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## Quaternary alkylammonium disinfectant concentrations in soils rise exponentially after long-term wastewater irrigation

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E-mail: [bheyd@envr.jlug.de](mailto:bheyd@envr.jlug.de)**Keywords:** pollution, contamination, water reuse, heavy metal, aridity, surfactants, COVID-19 pandemicSupplementary material for this article is available [online](#)

## Abstract

Quaternary alkylammonium compounds (QAACs) are used as disinfectants and surfactants worldwide, with their usage currently increasing as a result of the COVID-19 pandemic. QAACs are released into the environment with manure, sewage sludge and wastewater. The fate of QAACs in soils is poorly understood, although QAACs are inflicted in the selection of antibiotic-resistant bacteria. We studied the temporal accumulation of QAACs in soils of the Mezquital Valley that have been irrigated with Mexico City wastewater from 0 to 88 years. Concentrations of 16 QAACs, including alkyltrimethylammonium compounds (ATMACs), dialkyldimethylammonium compounds (DADMACs) and benzylalkyldimethylethylammonium compounds (BACs), were determined using HPLC-MS/MS after ultrasonic extraction. The most abundant QAAC-homologues in the soils were BACs > ATMACs > DADMACs. The concentrations of QAACs increased linearly and slowly during the first years of irrigation ( $\sum$ QAAC: 2–23  $\mu\text{g kg}^{-1}$ ), but after 40 years of wastewater irrigation we observed an exponential increase in QAAC concentrations (up to 155  $\mu\text{g kg}^{-1}$ ). QAACs accumulate in soils of the Mezquital Valley during long-term wastewater irrigation. In contrast to pharmaceuticals, no apparent ‘steady state’ concentration is reached after decades of wastewater irrigation.

## 1. Introduction

Quaternary alkylammonium compounds (QAACs), such as alkyltrimethylammonium compounds (ATMACs), dialkyldimethylammonium compounds (DADMACs) and benzylalkyldimethylethylammonium compounds (BACs), are used worldwide as surfactants in household chemicals, the chemical and food industry and the agricultural sector (Mulder *et al* 2018). They consist of a permanently positively charged nitrogen atom, which is the hydrophilic part of the molecule, and four covalently bound organic rests, such as methyl groups, benzyl group or alkyl-chains of variable length that form the hydrophobic part. Thus, they are amphiphilic compounds. The critical micelle concentration best describes their partitioning in a soil–aqueous system (table 1). Ismail *et al* (2010) described that CMC represents the hydrophobic as well as the ionic properties of QAAC.

The large scale production and use of QAACs started in the first half of the 20th century. QAACs were first described in the literature in 1928 as ‘saure seifen’ (acidic soaps) by Hartmann and Kägi (1928). Domagk (1935) described the use of ‘Zephirol’ in 1935, which is BAC-C12, as a new class of disinfectants. In the following years BAC-C12 was widely used in the medical sector (Frankl 1941). Botwright (1946) advocated the use of these tasteless, for humans non-toxic compounds as cost-effective germicides for the food industry. By the end of the 1940, QAACs were used in the whole food industry (quick-freezing, canning, baking, butcher-shops), at food-markets, in eating and drinking establishments, medicine, veterinary medicine and more (However, as early as 1961, first signs of resistance development of microorganism were observed (Lee and Fialkow 1961)).

Nevertheless, even today QAACs belong to the class of so-called high production volume chemicals

Table 1. Compound properties of QAACs.

	CAS #	mp (°C) <sup>a</sup>	CMC (mM)	Mol. mass
ATMAC-C8	2083-68-3	198–200	190 ± 10 <sup>c</sup>	252
ATMAC-C10	10108-87-9	N/a	60 ± 1 <sup>c</sup>	236
ATMAC-C12	112-00-5	37	15 ± 1 <sup>c</sup>	264
ATMAC-C14	4574-04-3	N/a	4.1 ± 0.1 <sup>c</sup>	292
ATMAC-C16	112-02-7	77	1.6 ± 0.1 <sup>c</sup>	320
BAC-C8	959-55-7	N/a	188 ± 16 <sup>b</sup>	284
BAC-C10	965-32-2	N/a	34 ± 1.8 <sup>b</sup>	312
BAC-C12	1390-07-1	42	8.3 ± 0.2 <sup>b</sup>	340
BAC-C14	139-08-2	63	1.8 ± 0.05 <sup>b</sup>	368
BAC-C16	122-18-9	59	0.4 ± 0.015 <sup>b</sup>	396
BAC-C18	122-19-0	57	0.1 ± 0.01 <sup>b</sup>	424
DADMAC-C8	3026-69-5	60–68	N/a	350
DADMAC-C10	7173-51-5	88	N/a	362
DADMAC-C12	3401-74-9	175	3.5 × 10 <sup>-2</sup> d	418
DADMAC-C14	68105-02-2	N/a	1.6 × 10 <sup>-3</sup> d	519
DADMAC-C16	70755-47-4	159–162	7.8 × 10 <sup>-5</sup> d	575

<sup>a</sup> Mulder *et al* (2018).<sup>b</sup> Mulder *et al* (2020).<sup>c</sup> Cepeda *et al* (2013).<sup>d</sup> Diress *et al* (2007).

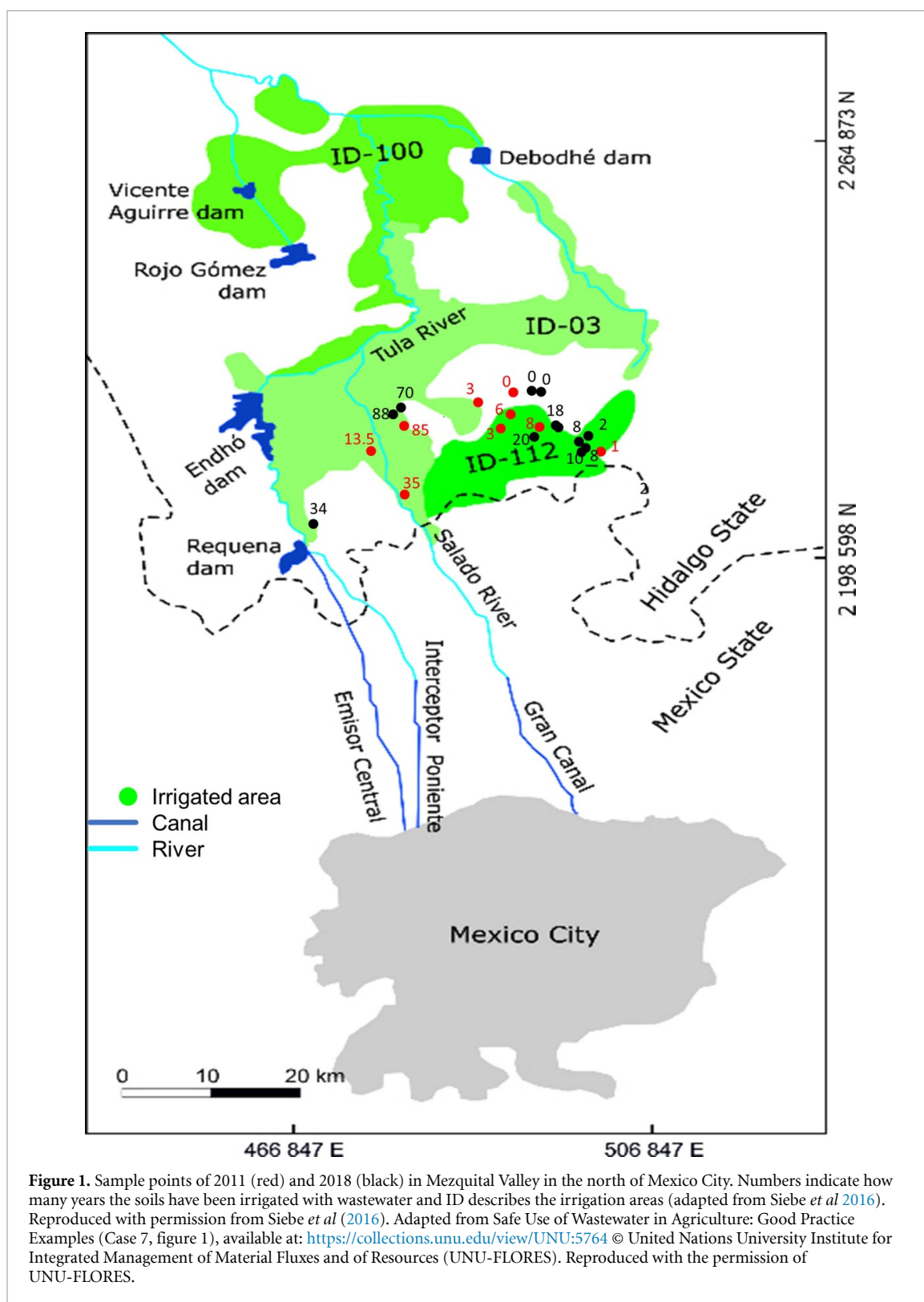
(HPVCs) (OECD 2004), because of their antimicrobial and surfactant properties. During the COVID-19 pandemic hygiene is one of the key measures for infection control and prevention. Consequently, the use of disinfectants has risen substantially, even though exact data on disinfectant consumption are difficult to obtain. Hora *et al* (2020) found that in the U.S the consumption of disinfection wipes of one manufacturer in May 2020 was 146% that of the year before. Almost half of all disinfectants (600 of 1285) listed by the German Association of Applied Hygiene (Association for Applied Hygiene 2020) contain QAACs as active ingredients. It should be expected that the amount of QAACs released into the environment is increasing as a consequence of the COVID-19 pandemic.

After their use, QAAC are introduced into the environment with wastewater, sewage sludge and manure (Mulder *et al* 2018). Data on the environmental concentrations and fate of QAACs are scarce and predominantly available for wastewater and sewage sludge (Merino *et al* 2003, Clara *et al* 2007, Ruan *et al* 2014), followed by data on river water and river sediments (Ferrer and Furlong 2002, Lara-Martín *et al* 2010). Information about their concentrations in soils is rarely available (Gerike *et al* 1994).

Studies have shown that microorganism can degrade QAACs under aerobic conditions with half-lives in the range of hours (Games *et al* 1982, Zhang *et al* 2015) in aerated laboratory systems. Regarding their effects in the environment, the main concern is that their presence promotes the selection and spread of antibiotic-resistant bacteria and resistance genes (Gaze *et al* 2005, Tandukar *et al* 2013, Mulder *et al* 2018). The ecotoxicological effects of QAACs in

soils and sediments are strongly reduced by their sorption. Previous work has shown, that QAACS can sorb in interlayer spaces of smectite soil clay minerals (Zanini *et al* 2013), which reduces their toxicological effects (and hence their bio-accessibility) at least under controlled laboratory conditions (Heyde *et al* 2020b). By reducing the bio-accessible concentration of molecules, sorption is also known to slow down the dissipation and degradation of organic compounds, thus increasing their persistence in strongly bound-forms (Rosendahl *et al* 2012). Sorption occurs via cation exchange (due to the positively charged N atom) and via hydrophobic interactions of the alkyl chains with organic matter (Ismail *et al* 2010, Ren *et al* 2011, Mulder *et al* 2018).

In semiarid and arid areas of the world, municipal wastewater is reused for irrigation of agricultural land (Asano 1998). The reuse of wastewater for irrigation is regarded as key for relieving regional water shortages, increasing food production and improving income and livelihoods of people (e.g. Bahri *et al* 2009, Drechsel *et al* 2015). Wastewater irrigation also has positive effects on the soil concentration of nutrients, the content of soil organic matter and the biomass as well as activity of soil microorganisms (Siebe 1998, Friedel *et al* 2000, Dalkmann *et al* 2012). Disadvantages of wastewater irrigation are the input of pollutants and the spread of resistance genes due to the input of pathogenic bacteria (Igbinosa *et al* 2011, Munir and Xagorarakis 2011, Dalkmann *et al* 2012). One of the largest agriculturally used areas under wastewater irrigation in the world (Siebe and Cifuentes 1995), the Mezquital Valley, covers an area of 900 km<sup>2</sup> and is located 80 km north of Mexico City (figure 1). Wastewater irrigation in this area started in 1912 and the irrigated



area has been growing over the past 100 years due to the expansion of Mexico City and is still expanding (Broszat *et al* 2014). Until 2017 most of the irrigated 80 000 ha land received untreated wastewater for irrigation; since 2018 approximately 60% of the wastewater is treated prior to irrigation (pers. Comm. Ing. Cruz Atienza, director of the wastewater treatment plant). The wastewater is pumped

and diverted frequently until it reaches the fields (Dalkmann *et al* 2012). While in the pipe system, the water is anaerobic until it reaches the fields where it is aerated. Main characteristics and metal concentrations of the water are provided in table S11 (available online at [stacks.iop.org/ERL/16/064002/mmedia](https://stacks.iop.org/ERL/16/064002/mmedia)). The concentrations of trace metals in the wastewater canals are high but below the Mexican wastewater

guidelines. The concentrations of Al, As, Pb and methylmercury in the Tula River, the river into which the wastewater is partially discharged, exceeded the surface water guidelines (Guédron *et al* 2014). Few trace metal concentrations ( $0.024 \text{ mg l}^{-1}$  Cd,  $0.510 \text{ mg l}^{-1}$  Pb) in the irrigation canal were exceeding the surface water guideline concentrations (Ramirez-Fuentes *et al* 2002).

Together with the wastewater, all kinds of chemicals that are used in households are introduced into the fields and soils. Siebe Grabach (1994) and Siebe and Cifuentes (1995) documented the accumulation of heavy metals in soils of the Mezquital Valley with increasing time under irrigation by sampling a chronosequence of soils for which irrigation started in different years in the course of the expansion of the irrigated area. The concentrations of heavy metals in the soils increased linearly with increasing time of irrigation, because these metals are continuously introduced and sorbed to clay, iron oxides and organic matter. Later studies showed that the soils are also enriched with pharmaceuticals and endocrine disruptors over time of irrigation (Durán-Alvarez *et al* 2009, Gibson *et al* 2010). Dalkmann *et al* (2012) revealed that concentrations of pharmaceutical residues reach an apparent steady state over time, which can be theoretically explained as an equilibrium reached between constant input and first order degradation (dissipation) of the organic compounds. QAAC concentrations in wastewater are known to be quite high, often an order of magnitude higher than commonly observed pharmaceuticals. For example, treatment plant influents in the range of  $2\text{--}6000 \text{ } \mu\text{g l}^{-1}$  were reported for Austria (Clara *et al* 2007, Martínez-Carballo *et al* 2007). Effluent concentrations between 14 and  $78 \text{ } \mu\text{g l}^{-1}$  are reported for Northern Europe by Kaj *et al* (2014).

Therefore, as was observed in the Mezquital Valley soils for pharmaceuticals, a similar pattern enrichment and attainment of apparent steady-state could also be expected for QAACs, which are also biodegradable under aerobic conditions (Tandukar *et al* 2013). We therefore hypothesized that (a) soil concentrations of QAACs increase with the duration of untreated wastewater irrigation and (b) the soil concentrations of QAAC will reach a steady state with time, analogously to the documented enrichment of pharmaceuticals in the Mezquital Valley. For testing these hypothesis we sampled an irrigation chronosequence of soils in 2018 and quantified concentrations of BACs, ATMACs and DADMACS. Results were confirmed and compared by extracting samples that were already analyzed for concentrations of pharmaceuticals by Dalkmann *et al* (2012). Finally, the accumulation of QAACs was compared to the accumulation of heavy metals with increasing time of irrigation.

## 2. Materials and methods

### 2.1. Study area description

The Mezquital Valley is mostly located in the north-eastern part of the Transmexican volcanic belt and extends into the Sierra Madre Oriental sedimentary system in its northern part. The valley bottom consists of extended piedmonts of relatively compacted and partly  $\text{CaCO}_3$ -cemented volcanoclastic sediments of Tertiary age which grade into fluvial and lacustrine Quaternary deposits in its lower parts. Climate is temperate (mean annual temperatures between  $16^\circ\text{C}$  and  $18^\circ\text{C}$ ) semi-arid in the South with annual mean precipitations ranging from up to 700 mm in the southern parts to less than 435 mm in the North concentrated in the summer months. Dominant soils are rendzic Leptosols, haplic, calcaric and vertic Phaeozems and pellic Vertisols. Irrigated areas are mostly cultivated with lucerne—maize rotations (3 years of lucerne followed by 2 years of maize combined with rye grass or different kinds of vegetables). Non-irrigated areas are nowadays scarce and used to cultivate dominantly rain-fed maize or agave species (Siebe Grabach 1994).

### 2.2. Soil samples

The first set of samples was taken in 2011 for the Dalkmann *et al* (2012) study from 0 to 30 cm depth from nine different fields in the Mezquital Valley representing eight periods of irrigation with untreated wastewater (0, 1, 3, 6, 8, 13.5, 35, 85 years). These samples were taken as composite samples with a soil auger ( $\sim 1 \text{ kg}$ ), collected in polyethylene bags and stored at  $-21^\circ\text{C}$ . The second set of samples was collected in 2018 as composite sample from 0 to 20 cm depth from ten fields representing nine irrigation durations (0, 2, 8, 10, 18, 20, 34, 70, 88 years). Sampling in 2018 was performed with a shovel ( $\sim 300\text{--}500 \text{ g}$ ) and the soil samples were wrapped in alumina foil and stored at  $-21^\circ\text{C}$  in polyethylene bags.

For all analyzes, except for pH measurements, the samples of 2018 and 2011 were freeze-dried (Beta 1 8 LSCplus, CHRIST, Osterode am Harz, Germany) in the lab for 5 d, sieved  $< 2 \text{ mm}$  (Retsch®, Haan, Germany) and stored in high density polyethylene (HDPE) containers.

### 2.3. Characterization of soil samples

Soil pH-values were determined with a pH electrode (SenTix® 940–3 WTW, Weinheim, Germany) and a pH meter (handylab 2, SCHOTT Instruments, Mainz, Germany) in  $0.01 \text{ M CaCl}_2$ . Five grams of air-dried ( $40^\circ\text{C}$  until constant weight) soil was mixed with  $12.5 \text{ ml CaCl}_2$  solution and shaken at 80 rpm in a horizontal shaker (KS 10, Edmund Buehler GmbH, Bodelshausen, Germany) for 30 min. After shaking,



suspensions were allowed to settle for 30 min and pH was determined in the supernatant.

Carbonates were determined volumetrically as CO<sub>2</sub> released from CaCO<sub>3</sub> with a Scheibler apparatus (Blume *et al* 1996, DIN EN ISO 1069 2014). Total carbon and total nitrogen content of the samples were determined from 5 mg soil using a CN analyzer with a thermal conductivity detector (Unicube®, Elementar, Langenselbold, Germany).

The organic carbon (C<sub>org</sub>) content was calculated by subtracting the content of carbonate-C from the total organic carbon content (Nelson and Sommers 2001).

For soil texture analysis all particles  $\geq 20 \mu\text{m}$  were separated with a wet sieving process and quantified gravimetrically, and particles smaller than  $20 \mu\text{m}$  were separated by sedimentation according to Köhn (1928) and quantified also gravimetrically. Prior to soil texture analysis, carbonates were destroyed with HCl (10%) and soil organic matter was destroyed with H<sub>2</sub>O<sub>2</sub> (30%). Tetrasodium pyrophosphate (0.4 mol l<sup>-1</sup>) was added as dispersion agent to prevent flocculation of soil particles (Jensen *et al* 2017).

Soil trace element contents were determined by inductively coupled plasma coupled to an optical emission spectrometer (Agilent 720ES) after microwave assisted aqua regia extraction of the pseudo-total metal content based on U.S. EPA. Method 3051A (2007) modified by Öztan and Düring (2012).

## 2.4. QAAC analyzes

The soils were analyzed for ATMACs (chain length C-8 to C-16), BACs (C-8 to C-18) and DADMACs (C-8 to C-16). Firstly, the soils were repeatedly extracted with acidified acetonitrile (99.9% AcN/0.1% HCl v/v) and ultrasonic irradiation according to Heyde *et al* (2020a). The extracts were cleaned with solid phase extraction (Chromabond CN, Machery Nagel, Dueren, Germany). The analytes were separated and quantified with high performance liquid chromatography (Waters™ alliance 2690, Eschborn, Germany) and a Waters XSelect CSH Phenyl-Hexyl-Column (130 Å, 150 mm length, 2.1 mm ID, 3.5  $\mu\text{m}$  particle size) with a column guard of the same material coupled to a mass spectrometer (Micromass Quattro Micro, Waters, Eschborn, Germany) following the method described elsewhere by Heyde *et al* (2020a).

A list of QAACs analyzed along with available compound parameters is provide in table 1.

## 2.5. Data evaluation

Peak integration of the QAAC analyzes was performed with Waters MassLynx 4.0, data evaluation and illustration with Systat Sigma Plot 12.0. RStudio 4.0.2 was used to perform correlation analysis i.e. the correlation matrix (tables SI2/SI3) and the correlograms (figures 2 and SI1). In order to analyze

the linear correlation between irrigation time, soil properties and QAAC concentration, the Pearson correlation coefficient ( $r$ ) was used. We tested the correlation of soil properties and QAAC irrigation time additionally with Spearman rank correlation to confirm the results (tables SI4, SI5).

Systat Sigma Plot 12.0 was also used to calculate regressions between (log) QAAC-concentrations ( $y$ ) and duration of irrigation ( $x$ ). The same was performed for the concentrations of the trace metals, pH, CaCO<sub>3</sub>, C<sub>org</sub>, Clay, and N<sub>total</sub> ( $y$ ) and the duration of irrigation ( $x$ ). We judged the increase of concentrations (values) with increasing duration of irrigation as significant, if the confidence intervals of the slope parameter of the regression did not overlap with zero. In this case the H<sub>0</sub>-hypotheses was: slope parameter  $b$  is 0, which means the slope did not differ significantly from 0. The level of significance was set to  $\alpha = 0.05$ . Hence, the increase of concentrations with duration of irrigation was significant if  $p < 0.05$ .

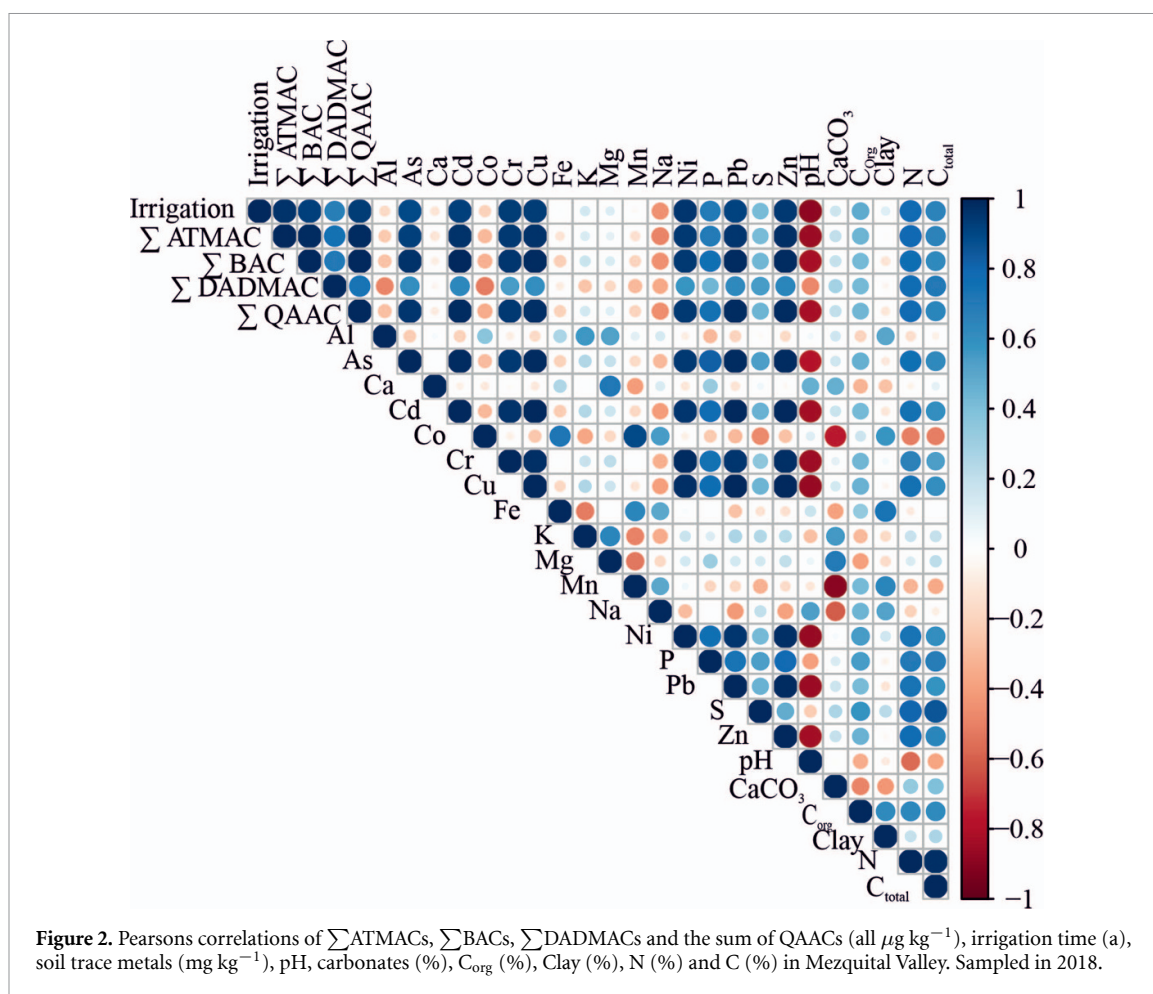
Multiple Regression was performed to test which variable (pH, irrigation time, clay content) explains most of the observed increase in the sum of QAAC concentrations ( $p < 0.05$ ).

# 3. Results and discussion

## 3.1. Accumulation of QAACs in wastewater-irrigated soils

The smallest total concentrations of QAACs were found in the samples of 2011 after 0 and 3 years of wastewater irrigation. Across both sample sets the most abundant QAACs belonged to the group of BACs (2018; 2.3–131.2 mg kg<sup>-1</sup>), followed by ATMACs (2018; 0.1–12.7 mg kg<sup>-1</sup>) and DADMACs (2018; 0–11.3 mg kg<sup>-1</sup>) (table 2). The prevalence of BACs was expected since they are widely used in households and four of six BAC homologues are HPVCs, whereas only two of the five analyzed ATMACs and DADMACs are HPVCs (Mulder *et al* 2018). Our results were in the same concentration range as data of Li *et al* (2018), who also found DADMACs in lowest concentrations among the three group of QAACs in sewage-impacted estuarine sediments.

In every single sample BAC-C12 was detected, which is one of the most commonly used QAACs in disinfectant agents (Wagner 2017). We also found BAC-C14 in all samples, with the exception of one sample of the 2011 sampling year. Both homologues were found at highest concentrations among all QAACs. The greatest concentration of each sum of the three homologue groups (ATMAC, BAC, DADMAC) was in the soils that were irrigated for 88 years. BAC-C12 was found in highest concentrations among all homologues in soil that was irrigated 88 years (83.6  $\mu\text{g kg}^{-1}$ ). The greatest increase of QAACs from 0 to 88 years of irrigation was observed for BAC-C12 (+4100%), BAC-C14 (+5500%) and ATMAC-C16



(+3500%). Concentrations of ATMAC-C8 and C10 (+0%) remained at a similarly low level.

In general, the samples taken in 2018 contained higher QAAC concentrations compared to those taken in 2011. This could be caused by aging effects of the soils and a loss due to microbial activity during storage, since QAACs are biodegradable by microorganisms (Nishihara *et al* 2000), especially by *Pseudomonas spec.* which can use QAACs as carbon source (Dean-Raymond and Alexander 1977, Geftic *et al* 1979, Kaech and Egli 2001, Takenaka *et al* 2007, Liffourrena *et al* 2008). Samples taken in 2011 were stored for 7 years longer before analysis than samples from 2018. Since we cannot rule out the suspected aging effects, we focus the discussion mainly on the samples of 2018.

The duration of irrigation was strongly and positively correlated to  $\Sigma$ ATMACs ( $r = 0.89$ ),  $\Sigma$ BACs ( $r = 0.89$ ) and  $\Sigma$ QAACs ( $r = 0.88$ ) (figure 2 and tables SI2, SI3), while for  $\Sigma$ DADMACs the correlation was weaker, with  $r = 0.60$ . This was supported by the data of the 2011 samples (figure SI1 and tables SI2, SI3). One possible reason is, as mentioned before, the lower production volumes of DADMACs (OECD 2004) resulting in lower discharges through the wastewater into soils. Further, DADMACs, especially those with alkyl chains longer

than 12 C atoms, have lower extraction recovery rates (Heyde *et al* 2020a) and possibly stronger interaction with soil particles since they have two hydrophobic alkyl chains. The time of irrigation showed the smallest  $p$ -values ( $p = 0.044$  in 2018 and  $p = 0.013$  in 2011), compared to pH and clay content ( $p = 0.355$ ;  $p = 0.272$  in 2018 and  $p = 0.0707$ ;  $p = 0.156$  in 2018) and hence explained most of the observed increase of the sum of QAAC concentrations in multiple linear regressions considering pH and clay content in addition to irrigation duration. The equation of the multiple linear regression of 2018 ( $R^2 = 0.76$ ) was:

$$\Sigma\text{QAAC} = 455.828 + (1.103 \times \text{irrigation}) - (55.331 \times \text{pH}) - (21.123 \times \text{Clay})$$

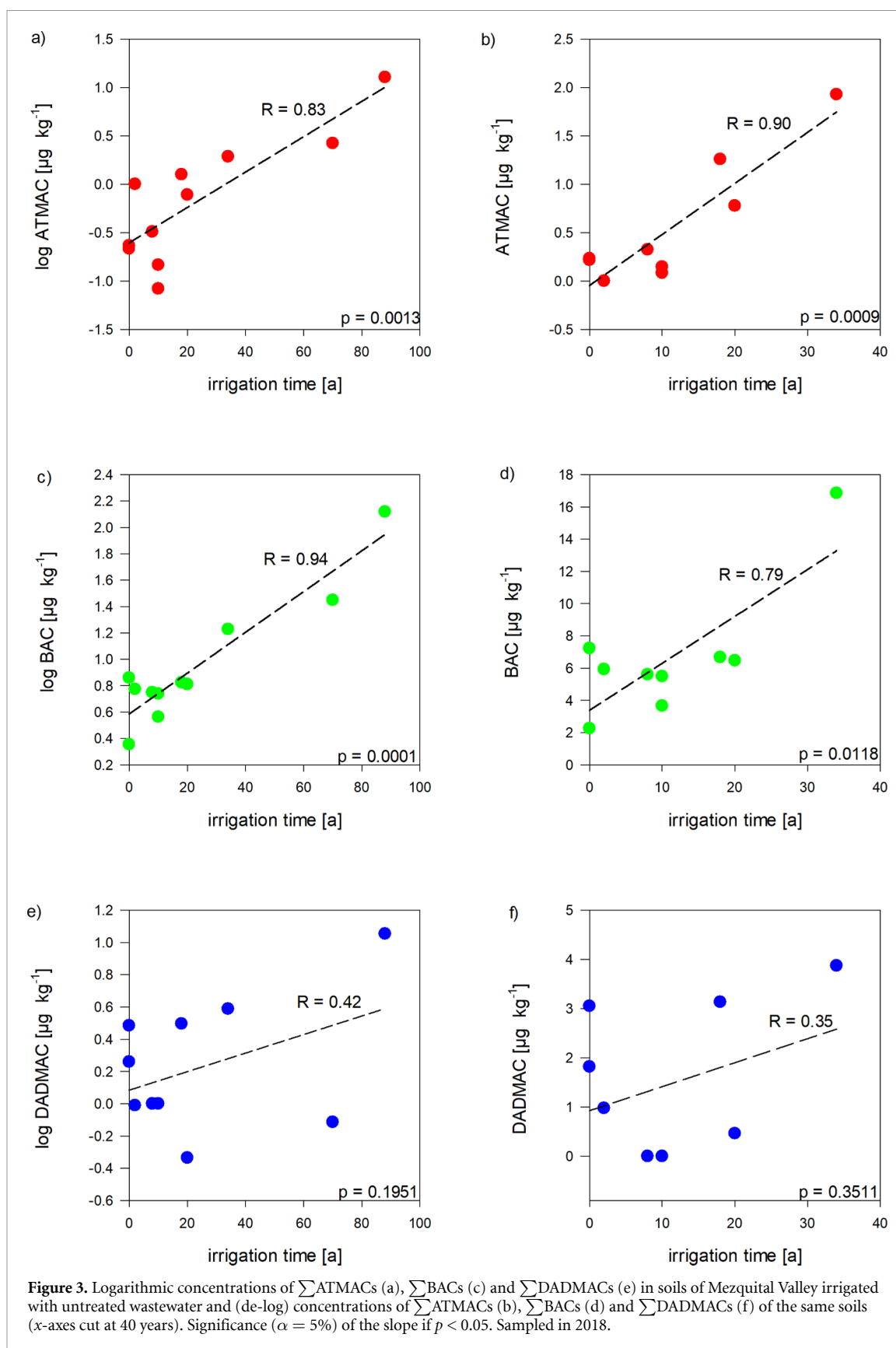
And in 2011 ( $R^2 = 0.92$ ):

$$\Sigma\text{QAAC} = -28.662 + (0.577 \times \text{irrigation}) + (6.135 \times \text{pH}) - (0.430 \times \text{Clay})$$

Plotting the logarithmic concentrations of  $\Sigma$ ATMAC and  $\Sigma$ BAC versus the irrigation time resulted in highly significant linear increases (figures 3(a) and (c)), which illustrates an exponential increase of these concentrations. This pattern was also observed in soils sampled in 2011 for all three classes of QAACs, including DADMACs (figures SI 3(a), (c), (e)).







When narrowed down to the first 40 years of irrigation, a closer look at the temporal trend of  $\sum \text{ATMAC}$  and  $\sum \text{BAC}$  concentrations during the first 40 years of irrigation revealed a linear increase with the duration of irrigation (figures 3(b), (d) and

SI 3(b), (d)). This suggested a biphasic accumulation in soil with time: an initial phase with linear accumulations, as typically observed for metals (Siebe Grabach 1994, Siebe and Cifuentes 1995), followed by an exponential rise of concentrations for time

**Table 3.** Soil properties of samples taken in 2011 and 2018. pH value was determined in 0.01 CaCl<sub>2</sub>. C<sub>total</sub> and N<sub>total</sub> were measured in triplicates with a standard deviation of 0.0.

	Irrigation time (years)	pH <sup>ab</sup>	CaCO <sub>3</sub> (wt. %)	C <sub>org</sub> (wt. %)	C <sub>total</sub> (wt. %) <sup>a</sup>	Clay (wt. %)	N <sub>total</sub> (wt. %)
Sampled in 2018	0	7.5	0.3	1.5	1.8	50	0.2
	0	7.5	0.2	1.3	1.5	71	0.1
	2	7.9	0.6	0.3	0.9	29	0.1
	8	7.7	0.7	0.4	1.1	38	0.1
	10	7.9	0.5	0.8	1.3	36	0.1
	10	7.8	0.2	2.1	2.3	55	0.2
	18	7.6	0.3	1.6	1.9	53	0.2
	20	7.7	0.1	1.9	2.0	57	0.2
	34	7.3	2.8	0.2	3.0	42	0.2
	70	7.3	0.1	2.1	2.2	50	0.2
	88	7.1	0.3	2.0	2.2	45	0.2
Sampled in 2011	0	7.8	0.0	0.9	0.9	43	0.1
	1	7.8	1.3	0.1	1.4	33	0.1
	3	7.9	0.2	1.3	1.4	40	0.1
	3	7.9	0.5	1.6	2.1	49	0.2
	6	7.8	0.4	1.3	1.7	53	0.1
	8	7.5	0.1	1.1	1.2	41	0.1
	13.5	7.9	0.9	1.0	1.9	36	0.2
	35	7.5	0.5	1.3	1.8	55	0.2
	85	7.1	0.7	1.7	2.4	41	0.2

<sup>a</sup> Statistically significant slope ( $p < 0.05$ ) of the regression ( $y =$  irrigation;  $x =$  soil property) in 2018.

<sup>b</sup> Statistically significant slope ( $p < 0.05$ ) of the regression ( $y =$  irrigation;  $x =$  soil property) in 2011.

periods >40 years. This observation is in contrast to the behavior of pharmaceuticals in those soils, for which an apparent ‘steady state’ is reached over time (Dalkmann *et al* 2012). We suppose the biphasic accumulation of BACs and ATMACs in soil during long-term irrigation with wastewater was caused either by (a) massive QAAC-inputs during the first half of the 20th century that ceased towards the end of the 20th century, or by (b) an increasing strength of QAAC sorption to the soils, slowing down their biodegradation in soils with a very long history of wastewater irrigation.

Indeed, QAACs were intensively used following their invention as disinfectants in 1935 (Domagk 1935) as described in the introduction. Speculatively, the upcoming concerns about resistance could then have led to a drop of consumption, with subsequently lower QAAC concentrations in the wastewater and eventually in the soils, which were first irrigated during the 2nd half of the 20th century or later. However, since BACs and ATMACs are biodegradable, their accumulation requires an efficient sequestration of these compound caused by an increasingly strong sorption.

Interestingly, Zanini *et al* (2013) described a shift in sorption processes with increasing concentration of BACs. They found that the sorption of BAC occurred at low concentrations to soil minerals and at higher concentration to humic acids. At low concentrations QAACs act as polar as molecules and behave like other (metal) cations, but at high concentrations they form micelles and act like a nonpolar compound, which changes their behavior in solutions

(Mulder *et al* 2020). Also the sorption to soil minerals occurred in two steps (Zanini *et al* 2013). At low concentrations, BACs were sorbed on the surface and in the interlayer of clay minerals and with rising concentrations the sorption occurred in bi-layers due to hydrophobic-hydrophobic interaction at the clay surface. However, it is unclear whether sorption to organic matter and in bi-layers would stabilize BACs against biodegradation. Sorption in the interlayer space of clay minerals is known to protect organic molecules against biodegradation (Amelung *et al* 2018). As we and others have shown in previous work, QAACs widen the interlayer spaces of clay minerals (Paiva *et al* 2008, Heyde *et al* 2020b). In those interlayer spaces they can form bilayers and paraffin-like structures (Zhu *et al* 2003), which are poorly accessible for enzymes and microorganisms. Possibly, such widening of interlayer spaces and the efficient diffusion of QAACs into these spaces requires the build-up of certain minimum QAAC concentrations and time, which are only given after long-term irrigation.

Since there is no ecotoxicological information available regarding no-effects concentrations of QAACs in soils, we cannot judge potential risks associated with the accumulation of the compounds in soils.

### 3.2. Change of soil properties with increasing duration of irrigation

The pH-values decreased the longer soils were irrigated (up to 85 years and 88 years, table 3). The duration of irrigation and pH-value were correlated

**Table 4.** Total elemental analysis of the soils ( $\text{mg kg}^{-1}$ ) in the Mezquital Valley, Sampled in 2018 and 2011.

Irrigation time (years)	Al	As <sup>b</sup>	Ca	Cd <sup>ab</sup>	Co	Cr <sup>ab</sup>	Cu <sup>ab</sup>	Fe	K <sup>a</sup>	Mg	Mn	Na	Ni <sup>ab</sup>	P <sup>ab</sup>	Pb <sup>ab</sup>	S <sup>a</sup>	Zn <sup>ab</sup>	
																		(mg kg <sup>-1</sup> )
Sampled in 2018	0	63 700	1.1	12 300	0.0	17.5	51.6	11.9	34 400	8000	9976	702	2700	22.3	243	3.8	150	66.8
	0	66 300	0.0	11 000	0.1	17.3	51.7	15.3	36 400	10 100	11 798	638	1200	25.9	448	3.3	248	80.0
	2	57 700	1.0	16 600	0.1	17.8	47.9	11.6	30 400	8700	9335	808	3500	17.8	434	3.7	179	64.5
	8	58 900	1.5	13 300	0.1	16.2	48.5	12.0	30 600	8500	9599	713	3200	17.6	454	4.9	217	66.3
	10	59 600	1.7	12 800	0.1	15.8	50.2	12.7	30 900	8400	9894	662	3400	17.9	482	3.2	245	68.3
	10	63 200	1.5	8800	0.1	16.1	48.7	16.4	32 300	9400	9161	693	2600	19.4	820	6.3	394	78.5
	18	58 000	0.4	8700	0.1	17.2	47.0	15.0	31 600	7200	7437	819	3000	19.9	542	6.8	290	72.3
	20	62 000	1.2	8000	0.1	15.3	46.4	15.0	32 900	7300	6601	672	3100	20.5	596	5.2	299	76.6
	34	49 300	7.8	27 500	0.3	14.2	53.1	22.8	29 400	7100	8523	617	2800	28.4	1025	6.4	476	97.8
	70	58 500	2.7	7700	1.4	16.1	80.3	44.0	32 900	7300	8012	755	2600	35.4	879	35.1	430	185
88	55 600	2.3	9900	1.2	15.7	74.6	50.6	33 600	7000	7671	702	3000	33.5	1303	37.5	532	215	
Sampled in 2011	0	56 600	1.4	15 200	0.0	19.5	52.8	12.0	36 500	5000	7711	880	4500	20.3	518	0.8	130	62.5
	1	59 800	1.3	16 000	0.1	15.3	44.8	12.6	29 800	9000	10 241	609	2500	17.6	514	3.2	234	67.0
	3	54 200	1.5	15 000	0.1	17.6	46.4	13.1	34 000	6200	8014	803	4400	19.8	920	0.8	202	65.9
	3	57 700	1.8	13 900	0.1	16.2	43.7	13.4	33 300	7000	8075	735	5200	19.9	746	3.5	727	71.7
	6	60 800	1.0	12 100	0.1	18.2	50.3	13.3	36 000	6500	8076	810	4000	21.3	546	1.7	241	70.2
	8	54 800	1.2	6700	0.1	16.7	42.6	13.8	29 900	6400	5626	828	3200	19.1	333	5.4	207	59.5
	13.5	51 400	1.3	15 300	0.1	14.9	42.6	11.7	33 400	4600	7213	676	3100	18.1	643	1.5	334	70.3
	35	59 200	1.4	13 200	0.1	18.2	54.2	15.6	38 500	6300	8171	867	3600	23.6	593	1.2	311	81.3
	85	55 000	5.1	12 900	2.5	15.9	102.7	58.0	32 100	7300	8520	735	2700	38.7	1191	57.3	548	242.5

<sup>a</sup> Statistically significant slope ( $p < 0.05$ ) of the regression ( $y = \text{irrigation}$ ;  $x = \text{trace metal concentration}$ ) in 2018.<sup>b</sup> Statistically significant slope ( $p < 0.05$ ) of the regression ( $y = \text{irrigation}$ ;  $x = \text{trace metal concentration}$ ) in 2011.

negatively in the samples of 2018 (figure 2), which was confirmed by the data of samples collected in 2011 (figure SI1). The range of pH was only from 7.1 to 7.9 in both sample sets, but the negative correlation corresponds to findings of Xu *et al* (2010), who showed that the pH-value of wastewater irrigated soils decreased in the upper 20 cm over time of irrigation. Siebe *et al* (2016) also observed this decrease in the range of neutral to slightly alkaline values due to wastewater irrigation in the Mezquital Valley. Hernandez-Martínez *et al* (2018) proposed that proton production by nitrification is accountable for the slightly changing pH values over time.

Apart from the soil that was irrigated for 34 years, all soils that were sampled in 2018 had a carbonate content below 1%. Among the samples from 2011, only one soil irrigated during 1 year had a carbonate content of 1.3%. Neither for the samples collected in 2011 nor for the ones collected in 2018, could we observe a significant correlation between the irrigation time and the  $\text{CaCO}_3$  content in the soils (figures 2 and SI1). These results are similar to those of Adrover *et al* (2012), who found no significant change in soil carbonate content after wastewater irrigation for 30 years.

$C_{\text{total}}$  and  $N_{\text{total}}$  were strongly correlated with each other with correlation coefficients of 0.93 (2018) and 0.97 (2011), but only weakly correlated with irrigation time in both sample sets.  $N_{\text{total}}$  ranged from 0.1% to 0.2% in 2018 and 2011 and  $C_{\text{total}}$  ranged from 0.9% to 3.0% in 2018 and up to 2.4% in 2011 (table 3 and figure SI2). Considering that  $C_{\text{org}}$  ranged from 0.3% to 2.1% in 2011 samples, the results are in good agreement with the results from Dalkmann *et al* (2014), who obtained the same concentrations of  $N_{\text{total}}$  and slightly lower  $C_{\text{org}}$  concentrations. The highest amounts of organic carbon with 3% and 2.4% were detected for a soil that was irrigated more than 34 years (2018) and one irrigated for 85 years (2011). An increasing  $C_{\text{org}}$  content with irrigation time was expected, since it is known that wastewater irrigation can drive the build-up of soil organic matter content (Friedel *et al* 2000). Sánchez-González *et al* (2017) observed that organic carbon stocks increase 1.5 fold after 40 years of irrigation and reach thereafter a new steady state in the Mezquital Valley.

The determined clay contents ranged from 36% to 57% in samples from 2018 and from 33% to 55% in 2011. An exception was the field that was irrigated for 0 years (table 3), where the soil had a clay content of 71%. Dalkmann *et al* (2014) described a clay content between 39% and 54% for soils in that area, which is close to our findings. Apparently, the clay content was independent of the irrigation duration, since the amounts of fine material introduced into the soils with wastewater were too small to increase the bulk mass of clay-sized material significantly. This is also in agreement with a study by Mamedov *et al* (2001), who found no significant difference in clay

content between wastewater and freshwater-irrigated soils.

### 3.3. Accumulation of trace metals with increasing duration of irrigation

The regression between soil concentrations and irrigation duration showed that concentrations of Cd, Cr, Cu, Ni, P, Pb and Zn increased significantly with time in both sets of samples (table 4). The concentrations of Cu, Mn, Zn, Cd, Cr, Co and Pb (table 4) were similar to those that were found by Cajuste *et al* (1991) in wastewater-irrigated soils in Mezquital Valley, but our Ni-concentrations were about four times higher ( $17.6\text{--}35.4\text{ mg kg}^{-1}$ ). Pb contents in the soils that were irrigated for 70 or more years ( $\geq 35.1\text{ mg kg}^{-1}$ ) were elevated. This coincided with the fact that the Pb-concentration in wastewater were increased. The lowest Cr-content that we found was  $42.6\text{ mg kg}^{-1}$  (table 4) and background concentration of rainfed soils were around  $50\text{ mg kg}^{-1}$ . These comparably large background concentrations of Cr were most likely inherited from the volcanic rocks in the Mezquital Valley area, which form the parent material for soil formation.

Strong positive correlations between duration of irrigation and the contents of Cd, Cr, Cu, Ni, P, Pb, S and Zn occurred for the samples of 2018 (figure 2). These correlations were confirmed by the data of the samples from 2011. This leads us to conclude, that metals were accumulated in the soils due to the irrigation with wastewater. Similar accumulation of Cu, Cr, Pb, Zn and Cd in wastewater irrigated soils of the Mezquital Valley was reported previously by Siebe and Cifuentes (1995). Hence, the temporal change of metal contents with increasing irrigation time underlines the suitability of our set of chronosequence samples for testing the potential accumulation of QAACs in wastewater-irrigated soils.

In summary, wastewater irrigation over a time period of 88 years leads to an accumulation of QAACs in soils. Contradictory to our second hypotheses, QAACs behaved differently to what we expected from pharmaceuticals, as their concentrations did not reach a steady state after 88 years of irrigation.

## 4. Conclusion

This study provides first evidence that wastewater irrigation leads to an increase of QAACs concentrations in the soil of the Mezquital Valley, Mexico. In fact, our study is to our knowledge is the first to report QAAC concentrations determined for an extended set of (unspiked) soil samples. We show that the concentrations of QAACs exceed the concentrations of other antibiotics and pharmaceuticals often by an order of magnitude, highlighting the need to keeping this group of substances on the radar when considering mechanisms of antibiotic resistance gene

evolution. The temporal trend of QAAC accumulation is opposite to the trend observed for pharmaceuticals. No 'steady state' concentration caused by a balance between inputs and dissipation is reached after 88 years of irrigation. Instead, QAAC concentrations in long-term irrigated soils rise exponentially, potentially due to massive inputs of QAACs into the soils in the first half of the 20th century or due to a strong sorption and effective sequestration (e.g. in clay mineral interlayer spaces).

The intensive use of disinfectants during the COVID-19 pandemic will likely leave a footprint of QAACs in wastewater-irrigated soils.

The fate of QAACs in soils is different to the fate of metal cations and pharmaceuticals. Future work should address the processes and kinetics of QAAC sorption and sequestration in soils with a focus on sorption and sequestration in clay mineral interlayers.

## Data Availability

All data that support the findings of this study are included within the article (and any supplementary files).

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