

Some Programs for Reduction of Environmental Pollution in Slovenia

Part II: Preliminary national list of dangerous substances for aquatic environment

Viktor Grilc

National Institute of Chemistry, Ljubljana, Hajdrihova 19, 1000 Slovenia

E-mail: vktor.grilc@ki.si

Received 08-06-2006

Abstract

Some actions towards reduction of aquatic and terrestrial environment pollution with dangerous substances, emitted from various sources, especially industrial and municipal, on the national level of Slovenia are presented and critically discussed. Industry and agriculture contributes mostly to the pollution of aquatic environment. Various intake routes are present: direct use of chemicals, emissions by wastewaters, air emissions and waste disposal. Most of surface and ground water bodies are affected. Regarding their protection, primary concern is given to the use of most dangerous substances and to the emission reduction of untreated wastewaters. A preliminary list of most dangerous substances for Slovene aquatic environment has been set up consisting 92 substances, based on exposure and immission data.

Keywords: aquatic pollution prevention, dangerous substances, national list

1. Control of Aquatic Pollution

Surface and ground waters are the environmental media, potentially vulnerable by harmful substances, originating from industry and other discrete sources. Basic EU environmental legislation, responsible for systematic control of aquatic pollution is the so-called *Dangerous Substance Directive*.¹ It contains two lists of dangerous substances (individual or grouped into families of substances):

- List I, containing 17 substances and groups of substances, selected on the basis of their toxicity, persistence and bioaccumulation, for which the larger polluters must prepare the release prevention programs. Common European emission standards have been agreed and enforced for these substances.
- List II, containing eight groups of substances, with much broader number of (potential) individual substances which emission may have a deleterious effect on the aquatic environment and for which common quality objectives were given. It is left to the member states to specify the relevant substances, set their limit emission values and establish emission prevention programs.

Both lists are shown in Table 1.

For the List I substances special daughter directives have been issued, laying down environmental quality objectives and emission limit values. Some substances were even banned from further use.

Water Framework Directive 2000/60/EC² has further extended both lists to the so-called priority substance list. It includes all substances from the List I, some from the List II and some new ones, altogether 33 compounds and groups of compounds.

2. Preliminary List of Dangerous Substances for Slovene Water Environment

2.1 Establishment of the list of relevant dangerous substances in Slovenia

By the time of final accession of Slovenia to EU, it had had to determine a list of relevant dangerous substances and prepare emission prevention programs for them. Ministry of environment has financed a project aiming to establish a national list of dangerous substances, most responsible for pollution of Slovene surface and ground waters. Determination procedure of nationally-relevant dangerous substances, as deduced after completion the work, is schematically shown in Figure 1.

Table 1: List I and II substances from the Dangerous Substance Directive.

List I Substances	
1	Organohalogen compounds and substances which may form such compounds in the aquatic environment: 1,2-dichloroethane, trichloroethene, trichloromethane, tetrachloromethane, tetrachloroethene, pentachlorophenol, heksachlorobenzene (lindane), heksachlorobutadiene, heksachlorocyclohexane
2	Organophosphorous compounds
3	Organotin compounds
4	Substances that posses carcinogenic properties in or via aquatic environment: Aldrin, Dieldrin, Endrin, Izodrin, DDT (DDD+DDE)
5	Mercury and its compounds
6	Cadmium and its compounds
7	Mineral oils and hydrocarbons of petroleum origin
8	Persistent synthetic substances which may float, remain in suspension or sink which may interfere with any use of waters
List II Substances	
1	Metals and metalloids: Zn, Se, Sn, V, Cu, As, Ba, Co, Ni, Sb, Be, Tl, Cr, Mo, B, Te, Pb, Ti, U, Ag
2	Biocides and derivatives not on the List I
3	Substances that have deleterious effect on taste or smell of the products for human consumption derived from the aquatic environment
4	Toxic or persistent organic compounds of silicon or which may give rise to such compounds in water
5	Inorganic compounds of phosphorus and elemental phosphorus
6	Non-persistent mineral oils and hydrocarbons of petroleum origin
7	Cyanides, fluorides
8	Substances that have adverse effect on the oxygen balance (ammonia, nitrites...)

2.1.1 Defining the list of candidate compounds

In the first step a candidate list of potentially polluting substances was established, which has taken into account:

- dangerous substances from the List I
- dangerous substances (individual, groups and families) from the List II
- additional List II substances, so far identified in other EU member states
- dangerous substances from the Priority list of the Water Framework Directive
- dangerous substances from other relevant lists (e.g. registered pesticides, used in Slovenia).

All together 171 candidate substances were selected and grouped upon chemical nature (CAS No.) or type of products: 22 heavy metals (and their compounds), 5 non-metal cations and anions, 63 organohalogen compounds, 13 mono- and polycyclic aromatic hydrocarbons, 40 organochlorine and organophosphorous pesticides, 9 organotin compounds, while the rest represent other, mainly organic compounds. It should be noted that situation is subject to relatively fast changes due to market situation and restrictive legislation.

2.1.2 Defining the list of relevant compounds

In second step selection of substances that represent evident threat to Slovene water environment was made, based on exposure of environment (intake and emission data) and their effect (immission data). Possible effects of all 171 candidate substances were checked in two ways:

- i) input-output mass balance of dangerous substances on the territory of Slovenia, and
- ii) extent of pollution of the Slovene water environment (emission and immission data).

Ad i) For all candidate substances an informative material balance (an input-output analysis) was made using data from an *ad hoc* national inventory investigation, including 1441 potential companies, involved in certain business activities with the substances. These were:

- all important import-export and retail companies, registered for trading chemicals etc.
- the main chemical manufacturing companies, that might use or produce chemicals
- agriculture firms.

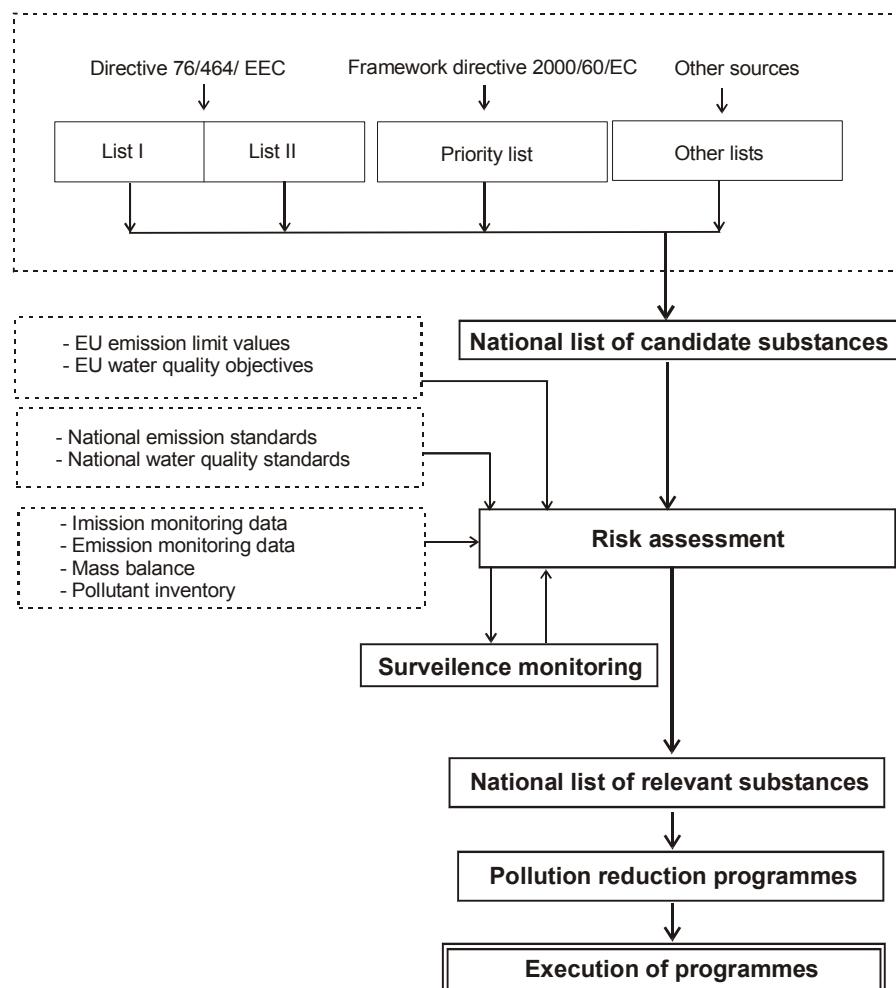


Figure 1: Determination of nationally-relevant polluting substances and their prevention programs

Using a special questionnaire they were asked to declare their annual quantities of import and export, production, store, use and emission of candidate substances into air, water and wastes. The response was quite good (67.6% companies had answered) and 47.2% of the respondents declared their involvement with one or more candidate compounds. Out of 171 candidate compounds, only 83 (48.8%) were confirmed to be present in amounts, potential to cause national-wide pollution. Substances above the threshold quantities of 1 ton (on stock, or handled per year), except for pesticides (200 kg), were onward considered.

Institutions that collect relevant data and run corresponding information systems were visited and interviewed:

- Ministry of Finance, General custom office. Data on import and export of chemicals are available only on aggregate level for groups of chemical, very seldom for individual ones. This data source was not exploited.

- Ministry of Agriculture, Office for crop prevention. They keep very good database about trade and use of phytopharmaceuticals and biocides since, which was extensively applied in this work.
- Ministry of Health, National Chemicals Bureau. The information system on chemicals (as defined in the Chemicals law) was still in construction; no reliable and complete data could have been provided.
- Ministry of Environment and Spatial Planning, Environment Agency. National immission monitoring data of surface/ground waters, as well as the wastewater emission from main polluters are maintained since 1995. Wastewater emission data from factories and other companies which are obliged to run operating wastewater monitoring have also been checked. Special attention was put to the emission of substances from the candidate list above or close to the permitted limit concentration or quantities.

However only about 40 out of 171 candidate substances are included in regular monitoring of surface waters. Some individual substances are lumped in group parameters (e.g. total pesticides, total detergents...); such data could not have been used in the study.

Ad ii) For the purpose of testing the data quality provided by dealers, the Slovenian surface water monitoring data were also addressed. The main source was national immission monitoring register of surface and ground waters, located at Environmental Agency. Data on well water and ground water quality were also provided from local municipal water supply companies. A substance was considered relevant, if it was regularly recorded in measurable quantities in any of Slovene surface, ground or spring waters (56 rivers and brooks and 26 of freshwater springs were included in regular monitoring). Broader list of potentially monitored parameters includes about 140 parameters, however only about 80 are practically measured. The monitoring frequency varies very much: for most important (e.g. heavy metals, toxic anions in rivers and springs) most often 2-6 times per year, but for many substances only sporadic surveillance measurements are performed. As above, some parameters are determined together, lumped in groups. Data are abundant, so that filtering by a computer program was made only for data from the last 5-6 years.

In the situation, where European as well as national water quality standards had been set for most of the candidate substance, the assessment criterion was determined following a combined procedure:

- Where available, the predicted no-effect concentrations from risk assessments studies were used.
- When the no-effect values were not available, the predicted values were taken from the COMMPS study on the selection of priority substances.³
- When no predicted values were available, the lowest target values from a collection of international quality objectives were selected.
- The assessment criterion was reduced by a factor of ten for monitoring stations at the Sava and Drava river basins.
- If for a particular substance the assessment criterion was lower than the detection limit of the respective analytical method, this limit was used as the assessment criterion.

Due to lack of data and resources no modeling of exposure – effect relationship could have been applied at this stage. The preliminary list of nationally relevant polluting substances included:

- all obligatory pollutants from the two basic water directives: List I and the Priority list, (by default) and
- other substances from the candidate list which were recorded in critical extent at least at one data source.

The list contains 92 relevant substances or groups of them. They are listed in alphabetical order, together with the CAS Numbers, remarks about listing status, remarks about national monitoring status, main uses and preliminary assessed risk potential for the water environment, based on annual quantity and toxicity of a substance. A part of the list is presented in table 2.

It should be noted that situation is subject to relatively fast changes due to market situation (especially regarding pesticides) and restrictive legislation. The list should be periodically updated, based on reliable monitoring and intake data and applying advanced risk assessment/ modeling methods.

For comparison, Austria has contemporarily set up their national list⁴ where 320 candidate substances were specified, among which 86 were qualified for the national relevant substance list. It should be noted however that five times higher threshold quantities were as used in their work as in the present one. Due to relative high level of uncertainty in available data, a precaution principle was thus provided in our case.

3. Preparation of Pollution Reduction Programs

The last step was preparation of pollution abatement action programs (so-called operating programs) for top pollutants from the preliminary relevant substance list. The prevention programs under Article 7 of the Dangerous Substance Directive must be prepared according to a special Guidance document⁵, which demands relatively precise specification and extent of the pollution prevention measures for each of the selected relevant substance. A substance dossier contains the following data:

- type and scope of the abatement program
- identification of the relevant pollutants
- quality objectives for surface waters
- monitoring of substances in surface waters
- authorization and provisions for specific discharges
- deadlines for measures
- communication to the Commission.

Ministry of the Environment and Spatial Planning had coordinated activities aimed to provide basic data and information, needed for elaboration of prevention programs, containing all the above mentioned contents.

Table 2: List of relevant dangerous substances for the Slovene aquatic environment

Substance	CAS No.	Status in EU*	Status in RS#	Main use
Alachlor	15972-60-8	PS	Y	herbicide
Aldrine	309-00-2	I	N	herbicide
Ammonia & its comps.		II	Y	fertilizer, fecal component
Antimony & its comps.		II	N	technical chemicals
Antracene	120-12-7	II, PS or PHS	Y	Solid fuel, tar/asphalt
Arsenium & its comps.		II	N	technical chemicals
Atrazine	1912-24-9	PS or PHS	Y	herbicide
Barium & its compounds		2	N	tech.chemicals, pigments
Benzene	71-43-2	PS, 2	Y	solvent, tech.chemical
Benzo(a)pyrene	50-32-8	PHS	Y	tar impurity
Benzo(b)fluorantene	205-99-2	PHS	Y	tar impurity
Benzo(ghi)perylene*	191-24-2	PHS	Y	tar impurity
Benzo(k)fluorantene*	207-08-9	PHS	Y	tar impurity
Boron & its compounds		2	Y	oxydiser, fertilisers
Brominated diphenyl ethers		PS or PHS	N	flame retardants
Cadmium & its compounds	7440-43-9	1, PHS	Y	tech. chemicals pigments, batteries
Captan	133-06-2	xx	N	fungicide
Chloralhydrate	302-17-0	2	N	dezinfektant
Chlorphenvinphos *	470-90-6	PS	N	insecticide
Chloroalcanes, C10-13	85535-84-8	PHS	N	tech.chemicals
Chlорpiriphos	2921-88-2	PS or PHS	N	insecticide
Chromium & its compounds		2	Da	tech. chemicals
Cobalt & its compounds		2	N	tech. chemicals
Copper & its compounds		2	N	tech.chemicals fungicides
Cyanides		2	N	tech.chemicals
Cyanuric chloride (trichlorotriazine)	108-77-0	2	N	dezinfectant
2,4-D	94-75-7	II	N	herbicide
DDT (DDD+DDE)*	50-29-3	1	N	insecticide
di-(2-ethylhexyl)-phtalate (DEHP)	117-81-7	PS or PHS	N	softener, additive
Dibutyltin oxyde	818-08-6	2	N	catalist
Dibutyltin compounds (others)		2	N	catalysts, tech. chemicals
Dieldrine*	60-57-1	1	N	insecticide
1,2-dichloroethane	107-06-2	I, PS	Y	technical chemical
Dichlorometane	75-09-2	PS, 2		solvent
Dichlorprop	120-36-5	2	N	herbicide
Diethylamine	109-89-7	2	N	tech. chemical
Dimethylamine	124-40-3	2	N	tech. chemical
Dimethoat	60-51-5	2	N	insecticide
Diuron *	330-54-1	PS or PHS	N	herbicide
Endosulfane (alfa + beta)	115-29-7	PS or PHS	N	insecticide
Endrine*	72-20-8	1	N	insecticide
Epichlorhydrine	106-89-8	2	N	tech. chemical
Ethylbenzene	100-41-4	2	N	solvent
Fentin hydroxide	76-87-9	2	N	fungicide
Fluorantene*	206-44-0	PS		tar impurity
Fluorides		2	N	tech. chemicals
Foxyme	14816-18-3	2	N	insecticide
Hexachlorobenzene*	118-74-1	1, PHS	Y	fungicide
Hexachlorobutadiene*	87-68-3	1, PHS	Y	fungicide
Hexachlorocikloheksane*	608-73-1	1, PHS	Y	insecticide
Hexachloroethane	67-72-1	2	N	solvent

Substance	CAS No.	Status in EU*	Status in RS#	Main use
Indeno(1,2,3-cd)pyrene*	193-39-5	PHS	Y	tar impurity
Izodrine	465-73-6	1	N	insecticide
Izoproturon	34123-59-6	PS or PHS	N	herbicide
Lead & its compounds		PS or PHS, 2	Y	tech. chemicals, accumulators
Lindane*	58-89-9	1, PHS	N	insekticide
Linurone	330-55-2	2	N	herbicide
MCPA	94-74-6	2	N	herbicide
Mecoprop	93-65-2	2	N	herbicide
Mercury & its compounds	7439-97-6	1, PHS	Y	teh.chemical, insecticide
Molibdene & its compounds		2	N	tech. chemicals
Naphthalene	91-20-3	PS or PHS, 2	Y	tech. chemical
Nickel & its compounds		PS, 2	Y	tech. chemicals
Nitrites		2	Y	fertilizers, tech.chemicals
4-Nonylphenol	104-40-5	PHS	N	technical chemical
Nonylphenols	25154-52-3	PHS	N	surfactants
Octylphenols	1806-26-4	PS or PHS	N	tech. chemicals
Omethoat	1113-02-6	2	N	insekticide
p-terc-Octylphenol	140-66-9	PS or PHS	N	tech. chemical
Oxydemethone-methyl	301-12-2	2	N	insecticide
Parathion	56-38-2	2	N	insecticide
Pentachlorobenzene *	608-93-5	PHS	N	insecticide
Pentachlorophenol*	87-86-5	1, PS or PHS	Y	insecticide
Phosphorous compounds		2		tech. chemicals
Polychlorinated biphenyls (PCB)	1336-36-3	2	Y	fertilizers, detergents
Selene & its compounds		2	N	technical oils
Silver & its compounds		2	N	tech. chemicals
Simazine	122-34-9	PS or PHS, 2	Y	tech. chemicals
Tetrachloroethene		1	Y	herbicide
Tetrachloromethane	56-23-5	1	N	solvent
Tin & its compounds		2	N	solvent
Titanium & its compounds	-	2	N	tech. chemicals
Toluene	108-88-3	2	N	pigments
Tributyltin-cation*	36643-28-4	PHS	N	solvent
1,2,4-trichlorobenzene	120-82-1	I, PS or PHS	Y	catalysts
Trichlorobenzenes – technical mixture*	12002-48-1	PS or PHS	Y	technical chemical
Trichloroethylene	79-01-6	1	Y	solvent
Trichlorophon	52-68-6	2	N	solvent
Trichloromethane	67-66-3	1, PS	Y	insecticide
Trifluraline	1582-09-8	PS or PHS, 2	N	solvent
Xylenes – technical mixture		2	N	tech. chemicals
Zinc & its compounds		2	Y	pigments, bateries

* which list they belong: I, II - lists I and II; PS- priority substances, PHS - priority hazardous substances

included in Slovene water monitoring regulation?

They were collected for most of the selected relevant substances, the action programs however were finalized only for 71 in due time. The programs were assessed by the European Commission according to the special procedure⁶, which tested their compliance with provisions of Article 7 of the Directive.

For the remaining 21 substances from the relevant list not enough reliable monitoring data was available.⁷ A surveillance monitoring had to be performed in 18 months period, after which decisions have to be made. Deadline for the completion of the programs is end of year 2006.

Activities have already commenced towards risk assessment and pollution abatement for most important Slovene river basins Save and Drava. These are included in international projects (Danube, Mediterranean).

4. Conclusions

Preparation works towards prevention programs for reduction of aquatic environment pollution with dangerous substances on the national level of Slovenia have commenced. Pollution from many sectors of economy, among them mainly industry and agriculture with their emissions, wastewaters and wastes contribute most significantly to the pollution of the aquatic environment, which may affect ground water quality and potable water resources. According to the Article 7 of the Dangerous Substance Directive evaluation of the surface and ground water pollution was made and preparatory actions taken in order to reduce the impact. The starting point is establishment of a preliminary national relevant substance list, for which discharge reduction programs are to be prepared and implemented. The study has disclosed nearly 200 dangerous substances that may be responsible for nationally significant pollution of the Slovene aquatic environment. From these 92 were selected as relevant for the concrete action.

Elements of pollution prevention programs were prepared and commissioned in which measures, responsible parties and deadlines were proposed. They are currently in execution; for some substances the surveillance monitoring is taking place. The actions should – beside other current activities - shortly contribute to significant pollution reduction and quality

improvement of the aquatic environment in Slovenia.

Further work is needed in order to provide regular update of the relevant substance list due to changing supply and consumption of these materials. Also national water quality objectives must be prepared, adapted to specific situation and demands. Relevance should be assessed based on stricter risk assessment methods, taking into account exposure-effect relationship for each river basin.

5. References

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Povzetek

Prikazan je potek izdelave preliminarnega nacionalnega seznama nevarnih snovi za onesnaževanje vodnega okolja, skladno s 7. členom Direktive o nevarnih snoveh in v soglasju s Krovno vodno direktivo. Na podlagi navskrižnega uzpoštevanja tokov nevarnih snovi (masna bilanca), emisijsko-imisijskih podatkov in razpoložljivih kvalitetnih standardov za vodno okolje je ugotovljeno 92 vrst nevarnih snovi, ki so prisotne in zaznavne v obsegu, kateri zahteva pripravo operativnih programov za njihovo zmanjševanje.