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Input and fate of anthropogenic estrogens and gadolinium in surface water and sewage plants in the hydrological basin of Prague (Czech Republic)

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Abstract

The concentration of the estrogens 17β-estradiol, estriol, estrone, 17α-ethinylestradiol, mestranol and norethisterone and of the anthropogenic gadolinium (Gd_{ant}) has been determined in the creeks and rivers, sewage treatment plants and water works of the city of Prague. The rapid degradation of estrogens in surface water allows the estrogen concentration gradient to be used as a very precise and sensitive guideline by which to pin-point sewage leaks into surface run-off water. The rather conservative behavior of Gd_{ant} in surface and ground water documents in the present case the presence of sewage water in the surface water cycle.

Introduction and problem

The well-defined hydrogeological basin of Prague, with its approximately 1.2 million inhabitants, many small creeks and the Vltava River as the major water collector, is an ideal location to study the input and environmental behavior of anthropogenic estrogens and gadolinium (Gd_{ant}) in surface water. The combined study of both estrogens and gadolinium is expected to yield information on the efficiency of sewage treatment plants (STP) in reducing these chemicals, on leakages of sewage collectors into surface water and ground water and on the quality of drinking water.

The concentration of 17β-estradiol, estriol, estrone, 17α-ethinylestradiol, mestranol, norethisterone and gadolinium has been determined in the creeks and rivers and in the city's sewage treatment plants and water works. 17β-estradiol, estriol and estrone are natural estrogens produced not only by the ovaries but also by the corpus luteum and the placenta of humans and other mammals. Mestranol is a synthetic estrogen consumed predominantly in the USA but not widely used in Europe. Norethisterone is a product typically used in drugs administered against menopause problems. The environmental behavior of these estrogens can be considered to be representative of the whole family of natural and synthetic estrogens.

The endocrine and reproductive effects of natural and synthetic estrogens found in the environment are due to their ability to: (1) mimic the effect of endogenous hormones, (2) antagonize the effect of endogenous hormones and (3) disrupt the synthesis and metabolism of endogenous hormones and of hormone receptors (Soto *et al.* 1994; Sonnenschein and Soto, 1998). In mid-1990s, various researchers suggested that environmental estrogens may be ethiological agents in several human diseases, including breast and testicular cancer and disorders in the male reproductive tract (Colburn *et al.* 1993; Jobling *et al.* 1995; Routledge and Sumpter, 1997; Routledge *et al.* 1998; Körner *et al.* 2000).

The natural secretion of such estrogens as 17β-estradiol, estriol and estrone by an individual woman varies between 25 and 100 μg per day. 17α-ethinylestradiol as a synthetic estrogen is found in nearly all commercial brands of contraceptive pills, but it is used also in drugs against endocrine diseases, such as acne. When it is taken into consideration that about 350,000 women between the ages of 15 and 54 years live in Prague (Czech Statistical Office), the total input of natural estrogens into the environment can be calculated to be about 2.1 g day^{-1}. Given that the flow rate of the sewage system of Prague is about 4.5 m^3 s^{-1} (City of Prague Civil Administration), this yields a total concentration of about 50 ng l^{-1} estrogens in the sewage. The fate of the estrogens in STP and sewage collection pipe systems is discussed by Johnson *et al.* (2000) Baronti *et al.* (2000), Stumpf *et al.* (1996), Ternes *et al.* (1999) and Körner *et al.* (2000, 2001), among others.

In unpolluted water gadolinium is found together with the other rare Earth elements (REE) as a geogenic component (Gd_{geo}) as a result of Gd leaching from the aquifer rocks. In the last decade, however, distinct, positive Gd_{ant} anomalies have been found in the normalized REE distribution pattern of river and lake water (Goering *et al.*, 1991; Bau and Dulski, 1996; Fuganti *et al.* 1996; Knappe *et al.* 1999; Kümmerer and Helmers, 2000; Möller *et al.* 2000, 2002; Nozika *et al.* 2000; Knappe *et al.* 2001). Such positive anomalies are produced by the commercial use of derivatives of gadopentetic acid, mostly in the form of salts of the Gd complex of the di-ethyl-tri-amin-penta-acetic acid (Gd-DTPA). One of the major sources of Gd-DTPA is the contrast agent in magnetic resonance imaging (MRI), which has been used in hospitals and some private medical clinics since 1988. The Gd complex is excreted in a non-metabolized form by the patients within a few hours and subsequently enters the hospital sewage system, the sewage collecting system and finally the sewage treatment plants, from where it enters the surface and ground water (Möller *et al.* 2003). Positive Gd_{ant} anomalies indicating an enrichment by a factor of nearly one thousand have been found in the surface waters of the area around the city of Berlin (Knappe *et al.*, 1999, 2001, 2005; Möller *et al.*, 2000). In order to calculate the amount of Gd_{ant}, the first step is to determine the Gd_{geo} content by a third order polynomial fit of the trend given by the PAAS-normalized La, Nd, Pr, Nd, Sm, Tb, Dy, Ho, Er, Yb and Lu contents of the water (Möller *et al.*, 2002). The PAAS-normalized $REEGd_{ant}$ anomaly is then calculated by subtracting Gd_{geo} from the analyzed total Gd (Gd_{tot}) content, as follows: $Gd_{ant} = Gd_{tot} - Gd_{geo}$.

Analytical procedures

Sampling and sample treatment

Estrogens

With two exceptions all water samples were collected using a suction hose connected to a peristaltic pump, immediately filtered in the field through 0.2-μm cellulose acetate filters (Sartobran; Sartorius, Goettingen, Germany) and stored in dark-brown glass flasks. Filtration removed the load of particulate matter including bacteria. The samples were kept in the dark at approximately 4°C and analyzed at the very latest 3 days after sampling.

Analysis of the hormones 17α-ethinylestradiol, 17β-estradiol, estrone, estriol, mestranol and norethisterone by gas chromatography/mass spectrometry (GC/MS) was carried out on a commercial basis at the Technologiezentrum Karlsruhe (Germany).

Rare earth elements and yttrium (REY)

Five liters of water were filtered on the sampling site, acidified to a pH of approximately 2 and spiked with 1 ml of 100 ppb thulium (Tm). At a rate of 1 l h^{-1}, each of the conditioned water samples was passed through a SepPac column (Waters Corp., Milford, Mass.) preconditioned with a mixture of ethyl-hexyl-phosphates in order to collect REY. The columns were later washed with 50 ml of sub-boiled 0.1 *M* HCl. The REY were eluted with 40 ml sub-boiled 6 *M* HCl. The eluate was evaporated to incipient dryness, and the residue was dissolved in 1 ml 10 *M* sub-boiled HNO_3 and transferred to a volumetric flask, where 1 ml of 100 ppb Rh and Ru spike was added for internal shift corrections; the flask was then filled up to 10 ml. REY were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer-Sciex, Foster City, Calif.). Details of the pre-concentration procedure and the corrections for molecular ion interferences are given by Bau and Dulski (1996) and Dulski (1994), respectively.

The uncertainty in the determination of Gd_{ant} is supposed to be less than 2 nmol m^{-3}.

Results and discussion

The results of the estrogen and Gd analyses are compiled in Table 1 and shown in Figures 1 and 2.

Mestranol and norethisterone levels were always below the detection limit (DL) and therefore are not given in Table 1. Individual samples differed in 17β-estradiol, estriol, estrone and 17α-ethinylestradiol content only. There was no significant correlation between the individual estrogens in any of the samples. For example, the sewage entering the STP on Cisarsky Island (sample no. 53) carried 466 ng l^{-1} total estrogen, and 360 ng l^{-1} estriol and 55 ng l^{-1} estrone, whereas the sewage leaving the local small Uhrineves STP (sample no. 74) had a total estrogen content of 344.9 ng l^{-1}, no estriol but 330 ng l^{-1} estrone.

Figure 1 shows the content of individual estrogens in water of the rivers and creeks, the effluents and the feed of the STP of the study area and the total estrogen content. The total estrogen content of the sewage entering the major STP of the city of Prague on Cisarsky Island (sample no. 53) was 466 ng l^{-1}. The total estrogen content in the effluent from the local STPs at Uhrineves (sample no. 74) was 344.9 ng l^{-1} and at Sedlec (sample nos. 73, 73a) it was about 287 ng l^{-1}. The total estrogen content in the effluent of the local Dolni Chabry STP (sample nos. 72, 72a) varied between 77.1 and 51.1 ng l^{-1}.

If the hormone load of 466 ng l^{-1}, as determined for the sewage input to the major STP (sample no. 53) of the city of Prague is considered typical for the sewage treated in the other STP studied, the estrogens are best removed by the plant on Cisarsky Island and the Dolni Chabry plant, followed by that of Sedlec. The Uhrineves STP seems to have the lowest efficiency in removing estrogens. The total estrogen content in the effluents of the STP is largely determined by high levels of estrone. A comparison of the 17β-estradiol and 17α-ethinylestradiol contents with the total estrogen content of different samples given in Table 1 shows that high total estrogen contents are mirrored in most samples by high 17β-estradiol contents.

The small creeks with their ponds draining the city of Prague and entering the Vltava differ markedly in estrogen content. The waters of the Kunraticky (sample no. 63), Zatisky (sample no. 64) and Lhotsky (sample no. 65) creeks have a total estrogen content below the detection limit of 1 ng l^{-1}, whereas the Kyjevsky pond on the Rokytka Creek (sample no. 71) and the Rokytka Creek itself (sample no. 67) show significant estrogen abundances of about 3 and 1.8 ng l^{-1} (Table 1). The estrogen contents found in the Kyievsky pond and the Rokytka Creek are produced by the effluents of the Uhrineves STP entering that river. Also, the Libussky (sample no. 66) and the Slivenecky (sample no. 68) creeks – with 8.8 and 4.6 ng l^{-1} – show remarkably high total estrogen contents, predominantly of the synthetic estrogen 17α-ethinylestradiol. In both cases no STP upstream of the sampling point was reported. The high levels of estrogen in the waters of the Libussky and Slivenecky creeks indicates that (1) sewage is seeping from the canalization into the creeks upstream of the sampling point or (2) an undetected direct input of sewage into the creeks exists.

The Zelivka dam is one of the major drinking water reservoirs of the city of Prague. It is found well outside of the city limits of Prague in a poorly populated agricultural area. Nevertheless, the water of the Zelivka dam (sample nos. 57, 58) was shown to contain 2.3 and 2.4 ng l^{-1} of synthetic 17α-ethinylestradiol. Contraceptive pills contain 17α-ethinylestradiol, consequently the presence of this substance in the water of the dam indicates an anthropogenic input. This anthropogenic input in the water of the Zelivka dam is also indicated by a Gd_{ant} content of 1.1 nmol m^{-3} (see below).

The water of the Vltava River at Jarov (sample no. 70) and at Zbraslav (sample no. 42) – a location upriver of the confluence with the Berounka river – had a total estrogen content below the detection limit of 1 ng l^{-1} (Figure 1). It may be possible to base an explanation for the estrogen content of 3.8 ng l^{-1} in the water of the Vltava at

Table 1. Sample numbers, sample locality and content of individual and total estrogens and of Gd_{ant} in waters of the rivers and creeks, the effluents and feed of the STP of the study area. (*DL* detection limit, *n.a.* not available).

Sample	Locality		17β-Estradiol (ng l^{-1})	Estriol (ng l^{-1})	Estrone (ng l^{-1})	17α-Ethinyl estradiol (ng l^{-1})	Total estrogens (ng l^{-1})	Gd_{ant} (nmol m^{-3})
40	Dalejsky Creek	Hlubocepy, confluence with Vltava River	DL	DL	DL	1.6	1.6	1.9
41	Berounka River	Lahovice, left bank, confluence with Vltava River	DL.	DL	DL	4.6	4.6	7.9
42	Vltava River	Upstream of the confluence with Berounka river at Zbraslav	DL	DL	DL	DL	DL	4.9
43	Vltava River	Veslarsky Ostrov Island	3.8	DL	DL	DL	3.8	5.6
44	Botic Creek	Confluence with Vltava River	1.5	1.7	DL	3.3	6.5	6.6
45	Kunraticky Creek	Downstream of Thomayer Hospital	DL	DL	DL	DL	DL	3.6
46	Vltava River	Podoli water treatment plant, raw water before treatment	n.a.	n.a.	n.a.	n.a.	n.a.	6.3
47	Vltava River	Podoli water treatment plant, tap water	2.6	DL	DL	DL	2.6	1.9
48	Brusnice Creek	Near springs at the Cloister of St. Marketa	2.6	DL	DL	DL	2.6	0.9
49	Motol Creek	Pool	n.a.	n.a.	n.a.	n.a.	n.a.	7.7
50	*Cisarsky Island*	*STP, first effluent discharging into the Vltava*	DL	DL	100	DL	100.0	273.1
51	*Cisarsky Isand*	*STP, second effluent discharging into the Vltava*	1.9	DL	75	2.1	79.0	250.5
52	*Cisarsky Island*	*STP, third effluent discharging into the Vltava*	2.3	DL	65	5.1	72.4	248.6
53	*Cisarsky Island*	*STP, feed of sewage*	DL	360	55	51	466.0	424.5
54	Sarecky Creek	Confluence with Vltava River at Podbaba	DL	DL	DL	DL	DL	3.6
55	Vltava River	At Roztoky	1.3	DL	DL	DL	1.3	18.8
56	Uneticky Creek	Confluence with Vltava River	DL	DL	DL	DL	DL	4.3
57	Zelivka dam	Tap water after treatment	DL	DL	DL	2.3	2.3	0.3
58	Zelivka dam	Raw water before treatment	DL	DL	DL	2.4	2.4	1.1
59	Vlastejovice	Spring water	n.a.	n.a.	n.a.	n.a.	n.a.	0
60	Karany	Water supply plant, tap water after treatment	DL	DL	DL	DL	DL	1.3
61	Karany	Water supply plant, raw water	n.a.	n.a.	n.a.	n.a.	n.a.	3.8
62	Vltava River	At Kralupy	3.4	DL	DL	DL	3.4	19.6
63	Kunraticky Creek	Confluence with Vltava River	DL.	DL	DL	DL	DL	4.6
64	Zatissky Creek	Confluence with Vltava River	DL	DL	DL	DL	DL	44.1
65	Lhotsky Creek	Confluence with Vltava River	DL	DL	DL	DL	DL	44.7
66	Libussky Creek	Confluence with Vltava River	DL	DL	7.4	1.4	8.8	8.1
67	Rokytka Creek	Confluence with Vltava River	DL	DL	DL	1.8	1.8	16.1
68	Slivenecky Creek	Confluence with Vltava River	1.3	DL	DL	3.3	4.6	1.8
70	Vltava River	At Jarov	DL	DL	DL	DL	DL	4
71	Rokytka Creek	Kyjevsky pond	3	DL	DL	DL	3.0	17.8
72	*Dolni Chabry*	*STP, effluent discharging into the Drahanske River, filtered*	9.9	10	53	5	77.9	16.1
72a	*Dolni Chabry*	*STP, effluent discharging into the Drahanske River, unfiltered*	4.2	DL	43	3.9	51.1	n.a.
73	*Sedlec*	*STP, effluent, filtered*	11	DL	280	DL	291.0	1
73a	*Sedlec*	*STP, effluent, unfiltered*	3	DL	280	DL	283.0	n.a.
74	*Uhrineves*	*STP, effluent, filtered*	11	DL	330	3.9	344.9	0
75	*Uhrineves*	*STP, effluent, filtered*	n.a.	n.a.	n.a.	n.a.	n.a.	0
76	Uhrineves	Dubec, creek	n.a.	n.a.	n.a.	n.a.	n.a.	6.2
77	*Dolni Chabry*	*STP, effluent discharging into the Drahanske River, filtered*	n.a.	n.a.	n.a.	n.a.	n.a.	0

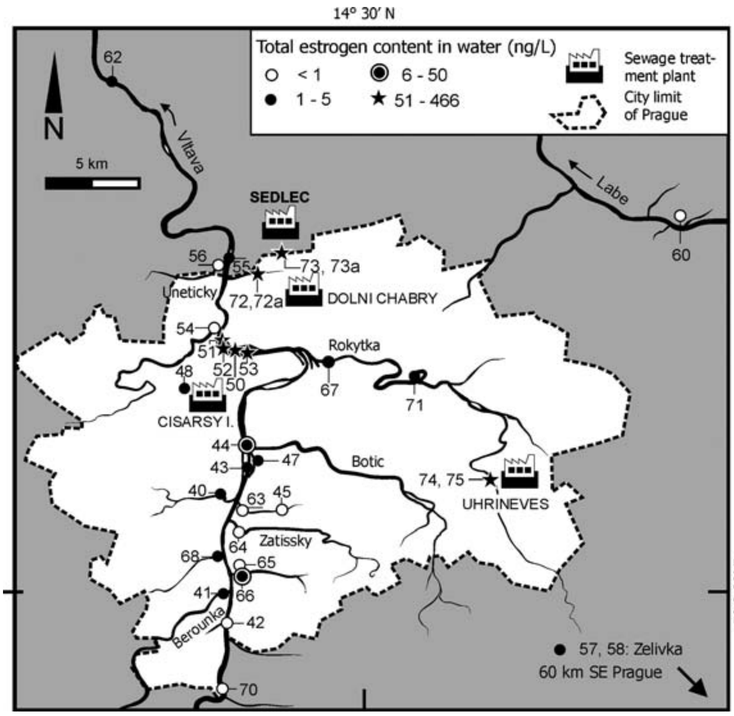

Fig. 1. Map showing total estrogen contents in water of the rivers and creeks, the effluents and feed of the STP of the study area.

Veslarsky Ostrov (sample no. 43) on the supply of estrogen-rich water by the Berounka River and also by small tributaries like the Zatissky Creek. However, when the individual estrogens are examined in detail, it is apparent that the estrogen content in the Vltava at Veslarsky Ostrov (no. 43) is totally represented by 17β-estradiol, whereas the tributaries have a very different estrogen composition. The estrogen contents of the Vltava at Veslarsky Ostrov (no. 43) cannot be explained, therefore, by a simple admixture of estrogens by the different tributaries. With the present dataset, we can provide no explanation of the observed differences in estrogen composition of the tributaries and Vltava.

The level of estrogen in the effluent water of the Cisarsky Island STP (sample nos. 50, 51, 52) as it flows to the Vltava was between 100 and 72.4 ng l^{-1}. Some 3 km downstream of that plant at Roztoky (sample no. 55), the estrogen content of the Vltava river was only 1.3 ng l^{-1}. About 10 km downstream of Roztoky, at Kralupy (sample no. 62), the estrogen content in the water of the Vltava again reached 3.4 ng l^{-1}.

The Gd_{ant} content of the Vltava river upstream of the confluence with the Berounka River (sample no. 70) amounted to 4 nmol m^{-3} (Figure 2), while that in the water of the Berounka River (sample no. 41) contained 7.9 nmol $m^{-3}{}_{Gdant}$. After the confluence, the Gd_{ant} in the Vltava River (sample no. 43) was 5.6 nmol m^{-3}. The Gd_{ant} content in the Vltava river stayed rather constant at 6.3 nmol m^{-3} until the Podoli water treatment plant (sample no. 46) and up to the water treatment plant on Cisarsky Island. The effluents of the Cisarsky Island STP contained 273.1, 250.5 and 248.6 nmol m^{-3} Gd_{ant} (sample nos. 50, 51, 52, respectively). The sewage entering the STP had the highest Gd_{ant} content of all the samples analyzed: 424.5 nmol m^{-3} (sample no. 53).

The G_{ant} and total estrogen content of the water of the Vltava River from its entrance to its exit from the city limits of Prague is given in Figure 3. The Gd_{ant} content in the Vltava increased slightly from the point it entered the city limits up to the Cisarsky Island STP. The effluents of the Cisarky Island STP entering the Vltava had a mean Gd_{ant} load of 57.4 nmol m^{-3}, which is a sudden increase over the 18.8 nmol m^{-3} in the Vltava River up to that point (sample no. 55). Downstream of the Cisarky Island STP, the Gd_{ant} content remained practically constant for approximately 30 km.

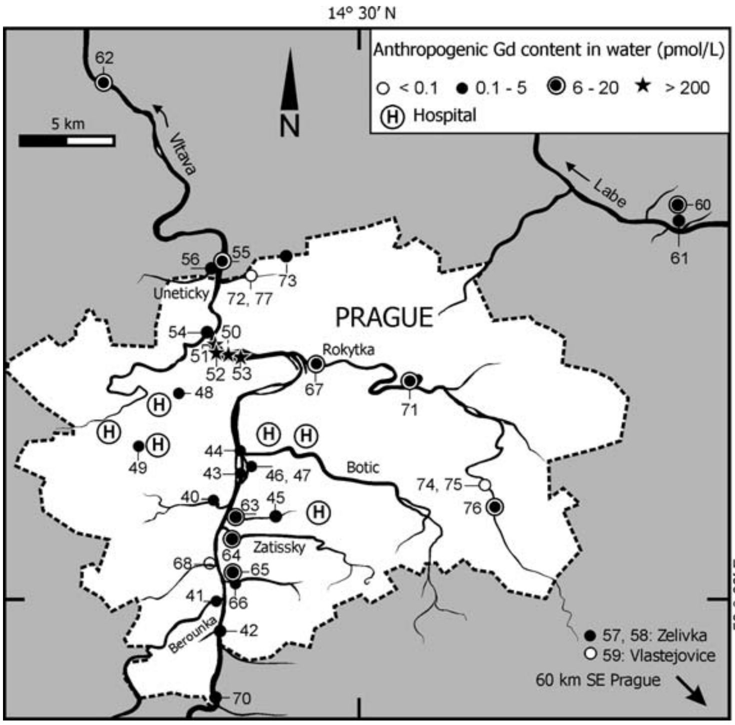

Fig. 2. Map showing the Gd_{ant} content in water of the rivers and creeks, the effluents and feed of the STP of the study area.

The Gd_{ant} content in the effluents of the small Dolni Chabri (sample no. 77) and Uhrineves (sample no. 74) STP were zero, while that of the effluents of Sedlec (sample no. 73) was 1 nmol m^{-3}. However, the Kyjevsky pond (sample no. 71) and the Rokytka Creek (sample no. 67), into which the Uhrineves STP discharges effluents, showed a significant level of Gd_{ant} – about 17 nmol m^{-3}. The Zatissky (sample no. 64) and Libussky (sample no. 66) creeks also showed high

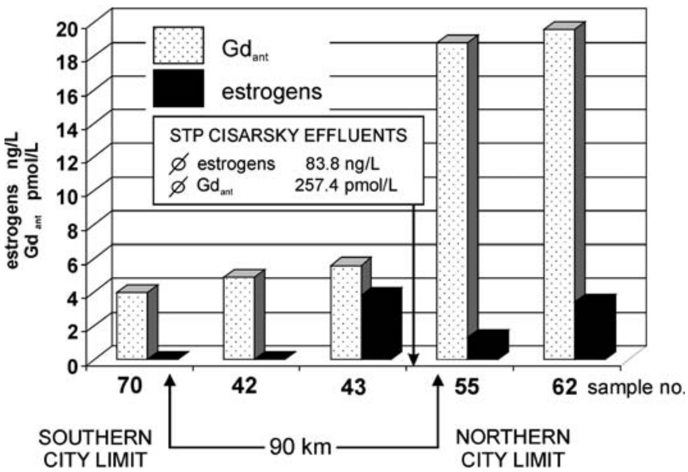

Fig. 3. Gd_{ant} and total estrogen content in the water of the Vltava River from the point it entered into Prague city limits to its exit and 20 km downstream. Between sample locations 43 and 55 the STP of Cisarsky Island discharges its effluents into the Vltava River. Notice the marked increase in Gd_{ant}, but a lack of increase in the estrogen contents downstream of the Cisarsky Island STP.

values of Gd_{ant}: about 44.1 and 8.1 nmol m^{-3}, respectively. Both creeks are not connected to an STP.

Conclusion

The different STP studied in this investigation show remarkable differences in their capacity to remove estrogens before discharging effluents into the surface water cycle. Our results demonstrate that the rivers have a measurable self-cleaning potential with respect to the natural and synthetic estrogens introduced via STP or leakages in the city sewage system. About 10 km downstream of the Cisarsky STP the total estrogen content in the Vltava river was only 1.3 ng l^{-1} even though the STP on Cisarsky Island discharges effluents containing between 100 and 72 ng l^{-1} of estrogens into the Vltava river. The tributaries entering the Vltava between the STP on Cisarky Island and 10 km further downstream are very small so that the great reduction in the estrogen content in the Vltava river water that we observed can not have occurred by simple dilution. The self-cleaning effect can also be recognized along the Rokytka Creek (Figures 1, 2). The Uhrineves STP (sample no. 74) discharges into Ricansky Creek, a tributary of Rokytka Creek, and the water had a total estrogen content of 344.9 ng l^{-1}. Some 10 km downstream of the Uhrineves STP, in Rokytka creek (sample no. 71), the estrogen content of the water was only 3 ng l^{-1} and a further 10 km downstream (sample no. 67), it was as low as 1.8 ng l^{-1} (Figures 1, 2). Nevertheless, one should not rely only on the self-cleaning capacity of rivers. The potential of activated sludge STP to efficiently remove steroid estrogens is fast becoming one of the key water quality issues in densely populated and water-deficient areas (Johnson *et al.*, 2000). This is a particularly interesting development because of the increasing number of cases where settlements rely on water works that obtain their drinking water from river bank filtration, rivers or lakes that suffer from the input of STP effluents.

The estrogen contents of the filtered (sample nos. 72, 73) and unfiltered (sample nos. 72a, 73a) effluent water from the small STP of Dolni Chabri and Sedlec were not very different. This leads to the conclusion that the suspended matter is not the dominant estrogen carrier in the effluents. The slightly lower estrogen content in the unfiltered samples can be explained by elevated bacterial activity and the consequent degradation of the estrogens in the unfiltered samples during the short time span between sampling and analysis despite the storage of all samples at temperatures near 0°C.

The Gd_{ant} contents of the surface waters of Prague ranged from 0 to 44 nmol m^{-3}. It was not only the Vltava and the Berounka rivers and some creeks into which the effluents of STP are discharged that showed increased Gd_{ant} contents; several creeks within Prague that are not connected with STP also had high Gd_{ant} values.

The cause of the exceptionally high estrogen level in the waters of the Libussky and Slivenecky creeks must relate to the seepage of sewage from the canalization into the creek upstream of the sampling point or to a direct input of sewage. This conclusion is supported by the elevated Gd_{ant} levels found in the waters of both creeks.

Based on the results of this study we conclude that the rapid degradation of estrogens in surface waters ensures that the estrogen concentration gradient is a very precise and sensitive guideline by which to pin-point sewage leaks into surface run-off and ground waters. The conservative behavior of Gd_{ant} enables an input of sewage to be followed, not only in the surface water cycle but also into aquifers used for drinking water production (Fuganti *et al.*, 1996; Möller *et al.*, 2003).

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