

## Review and Research Results

# Marine Macroalgae in Polar Regions as Natural Sources for Volatile Organohalogens

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**Abstract.** Marine macroalgae species from the polar regions were investigated for their importance as natural sources of volatile halogenated compounds released into the biosphere. Several different halogenated C<sub>1</sub> to C<sub>4</sub> hydrocarbons were identified and their release rates determined. The compounds contained mainly bromine and iodine, and form was the dominant compound released. Although an annual atmospheric input of approximately 10<sup>8</sup>-10<sup>10</sup> g bromine and 10<sup>7</sup>-10<sup>8</sup> g iodine was calculated from the release rates, marine macroalgae are apparently not the major source on a global scale, as the release is up to four orders of magnitude lower than a presumed annual flow from the oceans. Despite this, macroalgae may be more important on a local scale due to their occurrence at a high biomass in the coastal regions. The present paper gives an overview about studies done on the release of volatile halocarbons by macroalgae from polar regions. Furthermore, the function of these compounds in the macroalgal metabolism is discussed.

**Keywords:** Algal metabolism; bromoform; marine macroalgae; methyl halides; polar regions; volatile halocarbons

## Introduction

Stratospheric ozone depletion and volatile halogenated compounds are strongly connected with each other since the discovery that a massive loss of ozone in the polar stratosphere is catalyzed by halogen radicals derived from chloro and chlorofluorocarbons (CFCs) [1-3]. These compounds are released in high amounts into the environment by human activities. The threat that the protecting layer against certain wavelengths of ultra-violet (UV) radiation from the sun, e.g. UV-B, could disappear, kept researchers and politicians together working hand in hand for solutions. This unusual co-operation resulted in the Montreal Protocol (1987) [4] declaring that all industrial nations will stop the production of CFCs by 1996. A recently released report on Scientific Assessment of Ozone Depletion 1998 [5], prepared by the scientific assessment panel of the Montreal Protocol, stated a probable return of the halogenated ozone-depleting substances to its pre-1980 levels and a recovery of the ozone layer in 50 years, provided that parties fully adhere to the 1989 treaty [6]. However, it may be far too early to uncork the 'bottleneck' as there are still incalculable threats like il-

legal production of CFCs [7], large-area biomass burning [8], or natural events like major volcanic eruptions [9]. Furthermore, so far unknown natural sources of volatile organohalogens may also contribute to a further destruction of the ozone layer. Therefore, it is important to investigate a possible natural part of the halocarbon input into the environment. At present, known sources are terrestrial sources like forests [10-12] or rice fields [13], and the global oceans [14-16], where marine macroalgae [17-19], ice algae [20,21] and probably also phytoplankton [22,23] contribute to the halocarbon budget. In the polar regions, natural sources may be more important compared to others regions of the world due to their close-range location to major ozone destruction. Estimating the significance of marine macroalgae occurring in the polar regions as a source for volatile halocarbon, several different species of macroalgae were investigated and their release of volatile organohalogens determined.

## 1 Analytical Methods

The analytical methodology for the determination of volatile halocarbons in the environment is now well enough developed to allow ultra-sensitive and reliable measurements in remote areas like the polar regions. For field studies, intertidal macroalgae were collected in the Arctic (Ny-Ålesund, Svalbard) and in the Antarctic (King George Island, South Shetlands) at low tide, and species from deeper waters were collected by a benthic algal sampler or by scuba diving [17,18]. For culture experiments, macroalgae from the Arctic (Ny-Ålesund, Svalbard) and the Antarctic (King George Island, South Shetlands) were cultivated under optimized growth conditions in unialgal cultures mimicking the temperature and day-length conditions in the polar regions [24]. Details on the macroalgae and the incubation conditions are given in Table 2. To investigate the release of volatile halocarbons by macroalgae, complete algal thalli were incubated with no headspace in glass vessels filled with filtered natural seawater. For field studies, most of the macroalgae were too large for incubating a complete thallus. Therefore, pieces of alga were cut with a sharp scalpel and placed for not less than 24 h in running seawater before incubation. Enhanced release rates due to algal wounding were thereby avoided. The determination and verification of volatile halocarbons were carried out by stripping the incubation medium with purge-and-trap and analyzing the

separated volatile halocarbons by high resolution gas chromatography with electron capture detection and microwave-induced plasma atomic emission detection (p&t-HRGC-ECD/MIP AED) [24,25]. With this method, detection limits down to 1 pmol L<sup>-1</sup> were obtained, and several volatile halogenated compounds from chloromethane to 2-iodobutane were identified and their release quantified (see Table 1).

## 2 Results and Discussion

### 2.1 Methyl halides

Due to their role as a source for halogen radicals in the atmosphere, the methyl halides, methyl chloride, methyl bromide and methyl iodide received considerable interest over the last decades. Comparable to CFCs, especially methyl chloride and methyl bromide own a higher photochemical stability and therefore increase their importance in stratospheric photochemical reactions [8,26]. Both anthropogenic and biogenic sources of methyl halides have been identified [27-29]. For polar macroalgae, several different species were found to release methyl halides with methyl chloride as the dominant species [30]. Average release rates for the methyl halides of 1.68 to 34.7 pmol wet algal weight (waw) g<sup>-1</sup> d<sup>-1</sup> were measured (see Table 1). Compared to an earlier study on the release of these compounds by temperate macroalgae [31], polar macroalgae showed an approximately 10 to 50-fold lower release.

### 2.2 Volatile organobromine compounds

Various ranges of brominated and brominated-chlorinated compounds released by marine macroalgae from the polar regions have been identified (Table 1) [17,18]. Among the compounds found, the bromoform release dominated due to its up to 20 to 30-fold higher release rates compared to the other mainly released compounds of bromoethane and dibromomethane (Table 1). Investigations of different macroalgae species showed independent whether the alga belongs to the group of red, brown or green macroalgae that bromoform is the preferably released compound (Table 2). The release of volatile halocarbons by polar macroalgae predominantly occurred by brown and green macroalgal species, whereas red algal species showed only a low release. Data on subtropical and temperate macroalgae are still scarce due to missing screenings of different macroalgal species from these climatic regions. Similar to the methyl halides, macroalgae occurring in the Arctic and Antarctic revealed a lower release of organobromine compounds than macroalgae from temperate or subtropical regions. The release rates of bromoform, for example, are 2 to 5-fold lower compared to those determined for temperate macroalgae [30]. Interesting is that halocarbons like 1,2-dibromoethane (used as a gasoline additive), which were believed to have an anthropogenic origin only, are also formed biogenically [17]. Therefore, the occurrence of these compounds in oceanic or remote Antarctic regions [32,33] cannot automatically be assumed to be of industrial origin only.

**Table 1:** Various volatile halocarbons determined from different macroalgal species from polar regions. Values are the average release rates and variation of the release rates between the different algal species.

Compound detected	Formula	Release rate [pmol g <sup>-1</sup> wet algal weight day <sup>-1</sup> ]	
		average	range
methyl chloride	CH <sub>3</sub> Cl	35	0 - 2.8*10 <sup>3</sup>
methyl bromide	CH <sub>3</sub> Br	2.0	0 - 67
bromochloromethane	CH <sub>2</sub> BrCl	9.2	0 - 85
dibromomethane	CH <sub>2</sub> Br <sub>2</sub>	90	0 - 693
bromodichloromethane	CHBrCl <sub>2</sub>	23	0 - 145
dibromochloromethane	CHBr <sub>2</sub> Cl	48	0 - 600
bromoform	CHBr <sub>3</sub>	1.3*10 <sup>3</sup>	0 - 15.5*10 <sup>3</sup>
bromoethane	C <sub>2</sub> H <sub>5</sub> Br	719	0 - 3.5*10 <sup>3</sup>
1,2-dibromoethane	1,2-C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	41	0 - 266
methyl iodide	CH <sub>3</sub> I	1.7	0 - 63
chloriodomethane	CH <sub>2</sub> ClI	3.8	0 - 39
diiodomethane	CH <sub>2</sub> I <sub>2</sub>	68	0 - 183
iodoethane	C <sub>2</sub> H <sub>5</sub> I	6.0	0 - 36
1-iodopropane	1-C <sub>3</sub> H <sub>7</sub> I	0.48	0.03 - 1.4
2-iodopropane	2-C <sub>3</sub> H <sub>7</sub> I	1.25	0.03 - 11
1-chloro-3-iodopropane	1,3-C <sub>3</sub> H <sub>6</sub> ClI	not quantified	
1-iodobutane	1-n-C <sub>4</sub> H <sub>9</sub> I	0.27	0 - 0.58
2-iodobutane	2-n-C <sub>4</sub> H <sub>9</sub> I	0.08	0 - 0.20
1-iso-iodobutane	1-iso-C <sub>4</sub> H <sub>9</sub> I	0.07	0 - 0.25

**Table 2:** Main released volatile halocarbons from selected species of macroalgae occurring in the polar regions and corresponding incubation conditions. (Bold = major occurring macroalgae in the polar regions).

Macroalgae species	Main compound released	Release rate [pmol g <sup>-1</sup> waw d <sup>-1</sup> ]	Incubation conditions					
			A		T		P	
			L	F	L	F	L	F
<b>Phaeophyta (brown macroalgae)</b>								
<i>Desmarestia antarctica</i> Moe et Silva	CHBr <sub>3</sub>	253	-	x	-	24	-	nr
<i>Desmarestia anceps</i> Montagne	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub> , CHBr <sub>2</sub> Cl	15491, 693, 599	x	x	-	24	10	nr
<i>Desmarestia menziesii</i> J. Agardh	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub> , CHBr <sub>2</sub> Cl	5190, 390, 317	x	x	24	24	10	nr
<i>Himantothallus grandifolius</i> (A. et E.S. Gepp) Zinova	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub>	952, 144	x	x	24	24	25	nr
<i>Cystosphaera jaquinotii</i> (Montagne) Skottsberg	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub> , CHBr <sub>2</sub> Cl	3348, 620, 379	-	x	-	24	-	nr
<i>Fucus distichus</i> L.	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub>	45, 15	-	x	-	30	-	nr
<i>Dictyosiphon foeniculaceus</i> (Huds.) Grev	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub>	311, 19	-	x	-	30	-	nr
<i>Laminaria saccharina</i> (L.) Lamour.	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub> , 1,2-EtBr <sub>2</sub>	155, 62, 47	x	x	24	24	25	nr
<i>Laminaria solidungula</i> J.Ag.	CHBr <sub>3</sub> , 1,2-EtBr <sub>2</sub>	42, 13	-	x	-	32	-	nr
<i>Chordaria flagelliformis</i> (O.F. Müll.) C. Ag.	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub>	35, 4.6	-	x	-	30	-	nr
<i>Alaria esculenta</i> (L.) Greville	CHBr <sub>3</sub>	245	x	-	48	-	10	-
<b>Rhodophyta (red macroalgae)</b>								
<i>Kallymenia antarctica</i> Hariot	CHBr <sub>3</sub>	179	x	x	44	48	10	nr
<i>Plocamium coccineum</i> (Hudson) Lyngbye	CHBr <sub>3</sub>	226	-	x	-	72	-	nr
<i>Gymnogongrus antarcticus</i> Skottsberg	CH <sub>2</sub> I <sub>2</sub> , CH <sub>3</sub> Cl, CHBr <sub>3</sub>	29, 27, 15	x	x	45	72	10	nr
<i>Gigartina skottsbergii</i> (Bory) Setchell and Gardner	CHBr <sub>3</sub> , CH <sub>3</sub> Cl, CH <sub>2</sub> Br <sub>2</sub>	277, 30, 29	x	x	95	48	10	nr
<i>Iridaea cordata</i> Kützling	CHBr <sub>3</sub>	106	x	x	100	48	25	nr
<i>Palmaria decipiens</i> (Reinsch) Ricker	CHBr <sub>3</sub>	298	x	x	96	48	25	nr
<i>Myriogramme mangini</i> (Gain) Skottsberg	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub>	425, 94	x	x	93	72	10	nr
<i>Curdiea racovitzae</i> Hariot	CHBr <sub>3</sub> , CHBr <sub>2</sub> Cl, CH <sub>2</sub> I <sub>2</sub>	1254, 1401, 119	-	x	-	72	-	nr
<i>Devalaerea ramentacea</i> (L.) Guiry	CHBr <sub>3</sub>	17	-	x	-	48	-	nr
<i>Plocamium cartilagineum</i> (Linné) Dixon	CHBr <sub>3</sub>	72	x	-	48	-	10	-
<i>Pantoneuro plocamioides</i> Kylin	CHBr <sub>3</sub> , CH <sub>2</sub> I <sub>2</sub>	31, 28	x	-	48	-	10	-
<b>Chlorophyta (green macroalgae)</b>								
<i>Enteromorpha bulbosa</i> (Suhr) Montagne	CHBr <sub>3</sub> , CH <sub>2</sub> I <sub>2</sub>	219, 40	-	x	-	48	-	nr
<i>Enteromorpha compressa</i> (Linné) Greville	CHBr <sub>3</sub> , CH <sub>3</sub> Br	65, 3.7	x	x	98	36	15	nr
<i>Monostroma arcticum</i> Wittr.	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub> , 1,2-EtBr <sub>2</sub>	309, 42, 35	-	x	-	36	-	nr
<i>Blidingia minima</i> (Näg. ex Kütz.) Kylin	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub>	261, 14	-	x	-	48	-	nr
<i>Urospora penicilliformis</i> (Roth) Areschoug	CHBr <sub>3</sub>	64	x	x	24	48	50	nr
<i>Acrosiphonia sonderi</i> (Kütz.) Kornm.	CHBr <sub>3</sub> , CHBr <sub>2</sub> Cl	78, 7.1	-	x	-	48	-	nr
<i>Ballia callitricha</i> (C. Agardh) Kütz.	CHBr <sub>3</sub>	64	x	-	98	-	15	-
<i>Lambia antarctica</i> (Skottsberg) Delépine	CHBr <sub>3</sub>	30	x	-	98	-	15	-

waw = wet algal weight; A = samples; T = incubation period [hours]; L = laboratory cultures

F = field samples; nr = not recorded

P = photon flux [μmol m<sup>-2</sup> sec<sup>-1</sup>]. Values for culture samples only. Field samples were illuminated according to the light regime in the polar regions at the time of the studies.

### 2.3 Volatile organoiodine compounds

Different to chlorinated or brominated compounds, iodinated compounds play a more significant role in tropospheric chemistry. They are photodissociated faster than the corresponding chlorine and bromine compounds [34]. As no significant anthropogenic sources are known, it is assumed that iodinated compounds are exclusively of biogenic origin [35]. Marine macroalgae from the polar regions are a biogenic source for a variety of iodinated compounds [36]. Diiodomethane, iodoethane and methyl iodide are the major released compounds (see Table 1). However, compared to organobromine compounds, the release rates for iodinated hydrocarbons are up to 4 orders of magnitude lower. In contrast to the methyl halides and organobromine compounds, which were released at higher rates by temperate or subtropic macroalgae [30], polar macroalgae exhibited higher release rates for the organoiodine compounds [36]. A view on the total halocarbon release by subtropic and polar macroalgae (Fig. 1) showed a higher proportion of iodinated compounds on the release of halocarbons by polar macroalgae, possibly due to the increasing stability of iodinated hydrocarbons at lower temperatures.

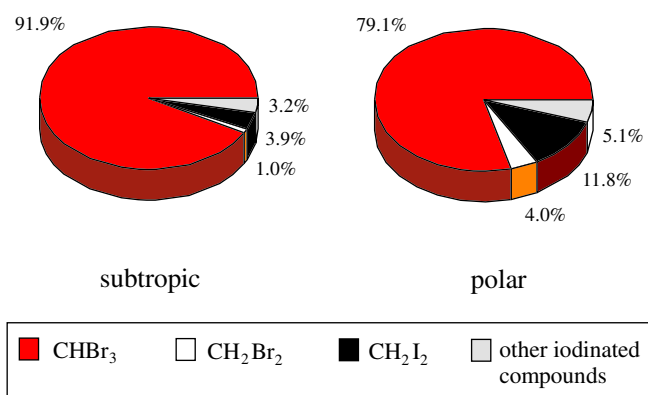


Fig. 1: Percentage of the single volatile organohalogen compounds released by polar and subtropic macroalgae during a 24 h period.

### 2.4 Influence of altered environmental conditions

In the polar environment, a possible influence of varying environmental conditions like temperature, photoperiods, salinity on the release of volatile halocarbons cannot be neglected. Whereas the water temperature remains fairly constant during the year, very high variations in salinity and photoperiods were found due to ice formation or melting, and very long (summer) or very short (winter) day-lengths, respectively [37,38]. However, salinity, air temperature and probably also nutrient availability may have a considerable influence only on macroalgae occurring in the tidal zone, whereas changes in photoperiods and also photon fluxes affected macroalgae in the whole marine habitat [38]. Determination of volatile halocarbons released by cultivated polar algae exposed to altered environmental conditions showed increasing release rates for both short-term (a few hours) and long-term (two month) exposition compared to rates obtained under standard culture conditions. For example, increasing release rates have been found when macroalgae were exposed to lower salinity or higher temperature [39]. Further-

more, macroalgae in the polar environment exhibited a higher halocarbon release at low photon fluxes. They even continued to release these compounds under the absence of light [40]. This is probably quite important for the polar regions, as a constant release of halocarbons during the winter may lead to a concentration build-up in the Antarctic environment. With sunrise in spring, these naturally-formed compounds may be more important for atmospheric photochemical reactions than generally assumed.

### 2.5 The function of volatile halocarbons for macroalgae

What is the function of volatile halocarbons in macroalgae? The puzzling question about the biological significance of these compounds in algal metabolism still remains unanswered. The extracts of some macroalgae exhibited a high antibiotic activity [41] and it has been suggested that halogen containing metabolites are synthesized as active messengers in an exocrine system involved primarily in chemical defense against, for example, microorganisms or herbivores [41]. The toxicity of halocarbons is caused by their ability to act as alkylating agents [42]. Narcotic effects of bromoform on some marine organisms were described by Gibson et al. [43]. A release of volatile halocarbons from all parts of the algal thalli [18] supported the theory of a function as a chemical defense. However, Iken [44] found trophic relations between herbivores and some Antarctic macroalgae like *Desmarestia anceps* or *D. menziesii*, which also showed high release rates of volatile halocarbons [17]. Antarctic macroalgae are believed to be an important food for a variety of marine herbivores, although they possess a high halocarbon formation. In general, naturally-produced semi-volatile and non-volatile halocarbons play an essential role in the survival of the organisms for chemical defense and food gathering [45]. Whether the volatile halocarbons also play an active part in this role remains to be seen. On the contrary, a constant release of bromoform or 1-iodobutane during a 24 h incubation period may be an indication that volatile halocarbons, or at least some of them, are only side-products in macroalgal metabolism. Pedersen et al. [46] assumed the halocarbon formation as a side step in the breakdown of surplus hydrogen peroxide released in the algae cells under oxidative stress. As high concentrations of hydrogen peroxide are toxic to the cells, macroalgae may use molecular iodine and probably also bromine to reduce the surplus hydrogen peroxide. Macroalgae have been found to accumulate high levels of iodine, which may serve for the formation of higher-molecular weight iodinated antimicrobial compounds [47]. Under normal conditions, hydrogen peroxide mainly formed by extracellular sources is used for the oxidation of iodide to hypoiodous acid and molecular iodine. This reaction is catalyzed by haloperoxidases located in the cell walls [48], leading to an intracellular accumulation of oxidized iodine in the algae. Under oxidative stress, iodine is mobilized and haloperoxidases can use the released iodine to catalyze the destruction of surplus hydrogen peroxide under formation of volatile halocarbons, which together with molecular iodine are released from the cells into seawater ('iodovolatilization') [47]. The same mechanism may also be in operation for bromine.

## 2.6 Global significance of marine macroalgae emissions

The question remains, whether marine macroalgae are important for the environmental halocarbon input on a global scale. Using a global algae biomass of  $6 \times 10^{13}$  g and assuming a 100% transfer of the released compounds from the oceans into the atmosphere, an annual input of  $10^8$ - $10^{10}$  g bromine originating to 73% from bromoform, and  $10^7$ - $10^8$  g iodine originating to 80% from diiodomethane can be calculated from the average release rates determined from macroalgae (Table 3). Compared to a presumed annual oceanic flow of  $10^{10}$ - $10^{12}$  g bromine and  $10^{11}$ - $10^{12}$  g iodine [36], the input estimated to be released from macroalgae is up to four orders of magnitude lower. Although the estimations have to be considered carefully, since the global macroalgae biomass can only be calculated very roughly, macroalgae apparently are not the main source of atmospheric bromine and iodine, even when considered that macroalgae from temperate zones revealed partly higher release rates than those found in polar regions [30]. Besides macro and ice algae, other so far unknown sources may also be involved in the release of these compounds. Recently, phytoplankton was reported to be able to form and release volatile halocarbons [22,23]. However, the investigations were done in laboratory experiments only. Field studies from the open oceans are still lacking and an extrapolation from these controlled culture experiments to the marine environment cannot yet be performed. If field data confirms the results from the laboratory experiments, phytoplankton may be a considerable source for the input of volatile halocarbons into the biosphere, due to their abundant occurrence in the whole area of the global oceans. Macroalgae may be more important for the local input in the coastal regions where they occur in considerable depth down to 30 m along thousands of kilometers of coastlines.

**Table 3:** Estimated annual atmospheric input of organic bromine and iodine released by marine macroalgae.

Marine macroalgae	Bromine [gr yr <sup>-1</sup> ]	Iodine [gr yr <sup>-1</sup> ]
marine algae* <sup>1)</sup>	$10^8 - 10^9$	$10^7 - 10^8$
marine algae** <sup>2)</sup>	$10^8 - 10^{10}$	
oceans <sup>1)</sup>	$10^{10} - 10^{12}$	$10^{11} - 10^{12}$
anthropogenic <sup>2)</sup>	$10^{10} - 10^{11}$	

<sup>1)</sup>Giese et al. [36]; <sup>2)</sup>Goodwin et al. [19]

\*polar, temperate, subtropic macroalgae

\*\*temperate kelp and non-kelp macroalgae

## 2.7 Uncertainties resulting from laboratory studies

Investigations of Wiencke [49] showed that the growth of macroalgae in laboratory experiments is comparable to the field. Therefore, the use of cultivated algae to investigate the release of volatile halocarbons is an acceptable and reliable procedure. However, when estimating the global input of organobromine and organoiodine from release studies obtained by cultivated macroalgae, it has to be considered that, different to the field, macroalgae from the laboratory were held under optimal culture conditions, i.e. constant temperature, constant photon flux adapted only to the day-

night-changes in the polar regions, optimum entrophication. Furthermore, cultivated macroalgae are free of epiphytes and the bacteria content is minimized due to filtration of the seawater and the use of sterile equipment. For some macroalgae species, the identical release of volatile halocarbons were found for the laboratory and the field (e.g. *Iridaea cordata* Kützing), whereas some species showed a much higher release in the field (e.g. *Desmarestia anceps* Moe et Silva). As the real conditions in the field cannot be simulated exactly, the global input of volatile halocarbons from field macrolage as a source may vary significantly from the one estimated from laboratory studies. This has to be considered carefully when discussing the global environmental input of volatile halocarbons from natural sources like marine macroalgae.

## 3 Conclusion

The studies showed that marine macroalgae in polar regions are an important natural source for volatile organohalogenes contributing to the release of these compounds into the biosphere. Although, at present, marine macroalgae are apparently not the major source on a global scale, they may become more important in the future due to the influence of changing abiotic factors such as photon fluence rate, nutrient concentration, temperature, and salinity on the formation of volatile organohalogenes. Global warming and further uncontrolled eutrophication of the oceans may result in an unknown increase of the emission of volatile organohalogenes into the global environment.

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