PRIORITY POLLUTANTS AND POP's AS INDICATORS OF WATER QUALITY IN THE VRBAS RIVER

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Abstract

The adoption of Water Framework Directive and Stockholm Convention, set the strategy against water pollution and requirements for further specific measures in pollution control. These are individual pollutants or groups of pollutants that pose significant risk for aquatic environment including drinking water. It is necessary to take actions for priority substances in order to achieve load reduction. The group of "priority pollutants" represents part of wider spectrum of compounds that need to be identified under the river basin management plan by every Member State and represent the so called "specific synthetic and non-synthetic pollutants". The research was carried out in collaboration with the Public institution „Vode Srpske". The main aim of monitoring was to collect data for the period of five years (2007-2011), on the presence of priority pollutants and specific substances, defined by Annex X of WFD as well as the POP's in the river Vrbas, in order to evaluate quality of water and to record significant changes in ecological status. Water samples were taken at three profiles in the Vrbas River (Novoselija, Delibašino selo and Razboj). Quantitative analyses of the presence of compounds from the list of 33 priority substances and additional compounds and the group of persistent and bioaccumulative substances which include: pesticides, aromatic and chlorinated hydrocarbons, polycyclic aromatic hydrocarbons and metals were performed in the research. Obtained results showed that there is no significant variation of values for many parameters, except Dis (2-ethylhexyl) phthalate. Its value increased slightly during September and October, in 2010 and 2011.

Key words

Pollutants; WFD; Stockholm Convention; River Vrbas

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1 INTRODUCTION

Adoption of the Water Framework Directive (2000/60/EC) of the European Parliament and of the Council established a strategy against water pollution and requirements for further specific measures to control pollution. The European legislation establishing measures for prevention of surface waters pollution is implemented at two levels:

- selection of substances of importance for achieving the "good status" of waters,
- defining measures that each Member State is required to take at the river basin level for prevention of pollution by certain hazardous substances.

A more extensive part of the strategy for prevention and control of surface waters pollution is found in the Article 16 of the Directive 2000/60/EC, which requires establishing the list of priority substances and procedures for identifying priority substances and priority hazardous substances, as well as adoption of specific measures for prevention of pollution by these substances.

Priority Substances are individual groups or pollutants that pose a significant risk to the water environment, also including risks to the water used for water supply. It is necessary to take measures for the progressive reduction of such substances. Among them, "priority hazardous substances" have been specifically defined. These substances are toxic, persistent and tend to bioaccumulate, or otherwise contribute to the level of concern, thus it is necessary to completely disrupt them or phase out their spilling, emissions and escapes, therefore completely prevent further pollution of the environment.

It should be noted that a group of "priority pollutants" is a smaller part of a larger group of compounds which must be identified within each river basin management plan by each Member State and it represents the so-called "specific synthetic and non-synthetic pollutants". The term "specific pollutants" includes priority substances and also additionally the substances relevant for the basin that must be identified during the preparation of river basin management plan.

The aim of the Vrbas river water monitoring was to gather data on the presence of priority substances and specific pollutants, defined by Annex X of the Framework Directive of the European Union (EU WFD 2000/60/EC) and POPs defined by the Stockholm Convention [1], [2], [3], [4]. The water quality status is monitored on selected river Vrbas profiles. Monitoring program included analysis of organic and inorganic pollutants four times a year. Sampling and analysis were carried out 12 times a year (from January to December). For the profile Razboj, which is also included in transnational monitoring network (TNM). Monitoring the status of water quality in Republic of Srpska underwent some changes after 2009, based on the fact that typology and defining the water bodies in accordance with the requirements of the Water Framework Directive was performed in the meantime. Monitoring the waters quality status in 2009 was conducted at specific measurement points of the water bodies, for certain types.

Analyses were interrupted during the war activities, and regular performance of monitoring was resumed again in 2000 for all the rivers in Republic of Srpska. The monitoring programme involved analysis of organic and inorganic pollutants four times a year.

Monitoring the water quality status of the Republic of Srpska watercourses was subjected to certain changes after 2009, based on the fact that typology and defining the water bodies in accordance with the requirements of the Water Framework Directive was performed in the meantime. Monitoring the waters quality status in 2009 was conducted at specific measurement points of the water bodies, for certain types [5], [6], [7].

2 MATERIAL AND METHODS

The research of the presence of priority pollutants and POPs in the river Vrbas was carried out in cooperation with the public institution "Vode Srpske". Water quality monitoring in Republic of Srpska has been performed systematically since 2000, including the analysis of biological, physical-chemical, chemical and microbiological parameters and specific pollutants, as well as POPs and the parameters from the list of priority pollutants (Annex X, WFD) from 2007. Quality assessment carried out in accordance with the Regulation on water classification and categorization of watercourses. The trends following in the field of water policy in 2007 introduce measurement of priority substances for all waterways in Republic of Srpska [8], [9],[10].

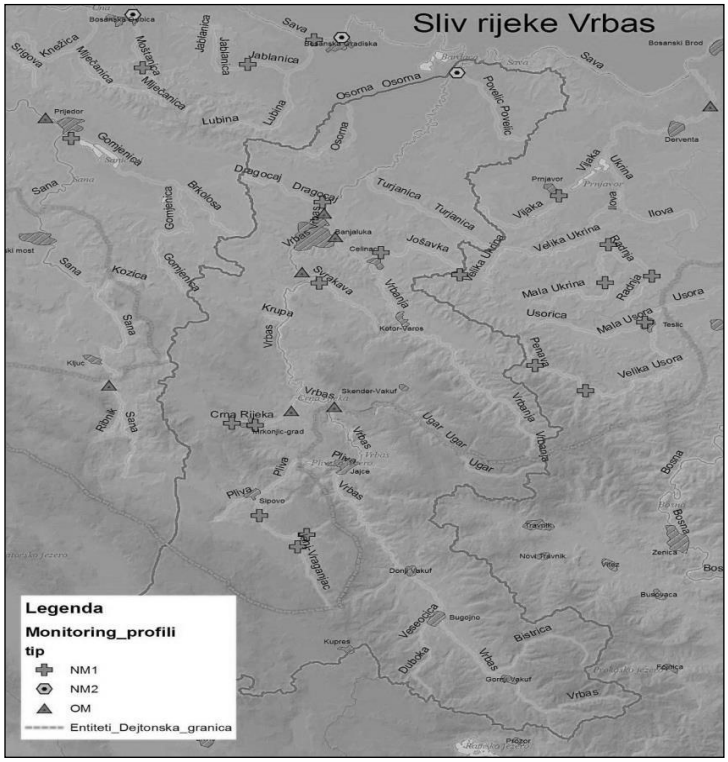

Fig. 1: Map of the catchment area of the river Vrbas

On the river Vrbas there is a total number of 13 measuring profiles monitored for the purposes of national, internationally controlled (TNMN-ICPDR) and also for the purposes of operational monitoring. The water sampling for analysis of the Vrbas River was performed on three measuring profiles (sites): Novoselija, Delibašino selo and Razboj.

Tab. 1: Measuring profiles on the river Vrbas monitored under the National Monitoring

X coord.	Y coord.	Name of profile	Name of river	Mark	Type	Type of water body
6,436,009.40	4,896,498.67	Previja	Glogovac	V31	NM1	WB_5.10
6,434,661.30	4,893,959.39	Đajići	Vaganec	V23	NM1	WB_4.7
6,428,694.73	4,900,507.34	Mujidžići	Janj	V22	NM1	WB_4.4
6,440,340.46	4,923,332.40	Ušće u Bočac	Ugar	V17	OM	WB_4.4
6,428,019.32	4,919,489.72	Mrkonjić Grad	Crna Rijeka	V15	NM1	WB_5.7
6,433,612.52	4,922,444.36	Ušće u Bočac - s.Bjelajci	Crna Rijeka	V14	OM	WB_4.4

6,438,029.72	4,949,330.21	Tijesno	Svrakava	V13	NM1	WB_4.4
6,435,323.89	**4,951,567.33**	**Novoselije**	**Vrbas**	**V03**	**OM**	**WB_2.14**
6,447,606.58	4,955,707.79	Stančići	Jošavka	V21	NM1	WB_5.16
6,440,503.18	4,958,998.48	Vrbanja	Vrbanja	V12	OM	WB_4.14
6,438,711.18	**4,963,921.89**	**Delibašino Selo**	**Vrbas**	**V02**	**OM**	**WB_2.14**
6,438,488.24	4,966,288.82	Zalužani	Dragočaj	V11	NM1	WB_4.13
6,459,397.62	**4,993,368.44**	**Razboj**	**Vrbas**	**V01**	**NM2**	**WB_2.14**

3 RESULTS AND DISCUSSION

The results include measurements made during the period from 2007 until 2011 in the Framework of Monitoring Surface Water Quality in Republic of Srpska. Responding to trends of water monitoring, since 2007 specific pollutants, priority substances as well as POP's analysis was introduced in practice. In 2007 there was just one sample taken in the profile downstream of Bočac. In 2008 the same practice continues. In 2009 the list of specific pollutants and priority substances has been significantly changed, with no consistency in sampling of the same parameters on the basis of which we could get a clearer picture of the chemical status of the river Vrbas. Only in 2010 and 2011 the list is fixed, where consistency in sampling and analysis of all parameters can be seen. Thus, inter alia, increased value of Dis (2-ethylhexyl) phthalate was noted during September and October 2010 and in March, September and October 2011 [11], [12], [13], [14], [15].

Phthalates are esters of the phthalic acid, used as plasticizers or softeners to increase the elasticity of the most common plastic materials. They are used in a large variety of products, including coatings of pharmaceutical pills as a dietary supplement to control viscosity, as gelling agent, stabilizer, lubricant, binder and emulsifier. The final applications include adhesives, electronics, agricultural additives, building materials, personal hygiene products, medical devices, packaging, children's toys, modelling clay, waxes, paints, printing inks and coatings, pharmaceuticals, food products and textiles. Negligent waste disposal into the rivers causes an increased amount of phthalates in water samples, especially in the rainy periods, which were recorded in September and October 2010 and March, September and October 2011.

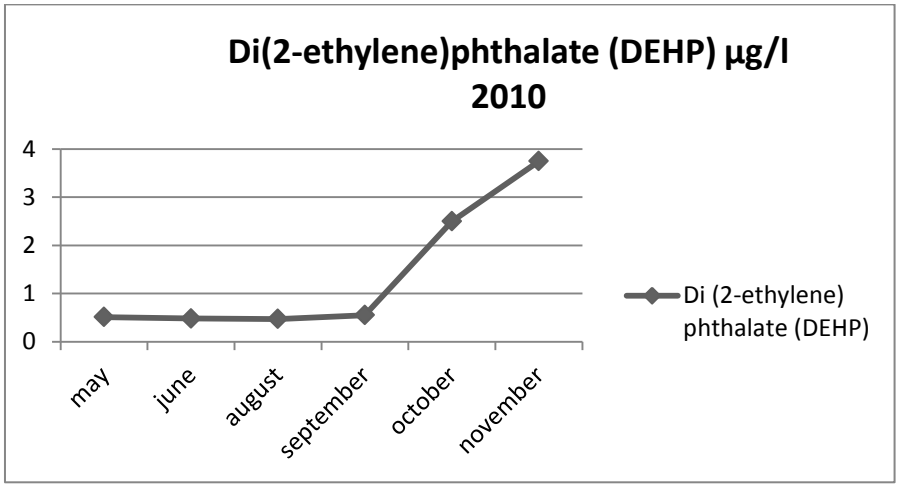

Fig. 2: Value Dis(2-etilheksil) phthalates for 2010

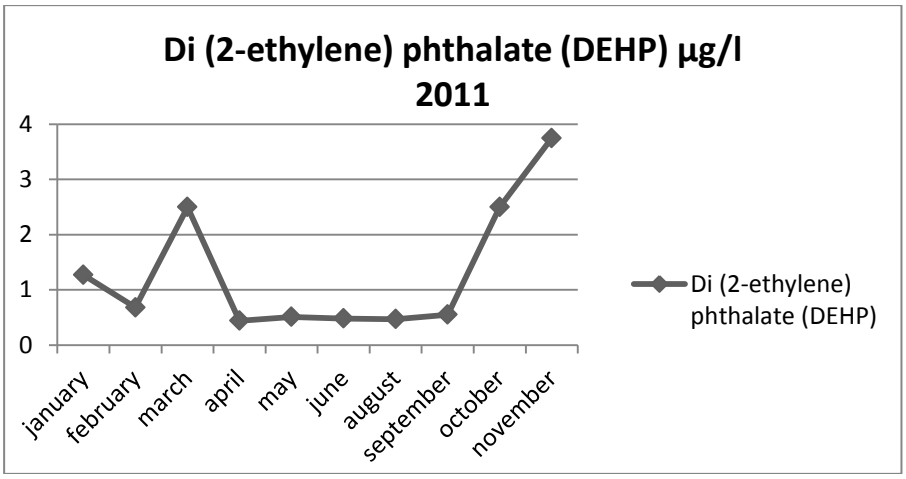

Fig. 3: Value Dis(2-etilheksil) phthalates for 2011

In the years 2010 and 2011 the value of Dis (2-ethylhexyl) phthalate increased. This pollutant was introduced on the list of tested parameters as late as in 2010. Value of Dis (2-ethylhexyl) phthalate shows increase for September and October 2010 and from March, September and October 2011 which is associated with precipitation that are most intense in this period of the year, during which the level of the river Vrbas is growing along with all the flotsam of plastic waste that washes from the nearby coast due to an increase in the level of the river.

The results show that there is no consistency in sampling for the same parameters for all five years. Because of all this, it is indicated which parameter is made in which year, hoping to change this practice in the coming Monitoring, and that same pollutants will be sampled continuously. As these are very expensive analyses and budget for performing these analyses is extremely limited, the analysis was performed only for those parameters the value of which could show increased variations in value. Expecting the practice for some specific pollutants and priority substances to improve both in terms of educating the staff and institutions, the results to date should have been taken as a pioneer ones, or they should have been considered as a zero condition, until this practice has improved and gained consistency in sampling and analysing these parameters [16].

4 CONCLUSION

The paper includes a chronological overview of the state of specific pollutants and priority substances and POP's since following up of surface water quality was introduced, in this case for the Vrbas river since 2007, following their values for five consecutive years (from 2007 until 2011). The results did not show significant differences for most examined parameters except Dis (2-ethylhexyl) phthalate the value of which has slightly increased. Banja Luka city, through the territory of which the Vrbas river flows and where the measurements of priority substances and specific pollutants for the three measuring profiles were performed, does not have any major potential and existing pollutants, for example industrial plants which by large produce waste waters as by-products.

Banja Luka city development carries accelerated industrialisation with it, as well as agricultural development. It is expected that the Vrbas river watercourse will be more polluted, knowing that Banja Luka city has no collectors for wastewater treatment and that all waste water will go directly into the river as the recipient. It is difficult to go along with the trends imposed by the Water Framework Directive (WFD) when we are encountering the problem where individual parameters' thresholds are not defined by the Regulation on

classification and categorization of watercourses, so that in this case we take the limit values laid down in the Water Framework Directive as guidance. The lack of adequate infrastructure and damage to the existing infrastructure during the war, together with the lack of maintenance led to the pollution of water resources, and thus to a deterioration in the quality of drinking water. More than 90% of household waste waters discharge without treatment directly into local surface water, and less than 3% of wastewater from households goes through full biological treatment. As far as industrial wastewater is concerned, the situation is slightly less alarming, mainly due to the fact that industrial production is at the level of less than 30% compared to the pre-war period. Taking into account the long-term effects of high levels of industrial pollution before the war, and the necessity of achieving economic growth in the future, the proportions of this crisis are rather clear.

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APPENDICES

Tab. 2: The results of analysis of specific pollutants in river Vrbas in 2007, 2008, 2009, 2010 and 2011

Specific pollutants	OBTAINED VALUES														
	Vrbas 2007			Vrbas 2008			Vrbas 2009			Vrbas 2010			Vrbas 2011		
	Minimum	Maxim. allowed concentration acc. to Directive 2008/105/EC	Results	Minimum	Maxim. allowed concentration acc. to Directive 2008/105/EC	Results	Minimum	Maxim. allowed concentration acc. to Directive 2008/105/EC	Results	Minimum	Maxim. allowed concentration acc. to Directive 2008/105/EC	Results	Minimum	Maxim. allowed concentration acc. to Directive 2008/105/EC	Results
Anthrancene (µg/l)	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.708
Atrazine (µg/l)	0.00	0.6	<0.1	0.00	0.6	<0.1	0.00	0.6	<0.1	0.00	0.6	<0.1	0.00	0.6	<2.18
(Benzo(a)pyrene) (µg/l)	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	-
(Benzo(b)fluoranthene) (µg/l)	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	<0.015	0.00	0.03	<0.436
(Benzo(g,h,i)perylene) (µg/l)	0.00	0.03	0.1	0.00	0.03	0.1	0.00	0.03	0.1	0.00	0.03	<0.008	0.00	0.03	<0.436
(Benzo(k)fluoranthene) (µg/l)	0.00	0.05	<0.1	0.00	0.05	<0.1	0.00	0.05	<0.1	0.00	0.05	<0.001	0.00	0.05	<0..815
(Benzo(a)pyrene) (µg/l)	0.00	0.02	<0.1	0.00	0.02	<0.1	0.00	0.02	<0.1	0.00	0.02	<0.008	0.00	0.02	<0.0545
Bis (2-ethylhexyl) phthalate (µg/l)	0.00	-	<100	0.00	-	1.15	0.00	-		0.00	-		0.00	-	-
Dibenzo (a.h) anthracene (µg/l)	0.00	-	<0,1	0.00	-	<0.1	0.00	-	<0.1	0.00	-	<0.1	0.00	-	-
Di (2-ethylene) phthalate DEHP (µg/l)	0.00	1.3	0.1	0.00	1.3	0.1	0.00	1.3	-	0.00	1.3	0.51	0.00	1.3	28.135
Diuron (µg/l)	0.00	0.20	<0.1	0.00	0.20	<0.1	0.00	0.20	<0.1	0.00	0.20	<0.01	0.00	0.20	<0.543
4.4 DDD (µg/l)	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	0.01
4.4 DDE (µg/l)	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	0.01
4,4 DDT (µg/l)	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	<0.01	0.00	0.01	0.01
(Indeno(1,2,3-cd)pyrene) (µg/l)	0.00	0.002	<0.1	0.00	0.01	<0.1	0.00	0.01	<0.1	0.00	0.01	<0.01	0.00	0.02	<0.0545
Endosulfan I (µg/l)	0.00	0.05	<0.01	0.00	0.05	<0.01	0.00	0.05	<0.01	0.00	0.05	<0.01	0.00	0.05	<0.0545
Endosulfan II (µg/l)	0.00	0.05	<0.1	0.00	0.05	<0.1	0.00	0.05	<0.1	0.00	0.05	<0.1	0.00	0.05	-
Endosulfan sulfate (µg/l)	0.00	0.05	<0.01	0.00	0.05	<0.01	0.00	0.05	<0.01	0.00	0.05	<0.01	0.00	0.05	-
Phenanthrene (µg/l)	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	-
Fluorene (µg/l)	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	-
Heptachlor (µg/l)	0.00	0.10	<0.01	0.00	0.10	<0.01	0.00	0.10	<0.01	0.00	0.10	<0.01	0.00	0.10	-
Hlorfenilfros (µg/l)	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.1	0.00	0.10	<0.02	0.00	0.10	<0.1
Hlorpirifros (-methyl) (µg/l)	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	<0.1	0.00	0.03	-
Lead (µg/l)	0.00	7.20	-	0.00	7.20	0.20	0.00	7.20	<0.1	0.00	7.20	<0.1	0.00	7.20	<0.05
Mercury (µg/l)	0.00	0.05	-	0.00	0.05	<0.1	0.00	0.05	<0.1	0.00	0.05	<0.1	0.00	0.05	<0.04
Nickel (µg/l)	0.00	20.00	<0.40	0.00	20.00	<0.01	0.00	20.00	<0.40	0.00	20.00	<0.40	0.00	20.00	<0.01
Naphthalene (µg/l)	0.00	1.20	<0.1	0.00	1.20	<0.1	0.00	1.20	<0.1	0.00	1.20	<0.1	0.00	1.20	<0.016

PCB s(µg/l)	0.00	<0.01	<0.01	0.00	<0.01	<0.01	0.00	<0.01	<0.01	0.00	<0.01	<0.01	0.00	<0.01	-
Simazine (µg/l)	0.00	1	<0.1	0.00	1	<0.1	0.00	1	<0.1	0.00	1	<0.4	0.00	1	2.178

Tab. 3: The frequency of sampling parameters for the period prior to the measurement

No.	CAS number (1)	EU number (2)	Names of Specific substances and priority pollutants and POPs	Monitoring				
				2007	2008	2009	2010	2011
				V-7 profile	V-7 profile	profile BAVRB1	profile BAVR	NV03
1	15972-60-8	240-110-8	Alachlor	-	+	-	+	+
2	120-12-7	204-371-1	Anthrancene	+	+	-	+	+
3	1912-24-9	217-617-8	Atrazine	-	+	+	+	+
4	71-43-2	200-753-7	Benzene	-	+	-	-	-
5	not applied	not applied	Brominated diphenylethe(**)	+	+	-	-	-
6	7440-43-2	231-152-8	Cadmium and its compounds	+	+	+	+	+
7	85535-84-8	287-476-5	Chloroalkanes C_{10-13}(**)	-	-	-	-	-
8	470-90-6	207-432-0	Chlorfenvinphos	+	+	-	+	+
9	2921-88-2	220-864-4	Chlorpyrifos	-	+	-	+	+
10	107-06-2	203-458-1	1,2-dichloroethane	-	-	-	+	+
11	75-09-2	200-838-9	Dichloromethane	-	+	-	+	+
12	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate	+	+	-	+	+
13	330-54-1	206-354-4	Diuron	+	+	-	+	+
14	115-29-7	204-079-4	Endosulfan	+	+	-	+	+
	959-98-8	not applied	(alfa-endosulfan)	-	-	-	-	-
15	206-44-0	205-912-4	Fluoranthene (*****)	+	-	-	+	+
16	118-74-1	204-273-9	Hexachlorobenzene	+	-	-	+	-
17	87-68-3	87-68-3	Hexachlorobutadiene	-	-	-	+	+
18	608-73-1	210-158-9	Hexachlorocyclohexane	-	-	-	-	-
	58-89-9	200-401-2	(gama-izomer, Lindan)	+	+	-	+	+
19	34123-59-6	251-835-4	Isoproturon	-	+	-	+	+
20	7439-92-1	231-100-4	Lead and its compounds	+	+	+	+	+
21	7439-97-6	231-106-7	Mercury and its compounds	+	+	+	+	+
22	91-20-3	202-049-5	Naphthalene	-	-	-	+	+
23	7440-02-0	231-111-4	Nickel and its compounds	+	+	+	+	+

24	25154-52-3	246-672-0	Nonylphenol	-	+	-	+	+
	104-40-5	203-199-4	(4-nonylphenol)	-	-	-	+	+
25	1806-26-4	not applied	Octylphenol	-	+	-	+	+
	140-66-9	not applied	(4-(1,1 ',3,3 '-tetramethylbutyl)-phenol)	-	-	-	+	+
26	608-93-5	201-778-6	Pentachlorobenzene	-	-	-	-	-
27	87-86-5	not applied	Pentachlorophenol	+	+	-	+	+
28	not applied	not applied	Polyaromatic hydrocarbons	+	+	-	+	+
	50-32-8	200-028-5	(Benzo(a)pyrene)	+	+	-	+	+
	205-99-2	205-911-9	(Benzo(b)fluoranthene)	+	+	-	+	+
	191-24-2	205-883-8	(Benzo(g,h,i)perylene)	+	+	-	+	+
	207-08-9	205-916-6	(Benzo(k)fluoranthene)	+	+	-	+	+
	193-39-5	205-893-2	(Indeno(1,2,3-cd)pyrene)	-	+	-	+	+
29	122-34-9	204-535-2	Simazine	+	-	-	+	+
30	688-73-3	211-704-4	Tributyltin compounds	-	-	-	-	-
	36643-28-4	not applied	(Tributyltin-cation)	-	-	-	-	-
31	12002-48-1	234-413-4	Trichlorobenzenes	-	+	-	-	-
	120-82-1	204-428-0	(1,2,4- trichlorobenzenes)	-	-	-	-	-
32	67-66-3	200-663-8	Trichloromethane (chloroform)	-	-	-	+	+
33	1582-09-8	216-428-8	Trifluralin	-	-	-	-	+