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A review of shellfish phycotoxin profile and toxic phytoplankton species along Croatian coast of the Adriatic Sea

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Toxin analyses along Croatian coast of the Adriatic Sea started in mid 1990s when okadaic acid has been determined in shellfish from Kaštela Bay (central Adriatic Sea). Since then, the toxin profile of Adriatic shellfish has become complex and the number of recorded toxic and potentially toxic species has increased over the time. Up to date, phycotoxins determined in Adriatic shellfish or phytoplankton belong to various groups od toxins: okadaic acid toxin group, saxitoxin group, domoic acid group, yessotoxins (YTXs), pectenotoxins (PTXs), gymnodimines (GYMs), spirolides (SPX) and palytoxins (PLTs). Toxins from okadaic acid group and YTXs are highlighted as the main phycotoxins in shellfish along Croatia coast of the Adriatic Sea. Toxins from okadaic acid group has been determined in high concentration that could endanger human health while YTXs have been determined more often in shellfish samples, comparing to other phycotoxins. Regarding toxic phytoplankton species reported in the Adriatic Sea, only for ten species toxin production has been confirmed and 20 species are suspected to be toxic. Toxicity has been confirmed for eight dinoflagellates species: Alexandrium minutum, Alexandrium ostenfeldii, Dinophysis fortii, Gonyaulax spinifera, Lingulodinium polyedrum, Ostreopsis cf. ovata, Prorocentrum lima, Protoceratium reticulatum *and two diatom species* Pseudo-nitzschia delicatissima *and* Pseudo-nitzschia multiseries*. Toxin profile has yet to be defined for other potentially toxic phytoplankton species found along Croatian coast of the Adriatic Sea. Most of those species are* Dinophysis *and* Pseudo-nitzschia *species, which are relatively common and abundant in this area as well as toxins from okadaic acid group in shellfish.*

Key words: Phycotoxins, shellfish toxicity, toxic phytoplankton, Croatian coast of the Adriatic Sea

INTRODUCTION

Phytoplankton is a major producer of organic compounds in the ocean and is crucial to the marine ecosystem. A proliferation of phytoplankton is usually beneficial for the marine ecosystem, except in the case of harmful species. Among approximately 4000 phytoplankton species described up to date (SIMON *et al.*, 2009), 300 of them are considered to be harmful (HALLEGRAEFF, 2003). Harmful algal blooms (HAB) affect marine ecosystem in various ways. In general, regarding the effect they cause harmful phytoplankton species can be observed as: high-biomass producers and toxin producers. First group includes species which are able to proliferate in abundance and thus form dense blooms (>10^6 cell L^{-1}). This can cause significant ecological problems such as hypoxia and anoxia due to degradation of organic matter or economic problems caused by discoloration of the seawater. Phytoplankton species producing phycotoxins could have a harmful effect on the ecosystem at much lower cell concentration causing so called "toxic bloom". This is referred to a threshold population density above which, its occurrence has harmful consequences (SMAYDA, 1997). According to HALLEGRAEFF (2003) there are about 80 species with the capacity to produce toxins. The majority are dinoflagellates. However, some species of diatoms, cyanobacteria, raphidophytes and prymnesiophytes are also able to synthesize toxins. Phycotoxins are their secondary metabolites, but it is important to notice that species toxicity may vary in different geographical areas and in different environmental conditions (AMATO *et al*., 2010; PISTOCCHI *et al.,* 2011; TRAINER *et al*., 2012). Generally, phycotoxins can be classified as: saxitoxin group (STX), domoic acid group (DA), okadaic acid group (OA), pectenotoxin group (PTX), yessotoxin group (YTX), azaspiracid group (AZA), brevetoxin group (BTX), ciguatera group (CTX), cyclic imines group and palytoxin group (PLT). Saxitoxin group and domoic acid toxin group are hydrophilic toxins while the others are lipophilic, except palytoxin which is a large molecule with both, hydrophilic and lipophilic areas. Until recently phycotoxins were usually classified regarding the symptoms they cause and the main groups were diarrhetic (DSP), paralytic (PSP), amnesic (ASP), neurotoxic (NSP), azaspiracid (AZA) shellfish poisoning and ciguatera fish poisoning (CFP). Yessotoxins and pectenotoxins together with okadaic acid and its derivates dinophysistoxins, were part of DSP toxins, but as yessotoxins and pectenotoxins don't cause diarrhea, today they are separate groups. The main phycotoxin groups and species that produce them are summarised in Table 1. Toxic blooms can cause wide-range of negative impacts, including human intoxications (GARCÌA *et al*., 2004; GALLITELLI *et al.,* 2005), harm to wildlife (SCHOLIN *et al*., 2000) and economic losses due to the closures of shellfish harvesting areas (HOAGLAND & SCATASTA, 2008; TRAINER *et al.,* 2012). In order to prevent human intoxication due to consumption of contaminated shellfish or other marine products, expensive monitoring programmes has been established worldwide.

Fig. 1. Map of the Adriatic Sea, indicating the approximate confines of the investigated areas: N) northern Adriatic Sea (Istria Peninsula); C) central Adriatic Sea (Šibenik and Kaštela Bays); S) southern Adriatic Sea (Mali Ston Bay)

In the Croatian part of the Adriatic Sea only two shellfish species are commercially cultured, black mussel *Mytillus galloprovincialis* and European flat oyster *Ostrea edulis*. The production relies only on seeds collected from nature and is located mostly in three main aquaculture areas: western coast of Istria Peninisula, in Šibenik Bay- river Krka estuary and in Mali Ston Bay. Annual production of 3000 tons of mussels and one million pieces of oysters is quite low comparing to other European countries, but due to coastline length and indentedness, Croatia has a great potential to increase shellfish production.

The first toxin analysis in Croatian waters started in the early 1990s and was related to DSP and PSP toxins (ORHANOVIĆ *et al*., 1996). Since 2000, Croatia has been conducting regular controls of shellfish and seawater quality.

The aim of this paper is to summarise the results of previous studies on phycotoxins and

Table1. Summary of main phycotoxin groups, symptoms which they induce and causative organisms

TOXIN GROUP	SYMPTOMS	CAUSATIVE SPECIES
Saxitoxin (STX)	Paralytic Shellfish Poisoning (PSP)	Several species of *Alexandrium*, *Gymnodinium catenatum*, *Pyrodinium bahamense*
Domoic acid (DA)	Amnesic Shellfish Poisoning (ASP)	Several species of *Pseudo-nitzschia*, *Nitzchia navis-varingica*, *Halamphora coffeaeformis*
Okadaic acid (OA), Dinophysistoxins (DTXs)	Diarrhetic Shellfish Poisoning (DSP)	Several species of *Dinophysis*, *Phalacroma* and *Prorocentrum*
Pectenotoxins (PTXs)	*	Several species of *Dinophysis*
Yessotoxin (YTXs)	*	*Gonyaulax spinifera*, *Lingulodinium polyedrum*, *Protoceratium reticulatum*
Azaspiracids (AZAs)	Azaspiracid Shellfish Poisoning (AZA)	*Azadinium spinosum*
Brevetoxins	Neurotoxic Shellfish Poisoning (NSP)	Several species of *Karenia*
Ciguatoxins (CTXs)	Ciguatera Fish Poisoning (CFP)	Several species of *Gambierdiscus*
Spirolides-SPXs, gymnodimines- GYM (part of cyclic imines group)	*Fast acting toxins	*Alexandrium ostenfeldii* (SPXs), *Karenia selliformis* (GYM)
Palytoxins (PLTs)		Several species of *Ostreopsis*

*adverse effect on human health has not yet been confirmed

toxic diatoms and dinoflagellates along the eastern Adriatic coast (Fig. 1) and to compare these results with the findings obtained along western coast of the Adriatic Sea in order to give a comprehensive overview.

Phycotoxins in shellfish from the Adriatic Sea

Okadaic acid toxin group, yessotoxins and pectenotoxins

Phycotoxin analysis in shellfish along the eastern Adriatic coast began in 1993. In the following year (1994) OA and dinophysistoxin1 (DTX1) were confirmed in mussels from Kaštela Bay (ORHANOVIĆ *et al.*, 1996). OA was confirmed in mussels from the same area also in 1995, 1997 and 2001 (MARASOVIĆ *et al.*, 1998; PAVELA-VRANČIĆ *et al.,* 2006).

The first case of dinophysistoxin2 (DTX2) in mussels from the Adriatic Sea was reported in 1997 (PAVELA-VRANČIĆ *et al.,* 2002). These phycotoxin studies were all based on analyses of shellfish from Kaštela Bay in the central part of the Adriatic Sea (see Fig.1, area C), but after the monitoring programme was established in year 2000, phycotoxin analysis extended to other areas. Since then, OA and DTXs have been detected in shellfish from the north-eastern Adriatic Sea (Istria Peninsula), in Šibenik Bay and in Mali Ston Bay, occasionally in concentrations that could endanger human health (NINČEVIĆ GLADAN *et al.*, 2008; NINČEVIĆ GLADAN *et al.*, 2010; NINČEVIĆ GLADAN *et al.*, 2011). The highest concentrations of OA and DTXs, above regulatory limit (160μg kg^{-1}), have been determined in mussels from Lim Bay in October 2006 and 2007, when levels of OA and DTXs were 1222 μg $kg^{-1}$and 1041 μg kg^{-1}, respectively (NINČEVIĆ GLADAN *et al.*, 2010; NINČEVIĆ GLADAN *et al.*, 2011). In summer of 2004 YTX and its analogs (carboxyyessotoxin (COOHYTX), 45-hydroxyyessotoxin (45-OH YTX) and homoyessotoxin (homoYTX)) were detected for the first time in mussels from north-eastern Adriatic (NINČEVIĆ GLADAN *et al.*, 2008). In the following period, from 2006 to 2008 YTXs were found in shellfish from other areas (ČUSTOVIĆ *et al.*, 2009; NINČEVIĆ GLADAN *et al.*, 2010, personal comm.). Concentration of YTXs (YTX, 45-OH YTX, homoYTX and 45-OH homoYTX) has never exceeded the regulatory limit (1000 μg kg^{-1}) although elevated concentration of carboxyhomoYTX has been determined in mussels collected from Medulin Bay in August of 2007 (NINČEVIĆ GLADAN *et al.*, 2010).

The first toxic event in the Adriatic Sea with accompanying human intoxication caused by consumption of contaminated shellfish with okadaic acid was recorded along Emilia-Romagna coast of Italy in 1989 (BONI *et al.*, 1992; FATTORUSSO *et al.*, 1992). This was the first evidence of any phycotoxin in mussels from the Adriatic Sea.

Yessotoxin (YTX) was detected for the first time in 1995 in shellfish from the same area, together with OA (CIMINIELLO *et al.*, 1997). Many YTX analogs have subsequently been successfully identified, some of which are unique for the Adriatic Sea, such as adriatoxin (ATX) (CIMINIELLO *et al.*, 1998). A detailed overview of YTXs detected in shellfish from this area is given by CIMINIELLO & FATTORUSSO (2004).

Pectenotoxins were found in shellfish and phytoplankton in the mid 1990s on both coasts of the Adriatic Sea. In 1994, pectenotoxin-2 (PTX-2) was identified in the phytoplankton species *Dinophysis fortii*, along the Emilia-Romagna coast of Italy (north-west Adriatic Sea). This was the first report of this toxin in Europe (DRAISCI *et al.*, 1996). The following year (1995), 7-*epi*-pectenotoxin-2-seco acid (7-epi-PTX-2SA), a PTX-2 derivate, was found in *M. galloprovincialis* from Kaštela Bay (PAVELA-VRANČIĆ *et al.*, 2006) and since then, PTXs have occasionally been found in Croatian shellfish in low concentrations (NINČEVIĆ GLADAN *et al.*, 2010; NINČEVIĆ GLADAN *et al.*, 2011).

Saxitoxin group and domoic acid toxin group

Since 2000, when Croatian regular controls of shellfish quality started, the PSP toxins were determined first time in winter of 2009 (UJEVIĆ *et al.*, 2012). This was recorded for the north-eastern part of the Adriatic Sea (Medulin Bay). Shellfish toxicity was prolonged from January to April 2009. During that period high levels of PSP toxins, above regulatory limit (800 μg STX eq. kg^{-1}) were determined with saxitoxin (STX) identified as the dominant toxin and followed by gonyautoxin2 (GTX2), gonyautoxin3 (GTX3) and deacrbamoylsaxitoxin (dcSTX). The highest concentration was recorded in February 2009 when total PSP toxicity was 1550.49 μg STX eq. kg^{-1} (UJEVIĆ *et al.*, 2012). In this study very low concentration of dcSTX, 8.68 μg kg^{-1} was reported in shellfish from Mali Ston Bay.

The first report of PSP toxins in shellfish along western coast of the Adriatic Sea (from the Emilia-Romagna coast) dates from 1993, when GTX2 and GTX3 were detected in low concentrations (CIMINIELLO *et al.*, 1995). The only case of shellfish toxicity in this part of the Adriatic Sea that involves PSP concentrations above the regulatory limit occurred in 1994, after bloom of *Alexandrium minutum* (HONSELL *et al.*, 1995).

Domoic acid (DA) was first found in shellfish in the early 2000s. Up to date, DA has been determined at low levels, well below regulatory limit of 20 μg g^{-1}, for entire Adriatic Sea. The first record of DA in shellfish from the Adriatic Sea was reported by CIMINIELLO *et al.* (2005). In Croatian waters, DA was first reported in 2006 from Šibenik Bay, and subsequently in shellfish from the northern part of the coast (UJEVIĆ *et al.*, 2010). At that time DA was present in mussels *M. galloprovincialis* from January till March of

2006 with the highest concentration, 6.5486 μg g^{-1} recorded in February.

Spirolides, Gymnodimines and Palytoxins

Along eastern Adriatic coast, for the first time, spirolides and gymnodimine were recorded in 2006, but in concentrations below limit of quantification. Traces of 13-desMethyl spirolide C (SPX-1) were found in mussels from the north-eastern part of the Adriatic coast, while GYM was reported in mussels from Šibenik Bay (NINČEVIĆ GLADAN *et al.*, 2011).

The first occurrence of spirolides in the Adriatic Sea was described by PIGOZZI *et al.* (2008), from mussels collected at the end of 2003 along the Emilia-Romagna coast. Further analyses of toxic shellfish confirmed the presence of three major spirolides: 13-desMethyl spirolide C (SPX-1), 13, 19-didesMethyl spirolide C and 27-hydroxy-13, 19-didesMethyl spirolide C (CIMINIELLO *et al.*, 2010a). Subsequently, spirolides have been sporadically detected in Italian shellfish, although in low concentrations (PISTOCCHI *et al.*, 2012).

Until now, the only report of palytoxin analogue determined in shellfish from the Adriatic Sea is reported by ACCORONI *et al.* (2011). Namely, ovatoxin-a (OVTX-a) has been determined in mussels collected from natural banks on Italian coast of the Adriatic Sea.

Potentially toxic phytoplankton species in the Adriatic Sea

Since the 1980s, massive blooms of phytoplankton species have become more frequent in the coastal waters of the eastern Adriatic Sea. These events took part in the most eutrophic areas such as Kaštela and Šibenik Bay. At that time intense summer blooms of *Lingulodinium polyedrum* were regular in Kaštela Bay (MARASOVIĆ *et al.*, 1991; MARASOVIĆ *et al.*, 1995) while *Prorocentrum minimum* blooms occurred in Šibenik Bay (MARASOVIĆ *et al.*, 1990). In the 1980, after intense bloom of *L. polyedrum*, massive mortally of fish and shellfish has been recorded as a consequence of significant decrease in oxygen concentration (MARASOVIĆ & VUKADIN, 1982). Since the 1990s, the intensity of these events has decreased, as a result of a reduction in anthropogenic impacts in these areas. However, the number of toxic and potentially toxic phytoplankton species has increased. In previous study MARASOVIĆ (1990a) listed a total of 14 potentially toxic species in the central Adriatic Sea, while more than 30 toxic or potentially toxic phytoplankton species have so far been found in the Adriatic Sea. This could be due to increasing scientific awareness and interest in toxic species resulting in the discovery of many new toxic compounds and toxic phytoplankton species, in this area and worldwide.

Potentially toxic dinoflagellates

Most of the toxic, and potentially toxic, phytoplankton species found in the Adriatic Sea are dinoflagellates. Out of 322 dinoflagellates reported from the Adriatic Sea (GÓMEZ, 2003) 20 toxic dinoflagellates have been recorded along Croatian part of the Adriatic Sea. Those species are summarised in Table 2, according to the areas where they are found and with corresponding citation. Toxicity of these species, listed in Table 2, has been already confirmed but not necessary in area of the Adriatic Sea so they are considered to be potentially toxic.

During last 12 years, since regular seawater analyses on Croatian shellfish breeding areas have begun (Fig. 1, area N, C and S), the most frequent and the most abundant toxic dinoflagellates were *Dinophysis* species. Six of them can be highlighted as regularly occurring in investigated areas: *Dinophysis acuta*, *Dinophysis acuminata*, *Dinophysis caudata*, *Dinophysis fortii*, *Dinophysis sacculus* and *Dinophysis tripos* and species *Phalacroma rotundatum* which has been, until recently, included in genus *Dinophysis* (SKEJIĆ *et al.*, 2006; MARASOVIĆ *et al.* 2007; NINČEVIĆ GLADAN *et al.* 2008; SKEJIĆ *et al.*, 2012). DSP shellfish toxicity was related to elevated abundance of *D. caudata* and *D. fortii* along the western coast of Istria Peninsula in 2005 (MARASOVIĆ *et al.* 2007). In shellfish from Lim Bay (Istria Peninsula) high levels of OA

Table 2. Toxic and potentially toxic dinoflagellates and diatoms reported along the Croatian coast of the Adriatic Sea. Area N) northern Adriatic Sea (Istria Peninsula); C) central Adriatic Sea (Šibenik and Kaštela Bays); S) southern Adriatic Sea (Mali Ston Bay) (see Fig. 1)

Potentially toxic dinoflagellates			
Alexandrium	**N**	**C**	**S**
A.minutum Halim	SKEJIĆ, 2004	MARASOVIĆ *et al.* 1995; SKEJIĆ 2004	
A.ostenfeldii (Paulsen) Balech i Tangen	NINČEVIĆ GLADAN *et al.* 2011		
A.pseudogonyaulax (Biecheler) Horiguchi ex Kita et Fukuyo	*	*	*
A.tamarense (Lebour) Balech	SKEJIĆ, 2004	BUŽANČIĆ *et al.* 2012	SKEJIĆ, 2004
A. taylorii Balech	*	*	
Dinophysis	**N**	**C**	**S**
D.acuminata Claparède & Lachmann	MARASOVIĆ *et al.* 2007; NINČEVIĆ-GLADAN *et al.* 2008	VILIČIĆ *et al.* 2002	VILIČIĆ *et al.* 2002
D. acuta Ehrenberg	MARASOVIĆ *et al.* 2007; NINČEVIĆ-GLADAN *et al.* 2008	NINČEVIĆ-GLADAN *et al.* 2008	VILIČIĆ *et al.* 1998
D. caudata Saville-Kent	MARASOVIĆ *et al.* 2007; NINČEVIĆ-GLADAN *et al.* 2008	NINČEVIĆ-GLADAN *et al.* 2008	VILIČIĆ *et al.* 1998; NINČEVIĆ-GLADAN *et al.* 2008; SKEJIĆ *et al.* 2012
D. fortii Pavillard	MARASOVIĆ *et al.* 2007; NINČEVIĆ-GLADAN *et al.* 2008	SKEJIĆ *et al.* 2006	VILIČIĆ *et al.* 1998; NINČEVIĆ-GLADAN *et al.* 2008; SKEJIĆ *et al.* 2012
D. sacculus Stein	MARASOVIĆ *et al.* 2007; NINČEVIĆ-GLADAN *et al.* 2008	MARASOVIĆ *et al.* 1998; SKEJIĆ *et al.* 2006	SKEJIĆ *et al.* 2006
D. tripos Gourret	MARASOVIĆ *et al.* 2007; NINČEVIĆ-GLADAN *et al.* 2008	NINČEVIĆ-GLADAN *et al.* 2008	VILIČIĆ *et al.* 1998; VILIČIĆ *et al.* 2002
Phalacroma	**N**	**C**	**S**
P. mitra Schütt	VILIČIĆ *et al.* 2002	VILIČIĆ *et al.* 2002	VILIČIĆ *et al.* 1998
P. rapa Jorgensen	VILIČIĆ *et al.* 2002	VILIČIĆ *et al.* 2002	
P. rotundatum (Claparède & Lachmann) Kofoid & Michener	MARASOVIĆ *et al.* 2007; NINČEVIĆ-GLADAN *et al.* 2008	VILIČIĆ *et al.* 2002	NINČEVIĆ-GLADAN *et al.* 2008; SKEJIĆ *et al.* 2012

	N	C	S
Gonyaulax spinifera Diesing	VILIČIĆ *et al.* 2002	VILIČIĆ *et al.* 2002	NINČEVIĆ GLADAN *et al.* 2010
Lingulodinium polyedrum (Stein) Dodge	VILIČIĆ *et al.* 2007; NINČEVIĆ GLADAN *et al.* 2010	MARASOVIĆ & VUKADIN 1982; MARASOVIĆ *et al.* 1995	VILIČIĆ *et al.* 1998; VILIČIĆ *et al.* 2002
Ostreopsis cf. *siamensis*	PFANNKUCHEN *et al.* 2012		
Ostreopsis cf. *ovata* Fukuyo	MONTI *et al.* 2007; PFANNKUCHEN *et al.* 2012	MARASOVIĆ, 1990a; MARASOVIĆ, 1990b	BRAVO *et al.*, 2012**
Prorocentrum lima (Ehrenberg) Stein	VILIČIĆ *et al.* 2002	MARASOVIĆ, 1990a	
Protoceratium reticulatum (Claparède i Lachmann) Bütschli	VILIČIĆ *et al*. 2002		
Potentially toxic diatoms	**N**	**C**	**S**
Halamphora coffeaeformis (Agardh) Levkov	VILIČIĆ *et al.* 2002;		
Pseudo-nitzschia calliantha Lundholm, Moestrup & Hasle	LJUBEŠIĆ *et al.* 2011 MARIĆ *et al.* 2011;	LUNDHOLM & MOESTRUP, 2003; BURIĆ *et al*., 2008***	
P. delicatissima (Cleve) Heiden	MARIĆ PFANNKUCHEN, 2013		
P. fraudulenta (Cleve) Hasle	LJUBEŠIĆ *et al.* 2011; MARIĆ PFANNKUCHEN, 2013		
P. pseudodelicatissima (Hasle) Hasle	LJUBEŠIĆ *et al.* 2011; MARIĆ PFANNKUCHEN, 2013		
P. pungens (Grunow ex Cleve) Hasle	LJUBEŠIĆ *et al.* 2011; MARIĆ PFANNKUCHEN, 2013		

* unpublished data, Laboratory of plankton and shellfish toxicity, IOF, Split; ** report from Dubrovnik (south from Mali Ston Bay, see Fig.1); *** report from Zrmanja River estuary (northeast from Zadar, see Fig.1)

have been determined after a bloom of *D. fortii* in 2006 and 2007 (NINČEVIĆ GLADAN *et al.*, 2010; NINČEVIĆ GLADAN *et al.*, 2011). In Mali Ston Bay, OA has been determined in shellfish when the species *D. caudata* was abundant in phytoplankton community (NINČEVIĆ GLADAN *et al.*, 2010).

Contrary to *Dinophysis* species, *Alexandrium* species are rare and less abundant in this area. Among 30 *Alexandrium* species known worldwide, out of which half of them are considered to be toxic (ANDERSON *et al.*, 2012), along Croatian coast of the Adriatic Sea five *Alexandrium* species were recorded: *Alexandrium minutum*, *Alexandrium ostenfeldii*, *Alexandrium pseudogonyaulax*, *Alexandrium tamarense* and *Alexandrium taylorii*. Presence of species *A. taylorii* and *A. pseudogonyaulax* along eastern Adriatic coast has been recently recorded, in 2010 and 2011, respectively (unpublished data, Laboratory of plankton and shellfish toxicity, IOF, Split). Several authors have already reported presence of *A. pseudogonyaulax* in the other parts of Adriatic Sea such as HONSELL *et al.* (1992) in the Gulf of Trieste, FRANCE & MOZETIČ (2006) along Slovenian coast of the Adriatic Sea and CAROPPO (2000) at southern coast of Italy. *A. taylorii* has been confirmed by PENNA *et al.* (2008).

The various strains of *A. ostenfeldii* usually only produce either toxins from saxitoxin group (New Zealand and Baltic Sea strains) or spirolides (Nova Scotia and Adriatic strains). Exceptions are Danish strains, which are known to produce both groups of toxins (ANDERSON *et al.*, 2012). Toxin analyses confirmed that Adriatic strain of *A. ostenfeldii* only produces spirolides (CIMINIELLO *et al.*, 2006; CIMINIELLO *et al.*, 2010b). In mussels from Lim Bay (north part of the Croatian coast of the Adriatic Sea) low concentrations of SPX-1 toxin have been related to presence of *A. ostenfeldii* in seawater (NINČEVIĆ GLADAN *et al.*, 2011). Toxin analyses of species *A. minutum* collected from the Gulf of Trieste in 1993 demonstrated the presence of four gonyautoxins (GTX1, GTX2, GTX3 and GTX4) (BEANI *et al.*, 2000).

Among species recorded along eastern coast of the Adriatic Sea toxin production has recently been confirmed or *Ostreopsis* spp. Samples were collected during a massive bloom noticed in September and October 2010, close to Rovinj at the western coast of Istria Peninsula (PFANNKUCHEN *et al.*, 2012). *Ostreopsis* cf. *ovata* has been determined as predominant species with low percentage of *Ostreopsis* cf. *siemensis* and *Coolia monotis*. Major toxin component was ovatoxin-a (OVTX-a) with its contribution up to 60% of total toxin content, followed by ovatoxin-b (OVTX-b), ovatoxin d+e (OVTX d+e) and ovatoxin c (OVTX-c) while putative palytoxin (p-PLTX) was determined in very low concentration (PFANNKUCHEN *et al.*, 2012). The first record of *Ostreopsis ovata* in the Adriatic Sea has been recorded from Kaštela Bay in 1984 by MARASOVIĆ (1990b).

As distribution of *Ostreopsis* species has increased significantly in last decade both worldwide and in the Mediterranean Sea (RHODES, 2011, PARSONS *et al.*, 2012), the number of records from the Adriatic Sea has risen too. In summer 2005 massive *Ostreopsis* bloom caused intoxication of hundreds of people after exposure to marine aerosol on the beach close to Genoa (Tyrhenian Sea, Italy). Putative palytoxin (p-PLT) was then determined in all phytoplankton samples (CIMINIELLO *et al.,* 2011) and this was the first evidence of the presence of palytoxin in the Mediterranean Sea. In Greece, ALIGIZAKI *et al.*, (2008) reported, for the first time in Mediterranean Sea, contamination of shellfish with p-PLT.

Human intoxication, related to high abundance of *Ostreopsis* species, was recorded during summer period in 2003 and 2004. As human symptoms appeared simultaneously while concentration of *Ostreopsis* cells were high and disappeared with decrease of *Ostreopsis* population this is probably the first recorded toxic bloom of *Ostreopsis* in the Adriatic Sea (GALLITELLI *et al.*, 2005). Since 2006, this genus has also been found in other areas along Adriatic coast of Italy. Toxin analyses on *Ostreopsis* cf. *ovata* confirmed OVTX-a as the main toxin followed by OVTX-b, OVTX-c, OVTX d+e and p-PLTX present in much lower concentrations then ovatoxins (ACCORONI *et al.,* 2011; PEZZOLESI *et al.,* 2012; VANUCCI *et al.,* 2012) which is in accordance with results reported by PFANNKUCHEN *et al.* (2012).

Up to date, toxin production has been confirmed for more species recorded along Italian coast of the Adriatic Sea. DRAISCI *et al.*, (1996) reported OA and PTX-2 in a natural phytoplankton community dominated by *Dinophysis fortii*. VANUCCI *et al.*, (2010) reported production of OA and DTX1 by cultured strains of *Prorocentrum lima*.

Since the mid 1990s, more attention has been given to YTXs producers as mussel contamination with YTX has become more frequent. Toxin production has been confirmed for all three known YTX producers: *Lingulodinium polyedrum* (DRAISCI et al., 1999), *Protoceratium reticulatum* (BONI *et al.* 2001; CIMINIELLO *et al.* 2003) and *Gonyaulax spinifera* (RICCARDI *et al.*, 2009). A comprehensive overview of the toxin profiles and cell toxin contents of YTXs producers was provided by PISTOCCHI *et al.* (2012). They reported that all 11 isolated and cultured strains of Adriatic *P. reticulatum* are toxic, with YTX being the main toxin while species *L. polyedrum* showed high variability in the toxicity governed by phosphorus concentration.

The majority of studies related to toxicity of particular species present in the Adriatic Sea have been carried out for the species recorded along Italian coast of the Adriatic Sea. Toxin profiles of dinoflagellates found along the Croatian coast have yet to be defined, although some species have been linked to specific toxins found in shellfish. Laboratory analyses on cultured species should be undertaken in order to confirm these reports.

Potentially toxic diatoms

According to the available literature, along eastern Adriatic coast there are six identified potentially toxic diatoms: *Halamphora coffeaeformis*, *Pseudo-nitzschia calliantha*, *Pseudo-nitzschia delicatissima*, *Pseudo-nitzschia fraudulenta*, *Pseudo-nitzschia pseudodelicatissima* and *Pseudo-nitzschia pungens*. Those species are summarised in Table 2, according to the areas where they are found and with corresponding citation. All of them are found in northern part while the only *P. calliantha* has been confirmed in Kaštela Bay (LUNDHOLM & MOESTRUP, 2003) and from Zrmanja River estuary (BURIĆ *et al*., 2008). Toxicity of these species has not yet been confirmed. The first report of DA in shellfish co-occurring and related with any *Pseudo-nitzschia* species in the Adriatic Sea was detected along the north-eastern Adriatic coast in 2007, after a bloom of *P. calliantha* (MARIĆ *et al,*. 2011). During this bloom, which lasted from August until October 2007, *P. calliantha* contributed up to 70% of the total phytoplankton abundance. However, as the authors themselves suggests, there is a need to further investigate possible linkage of toxin determined in shellfish and *P. calliantha* presence in seawater since toxicity of *P. calliantha* has not been yet confirmed in the Adriatic Sea. HONSELL *et al.* (2008) have been conducted one-year survey of *Pseudo-nitzschia* species and toxin analyses in phytoplankton and in mussels, in Gulf of Trieste. During this research two the most frequent species were *P. calliantha* and *P. decipiens*, but DA has not been determined neither in phytoplankton nor in mussels. The variability of toxicity between different strains of *Pseudo-nitzchia* species and including *P. calliantha* has been reported by several authors (ALVAREZ *et al*., 2009; ORLOVA *et al*., 2008; THESSEN *et al*., 2009). However, it is possible that *P. calliantha* from the Adriatic Sea might not be toxic. THESSEN *et al.* (2009) indicated that intraspecies variation in toxicity is larger than interspecies variation especially among low-toxin producing species.

In the other parts of the Adriatic Sea the presence and the toxicity of *P. delicatissima* (CAROPPO *et al.,* 2005; PENNA *et al*., 2013) and *Pseudo-nitzschia multistriata* (PISTOCCHI *et al*., 2012) have been confirmed.

CONCLUSIONS

Since the mid 1990s the toxin profile of Adriatic shellfish has become complex. Numerous types of toxins have been determined (in shellfish or phytoplankton), including toxins from okadaic acid group, saxitoxin group, domoic acid group, yessotoxins, pectenotoxins, gymnodimines, spirolides and palytoxins. Almost all phycotoxins have been determined in shellfish along both coasts of the Adriatic Sea. Exception is palytoxins which are, until now, along Croatia coast of the Adriatic Sea confirmed only in phytoplankton sample. Based on studies included in this review OA toxin group and YTXs are highlighted as the main phycotoxins. OA has been determined in high concentration, that could endanger human health and YTXs have been determined more often in shellfish samples comparing to other phycotoxins. The identification of new toxins in shellfish (such as palytoxins) along Croatian coast should come as no surprise, since the toxicity of *Ostreopsis* cf. *ovata* has been already confirmed. The number of toxic and potentially toxic, species has also increased over the time. To date, ten species were confirmed to produce toxins out of which there are eight dinoflagellates and two diatom species. Toxin production has been confirmed for *Alexandrium minutum*, *Alexandrium ostenfeldii*, *Dinophysis fortii*, *Gonyaulax spinifera*, *Lingulodinium polyedrum*, *Prorocentrum lima*, *Protoceratium reticulatum*, *Ostreopsis* cf. *ovata* and two diatom species *Pseudo-nitzschia delicatissima* and *Pseudo-nitzschia multistriata*. There are also 20 potentially toxic species recorded during last three decades. Toxin profile of those species reported along the Croatian coast of the Adriatic Sea is still quite unknown, so additional efforts should be made to ascertain the toxicity of these potentially toxic species. Most of them are *Dinophysis* and *Pseudo-nitzschia* species, which are relatively common in the Adriatic Sea as well as DSP toxins in Adriatic shellfish.

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Pregled fikotoksina u školjkašima i toksične fitoplanktonske vrste uzduž hrvatske obale Jadranskog mora

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SAŽETAK

Analize fikotoksina uzduž hrvatske obale Jadranskog mora započete su sredinom 1990-tih kada je okadaična kiselina određena u školjkašima iz Kaštelanskog zaljeva (srednji Jadran). Od tada, profil fikotoksina u školjkašima Jadranskog mora postao je složen kao što je tijekom vremena porastao i broj zabilježenih toksičnih i potencijalno toksičnih fitoplanktonskih vrsta. Do danas su u školjkašima ili u fitoplanktonu Jadranskog mora određeni toksini iz grupe okadaične kiseline, toksini iz grupe saksitoksina, te toksini iz grupe domoične kiseline kao i jesotoksini, pektenotoksini, gimnodimini, spirolidi i palytoksini. Toksini iz grupe okadaične kiseline i jesotoksini ističu se kao glavni fikotoksini zabilježeni u školjkašima uzduž hrvatske obale Jadranskog mora. Toksini iz grupe okadaične kiseline određeni su u visokim koncentracijama, opasnim za ljudsko zdravlje dok su u odnosu na ostale fikotoskine, jesotoksini češće zabilježeni u školjkašima. Među toksičnim vrstama zabilježenim u Jadranskom moru, samo je za deset vrsta potvrđeno da mogu stvarati toksine dok se 20 vrsta smatra potencijalno toksičnim. Toksičnost je potvrđena za osam vrsta dinoflagelata: *Alexandrium minutum*, *Alexandrium ostenfeldii*, *Dinophysis fortii*, *Gonyaulax spinifera*, *Lingulodinium polyedrum*, *Ostreopsis* cf. *ovata*, *Prorocentrum lima*, *Protoceratium reticulatum* i dvije vrste dijatomeja *Pseudo-nitzschia delicatissima i Pseudo-nitzschia multiseries*. Profil toksina za ostale potencijalno toksične vrste prisutne uzduž hrvatske obale Jadranskog treba tek definirati. Većina od njih su *Dinophysis* i *Pseudo-nitzschia* vrste koje su relativno česte i brojne na ovom području kao i toksini iz grupe okadaične kiseline u školjkašima.

Ključne riječi: fikotoksini, toksičnost školjkaša, toksični fitoplankton, hrvatska obala Jadranskog mora