

29 de JUNIO del 2022, Cipreses Cartago

RESPUESTA PÚBLICA A LA PRESIDENCIA DE ACUEDUCTOS Y ALCANTARILLADOS.

Ing Roberto Guzmán Gutierrez

Presidencia Ejecutiva Instituto Costarricense de Acueductos y Alcantarillados.

Cordiales saludos.

En respuesta al oficio PRE-2022-00572 con fecha del 27 de junio 2022 debemos aclarar lo siguiente:

Ante su preocupación sobre nuestro decir de los posibles impactos a la salud pública que el clorotalonil y sobre todo de los **productos de degradación** puedan ocasionar y de cara a responder su solicitud de evidencia científica que sustenta nuestro comunicado le respondemos:

Los primeros en hacer aseveraciones y alertar, muy responsablemente, de los impactos en materia de salud pública fueron los mismos técnicos de la institución que usted representa, tal y cual consta en el memorado técnico MEMORANDO No.GSD-UEN-GAR-2022-01098 (ver anexos). Copiamos a continuación textualmente lo que indica el documento del AyA:

"El clorotalonil y sus productos de degradación en el agua destinada al consumo humano, así como otros agroquímicos utilizados en la zona debido a las actividades productivas, han sido relacionados en investigaciones médicas con afectaciones graves al hígado y los riñones, además de ser un posible carcinógeno en humanos1, <u>por lo que es necesario que</u> <u>se evalúe la activación del Protocolo de Contaminación del AyA para asistir a la ASADA en</u> <u>una eventual solución, o mecanismo de mitigación de aplicación inmediata</u>. (1-B2 EPA-Estados Unidos)" El subrayado no consta en el texto original.

Le recomendamos empezar leyendo los informes técnicos que los mismos funcionarios del AyA han realizado sobre este tema ya que ustedes cuentan con excelentes profesionales que muchas veces no son atendidos con la diligencia del caso por asuntos políticos que



terminan entorpeciendo los debidos procedimientos. El caso de Cipreses es un ejemplo de lo anteriormente señalado.

Sobre La discusión científica que cuestiona ¿qué tan cancerígenos o dañinos pueden ser los productos de degradación del clorotalonil para la salud humana? y la forma en que usted nos increpa solicitando información científica también debemos decirle lo siguiente:

Esta es una discusión técnica muy reciente que apenas empieza en el mundo. Aún falta mucho por estudiar, pero con la evidencia científica que aportamos a continuación la Unión Europea y otros países más han decidido no autorizar o no renovar los permisos para el uso de clorotalonil. Con la evidencia científica que a continuación aportamos sobran elementos para aplicar el Principio de Precaución, el In Dubio Pro-Salud, el In Dubio Pro Aqua, el In Dubio Pro Vida, o mejor dicho el sentido común. Principios que incluso deberían estar siendo aplicados para proteger nuestra salud, pero que lamentablemente son diezmados por el oscurantismo burocrático de instituciones que se tiran la pelota una a otra desprotegiendo la salud de quienes recibimos agua con productos de la degradación de clorotalonil en nuestras casas.

Se adjunta el documento publicado en el Diario Oficial de la Unión Europea del 29 de abril de 2019 REGLAMENTO DE EJECUCIÓN (UE) 2019/677 DE LA COMISIÓN relativo a la no renovación de la aprobación de la sustancia activa clorotalonil con arreglo a lo dispuesto en el reglamento (CE) n.º 1107/2009 del Parlamento Europeo y del Consejo, Relativo a la Comercialización de Productos Fitosanitarios, y por el que se modifica el reglamento de ejecución (UE) n.º 540/2011 de la Comisión. Dicho documento indica textualmente en sus puntos 9 y 11:

 (9) La Autoridad identificó un problema crítico en relación con la contaminación de las aguas subterráneas por los metabolitos del clorotalonil. En particular, se prevé que los metabolitos R417888, R419492, R471811, SYN507900, M3, M11, M2, M7 y M10 aparezcan por encima del valor paramétrico de 0,1 μg/l en todos los escenarios pertinentes para todos los usos propuestos del clorotalonil. Por lo tanto, actualmente no puede afirmarse que la presencia de los metabolitos de clorotalonil en las aguas subterráneas no va a tener efectos inaceptables en las aguas subterráneas ni efectos nocivos para la salud humana a tenor del artículo 4, apartado 3, letra b),



del Reglamento (CE) n.º 1107/2009. Además, la Autoridad no pudo descartar un posible problema de genotoxicidad de los residuos a los que se verán expuestos los consumidores y detectó un alto riesgo para los anfibios y los peces en todos los usos evaluados. (el resaltado no es del original)

(11) Asimismo, el clorotalonil está clasificado como carcinógeno de categoría 2 de conformidad con el Reglamento (CE) n.º 1272/2008 del Parlamento Europeo y del Consejo (7), mientras que, en la conclusión de la Autoridad, se indica que el clorotalonil debe clasificarse como carcinógeno de categoría 1B. En los usos representativos considerados, no pudieron confirmarse los niveles de residuos a que se refiere el artículo 18, apartado 1, letra b), del Reglamento (CE) n.º 396/2005 en relación con los productos vegetales y animales debido a la falta de datos sobre la magnitud y la toxicidad de los metabolitos que se incluyen en la definición de residuo para la evaluación del riesgo. Por consiguiente, no se cumple el requisito establecido en el anexo II, punto 3.6.3, del Reglamento (CE) n.º 1107/2009.

Está claro que las autoridades europeas no están diferenciando entre la peligrosidad del clorpirifos y la de sus metabolitos a la hora de denegar la renovación del registro de este plaguicida, debido, en gran medida, a la alta probabilidad de contaminación de las aguas subterráneas con metabolitos del mismo. Tampoco diferencia la normativa costarricense de calidad de aguas, que establece los mismos valores máximos de admisibilidad (VMA) para las moléculas madre y sus metabolitos. Así también, las autoridades europeas dejan manifiesta su preocupación por los efectos que estos metabolitos puedan tener en las aguas subterráneas y en la salud humana.

Queremos también que sea de su conocimiento el artículo adjunto (ver anexo): Chlorothalonil transformation products in drinking water resources Widespread and challenging to abate publicado en Water Research 183 (2020), donde se documenta que el clorotalonil aplicado durante décadas en todo el mundo, ha sido prohibido recientemente en la Unión Europea (UE) y Suiza debido a su carcinogenicidad y la presencia de productos de transformación potencialmente tóxicos que contaminan las aguas subterráneas. ¿Qué tan tóxicos serán dichos productos de la transformación? Son muchos hay que analizarlo caso por caso, pero le insistimos en que el principio precautorio es el principio que debe imperar ante la incertidumbre científica y sobre todo ante la <u>incapacidad técnica del</u>



Laboratorio Nacional de Aguas de monitorearlos en Costa Rica, lo cual el AYA está reconociendo. Es de nuestra preocupación la poca capacidad del Laboratorio citado del AYA para analizar residuos de plaguicidas (solamente 24 moléculas) en un país que tiene más de 200 moléculas de plaguicidas en uso en la agricultura, con 161 moléculas altamente peligrosas, según se reporta recientemente por parte del PNUD. Pero, para empeorar las cosas, el AYA se niega a aceptar los resultados de laboratorios de universidades públicas nacionales, de gran prestigio, que tienen una mayor capacidad instalada, y esto lo usan como excusa para permitir que la población continúe consumiendo agua contaminada.

No saquen de contexto las cosas, en el comunicado anterior, claramente señalamos que la mamá de los chiquitos (productos de la degradación del clorotalonil) es la que se ha demostrado ampliamente como cancerígena y que lo que está apareciendo en el agua de nuestra comunidad son los productos degradación del clorotalonil. Mal intencionado es el intento de sacar de contexto las cosas, pero si es que a ustedes les preocupa nuestra aseveración a nosotros nos preocupa aún más que estén fumigando las áreas de protección de las nacientes con el clorotalonil y otros agroquímicos y se manipule y aplique esta sustancia altamente cancerígena en el área que por ley ha de ser respetada y no rociada de venenos. ¡Ojalá se preocuparan más por nuestra salud que por lo que decimos!

Ni pican leña ni prestan el hacha. Es realmente lamentable como nuevamente el AyA hace otro intento desesperado (porque no es el primero en este tema y de igual forma lo hicieron con el caso del bromacil) por disimular los hallazgos del IRET y por no aplicar el principio precautorio. No les ha bastado con desvirtuar cuatro análisis positivos de contaminación con productos de la degradación del clorotalonil en nuestras tomas de agua que desde el IRET dieron a conocer del 2020 hasta la fecha; sino que también insisten en ignorar los resultados positivos de la presencia de trece productos de la degradación del clorotalonil encontrados en el agua de Cipreses que fue enviada desde el IRET-UNA al laboratorio suizo EAWAG (Swiss Federal Institute of Aquatic Science and Technology, por sus siglas en inglés) en donde se encontró que también había otros productos de la degradación de clorotalonil y se confirmó el reiterado hallazgo del IRET.

Es obvio que les ha sido muy fácil lavarse las manos sacrificando en el altar de las famosas acreditaciones de ECA los resultados mencionados anteriormente. Flaco favor le hacen al



país y a la salud pública desde la comodidad de sus puestos asalariados y sus pretextos técnicos y burocráticos...

A manera de metáfora: como si a usted le encontraran un cáncer muy raro en un hospital muy moderno de Europa y regresara usted con los resultados a Costa Rica y la Caja Costarricense de Seguro Social al no tener las tecnologías ni herramientas necesarias para investigar el nuevo cáncer encontrado decidieran declararle sano, salvo y curado. Así mismo es lo que están haciendo con su respuesta pública que asegura que: "el agua de Cipreses es potable". Obviamente usan el criterio de potabilidad para tratar de alivianar la gravedad de lo que aquí se está discutiendo, pero basados en las limitadas capacidades de su propio laboratorio de análisis de aguas.

Con respecto al informe de la Unión Europea señalado: Final Renewal report for the active substance chlorothalonil del 22 de marzo del 2019 (ver anexo), indica usted señor Presidente Ejecutivo en el oficio PRE-2022-005 sobre el documento supra citado: "....*no puede ser tomado como referencia para el caso de Cipreses o de otros acueductos del país...*" ¿Nos interesa muchísimo entender el sustento de semejante aseveración? Podría usted indicarnos: ¿cómo se puede desestimar el criterio técnico de la Unión Europea bajo el cual se aplica el principio de precaución y no se renueva el permiso (registro) de uso de dicho fungicida para dar paso a la inacción por parte de su institución? Respondiendo a su pregunta y extendiendo la solicitada explicación le decimos: El documento se aportó de cara a evidenciar que dicho agrotóxico representa serios riesgos en materia de salud pública y que precisamente en Europa no se encuentra autorizado su uso precisamente por lo mismo que aquí está sucediendo con las aguas subterráneas. Si esa información les resulta irrelevante o incómoda pues que lástima, pero es lo que hay y la vamos a seguir dando a conocer.

Respecto a la afirmación en su comunicado respecto a que las autoridades europeas no recomiendan utilizar la información de su informe en terceros países, le aclaramos que hay que leer integralmente el texto y se puede dar cuenta que se refiere a usar tal reporte para efectos de registro de plaguicidas en un tercer país, por cuanto hay información confidencial, al menos parcialmente, que pertenece a terceros. Pero eso no implica invalidar la información técnica que el mismo documento contiene, sobre la cual se basó la resolución para no renovar el registro del agrotóxico en la Unión Europea.



Señor Presidente Ejecutivo del AyA: con todo respeto le decimos que está muy mal asesorado. Le recordamos que, según la Ley 7789, el principio de la carga de la prueba en materia de denuncias ambientales no recae en los denunciantes (nosotros el Frente Eco Cipreses), sino que más bien en los denunciados. *"Al efecto, el artículo 109 de la citada ley dispone: Carga de la prueba. La carga de la prueba, de la ausencia de contaminación, degradación o afectación no permitidas, corresponderá a quien solicite la aprobación, el permiso o acceso a la biodiversidad o a quien se le acuse de haber ocasionado daño ambiental". Así que le decimos: no ponga la carreta delante de los bueyes. Actúen con diligencia y en base al mandato constitucional que hoy está siendo lesionado bajo el oscurantismo de funcionarios públicos que lejos actuar se enfrascan en discusiones técnicas que decantan en ninguna solución concreta.*

Finalmente le hacemos las siguientes consultas.

- 1) ¿Cuánto tiempo más debemos esperar para que el Laboratorio Nacional de Aguas presente un informe con los resultados de laboratorios acreditados ante la contaminación de productos de la degradación de clorotalonil?
- 2) Sobre la recomendación del memorando No.GSD-UEN-GAR-2022-01098 que indica la "activación del Protocolo de Contaminación del AyA para asistir a la ASADA en una eventual solución, o mecanismo de mitigación de aplicación inmediata" ¿Qué van a hacer al respecto de la activación del Protocolo de Contaminación?

Respetuosos de sus oficios, solicitamos atentamente un **proceso de rendición de cuentas a la comunidad** donde se nos informe sobre cuáles han sido los resultados de la famosa Mesa Técnica que estableció la administración anterior. Sobre todo considerando que dos años después de nuestra primera denuncia pública y de tener un recurso de amparo a nuestro favor las áreas de protección siguen siendo fumigadas.

Dejamos en claro que nuestra organización se mantendrá firme utilizando las herramientas que el estado social de derecho nos confiere para hacer cumplir el artículo 50 de nuestra Constitución.



Atentamente: FRENTEECOCIPRESES

Para más información: <u>frente.ecologista.cipreses@gmail.com</u> Síguenos en Facebook: FRENTEECOCIPRESES



ANEXOS:

Se anexa comunicado de Presidencia del AyA que también estamos respondiendo en este escrito

Posición oficial sobre sit La salud de las per	tuación Asada de Cipreses: r sonas es nuestra prioridad
Desde la Presidencia de Ay comunicado de prensa titular en el agua de Cipreses.	A queremos aclarar varios puntos que el Frente EcoCipreses planteó la semana pasada en el do: Ministra de Salud pide al AYA investigar productos de la degradación del agrotóxico clorotalonil
Lo primero que debemos mar y de conformidad con los re- con la reglamentación nacio potabilidad.	nifestar es que para el AyA es prioritario que los ciudadanos cuenten con un servicio de agua potable sultados de las pruebas efectuadas por el Laboratorio Nacional de Aguas (LNA) en concordancia nal vigente, el agua que suministra el acueducto de Cipreses cumple con los parámetros de
Nos preocupó enormemente humana el consumo de clore renal y cáncer. Por este mo causa estos problemas de s toxicidad y sus repercusione	la aseveración de dicho grupo, en la que aseguró las afectaciones que puede provocar en la salud otalonil (no así de sus moléculas de degradación) destacando problemas hepáticos, insuficiencia tivo, les solicitamos que nos enviaran la evidencia científica que señala el nivel de toxicidad que salud, ya que ningún organismo internacional ha determinado hasta el día de hoy ese nivel de is.
Cabe destacar, que el inforr señalados, en su defecto in registro fuera el contexto o demostrado tener acceso mismo documento señala la la cual no se pudo demostra dicho informe no puede se país.	me de la Unión Europea que este grupo presentó en el comunicado no concluye los problemas ndica: "Se recomienda que este informe de revisión no se acepte para respaldar ningún de dicho Reglamento, por ejemplo, en terceros países, para los que el solicitante no haya reglamentario a la información en la que se basa este informe de revisión". Además, este necesidad de realizar más pruebas y una evaluación del riesgo de los metabolitos en humanos, ar y tampco se logró determinar la evaluación del riesgo por el consumo de agua. Por lo tanto, er tomado como referencia para el caso específico de Cipreses o de otros acueductos del
Seguimiento oportuno	
Sobre la solicitud hecha por la el Laboratorio Nacional de A y México de un laboratorio q análisis de las moléculas de	a señora ministra de Salud, esta tuvo respuesta desde el pasado 13 de junio de 2022 y paralelamente guas (LNA) realiza la búsqueda en países como Alemania, Holanda, Francia, Suiza, Reino Unido ue cuente con la Acreditación de la Norma Internacional INTE-ISO/IEC 17025:2017 que permite el degradación (metabolitos) del fungicida clorotalonil.
En este momento ni el Labora dicha prueba; es importante el agua y que está acreditad 38924-S y la Ley Nº 8279 Sis no se encuentra en el país.	atorio Nacional de Agua ni ningún otro laboratorio en el país, cuentan con la tecnología para realizar señalar, que el Laboratorio Nacional de Agua puede detectar la presencia de 24 agroquímicos en do para realizar estudios tal y como lo indica el Reglamento para la Calidad del Agua Potable N° stema Nacional para la Calidad, pero como se mencionó antes, la prueba para detectar metabolitos
Además, venimos trabajando estudios técnicos para valoro	o junto con la Asada en un plan para fortalecer el suministro de agua a la población que incluye ar el comportamiento de las fuentes actuales, su protección y definir posibles nuevas fuentes.
En el corto plazo iniciaremo Sistema Fitosanitario del Est tomar las mejores decisione	s mesas de trabajo que incluyan a todos los entes involucrados como el Ministerio de Salud, el tado del Ministerio de Agricultura, la Municipalidad de Oreamuno y otros entes, que nos permitan s y atender de forma adecuada la situación en la comunidad de Cipreses de Oreamuno.



INSTITUTO COSTARRICENSE DE ACUEDUCTOS Y ALCANTARILLADOS San José, Costa Rica Apartado 1097-1200. Teléfono 2591-7760 - vmesen@aya.go.cr

> MEMORANDO No.GSD-UEN-GAR-2022-01098

FECHA: 23 de marzo del 2022

- PARA: Susana Cambronero Blanco Laboratorio Nacional de Aguas Firmado digitalmente por VLADIMIR ALFONSO MESEN MONTENEGRO (FIRMA) Fecha y hora: 23/03/2022 11:44 AM
- DE: Vládimir Mesén Montenegro UEN Gestión de Acueductos Rurales

ASUNTO: Calidad del agua naciente conocida como Plantón – Sector Oratorio – Capira – Asada Cipreses de Oreamuno.

En seguimiento a los parámetros de calidad de agua de la naciente conocida como Plantón, la cual hace parte del sistema de abastecimiento de agua potable administrado por la ASADA Cipreses de Oreamuno, se han hecho de nuestro conocimiento los últimos análisis realizados por el Instituto Regional de Estudios en Sustancias Tóxicas de la Universidad Nacional (IRET-UNA), mediante el cual se efectuaron investigaciones en búsqueda de agroquímicos y sus metabolitos.

Lo cual consideramos debe ser de conocimiento por el Laboratorio Nacional de Aguas, en atención al oficio del 22 de marzo 2022 sobre el galardón del Programa de Calidad Sanitaria en la categoría de entes operadores, donde se otorga una calificación de 100 puntos en los parámetros obligatorios y 4 estrellas blancas a la Asada de Cipreses.

De acuerdo con lo que indica el Reglamento para la Calidad de Agua Potable en el **Anexo 1**, **cuadro 5. Parámetros de Calidad del Agua Nivel Cuarto (N4)**, los valores que se encuentran en los análisis realizados por el IRET-UNA sobrepasan tanto en la naciente Plantón como en la naciente Carlos Calvo el Valor Máximo Admisible (VMA), por lo que es necesario que la ASADA comunique directamente al AyA estos resultados en adelante, y que como ente operador del servicio de agua potable se tomen acciones inmediatas para comunicar a la población sobre el riesgo potencial.

A continuación, a manera de síntesis de los resultados anexos se muestran los parámetros tanto del Reglamento como los obtenidos por los estudios realizados por IRET-UNA.

Residuos de plaguicidas						
PARAMETRO	Valor Máximo Admisible (VMA) μg/					
Plaguicidas. (a)	0,1					
Plaguicidas organoclorados (b)	0,03					
Total de plaguicidas. (c)	0,5					

Tabla 1: Parámetros del Reglamento

"(a) Por "Plaguicidas" se entiende: insecticidas orgánicos, herbicidas orgánicos, fungicidas orgánicos, nematicidas orgánicos, acaricidas orgánicos, alguicidas orgánicos, rodenticidas orgánicos, molusquicidas orgánicos, productos relacionados (reguladores de crecimiento) **y sus pertinentes metabolitos y productos de degradación y reacción.** Sólo es preciso controlar aquellos plaguicidas que sea probable que estén presentes en un suministro dado. **De estar presentes en el suministro e implementado el sistema de tratamiento; estos deben ser evaluados con una frecuencia mensual.**²

(b) Sustancias de uso prohibido en el país, pero que debido a su persistencia en Costa Rica podrían encontrarse en aguas dada su larga vida media en el ambiente y su uso extensivo en épocas anteriores.

(c) Por "Total de plaguicidas", se entiende la suma de todos los plaguicidas detectados y cuantificados en el procedimiento de control."

En base al Reglamento citado supra, debe hacerse notar que los metabolitos están incluidos dentro de la definición de plaguicidas (ver a.), definiéndose un VMA de **0.1 µg/L** para estos compuestos.

A pesar de no encontrarse el pesticida investigado en su estado inicial (Clorotalonil), se ha confirmado en los análisis realizados por IRET una concentración de **6.4 \mug/L** del compuesto 1,3dicarbamoil-2,4,5,6-tetraclorobenceno y **0.13 \mug/L** del compuesto 4-Hidroxiclorotalonil en la naciente Plantón y **0.8 \mug/L** del compuesto 1,3-dicarbamoil-2,4,5,6-tetraclorobenceno, todos me-

¹ Según Reglamento para La Calidad del Agua Potable No 38924-S

² El resaltado no es original del Reglamento citado

tabolitos del fungicida de contacto Clorotalonil. Así mismo, en el caso de la naciente Plantón se detectan trazas (T) de varios tipos de agroquímicos a los cuales es importante dar seguimiento (ver página 3 de reporte anexo).

Ante esta evidencia la Norma indica que "*De estar presentes en el suministro e implementado el sistema de tratamiento; estos deben ser evaluados con una frecuencia mensual*" por lo que se requieren acciones urgentes por parte de la ASADA con acompañamiento del AyA, que permitan garantizar un monitoreo constante de estos parámetros.

La normativa define parámetros de plaguicidas para el control de la calidad del agua potable y si bien existen algunas sustancias orgánicas que tienen parámetros específicos donde se admiten concentraciones más altas, los metabolitos en cuestión no se encuentran dentro de esta lista, por lo que deben considerarse los VMA descritos en la tabla 1 del presente documento.

En la tabla a continuación se muestran los resultados del análisis de IRET-UNA, en muestreo realizado en octubre del año 2021, en la ASADA Cipreses de Oreamuno, cuyos resultados fueron comunicados el 17 de diciembre por parte del IRET-UNA a la ASADA.

Compuesto	Resultado	Análisis ¹
1,3-dicarbamoil-2,4,5,6-tetraclorobenceno	6.4 µg/L – Naciente Plantón	GC-MS
		LC- MSMS
4-Hidroxiclorotalonil	0.13 µg/L - Naciente Plantón	LC-MSMS
Total - Plaguicidas naciente Plantón	6.53 µg/L	-
		GC-MS
1,3-dicarbamoil-2,4,5,6-tetraclorobenceno	0.8 µg/L - Naciente Carlos	LC- MSMS
	Calvo	
Total - Plaguicidas naciente C. Calvo	0.8 µg/L	-

Tabla 2: Resultados análisis IRET-UNA

Como puede evidenciarse existen compuestos detectados, y confirmados mediante remuestreos, cuyas concentraciones exceden lo indicado por la Normativa.

Código: ADM-93-04-F5 - Versión: 02

¹ **GC-MS:** Cromatografía de gases con detector de masas; **LC-MSMS**: Cromatografía líquida con detector de masas en tándem

El Clorotalonil y sus productos de degradación en el agua destinada al consumo humano, así como otros agroquímicos utilizados en la zona debido a las actividades productivas, han sido relacionados en investigaciones médicas con afectaciones graves al hígado y los riñones, además de ser un posible carcinógeno en humanos¹, por lo que es necesario que se evalúe la activación del Protocolo de Contaminación del AyA para asistir a la ASADA en una eventual solución, o mecanismo de mitigación de aplicación inmediata.

Desde la ORAC Central Este se ha solicitado apoyo a la Subgerencia de Gestión de Sistemas Delegados, en particular a la Dirección de Fortalecimiento de Asadas y al señor Subgerente para definir los pasos a seguir, a fin de abordar el caso en conjunto con el Laboratorio Nacional de Aguas y establecer la hoja de ruta requerida, por lo cual se solicitó a la Subgerencia coordinar una reunión para atender el tema con el criterio de experto del Laboratorio Nacional de Aguas, la UEN Gestión Ambiental y el equipo experto de la Mesa Técnica del caso de la Asada de Cipreses, por lo que se procede a informar a las partes en apego al protocolo para la contaminación de fuentes, que se adjunta a la presente.

A su vez, se anexa el oficio UEN-GA-2022-00001 del 5 de enero 2022, donde la UEN Gestión Ambiental rechaza el estudio hidrogeológico presentado por la Asada de Cipreses, donde se indica que: "...desde el punto de vista hidrogeológico, se requiere la subsanación de los 10 puntos señalados para el estudio hidrogeológico de la naciente Carlos Calvo y los 10 puntos mencionados para el estudio de la naciente Plantón, por lo que el mismo no cumple técnicamente" (se adjunta oficio para su revisión).

Finalmente, la Mesa Técnica conformada por la Presidencia Ejecutiva sobre el caso de la Asada de Cipreses, concluye en su informe final del 5 de setiembre 2021: **"Se evidenció la presencia de productos de degradación de agroquímicos en las pruebas de calidad del agua** *para la Naciente Plantón, además se evidenció la presencia de coliformes fecales y niveles de cloro residual por encima y debajo del Reglamento de Calidad de Agua para mediciones puntales dentro de la red de distribución"*.

Se adjuntan los informes respectivos para la revisión y criterio del Laboratorio Nacional de Aguas, a fin de lograr una posición institucional al respecto, donde puedan participar todas las unidades competentes al caso.

¹ B2 EPA- Estados Unidos

Código: ADM-93-04-F5 - Versión: 02

Anexos

C.Gerardo Rivas Rivas - UEN Optimización de Sistemas GAM

Zaida Ulate Gutiérrez - Unidad Técnica de los Servicios de Abastecimiento de Agua Potable y de Saneamiento

Jorge Villalobos Madrigal - UEN Programación y Control

Esteban Vargas Rounda - UEN Programación y Control

Oscar Alonso Vásquez Saldaña - Unidad Técnica de los Servicios de Abastecimiento de Agua Potable y de Saneamiento

Adriana Maria Valverde Cortés - UEN Gestión de Acueductos Rurales

Christian Delgado Segura - UEN Gestión Ambiental

José Antonio Jiménez Gómez - UEN Gestión de Acueductos Rurales

Darner Mora Alvarado - Laboratorio Nacional de Aguas

Viviana Ramos Sánchez - Subgerencia Ambiental

Investigación y Desarrollo

Archivo

REGLAMENTO DE EJECUCIÓN (UE) 2019/677 DE LA COMISIÓN

de 29 de abril de 2019

relativo a la no renovación de la aprobación de la sustancia activa clorotalonil con arreglo a lo dispuesto en el Reglamento (CE) n.º 1107/2009 del Parlamento Europeo y del Consejo, relativo a la comercialización de productos fitosanitarios, y por el que se modifica el Reglamento de Ejecución (UE) n.º 540/2011 de la Comisión

(Texto pertinente a efectos del EEE)

LA COMISIÓN EUROPEA,

Visto el Tratado de Funcionamiento de la Unión Europea,

Visto el Reglamento (CE) n.º 1107/2009 del Parlamento Europeo y del Consejo, de 21 de octubre de 2009, relativo a la comercialización de productos fitosanitarios y por el que se derogan las Directivas 79/117/CEE y 91/414/CEE del Consejo (1), y en particular su artículo 20, apartado 1, y su artículo 78, apartado 2,

Considerando lo siguiente:

- La Directiva 2005/53/CE de la Comisión (2) incluyó el clorotalonil como sustancia activa en el anexo I de la (1)Directiva 91/414/CEE del Consejo (3).
- (2) Las sustancias activas incluidas en el anexo I de la Directiva 91/414/CEE se consideran aprobadas con arreglo al Reglamento (CE) n.º 1107/2009 y figuran en la parte A del anexo del Reglamento de Ejecución (UE) n.º 540/2011 de la Comisión (4).
- (3) La aprobación de la sustancia activa clorotalonil, que figura en la parte A del anexo del Reglamento de Ejecución (UE) n.º 540/2011, expira el 31 de octubre de 2019.
- (4) De conformidad con el artículo 1 del Reglamento de Ejecución (UE) n.º 844/2012 de la Comisión (5) y dentro del plazo previsto en dicho artículo, se presentó una solicitud de renovación de la aprobación del clorotalonil.
- Los solicitantes presentaron los expedientes complementarios exigidos de conformidad con el artículo 6 del (5) Reglamento de Ejecución (UE) n.º 844/2012. El Estado miembro ponente consideró que la solicitud estaba completa.
- (6) El Estado miembro ponente elaboró un informe de evaluación de la renovación junto con el Estado miembro coponente y, el 2 de septiembre de 2016, lo presentó a la Autoridad Europea de Seguridad Alimentaria («la Autoridad») y a la Comisión.
- La Autoridad comunicó el informe de evaluación de la renovación a los solicitantes y a los Estados miembros (7) para que formularan sus observaciones, y transmitió las observaciones recibidas a la Comisión. La Autoridad puso también a disposición del público el expediente complementario resumido.
- (8)El 6 de diciembre de 2017, la Autoridad comunicó a la Comisión su conclusión (6) sobre si cabía esperar que el clorotalonil cumpliera los criterios de aprobación establecidos en el artículo 4 del Reglamento (CE) n.º 1107/2009.

⁽¹⁾ DO L 309 de 24.11.2009, p. 1.

⁽²⁾ Directiva 2005/53/CE de la Comisión, de 16 de septiembre de 2005, por la que se modifica la Directiva 91/414/CEE del Consejo a fin de

incluir las sustancias activas clorotalonil, clorotoluron, cipermetrina, daminozida y tiofanato-metil (DO L 241 de 17.9.2005, p. 51). Directiva 91/414/CEE del Consejo, de 15 de julio de 1991, relativa a la comercialización de productos fitosanitarios (DO L 230 de 19.8.1991, p. 1).

⁽⁴⁾ Reglamento de Ejecución (UE) n.º 540/2011 de la Comisión, de 25 de mayo de 2011, por el que se establecen disposiciones de aplicación del Reglamento (CE) n.º 1107/2009 del Parlamento Europeo y del Consejo en lo que respecta a la lista de sustancias activas aprobadas (DO L 153 de 11.6.2011, p. 1).

⁽⁵⁾ Reglamento de Ejecución (UE) n.º 844/2012 de la Comisión, de 18 de septiembre de 2012, por el que se establecen las disposiciones necesarias para la aplicación del procedimiento de renovación de las sustancias activas de conformidad con el Reglamento (CE) n.º 1107/2009 del Parlamento Europeo y del Consejo relativo a la comercialización de productos fitosanitarios (DO L 252 de 19.9.2012, p. 26).

⁽⁹⁾ EFSA (Autoridad Europea de Seguridad Alimentaria), 2016. Conclusion on the peer review of the pesticide risk assessment of the active substance chlorothalonil (Conclusión sobre la revisión por pares de la evaluación del riesgo de la sustancia activa clorotalonil en plaguicidas). EFSA Journal 2018;16(1):5126, 40 pp. https://doi.org/10.2903/j.efsa.2018.5126.

ES

- (9) La Autoridad identificó un problema crítico en relación con la contaminación de las aguas subterráneas por los metabolitos del clorotalonil. En particular, se prevé que los metabolitos R417888, R419492, R471811, SYN507900, M3, M11, M2, M7 y M10 aparezcan por encima del valor paramétrico de 0,1 µg/l en todos los escenarios pertinentes para todos los usos propuestos del clorotalonil. Por lo tanto, actualmente no puede afirmarse que la presencia de los metabolitos de clorotalonil en las aguas subterráneas no va a tener efectos inaceptables en las aguas subterráneas ni efectos nocivos para la salud humana a tenor del artículo 4, apartado 3, letra b), del Reglamento (CE) n.º 1107/2009. Además, la Autoridad no pudo descartar un posible problema de genotoxicidad de los residuos a los que se verán expuestos los consumidores y detectó un alto riesgo para los anfibios y los peces en todos los usos evaluados.
- (10) Por otra parte, varios ámbitos de la evaluación del riesgo no pudieron finalizarse a causa de la insuficiencia de los datos del expediente. En particular, la evaluación del riesgo para los consumidores derivado de la exposición alimentaria no pudo completarse debido a la falta de datos para confirmar la definición del residuo en las plantas y la evaluación de la exposición del ganado, incluida la evaluación toxicológica de un metabolito.
- (11) Asimismo, el clorotalonil está clasificado como carcinógeno de categoría 2 de conformidad con el Reglamento (CE) n.º 1272/2008 del Parlamento Europeo y del Consejo (⁷), mientras que, en la conclusión de la Autoridad, se indica que el clorotalonil debe clasificarse como carcinógeno de categoría 1B. En los usos representativos considerados, no pudieron confirmarse los niveles de residuos a que se refiere el artículo 18, apartado 1, letra b), del Reglamento (CE) n.º 396/2005 en relación con los productos vegetales y animales debido a la falta de datos sobre la magnitud y la toxicidad de los metabolitos que se incluyen en la definición de residuo para la evaluación del riesgo. Por consiguiente, no se cumple el requisito establecido en el anexo II, punto 3.6.3, del Reglamento (CE) n.º 1107/2009.
- (12) La Comisión invitó a los solicitantes a presentar sus observaciones acerca de las conclusiones de la Autoridad y, de conformidad con el artículo 14, apartado 1, párrafo tercero, del Reglamento de Ejecución (UE) n.º 844/2012, a presentar observaciones acerca del proyecto de informe sobre la renovación. Los solicitantes presentaron observaciones, que se examinaron con detenimiento.
- (13) Sin embargo, pese a los argumentos presentados por los solicitantes, no pudieron descartarse los problemas relativos a esta sustancia.
- (14) Así pues, no se ha establecido que se cumplan los criterios de aprobación contemplados en el artículo 4 del Reglamento (CE) n.º 1107/2009 con respecto a uno o varios usos representativos de al menos un producto fitosanitario. Por tanto, de conformidad con el artículo 20, apartado 1, letra b), de dicho Reglamento, procede no renovar la aprobación de la sustancia activa clorotalonil.
- (15) Procede, por tanto, modificar el Reglamento de Ejecución (UE) n.º 540/2011 en consecuencia.
- (16) Debe darse suficiente tiempo a los Estados miembros para que retiren las autorizaciones de los productos fitosanitarios que contienen clorotalonil.
- (17) En el caso de los productos fitosanitarios que contienen clorotalonil, si los Estados miembros conceden un período de gracia de conformidad con el artículo 46 del Reglamento (CE) n.º 1107/2009, dicho período debe expirar, a más tardar, el 20 de mayo de 2020.
- (18) Mediante el Reglamento de Ejecución (UE) 2018/1262 de la Comisión (⁸) se prorrogó el período de aprobación del clorotalonil hasta el 31 de octubre de 2019, a fin de que pudiera completarse el proceso de renovación antes de que expirara la aprobación de dicha sustancia. Sin embargo, dado que se ha adoptado una decisión sobre la no renovación de la aprobación antes de la mencionada fecha de expiración prorrogada, el presente Reglamento debe aplicarse lo antes posible.
- (19) El presente Reglamento no excluye la presentación de una nueva solicitud de aprobación del clorotalonil con arreglo al artículo 7 del Reglamento (CE) n.º 1107/2009.
- (20) Las medidas previstas en el presente Reglamento se ajustan al dictamen del Comité Permanente de Vegetales, Animales, Alimentos y Piensos.

 ^{(&}lt;sup>7</sup>) Reglamento (CE) n.º 1272/2008 del Parlamento Europeo y del Consejo, de 16 de diciembre de 2008, sobre clasificación, etiquetado y envasado de sustancias y mezclas, y por el que se modifican y derogan las Directivas 67/548/CEE y 1999/45/CE y se modifica el Reglamento (CE) n.º 1907/2006 (DO L 353 de 31.12.2008, p. 1).
(⁸) Reglamento de Ejecución (UE) 2018/1262 de la Comisión, de 20 de septiembre de 2018, que modifica el Reglamento de Ejecución (UE)

^(*) Reglamento de Ejecución (UE) 2018/1262 de la Comisión, de 20 de septiembre de 2018, que modifica el Reglamento de Ejecución (UE) n.º 540/2011 por lo que respecta a la prórroga de los períodos de aprobación de las sustancias activas 1-metilciclopropeno, beta-ciflutrina, clorotalonil, clorotoluron, clomazona, cipermetrina, daminozida, deltametrina, dimetenamida-p, diurón, fludioxonil, flufenacet, flurtamona, fostiazato, indoxacarbo, MCPA, MCPB, prosulfocarb, tiofanato-metil y tribenurón (DO L 238 de 21.9.2018, p. 62).

ES

HA ADOPTADO EL PRESENTE REGLAMENTO:

Artículo 1

No renovación de la aprobación de una sustancia activa

No se renueva la aprobación de la sustancia activa clorotalonil.

Artículo 2

Modificaciones del Reglamento de Ejecución (UE) n.º 540/2011

En la parte A del anexo del Reglamento de Ejecución (UE) n.º 540/2011, se suprime la fila 101, relativa al clorotalonil.

Artículo 3

Medidas transitorias

Los Estados miembros retirarán las autorizaciones de los productos fitosanitarios que contengan la sustancia activa clorotalonil, a más tardar, el 20 de noviembre de 2019.

Artículo 4

Período de gracia

Todo período de gracia concedido por los Estados miembros de conformidad con el artículo 46 del Reglamento (CE) n.º 1107/2009 será lo más breve posible y expirará a más tardar el 20 de mayo de 2020.

Artículo 5

Entrada en vigor

El presente Reglamento entrará en vigor a los veinte días de su publicación en el Diario Oficial de la Unión Europea.

El presente Reglamento será obligatorio en todos sus elementos y directamente aplicable en cada Estado miembro.

Hecho en Bruselas, el 29 de abril de 2019.

Por la Comisión El Presidente Jean-Claude JUNCKER Water Research 183 (2020) 116066

ELSEVIER

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Chlorothalonil transformation products in drinking water resources: Widespread and challenging to abate



Karin Kiefer ^{a, b}, Tobias Bader ^c, Nora Minas ^a, Elisabeth Salhi ^a, Elisabeth M.-L. Janssen ^a, Urs von Gunten ^{a, b, d}, Juliane Hollender ^{a, b, *}

^a Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600, Dübendorf, Switzerland

^b Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, 8092, Zurich, Switzerland

^c Laboratory for Operation Control and Research, Zweckverband Landeswasserversorgung, 89129, Langenau, Germany

^d School of Architecture, Civil and Environmental Engineering (ENAC), École Polytechnique Fédérale de Lausanne (EPFL), 1015, Lausanne, Switzerland

ARTICLE INFO

Article history: Received 26 March 2020 Received in revised form 25 May 2020 Accepted 14 June 2020 Available online 17 June 2020

Keywords: Pesticide Metabolite Water treatment Groundwater Ozonation Activated carbon

ABSTRACT

Chlorothalonil, a fungicide applied for decades worldwide, has recently been banned in the European Union (EU) and Switzerland due to its carcinogenicity and the presence of potentially toxic transformation products (TPs) in groundwater. The spread and concentration range of chlorothalonil TPs in different drinking water resources was examined (73 groundwater and four surface water samples mainly from Switzerland). The chlorothalonil sulfonic acid TPs (R471811, R419492, R417888) occurred more frequently and at higher concentrations (detected in 65-100% of the samples, $<2200 \text{ ngL}^{-1}$) than the phenolic TPs (SYN507900, SYN548580, R611968; detected in 10-30% of the samples, $<130 \text{ ngL}^{-1}$). The TP R471811 was found in all samples and even in 52% of the samples above 100 ngL⁻¹, the drinking water standard in Switzerland and other European countries. Therefore, the abatement of chlorothalonil TPs was investigated in laboratory and pilot-scale experiments and along the treatment train of various water works, comprising aquifer recharge, UV disinfection, ozonation, advanced oxidation processes (AOPs), activated carbon treatment, and reverse osmosis. The phenolic TPs can be abated during ozonation (second order rate constant $k_{O3} \sim 10^4 \text{ M}^{-1} \text{s}^{-1}$) and by reaction with hydroxyl radicals (•OH) in AOPs $(k_{OH} \sim 10^9 \text{ M}^{-1} \text{s}^{-1})$. In contrast, the sulfonic acid TPs, which occurred in higher concentrations in drinking water resources, react only very slowly with ozone ($k_{O3} < 0.04 \text{ M}^{-1}\text{s}^{-1}$) and •OH ($k_{OH} < 5.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) and therefore persist in ozonation and •OH-based AOPs. Activated carbon retained the very polar TP R471811 only up to a specific throughput of 25 m³kg⁻¹ (20% breakthrough), similarly to the X-ray contrast agent diatrizoic acid. Reverse osmosis was capable of removing all chlorothalonil TPs by 298%.

© 2020 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Chlorothalonil, a broad-spectrum fungicide, has recently been banned in the EU and Switzerland because of its carcinogenic properties, the risks to fish and amphibians, and the expected contamination of groundwater with chlorothalonil TPs (BLW, 2019a; European Commission, 2019). In Switzerland, chlorothalonil had predominantly been used for grain and vegetable cultivation, but its use had also been approved for viticulture and non-agricultural land. Chlorothalonil has been applied in high amounts for decades (first registration in the USA in 1966) (EPA, 1999), as shown by the sales data in Switzerland (45 t/a, 2017) and Germany (1000–2500 t/a, 2017), where chlorothalonil was among the ten most sold pesticides in 2017 (BLW, 2019b; BVL, 2018).

Due to the toxicity of the parent compound and insufficient toxicological data for the TPs, the European Food Safety Agency (EFSA) recommended to provisionally classify chlorothalonil TPs as relevant pesticide TPs in 2018 (EFSA, 2018), implying an EU drinking water standard of 100 ngL⁻¹ (European Commission, 1998). To our knowledge, the EU member states have not yet decided on the drinking water relevance of chlorothalonil TPs; e.g. in Germany the previous classification as non-relevant or not evaluated still applies, resulting in a higher drinking water standard. However, some European countries, such as Denmark and France, apply the same

^{*} Corresponding author. Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600, Dübendorf, Switzerland.

E-mail address: juliane.hollender@eawag.ch (J. Hollender).

https://doi.org/10.1016/j.watres.2020.116066

^{0043-1354/© 2020} The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

drinking water standard of 100 ngL⁻¹ to all pesticide TPs. Some non-European countries, e.g. Australia and the USA, define individual, risk-based thresholds, but so far only for a limited number of pesticides and TPs (Laabs et al., 2015). As recommended by the European Commission (2019), Switzerland recently classified chlorothalonil as carcinogen category 1B, thereby declaring all groundwater TPs as relevant (irrespectively of their toxicity), following the EU guidance document Sanco/221/2000 –rev.10final (European Commission, 2003).

To reduce drinking water contamination with organic micropollutants, various treatment processes exist, such as (i) managed aquifer recharge (Hollender et al., 2018; Maeng et al., 2011), (ii) activated carbon treatment (Delgado et al., 2012; Westerhoff et al., 2005), (iii) ozonation (Hübner et al., 2012; von Gunten, 2003; von Sonntag and von Gunten, 2012; Westerhoff et al., 2005), (iv) AOPs, e.g. UV/H₂O₂, O₃/H₂O₂, UV/Cl₂ (Chuang et al., 2017; Guo et al., 2018; Huber et al., 2003; Miklos et al., 2018; Stefan, 2018; von Gunten, 2018), and (v) membrane processes such as nanofiltration and reverse osmosis (Taheran et al., 2016). Treatment efficiency strongly depends on physical-chemical properties of a compound. Managed aquifer recharge is most effective for less polar and well-degradable compounds (Benotti et al., 2012; Maeng et al., 2011); similarly, activated carbon filtration retains especially semi- to non-polar micropollutants (Westerhoff et al., 2005). While the oxidant ozone (O_3) selectively transforms mainly electron-rich compounds (e.g. phenols), •OH produced during ozone decomposition and in AOPs are less selective and react with a broader spectrum of organic compounds (von Sonntag and von Gunten, 2012). While these oxidative methods may only partially abate the micropollutant load and can produce reaction products, reverse osmosis is capable of removing most micropollutants to a large extent. However, operational costs of reverse osmosis systems are high (Taheran et al., 2016) and the highly-concentrated reject water that is produced requires disposal (Umar et al., 2014).

In a recent suspect screening for more than 1000 pesticide TPs (including >25 chlorothalonil TPs) in Swiss groundwater, we have detected eight different chlorothalonil TPs, six of them reported for the first time (Kiefer et al., 2019). The chlorothalonil TP R471811 was even found in all 31 groundwater samples with concentrations up to 2700 ngL⁻¹. Due to the high usage of chlorothalonil worldwide, chlorothalonil TPs may be a widespread threat for drinking water quality. However, the efficiency of water treatment processes to abate chlorothalonil TPs from drinking water have not yet been evaluated.

Therefore, we aimed to investigate the abatement of sulfonic acid- and phenol-containing chlorothalonil TPs from water in fullscale waterworks, pilot plants, and laboratory experiments. Our hypothesis was that the more electron-poor and more polar sulfonic acid TPs (exhibiting at least one sulfonic acid group; R471811-SA, R419492-SA, R417888-SA, and two isomers of R417888-SA; "SA" for sulfonic acid) are probably more recalcitrant during oxidative or adsorptive treatment. In contrast, the less polar phenolic TPs (SYN507900-Ph, SYN548580-Ph, R611968-Ph, "Ph" for phenol) are probably abated more efficiently by oxidation or adsorption, as previously shown for other phenolic compounds (Kovalova et al., 2013a; Lee et al., 2005). First, chlorothalonil TPs were monitored in different drinking water resources such as in lakes, rivers, and groundwater to obtain more information on the scope of chlorothalonil TPs contamination. Second, the fate of chlorothalonil TPs in a full-scale water treatment train consisting of activated carbon, ozonation, and UV disinfection was investigated. Additional laboratory and pilot-scale experiments were carried out to supplement the full-scale observations regarding activated carbon, ozonation, and UV disinfection and to test additional advanced treatment processes (AOPs, reverse osmosis).

2. Materials and methods

2.1. Drinking water resources and waterworks

To investigate the fate of chlorothalonil TPs in water treatment. samples were taken along the treatment train of eight waterworks (Table SI-A1) in February 2019. Waterworks A abstracts raw water from the river Rhine. Suspended matter is removed in a settling pond followed by a rapid sand filter. Then, the clarified water is infiltrated into the aquifer, abstracted again (average residence time: days to two months) and filtered via three granular activated carbon filters (specific throughput at the time of sampling: 25, 55, 305 m³kg⁻¹). A final disinfection is performed with a medium pressure UV lamp. Waterworks B treats raw water from a karstic spring with ozonation (0.8 g O_3 g⁻¹ DOC (dissolved organic carbon)) followed by two granular activated carbon filters (specific throughput at the time of sampling: 23, 215 m³kg⁻¹). Waterworks C uses Lake Zurich water (abstraction point 30 m below the lake surface), which is ozonated in two steps (pre- and intermediate ozonation) with different specific ozone doses (0.3 and 0.6 g O_3 g⁻¹ DOC). Ozonation is followed by twelve granular activated carbon filters (average specific throughput at the time of sampling: 1200 m³kg⁻¹, i.e. mainly biological and not adsorptive filters) and slow sand filtration. Waterworks D abstracts river bank filtrate from the river Limmat (outflow of Lake Zurich, Switzerland). The bank filtrate is disinfected (Cl₂/ClO₂), infiltrated into the aquifer and abstracted again. In addition, seven groundwater abstraction wells and four springs were sampled in Switzerland. The water from these wells or springs is delivered to the consumer as drinking water either without further treatment, with only minor treatment (UV disinfection), or after mixing with water from other sources (Table SI-A1, waterworks E-I).

Samples were collected in laboratory glass bottles (previously annealed at 500 °C; 500 mL bottles, SIMAX Kavalier, Czech Republic) in February 2019 and then frozen at -20 °C until sample enrichment and measurement. Six field blanks, consisting of ultrapure water (>18 M Ω cm, Barnstead Nanopure Diamond system and Elga Purelab Chorus) filled in sampling bottles, transferred to a second bottle during sampling, and frozen until enrichment and measurement, did not show detectable concentrations of the target analytes, demonstrating that no contamination occurred during sample handling and analysis. Furthermore, rain water from Dübendorf (vicinity of Zurich, 431 m above sea level, Switzerland) and Jungfraujoch (3571 m above sea level, Switzerland) was collected and analysed as background controls from hypothetically uncontaminated field sources. Since evian® water is used in many laboratories for calibration standard preparation, additionally evian® water (bottled in polyethylene terephthalate, PET) was enriched and analysed as a blank sample.

To investigate the occurrence of chlorothalonil TPs in groundwater (the major drinking water resource in Switzerland), we also present semi-quantitative data for 60 groundwater samples, collected in May and August 2018 within the Swiss National Groundwater Monitoring NAQUA (www.bafu.admin.ch/naqua). The 60 groundwater monitoring sites were selected based on longterm monitoring data. Twenty sites were known to have very low overall micropollutant concentrations, whereas 40 sites were chosen because micropollutants from urban or agricultural sources had been detected in the past. These samples were analysed using a comparable analytical method as described in section 2.4.

2.2. Stock solutions and chemicals

Stock solutions for liquid chromatography high-resolution tandem mass spectrometry (LC-HRMS/MS) analyses were prepared depending on compound solubility in ethanol, methanol or ethanol/water (1:1, volumetrically) at a concentration of 0.1 or 1 gL⁻¹. As organic solvents may influence ozonation and photo-degradation experiments, stock solutions for laboratory experiments (except for activated carbon) were prepared in water (20–100 μ M corresponding to 0.005–0.035 gL⁻¹). For details, see SI-A2.

Six chlorothalonil TPs (Fig. 1), reported by Kiefer et al. (2019) in groundwater and for which reference material was available (ASCA GmbH, Germany; Syngenta, Switzerland), were analysed in the environmental water samples (section 2.1). The TPs differ in their functional groups (Fig. 1). All TPs contain at least one amide group, three of the TPs have at least one hydroxyl group (phenolic TPs), whereas the other three TPs are characterized by at least one sulfonic acid group (sulfonic acid TPs). For the laboratory experiments, two phenolic TPs (R611968-Ph, SYN507900-Ph) and two sulfonic acid TPs (R471811-SA, R417888-SA) were selected as test compounds and it was assumed that structurally related TPs would behave similarly during water treatment. The four TPs were selected due to lower measurement uncertainty compared to R419492-SA and SYN548580-Ph.

2.3. Laboratory and pilot-scale experiments

Abatement of micropollutants with ozone or to a lesser extent with •OH or degradation by UV photolysis can depend on the speciation of organic compounds such as phenols. For the phenolic TPs considered here (R611968-Ph and SYN507900-Ph), experimentally determined acid-base equilibrium constants (pK_a) were not available, so the exact speciation under environmentally relevant pH values is not known. However, the predicted pK_a values (4.1 and 4.7, Fig. 1; predicted with JChem for Office, version 17.1.2300.1455, ChemAxon Ltd.) are more than two units below environmentally relevant pH values, indicating the dominance of the anionic phenolate species (>99%). To obtain data applicable to most waterworks, all laboratory experiments were conducted at pH 7.5 using a 5 mM phosphate buffer, unless stated otherwise. Laboratory experiments were performed individually for each compound, unless stated otherwise. Samples from laboratory or pilot-scale experiments were analysed without prior enrichment.

2.3.1. UVC irradiation

Photodegradation under UVC irradiation (four RPR-2537A lamps centered around 254 nm, Rayonet, Southern New England Ultraviolet Company, Branford, USA, emission spectrum in Fig. SI-A1) was carried out in a merry-go-round photoreactor (Rayonet, Southern New England Ultraviolet Company, Branford, USA) and by back-to-front light exposure. Temperature was kept constant $(12 \pm 2 \circ C, typical for groundwater in Central Europe)$. Depending on the reactivity, TPs (0.1 µM, pH 7.5) were irradiated for 40–150 min in quartz test tubes (diameter: 1.3 cm, length: 7 cm). Photon fluence rates were determined by chemical actinometry using atrazine as described by Zepp, 1978 (pH 7.0, 5 mM phosphate buffer; quantum yield: 0.046 molE⁻¹, Hessler et al. (1993), molar absorption coefficient: 3860 M⁻¹cm⁻¹ at 254 nm, Nick et al. (1992)). Atrazine shows similar phototransformation rates as the phenolic TPs, is easy to handle and analyse, and was successfully tested and compared to the actinometer hydrogen peroxide by Canonica et al. (2008). The photon fluence rate was $4.0-5.3 \times 10^{-5} \text{ Em}^{-2} \text{s}^{-1}$ (determined on different days). For details, including light emission spectra and absorbance spectra of



Fig. 1. Concentration distribution of different chlorothalonil TPs in 77 samples (73 x groundwater, 4 x surface water). Non-detects (LOQs: $0.2-5 \text{ ngL}^{-1}$) are not included in the boxplots. The sulfonic acid-containing TPs (on the left in green) were more frequently detected and at higher concentrations than the phenol-containing TPs (on the right in white). The red line marks the Swiss drinking water standard. The open circles represent outliers. The gray solid circles show the concentrations of individual samples. Dissipation time DT₅₀ from EFSA (2018), logD_{OW}, _{pH7} (water-n-octanol distribution coefficient considering the speciation at pH 7) and pK_a (acid dissociation constant) were predicted with JChem for Office (Version 17.1.2300.1455; ChemAxon Ltd.). *R419492: high measurement uncertainty (-0.5-2 × reported concentration). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

chlorothalonil TPs and data analysis for photon fluence rates, quantum yields, and photon fluence-based rate constants, see SI-A5.

2.3.2. Ozonation

To determine the second order rate constant (k_{03}) for the reaction of ozone with the slowly-reacting sulfonic acid TPs (R471811-SA, R417888-SA), TPs were exposed to ozone in excess at pH 2.3 (0.1 μ M TP, 100 μ M ozone, 10 mM phosphoric acid, 10 mM *tert*-butanol to scavenge •OH) in a 250 mL glass bottle with a dispenser system (Hoigné and Bader, 1994). Acidic conditions were selected as ozone is more stable at low pH (von Sonntag and von Gunten, 2012) and the sulfonic acid TPs do not change their speciation over a wide pH range (predicted pK_a –4.3, Fig. 1). The ozone concentration and TP abatement were monitored over 15 h (for details, see SI-A6).

The reaction kinetics for the faster reacting phenolic TPs (SYN507900-Ph, R611968-Ph) were investigated by competition kinetics using salicylic acid as a competitor ($k_{03} = 2.8 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$, Hoigné and Bader (1983)). Phenolic TPs (1 µM) and salicylic acid $(1 \mu M)$ were exposed to varying ozone doses $(0-4.5 \mu M)$ at pH 7.5 in 10 mL glass vials in presence of tert-butanol (50 mM, to scavenge •OH) (for details, see SI-A7). Other compounds for which reliable second order rate constants were reported (e.g. carbamazepine, clarithromycin) were also tested or considered as competitors but finally not used, either due to higher reactivity with ozone (carbamazepine, $k_{03} = 3 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$, Huber et al. (2003)) or analytical problems (clarithromycin). Direct measurement of the second order rate constant with ozone (similar approach as for the sulfonic acid TPs) was not feasible for the phenolic TPs because these reactions are too fast to be observed in batch reactors at environmentally relevant pH values.

2.3.3. Advanced oxidation

To evaluate the potential of AOPs, the second order rate constants were determined for the reactions of •OH (k_{OH}) with the TPs. •OH can be produced by a combination of hydrogen peroxide (H_2O_2) with UV irradiation or ozone, or at high pH directly from ozone (Rosenfeldt and Linden, 2004; Staehelin and Hoigne, 1982). Here, TPs (0.1 μ M) were exposed to H_2O_2 (1 mM) at pH 7.5 in a comparable reactor set-up as for UVC photodegradation experiments (section 2.3.1; here: UVA light with emission peak at 367 nm). To reduce the experimental effort, R471811-SA and SYN507900-Ph, and R417888-SA and R611968-Ph, respectively, were exposed to UVA/ H_2O_2 in the same vials. The second order rate constant k_{OH} was determined by competition kinetics using benzoic acid as a reference compound exhibiting similar reactivity as the TPs (10 μ M, $k_{OH} = 5.9 \times 10^9$ M⁻¹ s⁻¹, Buxton et al. (1988)) (for details, see SI-A9).

Using this experimental set-up, the sulfonic acid TPs showed no degradation, probably because the •OH concentration was too low (10⁻¹⁵ M). Thus, the second order rate constants for sulfonic acid TPs were determined by exposure to higher •OH concentrations produced from ozone (0–80 μ M) under alkaline conditions (pH ~10, 0.3 mM NaOH), with the X-ray contrast agent diatrizoic acid as a competitor. Diatrizoic acid was selected as a competitor due to its low reactivity ($k_{OH} = 5.4 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$, Real et al. (2009)), which is of similar order of magnitude as that expected for the sulfonic acid TPs. Degradation by ozone could be excluded due to the low stability of ozone at pH ~10 and the very low ozone reactivity of both diatrizoic acid (k_{O3} 0.05 M⁻¹s⁻¹, Real et al. (2009)) and sulfonic acid TPs (<0.04 M⁻¹s⁻¹, see section 3.3.1 and Table 1). For details, see SI-A8.

2.3.4. Activated carbon

The potential of adsorption to activated carbon was evaluated by conducting powdered activated carbon batch experiments. As the experimental set-up does not take into account kinetic effects. adsorption might be overestimated compared to granular activated carbon filters. In order to compare not only the adsorption behaviour between the chlorothalonil TPs but also relative to other micropollutants present in many waterworks, the herbicide atrazine and the X-ray contrast agent diatrizoic acid were also included in the experiments as reference compounds. Adsorption to activated carbon is affected by the water matrix and micropollutant concentration (Delgado et al., 2012; Knappe et al., 1998). To simulate real water conditions as closely as possible, groundwater (DOC 1.1 mgL⁻¹, electrical conductivity 840 μ Scm⁻¹) was spiked to a target concentration of ~500 ngL^{-1} for each TP (test solution <0.05% MeOH). Adsorption experiments were not performed for each chlorothalonil TP individually because it was assumed that the competition for adsorption sites between the chlorothalonil TPs and natural organic matter (NOM; low mgL⁻¹ range) and further anthropogenic micropollutants affects the adsorption to a larger extent than the competition between the individual chlorothalonil TPs (ngL^{-1} range). The test solution (17 mL spiked groundwater, $34-680 \,\mu\text{L}$ activated carbon suspension, $0-646 \,\mu\text{L}$ ultrapure water) was stirred for 42 h in closed glass vials with varying powdered activated carbon doses (0-40 mgL⁻¹, Eurocarb CC PHO 8x30, added as suspension). The chlorothalonil TP concentration in the supernatant solution was determined after filtration (Chromafil® Xtra RC-20/13, 0.2 µm).

2.3.5. Reverse osmosis

Reverse osmosis was investigated in a pilot-scale experiment at the waterworks E (Table SI-A1). Raw water originated from groundwater that was highly contaminated with chlorothalonil TPs (total concentration ~2000 ngL^{-1}). The raw water was pumped through a spiral wound reverse osmosis membrane (TMG20D-400, Toray Membrane Europe AG, Switzerland) with a pre-filter (PP95BL5L2005, Everblue, Italy), recovering 38–65% as permeate (permeate flow rate 12.9–14.0 Lmin⁻¹, for details, see SI–B10). Within a period of fourteen weeks, five raw water, five permeate, and three reject water samples were taken. Between sampling campaign two and three, the membrane was exchanged due to clogging because the antiscalant (ROPUR RPI-3000A, Toray Membrane Europe AG, Switzerland) had not correctly been dosed.

2.4. Analytical methods

2.4.1. Enrichment of environmental samples

Environmental samples were enriched via vacuum-assisted evaporative concentration using a Syncore® Analyst (BÜCHI, Switzerland) according to the method validated by Mechelke et al. (2019) with slight modifications. A sample volume of 120 mL was spiked with 221 isotope-labelled internal standards (100 ngL⁻¹) and evaporated into BÜCHI glass vials (1 mL appendix cooled at 7–10 °C) at 20 mbar and 45 °C to ~1 mL using a back-flush unit. The sample volume was adjusted to 1.2 mL with ultrapure water. To reduce analyte loss by sorption to the glass surface, the BÜCHI vials were rinsed thoroughly with the sample. Then, the sample was centrifuged at 3720 g (Heraeus Megafuge 1.0 R, Thermo Fisher Scientific, U.S.) for 15 min in annealed centrifuge vials. The supernatant was transferred to 1.5 mL vials (with screw caps; BGB Analytik AG, Switzerland) and kept at 8 °C until measurement. Analogous to the environmental samples, 17 calibration standards (0.1–2000 ngL⁻¹ in ultrapure water), seven laboratory and field blank samples, one evian(m, two rain water samples, and nine spiked samples (10, 100, 250, 500 ngL⁻¹) were prepared and analysed.

2.4.2. HPLC-MS/MS and HPLC-UV analyses

2.4.2.1. Environmental samples. Analytes were separated with high-performance LC (HPLC) on a reverse phase C18 column (Atlantis® T3 3 μ m, 3.0 × 150 mm; Waters, Ireland) with water and methanol as eluents, both modified with 0.1% concentrated formic acid. The injection volume was 150 μ L corresponding to 15 mL of the original water sample. Samples were analysed in sequence, first in negative, then in positive electrospray ionization mode (-2.5/3.5 kV) on an Orbitrap high-resolution mass spectrometer (Fusion Lumos, Thermo Fisher Scientific, U.S.).

2.4.2.2. Laboratory and pilot experiments. Samples from ozonation, UV irradiation and advanced oxidation experiments were spiked with isotope-labelled internal standards (2500 ngL⁻¹) and then measured with the same analytical method as the environmental samples, except for a lower injection volume (100 μ L). Additionally, the first 5 min of the HPLC run were directed to the waste to reduce interferences from the phosphate buffer. Samples from experiments conducted at elevated TP concentration (1 μ M) were diluted by a factor of ten.

The adsorption experiments with activated carbon (section 2.3.4) were measured with another analytical method at the Laboratory for Operation Control and Research (Zweckverband Landeswasserversorgung, Germany). For chromatographic separation an Ultra Aqueous C18 column (5 μ m, 4.6 \times 250 mm; Restek, U.S.) was used with an injection volume of 100 μ L and with water and acetonitrile as eluents, each acidified with 0.1% concentrated formic acid. Analytes were ionized using electrospray (4.5/-4.5 kV) in switching mode and detected with a triple quadrupole mass spectrometer (API 5500 Qtrap, Sciex, U.S.).

Samples from the reverse osmosis pilot plant were analysed at the Water and Soil Protection Laboratory (Office of Water and Waste Management of the Canton of Berne) for four pesticide TPs with high concentrations (chlorothalonil TPs R471811-SA and R417888-SA, chloridazon-desphenyl, chloridazon-desphenylmethyl) using a comparable LC-HRMS/MS method (injection volume 100 μ L; Atlantis® T3 3 μ m, 3.0 \times 150 mm; Waters, Ireland; QExactive, Thermo Fisher Scientific, U.S.). Selected samples were additionally measured at Eawag (comparable method to environmental samples, without enrichment). Major cations and anions were analysed at the Eawag apprenticeship laboratory.

The actinometer atrazine (section 2.3.1) was analysed on a Dionex UltiMate 3000 RS HPLC system coupled to a diode array detector (Thermo Fisher Scientific, U.S.) using a reverse phase C18 column (Atlantis® T3 3 μ m, 3.0 \times 150 mm; Waters, Ireland). Data was processed with the Chromeleon 7.2.1 Software. For details on HPLC-MS/MS and HPLC-UV analyses, see SI-A3.

2.4.3. Quantification

Samples measured with HPLC-MS/MS were quantified using TraceFinder 4.1 (Thermo Fisher Scientific, U.S.) and MultiQuant 3.0.3 (Sciex, U.S.), as appropriate. For each analyte and measurement, an isotope-labelled internal standard was selected for quantification that eluted at a similar retention time as the analyte and resulted in a relative recovery close to 100% and high reproducibility across different spiked samples (for more details, see Kiefer et al. (2019) or SI-A4). Quantification results including limits of quantification (LOQs, 0.2–10 ngL⁻¹ in environmental samples), relative recoveries (average 85–110% and relative standard deviation <20% across spiked samples in environmental samples) and isotope-labelled internal standards are provided in SI–B1 and

SI-B2

The chlorothalonil TPs R419492-SA and SYN548580-Ph were quantified retrospectively because reference material was received after analysis. For quantification and quality control, eleven calibration standards, one blank sample, six samples from drinking water treatment and six corresponding spiked samples were enriched and analysed (section 2.4.1 and 2.4.2). This calibration model was applied to the previously measured samples. The concentration of SYN548580-Ph deviated less than 20% in the six samples, which were measured twice. However, in case of R419492-SA, the concentration results differed by a factor of two. Due to the early retention time of R419492-SA, a suitable internal standard was not available. Therefore, R419492-SA concentrations were multiplied by two in the retrospectively quantified samples. It should be noted that measurement uncertainty for R419492 is expected to be higher ($\sim 0.5-2 \times$ reported concentration) than in case of the other chlorothalonil TPs (~0.7-1.5 \times reported concentration). The abatement of chlorothalonil TPs in the waterworks was compared to the abatement of the sweetener acesulfame and the X-ray contrast agent diatrizoic acid. In contrast to acesulfame, diatrizoic acid could not be guantified because reference material for diatrizoic acid was not included in the multi-component standard solution for quantification of the environmental samples. However, abatement was calculated from differences in the response ratios of diatrizoic acid and its structurally identical isotope-labelled internal standard before and after treatment.

To estimate the error of the calculated abatement efficiencies in water treatment due to measurement uncertainty, each sample taken along the treatment train was measured in triplicate. The uncertainty in removal was calculated based on the standard deviation of the measurement triplicates using Gaussian error propagation. In addition, three samples were enriched and measured in triplicate to assess the reproducibility of sample enrichment. The standard deviations of the triplicate measurement concentrations and the enrichment triplicates was comparable.

To determine the extent of chlorothalonil TPs in groundwater, concentrations were quantified in 60 groundwater samples (section 2.1) that have been analysed using a comparable method as the one used for the environmental samples in this study. The major differences were a lower enrichment factor (75 instead of 100) and a lower injection volume (140 instead of 150 μ L), corresponding to 10.5 mL of the original sample (instead of 15 mL). Additionally, only 35 isotope-labelled internal standards were spiked. The samples were analysed together with four calibration standards (1, 10, 100, 1000 ngL⁻¹) and three spiked samples (10, 100, 250 ngL⁻¹⁾, containing among other compounds the chlorothalonil TPs R471811-SA, R417888-SA, SYN507900-Ph and R61198-Ph. The concentrations of the chlorothalonil TPs R419492-SA and SYN545850-Ph were estimated based on the calibration standards measured separately (see above).

3. Results and discussion

3.1. Chlorothalonil TPs in drinking water resources

Fig. 1 illustrates the concentration ranges of the chlorothalonil TPs in different drinking water resources. In addition to the TPs presented in Fig. 1, the TPs R611965 (carboxylic acid) and R418503-SA were investigated with reference material (LOQ 10 ngL⁻¹) but never detected. SYN548581-SA, which is the R417888-SA isomer that we previously identified only tentatively based on comparison of the isotope pattern, predicted MS/MS spectrum and retention time (Kiefer et al., 2019), was now confirmed with reference material (Fig. SI-A9). As expected, none of the TPs were found above the LOQ of 0.2–10 ngL⁻¹ in rain water or ultrapure water. TP

R471811-SA was detected in all other samples, even in groundwater with very low anthropogenic impact, in surface water (river Rhine: 53 ngL^{-1} , Lake Zurich: 5 ngL^{-1}), and in bottled water (evian® water: 6 ngL^{-1}). The two other sulfonic acid TPs, R417888-SA and R419492-SA, were detected in 86% and 65% of samples (without rain and ultrapure water), whereas the phenols (R611968-Ph, SYN507900-Ph, SYN548580-Ph) were detected less frequently (in 10–30% of the samples) and at lower concentrations (Fig. 1). In the four surface waters investigated (3 rivers, 1 lake), all TPs had concentrations below 100 ngL⁻¹; whereas at least one TP was above 100 ngL⁻¹ in 40 out of 73 groundwater samples. It should be noted that concentrations in rivers may be subject to stronger seasonal fluctuations compared to concentrations in groundwater (for a compilation of all quantitative data, refer to SI–B1 and SI–B2).

Based on long-term monitoring data, the 60 groundwater monitoring sites were pre-classified as influenced by agricultural micropollutants (20 sites), micropollutants from wastewater (20 sites, often influenced by river bank filtration), or with only low anthropogenic influence (20 sites, section 2.1). As expected, the median concentration of the chlorothalonil TPs was higher in groundwater samples influenced by agriculture (515 ngL⁻¹) than in groundwater samples pre-classified as wastewater-impacted (99 ngL⁻¹) or in samples with only low anthropogenic influence (19 ngL⁻¹). The phenols play a minor role for the drinking water quality, since they exceeded 100 ngL⁻¹ in only 3% of samples, whereas the sulfonic acids R471811-SA, R417888-SA, and R419492-SA exceeded 100 ngL⁻¹ in 52%, 14%, and 14% of samples, respectively.

The concentration ratios between the TPs vary strongly from sample to sample (SI-B1). For example, TP R471811-SA was found at 2-50 times (median: 7.4) higher concentrations compared to its direct precursor compound, TP R417888-SA. These differences could be related to a different formation rate and/or transport behavior. The less polar TP R417888-SA is more affected by sorption than the more polar TP R471811-SA. Therefore, in case of TP R417888-SA, the degree of retardation during transport through the unsaturated zone might depend more strongly on the sitespecific soil/sediment characteristics (e.g. organic carbon) than in the case of TP R471811-SA. In addition, more R417888-SA will be oxidized to R471811-SA with increasing residence time (depending e.g. on size of soil/sediment particles) in the biologically more active aerobic top soil. Therefore, we speculate that the concentration ratio between the TPs R471811-SA and R417888-SA will increase with increasing organic carbon content and residence time in the unsaturated zone.

3.2. Abatement of chlorothalonil TPs during drinking water treatment

Fig. 2 provides an overview of the abatement by granular activated carbon filtration, ozonation and UV disinfection in different waterworks, while Fig. 3 illustrates the abatement of the three sulfonic acid TPs along the treatment train of waterworks A and B (phenolic TPs were not detected). Waterworks C and D showed only very low concentrations of chlorothalonil TPs in the raw water and were therefore not discussed in detail (Lake Zurich and river Limmat both \leq 7 ngL⁻¹, see SI–B2 for all quantitative data). Sand filtration and subsequent infiltration to the aquifer followed by abstraction did not lead to a decrease of the concentrations (Fig. 3, left), which is in accordance with the high mobility and persistence of the sulfonic acid TPs (EFSA, 2018).

Whereas the sulfonic acid TPs were stable during ozonation and UV disinfection, granular activated carbon filtration led to an abatement (Fig. 3). However, only very fresh activated carbon (specific throughput 23 and 25 m³kg⁻¹, waterworks A and B) was capable of sufficiently abating all sulfonic acid TPs (R471811-SA:

80% abatement; R417888-SA, R419492-SA: below LOQ). For slightly older activated carbon (specific throughput 55 $m^3 kg^{-1}$, waterworks A), no retention of R471811-SA was observed, whereas R419492-SA was still abated by 55% and R417888-SA was below LOQ. An activated carbon filter with a specific throughput of 215 $m^3 kg^{-1}$ (waterworks B) retained only the sulfonic acid TP with the highest water-n-octanol distribution coefficient considering the speciation at pH 7 (log D_{OW pH7}; R417888-SA, 58% abatement). The oldest activated carbon filter (specific throughput 305 $m^3 kg^{-1}$, waterworks A) had higher effluent than influent concentrations for all sulfonic acid TPs, indicating slight leaching from the filter.

The poor retention behaviour for R471811-SA was comparable to the breakthrough behaviour of the X-ray contrast agent diatrizoic acid (Fig. 2). Whereas both compounds were still abated by 80% by fresh activated carbon (specific throughput 25 m³kg⁻¹), neither R471811-SA nor diatrizoic acid were abated by slightly older activated carbon (specific throughput 55 and 305 m³kg⁻¹; diatrizoic acid was not present in the raw water of waterworks B). It should be noted that the results from the two waterworks A and B are in good agreement, although different granular activated carbons were used (waterworks A: bituminous coal, Filtrasorb® 400, Calgon Carbon Corporation; waterworks B: bituminous coal, Hydraffin® XC 30, Donau Carbon).

In intensively used agricultural areas, managed aquifer recharge can decrease groundwater contamination with chlorothalonil TPs by dilution because surface waters are usually less polluted with chlorothalonil TPs (section 3.1). Three of the investigated groundwater abstraction wells were close to a river (40–730 m), which was only slightly contaminated (concentration sum of chlorothalonil TPs 100 ngL^{-1} in a grab sample). With increasing distance to the river, the concentration sum of the chlorothalonil TPs in the abstracted groundwater increased (2 abstraction wells 40 m from river: 85 and 220 ngL^{-1} , concentrations may differ due to a different pumping regime before sampling, leading to different proportions of river water in the abstracted sample; abstraction well 730 m from river: 420 ngL⁻¹; SI–B2). However, managed aquifer recharge may introduce other organic micropollutants such as wastewaterderived compounds (Hollender et al., 2018). Accordingly, we observed higher concentrations of the sweetener acesulfame in abstraction wells close to the river compared to an abstraction well with larger distance to the river (grab sample in river: 280 ngL^{-1} ; 2 abstraction wells 40 m from river: 120 and 34 ngL⁻¹, concentrations may differ due to a different pumping regime before sampling; abstraction well 730 m from river: 11 ngL^{-1} ; SI-B2).

The phenolic TPs were partly abated by UV disinfection with a large variability (57 \pm 43%, Fig. 2, SI–B3, waterworks E and F). No clear difference in abatement between the UV disinfection systems with low pressure Hg lamps (monochromatic UV light, 254 nm) or medium pressure Hg lamps (polychromatic UV light) was observed (Fig. 2). UV systems at waterworks are usually installed for disinfection, requiring only low fluences, i.e. >400 Jm⁻² according to German, Austrian and Swiss legislation (DVGW, 2006; ÖNORM, 2001; SVGW, 2010). Despite the low fluences, abatement of some organic micropollutants has been reported. Scheurer et al. (2014) observed 30% abatement of the sweetener acesulfame at a waterworks in Basel, Switzerland, and similar acesulfame abatement (30–50%, Fig. 2) was observed at the UV disinfection systems in this study. In addition to acesulfame, we also observed partial abatement of diatrizoic acid (30–40%, Fig. 2). In contrast, UV disinfection did not affect the concentration of the sulfonic acid TPs (waterworks A, Fig. 3). The slight abatement or formation observed at three other UV systems (Fig. 2) likely reflects uncertainty from sampling and sample analysis.

It can be asked whether the investigated TPs may also be formed in the waterworks from chlorothalonil or chlorothalonil TPs.



Fig. 2. Abatements of chlorothalonil TPs by different treatment processes across multiple waterworks; for comparison acesulfame and diatrizoic acid are also included. Error bars indicate measurement uncertainty propagated from standard deviation of measurement triplicates (no triplicate measurements for diatrizoic acid). Uncertainty from sampling is not included. Abatement <LOQ is reported as 100%. The apparent formation of R417888-SA in ozonation was only observed in one sample with concentrations close to the LOQ (SI–B2) and is probably related to measurement uncertainty. GAC: granular activated carbon; LP: low pressure Hg lamp; MP: medium pressure Hg lamp; MP1&2: waterworks E, MP3: waterworks A, see Table SI-A1; (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Chlorothalonil itself was not analysed in this study as it does not ionize sufficiently in electrospray. However, based on laboratory and lysimeter experiments performed within the EU pesticide registration process (EFSA, 2018) and a German groundwater monitoring program (LUBW, 2011), the presence of chlorothalonil in the raw waters in relevant concentrations is unlikely. Accordingly, the water supplier operating waterworks B regularly checks for chlorothalonil in the raw water using gas chromatography electron ionization mass spectrometry, but has never detected this compound (LOQ = 20 ngL^{-1}). Furthermore, a formation of one target TP from another target TP was only observed in small amounts in the laboratory experiments, i.e. 2% R471811-SA was formed from R417888-SA at pH 10 (for each ozone dose, including the control without ozone, SI-A8), indicating very slow basic hydrolysis (section 3.3). Therefore, we expect that the results of our study are not influenced by chlorothalonil TPs formed in the waterworks.

3.3. Laboratory experiments

Table 1 provides the results from laboratory experiments with ozone, UV and AOPs and corresponding literature data for common micropollutants for comparison. SI–B4 to SI–B10 show the experimental data, SI-A5 to SI-A10 describe the calculations of the reported values.

3.3.1. UV irradiation

In full-scale water treatment, the phenolic TPs were partially abated by UV disinfection ($57 \pm 43\%$), whereas the sulfonic acid TPs were persistent (section 3.2, Fig. 2). The UVC irradiation experiments confirmed the higher photodegradability at 254 nm of the phenolic TPs, exhibiting higher photon fluence-based rate constants (Table 1). The fast decay of the phenolic TPs relates to their higher quantum yields compared to the sulfonic acid TPs, while all TPs have moderate to high molar absorptivities (Table 1, Fig. SI-A1 and SI-A2). Using the photon fluence-based rate constants determined, we calculated the theoretical abatement by UV disinfection (SI-A5), assuming an applied UV dose of 400 Jm⁻² as prescribed in

Switzerland, Germany and Austria (DVGW, 2006; ÖNORM, 2001; SVGW, 2010). Theoretically, <0.2% of the sulfonic acids and <2.5% of the phenols should be abated under such UV disinfection conditions (Table, SI-A10). However, abatement in full-scale treatment (Fig. 2) was higher compared to the estimates from UVC treatment alone. This difference might be explained by indirect phototransformation due to production of reactive intermediates that can contribute to the removal of micropollutants, i.e. reactions with radicals or triplet states generated by photoexcitation of dissolved organic matter or nitrate (Canonica et al., 1995; Mark et al., 1996; Zepp et al., 1987). Especially nitrate may play an important role, because groundwater polluted with chlorothalonil TPs often has elevated nitrate concentrations, since both originate from mainly agricultural sources (median of nitrate concentration in groundwater samples with phenolic TPs: 20 mgL $^{-1}$, SI–B1). In contrast, dissolved organic matter concentrations are usually low in groundwater (DOC in the 60 groundwater samples $<2.1 \text{ mgL}^{-1}$). Indirect phototransformation is especially important for compounds susceptible to oxidation such as phenols (Canonica et al., 2008).

In addition to disinfection, UV irradiation is used to generate •OH in UV-based AOPs. The fluence applied in UV-based AOPs (5000–10000 Jm⁻², Chuang et al. (2017)) are about 10–25 times higher compared to UV disinfection, so also direct photo-transfomation can become relevant in case of the phenols. An abatement of 24% for R611968-Ph and 37% for SYN507900-Ph is estimated for a UV dose of 7500 Jm⁻² and the respective rate constants. For 90% abatement of the phenolic TPs by direct photolysis, 38000–64000 Jm⁻² would be required; for the sulfonic acid TPs UV doses would need to be even ten times higher (Table SI-A10).

3.3.2. Ozonation

In the ozonation step of waterworks B, the sulfonic acid TPs were not degraded (section 3.2). This is in agreement with the very low second order rate constant for the reaction with ozone $(k_{03} < 0.04 \text{ M}^{-1}\text{s}^{-1}, \text{Table 1})$. Only micropollutants with second order rate constants $\gg 10 \text{ M}^{-1}\text{s}^{-1}$ are significantly abated during ozonation (von Sonntag and von Gunten, 2012); e.g. acesulfame



Fig. 3. Abatement of sulfonic acid chlorothalonil TPs along the treatment train of waterworks A (left) and B (right; calculated from one step to the next step). The UV disinfection system was equipped with a medium pressure Hg lamp. Phenolic TPs were not detected. logD_{OW, pH7} (water-n-octanol distribution coefficient considering the speciation at pH 7) predicted with JChem for Office (Version 17.1.2300.1455; ChemAxon Ltd.).

 $(k_{03} = 88 \text{ M}^{-1}\text{s}^{-1}$, Table 1) was abated by > 85% during ozonation (waterworks B and C; Fig. 2). The measured second order rate constants support our hypothesis that ozone only minimally reacts with the sulfonic acid TPs, because the benzene rings have six electron-withdrawing substituents such as chlorine, sulfonic acid, cyano- and/or amide-groups (Fig. 1). Ozone-refractory compounds (e.g. atrazine, Table 1) are mostly abated by •OH that are formed from ozone decay and ozone reactions with dissolved organic matter as secondary oxidants (von Sonntag and von Gunten, 2012). However, the sulfonic acid-containing TPs are also very refractory against •OH ($k_{OH} < 5.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, Table 1), explaining why no abatement was observed in waterworks B for these compounds.

In contrast, the more electron-rich phenolic TPs are clearly more reactive, as expected, both with ozone and •OH ($k_{O3} > 10^4 \text{ M}^{-1}\text{s}^{-1}$, Table 1). To what extent the phenolic TPs will be abated in full-scale treatment cannot be concluded from the data presented here because the concentrations of the phenolic TPs were <LOQ in the raw water of waterworks B and C. However, Hollender et al. (2009) showed for a wastewater treatment plant with $5.2 \pm 0.6 \text{ mgL}^{-1}$ DOC and hydraulic retention times of 3.7-10.1 min in the ozone reactor that micropollutants with $k_{O3} > 10^4 \text{ M}^{-1}\text{s}^{-1}$ are fully abated at ozone doses >0.4 g ozone g^{-1} DOC. Therefore, we assume that the phenols will be fully abated in waterworks B (0.8 g O₃ g⁻¹ DOC, contact time > 10 min) and C (pre-ozonation: 0.3 g O₃ g⁻¹ DOC, contact time >25 min; intermediate ozonation 0.6 g O₃ g⁻¹ DOC;

contact time >10 min).

For phenolic compounds, Lee and von Gunten (2012) developed quantitative structure-activity relationships (QSARs) based on substituent descriptors (Hammett constants) to predict the second order rate constants for the reactions with ozone. The proposed QSAR was applied to predict the second order rate constants of R611968-Ph and SYN507900-Ph, and in addition, of the phenolic TP, which was not investigated in laboratory experiments (SYN548580-Ph, see SI-A7). The second order rate constants of R611968-Ph and SYN507900-Ph predicted by QSAR were on average 2.4 times higher than the measured values. A factor 2.4 is within the uncertainty described by Lee and von Gunten (2012). The predicted second order rate constant of SYN548580-Ph was three to five times higher than the predicted second order rate constants of SYN507900-Ph and R611968-Ph, indicating higher abatement.

3.3.3. Advanced oxidation

Overall, a broader range of micropollutants can be transformed in AOPs compared to ozonation because the •OH generated in AOPs is a less selective oxidant (von Gunten, 2018). Moreover, direct phototransformation by UV irradiation can contribute to micropollutant abatement depending on the AOP applied (e.g. UV/H₂O₂, UV/free chlorine) (Katsoyiannis et al., 2011).

The second order rate constant for the reaction of R611968-Ph

Table 1

Rate constants and photochemical parameters determined in laboratory experiments in this study (chlorothalonil TPs) or from literature (other micropollutants): second order rate constant for the reactions of target compounds with ozone (k_{O3}) or •OH (k_{OH}), photon fluence-based rate constant k_E , molar absorptivity \mathcal{E}_{254nm} , and the quantum yield Φ ; \pm standard deviation or as reported in respective study.

Compound	Ozone k_{O3} in $M^{-1}s^{-1}$	•OH k_{OH} in $M^{-1}s^{-1}$	UVC $k_{\rm E}$ in ${\rm m}^2 {\rm einstein}^{-1}$	UVC \mathcal{E}_{254nm} in M^{-1} cm ⁻¹	UVC Φ in mol einstein ⁻¹
R471811-SA R417888-SA SYN507900-Ph R611968-Ph Acesulfame Atrazine Carbamazepine Diatrizoic Acid	$<0.04 <0.04 4.1 \times 10^{4*} (2.6 \pm 0.3) \times 10^{4*} 88 (a) 6 (e) ~3 \times 10^5 (h) 0.05 \pm 0.01 (i)$	$<5.0 \times 10^{7}$ $<5.0 \times 10^{7}$ not determined $(2.7 \pm 0.6) \times 10^{9}$ 4.55×10^{9} (a); $(3.8 \pm 0.3) \times 10^{9}$ (b) 3×10^{9} (c) $(8.8 \pm 1.2) \times 10^{9}$ (h) $(5.4 + 0.3) \times 10^{8}$ (i)	$1.1 \pm 0.1 \\ 1.9 \pm 0.1 \\ 30 \pm 1 \\ 17 \pm 1 \\ 130^{**} (c) \\ 41 \pm 1 \\ 1.0 (i) \\ 251 + 22 (i)$	710 8000 6900 5400 not reported 3860 (f) 6070 (i) 31200 (i)	$\begin{array}{c} (0.7\pm0.1)\times10^{-2}\\ (0.10\pm0.01)\times10^{-2}\\ (1.8\pm0.1)\times10^{-2}\\ (1.4\pm0.1)\times10^{-2}\\ (1.4\pm0.1)\times10^{-2}\\ 26\text{-}33(d)\\ (4.6\pm0.4)\times10^{-2}(g)\\ 0.06\times10^{-2}(i)\\ (3.5\pm0.3)\times10^{-2}(i) \end{array}$

* Value might be smaller (factor 10) due to conflicting values for k₀₃ of the competitor salicylic acid in Hoigné and Bader (1983), for details see SI-A7; ** calculated according to equation (SI-9) using values from Fu et al. (2019).

(a) Kaiser et al. (2013), (b) Toth et al. (2012), (c) Fu et al. (2019) (d) Scheurer et al. (2014), (e) Acero et al. (2000), (f) Nick et al. (1992), (g) Hessler et al. (1993), (h) Huber et al. (2003), (i) Pereira et al. (2007), (j) Real et al. (2009).

with •OH was $(2.7 \pm 0.6) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, which is similar to e.g. atrazine and many other micropollutants (Table 1; von Sonntag and von Gunten (2012)). For SYN507900-Ph, the second order rate constant could not be determined because it was already reacting by direct photochemical reactions during UVA irradiation and an enhancement of the decay rates could not be observed in UVA/H₂O₂ (SI-A9, SI-B8). However, because of their similar structures, we assume that the second order rate constant for the reaction of SYN507900-Ph with •OH is in the same range as for R611968-Ph. For a treatment plant with reverse osmosis followed by UV/H₂O₂, Marron et al. (2019) calculated pollutant abatement depending on their second order rate constants for the reaction with •OH, whereby they assumed that the UV/H₂O₂ reactor is designed to remove 1,4-dioxane by 70% through reactions with \cdot OH (i.e. 4 \times 10^{-10} Ms •OH exposure). Under these comparably favourable conditions (low •OH scavenging due to low DOC: $<0.5 \text{ mgL}^{-1}$), R611968-Ph (k_{OH} (2.7 ± 0.6) × 10⁹ M⁻¹s⁻¹) would be abated by 60–70% due to reaction with •OH. In contrast to the phenolic TPs, the abatement of the sulfonic acids ($k_{OH} < 5.0 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$) is expected to be negligible in O₃/H₂O₂ or UV/H₂O₂. Based on these low reactivities both with the rather unselective oxidant •OH and the selective oxidant ozone, it is likely that sulfonic acids are also persistent towards other oxidants such as HOCl, ClO₂ or sulfate radicals.

3.3.4. Activated carbon

Adsorption to powdered activated carbon was investigated in a natural groundwater (DOC 1.1 mgL⁻¹) spiked with four chlorothalonil TPs and, for comparison, with diatrizoic acid (anionic at pH 7; predicted log D_{OW pH7} -0.6) and atrazine (neutral at pH 7; predicted log D_{OW pH7} 2.2), two micropollutants with well-known adsorption behaviour. Fig. SI-A7 and SI-A8 show the abatement as a function of the powdered activated carbon dose. According to this, the affinity to activated carbon decreases in the following order: atrazine > R611968-Ph > R417888-SA \approx SYN507900-Ph > R4718111-SA \approx diatrizoic acid.

The laboratory experiments showed a higher activated carbon affinity of R417888-SA compared to R471811-SA, which was confirmed by the better retention of R417888-SA in the waterworks (section 3.2) and is in accordance with the higher hydrophobicity (Fig. 1, higher log $D_{OW pH7}$). However, hydrophobicity is not the only parameter governing adsorption to activated carbon (Kovalova et al., 2013b). Diatrizoic acid, which has a predicted log $D_{OW pH7}$ comparable to R417888-SA, showed similar adsorption behaviour to R471811-SA. This was observed as well in full-scale (section 3.2), i.e. diatrizoic acid can be used in waterworks as predictor for the expected breakthrough of R471811-SA.

3.3.5. Reverse osmosis

The reverse osmosis pilot plant was sampled five times over a period of fourteen weeks. The corresponding results are summarized in SI–B10. Chemical analyses focused on the two chlorothalonil TPs with the highest concentrations (R471811-SA, R417888-SA). Two additional pesticide TPs (chloridazon-desphenyl, log D_{OW pH7} -0.8; chloridazon-desphenyl-methyl, log D_{OW pH7} -0.6) and nitrate, which are typical groundwater contaminants in many agricultural areas, were also investigated.

The phenolic TPs were completely removed (not detectable in permeate, i.e. <10 ng/L, raw water: ~30–100 ng/L). Furthermore, the chlorothalonil TP R417888-SA and chloridazon-desphenylmethyl were not detectable in the permeate (raw water: 200–280 ngL⁻¹ and 30–33 ngL⁻¹), whereas the chlorothalonil TP R471811-SA was abated by \geq 98% (raw water: 1200–2100 ngL⁻¹; permeate: 15–20 ngL⁻¹), nitrate by 95–98% (raw water: 16.5–18.6 mgL⁻¹; permeate: 0.4–0.9 mgL⁻¹), and the pesticide TP

chloridazon-desphenyl was only abated by 87–94% (raw water: 440–560 ngL⁻¹; permeate: 30–63 ngL⁻¹). The lower removal of chloridazon-desphenyl compared to the chlorothalonil TPs may be related to differences in the molecular properties. In contrast to the chlorothalonil TPs, chloridazon-desphenyl is uncharged and has a smaller molecular mass and volume (R471811-SA: 348 gmol⁻¹, 23 nm³; chloridazon-desphenyl: 146 gmol⁻¹, 11 nm³; predicted by JChem for Excel, Version 17.1.2300.1455, ChemAxon Ltd.).

3.4. Practical implications

The sulfonic acid TPs are detected more frequently in drinking water resources than the phenolic TPs and exhibit higher concentrations, often exceeding the Swiss drinking water standard of 100 ngL⁻¹. Chlorothalonil has recently been banned in the EU and in Switzerland (BLW, 2019a; European Commission, 2019), so chlorothalonil will no longer be applied in large parts of Europe. However, it is difficult to predict how long these TPs will continue to be present in groundwater and for how long water suppliers will face raw water polluted with chlorothalonil TPs. The duration depends on various factors such as the exact dissipation time, groundwater recharge rate, groundwater residence time, and dilution with other water sources in the respective aquifer. Experience from other pesticides with similar properties related to biodegradability and application periods and polar TPs is scarce. However, studies in Germany and Switzerland showed no concentration decline for the TPs of the herbicide chloridazon within five years after the last application in two shallow aquifers with average groundwater residence times <15–20 years (Hintze and Hunkeler, 2019: Neukum and Meyer, 2019). Model predictions are uncertain but indicate that a decrease in chloridazon TP concentration by 90% will take more than 20 years (Neukum and Meyer, 2019).

Both sampling along water treatment trains and laboratory experiments indicate that the sulfonic acid TPs of chlorothalonil are persistent in most water treatment processes. Photochemical and oxidative processes (UV irradiation, ozonation, and AOPs based on •OH) are not able to abate the sulfonic acid-containing TPs. In contrast, activated carbon may offer a chance to abate the sulfonic acid TPs to a certain extent, but efficiency varies strongly among TPs. To remove all chlorothalonil TPs, activated carbon needs to be exchanged or regenerated very frequently, approximately as often as for the removal of the X-ray contrast agent diatrizoic acid, causing high economic and ecological costs. Reverse osmosis abated \geq 98% of chlorothalonil TPs; however, this is an energy intensive process and the reject water (20-30% of treated water) needs to be treated or disposed. Efficient post-treatment processes are not known and disposal to lakes and rivers is questionable because the pollutants are returned to the water cycle.

4. Conclusions

- Chlorothalonil TPs are widespread in drinking water resources. One TP (R471811-SA) was detected in all 77 samples, even in groundwater with low anthropogenic impact. The sulfonic acid containing TPs (R471811-SA, R419492-SA, R417888-SA) exceeded concentrations of 100 ngL⁻¹ in 14–52% of the samples, while the phenol-containing TPs (SYN507900-Ph, SYN548580-Ph, R611968-Ph) were less frequently detected; in 97% of samples the phenol-containing TPs were below concentrations of 100 ngL⁻¹.
- Although chlorothalonil has recently been banned in Europe, the TPs of chlorothalonil are expected to challenge drinking water suppliers for many years due to their persistence in the environment and in water treatment processes.

- The phenolic TPs can be removed by various treatment techniques such as ozonation, AOPs, and activated carbon. Even UV disinfection may lead to a certain extent of removal.
- In contrast to the phenolic TPs, the less electron-rich sulfonic acids are more persistent and can be removed neither by ozonation nor by •OH-based AOPs under typical water treatment conditions. The sulfonic acids adsorb to activated carbon to varying extents, depending on their polarity. For an efficient removal of the TP with the highest concentrations, granular activated carbon needs to be exchanged more frequently than for other common micropollutants.
- Reverse osmosis was able to abate the chlorothalonil TPs by \geq 98%. However, the reject water needs to be disposed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank all water suppliers, the Federal Office for the Environment (FOEN), and the cantonal authorities for providing samples, the Eawag apprenticeship laboratory for analysing DOC and nitrate as well as Heinz Singer and Philipp Longrée, Eawag, for discussion of the analytical methods. We acknowledge Miriam Reinhardt, FOEN, for selecting the 60 NAQUA groundwater monitoring sites and accompanying the project. We especially thank Roman Wiget, Seeländische Wasserversorgung, Jean-Julien Dessimoz, membratec, Marcel Leemann, Wasserversorgung Zürich, and Thomas Gabriel, Hardwasser AG, for providing detailed information on the reverse osmosis pilot plant or waterworks as well as Claudia Minkowski and Matthias Ruff (Water and Soil Protection Laboratory, Office of Water and Waste Management of the Canton of Berne) for analysing samples from the reverse osmosis pilot plant. Syngenta offered reference material if commercially not available. We acknowledge Jennifer Schollée, Eawag, for critically proofreading the manuscript. This project was partially funded by the FOEN.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.116066.

References

- Acero, J.L., Stemmler, K., von Gunten, U., 2000. Degradation kinetics of atrazine and its degradation products with ozone and OH Radicals: A predictive tool for drinking water treatment. Environ. Sci. Technol. 34 (4), 591–597.
- Benotti, M.J., Song, R., Wilson, D., Snyder, S.A., 2012. Removal of pharmaceuticals and endocrine disrupting compounds through pilot- and full-scale riverbank filtration. Water Sci. Technol. Water Supply 12 (1), 11–23.
- BLW, 2019a. Approval for chlorothalonil is withdrawn with immediate effect (Zulassung für Chlorothalonil wird mit sofortiger Wirkung entzogen). https:// www.blw.admin.ch/blw/de/home/services/medienmitteilungen.msg-id-77491. html. Accessed: 17/12/2019.
- BLW, 2019b. Sales per active ingredient (Verkaufsmengen je Pflanzenschutzmittel-Wirkstoff). Federal Office for the Agriculture. https://www.blw.admin.ch/blw/ de/home/nachhaltige-produktion/pflanzenschutz/pflanzenschutzmittel/ verkaufsmengen-der-pflanzenschutzmittel-wirkstoffe.html. Accessed: 06/01/
- 2020. Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical Review of rate
- constants for reactions of hydrated electrons, 17 (2), 513–886. BVL, 2018. Sales of plant protection products in the Federal Republic of Germany,
- Results of the notifications according to § 64 Plant Protection Act for the year 2017 (Absatz an Pflanzenschutzmittelen in der Bundesrepublik Deutschland, Ergebnisse der Meldungen gemäß § 64 Pflanzenschutzgesetz für das Jahr 2017). Federal Office of Consumer Protection and Food Safety. www.bvl.bund.de/

psmstatistiken.html. Accessed: 21/08/2019.

- Canonica, S., Jans, U., Stemmler, K., Jürg, H., 1995. Transformation Kinetics of Phenols in Water: Photosensitization by Dissolved Natural Organic Material and Aromatic Ketones. Environmental Science & Technology 29, 1822–1831.
- Canonica, S., Meunier, L., von Gunten, U., 2008. Phototransformation of Selected Pharmaceuticals during UV Treatment of Drinking Water. Water Research 42, 121–128.
- Chuang, Y.H., Chen, S., Chinn, C.J., Mitch, W.A., 2017. Comparing the UV/monochloramine and UV/free chlorine advanced oxidation processes (AOPs) to the UV/hydrogen peroxide AOP under scenarios relevant to potable reuse. Environ. Sci. Technol. 51 (23), 13859–13868.
- Delgado, L.F., Charles, P., Glucina, K., Morlay, C., 2012. The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon-a review. Sci. Total Environ. 435–436, 509–525.
- DVGW, 2006. W 294-2 Worksheet 06/2006: UV devices for disinfection in water supply; part 2: testing the quality, function and effectiveness of disinfection (W 294-2 Arbeitsblatt 06/2006: UV-Geräte zur Desinfektion in der Wasserversorgung; Teil 2: Prüfung von Beschaffenheit, Funktion und Desinfektionswirksamkeit).
- EFSA, 2018. Peer review of the pesticide risk assessment of the active substance chlorothalonil. EFSA Journal 16 (1), 1–40.
- EPA, 1999. Reregistration Eligibility Decision (RED) Chlorothalonil. United States Environmental Protection Agency. https://archive.epa.gov/pesticides/ reregistration/web/pdf/0097red.pdf.
- European Commission, 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Communities (L330).
- European Commission, 2003. Guidance Document on the Assessment of the Relevance of Metabolites in Groundwater of Substances Regulated under Council Directive 91/414/EEC. Sanco/221/2000 –rev.10- final.
- European Commission, 2019. Commission implementing regulation (EU) 2019/677 of 29 April 2019 concerning the non-renewal of the approval of the active substance chlorothalonil. In: Accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council Concerning the Placing of Plant Protection Products on the Market, and Amending Commission Implementing Regulation (EU) No 540/2011. Official Journal of the European Union.
- Fu, Y., Wu, G., Geng, J., Li, J., Li, S., Ren, H., 2019. Kinetics and modeling of artificial sweeteners degradation in wastewater by the UV/persulfate process. Water Res. 150, 12–20.
- Guo, K., Wu, Z., Yan, S., Yao, B., Song, W., Hua, Z., Zhang, X., Kong, X., Li, X., Fang, J., 2018. Comparison of the UV/chlorine and UV/H2O2 processes in the degradation of PPCPs in simulated drinking water and wastewater: kinetics, radical mechanism and energy requirements. Water Res. 147, 184–194.
- Hessler, D.P., Gorenflo, V., Frimmel, F.H., 1993. Degradation of aqueous atrazine and metazachlor solutions by UV and UV/H202 - influence of pH and herbicide concentration. Acta Hydrochim. Hydrobiol. 21 (4), 209–214.
- Hintze, S., Hunkeler, D., 2019. Long-term behaviour of PPP metabolites in groundwater (Langzeitverhalten von PSM-Metaboliten im Grundwasser). Aqua Gas 99 (11), 24–29.
- Hoigné, J., Bader, H., 1983. Rate constants of reactions of ozone with organic and inorganic compounds in water—II: dissociating organic compounds. Water Res. 17 (2), 185–194.
- Hoigné, J., Bader, H., 1994. Characterization of water quality criteria for ozonation processes. Part II: lifetime of added ozone. Ozone: Sci. Eng. 16 (2), 121–134.
- Hollender, J., Rothardt, J., Radny, D., Loos, M., Epting, J., Huggenberger, P., Borer, P., Singer, H., 2018. Comprehensive micropollutant screening using LC-HRMS/MS at three riverbank filtration sites to assess natural attenuation and potential implications for human health. Water Res. X 1, 1–12.
- Hollender, J., Zimmermann, S.G., Koepke, S., Krauss, M., McArdell, C.S., Ort, C., Singer, H., von Gunten, U., Siegrist, H., 2009. Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a fullscale post-ozonation followed by sand filtration. Environ. Sci. Technol. 43 (20), 7862–7869.
- Huber, M.M., Canonica, S., Park, G.-Y., von Gunten, U., 2003. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. Environ. Sci. Technol. 37 (5), 1016–1024.
- Hübner, U., Miehe, U., Jekel, M., 2012. Optimized removal of dissolved organic carbon and trace organic contaminants during combined ozonation and artificial groundwater recharge. Water Res. 46 (18), 6059–6068.
- Kaiser, H.-P., Köster, O., Gresch, M., Périsset, P.M.J., Jäggi, P., Salhi, E., von Gunten, U., 2013. Process control for ozonation systems: a novel real-time approach. Ozone: Sci. Eng. 35 (3), 168–185.
- Katsoyiannis, I., Canonica, S., von Gunten, U., 2011. Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O3/ H2O2 and UV/H2O2. Water Res. 45 (13), 3811–3822.
- Kiefer, K., Müller, A., Singer, H., Hollender, J., 2019. New Relevant Pesticide Transformation Products in Groundwater Detected Using Target and Suspect Screening for Agricultural and Urban Micropollutants with LC-HRMS. Water Res 165, 114972. Article number: 114972.
- Knappe, D.R.U., Matsui, Y., Snoeyink, V.L., Roche, P., Prados, M.J., Bourbigot, M.-M., 1998. Predicting the capacity of powdered activated carbon for trace organic compounds in natural waters. Environ. Sci. Technol. 32 (11), 1694–1698.
- Kovalova, L., Knappe, D.R., Lehnberg, K., Kazner, C., Hollender, J., 2013a. Removal of highly polar micropollutants from wastewater by powdered activated carbon.

Environ. Sci. Pollut. Res. Int. 20 (6), 3607-3615.

- Kovalova, L., Siegrist, H., von Gunten, U., Eugster, J., Hagenbuch, M., Wittmer, A., Moser, R., McArdell, C.S., 2013b. Elimination of micropollutants during posttreatment of hospital wastewater with powdered activated carbon, ozone, and UV. Environ. Sci. Technol. 47 (14), 7899–7908.
- Laabs, V., Leake, C., Botham, P., Melching-Kollmuss, S., 2015. Regulation of nonrelevant metabolites of plant protection products in drinking and groundwater in the EU: current status and way forward. Regul. Toxicol. Pharmacol. 73 (1), 276–286.
- Lee, Y., von Gunten, U., 2012. Quantitative structure-activity relationships (QSARs) for the transformation of organic micropollutants during oxidative water treatment. Water Res. 46 (19), 6177–6195.
- Lee, Y., Yoon, J., von Gunten, U., 2005. Kinetics of the oxidation of phenols and phenolic endocrine disruptors during water treatment with ferrate (Fe(VI)). Environ. Sci. Technol. 39 (22), 8978–8984.
- LUBW, 2011. Groundwater monitoring programme results from sampling campaign 2010 (Grundwasserüberwachungsprogramm - ergebnisse der Beprobung 2010). Reihe Grundwasserschutz 42, 1–98. http://www4.lubw. baden-wuerttemberg.de/servlet/is/208632/.
- Maeng, S.K., Sharma, S.K., Lekkerkerker-Teunissen, K., Amy, G.L., 2011. Occurrence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: a review. Water Res. 45 (10), 3015–3033.
- Mark, G., Korth, H.-G., Schuchmann, H.-P., von Sonntag, C., 1996. The photochemistry of aqueous nitrate ion revisited. J. Photochem. Photobiol. Chem. 101 (2), 89–103.
- Marron, E.L., Mitch, W.A., Gunten, U.V., Sedlak, D.L., 2019. A tale of two treatments: the multiple barrier approach to removing chemical contaminants during potable water reuse. Acc. Chem. Res. 52 (3), 615–622.
- Mechelke, J., Longree, P., Singer, H., Hollender, J., 2019. Vacuum-assisted evaporative concentration combined with LC-HRMS/MS for ultra-trace-level screening of organic micropollutants in environmental water samples. Anal. Bioanal. Chem. 411, 2555–2567.
- Miklos, D.B., Remy, C., Jekel, M., Linden, K.G., Drewes, J.E., Hübner, U., 2018. Evaluation of advanced oxidation processes for water and wastewater treatment – a critical review. Water Res. 139, 118–131.
- Neukum, C., Meyer, K., 2019. Chloridazon-metabolites in groundwater: coupled modelling for long-term estimation of transport behavior and concentration development in groundwater of a drinking water abstraction (Chloridazon-Metaboliten im Grundwasser: gekoppelte Modellierung zur langfristigen Abschätzung des Transportverhaltens und der Konzentrationsentwicklung im Grundwasser einer Trinkwassergewinnungsanlage). Grundwasser 24 (1), 73–81.
- Nick, K., Schöler, H.F., Mark, G., Söylemez, T., Akhlaq, M.S., Schuchmann, H.-P., Von Sonntag, C., 1992. Degradation of some triazine herbicides by UV radiation such as used in the UV disinfection of drinking water. J. Water Supply Res. Technol. -Aqua 41 (2), 82–87.

- ÖNORM, 2001. M 5873-1: Water disinfection systems using ultraviolet rays requirements and testing (Anlagen zur Desinfektion von Wasser mittels Ultraviolett-Strahlen - Anforderungen und Prüfung).
- Pereira, V.J., Weinberg, H.S., Linden, K.G., Singer, P.C., 2007. UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. Environ. Sci. Technol. 41 (5), 1682–1688.
- Real, F.J., Benitez, F.J., Acero, J.L., Sagasti, J.J.P., Casas, F., 2009. Kinetics of the chemical oxidation of the pharmaceuticals primidone, ketoprofen, and diatrizoate in ultrapure and natural waters. Ind. Eng. Chem. Res. 48 (7), 3380–3388.
- Rosenfeldt, E.J., Linden, K.G., 2004. Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. Environ. Sci. Technol. 38 (20), 5476–5483.
- Scheurer, M., Schmutz, B., Happel, O., Brauch, H.J., Wulser, R., Storck, F.R., 2014. Transformation of the artificial sweetener acesulfame by UV light. Sci. Total Environ. 481, 425–432.
- Staehelin, J., Hoigne, J., 1982. Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. Environ. Sci. Technol. 16 (10), 676–681.
- Stefan, M.I. (Ed.), 2018. Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications. IWA Publishing, London.
- SVGW, 2010. W13d: Guideline for UV disinfection in water supply (Richtlinie zur UV-Desinfektion in der Wasserversorgung). Schweizerischer Verein des Gasund Wasserfaches.
- Taheran, M., Brar, S.K., Verma, M., Surampalli, R.Y., Zhang, T.C., Valero, J.R., 2016. Membrane processes for removal of pharmaceutically active compounds (PhACs) from water and wastewaters. Sci. Total Environ. 547, 60–77.
- Toth, J.E., Rickman, K.A., Venter, A.R., Kiddle, J.J., Mezyk, S.P., 2012. Reaction kinetics and efficiencies for the hydroxyl and sulfate radical based oxidation of artificial sweeteners in water. J. Phys. Chem. 116 (40), 9819–9824.
- Umar, M., Roddick, F., Fan, L., 2014. Recent advancements in the treatment of municipal wastewater reverse osmosis concentrate—an overview. Crit. Rev. Environ. Sci. Technol. 45 (3), 193–248.
- von Gunten, U., 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Res. 37 (7), 1443–1467.
- von Gunten, U., 2018. Oxidation processes in water treatment: are we on track? Environ. Sci. Technol. 52 (9), 5062–5075.
- von Sonntag, C., von Gunten, U., 2012. Chemistry of Ozone in Water and Wastewater Treatment: from Basic Principles to Applications. IWA Publisher, London.
- Westerhoff, P., Yoon, Y., Snyder, S., Wert, E., 2005. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. Environ. Sci. Technol. 39, 6649–6663.
- Zepp, R.G., 1978. Quantum yields for reaction of pollutants in dilute aqueous solution. Environ. Sci. Technol. 12 (3), 327–329.
- Zepp, R.G., Hoigne, J., Bader, H., 1987. Nitrate-induced photooxidation of trace organic chemicals in water. Environ. Sci. Technol. 21 (5), 443–450.



Chlorothalonil SANTE/10186/2018 Rev 1 22 March 2019

Final Renewal report for the active substance chlorothalonil

finalised in the Standing Committee on Plants, Animals, Food and Feed at its meeting on 22 March 2019 in view of the non-renewal of the approval of chlorothalonil as active substance in accordance with Regulation (EC) No 1107/2009¹

1. Procedure followed for the re-evaluation process

This review report has been established as a result of the evaluation of **chlorothalonil**, in accordance with Regulation (EC) No $1107/2009^2$ and Commission Implementing Regulation (EU) No $844/2012^3$ following the submission of an application to renew the approval of this active substance expiring in October 2018.

Chlorothalonil is a substance that was included in Annex I to Council Directive 91/414/EEC concerning the placing of plant protection products on the market, by Commission Directive $2005/53/EC^4$. Chlorothalonil is deemed to have been approved under Regulation (EC) No 1107/2009 and is listed in Part A of the Annex to Commission Implementing Regulation (EU) No $40/2011^5$.

An application for renewal of the approval of chlorothalonil was submitted by Arysta LifeScience S.A.S, Oxon Italia S.p.A. and Syngenta Crop Protection AG in accordance with Article 1 of Regulation No. 844/2012.

Commission Implementing Regulation $2018/1262^6$ extended until 31 October 2019 the period of approval of chlorothalonil to allow the completion of its review.

¹ Renewal Report established in accordance with Art. 14 of Regulation (EU) No 844/2012; does not necessarily represent the views of the European Commission.

² OJ L 309, 24.11.2009, p. 1.

³ OJ L 252, 19.9.2012, p. 26.

⁴ Commission Directive 2005/53/EC of 16 September 2005 amending Council Directive 91/414/EEC to include chlorothalonil, chlorotoluron, cypermethrin, daminozide and thiophanate-methyl as active substances (OJ L 241, 17.9.2005, p. 51).

⁵ OJ L 153, 11.6.2011, p. 1.

⁶ Commission Implementing Regulation (EU) 2018/1262 of 20 September 2018 amending Implementing Regulation (EU) No 540/2011 as regards the extension of the approval periods of the active substances 1-methylcyclopropene, beta-cyfluthrin, chlorothalonil, chlorotoluron, clomazone, cypermethrin, daminozide, deltamethrin, dimethenamid-p, diuron, fludioxonil, flufenacet, flurtamone, fosthiazate, indoxacarb, MCPA, MCPB, prosulfocarb, thiophanate-methyl and tribenuron (OJ L 238, 21.9.2018, p. 62).

Commission Implementing Regulation (EU) No 686/2012⁷ designated the rapporteur Member States and the co-rapporteur Member States which had to submit the relevant renewal assessment reports and recommendations to the European Food Safety Authority (EFSA).

For chlorothalonil the rapporteur Member State was the Netherlands and the co-rapporteur Member State was Belgium.

The Netherlands finalised in September 2016 its examination, in the form of a renewal assessment report. This Report was sent to the Commission and the European Food Safety Authority on 2 September 2016 and included a recommendation concerning the decision to be taken with regard to the renewal of the approval of chlorothalonil for the supported uses.

In accordance with Article 13 of Implementing Regulation (EU) No 844/2012, the EFSA organised an intensive consultation of technical experts from Member States, to review the renewal assessment report and the comments received thereon (peer review).

The EFSA sent to the Commission its conclusion on the risk assessment (Conclusions regarding the peer review of the pesticide risk assessment of the active substance)⁸ on 6 December 2017. This conclusion refers to to several background documents: the draft assessment report including its addendum and the EFSA peer review report.

According to the provisions of Article 14 of Implementing Regulation (EU) No 844/2012, the Commission referred a draft renewal report on the renewal of approval to the Standing Committee on Plants, Animals, Food and Feed, for examination on 5 June 2018. The draft renewal report was finalised in the meeting of the Standing Committee on 22 March 2019.

The present renewal report contains the conclusions of the final examination by the Standing Committee. Given the importance of the conclusion of the EFSA, and its background documents, these documents are also considered to be part of this review report.

2. Purposes of this review report

This renewal report, including the background documents and appendices hereto, has been developed and finalised in support of **Commission Implementing Regulation (EU) 2019/677**⁹ concerning the non-renewal of approval of chlorothalonil as active substance under Regulation (EC) No 1107/2009.

This review report will be made available to the public.

The information in this review report is, at least partly, based on information which is confidential and/or protected under the provisions of Regulation (EC) No 1107/2009. It is therefore recommended that this review report would not be accepted to support any registration outside the context of that Regulation, e.g. in third countries, for which the applicant has not demonstrated to have regulatory access to the information on which this review report is based.

⁷ OJ L 200, 27.7.2012, p. 5.

⁸ EFSA (European Food Safety Authority), 2017. Conclusion on the peer review of the pesticide risk assessment of the active substance chlorothalonil. EFSA Journal 2018;16(1):5126, 47 pp. https://doi.org/10.2903/j.efsa.2018.5126.

⁹ OJ L 114, 30.4.2019, p. 15.

3. Overall conclusion in the context of Regulation (EC) No 1107/2009

As part of the updated evaluation of chlorothalonil the following reference values have been finalised:

ADI: 0.015 mg/kg bw per day, ARfD: 0.05 mg/kg bw, AOEL: 0.003 mg/kg bw per day, AAOEL: 0.01 mg/kg bw.

To note, the ARfD and AOEL have changed compared to the previous EU agreed reference value (0.05 mg/kg bw compared to 0.6 mg/kg bw for the ARfD and 0.003 mg/kg bw per day compared to 0.009 mg/kg bw per day for the AOEL) and an AAOEL has been set for the first time.

The overall conclusion of the evaluation, based on the information available and the proposed conditions of use, is that:

- the information available indicates that the approval criteria as set out in Article 4(1) to (3) of Regulation (EC) No 1107/2009 are not satisfied as concerns were identified with regards to:
 - The contamination of groundwater by metabolites of chlorothalonil. In particular, metabolites R417888, R419492, R471811, SYN507900, M3, M11, M2, M7 and M10 are predicted to occur above the parametric value of 0.1 μ g/L in all scenarios.
 - A genotoxicity concern could not be excluded for residues to which consumers will be exposed.
 - The risk to amphibians and fish.
 - The proposed classification of chlorothalonil by the peer review as carcinogen category 1B in accordance to the provisions of Regulation (EC) No 1272/2008 (while harmonised classification is category 2).
- **the information available is insufficient** to satisfy the requirements set out in Article 4(1) to (3) of Regulation (EC) No 1107/2009, in particular with regard to:
 - The analytical methods used in the toxicological studies were not identified and therefore not validated, this questions the validity of the studies, in particular repeated-dose dietary studies.
 - The need for further tests and risk assessment to unique human metabolites could not be finalised whilst an *in vitro* comparative metabolism study was not submitted.
 - The chronic risk to amphibians could not be finalised.
 - The consumer risk assessment from the consumption of water could not be finalised, whilst satisfactory information was not available to address the effect of water treatment processes on the nature of the residues that might be present in surface water, when surface water is abstracted for drinking water.
 - The consumer risk assessment could not be finalised as the residue definitions for risk assessment in plant and animal commodities are preliminary. In the absence of toxicological reference values for R182281 even an indicative consumer risk assessment using the preliminary residue definitions cannot be conducted.

In conclusion from the assessments made on the basis of the submitted information, no plant protection products containing the active substance concerned is expected to satisfy in general the requirements laid down in Article 29(1) of Regulation (EC) No 1107/2009 and the uniform principles laid down in Regulation (EU) No 546/2011.

The approval of chlorothalonil in accordance with Regulation (EC) No 1107/2009 should therefore not be renewed.