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Screening of pesticides, veterinary drugs and heavy metals in Baltic Sea waterways

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1. Introduction

A screening analysis for 275 pesticides, 101 veterinary drugs and 19 metals and metalloids was conducted on water samples taken from 8 different waterways leading to the Baltic Sea at locations close to their mouths. Samples were taken from rivers in the regions of Syddanmark and Midtjylland, both in Denmark, and from Schleswig-Holstein, Mecklenburg-Vorpommern and Brandenburg, in Germany. **Table 1** summarizes the details of the samples collected, including the precise coordinates and the time and date for each specimen taken. Samples were collected in two sets in autumn 2018 (25.10.2018 and 05.11.2018) by Greenpeace Denmark and Greenpeace Germany and received at the Greenpeace Research Laboratories 24h later (26.10.2018 and 06.11.2018, respectively) for sample preparation and analysis.

Figure 1. Sample being taken from Rarup A at As Vig (Midtjylland), Denmark.

Table 1. Samples analysed in the present work. Sampling local times and dates are provided; locations are defined by their coordinates.

Sample code	River name	Town (Region)	Country	Latitude	Longitude	Date	Time (local)
DK18004	Syltemade A	Vester Skerninge (Syddanmark)	Denmark	55° 03' 03.7" N	10° 27' 21.5" E	25-Oct-2018	9:35
DK18005	Rarup A	As Vig (Midtjylland)	Denmark	55° 46' 07.9" N	10° 00' 34.6" E	25-Oct-2018	10:45
DE18007	Kopendorfer Au	Fehmarn (Schleswig-Holstein)	Germany	54° 28' 38.0" N	11° 01' 59.6" E	25-Oct-2018	12:26
DE18008	Füsinger Au	Schaalby (Schleswig-Holstein)	Germany	54° 32' 08.6" N	9° 38' 33.5" E	25-Oct-2018	17:00
DE18009	Mühlenfließ	Bad Doberan (Mecklenburg-Vorpommern)	Germany	54° 07' 06.9" N	11° 54' 47.0" E	5-Nov-2018	8:30
DE18010	Warnow	Schwaan (Mecklenburg-Vorpommern)	Germany	53° 56' 20.2" N	12° 06' 38.7" E	5-Nov-2018	9:30
DE18011	Peene	Neetzow (Mecklenburg-Vorpommern)	Germany	53° 54' 55.8" N	13° 25' 32.2" E	5-Nov-2018	11:45
DE18012	West Oder	Mescherin (Brandenburg)	Germany	53° 14' 56.5" N	14° 26' 03.5" E	5-Nov-2018	15:15

2. Materials and methods

Pesticides and veterinary drugs were determined by liquid chromatography high resolution mass spectrometry (LC-Orbitrap-MS), after solid phase extraction (SPE) of the samples, following the method previously developed and validated in separate work (Casado et al., 2018). The concentrations of metals and metalloids were determined for all samples by inductively coupled plasma mass spectrometry (ICP-MS), following acidification.

High purity standards for the screened 275 pesticides, listed in **Table A1** in **Annex,** and 101 veterinary drugs, listed in **Table A2** in **Annex**, were obtained from Lab Instruments (Castellana Grotte, Italy). Mixtures of standards, dilutions and calibration solutions were prepared in methanol in the case of the pesticides and in acetonitrile/water (1:1) for the veterinary drugs.

Methanol (Optima), acetonitrile (Optima), formic acid (Optima) and ammonium hydroxide 28-30% solution in water were obtained from Thermo Fisher Scientific (Waltham, MA, USA). Ultrapure water was produced by a PureLab Elga-Veolia system (Paris, France) and SPE cartridges Oasis HLB 200 mg were purchased from Waters (Milford, MA, USA).

2.1. Analysis of pesticides and veterinary drugs

2.1.1. Sample preparation

Samples were extracted by SPE with an automatic AutoTrace system (Thermo Fisher Scientific).

In brief, Oasis HLB cartridges were firstly conditioned with 10 mL of methanol followed by 10 mL of ultrapure water adjusted to pH 3 with formic acid. Next, 200 mL of each water sample, previously filtered and acidified to pH 3, were loaded on the cartridge at a flow rate of 5 mL min^{-1}. Once the whole sample had passed through the extraction material, the cartridge was dried under a gentle nitrogen flow. Pesticides and veterinary drugs were then eluted with 10 mL of methanol. Finally, this 10-mL methanol extract was transferred into a TurboVap vessel and blown down, under a stream of nitrogen, to a final volume of 1 mL in the same solvent, avoiding the evaporation to dryness. Each individual sample was prepared and analysed in triplicate (i.e. extracting three separate aliquots from each sample) in order to assure the analytical quality of the measurement of the different parameters.

2.1.2. Determination conditions

Determination of the pesticides and the veterinary drugs was carried out using two independent methods with a liquid chromatography - electrospray ionisation – quadrupole Orbitrap tandem mass spectrometry (LC-ESI-Q-Orbitrap-MS) system (Thermo Fisher Scientific). In both cases, analytes were separated with an Accucore aQ C18 column (100 x 2.1 mm, 2.6 µm) LC column (Thermo Fisher Scientific) at 25 ºC with the same mobile phase constituents: water containing 2% methanol, 0.1% formic acid and 5 mM ammonium formate (phase A) and methanol containing 2% water, 0.1% formic acid and 5 mM ammonium formate (phase B). Two different gradients were applied to separate the pesticides and the veterinary drugs: 0 - 0.5 min 2% B, 7 min 70% B, 9 - 12 min 100% B for the pesticides and 0 - 0.5 min 2% B, 3 min 50% B, 6 - 10.5 min 100% B for the veterinary drugs. In both methods the column was re-conditioned to initial conditions between injections for 5 min. The mobile phase flow was 300 µL min^{-1} and the injection volume of the extract was 1 µL for the pesticides and 2 µL for the veterinary drugs.

The Orbitrap mass spectrometer was a Q Exactive Focus, furnished with a HESI-II electrospray ionisation source, a quadrupole mass filter, an HCD collision cell, a C-trap and the high-resolution Orbitrap mass analyser.

The source settings for the pesticides were: sheath gas flow 40 a.u., auxiliary gas flow 10 a.u. at 350 ºC, spray voltage 3.3 V and capillary temperature 325 ºC. The ionisation conditions of the veterinary drugs were: sheath gas flow 30 a.u., auxiliary gas flow at 5 a.u. at 450 ºC, spray voltage 3.5 V and capillary temperature 350 ºC.

The MS acquisition methods for pesticides and veterinary drugs were analogous. In both cases, full-scan data were collected at a resolution of 70,000 (FWHM at 200 Da) within the 80 – 1000 Da scan range. Simultaneously, the system acquired data-dependent tandem mass spectra (dd-MS^2) for each precursor ion at the different elution times at a resolution of 17,500 (FWHM at 200 Da).

The full-scan data was used for the quantification of 252 of the 275 detectable pesticides, while the dd-MS^2 spectra permitted the confirmation of their identities. In the case of the veterinary drugs only detection and identification were undertaken for all the 101 substances, using both the full-scan and the dd-MS^2 data. The quantification of the pesticides was performed with external calibration curves ranging from the LOQs to 2 µg L^{-1}.

2.2. Analysis of metals and metalloids

Concentrations of metals and metalloids were determined for all samples by ICP mass spectrometry (MS) following filtration and acidification. A portion of each sample was filtered through a 0.45 micron filter and then acidified by the addition of concentrated nitric acid to give a final concentration of 5% v/v.

Acidified samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilizing a collision cell with helium as the collision gas to minimize polyatomic interferences. Multi-element standards, matrix matched to the samples, at concentrations of 1, 10, 100 and 1000 µg/l respectively, other than for mercury (1, 2, 5, 20 µg/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 100 µg/l (Scandium, Germanium, Yttrium, Indium and Terbium). Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

One sample was prepared for ICP analysis in duplicate and analysed to verify method reproducibility. With the batch of samples, a blank sample (acidified deionised water) and two mixed metal quality control solution of 80 and 800 µg/l for each metal, other than mercury at 4 and 16 µg/l, were prepared and analysed in the same way as the samples.

Calibration of the ICP-MS was validated by the use of quality control standards at 80 µg/l and 800 µg/l (4 µg/l and 16 µg/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

3. Results and Discussion

3.1. Pesticides and veterinary drugs

The pesticide active ingredients detected, along with their quantified concentrations, are shown in **Table 2**. In total, 39 different pesticides were found in the analysed samples, 55% of them being herbicides, 25% fungicides and 20% insecticides. The highest detection frequency corresponds to the herbicides chlortoluron and prosulfocarb and the fungicide fluopyram, detected in 88% of the samples, followed by the herbicides bentazone and terbutryn and the fungicide tebuconazole, present in 75% of them.

In total, 11 of the 39 pesticides found in the samples are not approved by the EU, according to the EC regulation 1107/2009 (EC, 2009): carbendazim, dimethenamid, fenuron, griseofulvin, hexazinone, isoproturon, methabenzthiazuron, metolachlor, propazine, prometryn and terbutryn. The presence of these banned pesticides in the Baltic waterways might be related to an illegal use of these chemicals.

However, some can be formed as by-products of other substances, such as carbendazim which is a metabolite of benomyl (although the use of benomyl is not approved in the EU either). Others can be naturally generated, like griseofulvin.

In terms of concentrations, 66% of the total amount of pesticides (as ng L^{-1}) in the samples corresponded to herbicides, while 25% were fungicides and 9% insecticides. However, the highest concentration recorded corresponds to a fungicide, tebuconazole, 57.7 ng L^{-1} in sample DE18007, followed by the herbicides MCPA, 45.2 ng L^{-1} in the same sample (DE18007), and prosulfocarb, 27.6 ng L^{-1} in sample DK18005.

Figure 2 shows a map including blue bar-charts with the number of pesticides found at each site. All the analysed samples contained a mixture of several pesticides, ranging from the 6 pesticides present in sample DK18004 up to the 25 found in sample DE18012. The average number of pesticides found per sample was 14. On the other hand, the total concentration of pesticides varied widely from the 1.4 ng L^{-1} present in sample DE18009 to the 213.3 ng L^{-1} found in sample DE18007.

Figure 2. Sampling locations with horizontal bar-charts showing the number of pesticides (blue) and number of veterinary drugs (orange) found in each sample. Please, note that bar-chart scales differ among them, so it is not possible to make first glance comparisons between different samples.

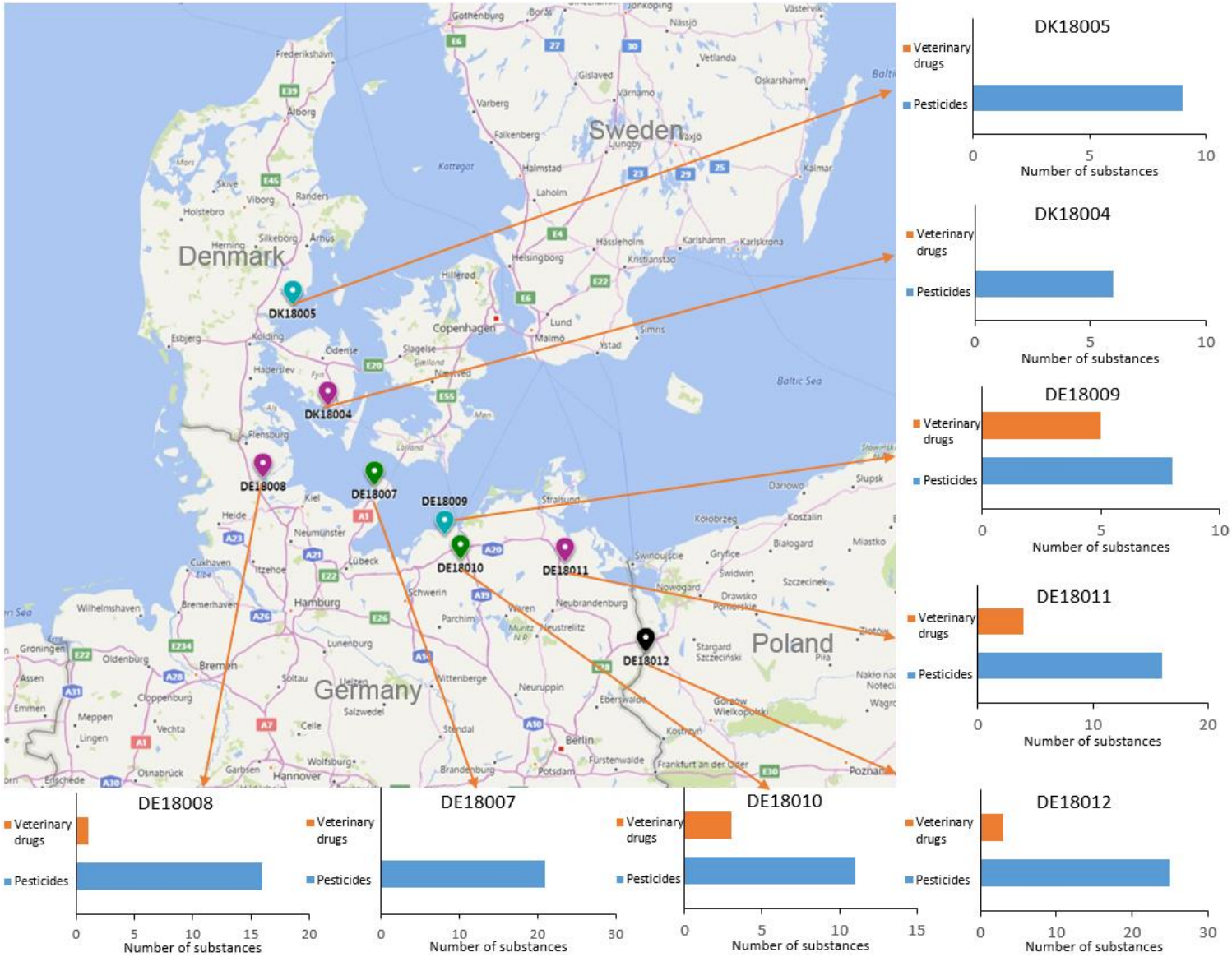

Table 2. Concentrations and standard deviations, in ng L^{-1}, of the pesticides found in the samples analysed. Pesticides are classified according to type and use (H: herbicide, F: fungicide, I: insecticide). Detection frequency of each pesticide (%), number of pesticides detected per sample and total concentration of pesticides per sample, in ng L^{-1}, are calculated.

Pesticide	Type	Use	LOQ (ng L^{-1})	Concentration ± Error (ng L^{-1})								Detection frequency (%)
				DK18004	DK18005	DE18007	DE18008	DE18009	DE18010	DE18011	DE18012	
Acetamiprid	Neonicotinoid	I	5								< LOQ	13%
Azoxystrobin	Strobilurin	F	0.5			0.9 ± 0.1				< LOQ	0.8 ± 0.1	38%
Bentazone	Benzothiazinone	H	2.5	2.7 ± 0.1	2.8 ± 0.1		5.1 ± 0.3		2.6 ± 0.4	5.3 ± 0.3	11.7 ± 0.1	75%
Boscalid	Carboxamide	F	2.5	< LOQ	< LOQ	4.6 ± 0.4						38%
Carbendazim	Benzimidazole	F	0.5								3.8 ± 0.2	13%
Chloridazon	Pyridazinone	H	2.5							< LOQ	< LOQ	25%
Chlortoluron	Urea (Benzoylurea)	H	2.5		< LOQ	< LOQ	15.5 ± 0.2	< LOQ	< LOQ	< LOQ	10.8 ± 0.2	88%
Clomazone	Isoxazolidinone	H	1			6.5 ± 0.3				< LOQ	2.2 ± 0.2	38%
Clothianidin	Neonicotinoid	I	5			9.7 ± 0.7						13%
Dimethenamid	Chloroacetamide	H	1				< LOQ					13%
Dimoxystrobin	Strobilurin	F	1			3.5 ± 0.1						13%
Diuron	Urea (phenylurea)	H	2.5				< LOQ	< LOQ	< LOQ		2.9 ± 0.2	50%
Epoxiconazole	Azole (Triazole)	F	2.5		< LOQ	4.1 ± 0.2	< LOQ					38%
Fenuron	Urea	H	1						1.2 ± 0.2		4 ± 0.3	25%
Flufenacet	Oxyacetamide	H	1			2.7 ± 0.3	21.1 ± 0.8					25%
Fluopyram	Benzamide	F	1	1.4 ± 0.2	2.1 ± 0.2	26.4 ± 0.7	< LOQ	< LOQ		< LOQ	< LOQ	88%
Formetanate	Formamidine	I	2.5						18.2 ± 1.3			13%
Fuberidazole	Benzimidazole	F	1							< LOQ	1.1 ± 0	25%
Griseofulvin	Benzofuran	F	1		1.4 ± 0.2	4.8 ± 0.4		1.4 ± 0.1		5 ± 0.3	< LOQ	63%
Hexazinone	Triazinone	H	0.5	< LOQ	0.5 ± 0.1							25%
Imidacloprid	Neonicotinoid	I	2.5				< LOQ	< LOQ			11.6 ± 0.7	38%
Isoproturon	Urea	H	2.5		< LOQ	< LOQ	< LOQ					38%
MCPA	Aryloxyalkanoic acid	H	20	< LOQ		45.2 ± 5.2						25%
Metazachlor	Chloroacetamide	H	2.5			23.2 ± 0.5	< LOQ			< LOQ	6.7 ± 0.2	50%
Methabenzthiazuron	Urea	H	0.5				< LOQ					13%
Methiocarb sulfoxide	Carbamate	I	1			1.2 ± 0.3						13%

Metolachlor	Chloroacetamide	H	0.5				4.3 ± 0.1				0.5 ± 0.1	25%
Nicosulfuron	Urea (Sulfonylurea)	H	5								7.6 ± 0.3	13%
Pirimicarb	Carbamate	I	1			1.2 ± 0.2						13%
Prometryn	Triazine	H	2.5					< LOQ	< LOQ	< LOQ	< LOQ	50%
Propazine	Triazine	H	1						< LOQ	1.4 ± 0	1.1 ± 0.1	38%
Propiconazole	Azole (Triazole)	F	2.5			< LOQ					2.5 ± 0.1	25%
Propyzamide	Benzamide	H	2.5			16.7 ± 0.8				< LOQ		25%
Prosulfocarb	Tiocarbamate	H	0.1	21.6 ± 0.7	27.7 ± 0.6	1.9 ± 0.3	4.9 ± 0.3		2.8 ± 0.6	2.9 ± 0.6	1.9 ± 0.2	88%
Tebuconazole	Azole (Triazole)	F H	5			57.7 ± 1.2	< LOQ	< LOQ	< LOQ	< LOQ	5.8 ± 0.2	75%
Terbuthylazine	Triazine	H	1				4 ± 0.2		1 ± 0.1	1.4 ± 0.1	1.9 ± 0.2	50%
Terbutryn	Triazine	H	2.5			< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	75%
Thiacloprid	Neonicotinoid	I	0.5			2.9 ± 0					< LOQ	25%
Thiamethoxam	Neonicotinoid	I	2.5								< LOQ	13%
Number of pesticides per sample				6	9	21	16	8	11	16	25	
Total concentration (ng L^{-1})				25.6	34.5	213.3	54.9	1.4	25.8	16.0	76.8	

< LOQ: detected below the limit of quantification

In parallel to the determination of pesticides, qualitative analysis of veterinary drugs was carried out in the same samples. The results obtained are summarized in **Table 3**. 6 different veterinary drugs were detected in the samples: 4 antibiotics and 2 non-steroidal anti-inflammatory drugs (NSAIDs). 3 of the antibiotics found belong to the group of sulphonamides: sulfadiazine, sulfamethoxazole and sulfapyridine; and the forth one, clarithromycin, is a macrolide. The 2 NSAIDs found were diclofenac and ketoprofen. All these 6 substances are also prescribed as pharmaceuticals in human medicine.

The veterinary drug presenting the highest detection frequency was diclofenac, present in 63% of the analysed samples, followed by sulfamethoxazole and sulfapyridine, found in 50% of them.

The number of veterinary drugs detected in each sample is represented by the orange bar-charts in **Figure 2**. 62% of the samples contained at least one veterinary pharmaceutical, the average number being 2 compounds per sample. Sample DE18009 carried a mixture of 5, 3 of them being antibiotics. Sample DE18011 contained a mixture of 4, 3 of them being antibiotics. Samples DE18010 and DE18012 had 3 veterinary drugs each, 2 of them being antibiotics. No veterinary pharmaceuticals were found in the samples collected in Denmark.

Table 3. Veterinary drugs identified in the samples. Compounds are classified according to their type and use. Detection frequency of each drug (%) and the total number of veterinary pharmaceuticals detected per sample are calculated.

Veterinary drug	Type	Use	DK18004	DK18005	DE18007	DE18008	DE18009	DE18010	DE18011	DE18012	Detection frequency (%)
Clarithromycin	Macrolides	Antibiotic					Detected				13%
Diclofenac	NSAIDS	NSAID				Detected	Detected	Detected	Detected	Detected	63%
Ketoprofen	NSAIDS	NSAID					Detected				13%
Sulfadiazine	Sulfonamides	Antibiotic							Detected		13%
Sulfamethoxazol	Sulfonamides	Antibiotic					Detected	Detected	Detected	Detected	50%
Sulfapyridine	Sulfonamides	Antibiotic					Detected	Detected	Detected	Detected	50%
Number of veterinary drugs per sample			0	0	0	1	5	3	4	3	

Taken into consideration both families of compounds analysed in this work, sample DE18007 carried the highest summed concentration of pesticides, 213.3 ng L^{-1} comprised of 21 active substances, but no veterinary drugs. Conversely, sample DE18009 contained the highest number of veterinary pharmaceuticals detected, a mixture of 5 biologically active compounds, but the lowest summed concentration of pesticides, 1.4 ng L^{-1} divided in 8 compounds. Between the two extremes, sample DE18012 combined 25 pesticides, with a total concentration of 76.8 ng L^{-1}, and 3 veterinary drugs, while sample DE18011 carried a mixture of 16 pesticides, with a summed concentration of 16.0 ng L^{-1}, and 4 veterinary active ingredients.

Finding mixtures of pesticides in rivers, often in combination with other biologically active substances (i.e. veterinary drugs), is indeed the most commonly encountered scenario (Altenburger et al., 2015; Malaj et al., 2014; Moschet et al., 2014; Schreiner et al., 2016). However, interactions between pesticides have to date been poorly studied (Hernández et al., 2013) and the presence of other biologically active substances in the same samples makes drawing any quantitative risk assessment even more complicated. Nonetheless, this is a serious matter because biological impacts arising from exposure to mixtures are expected to be significantly greater than for single compounds (Brack et al., 2015; Hernández et al., 2013; Schreiner et al., 2016).

3.2. Metals and metalloids

The concentrations of metals and metalloids in filtered water samples are reported in **Table 4**.

Table 4. Concentrations of metals and metalloids (µg/l) in filtered water samples from Denmark and Germany

Metal	DK18004	DK18005	DE18007	DE18008	DE18009	DE18010	DE18011	DE18012
Aluminium	11	9	2	3	2	1	2	2
Antimony	<0.02	0.09	0.06	0.03	<0.02	<0.02	0.05	0.11
Arsenic	1.20	0.80	1.46	0.79	0.70	0.84	0.90	1.16
Barium	91.4	184	52.1	65.1	63.5	61.4	55.7	67.6
Cadmium	0.01	0.03	<0.01	0.02	0.01	0.04	0.02	0.06
Chromium	0.09	0.05	0.04	0.07	0.05	<0.02	0.03	0.11
Cobalt	0.10	0.57	0.13	0.12	0.18	0.07	0.23	0.19
Copper	0.8	0.7	0.3	0.9	0.5	0.3	0.7	1.5
Iron	93	182	24	95	102	29	55	33
Lead	0.26	0.12	0.12	0.17	0.18	0.08	0.17	0.21
Manganese	47.4	667	2.70	4.80	169	7.36	62.7	58.4
Mercury	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Molybdenum	0.90	1.36	0.39	0.67	0.90	0.77	1.07	1.61
Nickel	0.45	1.53	0.71	0.67	0.65	0.25	0.54	1.58
Strontium	457	1600	874	398	505	606	588	665
Thallium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06
Uranium	0.87	1.00	1.90	0.73	1.04	0.81	1.09	0.65
Vanadium	0.32	0.20	1.08	0.46	0.20	0.20	0.30	0.34

Zinc	1.1	2.3	0.3	2.2	3.0	0.7	1.4	1.7

A summary of the range of concentrations, and the median value, for each metal or metalloid across all samples is given in **Table 5**, which also gives the range of concentrations and median values for European surface waters, from analysis of over 800 filtered stream water samples from second order drainage basins across Europe (Flem et al. 2018).

Just under half the dissolved concentrations of metals and metalloids in the samples were below the respective median values previously reported for European stream water samples from second order drainage basins, and for most cases the concentrations not more than three times these previously reported median values.

Concentrations of strontium in all samples were more than three times the second order drainage basins median, as were those of manganese and molybdenum in half or more of the samples, as concentrations of barium, cadmium, cobalt and uranium in one or two samples. For all these metals, however, concentrations in all samples were within the ranges reported for second order drainage basins in the EU, and commonly considerably below the upper end of those ranges.

Four of the metals (cadmium, lead, mercury and nickel) have environmental quality standards (EQS) set for inland waters in the EU (EU 2008). **Table 5** includes annual average EQS and the maximum allowable EQS for these metals. The samples analysed give an indication of the concentration for the various surface waters at a single point in time and are, therefore, not directly comparable with annual average limits, though the annual average EQS as well as the maximum allowable EQSs do provide useful context for the concentration found. None of the samples contained concentrations of these four metals higher than the EU annual average EQS, nor above the maximum allowable EQS concentrations.

Table 5. Median and range of concentrations of metals and metalloids (µg/l) for all filtered water samples, together with (a) medians and ranges for European stream waters from second order drainage basins (Flem et al. 2018) and (b) EU environmental quality standards (EQS) for inland waters (EU 2008).

Metal	Median	Range	Median for EU streams[a]	Range for EU streams [a]	EU EQS inland surface water	
					Annual average [b]	Maximum allowable concentration [b]
Aluminium	2	1 - 11	17.7	0.70-3370	-	-
Antimony	0.04	<0.02 - 0.11	0.07	0.005-2.91	-	-
Arsenic	0.87	0.07 - 1.46	0.63	<0.001-27.3	-	-
Barium	64.3	52.1 - 184	24.9	0.20-436	-	-
Cadmium	0.02	<0.01 - 0.06	0.010	<0.002-1.25	≤ 0.08	≤ 0.45
Chromium	0.05	0.03 - 0.11	0.38	<0.01-43.0	-	-
Cobalt	0.15	0.07 - 0.57	0.16	0.01-15.7	-	-

Copper	0.7	0.3 - 1.5	0.88	0.08-14.6	-	-
Iron	74	24 - 182	67.0	<1-4820	-	-
Lead	0.17	0.08 - 0.26	0.092	<0.005-10.6	7.2	not applicable
Manganese	53	2.7 - 667	15.9	<0.1-3010	-	-
Mercury	<0.05	<0.05 - <0.05	-	-	0.05	0.07
Molybdenum	0.90	0.39 - 1.61	0.220	0.005-16.0	-	-
Nickel	0.66	0.25 - 1.58	1.91	0.03-24.6	20	not applicable
Strontium	597	398 - 1600	109	1.00-13600	-	-
Thallium	<0.05	<0.05 - 0.06	0.005	<0.002-0.220	-	-
Uranium	0.93	0.65 - 1.9	0.320	<0.002-21.4	-	-
Vanadium	0.31	0.20 - 1.08	0.46	<0.05-19.5	-	-
Zinc	1.6	0.3 - 3.0	2.65	0.09-310	-	-

4. Conclusions

Waterways leading to Baltic Sea in Denmark and Germany were screened for pesticides and veterinary drugs in order to obtain a snapshot of the presence of these substances. All the analysed samples contained a mixture of different pesticides and most of German rivers also contained several veterinary drugs. However, no veterinary drugs were found in the Danish rivers at the time of sampling.

The dataset generated illustrates the need for more sustainable agricultural and livestock practices upstream which can prevent the contamination of watercourses with agrochemicals.

References

Altenburger, R., Ait-Aissa, S., Antczak, P., Backhaus, T., Barceló, D., Seiler, T.-B., Brion, F., Busch, W., Chipman, K., de Alda, M.L., de Aragão Umbuzeiro, G., Escher, B.I., Falciani, F., Faust, M., Focks, A., Hilscherova, K., Hollender, J., Hollert, H., Jäger, F., Jahnke, A., Kortenkamp, A., Krauss, M., Lemkine, G.F., Munthe, J., Neumann, S., Schymanski, E.L., Scrimshaw, M., Segner, H., Slobodnik, J., Smedes, F., Kughathas, S., Teodorovic, I., Tindall, A.J., Tollefsen, K.E., Walz, K.-H., Williams, T.D., Van den Brink, P.J., van Gils, J., Vrana, B., Zhang, X., Brack, W., 2015. Future water quality monitoring — Adapting tools to deal with mixtures of pollutants in water resource management. Sci. Total Environ. 512–513, 540–551. https://doi.org/10.1016/J.SCITOTENV.2014.12.057

Brack, W., Altenburger, R., Schüürmann, G., Krauss, M., López Herráez, D., van Gils, J., Slobodnik, J., Munthe, J., Gawlik, B.M., van Wezel, A., Schriks, M., Hollender, J., Tollefsen, K.E., Mekenyan, O., Dimitrov, S., Bunke, D., Cousins, I., Posthuma, L., van den Brink, P.J., López de Alda, M., Barceló, D., Faust, M., Kortenkamp, A., Scrimshaw, M., Ignatova, S., Engelen, G., Massmann, G., Lemkine, G., Teodorovic, I., Walz, K.-H., Dulio, V., Jonker, M.T.O., Jäger, F., Chipman, K., Falciani, F., Liska, I., Rooke, D., Zhang, X., Hollert, H., Vrana, B., Hilscherova, K., Kramer, K., Neumann, S., Hammerbacher, R., Backhaus, T., Mack, J., Segner, H., Escher, B., de Aragão Umbuzeiro, G., 2015. The SOLUTIONS project: Challenges and responses for present and future emerging pollutants in land and water resources management. Sci. Total Environ. 503–504, 22–31. https://doi.org/10.1016/J.SCITOTENV.2014.05.143

Casado, J., Santillo, D., Johnston, P., 2018. Multi-residue analysis of pesticides in surface water by liquid chromatography quadrupole-Orbitrap high resolution tandem mass spectrometry. Anal. Chim. Acta 1024, 1–17. https://doi.org/10.1016/j.aca.2018.04.026

Council European Union Regulation 1107/2009, L309/1, O. J. Eur. Union (24.11.09).

Flem, B., Reimann, C., Fabian, K., Birke, M., Filzmoser, P., Banks, D. (2018) Graphical statistics to explore the natural and anthropogenic processes influencing the inorganic quality of drinking water, ground water and surface water. Applied Geochemistry, 88(B), 133-148

Hernández, A.F., Parrón, T., Requena, M., Alarcón, R., López-Guarnido, O., 2013. Toxic effects of pesticide mixtures at a molecular level: Their relevance to human health. Toxicology 307, 136–145. https://doi.org/10.1016/J.TOX.2012.06.009

Malaj, E., von der Ohe, P.C., Grote, M., Kühne, R., Mondy, C.P., Usseglio-Polatera, P., Brack, W., Schäfer,

R.B., 2014. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc. Natl. Acad. Sci. 111, 9549 LP-9554.

Moschet, C., Wittmer, I., Simovic, J., Junghans, M., Piazzoli, A., Singer, H., Stamm, C., Leu, C., Hollender, J., 2014. How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality. Environ. Sci. Technol. 48, 5423–5432. https://doi.org/10.1021/es500371t

Schreiner, V.C., Szöcs, E., Bhowmik, A.K., Vijver, M.G., Schäfer, R.B., 2016. Pesticide mixtures in streams of several European countries and the USA. Sci. Total Environ. 573, 680–689. https://doi.org/10.1016/J.SCITOTENV.2016.08.163

Appendix

Table A1. Pesticides screened, name, CAS number, family, use and formula of each compound are provided.

Compound	CAS number	Family	Use	Formula
2,4-D	94-75-7	Alkylchlorophenoxy	Herbicide	C8H6Cl2O3
Acephate	30560-19-1	Organophosphate	Insecticide	C4H10NO3PS
Acetamiprid	135410-20-7	Neonicotinoid	Insecticide	C10H11ClN4
Acibenzolar-S-methyl	135158-54-2	Benzothiadiazole	Fungicide, Insecticide	C8H6N2OS2
Alachlor	15972-60-8	Chloroacetamide	Herbicide	C14H20ClNO2
Aldicarb-sulfone	1646-88-4	Carbamate (NMC)	Insecticide	C7H14N2O4S
Allethrin	584-79-2	Pyrethroid	Insecticide	C19H26O3
Ametryn	834-12-8	Triazine	Herbicide	C9H17N5S
Aminocarb	2032-59-9	Carbamate (NMC)	Insecticide	C11H16N2O2
Ancymidol	12771-68-5	Pyrimidinyl carbinol	Herbicide	C15H16N2O2
Anilofos	64249-01-0	Organophosphate	Herbicide	C13H19ClNO3PS2
Aramite	140-57-8	Sulphite ester	Insecticide	C15H23ClO4S
Atrazine	1912-24-9	Triazine	Herbicide	C8H14ClN5
Avermectin B1a	65195-55-3	Lactone	Insecticide	C48H72O14
Azaconazole	60207-31-0	Azole (Triazole)	Fungicide	C12H11Cl2N3O2
Azamethiphos	35575-96-3	Organophosphate	Insecticide	C9H10ClN2O5PS
Azinphos-ethyl	2642-71-9	Organophosphate	Insecticide	C12H16N3O3PS2
Azinphos-methyl	86-50-0	Organophosphate	Insecticide	C10H12N3O3PS2
Azoxystrobin	131860-33-8	Strobilurin	Fungicide	C22H17N3O5
Bendiocarb	22781-23-3	Carbamate (NMC)	Insecticide	C11H13NO4
Benodanil	15310-01-7	Anilide	Fungicide	C13H10INO
Benoxacor	98730-04-2	Benzoxazine	Safener	C11H11Cl2NO2
Bensulfuron-methyl	83055-99-6	Urea (Sulfonylurea)	Herbicide	C16H18N4O7S
Bentazone	25057-89-0	Benzothiazinone	Herbicide	C10H12N2O3S
Benzoximate	29104-30-1	Bridged diphenyl	Acaricide, Miticide	C18H18ClNO5
Benzoylprop-ethyl	22212-55-1	Arylanalnine	Herbicide	C18H17Cl2NO3
Bifenazate	149877-41-8	Hydrazine carboxylate	Insecticide	C17H20N2O3
Bitertanol	55179-31-2	Azole (Triazole)	Fungicide	C20H23N3O2
Boscalid	188425-85-6	Carboxamide	Fungicide	C18H12Cl2N2O
Brodifacoum	56073-10-0	Hydrocoumarin	Rodenticide	C31H23BrO3
Bromacil	314-40-9	Uracil	Herbicide	C9H13BrN2O2
Bromoxynil	1689-84-5	Hydroxybenzonitrile	Herbicide	C7H3Br2NO
Bromuconazole	116255-48-2	Azole (Triazole)	Fungicide	C13H12BrCl2N3O
Bupirimate	41483-43-6	Pyrimidinol	Fungicide	C13H24N4O3S
Buprofezin	69327-76-0		Insecticide	C16H23N3OS
Butachlor	23184-66-9	Chloroacetamide	Herbicide	C17H26ClNO2
Butafenacil	134605-64-4	Uracil	Herbicide	C20H18ClF3N2O6
Butocarboxim-sulfoxide	34681-24-8	Carbamate (NMC)	Insecticide	C7H14N2O3S
Butoxycarboxim	34681-23-7	Carbamate (NMC)	Insecticide	C7H14N2O4S

Carbaryl	63-25-2	Carbamate (NMC)	Herbicide, Insecticide	C12H11NO2
Carbendazim	10605-21-7	Benzimidazole	Fungicide	C9H9N3O2
Carbetamide	16118-49-3	Carbamate	Herbicide	C12H16N2O3
Carbofuran	1563-66-2	Carbamate (NMC)	Insecticide	C12H15NO3
Carbofuran,3OH-	16655-82-6	Carbamate (NMC)	Insecticide	C12H15NO4
Carfentrazone-ethyl	128639-02-1	Triazolone	Herbicide	C15H14Cl2F3N3O3
Carpropamid	104030-54-8	Cyclopropanecarboxamide	Fungicide	C15H18Cl3NO
Chlorantraniliprole	500008-45-7	Anthranilic diamide	Insecticide	C18H14BrCl2N5O2
Chlorbromuron	13360-45-7	Urea	Herbicide	C9H10BrClN2O2
Chlorfenvinphos	470-90-6	Organophosphate	Insecticide	C12H14Cl3O4P
Chlorfluazuron	71422-67-8	Urea (Benzoylurea)	Insecticide	C20H9Cl3F5N3O3
Chloridazon	1698-60-8	Pyridazinone	Herbicide	C10H8ClN3O
Chlormequat	999-81-5	Quatrenary ammonium	Herbicide	C5H12ClN
Chloroxuron	1982-47-4	Urea (Dimethylurea)	Herbicide	C15H15ClN2O2
Chlorpyrifos-Ethyl	2921-88-2	Organophosphate	Insecticide	C9H11Cl3NO3PS
Chlortoluron	15545-48-9	Urea (Benzoylurea)	Herbicide	C10H13ClN2O
Cinosulfuron	94593-91-6	Urea (Sulfonylurea)	Herbicide	C15H19N5O7S
Clethodim	99129-21-2	Cyclohexadienone	Herbicide	C17H26ClNO3S
Clomazone	81777-89-1	Isoxazolidinone	Herbicide	C12H14ClNO2
Clothianidin	205510-53-8	Neonicotinoid	Insecticide	C6H8ClN5O2S
Coumaphos	56-72-4	Organophosphate	Insecticide	C14H16ClO5PS
Crotoxyphos	7700-17-6	Organophosphate	Insecticide	C14H19O6P
Cumyluron	99485-76-4	Urea	Herbicide	C17H19ClN2O
Cyanazine	21725-46-2	Triazine	Herbicide	C9H13ClN6
Cyazofamid	120116-88-3	Azol (Cyanoimidazole)	Fungicide	C13H13ClN4O2S
Cycloate	1134-23-2	Carbamate (Thiocarbamate)	Herbicide	C11H21NOS
Cycluron	2163-69-1	Urea	Herbicide	C11H22N2O
Cyflufenamid	180409-60-3	Amidoxine	Fungicide	C20H17F5N2O2
Cyromazine	66215-27-8	Triazine	Insecticide	C6H10N6
Demeton-S-Methyl-Sulfone	17040-19-6	Organophosphate	Insecticide	C6H15O5PS2
Desmedipham	13684-56-5	Carbamate	Herbicide	C16H16N2O4
Desmethyl-pirimicarb	30614-22-3	Carbamate	Insecticide	C10H16N4O2
Desmetryn	1014-69-3	Triazine (Methylthiotriazine)	Herbicide	C8H15N5S
Diclobutrazol	75736-33-3	Azole (Triazole)	Fungicide	C15H19Cl2N3O
Dicrotophos	141-66-2	Organophosphate	Insecticide	C8H16NO5P
Diethofencarb	87130-20-9	Carbamate	Fungicide	C14H21NO4
Difenacoum	56073-07-5	Hydrocoumarin	Rodenticide	C31H24O3
Difenoconazole	119446-68-3	Azole (Triazole)	Fungicide	C19H17Cl2N3O3
Diflubenzuron	35367-38-5	Urea (Benzoylurea)	Insecticide	C14H9ClF2N2O2
Dimefuron	34205-21-5	Urea (phenylurea)	Herbicide	C15H19ClN4O3
Dimethametryn	22936-75-0	Triazine (Methylthiotriazine)	Herbicide	C11H21N5S
Dimethenamid	87674-68-8	Chloroacetamide	Herbicide	C12H18ClNO2S
Dimethoate	60-51-5	Organophosphate	Insecticide	C5H12NO3PS2

Dimethomorph	110488-70-5	Morpholine	Fungicide	C21H22ClNO4
Dimoxystrobin	149961-52-4	Strobilurin	Fungicide	C19H22N2O3
Diniconazole	83657-18-5	Triazole	Fungicide	C15H17Cl2N3O
Dinotefuran	165252-70-0	Neonicotinoid	Insecticide	C7H14N4O3
Dithiopyr	97886-45-8	Pyridine	Herbicide	C15H16F5NO2S2
Diuron	330-54-1	Urea (phenylurea)	Herbicide	C9H10Cl2N2O
DNOC	534-52-1	Dinitrophenol	Herbicide, Fungicide, Insecticide	C7H6N2O5
Dodemorph	1593-77-7	Morpholine	Fungicide	C18H35NO
Epoxiconazole	106325-08-0	Azole (Triazole)	Fungicide	C17H13ClFN3O
Esprocarb	85785-20-2	Carbamate (Thiocarbamate)	Herbicide	C15H23NOS
Etaconazol	60207-93-4	Azole (Triazole)	Fungicide	C14H15Cl2N3O2
Ethiofencarb	29973-13-5	Carbamate (NMC)	Insecticide	C11H15NO2S
Ethiofencarb sulfone	53380-23-7	Carbamate (NMC)	Insecticide	C11H15NO4S
Ethiofencarb sulfoxide	53380-22-6	Carbamate (NMC)	Insecticide	C11H15NO3S
Ethiprole	181587-01-9	Azole (Phenylpyrazole)	Insecticide	C13H9Cl2F3N4OS
Ethirimol	23947-60-6	Pyrimidinol	Fungicide	C11H19N3O
Ethofumesate	26225-79-6	Benzofuran	Herbicide	C13H18O5S
Ethoxyquin	91-53-2	Quinoline	Fungicide	C14H19NO
Etofenprox	80844-07-1	Pyrethroid	Insecticide	C25H28O3
Etoxazole	153233-91-1	Diphenyl oxazoline	Acaricide	C21H23F2NO2
Etrimfos	38260-54-7	Organophosphate	Insecticide	C10H17N2O4PS
Fenamidone	161326-34-7	Azole (Imidazole)	Fungicide	C17H17N3OS
Fenamiphos	22224-92-6	Organophosphate	Nematicide	C13H22NO3PS
Fenarimol	60168-88-9	Pyrimidine	Fungicide	C17H12Cl2N2O
Fenazaquin	120928-09-8	Quinazoline	Insecticide	C20H22N2O
Fenbuconazole	114369-43-6	Azole (Triazole)	Fungicide	C19H17ClN4
Fenhexamid	126833-17-8	Hydroxyanilide	Fungicide	C14H17Cl2NO2
Fenobucarb	3766-81-2	Carbamate	Insecticide	C12H17NO2
Fenoxanil	115852-48-7	Amide	Fungicide	C15H18Cl2N2O2
Fenoxycarb	72490-01-8	Carbamate	Insecticide	C17H19NO4
Fenpyroximate	134098-61-6	Pyrazolium	Insecticide	C24H27N3O4
Fensulfothion	115-90-2	Organophosphate	Insecticide	C11H17O4PS2
Fenthion	55-38-9	Organophosphate	Insecticide	C10H15O3PS2
Fenthion-sulfoxide	3761-41-9	Organophosphate	Insecticide	C10H15O4PS2
Fenuron	101-42-8	Urea	Herbicide	C9H12N2O
Flazasulfuron	104040-78-0	Urea (Sulfonylurea)	Herbicide	C13H12F3N5O5S
Florasulam	145701-23-1	Triazolpyrimidine	Herbicide	C12H8F3N5O3S
Fluazifop	69335-91-7	Aryloxyphenoxypropionate	Herbicide	C15H12F3NO4
Fluazinam	79622-59-6	Phenylpyridinamine	Fungicide	C13H4Cl2F6N4O4
Flubendiamide	272451-65-7	Benzene-dicarboxamide	Insecticide	C23H22F7IN2O4S
Flufenacet	142459-58-3	Oxyacetamide	Herbicide	C14H13F4N3O2S
Flufenoxuron	101463-69-8	Urea (Benzoylurea)	Insecticide	C21H11ClF6N2O3
Flumetsulam	98967-40-9	Cyclodiene	Herbicide	C12H9F2N5O2S

Fluometuron	2164-17-2	Urea (phenylurea)	Herbicide	C10H11F3N2O
Fluopicolide	239110-15-7	Benzamide	Fungicide	C14H8Cl3F3N2O
Fluopyram	658066-35-4	Benzamide	Fungicide	C16H11ClF6N2O
Fluoxastrobin	193740-76-0	Strobilurin	Fungicide	C21H16ClFN4O5
Fluquinconazole	136426-54-5	Azole (Triazole)	Fungicide	C16H8Cl2FN5O
Flurochloridone	61213-25-0		Herbicide	C12H10Cl2F3NO
Flusilazole	85509-19-9	Azole (Triazole)	Fungicide	C16H15F2N3Si
Flutriafol	76674-21-0	Azole (Triazole)	Fungicide	C16H13F2N3O
Forchlorfenuron	68157-60-8	Urea (phenylurea)	Herbicide	C12H10ClN3O
Formetanate	22259-30-9	Formamidine	Insecticide	C11H15N3O2
Formothion	2540-82-1	Organophosphate	Insecticide	C6H12NO4PS2
Fosthiazate	98886-44-3	Organophosphate	Insecticide	C9H18NO3PS2
Fuberidazole	3878-19-1	Benzimidazole	Fungicide	C11H8N2O
Furathiocarb	65907-30-4	Carbamate	Insecticide	C18H26N2O5S
Griseofulvin	126-07-8	Benzofuran	Fungicide	C17H17ClO6
Halofenozide	112226-61-6		Herbicide, Insecticide	C18H19ClN2O2
Haloxyfop	95977-29-0	Aryloxyphenoxypropionate	Herbicide	C15H11ClF3NO4
Haloxyfop-methyl	72619-32-0	Aryloxyphenoxypropionate	Herbicide	C16H13ClF3NO4
Heptenophos	23560-59-0	Organophosphate	Insecticide	C9H12ClO4P
Hexaconazole	79983-71-4	Azole (Triazole)	Fungicide	C14H17Cl2N3O
Hexaflumuron	86479-06-3	Urea (Benzoylurea)	Insecticide	C16H8Cl2F6N2O3
Hexazinone	51235-04-2	Triazinone	Herbicide	C12H20N4O2
Hexythiazox	78587-05-0	Carboxamide	Acaricide	C17H21ClN2O2S
Imazalil	35554-44-0	Azole (Imidazole)	Fungicide	C14H14Cl2N2O
Imazaquin	81335-37-7	Imidazolinone	Herbicide	C17H17N3O3
Imazethapyr	81335-77-5	Imidazolinone	Herbicide	C15H19N3O3
Imibenconazole	86598-92-7	Azole (Triazole)	Fungicide	C17H13Cl3N4S
Imidacloprid	105827-78-9	Neonicotinoid	Insecticide	C9H10ClN5O2
Indoxacarb	144171-61-9	Oxadiazine	Insecticide	C22H17ClF3N3O7
Ioxynil	1689-83-4	Hydroxybenzonitrile	Herbicide	C7H3I2NO
Iprovalicarb	140923-17-7	Carbamate	Fungicide	C18H28N2O3
Isocarbophos	24353-61-5	Organophosphate	Insecticide	C11H16NO4PS
Isoprocarb	2631-40-5	Carbamate	Insecticide	C11H15NO2
Isoprothiolane	50512-35-1	Phosphorothiolate	Herbicide, Fungicide	C12H18O4S2
Isoproturon	34123-59-6	Urea	Herbicide	C12H18N2O
Isoxaben	82558-50-7	Benzamide	Herbicide	C18H24N2O4
Isoxadifen-ethyl	163520-33-0		Safener	C18H17NO3
Kresoxim-methyl	143390-89-0	Strobilurin	Fungicide	C18H19NO4
Lenacil	2164-08-1	Uracil	Herbicide	C13H18N2O2
Malaoxon (Malathion-oxon)	1634-78-2	Organophosphate	Insecticide	C10H19O7PS
Mandipropamid	374726-62-2	Mandelamide	Fungicide	C23H22ClNO4
MCPA	94-74-6	Aryloxyalkanoic acid	Herbicide	C9H9ClO3
Mefenacet	73250-68-7	Oxyacetamide	Herbicide	C16H14N2O2S

Mepiquat	15302-91-7	Quarternary ammonium	Herbicide	C7H15N
Mepronil	55814-41-0	Benzanilide	Fungicide	C17H19NO2
Metamitron	41394-05-2	Triazinone	Herbicide	C10H10N4O
Metazachlor	67129-08-2	Chloroacetamide	Herbicide	C14H16ClN3O
Metconazole	125116-23-6	Azole (Triazole)	Fungicide	C17H22ClN3O
Methabenzthiazuron	18691-97-9	Urea	Herbicide	C10H11N3OS
Methamidophos	10265-92-6	Organophosphate	Insecticide	C2H8NO2PS
Methiocarb	2032-65-7	Carbamate	Insecticide	C11H15NO2S
Methiocarb-sulfone	2179-25-1	Carbamate	Insecticide	C11H15NO4S
Methiocarb-sulfoxide	2635-10-1	Carbamate	Insecticide	C11H15NO3S
Methomyl	16752-77-5	Carbamate	Insecticide	C5H10N2O2S
Methoprotryne	841-06-5	Triazine	Herbicide	C11H21N5OS
Methoxyfenozide	161050-58-4	Diacylhydrazine	Insecticide	C22H28N2O3
Metobromuron	3060-89-7	Urea	Herbicide	C9H11BrN2O2
Metolachlor	51218-45-2	Chloroacetamide	Herbicide	C15H22ClNO2
Metolcarb	1129-41-5	Carbamate	Insecticide	C9H11NO2
Metosulam	139528-85-1	Triazolopyrimidine	Herbicide	C14H13Cl2N5O4S
Metoxuron	19937-59-8	Urea	Herbicide	C10H13ClN2O2
Metrafenone	220899-03-6	Benzophenone	Fungicide	C19H21BrO5
Metsulfuron-methyl	74223-64-6	Urea (Sulfonylurea)	Herbicide	C14H15N5O6S
Mevinphos	298-01-1	Organophosphate	Insecticide	C7H13O6P
Mexacarbate	315-18-4	Carbamate	Insecticide	C12H18N2O2
Monocrotophos	6923-22-4	Organophosphate	Insecticide	C7H14NO5P
Monolinuron	1746-81-2	Urea	Herbicide	C9H11ClN2O2
Napropamide	15299-99-7	Alkanamide	Herbicide	C17H21NO2
Neburon	555-37-3	Urea	Herbicide	C12H16Cl2N2O
Nicosulfuron	111991-09-4	Urea (Sulfonylurea)	Herbicide	C15H18N6O6S
Nuarimol	63284-71-9	Pyrimidine	Fungicide	C17H12ClFN2O
Ofurace	58810-48-3	Phenylamide	Fungicide	C14H16ClNO3
Omethoate	1113-02-6	Organophosphate	Insecticide	C5H12NO4PS
Oxadixyl	77732-09-3	Phenylamide	Fungicide	C14H18N2O4
Oxamyl	23135-22-0	Carbamate	Insecticide	C7H13N3O3S
Paclobutrazol	76738-62-0	Azole (Triazole)	Herbicide, Fungicide	C15H20ClN3O
Penconazole	66246-88-6	Azole (Triazole)	Fungicide	C13H15Cl2N3
Pencycuron	66063-05-6	Urea (phenylurea)	Fungicide	C19H21ClN2O
Phenmedipham	13684-63-4	Carbamate	Herbicide	C16H16N2O4
Phenthoate	2597-03-7	Organophosphate	Insecticide	C12H17O4PS2
Phoxim	14816-18-3	Organophosphate	Insecticide	C12H15N2O3PS
Picoxystrobin	117428-22-5	Strobilurin	Fungicide	C18H16F3NO4
Piperonyl-butoxide	51-03-6		Safener	C19H30O5
Piperophos	24151-93-7	Organophosphate	Herbicide	C14H28NO3PS2
Pirimicarb	23103-98-2	Carbamate	Insecticide	C11H18N4O2
Pirimiphos-methyl	29232-93-7	Organophosphate	Insecticide	C11H20N3O3PS

Primisulfuron-methyl	86209-51-0	Urea (Sulfonylurea)	Herbicide	C15H12F4N4O7S
Prochloraz	67747-09-5	Azole (Imidazole)	Fungicide	C15H16Cl3N3O2
Profenofos	41198-08-7	Organophosphate	Insecticide	C11H15BrClO3PS
Promecarb	2631-37-0	Carbamate	Insecticide	C12H17NO2
Prometon	1610-18-0	Triazine (Methoxytriazine)	Herbicide	C10H19N5O
Prometryn	7287-19-6	Triazine	Herbicide	C10H19N5S
Propamocarb	24579-73-5	Carbamate	Fungicide	C9H20N2O2
Propazine	139-40-2	Triazine	Herbicide	C9H16ClN5
Propetamphos	31218-83-4	Organophosphate	Insecticide	C10H20NO4PS
Propiconazole	60207-90-1	Azole (Triazole)	Fungicide	C15H17Cl2N3O2
Propoxur	114-26-1	Carbamate	Insecticide	C11H15NO3
Propyzamide	23950-58-5	Benzamide	Herbicide	C12H11Cl2NO
Prosulfocarb	52888-80-9	Carbamate (Thiocarbamate)	Herbicide	C14H21NOS
Pymetrozine	123312-89-0	Pyridine	Insecticide	C10H11N5O
Pyraclostrobin	175013-18-0	Strobilurin	Fungicide	C19H18ClN3O4
Pyrimethanil	53112-28-0	Anilinopyrimidine	Fungicide	C12H13N3
Pyroxsulam	422556-08-9	Triazolopyrimidine	Herbicide	C14H13F3N6O5S
Quinoxyfen	124495-18-7	Quinoline	Fungicide	C15H8Cl2FNO
Quizalofop P	94051-08-8	Aryloxyphenoxypropionate	Herbicide	C17H13ClN2O4
Quizalofop-ethyl	76578-14-8	Aryloxyphenoxypropionate	Herbicide	C19H17ClN2O4
Resmethrin	10453-86-8	Pyrethroid	Insecticide	C22H26O3
Rimsulfuron	122931-48-0	Urea (Sulfonylurea)	Herbicide	C14H17N5O7S2
Rotenone	83-79-4		Insecticide	C23H22O6
Schradan	152-16-9	Organophosphate	Insecticide	C8H24N4O3P2
Sethoxydim	74051-80-2	Cyclohexadione	Herbicide	C17H29NO3S
Simeconazole	149508-90-7	Azole (Conazole)	Fungicide	C14H20FN3OSi
Simetryn	1014-70-6	Triazine	Herbicide	C8H15N5S
Spinosad A	131929-60-7		Insecticide	C41H65NO10
Spinosad D	131929-63-0		Insecticide	C42H67NO10
Spiromesifen	283594-90-1	Tetronic acid	Insecticide	C23H30O4
Spirotetramat	203313-25-1	Tetronic acid	Insecticide	C21H27NO5
Spiroxamine	118134-30-8	Morpholine	Fungicide	C18H35NO2
Sulfotep	3689-24-5	Organophosphate	Insecticide	C8H20O5P2S2
Sulprofos	35400-43-2	Organophosphate	Insecticide	C12H19O2PS3
Tebuconazole	107534-96-3	Azole (Triazole)	Herbicide, Fungicide	C16H22ClN3O
Tebufenozide	112410-23-8	Diacylhydrazine	Insecticide	C22H28N2O2
Tebufenpyrad	119168-77-3	Pyrazolium	Acaricide	C18H24ClN3O
Tebuthiuron	34014-18-1	Urea	Herbicide	C9H16N4OS
Teflubenzuron	83121-18-0	Urea (Benzoylurea)	Insecticide	C14H6Cl2F4N2O2
Tepraloxydim	149979-41-9	Cyclohexadione	Herbicide	C17H24ClNO4
Terbumeton	33693-04-8	Triazine	Herbicide	C10H19N5O
Terbuthylazine	5915-41-3	Triazine	Herbicide	C9H16ClN5
Terbutryn	886-50-0	Triazine	Herbicide	C10H19N5S

Tetraconazole	112281-77-3	Azole (Triazole)	Fungicide	C13H11Cl2F4N3O
Tetramethrin	7696-12-0	Pyrethroid	Insecticide	C19H25NO4
Thiabendazole	148-79-8	Benzimidazole	Fungicide	C10H7N3S
Thiacloprid	111988-49-9	Neonicotinoid	Insecticide	C10H9ClN4S
Thiamethoxam	153719-23-4	Neonicotinoid	Insecticide	C8H10ClN5O3S
Thidiazuron	51707-55-2	Urea (phenylurea)	Herbicide	C9H8N4OS
Thiobencarb	28249-77-6	Carbamate (Thiocarbamate)	Herbicide	C12H16ClNOS
Thiophanate-methyl	23564-05-8	Benzimidazole	Fungicide	C12H14N4O4S2
Tolfenpyrad	129558-76-5	Pyrazolium	Fungicide, Insecticide	C21H22ClN3O2
Tralkoxydim	87820-88-0	Cyclohexadione	Herbicide	C20H27NO3
Triadimefon	43121-43-3	Azole (Triazole)	Fungicide	C14H16ClN3O2
Triadimenol	55219-65-3	Azole (Triazole)	Fungicide	C14H18ClN3O2
Triazophos	24017-47-8	Organophosphate	Insecticide	C12H16N3O3PS
Trichlorfon	52-68-6	Organophosphate	Insecticide	C4H8Cl3O4P
Tricyclazole	41814-78-2	Triazolobenzothiazole	Fungicide	C9H7N3S
Tridemorph	24602-86-6	Morpholine	Fungicide	C19H39NO
Trietazine	1912-26-1	Triazine	Herbicide	C9H16ClN5
Trifloxystrobin	141517-21-7	Strobilurin	Fungicide	C20H19F3N2O4
Triflumizole	68694-11-1	Azole (Imidazole)	Fungicide	C15H15ClF3N3O
Vamidothion	2275-23-2	Organophosphate	Insecticide	C8H18NO4PS2
Zoxamide	156052-68-5	Benzamide	Fungicide	C14H16Cl3NO2

Table A2. Veterinary drugs screened, name, CAS number, family, use and formula of each compound are provided.

Compound	CAS	Family	Use	Formula
2-NP-AOZ	19687-73-1	Nitrofurans		C10H9N3O4
Acetylsalicylic acid	50-78-2	NSAIDS	Anti-inflammatory drug	C9H8O4
Albendazole	54965-21-8	Imidazoles	Antinematodal	C12H15N3O2S
Aminophenazone	58-15-1	NSAIDS	Anti-inflammatory drug	C13H17N3O
Amoxicillin	26787-78-0	β-lactams	Antibiotic	C16H19N3O5S
Ampicillin	69-53-4	β-lactams	Antibiotic	C16H19N3O4S
Beclomethasone dipropionate	5534-09-8	Cortiscosteroids	Anti-inflammatory drug	C28H37ClO7
Betamethasone dipropionate	5593-20-4	Cortiscosteroids	Anti-inflammatory drug	C28H37FO7
Carprofen	53716-49-7	NSAIDS	Anti-inflammatory drug	C15H12ClNO2
Chlortetracycline	57-62-5	Tetracyclines	Antibiotic	C22H23ClN2O8
Cinoxacin	28657-80-9	Quinolones	Antibiotic	C12H10N2O5
Ciprofloxacin	85721-33-1	Quinolones	Antibiotic	C17H18FN3O3
Clarithromycin	81103-11-9	Macrolides	Antibiotic	C38H69NO13
Cloxacillin	61-72-3	β-lactams	Antibiotic	C19H18ClN3O5S
Danofloxacin	112398-08-0	Quinolones	Antibiotic	C19H20FN3O3
Dexamethasone	50-02-2	Cortiscosteroids	Anti-inflammatory drug	C22H29FO5
Diclofenac	15307-79-6	NSAIDS	Anti-inflammatory drug	C14H11Cl2NO2
Dicloxacillin	3116-76-5	β-lactams	Antibiotic	C19H17Cl2N3O5S
Difloxacin	98106-17-3	Quinolones	Antibiotic	C21H19F2N3O3
Dimetridazole	551-92-8	Imidazoles	Antiprotozoal	C5H7N3O2
Doxycycline	564-25-0	Tetracyclines	Antiprotozoal	C22H24N2O8
Enoxacin	74011-58-8	Quinolones	Antibiotic	C15H17FN4O3
Enrofloxacin	93106-60-6	Quinolones	Antibiotic	C19H22FN3O3
Erythromycin	114-07-8	Macrolides	Antibiotic	C37H67NO13
Etodolac	41340-25-4	NSAIDS	Anti-inflammatory drug	C17H21NO3
Flubendazole	31430-15-6	Imidazoles	Antinematodal	C16H12FN3O3
Fludrocortisone acetate	514-36-3	Cortiscosteroids	Anti-inflammatory drug	C23H31FO6
Flumequine	42835-25-6	Quinolones	Antibiotic	C14H12FNO3
Flumethasone	2135-17-3	Cortiscosteroids	Anti-inflammatory drug	C22H28F2O5
Flunixin	38677-85-9	NSAIDS	Anti-inflammatory drug	C14H11F3N2O2
Furaltadone	139-91-3	Nitrofurans	Antiprotozoal	C13H16N4O6
Furazolidone	67-45-8	Nitrofurans	Antibiotic	C8H7N3O5
Hydrocortisone	50-23-7	Cortiscosteroids	Anti-inflammatory drug	C21H30O5
Ibuprofen	15687-24-1	NSAIDS	Anti-inflammatory drug	C13H18O2
Ipronidazole	14885-29-1	Imidazoles	Antiprotozoal	C7H11N3O2
Josamycin	16846-24-5	Macrolides	Antibiotic	C42H69NO15
Ketoprofen	22071-15-4	NSAIDS	Anti-inflammatory drug	C16H14O3
Lomefloxacin	98079-51-7	Quinolones	Antibiotic	C17H19F2N3O3
Maduramicin	84878-61-5	Ionophores	Antibiotic	C47H83NO17
Marbofloxacin	115550-35-1	Quinolones	Antibiotic	C17H19FN4O4
Mebendazole	31431-39-7	Imidazoles	Antinematodal	C16H13N3O3

Meloxicam	71125-38-7	NSAIDS	Anti-inflammatory drug	C14H13N3O4S2
Methylprednisolone	83-43-2	Cortiscosteroids	Anti-inflammatory drug	C22H30O5
Metronidazole	443-48-1	Imidazoles	Antibiotic	C6H9N3O3
Minocycline	10118-90-8	Tetracyclines	Antibiotic	C23H27N3O7
Mometasone furoate	83919-23-7	Cortiscosteroids	Anti-inflammatory drug	C27H30Cl2O6
Monensin	17090-79-8	Ionophores	Antibiotic	C36H62O11
Nafcillin	985-16-0	β-lactams	Antibiotic	C21H22N2O5S
Nalidixic acid	389-08-2	Quinolones	Antibiotic	C12H12N2O3
Naproxen	22204-38-7	NSAIDS	Anti-inflammatory drug	C14H14O3
Nitrofurantoin	67-20-9	Nitrofurans	Antibiotic	C8H6N4O5
Nitrofurazone	59-87-0	Nitrofurans	Antibiotic	C6H6N4O4
Norfloxacin	70458-96-7	Quinolones	Antibiotic	C16H18FN3O3
Ofloxacin	82419-36-1	Quinolones	Antibiotic	C18H20FN3O4
Oleandomycin	3922-90-5	Macrolides	Antibiotic	C35H61NO12
Orbifloxacin	113617-63-3	Quinolones	Antibiotic	C19H20F3N3O3
Oxacillin	66-79-5	β-lactams	Antibiotic	C19H19N3O5S
Oxibendazole	20559-55-1	Imidazoles	Antinematodal	C12H15N3O3
Oxolinic acid	14698-29-4	Quinolones	Antibiotic	C13H11NO5
Oxytetracycline	79-57-2	Tetracyclines	Antibiotic	C22H24N2O9
Paracetamol	103-90-2	NSAIDS	Anti-inflammatory drug	C8H9NO2
Penicillin G	61-33-6	β-lactams	Antibiotic	C16H18N2O4S
Penicillin V	87-08-1	β-lactams	Antibiotic	C16H18N2O5S
Phenylbutazone	50-33-9	NSAIDS	Anti-inflammatory drug	C19H20N2O2
Pipemidic acid	51940-44-4	Quinolones	Antibiotic	C14H17N5O3
Prednicarbate	73771-04-7	Cortiscosteroids	Anti-inflammatory drug	C27H36O8
Prednisolone	50-24-8	Cortiscosteroids	Anti-inflammatory drug	C21H28O5
Ronidazole	7681-76-7	Imidazoles	Antiprotozoal	C6H8N4O4
Salinomycin	53003-10-4	Ionophores	Antibiotic	C42H70O11
Sarafloxacin	98105-99-8	Quinolones	Antibiotic	C20H17F2N3O3
Spiramycin	8025-81-8	Macrolides	Antibiotic	C43H74N2O14
Sulfabenzamide	127-71-9	Sulfonamides	Antibiotic	C13H12N2O3S
Sulfacetamide	144-80-9	Sulfonamides	Antibiotic	C8H10N2O3S
Sulfachloropyridazine	80-32-0	Sulfonamides	Antibiotic	C10H9ClN4O2S
Sulfadiazine	68-35-9	Sulfonamides	Antibiotic	C10H10N4O2S
Sulfadimethoxine	122-11-2	Sulfonamides	Antibiotic	C12H14N4O4S
Sulfadoxine	2447-57-6	Sulfonamides	Antibiotic	C12H14N4O4S
Sulfaguanidine	57-67-0	Sulfonamides	Antibiotic	C7H10N4O2S
Sulfamerazine	127-79-7	Sulfonamides	Antibiotic	C11H12N4O2S
Sulfameter	651-06-9	Sulfonamides	Antibiotic	C11H12N4O3S
Sulfamethazine	57-68-1	Sulfonamides	Antibiotic	C12H14N4O2S
Sulfamethizole	144-82-1	Sulfonamides	Antibiotic	C9H10N4O2S2
Sulfamethoxazol	723-46-6	Sulfonamides	Antibiotic	C10H11N3O3S
Sulfamethoxypyridazine	80-35-3	Sulfonamides	Antibiotic	C11H12N4O3S

Sulfamonomethoxine	1220-83-3	Sulfonamides	Antibiotic	C11H12N4O3S
Sulfanilamide	63-74-1	Sulfonamides	Antibiotic	C6H8N2O2S
Sulfanitran	122-16-7	Sulfonamides	Antibiotic	C14H13N3O5S
Sulfaphenazole	526-08-9	Sulfonamides	Antibiotic	C15H14N4O2S
Sulfapyridine	144-83-2	Sulfonamides	Antibiotic	C11H11N3O2S
Sulfaquinoxaline	59-40-5	Sulfonamides	Antiprotozoal	C14H12N4O2S
Sulfathiazole	72-14-0	Sulfonamides	Antibiotic	C9H9N3O2S2
Sulfisoxazole	127-69-5	Sulfonamides	Antibiotic	C11H13N3O3S
Tetracycline	60-54-8	Tetracyclines	Antibiotic	C22H24N2O8
Thiabendazole	148-79-8	Imidazoles	Antinematodal	C10H7N3S
Tilmicosin	108050-54-0	Macrolides	Antibiotic	C46H80N2O13
Tinidazole	19387-91-8	Imidazoles	Antiprotozoal	C8H13N3O4S
Tolfenamic acid	13710-19-5	NSAIDS	Anti-inflammatory drug	C14H12ClNO2
Triamcinolone	124-94-7	Cortiscosteroids	Anti-inflammatory drug	C21H27FO6
Triamcinolone acetonide	76-25-5	Cortiscosteroids	Anti-inflammatory drug	C24H31FO6
Triclabendazole	68786-66-3	Imidazoles	Antinematodal	C14H9Cl3N2OS
Tylosin	1401-69-0	Macrolides	Antibiotic	C46H77NO17