Organic micropollutants in the assessment of groundwater quality

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Abstract The better the quality of raw water resources, the higher the safety of drinking water supply. In the Danube river basin more than 60% of the population depends on groundwater sources. Organic micropollutants play an important role in quality assessment since they might cause different toxic effects in humans. There are two groups of organic micropollutants: regulated and non-regulated. In recent years, a lot of scientific effort was made to quantify their risks. Their occurrence is site specific and depends on social and economic factors, industry, population density, environmental conditions etc. That is why legislation intervention is required both at national and international level. This paper presents a literature review on the presence and fate of organic micropollutants that have been recently investigated in numerous projects worldwide. Special attention is paid to their mobility and risk for groundwater resources. Data on Serbian groundwater quality is presented for the period 2004–2005. In comparison with knowledge in developed countries, one can conclude that there is a general lack of data. More data about organic micropollutants presence is required, as well as identification of the pressures which lead to quality deterioration. Future quality assessment should be based on evaluated risks made considering both experience from developed countries and local conditions.

Keywords Groundwater quality; monitoring; organic micropollutants; priority substances; water treatment

Introduction

It is estimated that about 60% of the population in the Danube River Basin depend on groundwater sources. Some countries in the Danube River Basin even use up to 95% groundwater sources for public water supply. Also, many people use groundwater from private wells for drinking water purposes. In Serbia more than 50% of the total water abstracted for public water supply is aquifer water. It is well known that the quality of groundwater abstracted from alluvial sources is greatly influenced by the quality of river waters and that groundwater in the Danube Basin is vulnerable to contamination due to porous and karstic aquifers. According to the European Environment Agency Report (2003) 180 different pesticides are analyzed at over 3000 locations in Europe at a frequency of 4 to 12 times per year. The herbicides diuron, isoproturon and mecoprop are found. However, for groundwater samples, less than 5% exceed 0.1 μg/L, while for freshwaters and marine waters, a higher percentage are above this level. In recent investigations in Germany 60 different substances from the group of plant protection products were detected in groundwater (Sturm and Kiefer, 2006). Most important findings were: desethylatrazine, atrazine, 2,6-dichlorbenzamide, simazine, diuron, bentazone, bromacil, isoproturon, desisopropylatrazine, mecoprop, hexazinon, propazine, terbutylazine, desethylterbuthylazine, 1,2-dichloropropane, chlorotoluon, lenacil, metalaxyl, methabenzthiazuron and dichlorprop.

Groundwater quality assessment regarding organic micropollution is a very complex issue that consists of several important topics which must be taken into account. First of all is the correct choice of substances which should be analyzed. It should be pointed out that
bearing in mind the state of instrumental analysis today, one can find in water only what one is looking for. This choice is strongly influenced by the purpose for which water is used and the corresponding water quality criteria which are developed and revised in accordance with the newest scientific results permanently regarding both substance identity and concentration of interest. Also, one has to pay attention on river basin specificity regarding the type of pollution which depends on social and economic factors, types of industry, population density, etc. A good example of such a complex issue is the case of the large Danube Basin, where for different regions one can expect different types of organic pollutants in water. They might differ from country to country, e.g. from region to region.

In general, we have two groups of organic pollutants: regulated and non-regulated. In recent research and monitoring programs it was shown that a large group of non-regulated substances exists, which seems to require legislative intervention. Among this group, wide attention is attracted to the endocrine disrupting compounds (EDC) and pharmaceuticals as well as personal care products (PPCPs). Before this intervention takes place it is necessary to quantify risks and determine predicted environmental concentrations (PEC) as well as predicted no-effect concentrations (PNEC). One of the preconditions to quantify the risks is the development of analytical standard methods which are still not developed for most of the non-regulated contaminants.

Recent research results worldwide
During the last several decades, most of the scientific and monitoring efforts have focused on the conventional “priority” pollutants, especially those acutely toxic/carcinogenic pesticides and industrial chemicals. However, this is only one part of the larger puzzle in “holistic” risk assessment according to Daughton and Ternes (1999). A more wider and diverse group of bioactive chemicals has become important in recent years, including pharmaceuticals (human and veterinary) and personal care products (PPCPs), (Ternes, 1998; Hirsch et al., 1999; Alder et al., 2003; Ternes et al., 2005). These compounds and their bioactive metabolites enter the aquatic environment as complex mixtures by both treated and untreated sewage. The effects of mixtures at low level concentrations (ppt and ppb ranges) are still unknown for the majority of substances. The possibility for continual but undetectable or unnoticed effects on aquatic organisms is worrying. In numerous reports one can find data about the amounts of drugs used in developed countries. Nearly 3000 different pharmaceutical ingredients are used in the EU (Ternes, 2005). In human medicine 30,000 t/year of different substances are used in Germany while the use of oral contraceptives is estimated at 50 kg/year (Heberer, 2002a). Personal care products in the nineties were used in quantities of 550,000 t/year (Ternes, 2005). In 2003, 86 t/year of diclofenac were used, 344 t/year of ibuprofen, 54 t/year sulfamethoxasole, etc. (Ternes and Rombke, 2005). Besides pharmaceuticals and personal care products, there are numerous reports on different industrial chemicals found in waters (Knepper et al., 2005; Friedrich, 2005). Recent investigations in USA (Kolpin et al., 2002) showed that the most frequently detected compounds among pharmaceuticals, hormones and other wastewater contaminants in water resources are coprostanol (fecal steroid), cholesterol (plant and animal steroid), N,N-diethyltoluamide (insect repellant), caffeine (stimulant), triclosan (antimicrobial disinfectant), tri(2-chloroethyl) phosphate (fire retardant) and 4-nonylphenol (nonionic detergent metabolite). The measured concentrations were generally low and below US-drinking water standards or aquatic life criteria, but for many compounds such guidelines are not established.

Their presence in groundwater is a consequence of penetration both from soil (e.g. accidents, use of pesticides) and from polluted surface water (e.g. infiltration, river bank filtration). The finding of such chemicals in recent years in groundwater and even tap water raised concern and initiated research activities. In 1993, clofibric acid was the
first PhAC ever to be detected in tap water, and was found in all tap water samples from the Berlin area up to 165 ng/L (Heberer, 2002b). It was found that the polar contaminants concentration in tap water of individual Berlin waterworks correlate well with the proportions of groundwater recharge used in drinking water production. Places with high proportions of bank-filtered water and located near water ways highly contaminated by municipal sewage effluents were in the worst situation. There were also findings of primidone and iodinated contrast agents detected in several groundwater samples in Germany. Webb et al. (2003) compared reported concentrations of pharmaceuticals in German drinking water and therapeutic dose. Potential daily exposure via drinking water was estimated at least three orders of magnitude below therapeutic dose. Drinking water examinations during 2003–2004 for antibiotics presence and the presence of iodinated contrast media in 55 waterworks within three categories regarding their size showed that in 11 cases out of 55 investigated, sulphometoxazol was identified (7–66 ng/L). Iodinated contrast media were found in concentrations up to 218 ng/L and carbamazepine up to a concentration of 150 ng/L (Ternes et al., 2005).

The recently published report “Behavior of selected human and veterinary pharmaceuticals in aquatic compartments and soil” (Ternes and Römbke, 2005) deals with the leaching behavior of six selected pharmaceuticals in different soils and four human metabolites presented in high portions (iopromid, diazepam, oxazepam, paracetamol, ibuprofen, 2-hydroxyibuprofen, clofibrac acid, carbamazepine and 10,11-dihydro-10,11-dihydroxy-carbamazepine). Their potential to contaminate groundwater was evaluated and was low for diazepam, ibuprofen, ivermectin and for carbamazepine. The last result was surprising, since carbamazepine is often detected in groundwater. This discrepancy is explained by the fact that the leaching tests were performed with topsoil, which is not the really the case when groundwater contamination occurs mainly over river sediments and subsoils from receiving waters. Clofibrac acid and iopromide were assessed as very mobile. Based on persistency testing it was concluded that an environmental risk cannot be excluded.

The findings from the European Poseidon project (Ternes, 2005) are that irrigation and soil passage might lead to pollution with iodinated contrast media, carbamazepine and sulfamethoxazole. Moreover, research of infiltration into unsaturated soil showed that acidic drugs such as diclofenac, bezafibrate and ibuprofen, which are removed easily during wastewater treatment, are subject to additional removal by polishing lagoon, gravel filter or infiltration pond. On the other hand, neutral substances such as diazepam and carbamazepine which hardly show any removal during wastewater treatment, remain stable during post treatment steps as well as in the groundwater.

A broad study on EDCs in drinking water treatment in the EU (Wenzel et al., 2003) showed that the raw water of waterworks can be contaminated by EDCs (especially the case if surface water is used). Data was provided from Austria, Denmark, Germany and the Netherlands and information on pesticide concentrations in groundwater of the United Kingdom was taken from another source. In groundwater, atrazine exceeded the limit for drinking water most frequently, but for diuron and isoproturon, maximal concentrations above 1 µg/L were also reported. The detection frequency of diuron, simazine, isoproturon, 3,4-dichloroaniline, lindane and linuron was in general below 1%. For the other pesticides with suspected endocrine activity selected for the questionnaire, no data was available. A data survey on tributyltin (TBT) and o-phenylphenol was performed. No data on o-phenylphenol in raw water and drinking water was reported. No groundwater data could be retrieved from literature and no information about TBT in surface, groundwater and drinking water was given in the questionnaires returned from authorities. Data on bisphenol A in groundwater was completely lacking. In the questionnaires returned from the waterworks 5 out of 51 waterworks reported determinations of bisphenol A in raw waters. Concentrations
above the limit of detection were reported from 2 waterworks ranging between 0.0025 µg/L and 0.009 µg/L. Alkylphenols were frequently detected in surface waters. Nonylphenols occur in the µg/L range, octylphenol was detected at lower concentrations in the ng/L range. Based on the presented data, a great variation of nonylphenol concentrations in European surface waters can be assumed, due to different efficiencies in the purification of sewage treatment plant discharge into rivers. For groundwater and drinking water little information is available. The reported concentrations are in the ng/L range. Tap water samples analyzed in the case study contained no nonylphenol and no octylphenol. 17β-estradiol can be present in surface waters in the lower ng/L range and in groundwater below 1 ng/L.

Recently Sacher (2005) reported several positive results of pharmaceuticals in groundwater and their maximal concentrations: sotalol (560 ng/L), phenazon (25 ng/L), diclofenac (590 ng/L), iopamidol (300 ng/L), amidotriazico acid (1100 ng/L), carbamazepine (900 ng/L), dehydrato-erythromycin (49 ng/L) and sulfamethoxazol (410 ng/L). Very important issue related to transport of pollutants from surface water to groundwater is their behavior in bank filtration. It is influenced by hydrogeological conditions, dispersion, diffusion, sorption, degradation, complexation, transport of coloids, as well as substance characteristics (e.g. polarity, hydrophobicity, solubility, biodegradability). Investigation of bankfiltration at rivers Rhein, Ruhr and Elbe under aerobic, suboxic, anoxic and anaerobic conditions (Schmidt, 2006) showed that carbamazepine, sulfamethoxazol, amidotriazico acid and iopamidol can be removed 70–100% in anoxic and anaerobic conditions. In aerobic and suboxic conditions carbamazepine was not removed at all, while the removal of the other substances increased from 10% to 50% (amidotriazico acid > sulfamethoxazol > iopamidol). Findings for EDTA showed that this compound can only be removed in aerobic and suboxic conditions. Some of investigated naphthalin-sulfonates had very low removal by bank-filtration regardless of redox conditions (e.g. naphthalin-1,5-disulphonate). Most of iodinated contrast media and pharmaceuticals had very good removal. It was confirmed that perfluorocanano and perfluorococtylsulfonate is not possible to remove by aerobic bank filtration while there is no data for other redox conditions.

Not only quality of surface water influences groundwater quality. Beside agricultural activities which might cause pollution with pesticides directly, one has to take into account possible leakage from sewers in urban settlements. Wolf and Gluner (2005) confirmed the significance of several groups of substances related to leakages from sewers: iodinated constrast media (most abundant amiditriazio acid), betablockers (metoprolol and sotalol), carbamazepine, clofibric acid, diclofenak and ibuprofen.

**Current status of water management**

**Danube river basin**

Referring to organic micropollutants, Anex X of the Water Framework Directive (Council Directive 2000/60/EC) contains a Priority pollutant list of 33 substances. Furthermore Dangerous Substance Directive remains in force for 13 years from the adoption of WFD and requires the identification of specific pollutants from the List II. Recently the European Commission decided to include 8 more substances from the groups of chlorinated aliphatic and aromatic components, mono and polyaromatic amines, mono and polyaromatic hydrocarbons, pesticides and hormone active substances (Puijker, 2005). According to the “Danube Basin Analysis (WFD Roof Report, 2004)” (ICPDR, 2005) “pollution loads of hazardous substances are significant although the full extent can not be evaluated to date”. There is a general lack of data but concern is also present about several substances that are stressed in the report: p, p’-DDT in the lower Danube, lindane, atrazine in some tributaries, alkyl phenols and δ [2-ethyl-hexyl] phthalate in sediments and suspended solids. Pesticide pollution is present as well, both by priority pesticides and other pesticides. In a
certain number of water samples, volatile organic compounds were detected above interim target values (e.g. chloroform, tetrachloroethylene) in river water. Monitoring of organic compounds which are not included in regular monitoring programs showed the presence of numerous classes of organic compounds (e.g. phthalates, fatty acids, aliphatic chlorohydrocarbons, sterols, hydrocarbons, phenols, hydroxy- and keto-aliphates and aromates, benzothiazoles, organophosphates etc) in river water. Regarding pharmaceuticals, it was shown that there are relatively low concentrations in the Danube comparing to the tributaries. However in almost all samples low concentrations of isopropylphenazone and N-acetyl-4-aminoantipyrine were found (ICPDR, 2002). No data for groundwater is presented. These findings are compared to findings at other large river basins. It seems there is a severe lack of data on organic pollutants content in Danube river basin at present both for surface and groundwater. All countries within the basin have stated that the water quality of many surface and groundwater bodies is not satisfactory. They gave the main reasons for the pollution of the water sources: insufficient wastewater collection and treatment on a municipal level, insufficient wastewater treatment at industrial enterprises, water pollution caused by intensive agriculture and livestock breeding, inappropriate waste disposal sites. Existing and planned measures for pollution reduction concentrate on municipal wastewater treatment, but expected development in agriculture is that fertilizer and pesticide use will again be a threat to the groundwater resources in the basin.

Moreover, there is certain number of substances which can not be removed with conventional wastewater treatment (Friedrich, 2005). These pressures, in combination with the high vulnerability of some aquifers, require the development of groundwater protection strategies. Although a monitoring network on water quantity and water quality exists, there is a need for further harmonization of methods at a basin-wide level in order to fulfill the demands of Water Framework Directive for the assessment of the risk of failure to reach the environmental objectives, both for groundwater quantity and quality. In accordance with EU developments and based on the results of screening at national levels it is expected that ICPDR gives final list of priority substances for the Danube Basin in future.

It is well known that the better the quality of raw water resources, the higher the safety of the drinking water supply. Organic micropollutants relevant for drinking water treatment are substances which are persistent but possible to remove by activated carbon (e.g. atrazine, tetrachloroethene or carbamazepine). However, high relevance for drinking water quality have those substances which are not adsorbable on activated carbon (EDTA, MTBE, amidotriazoate) and thus very difficult to remove from water (Brauch, 2006). Those three compounds were frequently found in river water and bank filtrate up to several µg/L (Rhein, Danube, Main, Elbe). The most important characteristics relevant for organic micropollutants assessment are human toxicity, ecotoxicity, persistence and bioaccumulation. Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet (IAWR) proposed including more substances on the WFD List: trialkylphosphates, alkylamines, complex compounds, aroylsulphonates, pharmaceuticals, X-ray contrast media, benzine derivatives, pesticides and hormone active substances. A statement from this organisation said that monitoring should be done 13 times per year and that beside ecotoxicological standards, the drinking water parameters should also be taken into account (IAWD and IAWR, 2005).

State of the art in Serbia

Groundwater quality in Serbia is monitored by the Republic Hydrometeorological Institute once per year in 9 regions: at Velika Morava, West Morava, South Morava, Kolu bara, Macva, Danube, Backa, Banat and Srem (Republic Hydrometeorological Institute of Serbia, 2005, 2006); 53 and 68 groundwater stations were evaluated in 2004 and 2005, respectively. The list of organic micropollutants which are used to assess the quality of
groundwater is identical to the list for surface water with exception that herbicides are evaluated in surface waters. This is in accordance with current Serbian legislation which is still not harmonized with European legislation in the field of water. Improvement of monitoring program is planned within the activities related to the implementation of the WFD in Serbia (Djuric, 2006). Referring to organic micropollutants, in 2004, the list of monitored parameters consisted of: MPAS, volatile phenols, mineral oils, lindane, heptachlor, aldrin, DDE, dieldrin, endrin, DDD, DDT, methoxychlor, hexachlorobenzene, heptachlor epoxide, BHC and PAH. In 2005, instead of PAH analysis, analysis of PCBs and triazine herbicides (atrazine, simazine and propazine) was made.

In 2004, among all the determinants, only the presence of volatile phenols was confirmed in the regions of Backa, Banat and Srem. Rare findings of mineral oils by IR spectroscopy after liquid-liquid extraction and filtration over Al₂O₃ (6 samples up to 0.021 mg/L), volatile phenols (in 13 stations up to several micrograms per litre) and BHC (2 samples up to 6 μg/L) occurred. All other parameters were below detection limits. In 2005, no organic micropollutants were found except: surface active substances in the regions of Backa and Banat (0.02-0.09 mg/L) and in a few samples, mineral oils in the Danube region (0.006 mg/L), Backa region (1 piezometer with a value of 0.014 mg/L) and the Banat region (1 piezometer with a value of 0.045 mg/L).

Besides these measurements of the Hydrometerological Institute of Serbia in the period 2000–2006, the Laboratory for Chemical Technology and Environmental Protection at the Faculty of Sciences of University of Novi Sad made numerous investigations of groundwater quality in regions where aquifers were endangered due to oil or waste water spillages (Dalmacija et al., 1997; Dalmacija et al., 2002; Dalmacija et al., 2003; PMF, PCO “Water Supply and Sewerage System” Novi Sad and SDC-Belgrade (2003); PMF, SDC-Belgrade (2003); PCO “Water Supply and Sewerage System” Novi Sad and UNEP-UNOPS (2004)). Within these investigations the presence of different compounds in groundwater at several locations was confirmed: organochlorine compounds (e.g. 1,2-dichlorethane), solvents, benzene and its derivates (BTEX), phthalates, PAHs, mineral oils, etc. Concentration ranges for almost all of them were from values below maximum permissible levels (MPLs) to the values which were significantly above MPLs, depending on the vicinity of the spillage to sampling location, age of pollution, river water influence, different degradation processes, etc. These findings at endangered locations confirmed the urgent need for the determination of the quantitative and qualitative status of groundwaters, risk assessment and protection measures. However, those projects were mainly oriented towards organic pollutants related to accidental oil and gasoline spillage at several locations. No detailed studies on the other organic micropollutants in groundwater were performed (e.g. pesticides, pharmaceuticals, personal care products, industrial chemicals etc) or in depth study of their fate and behavior.

It is expected that improvements in legislation dealing with water in general will introduce changes in organic pollutants monitoring issues in Serbia. In comparison with the list of priority substances, one can conclude that the list of parameters which are currently monitored should be significantly revised. It is necessary that at least the list of priority substances is taken into consideration concerning to assessment of groundwater chemical status. Moreover data about the presence of different classes of compounds is needed, as well as pressure identifications which can lead to groundwater quality deterioration (e.g. data on production, usage and emission of relevant chemicals). This means that the state of the art of the current monitoring program must be broadened with both surveillance and operational monitoring in accordance to the WFD, in terms of frequency, objectives and list of determinants. Data is needed about the presence of organohalogen compounds, organophosphorous compounds, organotin compounds, hydrocarbons, biocides and plant protection products and different endocrine disruption and carcinogenic agents.
In comparison with knowledge in developed countries and other river basins, one can conclude that a general lack of data exists, also regarding the new class of emerging pollutants. However, before broad analytical work is undertaken, assessment of the type of pollutants and their impact should be made for the region.

**Future needs**
In recent research and monitoring activities worldwide it was shown that relevant groups of substances for groundwater aquifer are: pesticides and their metabolites, complexing agents, MTBE, and some pharmaceuticals (e.g. carbamazepine, sulfamethoxazol and iodinated contrast media). Both lack of knowledge referring to chemical status of groundwater stressed in ICPDR report and WFD require further intensive activities in this field for the Danube basin. In order to assess groundwater quality in Serbia and protect it from deterioration, it is necessary to continue with local, regional and international efforts on identification of pressures regarding organic micropollution of water bodies, and strengthening both research and institutional capacities which are able to do so. Organic micropolllutants assessment should be made very carefully by paying attention both to local conditions and already gained knowledge in the developed part of the world. According to this two main goals should be achieved: firstly monitoring should be established in accordance with the Water Framework Directive with a core of priority substances, and furthermore, local risk assessment is needed for all regional specific and river basin relevant substances, also bearing in mind the new generation of emerging pollutants (EDCs, PhAC, veterinary drugs, industrial chemicals etc) and pesticides currently in use.

**Acknowledgment**
The authors acknowledge the financial support of the Humboldt Foundation through a research grant to Dr I. Ivancev-Tumbas and the support of the Ministry of Science of the Republic of Serbia through grant no ON142058.

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