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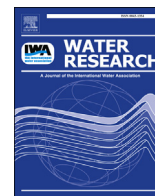
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Mercury loads and fluxes from wastewater: A nationwide survey in Switzerland

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ABSTRACT

Mercury (Hg) pollution threatens ecosystems and human health. Wastewater treatment plants (WWTPs) play a key role in limiting Hg discharges from wastewaters to rivers and lakes, but large-scale studies to estimate Hg loads and discharge at national levels are scarce. We assessed the concentration, flux, speciation, and removal of Hg in municipal wastewater throughout Switzerland by investigating 64 WWTPs in a pre-study and a subset of 28 WWTPs in the main study. We also studied the behavior and pathways of Hg along the various treatment steps in a state-of-the-art WWTP. The resulting dataset, representative of industrialized countries, provides an overview of (i) current Hg concentration ranges, (ii) average per capita loads, and (iii) wastewater Hg inputs into surface waters. The results allowed estimation of a total Hg (THg) load in Swiss wastewater of 130 ± 30 kg THg/year (15.7 mg/capita/y), of which $96 \pm 4\%$ is retained in sewage sludge. About 4.7 ± 0.5 kg THg/year (0.57 mg/capita/y) is discharged with the treated wastewater into surface waters. This corresponds to only 1.5–3% of the THg load carried by the major Swiss rivers, indicating that >95% of riverine Hg originates from other sources. Extrapolation to the population of Europe would yield a total amount of 11,700 kg THg/year in raw wastewater, with some 480 kg THg/year discharged to surface waters. Monomethyl mercury on average accounted for 0.23% of THg, and its fraction remained constant along the different treatment steps.

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1. Introduction

Mercury is classified as a priority hazardous substance by many countries, including Switzerland, the European Union, and the United States (EPA, 1972, 2002; Ritscher et al., 2018). The multiple environmental and health issues related to mercury (Hg) were addressed by the international Minamata Convention, which was reached in 2013 with the aim of reducing global anthropogenic Hg emissions (UNEP, 2013b). The convention came into force in 2017 and is currently signed by 128 countries and ratified by 118 countries, including Switzerland. Among the key convention objectives are the identification, quantification, control, and reduction of Hg

emissions to land and water and the attainment of a better understanding of Hg environmental distribution and transformation processes (EU, 2017; UNEP, 2013b).

In this context, wastewater treatment plants (WWTPs) play a key role in limiting Hg discharge to aquatic ecosystems. In the past, wastewater effluents were major pathways of Hg to surface waters (Balogh et al., 1999; Kocman et al., 2017). However, current legislation limits the maximum total Hg (THg) concentrations in surface waters to 30 ng/L in Switzerland (SFC, 2020), and 70 ng/L in the EU (EU, 2013). Therefore, removal of Hg by WWTPs must be effective. Most WWTPs receive mixed wastewaters of domestic and industrial origins, which include discharges from agriculture, hospitals, dentists, research institutions, households, and the chemical, cement, and metal industries, as well as landfill leachates and surface drainage (Balogh and Liang, 1995; Cantinho et al., 2016;

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Gbondo-Tugbawa et al., 2010; Koch, 2002; Sörme and Lagerkvist, 2002; UNEP, 2013a; Wang et al., 2004). The THg inputs from most of these sources have been significantly reduced due to stricter regulations (e.g., in Germany, Austria, Sweden, and the USA) (State of New Jersey, 2003; Swedish EPA, 2014; Wiechmann et al., 2013). Nevertheless, even today, THg concentrations in raw wastewater can still reach several $\mu\text{g/L}$ (Cantinho et al., 2016; Carletti et al., 2008; Goldstone et al., 1990; Liu et al., 2018; Mao et al., 2016), but concentrations in treated wastewater are often in the low ng/L range (Bodaly et al., 1998; Fricke et al., 2015; Stoichev et al., 2009; Zierhut et al., 2010). Hg is usually effectively retained in sewage sludge, with retention efficiencies often exceeding 95% (Fricke et al., 2015; Liu et al., 2018; Perusini, 2016; Stoichev et al., 2009).

Previous studies have reported Hg concentrations in sewage sludge between 0.4 and 7 mg THg/kg (Fricke et al., 2015; Hittinger and Pichler; Jones et al., 2014; Külling et al., 2002; Mattsson et al., 2017; Oliveira et al., 2007; Olofsson et al., 2012; Olofsson et al., 2013; Swedish EPA, 2014; Wiechmann et al., 2013). This Hg content is relevant, because many countries use sewage sludge for agricultural fertilization (e.g., 60% in the USA or 47% in the European Union) (Bianchini et al., 2016; Mattsson et al., 2017; NRC, 2002; Olofsson et al., 2012). In Switzerland, this practice was banned in 2006, and sewage sludge has been exclusively incinerated since then, with the ash and the flue gas treatment residue safely stored in managed landfill sites (FOEN, 2012; Ritscher et al., 2018; SFC, 2019).

In addition to THg concentrations, a number of studies have analyzed methyl-Hg (MeHg) compounds in wastewaters. MeHg can cause severe ecotoxicological effects through bioaccumulation and its high toxicity, thereby endangering humans via the food chain (Behra et al., 1993, 1994; Mahubub et al., 2017). The reported MeHg concentrations in raw wastewater range from 0.4 to 7.5 ng/L and they can be up to 2 ng/L in treated wastewater but are often very low due to a combination of limited occurrence and/or efficient degradation along the treatment chain (Balogh and Nollet, 2008a; Bodaly et al., 1998; Gilmour and Bloom, 1995; Mao et al., 2016). However, unlike THg, MeHg is often less effectively retained in sewage sludge (30–98%) (Balogh and Nollet, 2008a, 2008b; Bodaly et al., 1998; Gbondo-Tugbawa et al., 2010; Gilmour and Bloom, 1995; Stoichev et al., 2009), which may reflect the rather low binding affinity of MeHg to suspended solids. Based on the available studies, e.g. (Balogh and Nollet, 2008b; Bodaly et al., 1998; Fricke et al., 2015; Perusini, 2016), effluents of WWTPs are currently expected to be of minor importance in terms of the fluxes of Hg that currently occur in surface waters. However, comprehensive studies to substantiate this assumption are lacking.

In this context, Switzerland is uniquely suited for studies aimed at quantifying the contribution of WWTP effluents to Hg loads in surface waters. Nearly the entire Swiss population (~98%) (OECD, 2013) is connected to wastewater treatment systems and all major rivers have their origin in the country and are routinely monitored, thereby enabling the establishment of a rigorous mass balance. Therefore, in the present study, we quantified the Hg concentrations in both the raw and the treated wastewaters from representative WWTPs in Switzerland. We first screened samples from 64 WWTPs in a pre-study in 2016, and then focused on a subset of 28 WWTPs in 2017 for detailed sampling and investigation. We further determined the Hg speciation in the sewage sludge and assessed changes in concentrations and speciation along the different steps of the wastewater treatment process in a state-of-the-art WWTP. With this dataset, we were able to estimate (i) the total and per capita Hg loads to WWTPs, (ii) the Hg removal efficiencies of WWTPs, and (iii) the overall contribution of WWTP effluents to the riverine Hg load on a national scale.

2. Materials and methods

2.1. Studied WWTPs and sample collection

The locations and catchments of the studied WWTPs are shown in Fig. 1. In a pre-study, samples from 64 WWTPs were repeatedly collected in January, June, and July 2016 (Vriens et al., 2017). Raw wastewater, sewage sludge, and treated wastewater were collected again from 28 of the same WWTPs in June 2017 (see Fig. S4). Characteristic properties of the investigated WWTPs are listed in the supporting Tables S7 and S13. The WWTPs were selected to obtain a broad nationwide representation, based on geographical distribution, number of connected people, and industries in the catchment areas (Vriens et al., 2017). The communal and industrial WWTPs from both rural and urban areas represent a total of 2.6 million connected people, equivalent to 31% of the Swiss population (FOEN, 2017). The WWTPs all run similar mechanical and biological treatment processes with slight variations in their nitrate and phosphorus elimination schemes (see Table S7). The incoming raw wastewater and the outflowing treated wastewater (effluent) were collected as 24 h composite samples; the raw wastewater was sampled after the bar screens and sand trap, and the treated wastewater was collected after the final filtration step. Sludge treatment included anaerobic digestion with an average sludge age of 26 ± 11 days. Samples were shipped and processed within 24–72 h (see Supporting Information). In addition to the samples collected from WWTPs in 2017, the freeze-dried sewage sludge samples collected in 2016 from 64 Swiss WWTPs were also analyzed for THg contents and speciation for comparison (Vriens et al., 2017).

A detailed study was conducted at the state-of-the-art Zurich-Werdhoelzli WWTP in August 2017 to determine Hg concentrations, speciation, and retention along the successive treatment steps, and to determine the variability in Hg concentrations in the raw and the treated wastewaters over a period of eight days (24 h composite samples, 15-mins flow-proportional intervals, 15.–22.08.2017). Several grab samples were also taken throughout the treatment steps on the last sampling day.

2.2. Sample processing

Dissolved Hg in raw wastewater was analyzed after filtration (0.22 μm , Nylon, BGB) and acidification to 1% HCl (v/v; HCl 32–35%, Optima™, Fisher). Treated wastewater samples were kept unfiltered and were directly acidified. The content of THg in raw wastewaters was determined after microwave-assisted digestion (ETHOS 1, MSL GmbH) using aqua regia and hydrogen peroxide (H_2O_2 , traceselect®, Fluka) (Table S1). The maximum temperature was set at 110 °C to avoid Hg losses through volatilization (Lomonte et al., 2008). The particulate fraction of Hg was calculated as the difference between the total and dissolved Hg concentrations. Sewage sludge samples were freeze-dried (Hojdová et al., 2015), homogenized in an agate mortar, and digested by microwave similarly to the raw wastewaters (but without H_2O_2 , due to strong frothing). Digests were kept at 4 °C in the dark in borosilicate bottles sealed with Teflon-lined lids.

2.3. Analytics

The THg in the liquid samples (i.e., filtered raw wastewater, microwave-digested raw wastewater, microwave-digested sewage sludge, and treated wastewater) was analyzed with a triple-quadrupole ICP-MS (ICP-QQQ, Agilent 8900). To minimize Hg carry-over and losses, the Agilent ISIS sample introduction system was used with a HCl– HNO_3 carrier (2% HCl + 2% HNO_3) and an

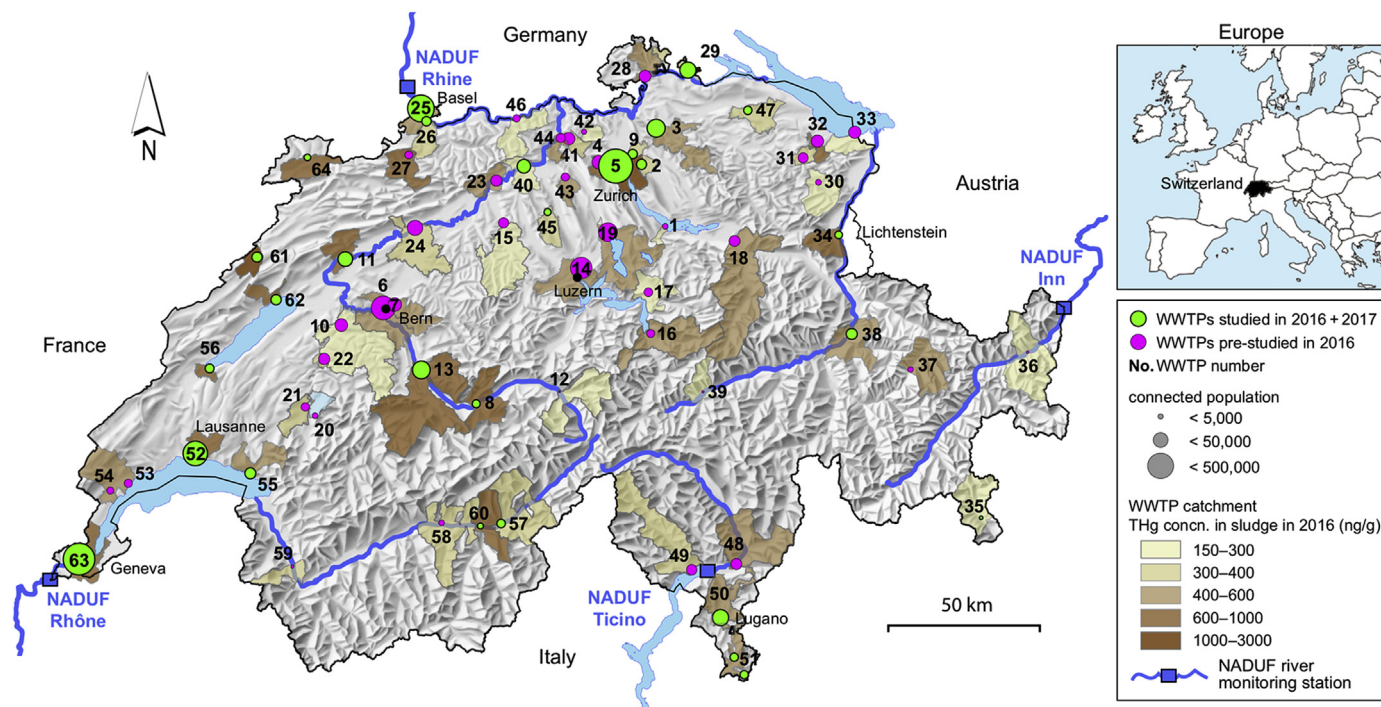


Fig. 1. Map of Switzerland depicting the locations of the 64 wastewater treatment plants (WWTPs) investigated in 2016 (pink and green dots) and of the subset of 28 WWTPs studied in detail in 2017 (green dots). The corresponding catchment areas are shown, along with the national monitoring sites (NADUF) of the four major rivers leaving Switzerland. The names of cities and towns are shown in the supporting Fig. S1. Selected characteristics of the investigated WWTPs are listed in the supporting Table S7 and Table S13. The size of the points reflects the number of connected inhabitants, and the yellow to brown colored catchment areas indicate the magnitude of the total mercury (THg) in the sewage sludge in 2016 (Table S13). The THg concentrations ranged from 160 to 2600 ng/g in sludge and were measured by total combustion using advanced mercury analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

optimized rinsing program for the needle and loop, using three rinsing steps (each 20s) with 2.5% HNO_3 /1% HCl, followed by 2% HCl, and finally 1% HCl, modified after (Agilent, 2011; Chen, 2009; Guo et al., 2011). Two Hg isotopes were recorded (^{201}Hg and ^{202}Hg) in collision/reaction modes, using helium or oxygen to remove interferences. The isotope m/z 201 was used for quantification, as it is essentially free of polyatomic interferences. More details about the ICP-QQQ instrument configuration can be found in the Table S2. Lutetium (^{175}Lu , 40 $\mu\text{g/L}$) was used as internal standard to correct for instrument drift. Matrix-matched calibrations were done using digestion blanks (Hg standard for ICP-MS analyses, Baker). The full details of the analytical methods are provided in the supplementary material, including Tables S1–S5.

THg concentrations in 2017 sewage sludge samples were determined by ICP-MS in digested samples (Table S1). In the sewage sludge samples from 2016, the THg concentrations were determined by direct combustion with an advanced mercury analyzer (AMA) (AMA-254, Altec, Prague, Czech Republic, LOD 6.7 ng/g) (Bravo et al., 2011). In the samples from 2017, monomethylmercury (MMHg) and inorganic mercury (IHg) were determined in acid extracts (6 M HNO_3 for sludge) or alkaline extracts (25% TMAH for fat samples) by isotope dilution GC-ICP-MS (LODs of 0.11 and 0.05 ng/g, respectively), as described previously (Bravo et al., 2011). Recoveries of MMHg determined with the certified reference materials IAEA-405 and IAEA-433 were $92 \pm 5\%$ for both materials.

2.4. Method performance and quality control

The limit of detection (LOD) for THg concentrations was determined according to the 3 sigma criterion (3 times the standard deviation of signal noise) of replicate blank measurements ($n > 10$,

see Tables S3 and S4). The limit of quantification (QL) was defined as 3.33 times the LOD.

The following certified reference materials (CRMs), representative of various matrices, were processed and analyzed in the same way as the samples: BCR 144 (municipal sewage sludge), NIST 2781 (domestic sewage sludge), NIST 2782 (industrial sewage sludge), ERM-CA615 (groundwater), and ERM-CA713 (raw wastewater). The recoveries of THg in the sewage sludge were $94 \pm 8\%$ for ICP-QQQ and $94 \pm 5\%$ for AMA (Table S5). Mean recoveries with ICP-QQQ for the groundwater and raw wastewater CRMs were $112 \pm 13\%$ and $111 \pm 5\%$, respectively. Sample replicates ($n = 4$) were processed at least 3 times within 2–5 h and yielded a mean recovery of $106 \pm 4\%$, showing that Hg was not lost by volatilization or accumulated by contamination during the ICP analyses. Sample spikes using the CRM CA713 and Hg^{2+} (Baker) were $88 \pm 13\%$ and $101 \pm 4\%$, respectively.

The comparison of THg analyses by AMA and ICP-MS were in agreement, with a statistical significance of 0.95, for the 28 sewage sludge samples from 2017 (paired sample *t*-test, $p < 0.05$) (Fig. S2). Verification cross-checks of other elements (i.e., P, Cu, Zn, and Cd) were in good agreement with long-term monitoring data of the WWTPs of Zurich (ZUE) and Duebendorf (DUE), as well as with the results from our previous study on trace elements by Vriens et al. (2017) (Fig. S3).

2.5. Ancillary data and statistics

Operational information on the size of the connected population, catchment area, wastewater flow rates, and sewage sludge quantities of all studied WWTPs were obtained from the Swisstopo geographic information system (Table S7) (FOEN, 2000). The Swiss map was created with ArcGIS software using data from the

Swisstopo geographic information system. Data on the connected population were obtained from the Swiss Federal Office for the Environment (FOEN) (FOEN, 2017). River water data were obtained from the National Long-term Surveillance of Swiss Rivers program (NADUF) (Zobrist et al., 2018). Hg concentrations have been recorded since 1994 on a monthly to bi-monthly basis in the Rhine River at Weil am Rhein (on the border of Switzerland and Germany) (Ruff et al., 2013).

Concentrations below the LOD in wastewater and sewage sludge were replaced by $\text{LOD}/\sqrt{2}$ (Newman et al., 1989). Statistical analyses were carried out with OriginPro V.9.1 (OriginLab Corporation). For correlation analysis, Spearman's rank correlations were performed at a significance level of 95% ($p = 0.05$). The Kolmogorov-Smirnov test was also used to identify the variability between data sets; the Mann Whitney, paired t-tests, and median tests were also used for data set comparison.

The THg loads entering the individual WWTPs with wastewater or leaving them with sludge were calculated by multiplication of the respective THg concentration (c_i) by the daily volume of wastewater inflow or the amount of daily sewage sludge production (V_i) (eq. (1)). The per capita THg loads were calculated by dividing the THg loads by the number of persons in the connected population (N_i) (eq. (2)). The weighted mean (WM) concentrations of THg in the raw wastewater and the sludge of the 28 WWTPs are the sum of individual THg loads divided by the sum of the individual wastewater volumes or sewage sludge masses per time (V_i) (eq. (3)). The THg load for all of Switzerland was calculated by multiplying the weighted mean values with the total Swiss wastewater flow (3.37 million m^3/d) or sewage sludge production (814 t/d) (FOEN, 2017) (eq. (4)) in 2017 ($V_{\text{Switzerland}}$).

$$\text{THg load WWTP}_i = c_i * V_i \quad (1)$$

$$\text{per capita THg load WWTP}_i = \frac{c_i * V_i}{N_i} \quad (2)$$

$$\text{WM of the 28 WWTPs} = \frac{\sum_n (c_i * V_i)}{\sum_n V_i} \quad (3)$$

$$\text{THg load of Switzerland} = \text{WM} * V_{\text{Switzerland}} \quad (4)$$

3. Results and discussion

3.1. Hg concentrations and loads in wastewaters

3.1.1. Raw wastewater

The THg concentrations in the inflows of the 28 WWTPs are shown in Fig. 2a (for abbreviations, see Table S7). They spanned two orders of magnitude, from 9 to 750 ng/L, with a median concentration of 57 ng/L; average 110 ng/L (Table 1 and Table S8). The dissolved Hg concentrations ranged from 0.6 to 59 ng/L and accounted for 1–27% of the THg (average 7%). Hence, Hg was predominantly bound to particulate matter ($93 \pm 6\%$), with a positive correlation of THg ($\rho = 0.5$, $p < 0.01$) with total suspended solids (TSS, 30–392 mg/L). When compared to studies in other countries, the average THg concentration in Switzerland is in the lower range and comparable with the literature values of WWTP inflows in Canada, England, or Brazil (Table S6) (Bodaly et al., 1998; Gardner et al., 2013; Hargreaves et al., 2016; Oliveira et al., 2007). It is interesting to note that this range is 1–2 orders of magnitude lower than values recently reported in a comprehensive study of China (average 3400 ± 2600 ng/L, max 15,000 ng/L) (Liu et al., 2018). The

four Swiss WWTPs with the highest determined THg concentrations (i.e., ChdF, VISP, VERN, and VEV; Fig. S1) are located in western Switzerland (Figs. 2a and S1). The region of ChdF, VERN, and VEV is known for its watch and jewelry industry, which may be a (legacy) source for Hg; however, this would need further investigation.

As with the THg concentrations in raw wastewaters, the daily loads of THg spanned over two orders of magnitude, from <0.05 to 39.5 g/d, with an average of 4.8 ± 7.7 g/d (Table S8). By comparison, the TSS loads were 150–52,100 kg/d.

3.1.2. Treated wastewater

The THg in the treated wastewaters ranged from $<\text{LOD}$ (0.3 ng/L) to 92 ng/L (Fig. 2a), with a volumetric weighted mean concentration of 3.8 ± 0.4 ng/L (Table S9). These concentrations of a few tens of ng/L correspond with references to WWTPs that efficiently remove Hg (Balogh and Nollet, 2008b; Bodaly et al., 1998; Fricke et al., 2015; Gbondo-Tugbawa et al., 2010; Mao et al., 2016; Stoichev et al., 2009) (see Table S6). Liu et al. (2018) recently reported an average of 160 ng/L THg in Chinese effluents together with an overall 95% removal efficiency, but the incoming concentrations are much higher than in Switzerland (see section 3.1.1 above). The daily loads of THg in treated wastewater (i.e., the WWTP effluents) ranged from 3 to 950 mg/d. Our data allowed an estimation of the wastewater-derived Hg discharge to surface waters for the entirety of Switzerland of 13 ± 1.3 g THg/d, equivalent to a per capita discharge of 1.6 ± 0.16 μg THg/capita/day (Table 1). The relevance of wastewater-derived Hg discharge to the aquatic environment is discussed in section 4.1.

3.1.3. Hg retention efficiencies

The studied WWTPs reveal an overall efficient Hg removal from wastewater of 85–99.7%, with an average of $96 \pm 4\%$. Interestingly, the lowest efficiencies (85–88%) were found in WWTPs that received the highest dissolved Hg concentrations in their inflowing wastewaters (i.e., 17–59 ng/L dissolved Hg, equal to 12–17% of THg), suggesting limited sorption of dissolved Hg to TSS and a consequently poor elimination efficiency of the dissolved Hg fraction.

3.2. Concentrations and speciation in sewage sludge

3.2.1. THg concentrations in sewage sludge

The concentrations in sludge from the 28 WWTPs are plotted in Fig. 2b, together with the percentage of MMHg. The THg concentrations of the 2017 campaign ranged from 320 to 1400 ng/g (median 675 ng/g), as shown in the corresponding box plot. For the WWTPs studied in 2016, the THg spanned a slightly wider range, from 160 to 2600 ng/g (median 445 ng/g) (see Fig. 1, Fig. S4, and Table S13). The variability between the two campaigns within individual WWTPs was about 20%, with the majority of the WWTPs (16 of 28) differing by less than 10%, thereby confirming small temporal variations, as reported by Vriens et al. (2017) for other major and trace elements. The measured THg concentrations are largely in line with long-term monitoring data of the Swiss cantons and with published data from various European countries (~ 100 –3000 ng/g) (AWEL, 2017; Canton de Vaud, 2017; Canton de Vaud, 2018; Clara and Scheffknecht, 2016; Hittinger and Pichler, 2007; Kanton Aargau, 2015; Wiechmann et al., 2013).

3.2.2. Hg speciation in sewage sludge

The only organic species found with GC-ICP-MS analysis was MMHg (no peaks that could correspond to ethylated or phenyl-Hg forms were present); the MMHg concentrations in sewage sludge ranged from $<\text{LOD}$ (0.11 ng/g) to 8.6 ng/g (median 0.7 ng/g). The GC-ICP-MS analyses further revealed that the majority of Hg was

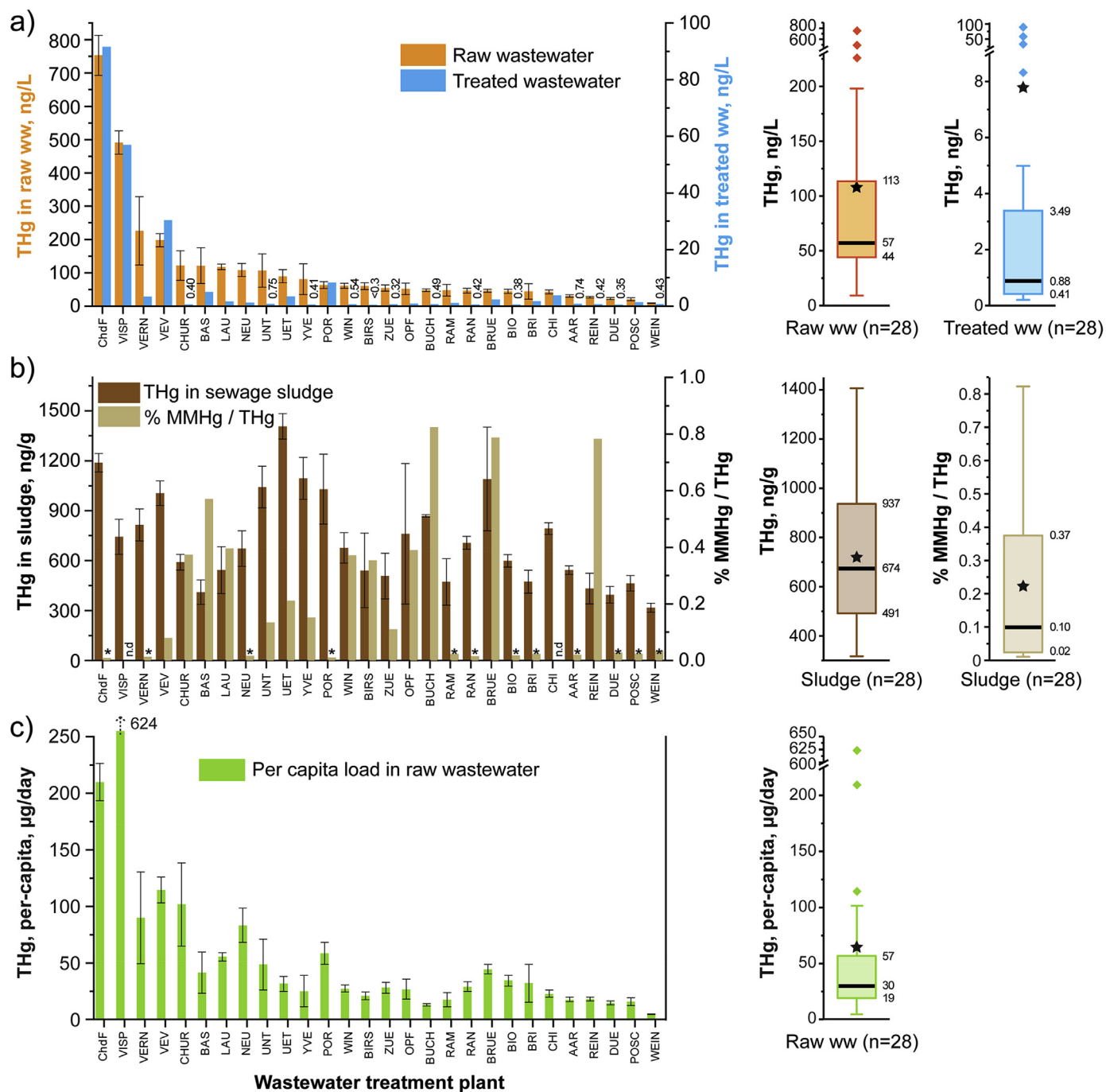


Fig. 2. a) THg concentrations in raw wastewaters and in treated wastewaters collected in 2017 from 28 Swiss wastewater treatment plants (WWTPs). The box plots show the medians (thick lines), means (stars), quartiles (25, 75%) (box), whiskers (1.5 times the interquartile range), and the outliers. The concentrations in the treated wastewater were below the detection limit (0.3 ng/L) in BIRS and ZUE. **b)** THg concentrations in sewage sludge and the percentage of monomethyl-Hg (MMHg) versus THg. MMHg concentrations that were below the detection limit were set to 0.08 ng/g (LOD/ $\sqrt{2}$); marked by a star. MMHg was not determined in VISP and CHI. **c)** Per capita THg loads calculated from the concentration in the raw wastewater inflow and the number of connected persons. The full names of the WWTPs are listed in the supporting Table S7, and their locations shown in the supporting Fig. S1.

present as IHg (median 84%, see Table S10). As shown in Fig. 2b, MMHg represented up to 0.8% of the THg. The determined MMHg concentrations are very similar to values reported in other studies from around the globe (Balogh and Nollet, 2008b; Bodaly et al., 1998; Gbondo-Tugbawa et al., 2010; Gilmour and Bloom, 1995; Liu et al., 2018; Mao et al., 2016). Such low MMHg concentrations in the sludges suggest that MMHg in the treated wastewater is most likely below the detection limit.

3.3. Detailed study of Hg loads and variability within the treatment process

3.3.1. Wastewater treatment chain

In raw wastewater of the Zurich-Werdhoelzli WWTP, which was continuously sampled for eight days, the THg varied between 45 and 73 ng/L on working days (average 59 ng/L), and between 29 and 32 ng/L on the weekend (see Fig. S5 and Table S11). Along the

Table 1
Summary of Hg concentration ranges and daily loads measured in raw wastewater (inflow), sewage sludge, and treated wastewater (outflow) of the 28 studied wastewater treatment plants, as well as loads extrapolated for the entire country of Switzerland based on the weighted means (WM).

	Raw wastewater	Sludge		Treated wastewater
	THg	THg	MMHg	THg
Range	9–750 ng/L	320–1400 ng/g	<LOD (0.11)–8.6 ng/g	<LOD (0.3)–92 ng/L
Average	110 ± 150 ng/L	720 ± 280 ng/g	1.6 ± 2.1 ng/g	8 ± 20 ng/L
Median	57 ng/L	674 ng/g	0.7 ng/g	0.9 ng/L
Weighted mean	104 ± 28 ng/L	656 ± 108 ng/g	1.5 ± 0.2 ng/g	3.8 ± 0.4 ng/L
Load of the entire country of Switzerland				
Daily load 2017 (g/d)	350 ± 90	530 ± 90	1.2 ± 0.2	13 ± 1.3
Annual load 2017 (kg/y)	130 ± 30	190 ± 30	0.5 ± 0.1	4.7 ± 0.5
Per-capita (µg/capita/d)	43 ± 11	64 ± 11	0.15 ± 0.03	16 ± 1.6

THg: total mercury; MMHg: monomethyl mercury.

treatment stages depicted in Fig. 3, the THg decreased from 52 ± 16 ng/L in the inflow to 22 ± 2 ng/L after the primary clarifier, to 9 ± 2 ng/L after the final sand filter, and to < LOD (0.3 ng/L) in the treated outflow (removal efficiency 99.5%). The highest THg concentrations along the treatment train (203 ± 56 ng/L) were present in the return sludge, which recirculates a major part of the activated sludge back to the bioreactor inflow to maintain microbial activity (Fig. 3). This loop causes an approximately 5-fold enrichment of Hg in the biological treatment stage (103 ± 3 ng/L, note that the median sludge age is 27 days).

Of the solids, the suspended solids of the preliminary clarifier were the most heavily burdened with THg (416 ± 28 ng/g), and hence contributed the largest share of THg in the dewatered sewage sludge (465 ± 40 ng/g, Fig. 3). In the activated sludge treatment (bioreactor), which includes nitrification, denitrification, and phosphorus precipitation, the THg in the suspended solids decreased to 163 ± 3 ng/g.

MMHg was also analyzed in the suspended matter and sewage sludge. The concentrations were between 0.2 and 1.6 ng/g, accounting for 0.1–0.9% of the THg (Fig. 3). The proportion of MMHg was therefore in the same range as found in the sewage sludge of the other 27 WWTPs. Further, MMHg remained quite stable along

the different treatment steps, indicating no significant transformation.

3.3.2. Sludge incineration

The Zurich-Werdhölzli WWTP incinerates its own dewatered sludge (29,970 t in 2017) and sludge from other WWTPs (53,670 t in 2017), with an estimated THg load of 37.1 kg/y (79,720 t of sludge in 2017, 465 THg ng/g). For the years 2016–2018, the reported THg concentration in the incineration ash was in the range of 100–430 ng/g, while the residues from flue gas treatment showed 100 times higher THg concentrations of 11–41 µg/g (Schafflützel, 2019). In Switzerland, the legal limit for THg in incineration exhaust is 0.05 mg/m^3 (SFC, 2018). The Zurich-Werdhölzli WWTP reported a daily average THg concentration in the exhaust gas of 0.016 mg/m^3 , which, in 2017, resulted in ~ 1.7 kg ($\sim 5\%$) THg expelled to the atmosphere (Abegglen, 2018). This indicates that most of the Hg is volatilized in the incineration process but is then recaptured in the flue gas treatment, after the separation of the fly and bottom ash (van Velzen et al., 2002). Hence, the major fraction of Hg is not found in the incineration ash, but in the flue gas treatment residues. The overall retention efficiency of the sewage sludge incineration was $\sim 95\%$. Combined with the $\geq 99.5\%$ removal by the wastewater

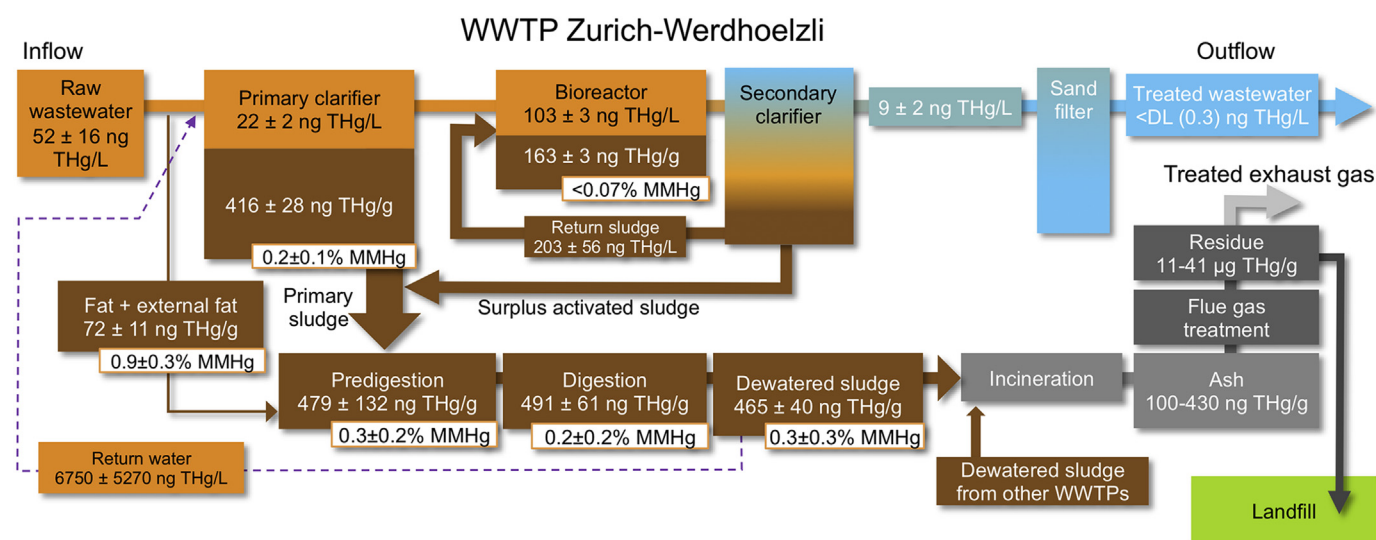


Fig. 3. Flowchart for total mercury (THg) concentrations, mercury speciation in sewage sludge, and wastewater along the treatment steps of the WWTP Zurich-Werdhölzli in September 2017 (detailed study, Table S12). The THg concentrations are given in ng/L for liquid phases (orange and blue) and in ng/g for solid phases (brown); the standard deviation was calculated from replicate digests and replicate samples. The percentage of monomethyl mercury (MMHg) is also indicated. The Hg follows the solid phase by sedimentation into the sludge digestion. The sewage sludge is incinerated after digestion. The THg retention efficiency of the Zurich-Werdhölzli WWTP was $\geq 99.5\%$ for the water treatment and about 95% for sludge incineration. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

treatment, a grand total of 95% of the Hg was therefore retained by the WWTP. Even though some THg is expelled to the atmosphere through sludge incineration, the WWTPs efficiently remove most THg from wastewater and allow its storage in hazardous waste landfills.

3.4. Total and per-capita loads in raw wastewater

The weighted mean THg concentration of raw wastewaters (104 ± 28 ng/L) and the total wastewater flow of Switzerland gave an estimated annual Hg input of 130 ± 30 kg/y (Table 1). For Switzerland, which has 8.29 million people connected (FOEN, 2017) to WWTPs (98% of population in 2016), this corresponds to a per-capita load of 43 ± 11 μ g/capita/d. Hence, the Swiss average is comparable with estimations made for Austria (55 μ g/capita/d) (Reisinger et al., 2009), the city of Frankfurt (59 μ g/capita/d) (Fricke et al., 2015), or Sweden (67 μ g/capita/d) (Sörme and Lagerkvist, 2002). Two of the 28 WWTPs, namely Visp (620 μ g THg/capita/d) and La Chaux-de-Fonds (ChdF; 210 μ g THg/capita/d), had exceptionally high per-capita loads; these WWTPs are located in catchments that are strongly influenced by chemical and watchmaking industries. By contrast, for the Zurich-Werdhoelzli WWTP that has a much smaller proportion of industrial wastewater, the THg flux in the raw wastewater was 8 ± 3 g THg/d, with a corresponding per capita load of 19 ± 6 μ g THg/capita/d (Table S11).

Since only a minor fraction of the total Hg input to WWTPs is released into surface waters, and since most THg is retained in the sewage sludge, the total mass of THg retained in the annually produced sewage sludge represents an independent estimate of the THg flow into Swiss WWTP. From the weighted mean THg concentration in sewage sludge and the annual Swiss sludge production, a THg load of 190 ± 30 kg/y was calculated (Table 1). This sludge-based estimate is about 50% higher than the THg load calculated from THg in raw wastewater. However, sludge is believed to provide a better estimate since the sludge samples integrate longer time periods than the aqueous phase.

4. Environmental implications

4.1. Relevance of wastewater-derived Hg discharge to the aquatic environment

In the following, we estimate the extent to which the discharge of wastewater can contribute to Hg amounts in riverine water. In 2017, the combined average flow of the four rivers that drain Switzerland was 194 million m³/d (NADUF, 2017), with the vast majority discharged by the Rhine (71%) and Rhone (23%) rivers (Fig. 1). The total treated wastewater discharge of the 28 WWTPs amounted to 1.28 million m³/d, or 0.49 m³/d per capita for the 2.6 million connected people. Hence, an amount of ≈ 4.1 million m³/d of wastewater is estimated for the entire country of Switzerland (8.29 million connected population in 2017), equaling $\approx 2.1\%$ of the average riverine discharge from Switzerland, as mentioned above (FOEN, 2017).

Recent THg measurements in Swiss surface waters are scarce, and the concentrations are often below the LOD (<10 , <5 ng/L) (Ritscher et al., 2018). However, the Rhine River monitoring station at the Swiss border with Germany has regularly measured THg in suspended solids and in water since 1994 (Fig. S6). For the period of 1994–2017, the range of 5-year averages of THg concentrations was 2.7–4.5 ng/L, with an average of 3.3 ± 0.8 ng/L in suspended solids, and below LOD (5 ng/L) for the truly dissolved THg in water (Mazacek, 2019). Yearly loads, calculated from the available THg concentrations, are shown in Fig. S6 and range from 30 to 378 kg/y (mean 137 ± 90 kg/y). Based on these long-term data for the Rhine

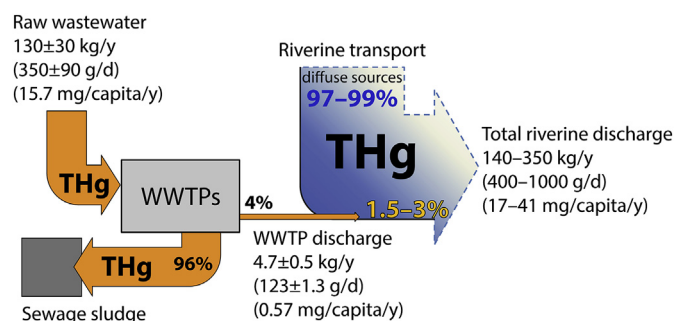


Fig. 4. Estimated total mercury (THg) loads of the Swiss WWTPs and their contribution to the THg load in surface waters at the Swiss border. The THg contribution of WWTPs to surface waters is small, at about 1.5–3%. Examples of potential diffuse sources are atmospheric deposition, soil erosion and runoff, agricultural chemicals, and historical sources, such as Hg in lake sediments from earlier sedimentation (Yernet and Thomas, 1972).

River, which actually captures 71% of the entire surface water discharge of Switzerland, we can conclude that the average THg concentrations in Swiss rivers range between 3.8 and 6.3 ng/L, equaling an estimated Hg discharge from Switzerland of some 160–290 kg/y (mean 197 kg/y).

Finally, the total flux of THg in treated wastewater from the 28 investigated WWTPs was calculated and extrapolated to the whole of Switzerland (note that $>97\%$ of the country is connected to WWTPs). The estimated combined THg discharged from all the WWTPs in Switzerland was 13 g/d (4.7 kg/y), which corresponds to a total Hg contribution from treated wastewater of some 1.5–3% (mean 2.4%) of the riverine Hg loads (Fig. 4).

The Swiss limit for Hg concentrations in surface water is defined as 30 ng/L THg and 10 ng/L dissolved Hg after thorough mixing of a potential wastewater inflow (EU max. yearly average is 50 ng/L) (Behra et al., 1993; Behra et al., 1994; EC, 2008; SFC, 2020). The THg contributions of the 28 WWTPs to the receiving rivers were calculated based on river water discharge being representative for 95% of the time (FOEN, 1992). The resulting THg concentrations of <0.01 –8.5 ng/L (THg) meet the legal requirements; however, in some cases, they are close to the ecotoxicological quality criterion of 10 ng/L (Behra et al., 1993; Behra et al., 1994; SFC, 2020). At present, no more Hg point sources are known that contribute to surface waters in Switzerland; therefore, diffuse sources are likely the main contributors to Hg in Swiss rivers. Potential diffuse sources could include atmospheric deposition, erosion and runoff, historical sources (e.g., Hg in lake sediments (Díez et al., 2018; Yernet and Thomas, 1972)), or other unspecified sources.

Although emissions of Hg have declined significantly in Switzerland in the last decade (EMEP, 2015), the mean direct atmospheric deposition rate to surface waters is still estimated at 11 g/km²/year (with more than 99% originating from emission sources outside the country) (EMEP, 2015). The total direct atmospheric deposition to the Swiss surface water bodies alone (1734 km²) therefore amounts to 52 g/d Hg, which is 5–27% of the riverine THg load (see above).

Soil erosion can also be a source of Hg to rivers. For an erosion rate of 0.4 t/y/ha (Mosimann et al., 1991) from Swiss farmland (4071 km²) (BFS, 2009) with a mean soil Hg content of 45 μ g/kg (range 20–70 μ g/kg) (Selin, 2009), this flux amounts to 20 g/d Hg, thereby accounting for 2–10% of the riverine THg loads (see above). Rainfall and glacier melt are likely only very minor contributors, at $<1\%$ (Blanc and Schädler, 2014), similar to exfiltration of groundwater (Fricke et al., 2015).

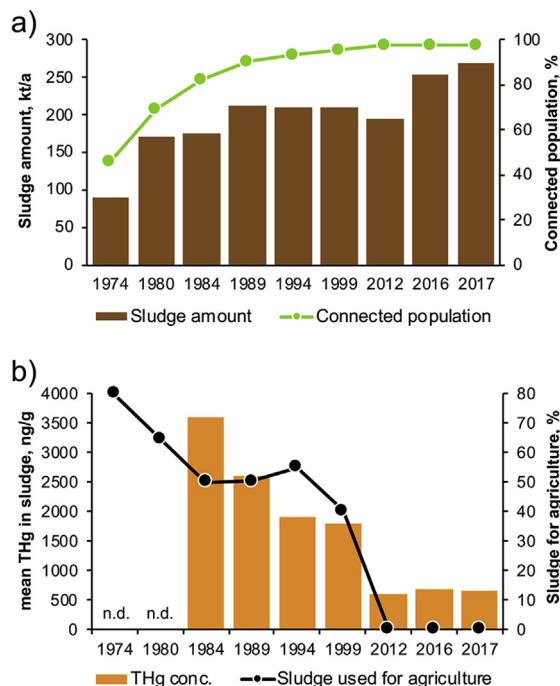


Fig. 5. Timeline for sludge production in Switzerland and annual total mercury (THg) concentrations (brown and orange columns, left y-axis) compared to the percentage of the population connected to WWTPs and the use of sludge in agriculture (green and black symbols, right y-axis), modified after (Külling et al., 2002). The use of sludge in agriculture has been prohibited in Switzerland since 2006. The data shown for 2016 and 2017 are data based on the calculated volume weighted means of 64 and 28 WWTPs in 2016 and 2017 (this study), respectively. THg concentrations in sludge were not determined in the years 1974 and 1980. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4.2. Contamination of soils by Hg in sewage sludge

Given its high content in essential elements, such as phosphorus, for which resources are getting more and more scarce (EC, 2018), sewage sludge is an attractive fertilizer in many regions worldwide (Mattsson et al., 2017; Mayer et al., 2016; Mulchandani and Westerhoff, 2016; Nancharaiyah et al., 2016a, 2016b; Olofsson et al., 2012; Vriens et al., 2017). As shown in Fig. 5, the estimated annual THg load of sewage sludge in Switzerland decreased from 612 kg/y in 1984 (170 kt/y of sludge, THg concentration 3600 ng/g) (Laube and Vonplon, 2004) to 176 ± 28 kg/y in 2017 (268 kt/y of sludge, THg concentration 656 ± 108 ng/g, this study). Hence, a significant reduction in both Hg concentrations and loads can be observed, despite the 50% increase in sewage sludge production in the same time period (Fig. 5) (Külling et al., 2002). Declining THg concentrations in sewage sludge were also observed in other countries, such as Germany (4.8 mg/kg in 1977 to 0.6 mg/kg in 2002–2006) (Wiechmann et al., 2013), Austria, the UK, Sweden (2.5 mg/kg in 1987 to 0.5 mg/kg in 2010–2012) (Swedish EPA, 2014), and the USA (e.g., New Jersey 3.6 mg/kg in 1983 to 1.47 mg/kg in 2003) (State of New Jersey, 2003). In Switzerland, as a result of application restrictions, the use of sewage sludge as a fertilizer strongly decreased from 70% to 20% between 1980 and 2002 (Fig. 5) (Laube and Vonplon, 2004). In 2006, sewage sludge spreading was completely banned in Switzerland and all sludge has since been incinerated (SFC, 2011).

Where sewage sludge is still used as a fertilizer in agriculture, Hg is distributed again in the environment and can pose a risk to human health and the ecosystem (EPA, 1972, 2002). In our study, THg concentrations in sewage sludge ranged from 320 to 1400 ng/g

THg/g (Table S10). Consequently, when compared to background soil and sediment concentrations (unpolluted soils 100 ng/g (Adriano, 1986) to 232 ng/g natural background (Remy et al., 2002, 2006)) or organic fertilizers (cattle and pig slurry 20–200 ng/g, manure 30–50 ng/g, bio compost 150 ng/g) (Hittinger and Pichler), sewage sludge can contribute substantially to Hg in agricultural soils. The THg concentrations and the ratios of MMHg/THg in sewage sludge were comparable to those in soils (0.6% MMHg) (Grigal, 2003) and sediments (up to 2% in lake sediments) (Jiang et al., 2011).

5. Conclusions

Our nationwide survey shows that THg concentrations in sewage sludge and treated wastewaters are in the same range as in other developed regions around the globe. The geographic setting of Switzerland, with its main rivers originating within the country, and with almost the entire population connected to WWTPs, allowed an estimation of the mean per-capita loads and the share of wastewater-derived Hg inputs to receiving rivers. Further, the well documented fluxes of wastewater, sewage sludge production rates, and river discharge in Switzerland, enabled a nationwide quantitative assessment of (i) the fluxes of Hg into WWTPs, (ii) the extent of Hg removal and the concomitant Hg accumulation in sewage sludge and (iii) the importance of wastewater treatment plants as sources for Hg in receiving streams.

The derived mean per-capita loads of ~16 mg/year in raw wastewater and 0.6 mg/year in treated wastewater are valuable proxies to estimate Hg loads elsewhere. For example, extrapolation to the population of Europe (746 million people in 2018) yields a total amount of 11,700 kg/year of Hg in raw wastewater, with 425 kg/year discharged to surface waters. Although these are considerable quantities, our study indicated that the amount of Hg discharged by WWTPs into rivers in Switzerland is marginal ($\leq 3\%$) compared to the total riverine Hg export from Switzerland. Thus, the main share of the riverine Hg originates from other diffuse and point sources (e.g., atmospheric deposition, erosion and runoff, legacy sites) that need further investigation.

Annual mean Hg concentrations in sewage sludge were significantly reduced (~fivefold) since the 1980s and have leveled at concentrations below 1000 ng/g for the past 10 years, demonstrating the effectiveness of the imposed regulations. Our survey further confirmed that WWTPs effectively reduce the release of Hg resulting from anthropogenic activities into surface waters, provided the sewage sludge is disposed of properly and not used as fertilizer in agriculture. This study provides valuable baseline estimates that contribute to the goals of the global Minamata Convention and will be of interest to stakeholders in the fields of wastewater treatment, environmental chemistry, ecology, toxicology, and environmental remediation related to mercury.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115708>.

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