Occurrence and Fate of Emerging Wastewater Contaminants in Western Balkan Region

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Abstract

There is a growing concern about possible ecotoxicological importance of various classes of emerging contaminants in wastewaters and receiving ambient waters. This paper reports on a comprehensive reconnaissance of more than seventy individual wastewater contaminants in the region of Western Balkan (Bosnia and Herzegovina, Croatia and Serbia), including some prominent classes of emerging contaminants such as pharmaceuticals and personal care products, surfactants and their degradation products, plasticizers, pesticides, insect repellents, and flame retardants. All determinations were carried out using a modern multiresidue analytical approach, based on the application of gas chromatographic and liquid chromatographic techniques coupled to mass spectrometric detection. The sampling strategy encompassed collection of primarily municipal wastewaters but wastewater effluents from some industries were also included. The results confirmed a widespread occurrence of the emerging contaminants in municipal wastewaters of the region with a great deal of similarities with the situation found in the Western Europe and USA. The most prominent contaminant classes, determined in municipal wastewaters, were those derived from aromatic surfactants, including linear alkylbenzene sulphonate (LAS) and alkylphenol polyethoxylates (APEO), with the concentrations in raw wastewater reaching into the mg/L range. All other contaminants were present in much lower concentrations, rarely exceeding few μg/L. The most abundant individual compounds belonged to several classes of pharmaceuticals (antimicrobials, analgesics and antiinflammatories, β-blockers and lipid regulators) and personal care products (fragrances). Due to the rather poor wastewater management practices in WB countries, with less than 5 % of all wastewaters being biologically treated, most of the contaminants present in wastewaters reach ambient waters and may represent a significant environmental concern. Moreover, the results indicated that the conventional biological wastewater treatment using activated sludge is relatively inefficient for the removal of some classes of emerging contaminants.

Keywords: emerging contaminants, pharmaceuticals, personal care products, surfactants, gas chomatography/mass spectrometry, liquid chromatography/tandem mass spectrometry, Western Balkan

1. **Introduction**

Wastewaters represent one of the main routes of input of anthropogenic organic and inorganic contaminants into the environment. Due to their distinct differences in composition and related specific treatment requirements, domestic and industrial wastewaters in developed countries are often kept in separate wastewater collection and treatment systems, which allows a more efficient source control and specific pollutant mitigation strategies. In contrast, municipal wastewaters in the developing countries such as those of the Western Balkan (WB) region (Bosnia and Hercegovina, Croatia, and Serbia) are mainly of mixed type and include both, domestic and industrial wastewaters (Kastelan-Macan et al., 2006). Moreover, a vast majority of wastewaters in the WB countries is released to the environment either without any treatment or after being treated only mechanically. For example, only a small fraction (4.4 %) of the collected municipal wastewaters in Croatia receives a complete mechanical and biological treatment. As a consequence of such poor wastewater management practices in WB countries, organic load discharged into the receiving waters, is often very high and characterised by a rather complex chemical composition. Like in many other regions of the world, besides various types of law-regulated contaminant classes, wastewaters in WB countries contain a large number of various specific organic constituents for which environmental quality criteria are yet to be determined. In the last decade, a growing number of reports on the occurrence of unregulated anthropogenic compounds, frequently referred to as novel or emerging organic contaminants, expressed concern

about their possible undesirable effects in the environment (Daughton and Ternes, 1999; Daugton, 2004; Fent et al., 2006)

The identification and determination of many previously undetected organic anthropogenic compounds in wastewaters, including a large number of pharmaceuticals and personal care products, has seen a dramatic progress in recent years along with a rapid development of new analytical techniques (Gros et al., 2006a; Gonzalez et al., 2007; Richardson, 2007). Several extensive national and multinational monitoring programs have been launched in the last few years in order to provide comprehensive reconnaissance of the occurrence of various pollutants, with a special emphasis on pharmaceuticals, hormones and other polar organic wastewater contaminants (Ternes, 1998; Kolpin et al., 2002; Reemtsma et al., 2006; Zuccato et al., 2006. All these studies confirmed the presence of complex mixtures of unregulated contaminants, having various origins, and raised concern about their potential interactive effects.

In contrast to rapidly accumulating information on emerging contaminants in the USA and Western Europe, the data on the occurrence and fate of individual organic contaminants in countries of the WB region are very scarce and limited in terms of number of compounds measured and geographic distribution of the sampling points (Terzic and Ahel, 2006). An exception is study on surfactant-derived alkylphenolic compounds in Croatia, which indicated their widespread occurrence in municipal wastewaters (Kvestak et al., 1994). Pharmaceutical compounds are another class of emerging contaminants for which some initial results from Croatia were reported (Ahel and Jelicic, 2001; Jelicic and Ahel, 2003; Ahel et al., 2004). Among different compounds, identified during extensive GC/MS-analyses at the main landfill of the city

of Zagreb, the over-the-counter analgesic propyphenazone and isopropylidene intermediates from the vitamin C production, were the most prominent individual contaminants in the landfill leachate and adjacent groundwater aquifer (Ahel et al., 1998). More recently, a comprehensive characterisation of the organic contaminants in the wastewater of the city of Zagreb, performed using an effects-directed analytical approach, showed a presence of numerous toxicants exhibiting either citotoxicity (measured as a loss of membrane integrity), estrogenicity as reflected by vitellogenin induction and 7-ethoxyresorufin-O-deethylase (EROD) activity in a culture of rainbow trout hepatocites (Grung et al., 2007).

To the best of our knowledge, there are no reports in the open literature, documenting the occurrence of emerging contaminants in domestic and industrial wastewaters in Bosnia and Herzegovina and Serbia. Only scarce reports, focused mainly on the distribution of classical pollutants such as pesticides (Gasic et al., 2002) and petroleum hydrocarbons (Dalmacija et al., 2003) in soils and receiving surface waters can be found.

Along these lines, this paper aims to fill the existing gap by providing for the first time a comprehensive report on the occurrence of a wide spectrum of individual organic wastewater contaminants in municipal and industrial wastewaters from the WB region, including various groups of emerging contaminants. Highly specific LC/MS/MS and GC/MS analyses were applied to determine the occurrence and behaviour of more than seventy individual organic trace contaminants in Croatian, Bosnian and Serbian wastewaters. The analytes included representatives of seven different classes of contaminants, including pharmaceuticals, surfactants, plasticizers, pesticides, repellents, flame retardants and fragrances.

2. Experimental part

2.1. Sampling sites

Sampling was performed in autumn 2004 and spring 2005 in the framework of the EU FP6 project on "Reduction of environmental risks posed by emerging contaminants through advanced treatment of municipal and industrial wastes" (EMCO) and included two sampling campaigns in Croatia (16 locations), and one in Bosnia and Herzegovina (6 locations) and Serbia (7 locations) (Figure 1). The majority of samples from Bosnia and Serbia were untreated municipal and industrial wastewaters, while in Croatia, effluents from the existing wastewater treatment plants (WWTPs) were also collected, which allowed the assessment of the removal efficiencies for the most prominent classes of emerging contaminants. The list of samples analysed is given in Table 1. It should be stressed that only few WWTPs (Cakovec and Bjelovar) contained facilities for 24-hour flow-proportional composite sampling, while on some other locations (Rijeka, Split, Varaždin) composite samples were prepared by mixing grab samples, taken over a diurnal cycle. For all other locations, only grab samples were available.

146 ***2.2. Sample pre-treatment and analysis***

147

148 The collected samples were analysed for the presence of a wide spectrum of
149 organic trace contaminants (Table 2). The main classes of target compounds included
150 pharmaceuticals, surfactants, plasticizers, pesticides and fragrances and involved several
151 analytical protocols for multi-residue analysis of different contaminant groups based on
152 GC/MS and LC/MS techniques. Before further analysis, all wastewater samples were
153 filtered through glass-fiber filters and thus represent only dissolved fraction.

154 The enrichment of all analytes from the collected wastewater samples was
155 performed by solid-phase extraction (SPE) following earlier developed analytical
156 protocols (for references see Table 2). Surfactant residues were enriched on C_{18}
157 cartridges, while other target analytes were extracted using Oasis HLB cartridges. The
158 Oasis extracts were divided into four identical aliquots and distributed to the participating
159 laboratories for analyses on different groups of target contaminants. The following
160 analytical methods were used for trace level quantification:

161

162 *Surfactants.* The determination of surfactant residues included two major types of
163 aromatic surfactants, anionic surfactants of linear alkylbenzene sulphonate (LAS) type
164 and nonionic surfactants of alkylphenol polyethoxylate (APnEO) type. A special
165 emphasis was on the comparatively persistent biotransformation products of APnEO
166 (Ahel et al., 1994), including nonylphenol (NP) and nonylphenoxy carboxylic acids
167 (NPnEC). The analyses of the parent NPEO were performed using HPLC with
168 fluorescence detection (Ahel et al., 2000), while LC/MS technique was used for

qualitative confirmation purposes. For LAS and NPEO biotransformation products, LC/MS/MS analytical procedures, based on electrospray ionisation in negative mode, have been adopted (Di Corcia et al., 1999; Petrovic et al., 2003).

Pharmaceuticals. A multiresidue LC/MS/MS method for simultaneous determination of 3 classes of antimicrobials, including 6 sulfonamides, trimethoprim, 3 fluroquinolones and 5 macrolides was developed (Senta et al., submitted) using a modification of the method, originally proposed by Goebel et al (2004).

Determination of all other pharmaceutical compounds was performed by multiresidue LC-MS-MS method developed by Gros et al. (2006b). This included a determination of trace level of 29 different pharmaceutical compounds, belonging to a wide range of different therapeutical classes.

Personal care products. A GC-MS multiresidue method for the analysis of fragrances, including polycyclic musks (galaxolide, tonalide, traseolide, and HHCB lactone), nitro musks (musk xylene), amberonne and acetyl cedrene, was applied as described in details by Mitjans and Ventura (2005). Insect repellents, including DEET and Bayrepel were also determined using GC/MS technique (Knepper, 2004).

Other contaminants. The plasticizer bisphenol A was determined along with other alkylphenolic compounds derived from APEO surfactants using the same electrospray LC/MS/MS method in negative ionization mode (Petrovic et al., 2003).

191 The organophosphate flame retardants were determined using GC/MS technique as
192 described by Meyer and Bester (2004).
193 Pesticides, including triazine herbicides and their metabolites, triazole fungicides and
194 organophosphate acaricide dimethoate, were determined by a multiresidue GC/MS
195 methods as described in Peschka et al (2006a).
196
197
198 **3. Results and discussion**
199
200 ***3.1. Occurrence of emerging contaminants in wastewaters***
201
202 As can be seen from Table 1, the present study encompassed two distinct types of
203 wastewaters, i.e. municipal and industrial wastewaters. Since the two types of
204 wastewaters differ significantly with respect to the complexity of contaminants present,
205 levels of specific classes of emerging contaminants and management requirements, for
206 sake of clarity, the results for each group are discussed separately. Nevertheless, it should
207 be kept in mind that municipal wastewaters, which contain mainly domestic sewage, in
208 WB countries often include a significant contribution of wastewaters having industrial
209 and institutional origin (Kastelan-Macan et al., 2006).
210
211 *3.1.1 Municipal wastewaters*
212 A summary of the results, obtained during the reconnaissance of the selected contaminant
213 classes in municipal wastewaters in WB countries, showing concentration ranges and

214 mean values for individual chemical compounds, is given in Table 3. Fig. 2 shows the
215 frequency of detection of individual analytes. For sake of clarity, the data presented in
216 Fig. 2 were divided into two groups, the first one corresponding to pharmaceuticals as the
217 most numerous contaminant class investigated (Fig. 2A) and the second one covering all
218 other non-pharmaceutical classes (Fig 2B). The results presented in Table 3 and Fig. 2
219 refer only to raw wastewater samples and represent only dissolved fraction, since all
220 samples were filtered before the SPE enrichment. Since most of the target compounds
221 belong to the relatively polar chemicals, the dissolved fraction is expected to correctly
222 reflect the total contaminant loads in analysed wastewaters.

223 Overall, the results showed that the levels of wastewater contaminants, found in
224 raw municipal wastewaters of WB countries were rather similar to the levels found in
225 other European regions. Fifty six (56) out of 76 target compounds were confirmed in at
226 least one sample. The concentrations as well detection frequencies of individual
227 compounds were highly variable.
228
229 ***Surfactants***. Surfactants were clearly the most abundant chemical class in all
230 examined wastewaters, ranging from 330-9450 μg/l for linear alkylbenzene sulphonates
231 (LAS) and 5-395 μg/l for nonylphenol polyethoxylates (NPEO). Analyses of LAS
232 revealed that these anionic surfactants belong to the most abundant anthropogenic
233 compounds in wastewaters. All examined municipal wastewaters are of the mixed type
234 and show relatively uniform LAS levels.
235 Analyses of surfactant-derived alkylphenolic compounds confirmed earlier
236 findings on their widespread occurrence in Croatian wastewaters, however the

237 concentration levels were relatively low and suggest a decreasing trend in comparison to
238 some previous campaigns conducted in early 1990s (Kvestak et al., 1994). The
239 concentration of nonylphenol (NP), as the most toxic and most potent estrogen disrupting
240 compound derived from NPEO surfactants (Jobling et al., 1996), was present in
241 concentrations up to 4.4 μg/l with an average value of 1.7 μg/l. It is interesting to mention
242 that Croatia was one of the first countries, which introduced water quality criteria for NP
243 with a maxiumum permissible concentration in ambient water of 1 μg/l (Croatian
244 Ordinance, 1984), fifteen years before it was accepted as a priority pollutant in the EU
245 Water Framework Directive. Besides NP, all municipal wastewaters contained
246 measurable levels of other metabolites derived from NPEO surfactants, in particular
247 nonylphenoxy carboxylic acids (NPEC). The composition of alkylphenolic compounds
248 was highly variable and revealed a strong impact of various biotransformation and
249 physico-chemical processes on the distribution of individual alkylphenolic compounds in
250 various types of wastewater samples. The most abundant alkylphenolic species in non-
251 treated wastewaters was NP, while NPEC were the dominant species in biologically
252 treated effluents, which is in agreement with earlier reports on this subject (Ahel et al.,
253 1994).

254 Octylphenolic analogues of NPEOs and their metabolites represented only a small
255 percentage of the total alkylphenolic compounds in all analysed samples, typically less
256 than 10 %. This is important for the assessment of the endocrine disrupting potential
257 associated with APEO surfactants and their metabolites, because OP is 4 time more
258 potent endocrine disrupting compound (EDC) as NP (Jobling et al., 1996). On the other
259 hand, another widespread alkylphenolic xenoestrogen, bisphenol A (BPA), was found in

260 the concentrations, ranging typically from 60 to 300 ng/l with only three samples with
261 concentrations above 1 μg/l. This compound is applied as plasticizer and thus has a
262 different origin from NP, but their similar modes of action in biological systems justifies
263 considering possible additive effects.
264
265 ***Pharmaceuticals***. Except surfactants, all other compounds were present in much
266 lower concentrations, being mainly in the range of low ng/l to few ug/l, with
267 pharmaceuticals and fragrances being the most abundant groups. Thirty one (31) out of
268 forty four (44) analysed pharmaceutical compounds were detected at concentration above
269 the detection limit (typically 1-10 ng/l). The most abundant drug groups included
270 analgesics and antiinflammatories, antimicrobials, β-blockers and lipid regulators (Fig.
271 2A).
272 The concentration of analgesics and antiinflammatories, was relatively high as
273 compared to other pharmaceutical compounds as it can be usually expected for non-
274 prescription over-the-counter drugs (Reemtsma et al., 2006). The most abundant
275 compounds in this group were diclofenac (0.050-4.20 μg/l) and ibuprofen (bld-11.9 μg/l).
276 These levels seem to be a bit lower than those reported in Westen Europe (see the
277 compilation by Fent et al. (2006), indicating lower usage rates of pain-killers in WB
278 countries. Some other analgesic compounds, including ketoprofen (KET), naproxen
279 (NAP), indomethacine (IND), mefenamic acid (MFA) and propyphenazone (PRO) were
280 also found in detectable concentrations. The levels of PRO (bld-461 ng/l) are in
281 agreement with an earlier study in Croatia (Jelicic and Ahel, 2003) based on GC/MS
282 determinations and reflect its widespread use in WB countries. It should be noted that

283 phenazone analgesics are still used in pain-killer pills produced by the local
284 pharmaceutical industries in WB countries although they were phased-out in some
285 countries due to the therapeutical side-effects.

286 Among different antimicrobials, the most abundant ones were sulfonamides, in
287 particular sulfamethoxazole (SMX; 0.019-11.6 μg/l) and sulfapyridine (SPY; bld-0.93
288 μg/l) as the most prominent representatives. It should be stressed that the main form of
289 SMX in raw influent wastewater is its metabolite N-acetylsulfamethoxazole (Goebel et
290 al., 2005), so that the concentration levels of the free SMX often underestimate the total
291 load. Expectedly, SMX was accompanied by significant levels of trimethoprim (TMP;
292 0.035-2.55 μg/l) because these two antimicrobials are used in the same drug, which is still
293 widely used in human medicine. Other detectable sulfonamides included sulfadiazine
294 (SDZ) and sulfamethazine (SMZ), while sulfathiazole (STZ) and sulfamerazine (SMR)
295 were below the detection limit in all samples. The concentration levels of sulfonamide
296 antimicrobials were significantly higher than those reported for some other European
297 countries (Golet et al., 2002).

298 Two types of antibiotics, fluoroquinolones (FQ) and macrolides (MAC), were
299 encompassed by this study, showing their widespread use in the WB region. The analyses
300 of FQ antibiotics confirmed a widespread use of norfloxacine (NOR; 0.016-2.94 μg/l)
301 and ciprofloxacine (CIP; bld-2.61 μg/l), while ofloxacin (OFL) was not found in any of
302 the analysed samples and apparently is not being used in the region. Enrofloxacin (ENR),
303 which has only application in veterinary medicine, was detected at relatively low
304 concentrations (bld-20 ng/l).

305 Observed levels of NOR (average concentration 979 ng/l) were higher than those
306 reported for Swiss raw sewage (Golet et al. 2002), while the levels of CIP (average
307 concentration 400 ng/l) were very similar. A significantly different NOR-to-CIP ratio in
308 the WB indicates probably some region specific usage pattern.

309 Significant differences in the usage patterns between WB and the Western Europe
310 were even more pronounced for MAC antibiotics. MAC are an important group in
311 Croatia, reflecting the fact that one of the most important world manufacturers of AZI,
312 pharmaceutical industry PLIVA, is located in Zagreb (Croatia). Consequently, the most
313 prominent representatives of MAC antibiotics were azithromycin (AZI; 0.006-1.14 μg/l)
314 and erythromycin (ERY; 0.024-0.420 μg/l), while only traces of other MAC, including
315 tylosin (TYL), josamycin (JOS) and roxitromycin (ROX) were detected. The composition
316 of MAC antibiotics in WB region was significantly different from the one observed in
317 Switzerland where the most abundant MAC was clarithromycin (CLA), while ERY and
318 AZI were significantly lower (Goebel et al., 2005).

319 The drugs belonging to the class of β-blockers were identified in all analysed
320 samples and the most abundant ones were atenolol and metoprolol with average
321 concentrations of 1.88 and 0.95 μg/l, respectively, while lower levels of sotalol (0.22
322 μg/l) and propranolol (0.13 μg/l) were also detected. The levels of the selected β-blockers
323 appear to be significantly lower than those reported in some earlier studies in Western
324 Europe (see compilation by Diaz-Cruz and Barcelo, 2004) or in the USA (Vanderford
325 and Snyder, 2006).

326 Among five different lipid regulators and cholesterol lowering drugs monitored,
327 the most frequent lipid-regulating drug was gemfibrozil (GEM; bld-1.7 μg/l), which was

328 detected in almost all samples. Clofibric acid (CLO) and bezafibrate (BEZ) were detected
329 in less than 30 % of the samples with concentrations rarely exceeding 100 ng/l, while
330 pravastatin (PRAV) and mevastatin (MEV) were never detected. The observed
331 composition of lipid regulators is rather different and the concentrations lower than those
332 from some earlier reports in Western Europe (see review by Diaz-Cruz and Barcelo,
333 2004) and indicates the prevalence of older types of lipid-lowering drugs.

334 Analyses of psychiatric drugs confirmed the presence of carbamazepine (CARB)
335 in all analysed samples (0.120-1.55 μg/l), with an average concentration of 420 ng/l. The
336 widespread occurrence of CARB in municipal wastewaters was confirmed by many other
337 studies in Europe (see review by Diaz-Cruz and Barcelo, 2004) and N. America
338 (Metcalfe et al., 2003). The other two selected representatives of psychiatric drugs,
339 fluoxetine (FLU) and paroxetine (PAR), were not detected in any of analysed samples.
340 Barbiturates, as a special category of psychiatric drugs, were also not detectable in
341 wastewaters from WB, which reflects the fact that they were phased out from the use in
342 most of the European countries. Their occurrence on some locations in Germany was
343 shown to be associated with an old disposal site (Peschka et al., 2006b).

344 The most prominent antihistaminic drug was ranitidine (RAN), which was detected in 70
345 % of the samples and reached average concentration of 250 ng/l. The other related drugs,
346 anti-histaminic loratadine (LOR) and the ulcer-healing lansoprazole (LANS), were not
347 detected in any of the analysed samples.

348 ***Personal care products, flame retardants and pesticides.*** As to the personal care
349 products, fragrance compounds exhibited a widespread occurrence in municipal waters
350 with maximal concentrations, ranging from 0.337 μg/l for traseolide (TRA) to 16.7 μg/l

351 for amberonne (AMB). Most of the determined fragrances were detected at high
352 frequencies (>90 %). Among polycyclic musks, galaxolide (HHCB) was the most
353 abundant representative with average levels of 630 ng/l. A lactone metabolite of HHCB
354 and tonalide (TON) were also detected in the samples. Other prominent fragrances
355 included AMB, acetyl cedrene (AC) and musk xylene (MX) with average concentrations
356 of 2.8 μg/l, 1.6 μg/l and 0.13 μg/l, respectively. The observed levels and composition of
357 fragrances in wastewaters of WB countries confirm findings from some other studies
358 (Mitjans and Ventura, 2005).

359 Another widespread class of personal care products determined in this study were insect
360 repellants, including DEET and Bayrepel. DEET was detected in 67 % of the samples
361 with average concentration of 840 ng/l, while Bayrepel was detected in only 3 samples.
362 The maximum concentrations (6.7 μg/l DEET and 2.2 μg/l Bayrepel) were determined in
363 the samples from eastern part of Croatia (Osijek and Belisce), which is known for its
364 problems with mosquitos.

365 The two organophosphate flame retardants were also determined in most of the WB
366 municipal wastewaters. TCPP was detected more frequently and its average
367 concentration (460 ng/l) was somewhat higher than that of TCEP (190 ng/l). A very
368 similar situation was recently reported as a result of a Western European survey
369 (Reemtsma et al., 2006).

370 This study encompassed also several classes of pesticides, including triazines and their
371 metabolites, dimethoate (DIM) and triazole fungicides and postemergence herbicide
372 picolinafen (PIC). The most frequently detected class was chlorotriazine herbicides but
373 even this class was, generally, not very abundant in analysed municipal wastewaters.

374 Atrazine (ATR), simazine (SIM), terbutylazine (TBA) and terbutryn (TBN) were present
375 usually in rather low concentrations (<250 ng/l). This is probably a consequence of the
376 fact that sampling campaigns were performed out of the main pesticide application
377 season. High concentration of atrazine (28 μg/l) was observed only in the wastewater of
378 the city of Sisak (Croatia), probably due to the contribution of industrial waste from the
379 herbicide manufacture at that location. All other pesticide classes were not detected.

380

381 *3.1.2 Industrial wastewaters*

382 As can be seen in Table 1, wastewater from different industries, including
383 pharmaceutical industry, tannery, iron smelter, textile industry, cellulose production,
384 dishes factory, pulp and paper factory, were analysed. It should be stressed that this study
385 was not directed to perform a detailed screening of the main contaminants typical for
386 each of the individual industries, but the samples were analysed for preselected
387 compound classes as described for municipal wastewaters. As expected, most of the
388 industrial effluents contained very low levels of pharmaceuticals, mainly few over-the-
389 counter analgesics. However, it is interesting to look for the presence of selected
390 pharmaceutical compounds in wastewater effluents from the pharmaceutical industries,
391 since these may represent significant specific sources of such contaminants. The results
392 for pharmaceutical industries Bosnalijek in Sarajevo and Galenika in Belgrade are
393 presented in Fig. 3. As can be seen, composition of the detectable pharmaceuticals is
394 much simpler than in the municipal wastewater, and reflects production assortments of
395 the given industry. However, the concentrations for most of the selected target
396 compounds were relatively low in terms of expected strongly enhanced values, which can

occur periodically in industrial effluents. Only few compounds such as acetaminophen (ACE; up to 4 ng/l), ibuprofen (IBU; 0.42 ng/l) and propyphenazone (PRO; 0.18 ng/l), were present in concentrations above 0.1 ng/l, while some other les abundant compounds (KET, DCF, TMP and SMX) were still present in much higher concentrations (5-50 μg/l) as compared to municipal wastewaters. Such a picture indicates very likely that the discharges from the different production facilities are not continuous.

Due to their widespread use in various industrial applications, surfactants are supposed to be relatively common constituents of industrial wastewater effluents. The results of the analyses of aromatic surfactants in effluents of five different industries from Bosnia and Herzegovina are presented in Fig. 4. The concentrations of both LAS and NPEO vary over wide ranges with LAS being significantly higher in all effluents. The LAS concentration was the highest in effluents from the textile (16.9 ng/l) and pharmaceutical industry (7.7 ng/l), while effluents from the cellulose production and iron smelter showed relatively low levels (0.04 and 0.22 ng/l). The distribution of NPEO surfactants showed also the lowest abundance in the effluents from the cellulose production and iron smelter however their concentration was significantly enhanced in the effluents from the textile industry and tannery. This is in a good agreement with the reported most common industrial applications of NPEO. With respect to the transformation products of NPEO, the most abundant ones were NP and NP1EC. The concentrations of NP in the effluents from the textile industry reached very high levels, exceeding 100 μg/l, which suggests that this location requires a particular attention, since such concentrations are considered harmful for aquatic life (see review by Servos, 1999).

420

421 *3.1.3 Removal during wastewater treatment*

422 Study of the behaviour and fate of various types of emerging compounds, performed in
423 some Croatian WWTPs indicated that the removal rates of individual compounds may
424 vary significantly. Both classes of aromatic surfactants (LAS and NPEO) were
425 biotransformed very efficiently during activated sludge treatment. However, this
426 transformation was accompanied by a significant formation of relatively stable
427 metabolites, which significantly reduced the overall removal efficiency. The behaviour of
428 these two compound classes in WWTPs is well-described in the literature (Di Corcia et
429 al. 1999; Ahel et al. 1994) and will not be discussed here in detail.

430 On the contrary, behaviour of pharmaceuticals in WWTPs is still a matter of
431 intensive research. The concentrations of the most prominent representatives of
432 pharmaceuticals in raw influent water and secondary effluent as well as resulting removal
433 rates in the WWTP Cakovec (Croatia) are presented in Fig. 5. This WWTP was chosen
434 for detailed assessment of removal efficiencies because it includes both mechanical and
435 biological treatment and allows collection of flow-proportional composite samples of
436 wastewater effluents. As it can be observed, only few compounds showed good
437 elimination (e.g. IBU and GEM), while most of the other compounds showed low
438 removal (KET, DCF, CLO, CARB, ATE, SOT, TMP, AZI, ERY). It should be
439 mentioned that in some cases (ATE, DFC, TMP, AZI, ERY), effluent concentrations
440 were higher than in the influents, which could be explained either by sampling inaccuracy
441 (erroneous estimate of hydraulic retention time) or also by deconjugation or
442 retransformation of conjugated compounds during treatment into the original compounds.

443 Since these conjugates were not included in the analysis, no reliable conclusion about
444 their biotransformation could be made.

445 Reemtsma et. al. (Reemtsma et al., 2006) recently proposed the use of water cycle
446 spreading index (WCSI) to assess the potential of a contaminant category to reach
447 ambient waters. The WCSI is a simple combination of the typical (average)
448 concentrations in wastewater effluents and their estimated removal efficiencies at
449 prevailing wastewater treatment practices. Taking into account the rather low removal
450 rates shown in Fig 5, it can be estimated that WCSI for the selected pharmaceutical
451 compounds is relatively high, supporting the suggestions on their relevance as water
452 contaminants of high environmental concern.

453

454 **4 Conclusions**

455 There is a growing concern about possible ecotoxicological importance of various classes
456 of emerging contaminants in wastewaters and receiving ambient waters, however, most
457 of the published reports refer to the most developed regions of the world, while the data
458 from developing countries are very scarce. The results obtained in this study confirmed a
459 widespread occurrence of the emerging contaminants in municipal wastewaters of the
460 WB region. Regarding raw wastewaters, the situation is similar to that in the Western
461 Europe and USA. However, due to the rather poor wastewater management practices in
462 WB countries, there is a significant difference with respect to the increased percentage of
463 wastewater contaminants that ultimately reach the ambient waters in WB countries.
464 Futhermore, this study confirms that the removal rates for some of the emerging
465 contaminants, including numerous pharmaceuticals, in WWTPs using conventional

466 activated sludge treatment are very low, which indicates that more advanced treatment
467 methods might be necessary to cope with the increasing inputs of such contaminants.
468
469 **Acknowledgements**
470 This work was performed within the framework of the EU FP6 STREP project on the
471 Reduction of Environmental Risks, Posed by Emerging Contaminants, through Advanced
472 Treatment of Municipal and Industrial Wastes (EMCO) (INCO-CT-2004-509188). The
473 financial support of Croatian Ministry of Science, Education and Sports (Project No. 098-
474 0982934-2712) is also acknowledged.

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602 Table 1. List of sampling sites and types of samples analysed

603

No	Sampling site	Type of WW	WWT	Sample analyzed
Bosnia and Herzegovina				
1	Sarajevo –main sewer	Municipal	No	Raw water
2	Pharmaceutical industry Bosnalijek, Sarajevo	Industrial	No	Raw water
3	Tannery KTK, Visoko	Industrial	No	Raw water
4	Textile industry Viteks, Visoko	Industrial	No	Raw water
5	Main sewer of the iron smelter, Zenica	Industrial	No	Raw water
6	Cellulose production Natron, Maglaj	Industrial	No	Raw water
Croatia				
7	Velika Gorica	Municipal	Yes	1) Raw water; 2) Primary effluent; 3) Secondary effluent
8	Bjelovar	Municipal	Yes	1) Raw water; 2) Secondary effluent
9	Cakovec	Municipal	Yes	1) Raw water; 2) Secondary effluent
10	Varazdin	Municipal	Yes	1) Raw water; 2) Secondary effluent
11	Vinkovci	Municipal	Yes	1) Raw water; 2) Secondary effluent
12	Pula	Municipal	Yes	1) Raw water; 2) Primary effluent
13	Rijeka	Municipal	Yes	1) Raw water; 2) after mechanical treatment
14	Split	Municipal	Yes	1) Raw water; 2) after mechanical treatment
15	Split – sewer center	Municipal	No	Raw water
16	Zagreb	Municipal	Yes	Raw water
17	Novi Zagreb	Municipal	No	Raw water
18	Karlovac	Municipal	No	Raw water
19	Sisak	Municipal	No	Raw water
20	Osijek	Municipal	Yes	Raw water
21	Belišće	Municipal	No	Raw water
22	Zadar	Municipal	No	Raw water
23	Slavonski Brod	Municipal	No	Raw water
Serbia				
24	Belgrade- sewer center	Municipal	No	Raw water
25	Dishes factory, METALAC, Gornji Milanovac	Industrial	Yes	Raw water
26	Pulp and paper factory, UMKA, umka	Industrial	Yes	1) before WWT 2) after WWT
27	Factory of herbicides, FITOFARMACIJA, Zemun	Industrial	No	After washing of machines and reactors and after recycling
28	Pharmaceutical Industry GALENIKA, Zemun	Industrial	Yes	1) before WWT 2) after WWT
29	Public Railway Transport Enterprise, Washing Center, Belgrade,	Technical	No	Washing effluent

604 WWT-waste water treatment

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606

607 Table 2. List of contaminants analysed and analytical methods used

Target compounds	Acronym	Analytical technique	References
Acetaminophen	ACE	LC/MS/MS	Gros et al., 2006b
Acetyl cedrene	AC	GC/MS	Mitjans and Ventura, 2005
Amberonne	AMB	GC/MS	Mitjans and Ventura, 2005
Aprobarbital	AB	GC/MS	Peschka et al., 2006b
Atenolol	ATE	LC/MS/MS	Gros et al., 2006b
Atrazin	ATR	GC/MS	Peschka et al., 2006a
Atrazin-desethyl	DEA	GC/MS	Peschka et al., 2006a
Atrazin-desisopropyl	DIA	GC/MS	Peschka et al., 2006a
Azithromycin	AZI	LC/MS/MS	Senta et al., 2007
Bayrepel	BAY	GC/MS	Knepper, 2004
Bezafibrate	BEZ	LC/MS/MS	Gros et al., 2006b
Bisphenol A	BPA	LC/MS/MS	Petrovic et al.,2003
Bultalbital	BB	GC/MS	Peschka et al., 2006b
Carbamazepine	CARB	LC/MS/MS	Gros et al., 2006b
Clofibric acid	CLO	LC/MS/MS	Gros et al., 2006b
Ciprofloxacin	CIP	LC/MS/MS	Senta et al., 2007
Diclofenac	DCF	LC/MS/MS	Gros et al., 2006b
Dimethoat	DIM	GC/MS	Peschka et al., 2006a
Enrofloxacin	ENR	LC/MS/MS	Senta et al., 2007
Epoxiconazole	EPO	GC/MS	Peschka et al., 2006a
Erythromycin	ERY	LC/MS/MS	Senta et al., 2007
Famotidine	FAM	LC/MS/MS	Gros et al., 2006b
Fluoxetine	FLU	LC/MS/MS	Gros et al., 2006b
Galaxolide	HHCB	GC/MS	Mitjans and Ventura, 2005
Gemfibrozil	GEM	LC/MS/MS	Gros et al., 2006b
Hexobarbital	HB	GC/MS	Peschka et al., 2006b
HHCB Lactone	HHCBL	GC/MS	Mitjans and Ventura, 2005
Ibuprofen	IBU	LC/MS/MS	Gros et al., 2006b
Indomethacine	IND	LC/MS/MS	Gros et al., 2006b
Josamycin	JOS	LC/MS/MS	Senta et al., 2007
Ketoprofen	KET	LC/MS/MS	Gros et al., 2006b
Lansoprazole	LANS	LC/MS/MS	Gros et al., 2006b
Linear alkylbenzene sulfonates	LAS	LC/MS/MS	Di Corcia et al., 1999
Loratidine	LOR	LC/MS/MS	Gros et al., 2006b
Mefenamic acid	MFA	LC/MS/MS	Gros et al., 2006b
Metamitron	MTM	GC/MS	Peschka et al., 2006a
Metoprolol	MTP	LC/MS/MS	Gros et al., 2006b
Mevastatin	MEV	LC/MS/MS	Gros et al., 2006b
Musk Xylene	MX	GC/MS	Mitjans and Ventura, 2005
N-diethyl-m-toluamide	DEET	GC/MS	Knepper, 2004
Naproxen	NAP	LC/MS/MS	Gros et al., 2006b
Nonylphenol	NP	LC/MS/MS	Petrovic et al.,2003
Nonylphenol ethoxylates	NPEO	HPLC; LC/MS	Ahel et al., 2000
Nonylphenoxy acetic acid	NP1EC	LC/MS/MS	Petrovic et al.,2003
Nonylphenoxyethoxy acetic acid	NP2EC	LC/MS/MS	Petrovic et al.,2003
Norfloxacin	NOR	LC/MS/MS	Senta et al., 2007
Octylphenol	OP	LC/MS/MS	Petrovic et al.,2003

Octylphenoxy acetic acid	OP1EC	LC/MS/MS	Petrovic et al.,2003
Ofloxacin	OFL	LC/MS/MS	Gros et al., 2006b
Paroxetine	PAR	LC/MS/MS	Gros et al., 2006b
Pentobarbital	PB	GC/MS	Peschka et al., 2006b
Picolinafen	PIC	GC/MS	Peschka et al., 2006a
Prapranolol	PROP	LC/MS/MS	Gros et al., 2006b
Pravastatin	PRAV	LC/MS/MS	Gros et al., 2006b
Propiconazole	PCZ	GC/MS	Peschka et al., 2006a
Propyphenazone	PRO	LC/MS/MS	Gros et al., 2006b
Ranitidine	RAN	LC/MS/MS	Gros et al., 2006b
Roxithromycin	ROX	LC/MS/MS	Senta et al., 2007
Secobarbital	SB	GC/MS	Peschka et al., 2006b
Simazin	SIM	GC/MS	Peschka et al., 2006a
Sotalol	SOT	LC/MS/MS	Gros et al., 2006b
Sulfadiazine	SDZ	LC/MS/MS	Senta et al., 2007
Sulfamerazine	SMR	LC/MS/MS	Senta et al., 2007
Sulfamethazine	SMZ	LC/MS/MS	Senta et al., 2007
Sulfamethoxazole	SMX	LC/MS/MS	Senta et al., 2007
Sulfapyridine	SPY	LC/MS/MS	Senta et al., 2007
Sulfathiazole	STZ	LC/MS/MS	Senta et al., 2007
Tebuconazole	TEB	GC/MS	Peschka et al., 2006a
Terbutryn	TBN	GC/MS	Peschka et al., 2006a
Terbutylazin	TBA	GC/MS	Peschka et al., 2006a
Terbutylazin-desethyl	DET	GC/MS	Peschka et al., 2006a
Tonalide	AHTN	GC/MS	Mitjans and Ventura, 2005
Traseolide	TRA	GC/MS	Mitjans and Ventura, 2005
Trimethoprim	TMP	LC/MS/MS	Senta et al., 2007
Tris-2-chloroethyl phosphate	TCEP	GC/MS	Meyer and Bester, 2004
Tris-2-chloropropyl phosphate	TCPP	GC/MS	Meyer and Bester, 2004

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611 Table 3. List of contaminants analysed and their concentration ranges in raw municipal
612 wastewaters (n=24 for surfactants, pesticides, repellents and flame retardants and
613 pharmaceuticals except barbiturates; n= 17 for barbiturates; n = 18 for fragrances).

614

Compound class	Analyte	LOD (µg/l)	No positive samples	Conc. range (µg/l)	Mean value (µg/l)*
PHARMACEUTICALS					
Antimicrobials Sulfonamides	TMP	0.012	24	0.035-2.55	0.781
	SDZ	0.001	24	bld-0.132	0.026
	STZ	0.001	3	bld-0.004	0.002
	SPY	0.004	22	bld-0.931	0.339
	SMR	0.001	4	bld-0.020	0.006
	SMZ	0.002	11	bld - 0.186	0.047
	SMX	0.001	24	0.019-11.6	1.18
	ERY	0.001	24	0.024-0.420	0.134
	AZI	0.002	24	0.006-1.14	0.456
	JOS	0.008	4	bld-0.016	0.013
	ROX	0.001	3	bld-0.050	0.031
Fluoroquinolones	NOR	0.003	23	0.016-2.94	0.976
	CIP	0.007	21	bld-2.61	0.405
	ENR	0.002	8	bld-0.018	0.012
	OFL	0.042	0	bld	-
Analgesics and antiinflammatories	KET	0.028	19	bld-1.52	0.561
	NAP	0.009	22	bld-1.55	0.335
	IBU	0.012	23	bld-11.9	3.20
	IND	0.007	3	bld-0.240	0.177
	DCF	0.010	24	0.050-4.20	0.859
	MFA	0.003	9	bld-0.120	0.053
	PRO	0.007	12	bld-0.461	0.083
Psychiatric drugs	CARB	0.018	24	0.120-1.55	0.419
	FLU	0.035	0	bld	-
	PAR	0.006	0	bld	-
Antiulcer agent	LANS	0.014	0	bld	-
Histamine H1 and H2 receptor agonists	LOR	0.004	0	bld	-
	FAM	0.012	3	Bld-0.12	0.059
	RAN	0.024	3	bld-0.758	0.253
β-blockers	ATE	0.042	23	bld -7.56	1.88
	SOT	0.029	13	bld -1.08	0.221
	MTP	0.012	5	bld -4.68	0.953
	PROP	0.012	5	bld -0.255	0.132
Lipid regulator and cholesterol lowering drugs	CFA	0.002	7	bld–0.110	0.057
	GEM	0.003	23	bld -1.70	0.377
	BEZ	0.009	7	bld -0.260	0.065
	PRAV	0.060	0	bld -1.17	-
	MEV	0.018	0	bld	-
Barbiturates	AB	0.080	0	bld	-
	BB	0.080	0	bld	-
	HB	0.080	0	bld	-
	PB	0.080	0	bld	-
	SB	0.080	0	bld	-

SURFACTANTS	LAS	0.200	24	0.242-9450	2903
	NPEO	0.100	24	5-392	89
Metabolites	NP	0.069	24	0.460-4.40	1.66
	OP	0.017	24	bld-0.272	0.128
	NP1EC	0.001	22	bld-3.20	0.741
	NP2EC	0.001	17	bld-4.37	0.586
	OP1EC	0.002	4	bld-0.107	0.050
PLASTICIZERS	BPA	0.013	22	bld-2.06	0.510
PESTICIDES	DIM	0.080	1	bld-0.80	-
	SIM	0.080	2	bld-0.50	0.3
	ATR	0.080	9	bld-28.0	3.3
	TBA	0.080	1	bld-0.10	-
	TBN	0.080	2	Bld-0.15	0.1
	MTM	0.150	0	bld	-
	PCZ	0.080	0	bld	-
	TEB	0.080	0	bld	-
	EPO	0.080	0	bld	-
	PIC	0.080	0	bld	-
Metabolites	DEA	0.100	0	bld	-
	DIA	0.100	0	bld	-
	DET	0.100	0	bld	-
INSECT REPELLENTS	DEET	0.080	16	Bld-6.9	0.84
	BAY	0.100	3	Bld-2.2	1.3
FLAME RETARDANTS	TCEP	0.080	9	Bld-0.5	0.19
	TCPP	0.080	22	Bld-2.5	0.46
FRAGRANCES					
Polycyclic musks	HHCB	0.006	18	0.03-2.67	0.63
	AHTN	0.007	17	0.052-0.86	0.25
	HHCBL	0.010	17	bld-1.21	0.57
	TRA	0.005	12	bld-0.34	0.12
Nitro musks	MX	0.009	16	bld-0.56	0.17
Other fragrances	AC	0.005	17	bld-13.9	1.6
	AMB	0.008	17	bld-16.5	2.8

615 *Mean value was calculated as an arithmetic mean of all values above a detection limit.
616

Figure captions

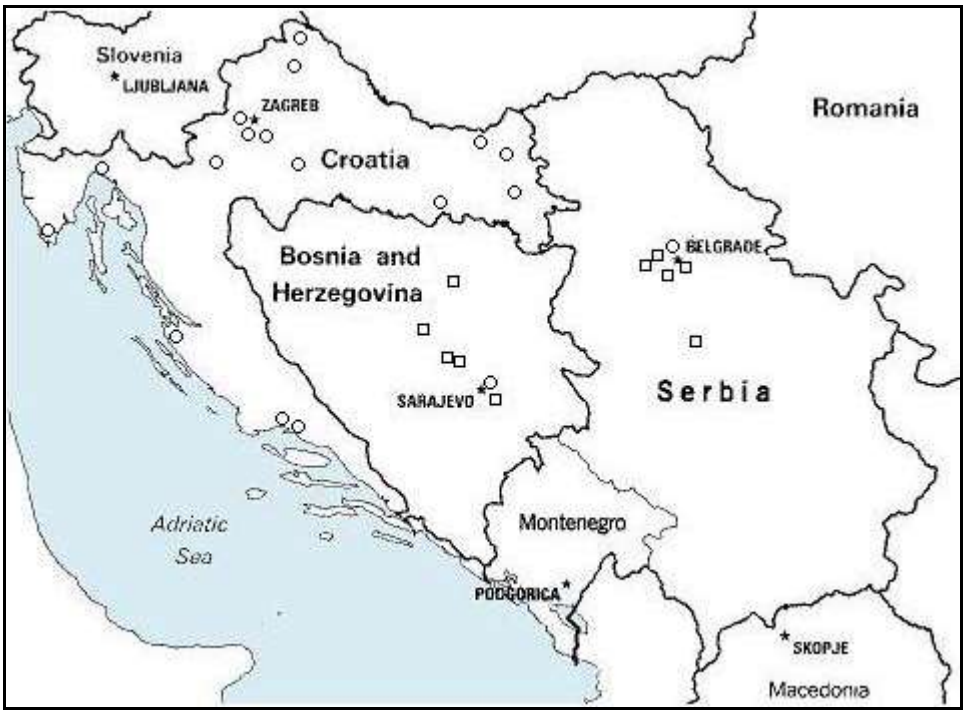
Fig. 1 Map of the region with indicated sampling locations for wastewater monitoring campaigns in Bosnia and Herzegovina, Croatia and Serbia; Legend: municipal wastewaters (circles); industrial wastewaters (squares).

Fig. 2 Frequency of detection for individual emerging contaminants (%). A) Pharmacueticals; B) Surfactants, fragrances, flame retardants, insect repellents and pesticides

Fig. 4 Concentration of different types of surfactants and surfactant-derived compounds in several types of industrial waters in Bosnia and Herzegovina (see Table 1).

Fig. 3 Occurrence of pharmaceuticals in wastewaters of pharmaceutical industries Galenika (Serbia) and Bosnalijek (Bosnia and Herzegovina)

Fig. 5. Occurrence and elimination efficiencies of pharmaceuticals in the municipal WWTP of the city of Čakovec (Croatia). A) October 2004; b) May 2005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LJUBLJANA
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Croatia
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Herzegovina
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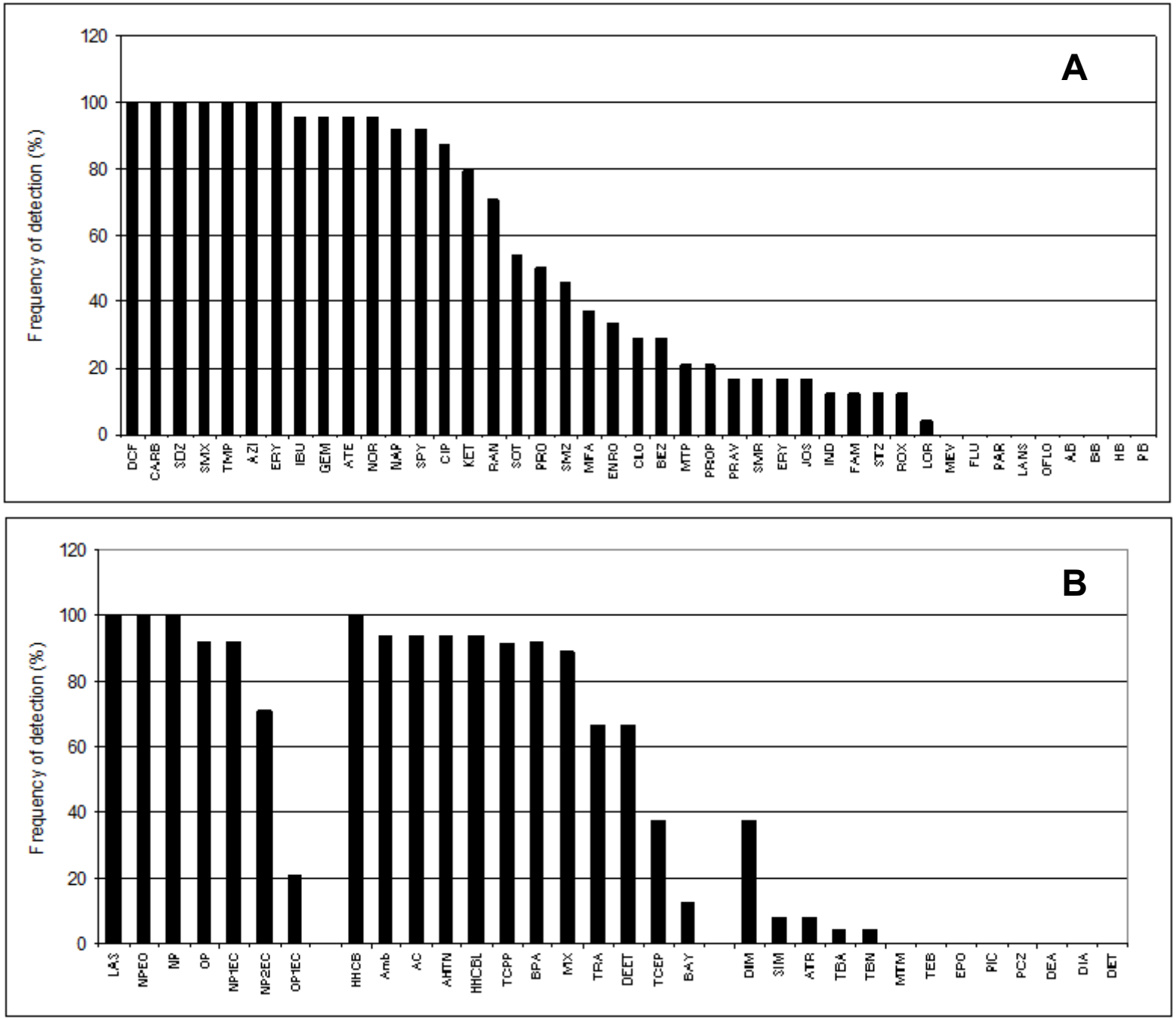
Sea
Montenegro
PODGORICA
SKOPJE
Macedonia

Fig. 1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Frequency of detection (%)
120
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Frequency of detection (%)
120
100
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LAS
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OP
NP1EC
NP2EC
OP1EC
HHCB
Amb
AC
AHTN
HHCBL
TCPP
BPA
MIX
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652 Fig. 2

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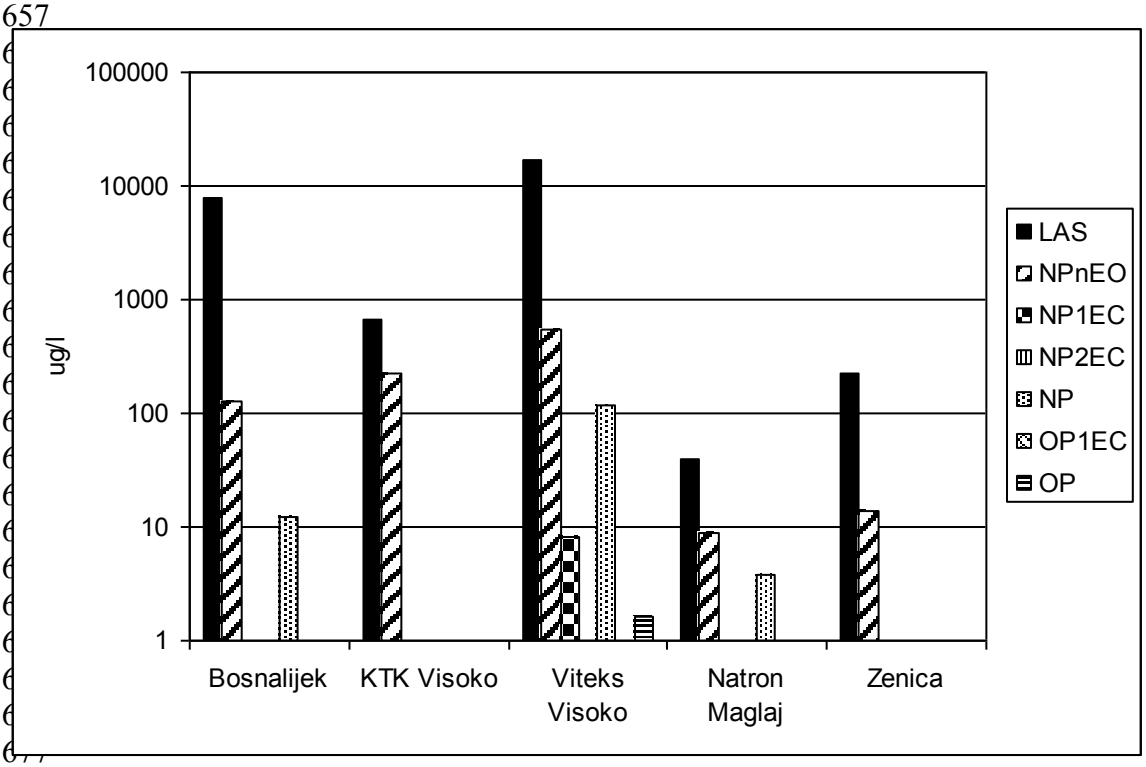

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682 Fig. 4.
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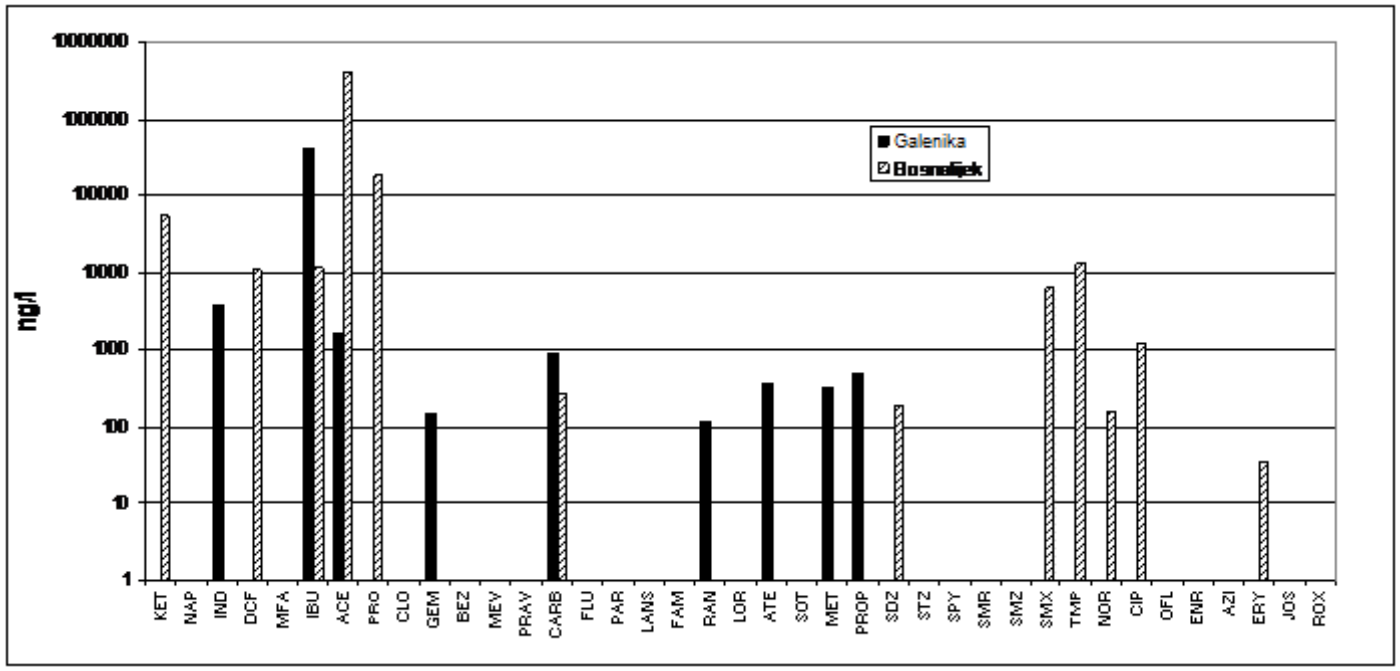

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686 Fig. 5.
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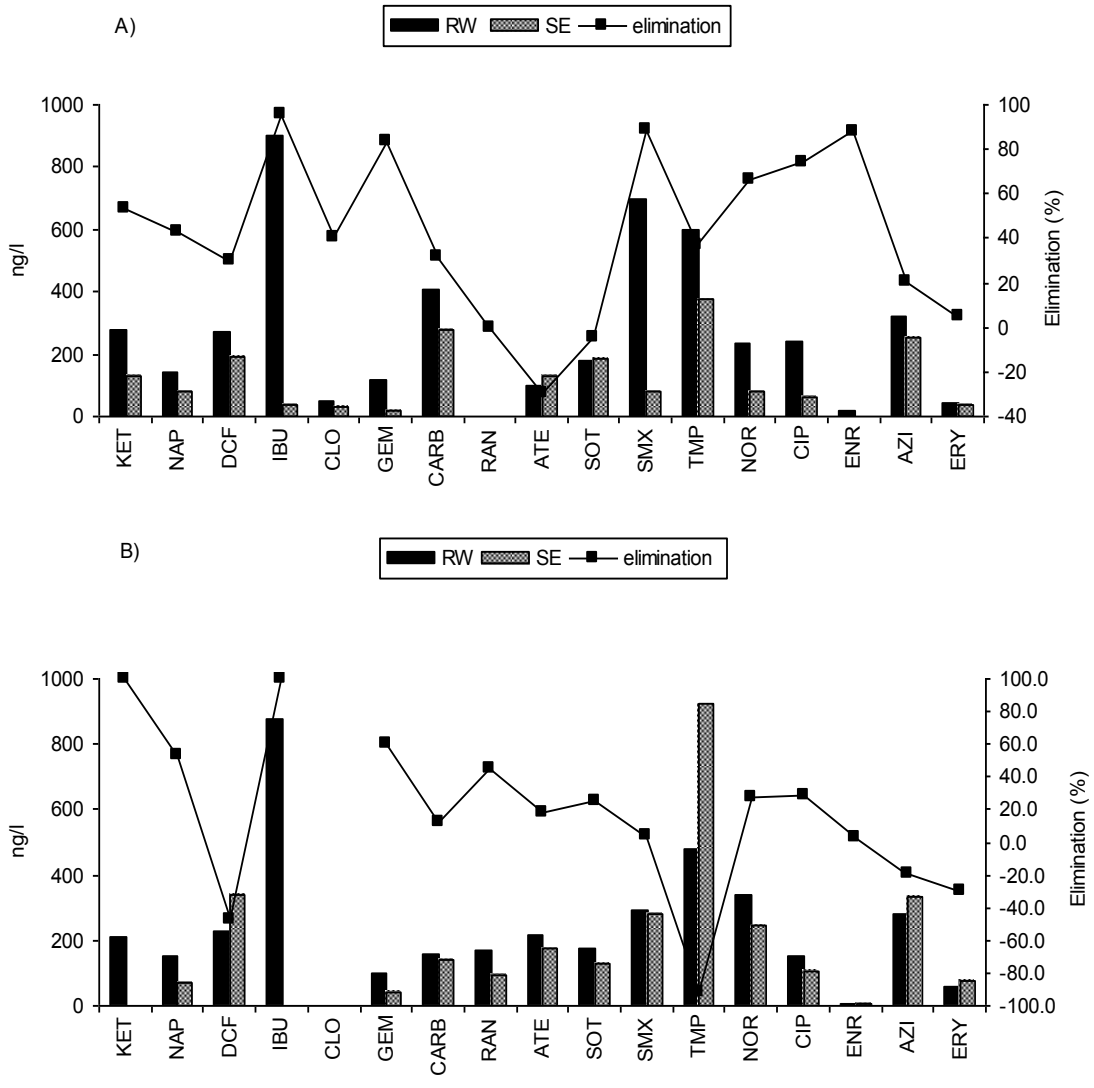

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