Quantification of Element Fluxes in Wastewaters: A Nationwide Survey in Switzerland

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ABSTRACT

The number and quantities of trace elements used in industry, (high-tech) consumer products, and medicine are rapidly increasing, but the resulting emissions and waste streams are largely unknown. We assessed the concentrations of 69 elements in digested sewage sludge and effluent samples from 64 municipal wastewater treatment plants, as well as in major rivers in Switzerland. This dataset, representative of an entire industrialized country, presents a reference point for current element concentrations, average per-capita fluxes, loads discharged to surface waters, and economic waste stream values. The spatial distribution of many individual elements could be attributed either to predominant geogenic or to anthropogenic inputs. Per-capita element fluxes ranged from $<10 \mu\text{g day}^{-1}$ (e.g., Au, In, Lu) to $>1 \text{ mg day}^{-1}$ (e.g., Zn, Sc, Y, Nb, and Gd) and $>1 \text{ g day}^{-1}$ (e.g., for P, Fe, and S). Effluent loads of some elements contributed significantly to riverine budgets (e.g., 24% for Zn, 50% for P, and 83% for Gd), indicating large anthropogenic inputs via the wastewater stream. At various locations, precious metal concentrations in sludge were similar to those in profitable mining ores, with total flux values of up to $6.8 \text{ USD capita}^{-1} \text{ yr}^{-1}$ or $15 \text{ USD metric ton}^{-1}$ dry sludge.

INTRODUCTION

Trace elements are of great importance for a variety of applications in electronics, optics, catalysts, ceramics, and pharmaceuticals. The global use of trace elements in industry and (high-tech) consumer products has increased tremendously due to economic and population growth over the last decades [1-3]. This increase applies not only to classical trace metal pollutants such as Ni, Cu, Zn, Pb, or Cd, but also to rare earth elements (REE) and platinum group elements (PGE), as well as Ag, Au, and other generally less well-studied elements, such as Nb, Ta, Ga, Ge, In, Tl, or Te. Many of the aforementioned elements are critical for applications in emerging technologies in communications, energy, and mobility [1-3]. The anthropogenic use of some REE [8, 9], platinum group elements [10, 11], and other trace elements, such as In [12] has recently been quantitatively described. The current societal use of certain trace elements (e.g., Hg, Pb, Zn or Os) is so large that it may affect their global distribution [13, 14]. The increasing use of trace elements may cause increases in emissions to the environment, which can occur during the mining of raw (ore) materials [4] and during manufacturing and application [5], as well as during recycling or degradation of e-waste [6, 7].

Despite the awareness of the increased use of trace elements and the potential environmental impact thereof, the quantitative understanding of the scale of trace element emissions and associated environmental impacts and health risks is currently quite limited. Many trace elements are viewed as emerging pollutants [5,7], but a profound understanding of the biogeochemical behavior and toxicology [15] of most of these trace elements is missing, which obstructs the forecasting of potential ecotoxicological consequences of their emissions. Prevention of human-induced adverse impacts on the environment requires a thorough understanding of the environmental behavior of trace elements and a quantification of their fluxes.

44 The presence of pollutants in wastewater is an indicator of societal use. Good examples are
45 pharmaceuticals and personal care products [16], flame retardants and surfactants [17, 18],
46 and engineered nanoparticles [19, 20]. Similarly, the growing use of trace elements may lead
47 to increasing loads in wastewater treatment plants (WWTP), since the trace elements used in
48 society often find their way into municipal and industrial wastewater streams. Unfortunately,
49 only a few studies have investigated the concentration ranges of trace elements in wastewater
50 and their behavior during wastewater treatment [21-23], and these studies usually considered
51 only one or a few selected WWTP. Furthermore, previous studies have focused mainly on the
52 fluxes and behavior of ‘classical’ trace elements such as metals [24] or precious metals—the
53 latter receiving attention because of their potential recovery value from sewage sludge [25-
54 28]. Comparable quantitative information on concentration ranges and fluxes for most other
55 trace elements is missing; the few existing surveys (e.g., from Sweden [29] and the U.S. [30])
56 are over a decade old. Quantitative information on the present concentrations of trace
57 elements in wastewater streams is thus critically needed.

58 Here, we quantified the concentrations of 69 major and trace elements in 64 communal and
59 industrial WWTP and in the major rivers in Switzerland (194 samples in total). This dataset,
60 representative of an industrialized country in its entirety, allows us to present estimates of i)
61 the current ranges of trace element concentrations in wastewater, ii) the per-capita element
62 fluxes, and iii) the wastewater discharge value estimates for selected precious trace elements.
63 We use this dataset to calculate the contributions of WWTP effluent fluxes to riverine fluxes.
64 Switzerland is uniquely suited for this, since virtually the entire Swiss population (~98% [73])
65 is connected to wastewater treatment systems, all major rivers have their origin in the country,
66 and these rivers are continuously monitored at Switzerland’s border.

MATERIALS AND METHODS

Sample collection

Samples of digested sewage sludge and treated wastewater (effluent) were collected from 64 WWTP in Switzerland (Figure 1) between February and March 2016 (one sludge sample and one effluent sample per WWTP). The sampled WWTP were selected to guarantee a broad nationwide representation, based on geographical distribution, numbers of connected people and industries in the catchment areas, and treatment types employed by the WWTP. Communal and industrial WWTP from both rural and urban areas were included, representing a total of 3.94 million connected population equivalents (54% of the country, Table S1). Average daily wastewater inflow and sludge production rates of the sampled WWTP are given in Table S1. Digested sludge samples were collected after anaerobic digestion and dewatering through centrifugation, pressing, or additional drying. The average age of the investigated sludges was 30.6 days. The effluent waters consisted of composite samples of one- to seven-day periods to account for diurnal variation in wastewater composition. The seasonal variation of element concentrations was monitored by collecting and investigating additional sludge and effluent samples from ten selected WWTP (Figure 1) two more times, in June and July 2016.

All sampling material was pre-cleaned by acid washing in 1% ultrapure HNO_3 (ROTIPURAN[®] $\geq 65\%$, Carl Roth GmbH, Germany) and rinsing with ultrapure water (NANOpure, Thermo Scientific). The sludge samples were collected in pre-cleaned 200 mL polypropylene boxes (Semadeni, Switzerland). The effluent water samples were collected in pre-cleaned 250 mL PFA flasks equipped with a PTFE cap (Semadeni, Switzerland). The WWTP effluent samples were immediately acidified by adding 2.5 mL concentrated ultrapure HNO_3 and subsequently filtered through 0.45 μm Teflon filters (Faust AG, Switzerland). The sludge samples and effluent samples were stored in the dark at -20°C and 4°C , respectively, until analysis.

Water samples from the four major rivers that drain Switzerland (i.e., Rhine, Rhône, Inn and Ticino) were obtained from the Swiss National River Monitoring and Survey Program (NADUF) [31] between March and August 2016, a period roughly corresponding to the period in which the WWTP samples were collected. Flow-proportional (discharge-weighted) biweekly collective river water samples were collected from the national monitoring stations at Weil am Rhein (Rhine), Chancy (Rhône), Riazino (Ticino), and Martinsbruck (Inn), which are located at the respective outflows at the Swiss border (Figure 1). These river water samples were acidified with 1% concentrated ultrapure HNO_3 , filtered through $0.45\ \mu\text{m}$ Teflon filters (Faust AG, Switzerland) and subsequently stored in the dark at 4°C until further use.

Acid digestion of sludge samples

Because the sludge samples had a variable water content (3–76%), aliquots (~10 g each) of the sludge samples were freeze-dried under vacuum to constant dry weight at -20°C for 48 h (LyoAlpha 10-55, Telstar, Madrid, Spain) and subsequently homogenized using a ceramic mortar. The total element fractions were quantitatively recovered using different acid-digestion methods from which at least one method guaranteed element stability for long periods of time. Three digestion techniques were applied: i) acid-digestion with hydrogen peroxide (H_2O_2) and nitric acid (HNO_3), ii) acid-digestion with H_2O_2 , HNO_3 and hydrofluoric acid (HF), and iii) acid-digestion with H_2O_2 and *aqua regia* (1:3 v/v mixture of HNO_3 and hydrochloric acid (HCl)). All chemicals were of ultrapure grade: ultrapure HF (47–51%) and ultrapure H_2O_2 ($\geq 30\%$) from Sigma-Aldrich and ultrapure HNO_3 ($\geq 65\%$) and HCl ($\geq 32\%$) from Carl Roth GmbH, Germany.

For acid-digestion methods 1 and 2, 50 mg of dried sludge was mixed with 1 mL concentrated H_2O_2 and 5 mL concentrated HNO_3 and, for acid-digestion method 2, 0.3 mL concentrated HF was added to this mixture. These mixtures were subsequently digested at 230°C and 130 bar for 45 min in 15 mL Teflon-tetrafluorometoxil (PTFE-TFM) tubes using an

MLS UltraClave 4 (Milestone, Shelton, USA). For acid-digestion method 3, 100 mg of dried sludge was mixed with 1 mL concentrated H_2O_2 , 2 mL concentrated HNO_3 , and 6 mL concentrated HCl and subsequently digested at 210 °C and 130 bar for 45 min in 50 mL TFM tubes using an Ethos 1 Microwave digestion oven (MLS GmbH, Heerbrugg, Switzerland). In all acid-digestion methods, the peroxide and acids were added slowly to prevent loss of sample due to the vigorous reaction with the organic matter in the sludge samples and resulting release of CO_2 . After acid-digestion, the digests were diluted with ultrapure water to 50 mL in 50 mL Greiner tubes. All vials and tubes were acid washed in 1% ultrapure HNO_3 and rinsed with ultrapure water before use.

For quality control, selected samples were acid-digested in triplicate, and three certified reference materials were acid-digested with each sample series: European Community Bureau Reference Standard BCR 145R (sewage sludge of mixed origin), NIST 2781 (domestic sewage sludge), and NIST 2782 (industrial sewage sludge). The recovery of the certified elements using the most suitable of the investigated acid-digestion methods ranged between 45 and 139% for the individual elements (see complete overview in Table S2).

Elemental analyses of sludge and water samples

The concentrations of 69 elements were quantified in the digested sludge samples and in the acidified and filtered WWTP effluents and river water samples using a quadrupole dynamic reaction cell ICP-MS (Agilent 7500cx). Two ICP-MS methods were used: ICP-MS method A included 48 target elements, with 1 mg L^{-1} Nb and Au as internal standards, and ICP-MS method B included 21 target elements, with 10 mg L^{-1} Sc and 1 mg L^{-1} Lu as internal standards. Multiple isotopes of each element were recorded to monitor interferences, but a single isotope was used for element quantification. The selected isotope was typically the one with the highest abundance, the lowest detection limit, and/or the best agreement with the certified reference materials. The digests from the three acid-digestion methods were analyzed with both ICP-MS methods, but each element was quantified only in the matrix resulting from

the most appropriate acid-digestion method as indicated in Table S2. Details of both ICP-MS methods (e.g., the measured target masses, used calibration standards, and matrix composition resulting from acid-digestion) are provided in Table S3. The digests from methods 1 and 2 were analyzed without further dilution (matrices were 10% HNO₃ for method 1 and 10% HNO₃ and 0.6% HF for method 2), while the digests from method 3 were diluted 1:10 with ultrapure water before analysis (yielding a matrix with 0.4% HNO₃ and 1.2% HCl). The acid concentrations in the corresponding calibration standards were similar. The element concentrations in the acidified and filtered WTP effluent samples and river water samples were measured without further dilution (1% HNO₃ matrix). Since the effluent samples and river water samples were acidified prior to filtration, the concentrations reported for these samples reflect, per methodological definition, a total element concentration (including elements from particles such as organic colloids that may have dissolved upon acidification), rather than a dissolved element concentration. The limits of detection for the investigated elements in both the digested sludge samples and the acidified water samples are listed in Table S4. The ICP-MS was tuned daily using a solution consisting of 1 ppb Sc, Rh, In, U, Y, and Lu and 5 ppb Li and Ba in 1% HNO₃. Quality control of the ICP-MS measurements was conducted by analyzing triplicate samples of selected sludge and effluent samples (<15% RSD for all elements), as well as by co-analyzing in-house (ARS-29 and ARS-32) and commercial (Merck 1643f and Environment Canada 51.2) aqueous reference standards.

Data processing

Correlations between the measured concentrations in the sludge and the effluent samples were analyzed using multivariate regression. For regression analysis, concentrations were treated as continuous numeric variables and scaled through log-normalization because their distributions were usually highly skewed. Non-detects (from measurements below the analytical detection limit) were log-normalized after adding a very small positive value (i.e.,

170 MDL/100). Statistical operations were executed using JMP 11 (SAS Institute Inc.,
171 Buckinghamshire, UK).
172

RESULTS AND DISCUSSION

Element concentrations in the WWTP

The concentration ranges of the elements quantified in sludge and effluent water samples are depicted as box plots in Figures 2 and 3, respectively. A summary of the concentration ranges of all 69 measured elements is given in Table S5, and individual values for each WWTP are provided in Table S6. The sludge samples show differences of over 6 orders of magnitude between the concentration ranges of the most abundant elements (e.g., Fe, P, and Ca, 10–100 g kg⁻¹ range) and those of the rarest trace elements (e.g., Pt, Au, and Pd, <10–100 µg kg⁻¹ range). The span in concentrations differs by as much as 8 orders of magnitude in the effluent waters, where the most abundant elements are Na, Ca, and S (10–100 mg L⁻¹ range) and the least abundant are REE and PGE (<0.1–10 ng L⁻¹ range). The PGE concentrations in the sludges and WWTP effluents were very low (>50% of all measurements <MDL, with the extreme case of Os being <MDL in all effluent samples) and their (indicative) concentration ranges should be further investigated using specialized analytical techniques. Since values <MDL will range between 0 and the corresponding MDL, concentration ranges are reported with non-detects being either ignored (Table S5, Figures 2 and 3) or considered being 0 (Table S5).

The element concentrations measured in sludge and effluent samples from the recurrently sampled WWTP generally varied by less than two orders of magnitude over the three sampling occasions: the correspondence between the measured concentrations at the three sampling occasions, averaged over all elements, was 98% and 113% for the sludges and effluents, respectively, while the maximum observed deviation was a factor of 6.1 (for Ca) and a factor of 50 (for Sm), respectively (see details in Table S7). This suggests representative sampling and relatively little temporal variation in most element concentrations in sludge and effluent samples throughout different times of the year (January–February versus June–July).

198 The distribution of the element concentrations is generally highly skewed, due to some
199 WWTP exhibiting concentrations exceeding the median value by up to 100 times. In sludge
200 samples, these conspicuous concentrations were observed, for instance, in La-Chaux-de-
201 Fonds (Ru, Rh, and Au), Porrentruy (Zr, Pd, and Hf), Mendrisio (Pt, Au, In, and Cu),
202 Uetendorf (Zr), Yverdon (Ce), and Poschiavo, Disentis, and Evionnaz (As) (Table S6).
203 Effluent samples with element concentrations clearly exceeding the median include Kaisten
204 (Li), Reinach (Cr), Locarno (REE), Visp (Li, Mn, Mo, and Cr), and Buchs and Porrentruy (Sn
205 and Cd) (Table S6). These elevated concentrations were verified by analyzing the digests
206 obtained using the three different digestion methods, as well as by analyzing the additional
207 samples collected for a limited number of WWTP (see Table S7). Multiple elements were
208 enriched simultaneously in only a few WWTP (e.g., Porrentruy and Mendrisio), suggesting
209 that most of the elevated concentrations of individual elements originate from different
210 (catchment area-specific) sources.

211 The high Fe concentrations in sludge samples originate from the use of Fe precipitation for
212 P removal [32], although no relation between P and Fe concentrations in the sludge samples
213 was observed. In addition, Fe is poorly correlated with Mn and with other metals that sorb to
214 Fe (e.g., Ni, Cr, Co or As; see Figure S1). However, the rank order of the concentrations of
215 most metals in the sludge samples ($\text{Zn} > \text{Cu} > \text{Cr} > \text{Ni} > \text{Cd}$) is consistent with trends for
216 sewage sludges reported elsewhere [24, 27, 33-36]. Concerning emerging trace elements,
217 multivariate correlations revealed that most REE correlate relatively well ($R^2 = 0.5\text{--}1.0$) with
218 each other in the sludge and effluents due to their similar chemistry (Figure S1). Other trace
219 elements were poorly correlated with each other and with major elements like Fe, Ca, or Si, as
220 can be expected with the large variety of WWTP treatment processes and the variability in the
221 chemical composition of the incoming wastewaters.

222 **Comparison of element concentrations with previous studies and legal guidelines**

Despite the locally elevated occurrence of some elements, the concentrations measured in our Swiss study are in the same range as those previously reported in Switzerland, as well as in Sweden, France, Luxembourg, Japan, Slovenia, China, and the U.S. (see literature comparison and references in Table S8). Previous studies have observed temporal variations in the element concentrations in WWTP on time scales ranging from decades (e.g., Cu, Zn, and Pb decline over the last decades [37, 38]) to weeks (e.g., Cu and Ni [39, 40]). However, few data exists for elements other than metals, and the number of studies is too limited to discern a systematic (international) increase or decrease in trace element levels in WWTP over the past decades. Furthermore, few of the above-mentioned studies report the number of connected population equivalents, so that per-capita fluxes, arguably a more accurate measure for societal use of elements, cannot be calculated and compared (see below). Additional multi-element measurements from long-term WWTP monitoring programs are therefore critically needed.

In contrast to EU legislation [42], the Swiss Chemical Risk Reduction Ordinance (ORRChem) and *Abfallverordnung* (VVEA) have prohibited the agricultural use of sewage sludge since 2006 and consider sewage sludge as a municipal waste [43, 44]. However, regular inspection of the quality of the sludge is still mandated. In Table 1, the element concentrations are compared with the former legal limits from the transitional provisions contained in the ORRChem [43], with the guidelines for surface water quality from the Swiss Waters Protection Ordinance (WPO) [45, 46], and with the guidelines from the EU Sludge Directive [42] and the German Sewage Sludge Ordinance (AbfKlärV) [47]. The great majority of investigated WWTP complies with Swiss legal limits for metal concentrations in sludge and effluents, except for 17 WWTP and 38 WWTP that exceeded Swiss WPO limits for Cu and Zn concentrations in effluents, respectively. In sludge, Cd and Cu concentrations each exceed the former limit values of the ORRChem in 5 WWTP (Table 1). The elevated levels of Cu and Zn in effluents may be (partially) explained by the fact that the

concentrations reported in this study reflect total (dissolved and particulate) rather than just dissolved element concentrations, and that mixing and dilution with the receiving surface waters (as specified in the WPO) was not considered [45]. Elevated Cd and Cu concentrations may be an issue in countries that use sludge as a fertilizer in agriculture. As far as toxicological data of trace elements and their speciation exist, no measures for further reduction in the concentrations of potentially toxic elements from wastewater in Switzerland seem currently required. The sludge and effluent concentrations of REE, for example, are well below previously published ecotoxicological concentration limits [48]. However, adequate toxicological data or legislation are lacking for many other trace elements and the need for legal guidelines for these other trace elements should be further investigated.

Per-capita element fluxes in WWTP

The population-weighted median flux of each element (if detected in >50% of the measured sludge samples) was calculated by dividing the total element flux through all sampled WWTP (sludge plus effluent fraction) by the sum of the connected population equivalents using the following equation:

$$J_X = \frac{\sum[(F_{sludge} \times [X]_{sludge}) + (F_{effluent} \times [X]_{effluent})]_{64 \text{ WWTP}}}{\sum[population \text{ equivalent}]_{64 \text{ WWTP}}}$$

in which F_{sludge} and $F_{effluent}$ are the digested sludge production rates (dry weight) and wastewater effluent rates of the individual WWTP, respectively (Table S1), and $[X]_{sludge}$ and $[X]_{effluent}$ the element concentrations in the sludges (dry weight) and effluents of the individual WWTP, respectively (Table S6). The population-weighted fluxes over all 64 WWTP vary from several $\text{g capita}^{-1} \text{ d}^{-1}$ for major elements (e.g., 36 g and 22 $\text{g capita}^{-1} \text{ d}^{-1}$ for Na and Ca, respectively) to less than 10 $\mu\text{g capita}^{-1} \text{ d}^{-1}$ for trace elements like Au, Lu or In (see Figure 4 and details in Table S9). The per-capita fluxes of (ultra-)trace elements such as Re, Os, or Ir are most likely even lower but could not be reliably estimated as >50% of the sludge concentrations were <MDL.

The incorporation of both communal and industrial WWTP from both rural and urban areas and the large number of population equivalents (3.94 million) sampled in this study allow the consideration of these population-weighted element fluxes as typical for an industrialized country. This representativeness is illustrated by the fact that the population-weighted P flux calculated in this study ($2.5 \text{ g P capita}^{-1} \text{ d}^{-1}$) quantitatively agrees with the P fluxes for domestic sewage (between $1.4 \text{ g P capita}^{-1} \text{ d}^{-1}$ and $4.1 \text{ g P capita}^{-1} \text{ d}^{-1}$) calculated by previous studies [49-51] and with previous estimates for P fluxes in Switzerland [52, 53]. Furthermore, the calculated population-weighted fluxes for metals in our study are in line with those calculated for single WWTP and with estimates for metal household emissions to wastewater (Table S10). Hence, the population-weighted averages represent a first reliable estimate of trace element fluxes in wastewater streams. Several trace elements have considerable fluxes (e.g., $0.1\text{--}1 \text{ mg capita}^{-1} \text{ d}^{-1}$ for the elements Sc, Y, La, Nb, Ag, Ga, Ge, and some of the light REE), which are comparable to fluxes of metals like Cd and Co. Some of the heavy REE and elements like Te, In, Tl, and Ta, by contrast, have substantially smaller fluxes (down to $0.03 \text{ } \mu\text{g capita}^{-1} \text{ d}^{-1}$; Table S9). The calculated element fluxes show a large variability and skew (Table S9), which may explain the poor correlations observed between the element fluxes of individual WWTP and the connected population, the applied treatment technology, or the size of the catchment area (data not shown).

Relevance of element fluxes from WWTP effluents

Particularly in urban areas, WWTP effluent fluxes can significantly contribute to surface water stream flows and riverine discharges, as has been shown for urban areas (e.g., Canada [54], France [55], and China [56], among others). Between January and July 2016, the combined average discharge of the four rivers that drain Switzerland was $193,622,400 \text{ m}^3 \text{ d}^{-1}$ [31], with 71% discharged by the Rhine and 23% by the Rhône. In the same period, the average discharge from the investigated 64 WWTP amounted to $2,195,000 \text{ m}^3 \text{ d}^{-1}$, or $0.558 \text{ m}^3 \text{ d}^{-1}$ per capita for the connected 3,936,000 population equivalents (Table S1). Hence, the

amount of 4,237,000 m³d⁻¹ of wastewater is estimated for the entire country of Switzerland (~7,598,000 connected population equivalents in 2016), equaling ~2.2% of the average riverine discharge from Switzerland, as mentioned above.

The total riverine element fluxes in Switzerland were calculated from concentrations measured in the river water samples and the recorded water discharges during the time of sampling (details provided in Table S11). The total WWTP effluent fluxes (equal to the element loads in effluent ('treated') wastewater) were calculated from the investigated 64 WWTP and extrapolated to the whole of Switzerland (note that 98% of the country is connected to WWTPs [73]). The derived wastewater-borne contributions to riverine element fluxes are presented for each element in detail in Table S12. Because a discussion of all investigated elements is beyond the scope of this paper, the fluxes of the following four elements, which show widely different effluent flux contributions and elemental sources to WWTP, are discussed in detail: the major nutrient P (mainly from anthropogenic inputs), the trace element As (mainly geogenic inputs), the metal Zn (mainly from industrial inputs and applications), and the REE Gd (mainly from medical applications).

Phosphorus. The contribution of WWTP effluent-sourced P to the total Swiss riverine P flux (50%, Figure 5) is considerably higher than what might be expected based on the fraction of WWTP effluent in riverine discharge (~2.2%) and demonstrates that over half of the Swiss riverine P may originate from wastewater effluents. The relatively high P levels in wastewater reflect the importance of P as a fertilizer in industrialized agricultural production and of organophosphorus compounds in detergents and pesticides. Although agricultural P runoff may be primarily unchanneled (previous studies have shown that the leaching of fertilizer from agricultural soils, at 1,071±238 metric ton P yr⁻¹, contributes ~50% to the Swiss riverine P flux [52]), the calculated P input from (channeled) WWTP effluents (1,243 metric ton P yr⁻¹) appears to be at least an equally important anthropogenic P source, which supports the extensive efforts for P recovery from the wastewater stream [52, 53].

Arsenic. The contribution of As from WWTP effluents to the total Swiss riverine As flux appears to be insignificant when compared to other As sources (1%, Figure 5). Environmental As budgets for Switzerland are lacking, but previous studies have shown that elevated As concentrations in drinking water resources in Switzerland stem from As-rich ore deposits (e.g., from brown limestones of the Dogger formation and from yellow limestones of Cretaceous and Bohnert formations, as well as from the granites and shales of the Schwarzwald Massif [57, 58]); therefore, As levels in wastewater are also likely to be related to these same natural sources. Indeed, the geographic distribution of As shows generally higher sludge concentrations in the Alpine regions, where these As deposits occur, than in the lower regions of Switzerland (Figure S2). In addition to As, various other elements for which significant geogenic contributions may be expected (e.g., U, Al, or Ti) have small WWTP effluent contributions (1 to 3%, Table S12).

Zinc. The WWTP effluent flux of Zn (32 metric tons yr^{-1}) contributes 24% to the total riverine Zn flux in Switzerland (Figure 5), which, compared to other estimates for Zn inputs to the Swiss rivers (39 metric tons yr^{-1} from road runoff [59] and 2.6 metric tons yr^{-1} from leaching of agricultural soils [60]), shows that the WWTP effluent flux of Zn is significant. This importance may partially be explained by the various societal and industrial applications of Zn (e.g., in metallurgy and electronics), but may also be due to the occurrence of geogenic Zn in influent wastewater. Interestingly, the metals Ni, Cu, and Co also have relatively large WWTP effluent contributions (11, 7, and 8%, respectively), while other metals do not (Cr, Cd, Pb; all <3%, see Table S12). Such low effluent contributions may suggest either highly efficient removal during the wastewater treatment process and/or the presence of other (undocumented geogenic or anthropogenic) contributing factors to riverine fluxes. Such additional inputs (e.g., from road run-off [71, 72]) may be elucidated via advanced source tracking and spatial analysis or by investigation of chemical speciation or isotopic composition.

Gadolinium. Most REEs have small WWTP effluent contributions (<1%, Table S12), suggesting that WWTP effluents, in contrast to other sources such as natural weathering, are negligible sources of riverine REE fluxes. However, a striking exception is the element Gd, for which WWTP effluents contribute over 83% to the riverine Gd discharge (Figure 5). This dissimilar behavior likely reflects the use of Gd in medicine, in the form of highly stable organic Gd complexes as contrast media for magnetic resonance imaging, and that these complexes are poorly eliminated during the wastewater treatment process [8, 9, 61]. The relevance of these medicine-derived Gd complexes has been demonstrated in wastewaters in Switzerland and elsewhere [62, 63]. Hence, the fluxes determined in our study (650 kg Gd yr⁻¹, Table S12) as well as previously published estimates of hospital-derived Gd in Switzerland (157 kg Gd yr⁻¹ [62, 63]), illustrate that Gd is predominantly of anthropogenic origin.

Potential recovery of valuable elements from WWTP sludge

The recovery of valuable elements from sewage sludge has been the topic of extensive investigation, and previous studies have indicated that recovery of major elements (e.g., Fe, P, and Al) and of precious trace metals (e.g., Cu, Pd, Au, and Ag) from digested sewage sludge or from ashes of incinerated sludge may be economically worthwhile [27, 28]. Although individual WWTP effluent fluxes may be significant for the riverine budgets of selected elements (see above), most total WWTP element fluxes (equal to the entire load through a WWTP, i.e. the influx or the sum of the effluent and sludge fluxes) are probably of minor economic importance, which is illustrated by juxtaposition onto recent import and export data and commodity prices of raw materials. For instance, the total WWTP Al and Cu fluxes (18 metric tons yr⁻¹ and 92 metric tons yr⁻¹, respectively, Table S9) equal only 0.2% and 3.9% of the annual Swiss Al and Cu imports in 2015 [66]. Considering recent raw metal prices of 1,650 USD metric ton⁻¹ for Al and 4,800 USD metric ton⁻¹ for Cu [67], the wastewater-derived Al and Cu fluxes of Switzerland would only have values of some 29,700 USD yr⁻¹ and 455,000 USD yr⁻¹, respectively. The economic feasibility of any metal recovery practice

will also depend on the amount of sludge and metal extractability, but these numbers suggest that metal recovery from wastewater streams may not be worthwhile [28].

However, total WWTP Fe fluxes (present in high concentrations in sludge due to its addition as a flocculant for P [64, 65]) and the total WWTP fluxes of precious metals represent considerably higher economic values. For instance, using recent commodity prices of 0.51 USD g⁻¹ for Ag and 40 USD g⁻¹ for Au [67], average wastewater stream values of 1,568,000 USD yr⁻¹ for Ag and 1,671,000 USD yr⁻¹ for Au can be calculated for Switzerland. This recovery potential (roughly 0.43 USD capita⁻¹ yr⁻¹ for these two precious metals combined) was lower than the 2.6 USD capita⁻¹ yr⁻¹ calculated in the U.S. for the recovery potential of Au and Ag from sludge alone [27]. However, the concentrations of precious metals in some WWTP sludges in Switzerland were significantly higher than the median concentrations found in Switzerland. At these few sites, Au concentrations reached as high as several hundreds of µg kg⁻¹ sludge (Table S6), most probably originating from precious metal refineries and processing facilities near these sites [68, 69]. The precious metal content in these locations is actually similar to that found in profitable mining ore [70] and to that found in incineration residues, such as fly ash and bottom slag (e.g., on average 0.4 mg kg⁻¹ of Au, in some fractions up to 40 mg kg⁻¹ of Au [65]), which are commonly considered the waste fractions of choice for the recovery of valuable precious metals. Considering the previously mentioned precious metal prices and the sludge production rates shown in Table S1, up to 155,000 USD yr⁻¹ worth of precious metals could theoretically be recovered from the WWTP sludges of these locations, with combined precious metal flux values of up to 6.8 USD capita⁻¹ yr⁻¹ and up to 15 USD metric ton⁻¹ of dry sludge. Thus, if the recovery of valuable metals from WWTP sludge is to be competitive with that from incineration products or e-waste, it should preferably be focused on those WWTP with elevated precious metal concentrations [27, 28, 64]. However, element recovery from sewage sludge may not only be interesting economically, but may also serve to close element cycles.

Environmental relevance

The presented nationwide survey shows that the element concentrations in sewage sludges and effluents of the great majority of Swiss WWTP are similar to those reported in previous studies. In addition, as far as toxicological data and legal guidelines exist, no additional measures appear to be currently required for further reduction of the concentrations of metals and other (trace) elements in Swiss WWTP sludges and effluents. Exceptions include Cu and Zn, whose concentrations exceeded the legal limits in effluents or sludges in multiple WWTP. However, for other (potentially toxic) trace elements and particularly their organic and inorganic species, toxicological information and knowledge of the biogeochemical behavior is scarce; therefore, additional research is required to determine whether the observed elevated concentrations pose reason for concern.

The volumetric fluxes of the investigated WWTP and rivers are well documented; therefore, this study provides the first quantitative assessment of the trace element fluxes from WWTP and inputs to rivers for an entire industrialized country. Analyses of the element mass budgets on a nationwide scale shows that WWTP effluent fluxes (i.e., treated wastewater inputs) can significantly affect nationwide riverine budgets when elements are released predominantly from anthropogenic sources (e.g., Cu, Ni, Sb, and Gd). The origin of these elements in wastewater, as well as their (biogeochemical) fate during wastewater treatment and after emission via effluents, needs further investigation. Nonetheless, this study shows that WWTP can be used to identify elements for which WWTP effluent fluxes may have significant environmental impacts. Local and federal governments may therefore use continued elemental screening of sewage sludge and treated wastewater as a way to monitor the (long-term) temporal trends of selected elements of interest, after optimization of analytical methods. Such continuous screening may subsequently be used in combination with spatial analysis to detect, quantify, and back-track potential inputs of anthropogenic contaminants into the environment via wastewater streams.

429

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Figures captions

Figure 1. Map of Switzerland showing the locations of the 64 studied WWTP, their corresponding catchment areas, and the national monitoring stations (NADUF) of the four major rivers leaving Switzerland. The WWTP depicted by black dots and dashed underlines were investigated three times. The size of the WWTP dots correspond to the number of connected population equivalents. A selection of WWTP properties is listed in Table S1, according to the indicated WWTP numbers.

Figure 2. Concentration ranges of elements measured in sludge samples (dry weight basis) from 64 WWTPs in Switzerland. The thicker gray bars mark the median, the boxes the 0.25 and 0.75 percentiles, and the whiskers the lowest and highest values within 1.5 times the interquartile range. Outliers are indicated by circles, or by arrows above the graph when outliers exceeded the shown log scale. For statistical analysis, only values above the method detection limit (MDL), indicated by triangles in the figure (values in Table S4) were considered; the fraction of measurements >MDL is indicated by red digits. A summary of the concentration ranges of all elements is given in Table S5.

Figure 3. Concentration ranges of elements measured in effluent water samples from WWTP in Switzerland (N=64). Figure and explanations analogous to Figure 2; the fraction of measurements >MDL is indicated by blue digits. A summary of the measured concentration ranges of all elements is given in Table S5.

Figure 4. Median per-capita (population-weighted) fluxes of 69 elements discharged by wastewater in Switzerland (based on fluxes in 64 WWTP). The range of the element fluxes is illustrated by the color scaling of the periodic table. Details of the calculated element fluxes are given in Table S8 and a comparison with fluxes calculated in previous studies is given in Table S9.

Figure 5. Illustration of the contributions of element fluxes from WWTP effluents to riverine element budgets in Switzerland for the elements P, As, Zn, and Gd. The red arrows represent the fraction from

675 *WWTP effluents and the black arrows indicate other inputs. Details of the calculations are provided in*
676 *Table S12.*
677

678 **Tables****Table 1.** Comparison of measured element concentrations in sludges and effluents with legal limits.

Element	Element concentrations (N=64)				Legal guidelines					Number of WWTP above Swiss limits
	Sample *	Unit	Median	Max	Swiss ORRChem 2005	Swiss WPO 2016	EU Sludge Directive	German AbfKlärV	EU UQN (MAS-EQS) surface water	
Cr	Sludge	mg kg ⁻¹	46	267	500			900		0
	Effluent	µg L ⁻¹	0.2	3.6		5				0
Ni	Sludge	mg kg ⁻¹	13	67	80		300-400	200		0
	Effluent	µg L ⁻¹	3	48		10			20	3
Co	Sludge	mg kg ⁻¹	7	43	60					0
	Effluent	µg L ⁻¹	0.3	3						
Cu	Sludge	mg kg ⁻¹	301	1963	600		1000-1750	800		5
	Effluent	µg L ⁻¹	4	52		5				17
Zn	Sludge	g kg ⁻¹	1	2	2		2.5-4	2.5		0
	Effluent	µg L ⁻¹	22	59		20				38
Cd	Sludge	mg kg ⁻¹	1.4	8	5		20-40	10		5
	Effluent	ng L ⁻¹	11	365		200			<450-1500	1
Pb	Sludge	mg kg ⁻¹	38	232	500		750-1200	900		0
	Effluent	µg L ⁻¹	0.06	1.9		10			7.2	0

* Sludge concentrations reported on a dry weight basis

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681 **TOC-Art****Per-capita element loads in wastewater**

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Map of Switzerland showing the locations of the 64 studied WWTP, their corresponding catchment areas, and the national monitoring stations (NADUF) of the four major rivers leaving Switzerland. The WWTP depicted by black dots and dashed underlines were investigated three times. The size of the WWTP dots correspond to the number of connected population equivalents. A selection of WWTP properties is listed in Table S1, according to the indicated WWTP numbers.

247x130mm (300 x 300 DPI)

255x99mm (300 x 300 DPI)

Concentration ranges of elements measured in effluent water samples from WWTP in Switzerland (N=64). Figure and explanations analogous to Figure 2; the fraction of measurements >MDL is indicated by blue digits. A summary of the measured concentration ranges of all elements is given in Table S5.

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Median per-capita (population-weighted) fluxes of 69 elements discharged by wastewater in Switzerland (based on fluxes in 64 WWTP). The range of the element fluxes is illustrated by the color scaling of the periodic table. Details of the calculated element fluxes are given in Table S8 and a comparison with fluxes calculated in previous studies is given in Table S9.

167x64mm (300 x 300 DPI)

Illustration of the contributions of element fluxes from WWTP effluents to riverine element budgets in Switzerland for the elements P, As, Zn, and Gd. The red arrows represent the fraction from WWTP effluents and the black arrows indicate other inputs. Details of the calculations are provided in Table S12.

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Per-capita element loads in wastewater

Graphical Abstract / TOC-Artwork

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