Rudolf Kiralj

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ON QUANTITATIVE RELATIONSHIPS BETWEEN CHEMICAL STRUCTURE AND PHYSICO-CHEMICAL PROPERTIES OF CHEMICAL PRODUCTS. THE CASE STUDY: BJELOVAR-BILOGORA COUNTY

Summary

Even small areas as Bjelovar-Bilogora County (BBC) are affected by increasing local and regional pollution. A large variety of organic compounds exists in all parts of the atmosphere, waters and soil, accumulates in living organisms and on anthropogenic objects. This work investigates organic pollutants in BBC in relation to their spread, behavior and chemical properties, based on literature data in absence of experimental measurements. More than 230 organic pollutants were identified in BBC: simple compounds, benzene derivatives, polycyclic aromatic hydrocarbons, polychlorinated and other biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, halogenated alkanes and alkenes, diverse pesticides and antimicrobials. Geographic distribution of organic pollutants was investigated in relation to population density, agricultural activity, position of volatile organic compounds emitters, annual traffic data, and night sky brightness levels as light pollution. It is visible that towns and larger villages as well as main roads are emitters of various organic pollutants and smog generators, whilst typically rural regions are more characterized by pesticides pollution. Three examples for QSPR (Quantitative Structure-Property Relationship) are described and investigated in terms of their statistics (sign change problem) and chemical interpretability: 1) a partial least squares (PLS) regression model for boiling point of polycyclic aromatic hydrocarbons; 2) a multiple linear regression (MLR) model for micellar phase-water partition coefficient of diverse solutes; 3) a MLR model for bioconcentration factor of nonpolar organic compounds. Several samples in the models were already identified as existing pollutants in BBC. Models 2) and 3) failed in the sign check, for which explanations are given and remedies are proposed.

Keywords: environment; Bjelovar-Bilogora County; organic pollutants; regression analysis; descriptors; structure-property relationship; validation.

1. Introduction

A famous Swedish chemist Jöns Jacob Berzelius, one of the fathers of modern chemistry, coined the term *organisk kemi* (*organic chemistry*) in his native Swedish in

1806 (Berzelius, 1806., p. 6). This way, he baptized a part of chemistry which was dealing with chemical compounds that could not be synthesized from inorganic materials at that time, but were extracted from animals and plants, all compounds containing carbon, hydrogen, oxygen and nitrogen. The choice of the name *organic* was made from the point of view of vitalism, a doctrine according to which organic compounds could be synthesized only by "vital force" in living organisms. A Berzelius' student Friedrich Wöhler was one of a few chemists and probably the most known that has seriously undermined this doctrine in 1828, by showing that an inorganic compound, ammonium cyanate NH_4CNO, could be transformed into an organic compound urea $CO(NH_2)_2$ (Wöhler, 1828.). Since the mid of the XIX century numerous compounds which existed in living organisms and others unknown before were synthesized in laboratory, but the historical term *organic compound* has persisted up to today. According to the CAS statistics (Chemical Abstract Service, 2012.), more than 65 million of inorganic and organic compounds as well as about 63 million protein sequences are known up today. The number of new chemicals increases exponentially (Binetti et al., 2008.), but the unclear borderline between "organic" and "inorganic" nature of compounds since the Wöhler's time still remains, in spite of various definitions proposed (Wikipedia 1, 2012.). It is certain that the majority of carbon compounds are studied by organic chemistry, and that the rest of compounds belongs to carbon inorganic chemistry, but there are some compounds that can be considered both organic and inorganic.

Modern lifestyle is marked by intensive if not excessive use of organic compounds in all spheres of life. To name some of them, such as plastics, nylons, colorants and dyes, medicaments, food additives, detergents and soaps, disinfectants, cosmetic products, and materials for construction. However, this progress has its bad side with respect to its undesired effects on the environment, i.e. on the planet Earth as the world is being more and more globalized, and directly or indirectly on human health and society. Among organic compounds causing such effects one can enumerate pesticides still in use and those already forbidden, halogenated hydrocarbons used as refrigerants, industrial waste chemicals, gases and vapors from vehicles and various anthropogenic sources, among others. Numerous organic compounds do not decompose quickly or not at all by chemical, biological or photolytic processes of environmental degradation, thus being called Persistent Organic Pollutants (POPs) (Wikipedia 2, 2012.). They are some pesticides used in past, industrial solvents, chlorinated organic compounds, pharmaceuticals, and a large variety of other compounds. Diverse organic pollutants that easily evaporate or sublimate into the atmosphere are called Volatile Organic Compounds (VOCs) are, for example, lower hydrocarbons, halogenated compounds and aldehydes (Wikipedia 2, 2012.). These and several other types of organic and inorganic pollutants participate in atmospheric physical processes and chemical reactions, resulting in the ozone depletion and

generation of harmful ground-level ozone, enhancement of the natural greenhouse effect, dry and wet deposition on the soil and waters etc. Other compounds pollute the hydrosphere and lithosphere directly. All pollutants are harmful to life, destroy the natural order in the biosphere, change physical and chemical characteristics of the planet, corrode and decompose anthropogenic objects and at the end, threat to the existence of mankind.

This work deals with organic compounds – pollutants which can be found in soil, waters and air, and are of environmental importance for Croatia, in particular for Bjelovar-Bilogora County (BBC). The county is situated in the west-central part of Croatia, with a peculiar position that have only the Zagreb district and Požega-Slavonia County: it makes borders only with Croatian counties and not with neighboring countries and international sea. The County has five towns, among which Bjelovar holds the county seat, and 18 municipalities, comprising in total 323 populated places. In total it has area of 2640 km^2 and 123390 inhabitants (Statistički ljetopis RH, 2011., Popis stanovništva, 2011.). It is interesting to inspect the environmental situation in BBC in terms of potential local pollution sources, such as agricultural activities, industry, urban centers, and traffic, as well as regional pollution affecting BBC. In this sense, this work gives some insights into organic pollution in BBC and its geographical tendencies, and shows some examples about how quantitative relationships between molecular structure and macroscopic properties of organic pollutants should be correctly understood and applied in practice.

2. Organic pollutants in Bjelovar-Bilogora County and their distribution

An extensive literature search for attested organic pollutants in BBC was carried out, with the purpose to identify classes of pollutants and have deeper insight into the environmental situation of the studied area.

To distinguish organic from inorganic pollutants, the following search criteria were applied. First, all carbon-containing compounds with C-H bonds were considered organic and the same was valid for perhalogenated compounds, with except of compounds considered traditionally as inorganic (hydrogen cyanide HCN and phosgene $COCl_2$). Second, an organic pollutant was identified via its CAS (Chemical Abstracts Service) number as a pure substance, i.e. one compound, and not a mixture of racemates, other isomers, or other structurally similar compounds.

In total, 236 organic pollutants have been found in 20 literature sources (Table 1). Six sources reported analyses carried out for BBC: three were county official documents (Izvješće o stanju okoliša, 2007., Plan intervencija u zaštiti okoliša, 2004., Program zaštite okoliša BBŽ, 2003.), two were environmental reports for Croatia (Pregled podataka o emisijama u zrak, 2005., Jerman, 2003.), and one was a scientific article (Senta et al., 2009). Most document reported situation for the entire territory of Croatia, meaning that mentioned pollutants were indeed present in BBC. Some

of these were official governmental documents (Emisija onečišćujućih tvari u zraku, 2005., Pravilnik o registru onečišćivanja okoliša, 2008., Plan zaštite i poboljšanja kakvoće zraka, 2008., Prijedlog nacionalnog plana za provedbu Stockholmske konvencije, 2008., pp. 67-71, Pravilnik o najvećim količinama štetnih tvari, 1992., Pravilnik o najvećim količinama rezidua, 2008.). Among other documents, there were scientific conference abstracts and proceedings, Sedmi skup Zaštita zraka '11, 2011. (Sinovčević, 1998.), scientific articles (Drevenkar, Fingler, 2000., Šišović, 2000.), projects (Project Development of the Croatian Soil Monitoring, 2008., Konačni nacrt priručnika za izvješćivanje o vodama, 2009.), and national statistical data (Statistički ljetopis RH, 2011.). Finally, there was a report about pollution for the entire Danube basin, in which the environmental situation in BBC was included (Fabianova et al, 2009.). In reality, BBC might contain thousands of organic pollutants, but they were not identified as single compounds with unique CAS numbers.

Table 1. Organic pollutants in Bjelovar-Bilogora County according to literature

Name[a]	Abbr.[b]	CAS[c]	Name[a]	Abbr.[b]	CAS[c]
Simple organic compounds					
acetone		67-64-1	formaldehyde		50-00-0
acetone cyanohydrin	ACH	75-86-5	methane		74-82-8
acetylene		74-86-2	methanol		67-56-1
acrolein		107-02-8	methyl isocyanate	MIC	624-83-9
acrylonitrile		107-13-1	*N*-nitrosodi-*n*-butylamine	NDBA	924-16-3
n-butanol		71-36-3	*N*-nitrosodiethylamine	NDEA	55-18-5
butyl acetate		123-86-4	*N*-nitrosodimethylamine	NDMA	62-75-9
ethyl acetate		141-78-6	*N*-nitrosopyrrolidine	NPYR	930-55-2
ethyleneimine (aziridine)		151-56-4	propylene oxide		75-56-9
ethylene oxide (oxirane)		75-21-8			
Benzene and its simple derivatives					
benzene		71-43-2	2,4,5-trichlorophenol		95-95-4
pentachlorobenzene	PeCB	608-93-5	pentachlorophenol	PCP	87-86-5
hexachlorobenzene	HCB	118-74-1	*o*-nitrophenol		88-75-5
ethylbenzene		100-41-4	*m*-nitrophenol		554-84-7
2-chloroaniline		95-51-2	*p*-nitrophenol		100-02-7
o-aminophenol		95-55-6	2,4-dinitrophenol		51-28-5
m-aminophenol		591-27-5	picric acid		88-89-1
p-aminophenol		123-30-8	styrene		100-42-5
o-cresol		95-48-7	toluene		108-88-3
m-cresol		108-39-4	2,4-toluene diisocyanate	2,4-TDI	584-84-9
p-cresol		106-44-5	2,6-toluene diisocyanate	2,6-TDI	91-08-7
4,6-dinitro-o-cresol		534-52-1	*o*-xylene		95-47-6
2-chlorophenol		95-57-8	*m*-xylene		108-38-3
2,4-dichlorophenol	2,4-DCP	120-83-2	*p*-xylene		106-42-3
Polycyclic aromatic hydrocarbons (PAHs)					
acenaphthylene		208-96-8	acenaphthene		83-32-9
anthanthrene		191-26-4	anthracene		120-12-7
benz(a)anthracene		56-55-3	benzo(a)pyrene		50-32-8
benzo(b)chrysene		214-17-5	benzo(b)fluoranthene		205-99-2
benzo(e)pyrene		192-97-2	benzo(ghi)perylene		191-24-2
benzo(k)fluoranthene		207-08-9	chrysene		218-01-9
coronene		191-07-1	dibenzo(a,h)anthracene		53-70-3

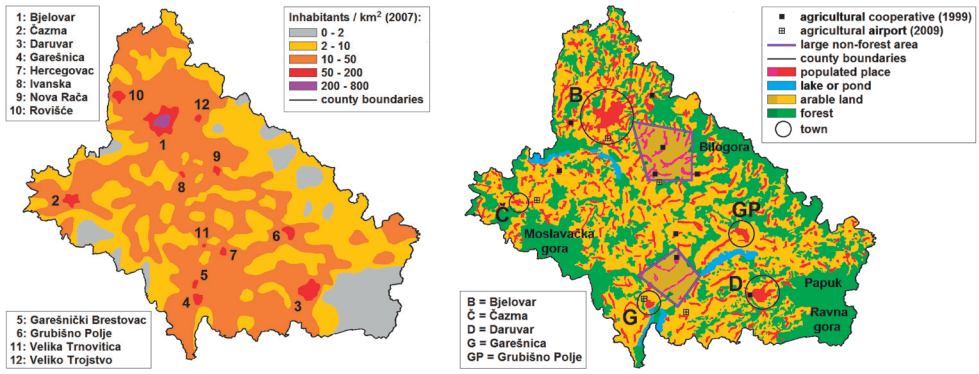
Name[a]	Abbr.[b]	CAS[c]	Name[a]	Abbr.[b]	CAS[c]
fluoranthene		206-44-0	indeno(1,2,3-cd)pyrene		193-39-5
naphthalene		91-20-3	phenanthrene		85-01-8
pyrene		129-00-0			
Polychlorinated biphenyls (PCBs) and other biphenyls					
2,4,4′-triCB	PCB28	7012-37-5	2,2′,3,4,4′,5-hexacCB	PCB138	35065-28-2
2,2′,5,5′-tetraCB	PCB52	35693-99-3	2,2′,4,4′,5,5′-hexaCB	PCB153	35065-27-1
2,3,4,4′-tetraCB	PCB60	33025-41-1	2,3,3′,4,4′,5-hexaCB	PCB156	38380-08-4
2,4,4′,5-tetraCB	PCB74	32690-93-0	2,3,3′,4,4′,5′-hexaCB	PCB157	69782-90-7
3,3′,4,4′-tetraCB	PCB77	32598-13-3	2,3′,4,4′,5,5′-hexaBP	PCB167	52663-72-6
2,2′,4,5,5′-pentaCB	PCB101	37680-73-2	3,3′,4,4′,5,5′-hexaBP	PCB169	32774-16-6
2,2′,4,5,6-pentaCB	PCB102	68194-06-9	2,2′,3,3′,4,4′,5-heptaBP	PCB170	35065-30-6
2,3,3′,4,4′-pentaCB	PCB105	32598-14-4	2,2′,3,4,4′,5,5′-heptaCB	PCB180	35065-29-3
2,3,4,4′,5-pentaCB	PCB114	74472-37-0	2,3,3′,4,4′,5,5′-heptaCB	PCB189	39635-31-9
2,3′,4,4′,5-pentaCB	PCB118	31508-00-6	benzidine		92-87-5
2′,3,4,4′,5-pentaCB	PCB123	65510-44-3	3,3′-dichlorobenzidine		91-94-1
3,3′,4,4′,5-pentaCB	PCB126	57465-28-8			
Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)					
2,3,7,8-tetraCDD		1746-01-6	2,3,4,7,8-pentaCDF		57117-31-4
1,2,3,7,8-pentaCDD		40321-76-4	1,2,3,4,7,8-hexaCDF		70648-26-9
1,2,3,4,7,8-hexaCDD		39227-28-6	1,2,3,7,8,9-hexaCDF		72918-21-9
1,2,3,6,7,8-hexaCDD		57653-85-7	1,2,3,6,7,8-hexaCDF		57117-44-9
1,2,3,7,8,9-hexaCDD		19408-74-3	2,3,4,6,7,8-hexaCDF		60851-34-5
1,2,3,4,6,7,8-heptaCDD		35822-46-9	1,2,3,4,6,7,8-heptaCDF		67562-39-4
octaCDD		3268-87-9	1,2,3,4,7,8,9-heptaCDF		55673-89-7
2,3,7,8-tetraCDF		51207-31-9	octaCDF		39001-02-0
1,2,3,7,8-pentaCDF		57117-41-6			
Halogenated methanes					
bromochloromethane	Halon1011	74-97-5	difluorochlorobromo-methane	Halon1211	353-59-3
bromodichloromethane	Halon1021	75-27-4	dichloromethane	Freon 30	75-09-2
bromomethane	Halon1001	74-83-9	difluoromethane	Freon 32	75-10-5
carbon tetrachloride	Freon 10	56-23-5	fluoroform	Freon 23	75-46-7
carbon tetrafluoride	Freon 14	75-73-0	fluoromethane	Freon 41	593-53-3
chlorodifluoromethane	Freon 22	75-45-6	trichlorofluoromethane	Freon 11	75-69-4
chloroform	Freon 20	67-66-3	trifluorobromomethane	Halon1301	75-63-8
dichlorodifluoromethane	Freon 12	75-71-8			
Halogenated ethanes and ethenes					
1,1-difluoroethane	Freon152a	75-37-6	pentafluoroethane	Freon125	354-33-6
1,2-dichloroethane	Freon 150	107-06-2	perchloroethane	PCA	67-72-1
1,1,1-trichloroethane	TCA	71-55-6	hexafluoroethane	Halon2600	76-16-4
1,1,1-trifluoroethane	HFC 143a	420-46-2	chloropentafluoroethane	Freon 115	76-15-3
1,1,2-trifluoroethane	HFC 143	430-66-0	1,2-dichloro-1,1,2,2-tetra-fluoroethane	Freon 114	76-14-2
1-chloro-1,1-difluoro-ethane	Freon 142	75-68-3	1,1,2-trichloro-1,2,2-tri-fluoro-ethane	Freon 113	76-13-1
1,1-dichloro-1-fluoro-ethane	Freon 141	1717-00-6	1,1,2,2-tetrafluoro-1,2-di-bromoethane	Halon2402	124-73-2
1,1,1,2-tetrafluoroethane	HFA 134a	811-97-2	vinyl chloride	VCM	75-01-4
1,1,2,2-tetrachloroethane	1122TTCA	79-34-5	trichloroethylene	TCE	79-01-6
1,1,2,2-tetrafluoroethane	HFA 134	359-35-3	perchloroethylene	PCE	127-18-4
Halogenated higher alkanes and alkenes					
1,1,2,2,3-pentafluoro-propane		679-86-7	octafluorocyclobutane	FreonC318	115-25-3
1,1,1,3,3,3-hexafluoro-propane	HFC 236fa	690-39-1	1,1,1,2,2,3,4,5,5,5-deca-fluoro-pentane		138495-42-8
1,1,1,2,3,3,3-heptafluoro-propane	HFC 227	431-89-0	perfluoropentane		678-26-2
octafluoropropane	Freon 218	76-19-7	perfluorohexane	FC 72	355-42-0

Name[a]	Abbr.[b]	CAS[c]	Name[a]	Abbr.[b]	CAS[c]
1,1,1,3,3-pentafluoro-butane		406-58-6	hexachloro-1,3-butadiene	HCBD	87-68-3
perfluorobutane		355-25-9			
Pesticides containing aromatic rings in structure					
acetochlor		34256-82-1	fenthion		55-38-9
acifluorfen		50594-66-6	isoproturon		34123-59-6
alachlor		15972-60-8	linuron		330-55-2
bentazon		25057-89-0	(*R*)-mecoprop		16484-77-8
bifenthrin		82657-04-3	(*S*)-mecoprop		25333-13-5
clofenvinfos		470-90-6	methoxychlor		72-43-5
deherban		66767-23-5	2-methyl-4-chlorophen-oxy-acetic acid	MCPA	94-74-6
dicamba		1918-00-9	metolachlor		51218-45-2
dichlorodiphenyldichlo-ro-ethane	DDD	72-54-8	4-nonylphenol		68152-92-1
dichlorodiphenyldichlo-ro-ethylene	DDE	72-55-9	parathion		56-38-2
dichlorodiphenyltrichlo-ro-ethane	DDT	50-29-3	pendimethalin		40487-42-1
di-(2-ethylhexyl)phthalate	DEHP	117-81-7	4-tert-octylphenol		140-66-9
dichlorprop		120-36-5	trifuralin		1582-09-8
diuron		330-54-1			
Pesticides containing heteroaromatic rings in structure					
atrazine		1912-24-9	prometryn		7287-19-6
chlorpyrifos		2921-88-2	propazine		139-40-2
cyanazine		21725-46-2	pyridate		55512-33-9
deisopropylatrazine		1007-28-9	sebuthylazin		7286-69-3
desethylatrazine		6190-65-4	simazine		122-34-9
fluroxypyr		69377-81-7	terbuthylazine		5915-41-3
metamitron		41394-05-2	terbutryn		886-50-0
Pesticides containing strained rings in structure					
aldrin		309-00-2	endosulfan		115-29-7
chlordane		57-74-9	heptachlor		76-44-8
chlordecone		143-50-0	heptachlor epoxide		1024-57-3
dieldrin		60-57-1	isodrin		465-73-6
endrin		72-20-8	mirex		2385-85-5
Other pesticides					
chlorpicrin	PS	76-06-2	δ-hexachlorocyclohexane	δ-HCH	319-86-8
dichlorvos	DDVP	62-73-7	lindane	γ-HCH	58-89-9
α-hexachlorocyclohexane	α-HCH	319-84-6	malathion		121-75-5
β-hexachlorocyclohexane	β-HCH	319-85-7	trichlorfon		52-68-6
Antimicrobials in human medicine					
azithromycin		83905-01-5	norfloxacin		70458-96-7
ciprofloxacin		85721-33-1	sulfadiazine		68-35-9
enrofloxacin		93106-60-6	sulfamethoxazole		723-46-6
erythromycin		114-07-8	trimethoprim		738-70-5
Antimicrobials and other medications in agriculture and veterinary medicine					
bacitracin		1405-87-4	gamithromycin		145435-72-9
chloramphenicol		56-75-7	metronidazole		443-48-1
chlorpromazine		50-53-3	nitrovin		804-36-4
colchine		64-86-8	ronidazole		7681-76-7
dapsone		80-08-0	rumensin		22373-78-0
dimetridazole		551-92-8	tilosyn phosphate		1405-53-4
flavomycin		11015-375	virginiamycin		11006-76-1
furazolidone		67-45-8			

[a] Systematic or trivial name. [b]Abbreviation or short commercial name. [c]CAS registry number.

The 236 identified pollutants were divided into 14 classes based on molecular structure, properties and use. Besides simple organic compounds (19), benzene and its simple derivatives (28) and polycyclic aromatic hydrocarbons (PAHs) (19), there were three groups of classes. One group consisted mainly of chlorinated hydrocarbons and similar compounds: polychlorinated and other biphenyls (23), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (17), halogenated methanes (15), halogenated ethanes and ethenes (20), and halogenated higher alkanes and alkenes (11). The other group was formed by pesticides with aromatic (27), heteroaromatic (14), and strained (10) rings in structure, and other pesticides (8). The last group contained antimicrobials used in human medicine (8), and antimicrobials and other medications used in agriculture and veterinary medicine (15). VOCs are compounds with relatively small molecules, found in Table 1 among some simple organic compounds, benzene derivatives, halogenated methanes, ethanes and ethenes. Several compounds from these classes are used as refrigerants and solvents and, because of containing carbon-halogen chemical bonds act as ozone depleting substances. POPs in Table 1 are more numerous because all polychlorinated biphenyls, dibenzo-*p*-dioxins and dibenzofurans are persistent to environmental degradation. Some very important POPs exist among halogenated non-aromatic hydrocarbons (methanes, alkanes and alkenes), antimicrobials in human medicine, and especially among pesticides (all such POPs contain chlorine). Carbon-halogen bonds are very stable and can decompose only at extreme conditions of intensive radiation in the stratosphere and upper layers of the atmosphere.

Spatial preferences for distribution of organic pollutants in BBC can be rationalized using specific maps designed for such purposes. Population density map (Fig. 1a) for year 2007 was made as a compilation of an electronic map (Population density, 2007.). Maps for agricultural activity (Fig. 1b), annual traffic statistics (Fig. 2a) and VOCs emitters (Fig. 2b) were based on compilation of an electronic map (Bjelovarsko-bilogorska županija map, 2005.). Other data were added posteriori: location of registered agricultural cooperatives (Popis poljoprivrednih zadruga, 1999.) and agricultural airports (Kunst, Tomljenović, 2009., p. 21) (Fig. 1b); active railways (Karta pruga, 2011) and roads with annual average daily traffic (Božić et al., 2010., p. 60) (Fig. 2a); location of VOCs emitters (Registar postrojenja, 2007.). Boundaries of the regions of air pollution at the local level were drawn at 5 km distance around PAHs emitters (roads and railways, Fig. 2a) and VOCs emitters (Fig. 2b) according to recommendations (Inglezakis, Poulopoulos, 2006., p. 3). Two maps for light pollution, given as artificial night sky brightness relative to the natural night sky brightness level (an average sky brightness below the atmosphere, equal to 252 $\mu cd\ m^{-2}$) (Cinzano et al., 2001a) were compilations of maps showing the situation in 1998 (Cinzano et al., 2000) and prediction for year 2025 (Cinzano et al., 2001.b).



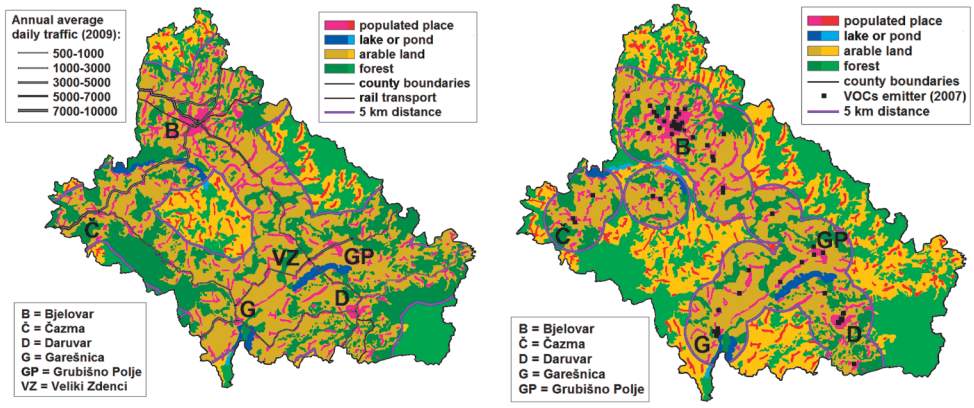
a) b)

Figure 1. a) Population density of Bjelovar-Bilogora County in 2007. b) Agricultural regions in Bjelovar-Bilogora County. Towns and particular villages are marked with numbers or initials.

Population density (Fig. 1a) reflects the geographical features of BBC. The least populated areas (gray) are located on mountain regions, along the county northeast boundaries (Bilogora low mountain), at the southeast mountains (Papuk and Ravna gora), at the southwest mountain (Moslavačka gora), and at the west border where the former swamp and lake region of the river Česma was transformed into ponds for recreational fishing. The most populated places are the capital Bjelovar located on the north of BBC, the town of Čazma at the west, three other towns (Daruvar, Garešnica and Grubišno Polje) located in the southern part of BBC, and larger villages that are placed around Bjelovar and also between Bjelovar and Garešnica. It is reasonable to suppose that the mountainous regions are the least polluted, whilst highly populated parts of BBC are the most polluted areas. Cities and larger villages are usually sources of various organic pollutants, due to industrial and craft activities, heavy traffic and heating based on combustion of fossil fuels. Considering compounds in Table 1, the following can be associated with the peaks of the population density. First, PAHs are generated in incomplete burning of fuels. Then, polychlorinated biphenyls are used in electric devices such as capacitors, electric transformers and electric motors. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are generated in pyrolysis of biphenyls, polyvinyl chloride and other chlorinated hydrocarbons. Halogenated lower hydrocarbons are used as refrigerants and solvents. Finally, there are antimicrobials released from hospitals.

Contrary to cities, rural regions (Fig. 1b) are sources of various pesticides and antimicrobials and other medications used for treating health and growth of animals. Typical agricultural areas in BBC are located around the five towns as well as

between Bjelovar and the three southern towns. There are two agricultural areas of considerable size, shown by a trapezoid southeast to Bjelovar and by another one northeast to Garešnica.



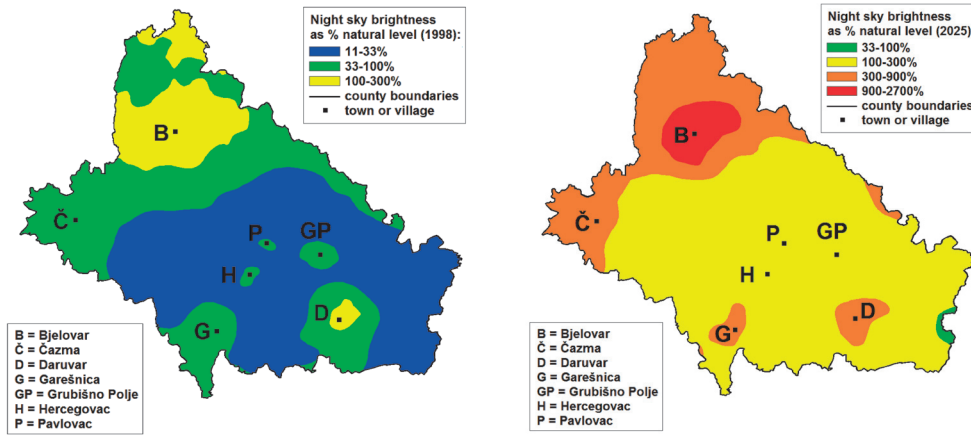
a) b)

Figure 2. a) Annual average daily transport in Bjelovar-Bilogora County in 2009. b) Distribution of VOCs in Bjelovar-Bilogora County in 2007. Towns and particular villages are marked with numbers or initials.

Road and railway traffic intensity and the polluted regions 5 km from the roads and railways are shown in Fig. 2a. Internal combustion engines in vehicles are known as emitters of various hydrocarbons, especially PAHs that deposit in the regions around the roads and railways, CO, CO_2 and nitrogen oxides, what finally results in complex photochemical reactions in the atmosphere producing photochemical smog, ground-level ozone and various hazardous secondary pollutants. Most area of BBC is affected by traffic pollution, only some mountainous regions at the county's boundaries are out of the risk, and the same is valid for a smaller central region (center of the Bjelovar subdepression). It is important to emphasize that the roads connecting BBC with western and northern neighbors, namely roads Zagreb-Bjelovar and Čazma-Ivanić Grad, have more than 9 and 7 thousand vehicles per day, respectively (Božić et al., 2010., p. 60). Somewhat less vehicles pass the roads Bjelovar-Đurđevac, Čazma-Bjelovar, and the first third of the road Bjelovar-Daruvar (Bjelovar-Bulinac), between 4 and 6 thousand vehicles. In fact, the values of annual average daily traffic (Fig. 2a) are well related to population density (Fig. 1a) and geographical position of the five towns.

Geographical distribution of VOCs emitters, industry and crafs (Fig. 2b), shows clearly that the size of populated places defines the concentration of the emitters. Therefore, Bjelovar and its vicinity leads in the number of VOCs emitters, then follow

Daruvar, Garešnica, Grubišno Polje and Čazma. The remaining VOCs emitters are located in some larger villages, situated mainly along the roads Bjelovar-Daruvar and Garešnica-Grubišno Polje, whilst some emitters are positioned northeast and east to Čazma. VOCs in BBC are released in procedures using dyes and paints, chemical cleaning, printmaking, and making plastic, wooden and rubber products (Registar postrojenja, 2007.). Carbon compounds in the atmosphere, including VOCs, CO_2 and CO in reaction with nitrogen oxides produce ground-level ozone.



a) b)

Figure 3. Artificial night sky brightness levels in Bjelovar-Bilogora County. a) Situation in 1998. b) Prediction for year 2025. Towns and particular villages are marked with numbers or initials.

Light pollution is a side effect of industrial civilization, in the form of excessive and obtrusive artificial light. There are several negative consequences of this type of pollution, such as energy waste, adverse effects on animal and human health and psychology, disruption of ecosystems, difficulties in astronomical observations and finally, increased atmospheric pollution. In fact, light pollution destroys nitrate radicals thus preventing the normal night time reduction of atmospheric smog produced by fumes emitted from vehicles and industry (Stark et al., 2011.). The current situation of the light pollution in BBC can be discussed in terms of the artificial night sky brightness relative to the natural level, as a situation between that from 1998 (Fig. 3a) and projected situation for year 2025 (Fig. 3b). It is evident that in 1998 the highest sky brightness levels were elevated in Bjelovar and its surroundings, and at the county borders with the northern and western neighbors, and at Daruvar, whilst some local maxima were noticed in the largest populated places in the southern half of BBC. The lowest sky brightness characterized the mountain regions and in gene-

ral southern half of BBC. However, predictions the 2025 year indicated a nine-fold increase of sky brightness in Bjelovar, an at least three-fold increase in the north and westernmost parts of BBC and at towns Daruvar and Garešnica, whilst only symbolic minimum was found between mountains Papuk and Ravna gora. Therefore, the current situation must be much worse than that from 1998. Both maps show that light pollution is not only a local but also regional problem because it is a characteristic of a continuous network of cities or towns. In the present case, BBC is clustered with Zagreb County and Koprivnica-Križevci County in terms of the highest night sky brightness levels.

3. Quantitative Structure-Property Relationships (QSPR): theory and application

In the previous section organic pollutants in BBC, detected by sensitive analytical methods and reported in literature, were listed with unique CAS numbers (Table 1), and tendencies in their geographical distribution were discussed. Third important issue, concentration of these pollutants with respect to environmental standards is out of the scope of this work. In further text the fourth essential issue, behavior of organic pollutants, will be presented in the light of their chemical structure. It is important to know how to connect molecular structure with behavior of pollutants in nature, and find applications of this knowledge in County's economy, ecology and environmental issues, traffic, public health and tourism (BBC possesses numerous fish ponds and hunting areas).

This connection is called Quantitative Structure-Property Relationship (QSPR) (Ferreira, 2001., Ferreira, Kiralj, 2011.), a multivariate regression equation by which a macroscopic property of interest y in vector form $\mathbf{y}$, usually a measured (sometimes calculated or extracted from literature) physico-chemical property of n chemicals, is modeled from two or more (m) molecular descriptors forming a matrix $\mathbf{X}$. A multivariate linear regression equation has a general form

$$\mathbf{y}_{\mathbf{pr}} = \alpha + \beta_1 \mathbf{x}_1 + \beta_2 \mathbf{x}_2 + \ldots + \beta_m \mathbf{x}_m \quad (1)$$

in which $\alpha = 0$ when the data ($\mathbf{y}$ and $\mathbf{X}$) are normalized or autoscalled, i.e. elements of each data column are reduced by the average value and then divided by standard deviation. Molecular descriptors in vector form are $\mathbf{x}_1$, $\mathbf{x}_2$, …, $\mathbf{x}_m$, and $\mathbf{y}_{\mathbf{pr}}$ is the vector of predicted y. A chemical product or chemical in QSPR is a simple substance, mostly chemical compound and rarely chemical element, and sometimes a mixture of known quantities of simple substances. The dependent variable y can be a simple property of chemicals such as boiling or melting point, a more complex property as soil sorption which measures the ability of chemicals to deposit on soil, and even a very complex feature as electropassivation power in the chemical processing of potable water (Teófilo et al, 2008.). The independent variables (molecular descriptors) are usually calculated microscopic properties of substances, sometimes extracted

from literature or even measured. There is no clear borderline between QSPR and QSAR (Quantitative Structure-Property Relationship) (Ferreira, 2002.), in which *y* is a biological activity, an effect of chemicals on living organisms, modeled in the same way from molecular descriptors.

QSPR and QSAR studies consist of three main phases, briefly described as follows. In the first one the data, *y* and *m* descriptors are generated or collected (calculated, extracted from literature or databases, measured). This phase also includes data preprocessing (autoscalling or another one) and sometimes mathematical data transformation into an appropriate form for regression analysis. The next step is the regression modeling, which includes variable selection, regression analysis, and model validation. In variable selection, independent variables are selected if having important features in relation to *y*, such as interpretability, easy generation for future applications, and statistically significant correlation to *y*, which can be obtained from simple linear regression:

$$\mathbf{y}_{pr} = \alpha + \beta\, \mathbf{x} \qquad (2)$$

In this equation, $\alpha = 0$ and $\beta = r$ when the data are autoscalled, and r is the Pearson correlation coefficient, a statistical index which measures the degree and direction of the association of x and y. A multivariate linear regression modeling can be carried out by diverse regression methods, such as Multiple Linear Regression (MLR) and Partial Least Squares (PLS) regression (Beebe et al., 1998., Ferreira et al, 1999., Ferreira, 2002.). For a given set of descriptors, the model obtained is tested by appropriate statistical methods, with the purpose to decide about which descriptors should be used to improve the model, and eventually which samples (chemicals) should be excluded. The finally obtained model is then checked by various statistical methods known as model validation (Kiralj, Ferreira, 2009.), the explanation of which is out of the scope of this work. After obtaining the best model, the last step in QSPR and QSAR includes the model interpretation and application, i.e. predicting *y* for new substances.

QSPR is used in various areas dealing with new materials, industrial or technological processes, and other areas where physico-chemical properties of chemicals are of special interest. QSAR is used as an auxiliary tool in drug design and in predicting pharmacological properties of drugs, but besides human medicine it can be employed in other biosciences and related areas (agriculture, veterinary medicine). Both QSPR and QSAR are useful in environmental sciences, because chemicals act both on living beings and their environment, and this position has been taken by OECD (Organisation for Economic Co-operation and Development) for some years already (Guidance document of OECD, 2007.). In this sense, QSPR/QSAR should be considered as a tool for investigation of three entities: chemicals, objects on which they act (organisms, nature, anthropogenic objects), and effects of this action. In spe-

cial case, when physico-chemical properties of chemicals are modeled via QSPR, chemicals and objects of action are identical. Therefore, one should have in mind the triple purpose of QSPR/QSAR. First, it is used for prediction of properties of new chemicals, i.e. unknown, expensive to test, unstable and other problematic substances that belong to the same set of chemicals which was used to build the model. Second, it is useful for inspection of the behavior of chemicals to make important decisions about the problem under study. Third, it means studying the behavior and properties of the objects, what is also important to make right decisions. When talking about the environmental situation in Bjelovar-Bilogora County, one should have in mind that there are no QSPR/QSAR studies nor measurements of interesting property y useful for eventual QSPR/QSAR. Measuring y in the area of interest is always a better solution that using literature data, because values of measured y are obtained for concrete chemicals and objects from the area in question, and they already incorporate specific biological (organisms: species and strains), geographical, geological, climatic and other features of the studied area.

In absence of such data, three literature examples of QSPR are described and investigated in this work, related to several chemicals listed in Table 1. The QSPRs are inspected in terms of their statistics (sign change problem, SCP) (Kiralj, Ferreira, 2010.) and chemical interpretability: 1) a PLS regression model for boiling point of PAHs (Ferreira, 2001.), 2) a MLR model for micellar phase-water partition coefficient of diverse solutes (Sprunger et al, 2009.); and 3) a MLR model for bioconcentration factor of nonpolar organic compounds (Qin et al, 2010.). The simple check for SCP consists of comparing signs of correlation coefficient r (Eq. 2) and regression coefficient b (Eq. 1) for each descriptor. A multivariate regression model is considered free of SCP when there is no sign difference for all descriptors. The essence of this test is based on the fact that a molecular descriptor x in QSPR/QSAR is a real or related to real property of a pure substance which, in relation to y, must have statistically clear direction of correlation in all linear regressions which use the same x and y. When x is increasing, y is either increasing or decreasing, it is not possible that both trends exist at the same time. Data for the three investigated QSPRs were autoscaled in this work, and a chemometrics software (Pirouette, 2009.) was used to build all simple and multivariate regression models. The original SCP (Kiralj, Ferreira, 2010.) is extended in this work for all combinations of selected descriptors, i.e. bivariate, trivariate, tetravariate etc. regression models, from which all are tested for SCP.

4. Inspection of QSPR model 1: boiling points of PAHs

Data set 1 (Ferreira, 2001.) consists of boiling point T_b and four molecular descriptors (EA, X_e, SArea, log$W$) for 23 PAHs, which have from one (benzene) to seven aromatic hexagons in molecular structure (Fig. 4). There are 13 PAHs in common

with those from Table 1 (which contains 19 PAHs and benzene), i.e. the following 7 PAHs from Table 1 are not in data set 1. These are: a) six PAHs with one pentagon in structure: acenaphthylene, acenaphthene, indeno(1,2,3-cd)pyrene, benzo(b) fluoranthene, benzo(k)fluoranthene, and fluoranthene; and b) one PAH having only hexagons, benzo(b)chrysene.

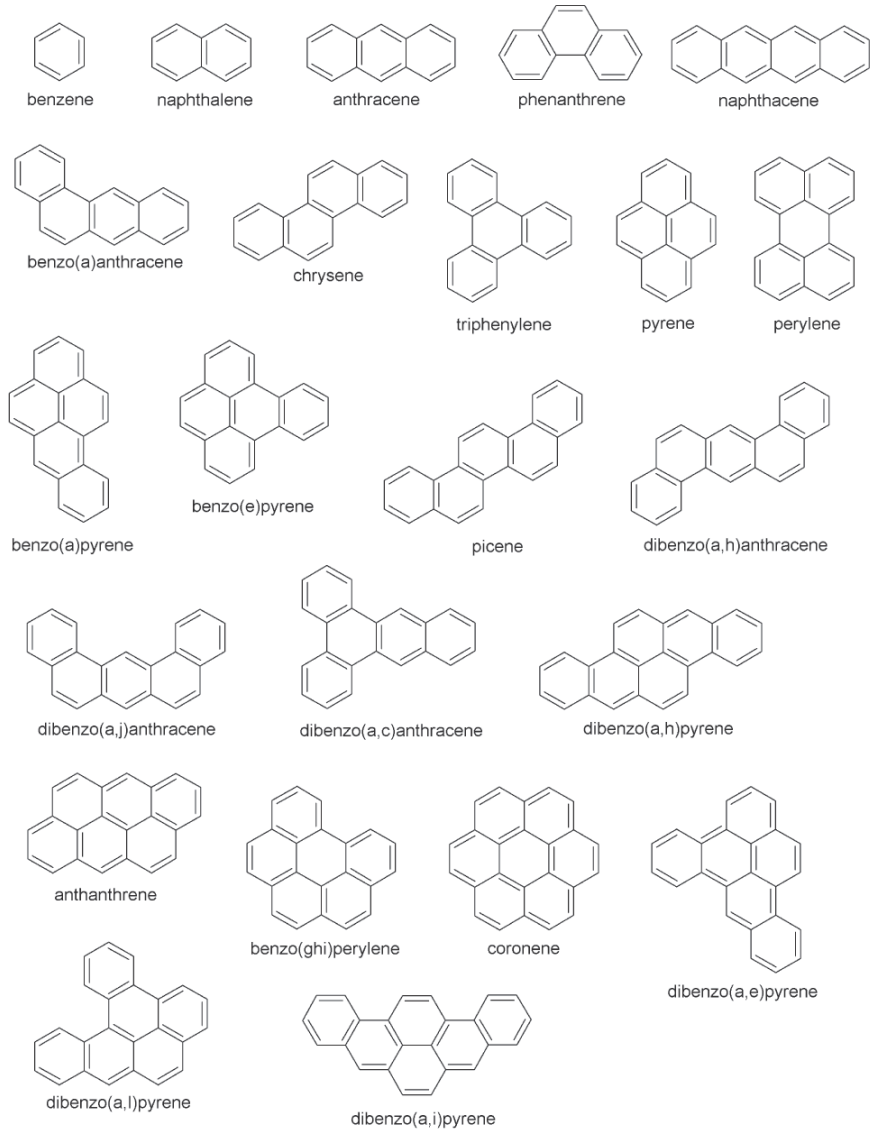


Figure 4. Chemical formula presented with Kekulé structures and names of polycyclic aromatic hydrocarbons (data set 1).

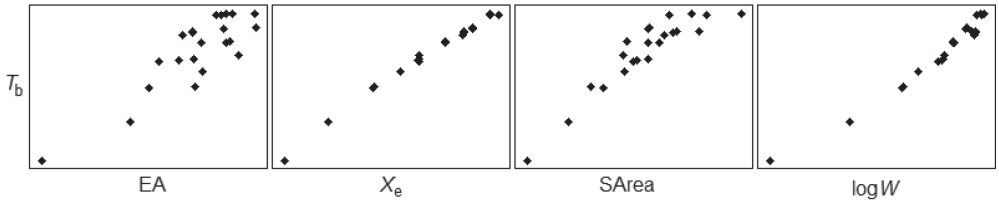


Figure 5. Scatteplots showing correlations between four descriptors and T_b (data set 1).

Scatterplots (Fig. 5) show that correlations between descriptors and T_b are well-defined, because data points exhibit linear relations, i.e. they are placed on elongated or very elongated concentric ellipses. Corresponding correlation coefficients (Table 2), calculated as regression coefficients for autoscalled data (Eq. 2) are all positive and very high ($r > 0.86$), meaning that relations between descriptors and T_b are extremely statistically significant. The published PLS model with four descriptors and four latent variables had very high coefficient of determination $R^2 = 0.9992$ and coefficient of leave-one-out crossvalidation $Q^2 = 0.9988$, and there were no extremely small regression coefficients, meaning that all descriptors were important. This model had reasonable prediction errors, yielded good predictions for new compounds, and had similar performance as another model with less samples (Ferreira, 2001). According to information presented, the model has good performance in validation and is useful for practical purposes.

Table 2. Full sign change problem check for model 1 (boiling points of PAHs).

Model(s)	**LVs**[a]	**R**[2b]	**EA**	**X$_e$**	**SArea**	**logW**
Univariate	-	0.735	0.8576			
	-	0.991		0.9953		
	-	0.853			0.9237	
	-	0.961				0.9804
Bivariate	2	0.995	0.1140	0.9013		
	1	0.935	0.5050		0.5439	
	2	0.963	0.0708			0.9198
	2	0.991		0.9499	0.0494	
	2	0.997		0.70291		0.3038
	1	0.956			0.4869	0.5168
Trivariate	3	0.996	0.1327	0.7931	0.1008	
	3	0.999	0.0664	0.7014		0.2484
	2	0.972	0.2020		0.3998	0.4382
	3	0.998		0.6845	0.0244	0.2996
Multivariate	4	0.999	0.999	0.0828	0.6536	0.2239
No. sign changes			0	0	0	0
%Sign changes		0	0	0	0	0

[a] Number of latent variables. [b]Coefficient of (multiple) determination.

The simple SCP check (Kiralj, Ferreira, 2010.), when applied to this QSPR model, shows that there are no sign changes between simple linear (Eq. 2) and multivariate (Eq. 1) models, as is visible from Table 2. A more rigorous, full SCP check can be made when all combinations of selected descriptors are used to build and test models. In this sense, the number of univariate (simple linear), bivariate, trivariate and tetravariate (the final multivariate) models is 4, 6, 4 and 1, respectively. These numbers of *k*-variate models are binomial coefficients, which can be calculated as *k*-combinations for *m* elements, or simply used as elements of the (*m*+1)-th row of Pascal's triangle, with exception that the first element of this row (the *m*-combination for *m* elements) must be discarded. This way, the number of all tested models is $2^m - 1$, and of all multivariate models is $2^m - m - 1$, from which it is visible that these numbers grow exponentially or predominantly exponentially with the number of descriptors *m* and so, chances for sign changes are greatly augmented. As can be seen from Table 2, regression coefficients from bivariate and trivariate models, when compared to the correlation coefficients, show no sign change for any descriptor. Concluding, the full SCP check confirmed the result of the simple SCP check, by which the published model is correct. This is the reason to consider the QSPR model reliable, and its interpretation can be presented in the light of the environmental situation in BBC.

The studied PAHs differ substantially in molecular structure (Fig. 4), ranging from very small to large molecules, and have diverse molecular shapes such as linear, bent, branched, circular, zig-zag, and even more complicated. The molecules are divided into catacondensed which have "bays" (internal vertices or carbon atom not bound to hydrogen), and more compact pericondensed PAHs without such "bays" (only external carbons are present, i.e. those involved in C-H bonds). PAH molecules are flat due to the nature of aromatic rings, but they are not always planar. Catacondensed PAHs possess bay hydrogens in steric hindrance, which contribute to molecular non-planarity. In case of dibenzo(a,l)pyrene, the bay is deep and so, the molecule is substantially non-planar. Molecular size, shape and electronic features are well encoded in four selected descriptors: a) SArea - molecular surface area, b) size-shape or topological descriptors X_e (edge-connectivity index) and log*W* (logarithm of the Wiener index *W*); c) electronic affinity EA (negative energy of the lowest occupied molecular orbital). Scatterplots (Fig. 4) show that boiling point increases mainly with molecular size, but there is also some dependence on molecular shape and electronic features. The reason for this lies in intermolecular interactions in which PAH molecules participate. There are two main geometrical arrangements of two flat systems. First, it is the face-to-face or $\pi \ldots \pi$ stacking interactions, in which two molecules are "glued" one onto another, with possibility to form stacks when more molecules interact. Second, it is the edge-to-face interactions, in which hydrogens from C-H bonds of one molecule face the aromatic system of the another one, in which C-H are nearly perpendicular to the π-system, so C-H$\ldots\pi$ hydrogen bonds

are formed. Smaller number of intermolecular interactions means lower T_b, as is the case of small molecules, pericondensed, brached and non-planar molecules that cannot pack tightly.

What is finally the relationship between presented QSPR model and Bjelovar-Bilogora County? First, boiling point ranges from 80 to 600°C, meaning that depending on molecular characteristics and atmospheric conditions (temperature, pressure), simpler PAHs will tend to behave as VOCs, and higher PAHs will more deposit on on soil and water, and there will be also differentiation in PAHs spread through air and solubility in water. Second, as PAHs are relatively simple molecules, consisting of only carbon and hydrogen, being aromatic compounds involved in a few types of intermolecular interactions, several properties (physico-chemical and molecular) are well correlated with each other (Ferreira, 2001.). Consequently, knowing about boiling point will aid in understanding other properties and behavior of PAHs in the environment. BBC has three types of PAHs emitters. One is rural areas in which wood is still traditionally used for heating and cooking. Then, there are roads between towns, from which some have more than 7 thousand vehicles per day (Božić et al., 2010., p. 60), what is comparable to the values for roads around the largest cities in Croatia except Zagreb, and is only 5-6 times smaller than the highest value in Croatia (about 40-41 thousand vehicles per day) for the highway portion Zagreb-Velika Mlaka. Finally, urban centers are multiple PAH emitters: heavy traffic, coal or wood burning for heating, and industrial and other activities involving pyrolysis and other procedures in which PAHs are released. Various carbonaceous materials, for example, smoke, soot, and particulate matter than can also come from other, more industrialized counties (Sisak-Moslavina County, Zagreb County and the city of Zagreb) and contain PAHs, among which several are carcinogenic. Within the area of 5 km from the main roads in BBC (Fig. 2a) there are forests, rivers and fish ponds, hunting areas, and in some cases the roads pass nearby or through forest, and frequently villages are located along such roads. Recent studies discuss mathematical relationship between PAHs emission around roads and the number of vehicles (Kumari et al., 2011.), as well as the probability for lung cancer provoked by PAHs exposure (Liao et al., 2011.). It is known that PAHs molecules interact with organic matter such as humic and fulvic acids in soil via $\pi \ldots \pi$ stacking and C-H… π interactions (Saparpakorn et al., 2007.). PAHs also bind to inorganic materials in soil via O-H… π hydrogen bonds, cation… π, anion… π or other interactions (Tunega et al., 2009., Keiluweit, Kleber, 2009.). This explains why PAHs deposit well on soil and anthropogenic objects and water, and how to accumulate in living organisms. All these literature findings and observations in this work suggest measuring PAHs concentrations and other characteristics in order to have more insight into PAHs presence in BBC and their effect on human health, economy and tourism.

5. Inspection of QSPR model 2: micellar phase-water partition coefficient of solutes

Data set 2 (Sprunger et al, 2009.) consists of LogP_x – logarithm of P_x, mole fraction water-to-aqueous CTAB (cetytrimethylammonium bromide) micellar partition coefficient, and five molecular descriptors (E, S, A, B, V) for 64 diverse solutes. Among solutes, two are chemical elements (oxygen and argon), whilst organic compounds belong to more than seven various classes (hydrocarbons, halogenated hydrocarbons, alcohols, aldehydes, ketones, nitro-compounds, etc.). There are 14 organic compounds in common with those from Table 1: simple organic compounds (methane, methanol, *n*-butanol), chlorinated hydrocarbons (dichloromethane, chloroform, trichloroethylene), benzene and its derivatives (ethylbenzene, toluene, *p*-cresol, *p*-xylene) and PAHs (anthracene, naphthalene, pyrene). CTAB is an amphiphilic compound acting as detergents, i.e. it consists of hydrophilic and hydrophobic parts, what makes it an effective means to capture diverse pollutants from water in the form of micelles. This is an important issue for remediation of contaminated waste sites and removal of hazardous materials from industrial, hospital and other waste effluents.

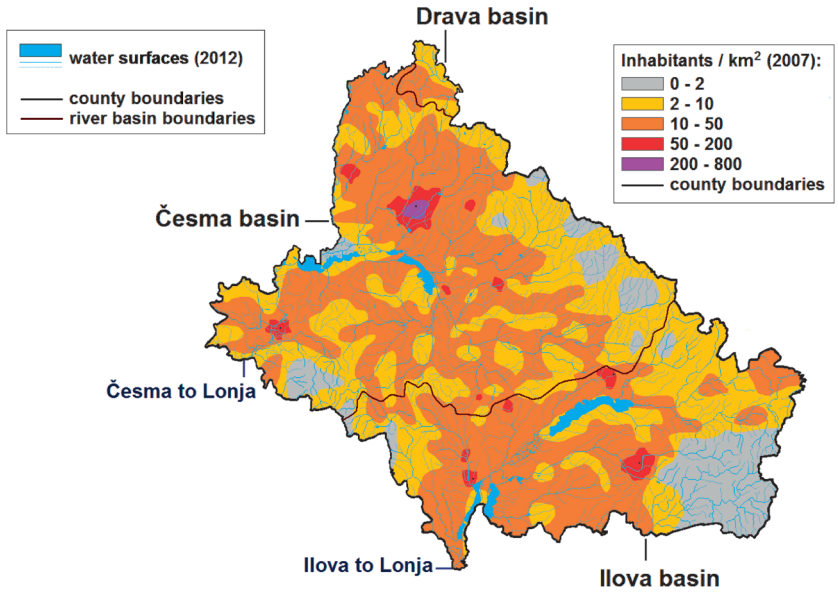


Figure 6. Water surfaces distribution in Bjelovar-Bilogora County overlapped with population density. Three river basins are separated with brown lines. Rivers Česma and Ilova are marked at County boundaries as tributaries of Lonja.

The importance of water in relation to pollution can be seen from the map of water surfaces in BBC (Fig. 6) overlapped with population density (Fig.2 a). The data for all water surfaces, including large and small ponds, rivers, canals, permanent and temporary streams, were used from a topographic map of Croatia (Topografska karta 1:100000, 1998), with corrections added according to the newest satellite photographs (Google Earth, 2012.). The map shows how rivers, streams and canals meet in the Bjelovar subdepression, where river lakes and ponds are mainly concentrated. The county consists of two main basins, Česma (northern) and Ilova (southern) basins, whilst Drava basin is of minor importance. Česma and Ilova are tributaries of Lonja, a left tributary of Sava, an important right side tributary of the Danube river at Belgrade. The areas with the highest population density are split by rivers and canals, and are close to the largest lakes and ponds. This means that urban regions contribute to water pollution (emitters of diverse pollutants), as well as happens to rural regions (emitters of PAHs and pesticides) and important roads (mainly PAHs emitters). Česma and Ilova may be collectors of pollutants, transferring them into the Sava river. Systematic experimental measurements of water samples could reveal the real situation.

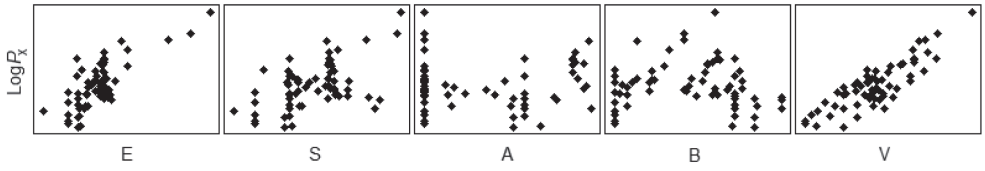


Figure 7. Scatteplots showing correlations between five descriptors and LogP_x (data set 2)

Scatterplots (Fig. 7) show that correlations between descriptors and LogP_x are well-defined for V and maybe for E, whilst descriptor S is problematic, B exhibits non-linear tendencies, and A has no acceptable scatterplot for regression analysis. Absolute values of the corresponding correlation coefficients (Table 3) are very small for A and B ($r < 0.3$), meaning that relations between these descriptors and LogP_x are not statistically significant (Kiralj, Ferreira, 2009., Kiralj, Ferreira, 2010.). In original publication (Sprunger et al, 2009.), the MLR model had very high coefficients R^2 = 0.9761and Q^2 = 0.9702, had *F*-ratio equal to 474, showed good agreement between experimental and calculated values of LogP_x in graphical form, but additional model validations were not performed and correlations between descriptors and LogP_x were not presented and discussed. According to information obtained from inspecting the model in this work, the model is not valid for practical purposes. The same conclusion can be made when the simple SCP check is made (Table 3), from which it is clear that there is one descriptor (S) with sign changed. When the full SCP check, a more rigorous criterion is applied, it is apparent that the MLR model fails in two

descriptors (S and A) with high sign change frequency in all 26 checked multivariate models (10 bivariate, 10 trivariate, 6 tetravariate models and the final multivariate model). Concluding, the published MLR model fails in the sign change problem check. Descriptors S, A and B are not useful for regression, whilst E and V are good, as was already seen in the scatterplots.

Table 3. Full sign change problem check for model 2 (micellar phase-water partition coefficient of solutes).

Model(s)	R^{2a}	E	S	A	B	V
Univariate[b]	0.566	0.7525				
	0.280		0.5294			
	0.001			0.0286		
	0.003				-0.0550	
	0.731					0.8549
Bivariate	0.590	0.9709	-0.2665			
	0.573	0.7581		0.0811		
	0.600	0.7836			-0.1862	
	0.771	0.2885				0.6484
	0.289		0.5517	-0.0975		
	0.434		0.7717		-0.4607	
	0.744		-0.1639			0.9718
	0.008			-0.0085	-0.0085	
	0.756			-0.1609		0.8892
	0.944				-0.5099	1.0714
Trivariate	0.622	1.1350	-0.4489	0.2097		
	0.601	0.8494	-0.0873		-0.1512	
	0.869	0.6531	-0.5753			0.7980
	0.651	0.8293		0.2756	-0.3452	
	0.781	0.2408		-0.1050		0.7049
	0.957	0.1531			-0.4844	0.9510
	0.450		0.7843	0.1519	-0.5508	
	0.765		-0.1406	-0.1496		0.9871
	0.946		0.0770		-0.5309	1.0253
	0.953			0.1151	-0.5744	1.0742
Tetravariate	0.657	0.9759	-0.1909	0.2930	-0.2789	
	0.871	0.6997	-0.6125	0.0506		0.7804
	0.957	0.2387	-0.1151		-0.4389	0.9525
	0.971	0.2022		0.1572	-0.5643	0.9163
	0.957		0.0906	0.1214	-0.6025	1.0201
Multivariate	0.976	0.3377	-0.1753	0.1734	-0.5031	0.9150
No. sign changes		0	10	5	0	0
% Sign changes		0	38	19	0	0

[a] Coefficient of (multiple) determination. [b] Correlation coefficients for statistically not significant correlations between descriptors and the dependent variable are typed bold.

It is visible from Table 3 that descriptors E and V alone give a model with reasonable coefficient of determination $R^2 = 0.771$, meaning that the remedy for the false multivariate model must be based on extending this bivariate model with some other descriptors having statistically significant correlations with LogP_x. In this sense, only a partial interpretation of the published multivariate model can be made. Higher LogP_x values mean that solutes are better soluble in CTAB micelles than in water and so, can be easier removed from contaminated water than solutes poorly associated with CTAB but well with water (Sprunger et al, 2009.). Descriptor V is the McGowan volume of the solute, a steric (size-shape) molecular descriptor, and E is the excess molar refraction of the solute, an electronic descriptor that quantifies the solute's ability to interact with solvent through π-electrons and lone pair electrons. Their positive correlations with LogP_x mean that larger molecules and molecules with larger number of π-bonds (aromatic and other unsaturated systems) and heteroatoms better interact with CTAB. Among studied solutes, such molecules are predominantly hydrophobic and aromatic, whilst small molecules are usually those interacting well with water. S is dipolarity/polarizability of the solute, which quantifies the ability of the solute to stabilize a charge or dipole. A and B are hydrogen bonding descriptors of the solute, measuring hydrogen bonding acidity and basicity, respectively. Why S, A and B are not good descriptors, although they are chemically very meaningful? One reason for this is the fact that the studied molecules make a very heterogeneous set, containing diverse organic compounds and even two elements. The other reason is the fact that several small and large molecules, well differentiated by V and E, act in a similar way when the presence or absence of polar and hydrogen bonding groups (hydroxyl, carbonyl, amino etc.) is considered. Anyway, it is worth to comment the false QSPR model which is partially meaningful. The model raises another question, and this is the current environmental situation in BBC in terms of water pollution. Determination of pollutants in water samples from several locations should be made, because BBC is a water-rich area (Fig. 6).

6. Inspection of QSPR model 3: bioconcentration factor of nonpolar organic compounds

Data set 3 (Qin et al, 2010.) contains logBCF – logarithm of the bioconcentration factor BCF (related to toxicant accumulation in fish), and five molecular electronegativity distance vector (MEDV) descriptors (x_{15}, x_{25}, x_{26}, x_{27}, x_{36}) for 114 nonpolar organic compounds (NPOCs). Studied NPOCs are hydrophobic compounds that belong to at least eight organic classes or groups (alkanes, haloalkanes, biphenyls, halogenated biphenyls, chlorinated naphthalenes, benzene derivatives, PAHs, chlorinated pesticides). There are 31 compounds in common with those from Table 1: benzene and its 7 derivatives, 8 PAHs, 6 chlorinated biphenyls, 3 other chlorinated hydrocarbons, and 6 chlorinated pesticides. Pollutants in water such as NPOCs are

absorbed by fish or another aquatic organism through skin or gill (by respiration). BCF of a pollutant is simply the ratio of concentration in the organism and the surrounding water. NPOCs, due to their relatively high hydrophobicity, interact well with and bind to lipophilic substances such as fats and lipid bilayers of various biological membranes (Mackay, Fraser, 2000.). Molecular size is an important characteristic for bioconcentration in fish (Sakuratani et al., 2008.).

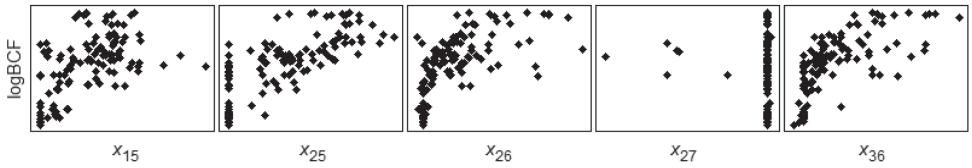


Figure 8. Scatteplots showing correlations between five descriptors and logBCF (data set 3)

Scatterplots (Fig. 8) show that correlations between all descriptors and logBCF are not well-defined. The relationship between x_{27} and logBCF is not statistically significant (r = -0.044, Table 4). Data points in scatterplots for x_{26} and x_{36} form smoke-stack plumes shape and not ellipses. Scatterplots for x_{15} and x_{25} seem acceptable for regression, although in that for x_{25} there is a large group of samples with constant value of x_{25}. The MLR model presented in the original publication (Qin et al, 2010.) had very high coefficients R^2 = 0.9280 and Q^2 = 0.9180, F-ratio equal to 275, and had good agreement between experimental and calculated values of logBCF in graphical form, and a similar model had good performance in external validation. In spite of all this, the conclusion based on inspecting correlations in this work is that the model is not valid for practical purposes. One comes to the same conclusion when the simple SCP check is made (Table 4) because two descriptors (x_{26} and x_{27}) have signs changed. Furthermore, when the full SCP check is made, these two descriptors have high frequency of sign changes in 26 models tested, and a third descriptor with lower frequency appears (x_{36}).

MEDV descriptors, although not too complicated for calculation, are not easy to interpret. They mean the "strength" of interactions between two specific atom types in a molecule, analogously to Coulomb forces, and take into account chemical bond types, atom types, and other topological and electronic features. Five selected descriptors are related to interactions between methylene group -CH_2-, tertiary carbon -C(H)--, quaternary carbon --C-- and chlorine -Cl. The interactions of interest are between -CH_2- and -C(H)--, -CH_2- and -Cl, -C(H)-- and -C(H)--, -C(H)-- and --C--, and -C(H)-- and -Cl for descriptors x_{15}, x_{25}, x_{26}, x_{27}, and x_{36}, respectively. Why only x_{15} and x_{25} are useful descriptors? A reasonable explanation is that variations in interactions involving only internal carbons (-C(H)-- and --C--) are too small to be used as descriptors: such atoms have small partial charges and are relatively close.

Table 4. Full sign change problem check for model 3 (bioconcentration factor of nonpolar organic compounds)

Model(s)	R^{2a}	x_{15}	x_{25}	x_{26}	x_{27}	x_{36}
Univariate[b]	0.278	0.5274				
	0.557		0.7461			
	0.408			0.6389		
	0.002				**-0.0436**	
	0.449					0.6704
Bivariate	0.636	0.3017	0.6396			
	0.519	0.3536		0.5209		
	0.317	0.5837			-0.2043	
	0.809	0.6033				0.7328
	0.796		0.6376	0.5007		
	0.565		0.7519		-0.0912	
	0.745		0.5814			0.4641
	0.409			0.6381	-0.0257	
	0.488			0.3047		0.4378
	0.497				0.2341	0.7563
Trivariate	0.818	0.1679	0.5881	0.4554		
	0.667	0.3541	0.6326		-0.1812	
	0.913	0.4540	0.3791			0.5829
	0.537	0.3982			0.5021	-0.1392
	0.870	0.8104		-0.4964	1.1331	0.8699
	0.814	0.5857			0.0734	0.7580
	0.800		0.6427	0.4976	-0.0704	
	0.806		0.6051	0.3831		0.1633
	0.755		0.5572		0.1094	0.5128
	0.510			0.1982	0.1763	0.5838
Tetravariate	0.833	0.2092	0.5852	0.4387	-0.1260	
	0.922	0.5719	0.3130	-0.2201		0.7865
	0.914	0.4490	0.3754		0.0269	0.5936
	0.896	0.8143		-0.6150	0.1899	1.2938
	0.806		0.6096	0.3940	-0.0172	0.1471
Multivariate	0.928	0.608	0.268	-0.323	0.101	0.922
No. sign changes		0	0	4	7	2
% Sign changes		0	0	15	27	8

[a] Coefficient of (multiple) determination. [b] Correlation coefficient for statistically not significant correlation between a descriptor and the dependent variable is typed bold.

Interactions involving -CH_2- and -Cl have the opposite characteristics. Therefore, the bivariate model based on x_{15} and x_{25}, and which has a modest statistics (R^2 = 0.636) should be extended with some other MEDV descriptors or even descriptors of other nature, having statistically significant correlations with logBCF. Another reason why the three descriptors are not useful is the relative heterogeneity of the studied set of pollutants. For example, the scatterplot for descriptor x_{27} shows that most data points are placed at x_{27} = 0, and the rest is spread over the whole range of x_{27}, because these few sample are the only molecules which have sp^3 carbon with two chlorines. The presented QSPR model, although being false is interesting for ecology. First, because it is partially meaningful, and second, it points out a general problem about interactions between aquatic organisms and NPOCs. BBC has large commercial and recreational fish ponds and numerous small ponds only for recreational fishing (Fig. 6). This is the reason why fish populations should be tested for NPOCs and NPOCs emissions should be controlled if necessary.

7. Conclusion

This work is a tentative of assessing the current environmental situation in Bjelovar-Bilogora County based on literature data. Organic pollutants were identified, their geographical distribution was discussed, and potential emitters were indicated. The role of chemical structure in behavior of organic pollutants was illustrated by three Quantitative Structure-Property Relationships. These regression models were tested by sign chance problem checks, a simple method to verify whether a literature or new regression model is valid for using it in practice. Conclusions in this work are directed towards the necessity to collect air, water and soil samples, samples taken from anthropogenic objects and organisms within the whole area of Bjelovar-Bilogora County. The purpose of these measurements would be to identify organic chemicals, determine their concentrations, and establish useful mathematical relationships between their effects on the environment and chemical structure.

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O kvalitativnim odnosima između kemijske strukture i fizičko-kemijskih svojstava kemijskih proizvoda. Studij slučaja: Bjelovarsko-bilogorska županija

Sažetak

Čak i mali krajevi kao Bjelovarsko-bilogorska županija sve su više pogođeni lokalnim i regionalnim zagađenjem. Razna zagađivala iz mnogih grupa organskih spojeva rasprostranjena su u svim dijelovima atmosfere, u vodama i tlu, te se nagomilavaju u živim organizmima i na površinama antropogenih objekata. U ovom radu proučavaju se načini širenja i ponašanja te kemijska svojsta organskih zagađivala u Bjelovarsko-bilogorskoj županiji na temelju literaturnih podataka pošto ne postoje eksperimentalna mjerenja. Pronađeno je više od 230 organskih zagađivala u Bjelovarsko-bilogorskoj županiji, a to su: jednostavni spojevi, derivati benzena, policiklički aromatski ugljikovodici, poliklorirani i drugi bifenili, poliklorirani dibenzo-*p*-dioksini i dibenzofurani, halogenirani alkani i alkeni, te razni pesticidi i antimikrobni spojevi. Geografska rasprostanjenost organskih zagađivala proučavana je u odnosu na gustoću naseljenosti, poljoprivrednu djelatnost, položaj izvora hlapivih organskih spojeva, prosječan godišnji dnevni promet, te razine svjetla na noćnom nebu kao svjetlosno zagađenje. Vidljivo je da su gradovi, veća sela i glavne ceste izvori raznih organskih zagađivala i proizvođači smoga, dok su tipično seoska područja više zagađena pesticidima. Tri su primjera za KOSS (kvantitativni odnos stukture i svojstva) opisana i istražena u smislu njihove statistike (problem promjene predznaka) i kemijskog tumačenja: 1. regresijski model parcijalnih najmanjih kvadrata (PNK) za vrelište policikličkih aromatskih ugljikovodika; 2. model višestruke linearne regresije (VLR) za koeficijent raspodjele micelarna faza-voda raznih topivih spojeva; 3. model VLR za faktor biokoncentracije nepolarnih organskih spojeva. Mnogi su uzorci u modelima već utvrđena zagađivala u Bjelovarsko-bilogorskoj županiji. Modeli 2. i 3. zakazali su u provjeri predznaka za što se daju objašnjenja te se preporučuju popravci.

Ključne riječi: okoliš; Bjelovarsko-bilogorska županija; organska zagađivala; regresijska analiza; opisivači; odnos struktura-svojstvo; validacija.

Dr. sc. Rudolf Kiralj
Bedenik 13, 43273 Bulinac
Tel.: ++385 043 254-110
rkiralj@yahoo.com

ISKUSTVA