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Groundwater from Infiltration Galleries Used for Small Public Water Supply Systems: Contamination with Pesticides and Endocrine Disruptors

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Abstract Infiltration galleries are among the oldest known means used for small public water fountains. Owing to its ancestral origin they are usually associated with high quality water. Thirty-one compounds, including pesticides and estrogens from different chemical families, were analysed in waters from infiltration galleries collected in Alto Douro Demarcated Wine region (North of Portugal). A total of twelve compounds were detected in the water samples. Nine of these compounds are described as presenting evidence or potential evidence of interfering with the hormone system of humans and wildlife. Although concentrations of the target analytes were relatively low, many of them below their limit of quantification, four compounds were above quantification limit and two of them even above the legal limit of 0.1 μg/L: dimethoate (30.38 ng/L), folpet (64.35 ng/L), terbuthylazine-desethyl (22.28 to 292.36 ng/L) and terbuthylazine (22.49 to 369.33 ng/L).

Keywords Infiltration galleries · Pesticides · Endocrine disruptors · Groundwater · GC-MS

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Infiltration galleries are permeable, horizontal or inclined conduits, into which water can infiltrate from an overlying or adjacent source, characterized by providing a continuous source of water supply that is diverted to the point of interest by gravity through channels/pipelines (Kresic 2007). They are among the oldest known means utilized for small public water supply systems in small villages in the North of Portugal, namely in the Alto Douro Demarcated Wine region.

Routine microbiological and chemical analysis of water supplies from infiltration galleries are regularly applied only when no other water supply is available in the region. Concerning the chemical quality of the water produced by a gallery it is dependent upon the chemical quality of the groundwater present locally, and the chemical quality of the surface source from which infiltration is received. Nowadays there are thousands of anthropogenic compounds mixed in our environment whose possible mechanisms of toxicity, endocrine disruption and physiological outcomes have converted this subject in an emerging study field (Díaz et al. 2009). Owing to ancestral origin of infiltration galleries, inhabitants of these small villages, like many others around the world, associate this type of water with high purity water. However, no studies were found about quantification of pesticides and endocrine disruptor compounds (EDCs) in these waters collected in a region of intense agricultural activity dedicated to viniculture.

The presence of pesticides in waters for human consumption is regulated by national and international rules that establish the maximum concentration of each pesticide at 0.1 μg/L and the total amount of pesticides at 0.5 μg/L in drinking water. For some organochlorines, as aldrin or dieldrin, the maximum individual concentration is even lower 0.03 μg/L (Mansilha et al. 2010).

EDCs, or potential endocrine disruptors include not only pesticides, but other compounds such as polycyclic aromatic hydrocarbons, some heavy metals and steroid hormones (e.g., estrogens) (Birkett and Lester 2003). Concerning the estrogens, there are no parametric values, however, because their estrogenic potency is often several orders of magnitude higher than that of the pesticides, their significantly lower environmental concentrations and relative resistance to biodegradation might, in fact, have a greater environmental impact (Gomes et al. 2003; Sumpter 2005). So, there is concern about the presence of estrogens in drinking water even at nanogram concentrations that may be enough to present a health impact (Stahlschmidt-Allner et al. 1997).

The goal of this work was the evaluation of water quality in small public water fountains of infiltration galleries, located in small villages in the North of Portugal. Trace analysis of thirty-one compounds, including estrogens and pesticides from different chemical families, some of them with endocrine disrupting properties were performed by gas chromatography–tandem mass spectrometry.

Materials and Methods

Reference standards of estrogens (Estrone, Estradiol) and pesticides from different chemical families (EPTC, Folpet, Phosmet, 2,4-D, Atrazine-desethyl, Terbuthylazine-desethyl, Iprodione, Dimethoate, Atrazine, Atrazine-d_5, Cyromazine, Terbuthylazine, Pirimicarb, Alachlor, Metalaxyl, Linuron, S-Metolachlor, Aldrin, Thiamethoxam, Pendimetaline, Cyprodinil, Tolyfluanid, Fludioxonil, Dieldrin, Endrin, o.p′-DDT, Fenehexamid, Acetamiprid, Methoxychlor, Azoxystrobin) with purity > 98% were obtained from Sigma–Aldrich (St. Louis, MO, USA). Solvents were organic trace analysis grade SupraSolv from Merk. Ultrapure water (0.054 μS/cm) was obtained by using a Milli-Q system from Millipore (Milford, MA, USA).

Individual stock standard solutions of 250 mg/L were prepared in methanol by exact weighing of the high-purity substances and accurate dilution. A mixture was then prepared, also in methanol, containing 1.5 mg/L of each individual compound. Calibration standard solutions, with concentration levels ranging from 15 μg/L to 360 μg/L were prepared by appropriate dilution of the 1.5 mg/L mixture with methanol in 10 mL volumetric flasks. Stock standard solutions were stored in amber glass-stoppered flasks at 4°C.

Matrix-standard calibration solutions (residue-free matrix spiked with standards) with concentration levels ranging from 15 to 360 μg/L were prepared by spiking 500 mL of water with different volumes of the 1.5 mg/L mixture just before extraction.

Nine water samples were collected in small villages in the North of Portugal near Douro River (Fig. 1, Table 1), in July 2009. Prior to extraction, 500 mL volume of water samples were filtered through glass fibber filters (Whatman, GF/F 47 mm, Maidstone, England) and spiked with the internal standard (atrazine-d_5 or 2-Chloro-4-pentadeuteroethylamino-6-isopropylamino-1,3,5-triazine) at 240 μg/L. Blank samples were prepared by adding the internal standard to residue-free water matrix.

Solid phase extraction was conducted in LiChrolut EN RP-18 SPE cartridges (100 mg/200 mg, 6 mL) from Merck (Darmstadt, Germany) using the following conditions: (a) conditioning step, by the sequential addition of 7 mL of ethyl acetate, 7 mL of methanol and 7 mL of Milli-Q water at a flow rate of 1 mL/min; (b) loading step, by passing 500 mL of the sample through the cartridge at a flow of 5 mL/min; (c) washing step, by rinsing the cartridge with 5 mL water and dried by vacuum pressure during approximately 60 min; and (d) elution performed with 2 × 2.5 mL of methanol and 2 × 2.5 mL acetonitrile, at a flow of 1 mL/min. After elution, the extracts were evaporated to dryness in a rotative evaporator (Buchi/Brinkman Rotavapor RE-111 & Water Bath B-461) and then re-suspended until a final volume of 500 μL in methanol and directly analyzed by GC/MS.

Chromatographic analyses were carried out in a Shimadzu GCMS-QP2010 Gas Chromatograph Mass Spectrometer equipped with a fused-silica capillary column coated with 5% diphenylmethylsiloxane, VF-5 MS (30 × 0.25 mm I.D., 0.25 μm film thickness) from Varian. High-purity helium (99.9999%) at a constant flow rate of 1.5 mL/min was used as the carrier gas.

For injection an AOC-5000 auto injector was used. Injections (1 μL) were made in the splitless mode with a 1.0 min purge-off time and injector temperature set at 275°C.

Samples were analyzed using the following oven temperature programme: initial temperature 60°C (held for 2 min), increased by 10°C/min to 200°C (held for 1 min), increased again by 10°C/min to 275°C and held at this temperature for 10 min.

GC was directly interfaced to a Shimadzu QP 2010 quadrupole mass spectrometer with an interface temperature of 250°C, and ionization by 70 eV electron impact. The transfer line was set at 275°C and the source at 200°C.

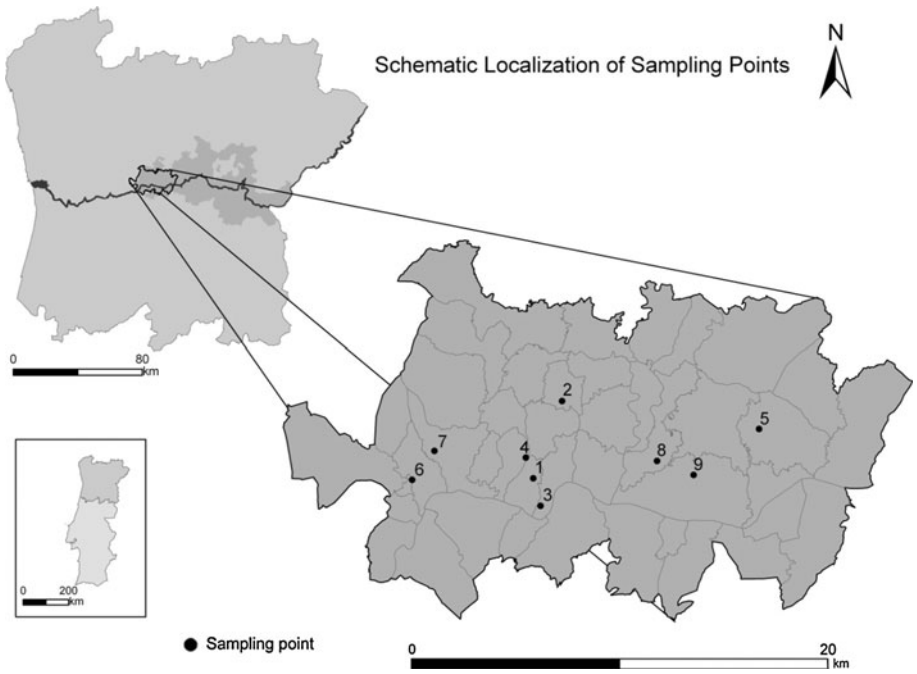

Fig. 1 Schematic localization of 9 infiltration galleries (fountains for public supply) sampled in the 'Alto Douro Demarcated Wine region' (marked on dark grey)

Table 1 Infiltration galleries (fountains for public supply) sampling location data

Sample code	Coordinates: latitude/longitude	Area name
1	41°09′49.40″N 7°49′06.95″W	Fontelas
2	41°11′06.95″N 7°48′27.84″W	Loureiro
3	41°09′06.40″N 7°48′51.04″W	Cederma
4	41°10′21.52″N 7°49′48.52″W	Oliveira
5	41°11′04.67″N 7°41′21.07″W	Galfura
6	41°09′47.84″N 7°53′15.79″W	Mesão Frio
7	41°10′32.70″N 7°52′29.73″W	Vila Marim
8	41°10′15.64″N 7°44′51.27″W	Vilarinho
9	41°09′53.98″N 7°43′36.18″W	Canelas

Positive fragment ions (*m/z*—ions mass/charge ratio) were analyzed over 43–500 m/z mass range in SCAN mode and in selected-ion monitoring (SIM) mode.

The chromatographic method gives, as usual, response to several substances simultaneously, including analytes and interferences; thus, it is important to assess specificity/selectivity. This can be done by comparison of mass spectra of chromatographic peaks with referenced standards. As acceptance criteria the responses of interfering peaks at the retention time of the analyte should be less than 30% of the response of the limit of quantification standards (SANCO 2009).

One of the most common definition of limit of quantification (LOQ) assumed to be the lowest amount of an analyte in a sample that can be quantified with acceptable precision and accuracy whereas the limit of detection (LOD) is the lowest concentration of an analyte that can be reliably differentiated from the background noise but not necessarily quantified as an exact value (ICH 2005). Both can be calculated based on the calibration curve parameters (ICH 2005; Miller and Miller 2005; NCCLS 2004).

Measurements by mass spectrometry coupled with chromatographic separation technique provided data on retention times, ions mass/charge ratio, abundance and ionization profile as described in Table 2.

The chromatographic peaks of the analytes must have a signal/noise ratio (S/N) greater than 3:1 and a shape and retention time similar to those obtained from calibration standards within a specified range of variations with $\pm 0.5\%$ tolerance for GC (SANCO 2009). When the identification is carried out in SIM mode, ions must meet the calibration standards measured under the same conditions. Intensity ratios for principal ions should be within the limit of tolerance of 25%. A minimum of four ions must be present with a relative intensity $\geq$ 10% of the base peak and the molecular ion should be included, if present, in the reference spectrum with a relative intensity also above 10%.

Several spectral libraries were used (NIST, PEST, PESTEI_3, PESTNCI3, WILEY229, SZTERP). Additionally, a library was created for comparison purposes with mass spectra of the pure standards used in this work.

Results and Discussion

Trace analysis of thirty-one compounds was performed by GC/MS in nine samples of water from small public

Table 2 Method validation data

	EDC/pesticides	$b_w \pm t_{(n-2)}.S_{(b)w}$ (95%)	$a_w \pm t_{(n-2)}.S_{(a)w}$ (95%)	$S_{(y/x)w}$	r_w	LOD (ng/L)	LOQ (ng/L)
1	EPTC	143.57 ± 4.16	−781.11 ± 796.79	437.09	0.9965	9.10	30.40
2	Folpet	73.77 ± 5.03	1502.26 ± 999.45	460.83	0.9938	18.70	62.50
3	Phosmet	215.61 ± 10.88	257.38 ± 2161.83	996.80	0.9963	13.90	46.20
4	2,4-D	11.38 ± 0.24	−16.41 ± 45.19	24.79	0.996	6.50	21.80
5	Atrazine-desethyl	155.17 ± 2.69	−884.61 ± 516.10	283.12	0.9987	5.50	18.20
6	Terbuthylazine-desethyl	204.23 ± 3.68	−336.09 ± 705.44	386.98	0.9995	5.70	18.90
7	Iprodione	40.11 ± 0.87	449.60 ± 173.41	79.96	0.9994	6.00	19.90
8	Dimethoate	154.23 ± 1.27	−1113.67 ± 242.28	132.91	0.9992	2.60	8.60
9	Atrazine	161.08 ± 3.09	−602.15 ± 592.67	325.12	0.996	6.10	20.20
10	Cyromazine	22.80 ± 2.08	−210.07 ± 413.60	218.60	0.9966	28.80	95.90
11	Terbuthylazine	207.47 ± 1.05	−245.39 ± 200.61	110.05	0.9999	1.60	5.30
12	Pirimicarb	640.96 ± 11.40	−779.31 ± 2265.43	1044.56	0.9984	4.90	16.30
13	Alachlor	189.68 ± 2.02	1276.34 ± 387.33	212.48	0.9977	3.40	11.20
14	Metalaxyl	142.94 ± 9.19	−539.94 ± 1827.37	842.58	0.9968	17.70	58.90
15	Linuron	184.07 ± 3.19	−125.53 ± 611.02	335.19	0.9983	5.50	18.20
16	S-Metolachlor	178.01 ± 2.60	−834.52 ± 497.18	272.74	0.9984	4.60	15.30
17	Aldrin	19.91 ± 1.15	−114.13 ± 219.90	120.63	0.9988	18.20	60.60
18	Thiamethoxam	96.61 ± 1.97	−159.94 ± 391.89	180.69	0.9977	5.60	18.70
19	Pendimethalin	34.06 ± 1.01	236.39 ± 193.19	105.98	0.9982	9.30	31.10
20	Cyprodinil	886.28 ± 12.07	−2042.23 ± 2398.71	1106.02	0.9988	3.70	12.50
21	Tolyfluanid	110.48 ± 4.06	924.17 ± 806.44	371.84	0.9976	10.10	33.70
22	Fludioxonil	310.56 ± 4.90	−747.35 ± 974.07	449.13	0.9994	4.30	14.50
23	Dieldrin	133.93 ± 1.81	490.24 ± 345.93	189.77	0.9997	4.30	14.20
24	Endrin	23.66 ± 1.27	782.46 ± 242.52	133.04	0.9995	16.90	56.30
25	o.p′-DDT	64.67 ± 0.98	−135.30 ± 188.40	103.35	0.9997	4.80	16.00
26	Fenehexamid	30.22 ± 1.42	74.06 ± 282.55	130.28	0.9953	12.90	43.10
27	Acetamiprid	53.47 ± 3.13	−357.54 ± 621.68	286.65	0.9976	16.10	53.60
28	Methoxychlor	153.73 ± 4.71	216.13 ± 901.08	494.30	0.998	9.60	32.20
29	Estrone	90.79 ± 1.88	−542.32 ± 359.99	197.48	0.9982	6.50	21.80
30	Estradiol	76.11 ± 1.21	−553.75 ± 230.97	126.70	0.9988	5.00	16.60
31	Azoxystrobin	56.07 ± 3.54	−370.69 ± 704.02	324.62	0.9972	17.40	57.90

Calibration parameters and related uncertainties

b_w—weighted slope, a_w—weighted intercept, r_w—weighted correlation coefficient; $S(b)_w$ and $S(a)_w$—standard deviations of the weighted slope and weighted intercept, $S(y/x)_w$—standard deviation of y-residuals of weighted regression line. LOD—limit of detection; LOQ—limit of quantification

fountains of infiltration galleries. The methodology was previously validated by us according mainly the International Conference on Harmonisation recommendations (Mansilha et al. 2010) using a weighted least squares linear regression procedure as heteroscedasticity has been verified for the target analytes. Calibration parameters are shown in Table 2.

A total of twelve compounds (folpet, 2,4-D, atrazine-desethyl, terbuthylazin-desethyl, dimethoate, terbuthylazin, dieldrin, endrin, o.p′-DDT, methoxychlor, estrone, estradiol) were detected in the nine water samples analysed. The remaining nineteen compounds screened by the GC-MS method were not detected in any sample. The concentrations of the target analytes were relatively low, many of them being frequently below their LOQ (2,4-D, atrazine-desethyl, dieldrin, endrin, o.p′-DDT, methoxychlor, estrone, estradiol). Only four compounds were above the LOQ (Table 3).

The calculation of analytes concentration in samples has an error associated with concentration estimation. Slope, intercept and the instrumental signal are subject to random errors that should not be ignored. Thus, this determination is complex but important to guarantee the reliability of results. Associated Errors Measurement (AEM) ranged between 0.57 and 6.78 ng/L, corresponding to a value around 2% of the concentration levels. It was lower than 10% in all measurements (Table 3).

In addition, deuterated-atrazine was used as a quality control internal standard, so-called procedural or instrument internal standard, for process evaluation through recovery studies, being added in a constant amount to samples and

Table 3 Results obtained in the analysis of estrogens and pesticides from different chemical families (some of them with endocrine disrupting properties) in waters from infiltration galleries used for small public water supply systems in small villages in the North of Portugal

EDCs/ pesticides	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6		Sample 7		Sample 8		Sample 9	
	Conc. (ng/L)	AEM (ng/L)	Conc. (ng/L)	AEM (ng/L	Conc. (ng/L)	AEM (ng/L)	Conc. (ng/L)	AEM (ng/L)	Conc. (ng/L)	AEM (ng/L)	Conc. (ng/L)	AEM (ng/L	Conc. (ng/L)	AEM (ng/L)	Conc. (ng/L)	AEM (ng/L)	Conc. (ng/L)	AEM (ng/L)
Folpet	n.d.	–	n.d.	–	n.d.	–	64.35	± 6.78	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
2,4-D	12.43	*	n.d.	–	n.d.	–	n.d.	–	6.54	*	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Atrazine-desethyl	n.d.	–	n.d.	–	n.d.	–	n.d.	–	9.25	*	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Terbuthylazin-desethyl	n.d.	–	n.d.	–	n.d.	–	292.36	± 4.70	n.d	–	n.d.	–	22.28	± 2.05	108.77	± 2.44	n.d.	–
Dimethoate	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d	–	30.84	±1.97	n.d.	–	n.d.	–	n.d.	–
Terbuthylazin	n.d.	–	n.d.	–	n.d.	–	369.33	± 2.21	n.d	–	n.d.	–	3.78	*	22.49	± 0.57	n.d.	–
Dieldrin	n.d.	–	n.d.	–	n.d.	–	11.96	*	n.d	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Endrin	n.d.	–	n.d.	–	n.d.	–	n.d.		n.d	–	n.d.	–	n.d.	–	n.d.	*	24.15	*
o.p′-DDT	n.d.	–	n.d.	–	n.d.	–	7.95	*	n.d	–	n.d.	–	6.47	*	n.d.	–	n.d.	–
Methoxychlor	n.d.	–	n.d.	–	n.d.	–	11.56	*		–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Estrone	n.d.	–	n.d.	–	n.d.	–	18.30	*	7.44	*	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Estradiol	n.d.	–	n.d.	–	n.d.	–	n.d.	–	8.10	*	n.d.	–	n.d.	–	n.d.	–	n.d.	–

AEM—Associated error measurement applying de equation $S_{x_{0w}} = \frac{S_{(y/x)w}}{b}\sqrt{\frac{1}{w_0}+\frac{1}{n}+\frac{(y_0-\overline{y_w})^2}{b^2\sum_i\left(w_i x_i^2 - n\overline{x_w^2}\right)}}$, *AEM cannot be estimated when measurement is below LOQ

calibration standards prior to extraction. The mean recovery and standard deviation was 90.74 ± 12.08% with a coefficient of variation (CV) of 13.31%. The control limits established are set between 70 and 120%, with CV ≤ 20% according to SANCO (2009).

None of the compounds under study were detected in samples 2 and 3. One single pesticide was detected in three other samples, but each one presented a different compound (2,4-D, dimethoate and endrin, respectively in samples 1, 6 and 9). However, only dimethoate was above the limit of quantification. Estrone and estradiol and two pesticides (2,4-D, atrazine-desethyl) were detected in sample 5, but below quantification limits. Samples 7 and 8 presented three pesticides, two of them were common in these two samples, namely, terbuthylazine-desethyl and terbuthylazine. DDT was detected below quantification limit in sample 7 and endrin was detected in sample 8. The most contaminated sample was sample 4, with seven compounds including EDCs and other pesticides: folpet, terbuthylazine-desethyl and terbuthylanzin were quantified and dieldrin, o.p′-DDT, methoxychlor and estrone were below quantification limit.

The maximum concentration of each pesticide is 0.1 μg/L with a total amount of pesticides of 0.5 μg/L for drinking water. Sample 4 exceed the parametric values for terbuthylazine-desethyl and terbuthylazine (0.292 and 0.369 μg/L, respectively) and for the total amount of pesticides (0.661 μg/L). Sample 8 exceed the parametric value for terbuthylazine-desethyl (0.108 μg/L). All other samples are in agreement with legislation.

Nine compounds that presented evidence or potential evidence of being EDCs (estrone, estradiol, o.p′-DDT, methoxychlor, dieldrin, endrin, 2,4-D, dimethoate, folpet) were detected in samples under study (the first four were classified as Cat 1, the other four were classified as Cat 2 by EU, the last compound was highlighted by EPA, COM 1999, SEC 2007).

Among of the most important group of chemicals considered as EDCs are steroids (Zarzycki et al. 2009). Residual levels of estrone and estradiol were detected in two water samples.

Folpet is a potential EDC (EPA 2004) that has been used in agricultural practices for the past 50 years. Studies performed in vitro have found folpet to induce cell-cycle deregulation (Canal-Raffin et al. 2008). This compound was quantified within the legal limits in one sample. Moreover, some pesticides detected at residual level in the water samples are not allowed in European agriculture, however, it analysis is justified because they are very persistent and present a long half-life: DDT, methoxychlor, dieldrin and endrin. Despite the fact that the use of these compounds ceased many years ago, they are very persistent in the environment and are still present in nature from former applications (Tiemann 2008, Buser et al. 2009; Matsumoto et al. 2009).

The general idea that water from infiltration galleries present always high quality was not confirmed. The sampling region chosen for this study was located in a small area (around 100 km^2). However, the qualitative and quantitative pesticide profile of water samples analysed and, therefore, its quality was clearly different. Target EDCs and other pesticides were found in seven of the nine samples and the most frequent was terbuthylazine and its metabolite terbuthylazine-desethyl that exceeded, in two samples, the 0.1 μg/L EU limit for individual pesticides. The intensive character of the local agriculture contributed to the diversity of pesticides that were detected and quantified. Winegrowers use different pesticides to control the diverse pest that affect the wine.

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References

Birkett JW, Lester JN (2003) Endocrine disrupters in wastewater and sludge treatment processes. CRC Press LLC Lewis Publishers, Florida

Buser HR, Müller MD, Buerge IJ, Poiger T (2009) Composition of aldrin, dieldrin, and photodieldrin enantiomers in technical and environmental samples. J Agric Food Chem 57:7445–7452

Canal-Raffin M, l'Azou B, Jorly J, Hurtier A, Cambar J, Brochard P (2008) Cytotoxicity of folpet fungicide on human bronchial epithelial cells. Toxicology 249:160–166

COM (1999) 706, Commission of the European Communities (1999). Community strategy for endocrine disrupters a range of substances suspected of interfering with the hormone systems of humans and wildlife. Communication from the commission to the council and the European parliament. Brussels, Belgium

Díaz G, Ortiz R, Schettino B, Vega S, Gutiérrez R (2009) Organochlorine pesticides residues in bottled drinking water. Bull Environ Contam Toxicol 82:701–704

Gomes RL, Scrimshaw MD, Lester JN (2003) Determination of endocrine disrupters in sewage treatment and receiving waters. Trend Anal Chem 22:697–707

ICH, International Conference on Harmonisation (2005) Harmonised tripartite guideline. Validation of analytical procedures: text and methodology Q2(R1)

Kresic N (2007) Hydrogeology and groundwater modeling, 2nd edn. CRC Press-Taylor & Francis Group, Florida

Mansilha C, Melo A, Rebelo H, Heitor A, Ferreira IMPLVO, Pinho O, Domingues V, Pinho C, Gameiro P (2010) Quantification of endocrine disruptors and pesticides in water by gas chromatography-tandem mass spectrometry. Method validation using weighted linear regression schemes. J Chromatogr A 1217:6681–6691

Matsumoto E, Kawanaka Y, Yun SJ, Oyaizu H (2009) Bioremediation of the organochlorine pesticides, dieldrin and endrin, and their occurrence in the environment. Appl Microbiol Biot 84:205–216

Miller JN, Miller JC (2005) Statistics and chemometrics for analytical chemistry, 5th edn. Pearson Education Limited, England

NCCLS, National Committee for Clinical Laboratory Standards (2004) Approved Guideline, EP17-A. Protocols for Determination of Limits of Detection and Limits of Quantitation

SANCO/10684/2009 of European Union (2009) Method validation and quality control procedures for pesticide residues analysis in food and feed

SEC (2007) 1635. Commission of the European Communities (2007). Commission staff working document on the implementation of the Community Strategy for Endocrine Disrupters—a range of substances suspected of interfering with the hormone systems of humans and wildlife. Brussels, Belgium

Stahlschmidt-Allner P, Allner B, Rombke J, Knacker T (1997) Endocrine disrupters in the aquatic environment. Environ Sci Pollut R 4:155–162

Sumpter JP (2005) Endocrine disrupters in the aquatic environment: an overview. Acta Hydroch Hydrob 33:9–16

Tiemann U (2008) In vivo and in vitro effects of the organochlorine pesticides DDT, TCPM, methoxychlor, and lindane on the female reproductive tract of mammals: a review. Reprod Toxicol 25:316–326

Zarzycki PK, Wlodarczyk E, Baran M (2009) Determination of endocrine disrupting compounds using temperature-dependent inclusion chromatography. I. Optimization of separation protocol. J Chromatogr A 1216:7602–7611