation of superoxide has been postulated as the main source of
262 hydrogen peroxide in the open ocean (Petasne and Zika, 1987). Hydrogen peroxide is produced by
263 photochemical reactions in surface waters and occurs at concentration levels between 10^{-6} and 10^{-8} mol L^{-1}
264 (Sulzberger et al., 1997). The redox reaction of transition metals could induce the species transformation of
265 chromium. For example, Fe(II) has been shown to act as the electron donor in Cr(VI) reduction (Gaberell et al.,
266 2003) and the excited Fe(III) complexes, e.g. $[\text{Fe}(\text{edta})\text{OH}]^{2-}$ behave as even stronger electron donors towards
267 Cr(VI) (Cieřla et al., 2007; Kocot et al., 2007).

268 The electronic shell distribution and organic ligands of iron, copper and manganese are different. The value
269 of E^0 , i.e., the ability of coordinated complex to accept or donate electron is different, so the effect of different
270 transition metals on the photo-reduction of Cr(VI) is quite different. The conversion ratio and redox
271 equilibration time were listed in Table 1.

272 In the single transition metal experiments, copper showed the strongest photochemical activity and
273 manganese the weakest. In the presence of two transition metals, the photo-oxidation activity was higher than
274 the respective single metal. When all the three transition metals were present, the conversion ratio of chromium
275 was higher than that of each of the single metal and two metal pair. Though all of the transition metals,
276 including iron, copper and manganese, have photochemical activity, the co-existence of bi- or tri-valent

277 elements could increase the yield of radicals. At the same time, collisional deactivation of radicals could also
278 occur. Therefore, the co-existence of transition metals did not simply show additive property or synergistic
279 effect on the photo-oxidation activity.

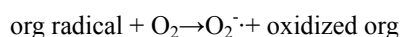
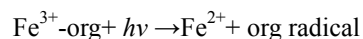
280 3.3. Combined effect of marine phytoplankton and transition metals on the reduction of Cr(VI)

281 The photo-reduction of Cr(VI) was facilitated not only by marine phytoplankton, but also by transition metals; the
282 combination effects of both were shown in Fig.3. It could be seen from Fig.3 that the reduction behavior of
283 Cr(VI), including conversion ratio, conversion rate and redox equilibration time varied with the constituents of
284 the photochemical system that was made up of same transition metals and different species of marine
285 phytoplankton or same species of marine phytoplankton and different transition metals. The difference of the
286 combined effect of marine phytoplankton and transition metals on the reduction of Cr(VI) was due to two
287 reasons: (a) if the species of marine phytoplankton is different, the influence factors of marine phytoplankton on
288 the photochemical reduction of Cr(VI) as mentioned above were all different; and (b) if the transition metal is
289 different; the complexing reaction with marine phytoplankton is different, too.

290 Chromium(VI) could be reduced to Cr(III) by the marine phytoplankton-light, transition metals-light, and
291 marine phytoplankton-transition metals-light systems. The photochemical activity for the reduction of Cr(VI)
292 was analyzed and compared in Table 2. The photochemical behaviors of marine phytoplankton-transition
293 metals-light systems (S_3) on the conversion ratio of Cr(VI) were the combination effects from the
294 photoreduction activity of marine phytoplankton (S_1), as the main contributor, and the photoreduction activity of
295 transition metals (S_2).

296 The photoreduction activity of the marine phytoplankton-transition metals-light system was higher than
297 that in the transition metals-light system, i.e., the value of (S_3-S_2) in Table 2, for three reasons: (a) marine
298 phytoplankton on its own has photoreduction activity, especially for photo-production of hydrated electrons and
299 releasing of the electron donors; (b) marine phytoplankton could adsorb, concentrate and coordinate transition

300 metals and chromium and thus change the redox potentials of transition metals and chromium; and (c) the
 301 content of the potential Cr(VI) reductants, including Fe(II), Cu(I), Mn(II) and O_2^- by transition metals might be
 302 enhanced by their organic ligands. For example, organic Fe(III) complexes (Fe^{3+} -org) are the main species of
 303 Fe(III) in the solution of Fe^{3+} with algae (Zuo and Hoigné, 1992; Zuo and Hoigné, 1993; Zuo and Jones, 1997;
 304 Liu et al., 2004). The effects of Fe^{3+} are described below.



307 The presence of transition metals increases the Cr(VI) reduction for 3 of the algae (A, C and G), has no
 308 impact for the algae B, but inhibits the reduction for 3 of the alga (D, E and F), according to the values of (S_3 - S_1)
 309 in Table 2. The species and concentration of Cr(VI) on the surface of algae or transition metal complexes might
 310 be affected by the coexistence of the alga and transition metal. A different mechanism is probably responsible
 311 for the Cr(VI) reduction by absorbing surfaces such as alga, transition metal complexes.

312 In marine phytoplankton-transition metals-light systems which are very close to the sunlit surface seawater,
 313 Cr(VI) was transformed into Cr(III) by photo-reduction. The ratio of Cr(VI) to Cr(III) was 0.48 for
 314 *Phaeodactylum tricornutum* (diatom), 0.71 for *Porphyridium purpureum* (red alga), and ranged from 1.45 to
 315 2.16 for five green algae (*Tetraselmis levis*, *Chlorella autotrophica*, *Dunaliella salina*, *Nannochloropsis sp.* and
 316 *Tetraselmis subcordiformis*). The most effective at reducing Cr (VI) was a diatom that are known to produce
 317 high concentrations of organic matter in the form of transparent exopolymer particles (Passow et al. 1994),
 318 dissolved organic matter mediated control of Cr reduction might be possible. The results were listed in Table 3,
 319 providing explanation for the distribution of Cr(VI) and Cr(III), obtaining useful information to understand the
 320 biogeochemical cycle of chromium. This study is beneficial to deal with assessment of the risk/bioavailability
 321 of Cr(VI)/Cr(III) in sunlit surface seawater.

322 4. Summary

323 The influence of marine phytoplankton itself (excluding its exudates such as DOM) on the photo-reduction of
324 trace metals was confirmed for the first time. The conversion ratio of Cr(VI) to Cr(III) increased with increasing
325 algae concentration and irradiation time. Different species of marine phytoplankton were found to have
326 different photo-reducing abilities. In addition to the photo-production of hydrated electrons, marine
327 phytoplankton could adsorb, concentrate and coordinate transition metals and chromium, change their redox
328 potentials, and affected their photochemical activities. The effect of the marine phytoplankton-transition
329 metal-light system on the chromium species transformation, especially the addition of marine phytoplankton,
330 was most important. We tried to interpret the observed relationships between Cr(VI) and Cr(III), and provided
331 further information for the understanding of the biogeochemical cycle of chromium, as well as for the risk
332 assessment of chromium in the sunlit surface seawater.

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Table 1

Photoreduction of Cr(VI) by transition metals

Transition metals	Fe(III)	Cu(II)	Mn(II)	Fe(III)+Cu(II)	Fe(III)+Mn(II)	Cu(II)+Mn(II)	Fe(III)+Cu(II)+Mn(II)
Conversion percent (%)	8.1	10.8	6.8	12.5	10.0	11.2	13.3
Redox equilibration time (hour)	3 h	5 h	6 h	5 h	6 h	6 h	6 h

Table 2

Photoreduction of Cr (VI) by marine phytoplankton, transition metals, marine phytoplankton and transition metals

Photoreduction System	Conversion percent (%)						
	<i>Phaeodactylum tricornutum</i>	<i>Porphyridium purpureum</i>	<i>Tetraselmis levi</i>	<i>Chlorella autotrophic</i>	<i>Dunaliella salina</i>	<i>Nannochloro psis sp.</i>	<i>Tetraselmis subcordiformis</i>
Alga and Cr(VI)(S ₁) Fe(III),Cu(II),Mn(II) and Cr (VI) (S ₂)	46.9	56.7	32.9	47.1	52.9	44.3	26.4
Alga,Fe(III),Cu(II),Mn(II) and Cr (VI) (S ₃)	67.6	58.7	40.9	31.7	35.1	33.3	32.4
S ₃ - S ₁	20.7	2.0	8.0	-15.4	-17.8	-11.0	6.0
S ₃ - S ₂	54.3	45.4	27.6	18.4	21.8	20.0	19.1

The content of marine phytoplankton was 10 ng/mL. The concentration of Fe(III), Cu(II) and Mn(II) was 55, 250 and 14 ng/L, respectively.

Table 3

Ratio of Cr (VI) to Cr(□) after photoreduction by marine phytoplankton-transition metals-light system

Alga	<i>Phaeodactylum tricornutum</i>	<i>Porphyridium purpureum</i>	<i>Tetraselmis levi</i>	<i>Chlorella autotrophic</i>	<i>Dunaliella salina</i>	<i>Nannochloropsis sp.</i>	<i>Tetraselmis subcordiformis</i>
Ratio of Cr(VI) to Cr(III)	0.5	0.7	1.4	2.2	1.8	2.0	2.1

The content of marine phytoplankton was 10 ng/mL. The concentration of Fe(III), Cu(II) and Mn(II) was 55, 250 and 14 ng/L, respectively.

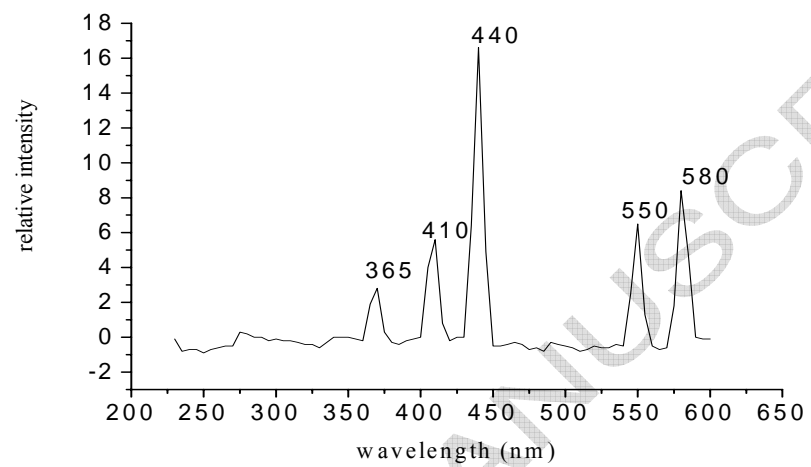


Fig. 1. Emission spectrum of the high-pressure mercury lamp

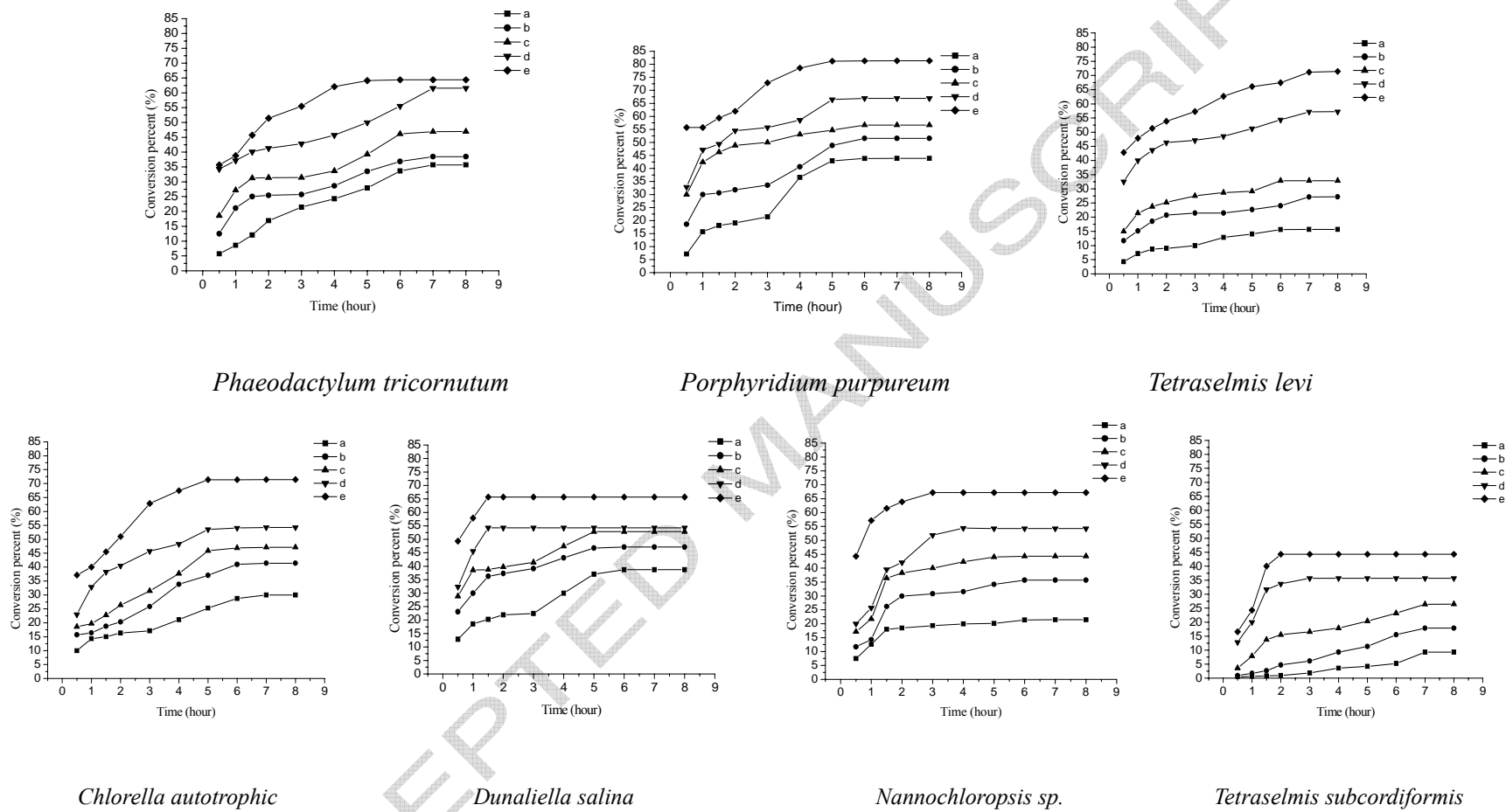


Fig. 2. Photoreduction of $5 \mu\text{g L}^{-1}$ Cr(VI) in the presence of marine phytoplankton at concentrations of a) 5, b) 8, c) 10, d) 15 and e) 20 ng ml^{-1}

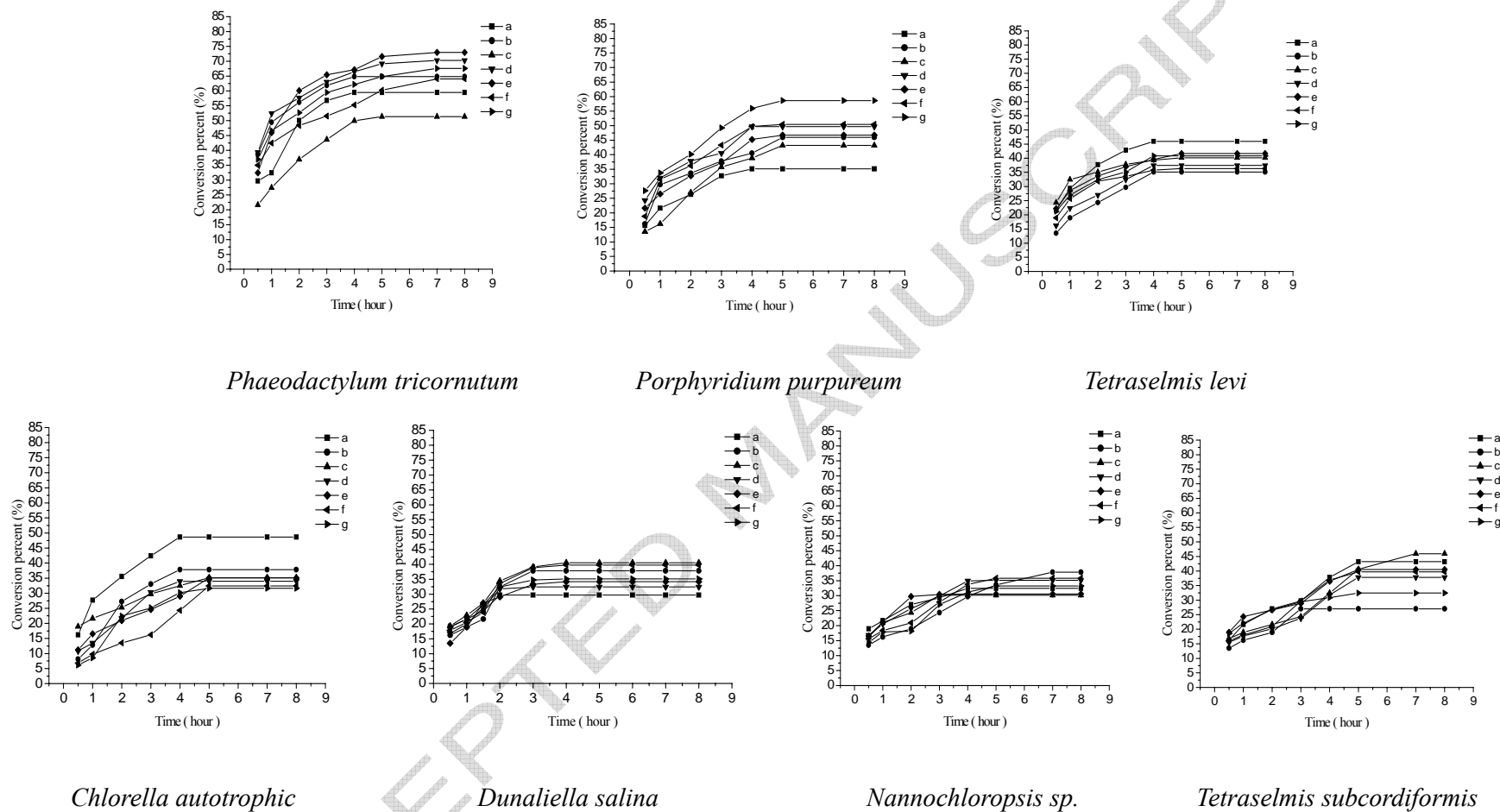


Fig. 3. Photoreduction of Cr(VI) ($5 \mu\text{g L}^{-1}$) in the presence of marine phytoplankton and transition metals. The content of marine phytoplankton was 10 ng ml^{-1} . The concentration of Fe(III), Cu(II) and Mn(II) is 55, 250 and 14 ng L^{-1} , respectively. a: Fe(III) b: Cu(II) c: Mn(II) d: Fe(III) and Cu(II) e: Fe(III) and Mn(II) f: Cu(II) and Mn(II) g: Fe(III), Cu(II) and Mn(II)