Groundwater: Does The Danish Regulation Of Pesticides Protect Human Health?

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INTRODUCTION

Groundwater is the sole source for drinking water in Denmark where 98% of the Danish population drink water from public abstraction wells. The Danish regulation of pesticides are among the strictest in the world, but residues from pesticides are regularly found in groundwater. We asked ourselves whether the Danish regulations do protect human health from harmful residues of pesticides in drinking water? Having access to GEUS Jupiter data base[1], we used chemical data from groundwater as a proxy for exposure from drinking water.

Since the 1980's samples from water abstraction wells, and later from the superficial groundwater, were analysed for pesticide residues. In 1986 the first in a row of *Pesticidplaner* (Pesticide Plans) were passed[2]. Highly watersoluble pesticides were banned and from 1999 a system (PLAP) was organized for monitoring leaching of allowed pesticides [3]. If residues from allowed field spraying exceed 0,1 µg/l in the superficial groundwater, steps will be taken to restrict or to ban the pesticide.

Launching the Drinking Water Directive in 1998[4] the EU set common requirements for drinking water. For chemical contaminants health-based guidance values were set, but pesticides – including relevant metabolites - would share a common precautionary guidance value of 0,1 µg/l. For most pesticides this is well below a toxicologically derived guidance value based on hazards to human health. In Denmark all metabolites are treated as "relevant" sharing the drinking water guidance value of 0,1 µg/l[5]. Groundwater as such do not have a guidance value. When the EU in 2017 consulted WHO about the revision of the Drinking Water Directive, WHO suggested pesticides be regulated like other anthropogenic chemicals using health-based guidance values[6]. In the EU though, the precautionary principle is still being used.

METHODS

The primary data analysis was carried out on the publicly available JupiterXL dataset from GEUS[1] receiving supplemental data on compounds from other sources.

Tests for pesticides in abstraction wells (AWs) providing drinking water to public waterworks were singled out. Samples not approved were omitted. Concentration units were unified to µg/l. Some historical datapoints are lost over time due to AWs being abandoned or repurposed and the data lacking the dimension of status changes over time.

The compounds analyzed are determined from GEUS' category "pesticides, metabolites and related compounds", including a total of 948 different compounds. Only compounds that were analysed in the years 2010-2021 are included. As each AW would be analysed every 3-5 years[4], all AWs should be represented by at least 2-3 samples.

The dataset used as basis for this analysis spans:

- 5.926 abstraction wells in which,
- 36.329 groundwater samples were taken, on which
- 838.720 chemical analysis have been performed, for
- 593 different pesticides, metabolites and related compounds.

Toxicological data were obtained mainly from the EU pesticide registrations. Where not available, from the US-EPA or WHO. From these sources, the toxicological guidance values for drinking water or the ADI (acceptable daily intake) was derived. Data on the use of pesticides were primarily from *Miljøstyrelsen*[7] and *Middeldatabasen*[8].

RESULTS

We analysed Danish drinking water abstraction wells for exceedances of both the common guidance values (GV) and toxicological guidance values (TGV).

Table 1. Pesticides, metabolites and related compounds detected or exceeding the guidance value (GV) of 0,1 ug/l in drinking water abstraction wells (AW).

	#	*detects*	*> GV*
Pesticides and metabolites	593	85 *(14%)*	40 *(7%)*
Abstraction wells (AW)	5.926	2.355 *(40%)*	607 *(10%)*

*Table 2. A*bstraction wells with residues from parent compounds of pesticides not allowed / allowed or restricted / non-pesticides at concentrations exceeding the guidance value / the toxicological guidance value. The 2 allowed pesticides have current uses that do not threaten the groundwater[2]. 6 residues are not from pesticides or have major non-pesticide sources[9].

Parent compounds	*total*	*AW*	*>GV*	*>TGV*	*highest conc.*
Not allowed	25	5.929	582 *(9,8%)*	3	13,5 µg/l
Allowed or restricted	2	5.876	20 *(0,3%)*	0	2,5 µg/l
Non-pesticides	6	5.876	15 *(0,3%)*	3	1,9 µg/l

Table 3. 85% of all exceedances (in 8,7% of AWs) are caused by 5 metabolites from 3 pesticides, having 5%, 4% and 2% of wells exceeding the guidance value (GV). All are non-relevant metabolites according to the EU[10] and do not exceed their toxicological guidance values.[11] [12] [13]

metabolite	*parent*	*used for*	*# AW*	*>GV*	*max amount*	*TGV*	*by*
N,N-Dimethylsulfamid (DMS)	Tolylfluanid	paint, wood preservation, AG until 2007	4.835	260	2,9 µg/l	10 ug/l	DK
Desphenyl chloridazon (DPC)	Cloridazon	AG Herbicide (tubers and onions)	5.149	210	11,0 µg/l	50 ug/l	DK
Methyl-desphenyle-chloridazon		sales stopped i 1997	5.085	24	1,2 µg/l	50 ug/l	DK
2,6-Dichlorbenzamide (BAM)	Dichlobenil	pre-emergency herbicide, widely used	5.883	116	1,7 µg/l	8 ug/l	US
2,6-Dichlorbenzoic acid		public areas, water abstraction sites	5.819	1	0,11 µg/l	8 ug/l	

Table 4: 0,17% of abstraction wells (AWs) have compounds exceeding their toxicological guidance values (TGVs):

compound	*# AW*	*>TGV*	*max amount*	*TGV*	*hazards*
Ethylen thiourea (ETU)	5.829	2 *(0,03%)*	13,5 µg/l	1,0 µg/l US	reproductive
Dinoterb	67	1 *(1,5%)*	0,68 µg/l	0,1 µg/l DK	persistent
Pentachlorophenol (PCP)	1.198	3 *(0,3%)*	0,1 µg/l	0,01 µg/l DK	carcinogen

DISCUSSION

Figure 1.

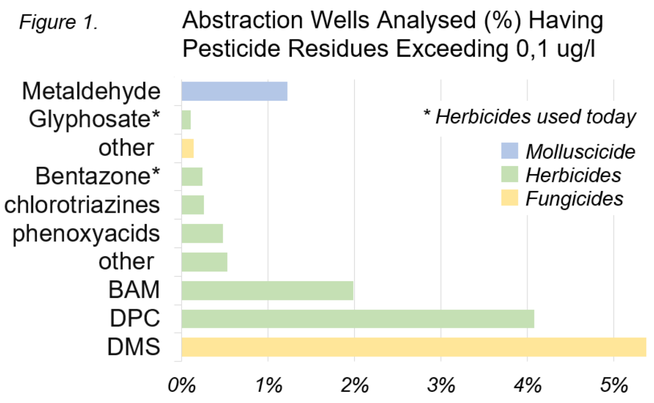


Figure 1.
The distribution of residues from pesticides exceeding the guidance value (GV) of 0,1 µg/l but not the toxicological guidance value (TGV). % of abstraction wells (AWs) analysed.

25 pesticides are not allowed. The 2 in use are not expected to contribute to future exceedances of the GV as they leach less than 0,1 µg/l in PLAP [3].

The majority of AWs are analysed for most residues but samples from 82 AWs only were analysed for the molluscicide Metaldehyde.

Pesticide (and chemical) residues exceeding the toxicological guidance value (TGV):

Ethylenethiourea (**ETU**): An industrial chemical used for production of neoprene and a metabolite of two fungicides (Maneb and Mancozeb), sold until 1998 and 2013[8]. ETU has a safety factor of 100[14], and a short-time exposure above the TGV is not likely to do harm.
Dinoterb: Very toxic. Appears on the UN list of Dangerous Substances[15]. If more AWs could be contaminated, the monitoring program should address this. For both compounds further risk assessment should be carried out.

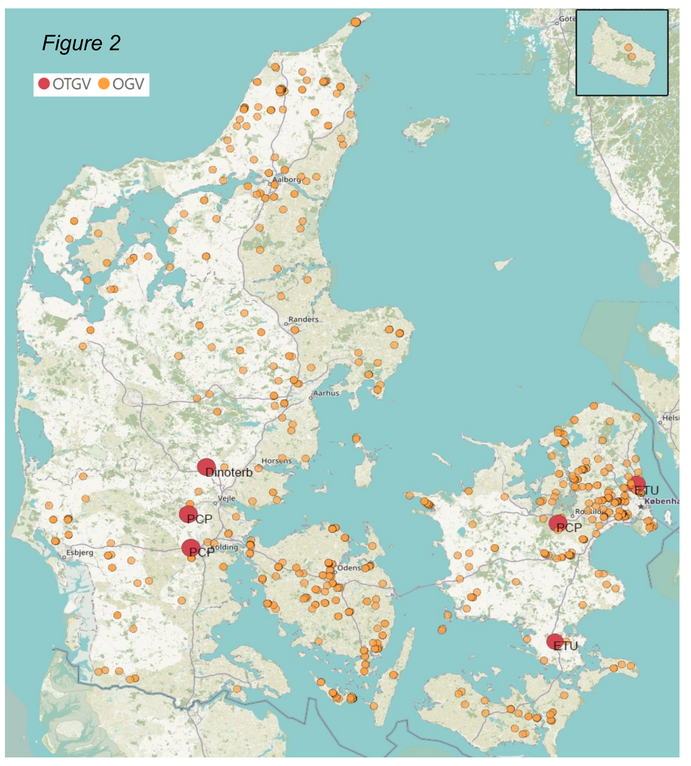
Pentachlorophenol PCP:
A Dangerous Substance[15] and a Persistent Organic Pollutant[16]. PCP has a known cancer risk. The Danish TGV is 0,01µg/L[4]. Exposure to the TGV would induce cancer (statistically) in 1 of 10 mil. people[17]. Surprisingly only 20% of AWs were analysed for PCP, a chemical been used for utility-poles and tiles for many decades.

Figure 2.
Years 2010-21:
Spatial distribution of groundwater data from abstraction wells providing 98% of the Danish population with drinking water.

Abstraction wells in which pesticides, metabolites or related compounds exceed the common guidance value (GV) of 0,1µg/l for one or more compounds.

5.926 abstraction wells were analysed for 593 different compounds of which 40 residues from 27 pesticides and 6 other chemical compounds tested above the common guidance value *(orange dots).*

In 6 abstraction wells, residues from 3 pesticides (Dinoterb and ETU) and one chemical (PCP) were measured in concentrations above their toxicological guidance value *(red dots).*



CONCLUSIONS

- In 2010-21 pesticide residues above the precautionary guidance value for drinking water of 0,1 µg/l were found in *10%* of Danish public drinking water abstraction wells. *9.8%* from residues of 25 pesticides not allowed, the majority *(8,7%* of wells and *85*% of exceedances) being non-EU-relevant metabolites from 3 pesticides. *0,3*% of wells held residues from 2 pesticides having current uses not exceeding 0,1 µg/l in groundwater. In 3 wells *(0,17%)* the toxicological guidance value was exceeded for residues from 3 pesticides not allowed.

- The Danish regulation of pesticides generally protect the population from harmful concentrations of pesticide residues in groundwater from public abstraction wells. Residues from 3 pesticides, not allowed, may pose a risk to human health. For those a refined exposure assessment should be carried out in order to characterize the risk.

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