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Ionic strength of the liquid phase of different sludge streams in a wastewater treatment plant

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ABSTRACT

In a wastewater treatment plant (WWTP), several sludge streams exist and the composition of their liquid phase varies with time and place. For evaluating the potential for formation of precipitates and equilibria for weak acids/bases, the ionic strength and chemical composition need to be known. This information is often not available in literature, and even neglected in chemical model-based research. Based on a literature review, we proposed three ranges of concentration (low, typical and high) for the major constituents of the liquid phase of the different streams in a WWTP. The study also discusses the reasons for the concentration evolution, and the exceptional cases, to allow readers to consider the right range depending on their situation. The ionic strength of the different streams and the contribution of its constituents were calculated based on the ionic composition. The major contributors to the ionic strength for the wastewater-based streams (influent, effluent and mixed sludge) were Na^+, Cl^-, Mg^{2+} and Ca^{2+}, representing 50–70% of the ionic strength. For digestate, NH_4^+ and HCO_3^- accounted for 65–75% of the ionic strength. Even though the ionic strength is recognized to impact several important wastewater treatment processes, its utilization in literature is not always adequate, which is discussed in this study.

Key words: conductivity, CPR, digestion, EBPR, wastewater composition, WWTP

HIGHLIGHTS

- The ionic strength for wastewater-based streams ranges from 0.003 to 0.1 M.
- Na^+, Cl^-, Mg^{2+} and Ca^{2+} make 50–70% of the wastewater-based streams' ionic strength.
- The ionic strength for digestates ranges from 0.02 to 0.17 M.
- NH^{4+} and HCO_3^- account for 65–75% of the ionic strength of digestates.
- Ionic strength is rarely determined and often misused in literature.

GRAPHICAL ABSTRACT
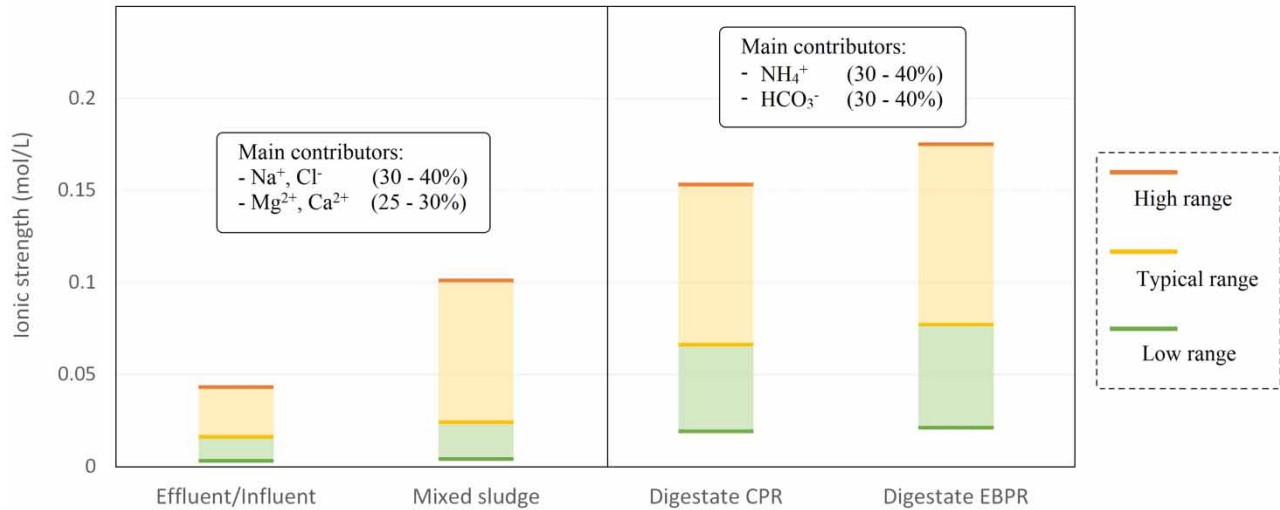
INTRODUCTION

The last decades saw a great development in the amount of wastewater treated. In Europe, 95% of the households were connected to a collection system in 2014, representing 517 million people (European commission 2017). China bears the world's largest municipal wastewater infrastructure, and over 90% of the country's wastewater was treated in 2018 (Qu *et al.* 2019). The wastewater composition can vary strongly depending on the location of the wastewater treatment plant (WWTP) and the type of influent streams. For instance, high concentrations of SO_4^{2-}, Na^+ and Cl^- can be expected in coastal WWTPs, where seawater intrusions can occur (Osman *et al.* 2017). Even higher salt loads can be found in specific places like Hong-Kong, where seawater is directly used to flush toilets (Wright & Colling 1995; Yu *et al.* 2002; Liu *et al.* 2019). It is also common for WWTPs to process some industrial wastewater, which can bear important loads of diverse elements, depending on the type of industry.

During municipal wastewater treatment, the pollutant load is oxidized or ends up in the sludge fraction, while the treated water is discharged. The composition of the solid fraction of the sludge does not evolve a lot through the different sludge treatment steps, except during digestion, where organic matter is transformed into biogas. However, the liquid fraction of the sludge flows is more dynamic, and its composition varies greatly in the different units. For example, when the sludge encounters anaerobic conditions (typically during thickening and digestion), fermentation occurs and volatile fatty acids (VFA) are progressively produced (Soares *et al.* 2010; Astals *et al.* 2012). It creates a pH drop that influences the solubility of several inorganic compounds present in the sludge, and thus the composition of the liquid fraction. Digestion is usually the final solid treatment step and provokes a big increase in bicarbonate and ammonium concentration associated with a slight increase in pH (Roldán *et al.* 2020). Additionally, WWTPs' process designs are numerous, and different succession of units will lead to different soluble phase composition. For example, a digestate contains higher P and K concentrations if produced in a WWTP using Enhanced Biological Phosphorus Removal (EBPR) compared to Chemical Phosphorus Removal (CPR) (Jardin & Pöpel 1994). Considering that the composition of wastewater and sludge soluble phase can vary a lot, evaluating their typical composition is complicated.

Ionic strength can be deduced from the composition of the soluble phase. Ionic strength is an important parameter in wastewater treatment, since it impacts, for example, nitrogen removal (Zhu & Liu 2017; Li *et al.* 2018) or the stability of sludge flocs (Zita & Hermansson 1994; Moghadam *et al.* 2005). Especially all kind of precipitation reactions will strongly depend on the ionic strength of the solution since the activity coefficients are calculated from ionic strength (Stumm & Morgan 1996). However, ionic strength is often misused in literature, by considering extremely wide ranges (Zita & Hermansson 1994; Moghadam *et al.* 2005) or unrealistic values (Song *et al.* 2002; Lei *et al.* 2017), for example. Moreover, the liquid composition of the different sludge streams, and thus their ionic strength, is not widely available in literature. Ionic strength should preferably be deduced from thorough analyses of the liquid phase composition, but this is not always the case or

possible. The lack of complete data on the composition of wastewater and sludge streams is likely due to the low interest in the concentration of the 'background ions' (like Na^+, Cl^-, K^+ and HCO_3^-) that do not directly influence the treatment processes and therefore, are not of direct relevance.

The current study aims to raise awareness on the importance of evaluating the ionic strength and provide a detailed composition of the liquid phases of the different flows at a WWTP. Literature was reviewed for data on the main compounds influencing the ionic strength of wastewater and sludge, and the data were critically evaluated. Ionic strength ranges were eventually calculated based on the composition of the streams and used to evaluate the current choices of ionic strength in literature. Besides highlighting the lack of data on ionic strength in wastewater systems, this study offers the possibility to the reader to quickly estimate the ionic strength of a sludge stream without the need of a complete characterization.

METHOD

To evaluate the composition of the different liquid streams in a WWTP, information from literature was collected. The study focuses on the dissolved compounds that have the biggest influence on the ionic strength: SO_4^{2-}, Na^+, Cl^-, PO_4^{3-}, Mg^{2+}, Ca^{2+}, K^+, VFA, NH_4^+, HCO_3^-. Values for pH were also collected, since it is an important global parameter and it influences, for example, the ionic speciation. Single or multiple concentrations were gathered for all the elements studied, and three ranges (low, typical, high) were determined from the entire dataset. In general, the ranges were built for each parameter on information collected from 10–20 WWTPs (Table 7). The ionic strength was later calculated from the composition of the different sludge streams.

For a matter of clarity, the studied streams can be broken down into three categories depending on their ionic strength:

- Low ionic strength: influent and effluent. The concentration of the soluble species is low compared to the liquid fraction of the sludge. Even though the compositions of the influent and effluent are different, the elements that contribute the most to their ionic strength (e.g., Na^+, Cl^-) present similar concentrations.
- Median ionic strength: soluble fraction of sludge before digestion. This category comprises primary sludge, waste activated sludge and any mix of undigested sludge. For those streams, biological activity has already started (especially after thickening), which increases the concentration of some parameters (P, VFA…). When possible, a distinction between primary and secondary sludge was made.
- High ionic strength: soluble fraction of sludge after digestion. Due to the biological activity, anaerobic conditions, and high solid retention time (20–30 days), the composition of the digestate is significantly different from the non-digested streams. Data were gathered from digestate or reject water (after dewatering). Moreover, clear differences were noticed for some compounds whether the digestate was from a EBPR or CPR plant; therefore, both streams are presented separately.

It was observed that some parameters were constant for the low and median ionic strength streams; thus, those parameters are presented in a unique range. A similar observation was made for the CPR and EBPR digestates: several compounds present similar concentration and are therefore presented together.

For each stream, three concentration ranges were given: low, typical, and high. The ranges are wide to cover most of the situations in WWTPs. However, they do not cover extreme cases, but these are discussed when possible. As much as possible, references giving an overview of several installations were prioritized. For some parameters, data are not widely available, but the value given was always based on a minimum of three different sources. It is important to note that different analytical techniques were employed to measure the same parameter depending on the reference, which can lead to differences in the concentration ranges obtained.

RESULTS AND DISCUSSION

Constant parameters in non-digested streams

In all the streams before digestion, references show that the concentration of sulphate, sodium and chloride stays relatively constant (Table 1). A well-documented source of these three elements is the intrusion of seawater or brackish groundwater in the sewer system. The concentration for these elements can be 5–10 times higher than the maximum range given if seawater is used as flushing water like in Hong-Kong (Wright & Colling 1995; Yu *et al.* 2002; Liu *et al.* 2019). Sulphate and chloride are also commonly added in WWTPs as counter-ion of iron or aluminium (used to flocculate the sludge and remove phosphate), and present in industrial wastewater (Rubio Rincon 2017).

Table 1 | Ranges for the compounds whose concentration is identical in all non-digested streams. The ranges presented are for influent, effluent and non-digested sludge.

	Low	Typical	High	Reference
SO_4^{2-} (mg S/L)	10	30	60	Andersen *et al.* (2014), Du & Parker (2013), Fisher *et al.* (2017), Kumar *et al.* (2018), Pathak *et al.* (2018), STOWA (2011), Wastewater characteristics and effluent quality parameters, Wilfert *et al.* (2016), Wilfert *et al.* (2018)
Na^+ (mg/L)	40	100	400	Andersen *et al.* (2014), Wastewater characteristics and effluent quality parameters, Wilfert *et al.* (2016), Wilfert *et al.* (2018), Arienzo *et al.* (2009), Kazadi Mbamba *et al.* (2016) and Novak & Park (2004)
Cl^- (mg/L)	30	300	600	Andersen *et al.* (2014), Wastewater characteristics and effluent quality parameters, Genz *et al.* (2004), Henze *et al.* (2008) and de Vries *et al.* (2009)

Several sources suggest that these elements go untreated during the wastewater treatment process (besides H_2S oxidation), explaining why their concentration does not vary in non-digested streams (United States Environmental Protection Agency (EPA) 1975; Dewil *et al.* 2008; Madison metropolitan sewer district. 2015; Wilfert *et al.* 2016; Fisher *et al.* 2017; Roldán *et al.* 2020). The dissolved sulphur in the influent is mainly present as SO_4^{2-} (Dewil *et al.* 2008; Fisher *et al.* 2017). Almost all sulphur is also present as SO_4^{2-} in secondary sludge, and reduction of sulphate to sulfide gradually happens during gravity-thickening (Dewil *et al.* 2008): for example, 60–80% of the dissolved sulphur can be sulphide after thickening of primary sludge (PS) and waste activated sludge (WAS) (Fisher *et al.* 2017). Then, dissolved sulphide can be eliminated by precipitation as FeS, provided enough iron is present or dosed to prevent H_2S in the biogas.

Variable parameters in non-digested streams

The concentrations of PO_4^{3-}, Mg^{2+}, Ca^{2+}, K^+, VFA, NH_4^+ and HCO_3^- are usually lower in influent/effluent than in the mixed sludge; therefore they are presented separately (Tables 2 and 3). Nitrogen and phosphorus species are always low in the effluent since they need to be removed to avoid eutrophication in the water bodies where the water is discharged. 70–80% of the influent nitrogen is ammonia (Kazadi Mbamba *et al.* 2016), while nitrate (Yu *et al.* 2002; Sattayatewa *et al.* 2010) or dissolved organic nitrogen (Pagilla *et al.* 2008) are the major nitrogen compounds in the effluent. Typical values for phosphorus in effluent in Europe are 1 mg/L (European Commission 1991) and will depend on the local legislation. For example, countries bordering the Baltic Sea, designated as a sensitive area, have to cope with more stringent discharge limits for phosphorus (and nitrogen) to control eutrophication (European Commission 2020). The concentration of magnesium in the influent is greatly influenced by the presence of seawater (up to 350 mg/L) (Wright & Colling 1995; Yu *et al.* 2002; Liu *et al.* 2019), while potassium is mainly influenced by the presence of industrial wastewater (up to 3,000 mg/L) (Arienzo *et al.* 2009). Similarly to calcium, magnesium and potassium usually go untreated from the influent to the effluent (Wilfert *et al.* 2016; Roldán *et al.* 2020). A small decrease in their concentration can be sometimes observed (Wilfert *et al.* 2016; Roldán *et al.* 2020), possibly due to their accumulation by Phosphate Accumulating Organisms (PAOs) as counter ion for the negatively charged polyphosphates (Jardin & Pöpel 1994). We expect this decrease to be more important for WWTPs using EBPR, but no full-scale experimental data were found to confirm it.

Under aerobic conditions, NH_4^+ is gradually oxidized to NO_2^- and NO_3^-, consuming 7.14 g of alkalinity per gram of N oxidized. In the later anoxic conditions, NO_3^- is reduced to N_2O and then released as gaseous N_2, producing 3.57 g of alkalinity per gram of N reduced (Li & Irvin 2007). Alkalinity represents the internal pH buffer of a system and is mainly influenced by HCO_3^-, NH_4^+, PO_4^{3-} and VFA concentrations in a WWTP (Barajas *et al.* 2002). During the oxidation of the biodegradable organic matter in activated sludge systems, 1.375 kg of CO_2 is produced per kg of Biological Oxygen Demand (BOD) (Denkert & Schulte 2010). The effect of this large CO_2 release on the alkalinity does not appear to be important: desorption predominates in weakly alkaline solution (like wastewater), meaning that CO_2 is emitted in the air and does not greatly influence the pH (Lijklema 1971). As soon as anaerobic conditions are present, fermentation can occur and significant release of some compounds can be observed, mainly due to biological activity. VFA concentration can strongly increase, especially during prefermentation, due to the decomposition of organic matter (Roldán *et al.* 2020) that mainly takes place during the first two days of fermentation (Soares *et al.* 2010; Yuan *et al.* 2011). The VFA produced, composed of

Table 2 | Ranges for the compounds whose concentration differs between influent/effluent and non-digested sludge. The ranges presented are for influent and effluent. We believe that these concentrations generally represent the poorly-loaded streams that can be found before digestion.

	Low	Typical	High	Reference
pH	6.5	7.5	8.5	Andersen *et al.* (2014), Kumar *et al.* (2018), Wilfert *et al.* (2016), Henze *et al.* (2008) and Barajas *et al.* (2002)
PO_4-P (mg/L)	0.1	5	15	Andersen *et al.* (2014), Wastewater characteristics and effluent quality parameters, Wilfert *et al.* (2016), Kazadi Mbamba *et al.* (2016), Henze *et al.* (2008), Barajas *et al.* (2002) and Hvitved-Jacobsen *et al.* (2013)
Mg^{2+} (mg/L)	1	15	60	Roldán *et al.* (2020), Andersen *et al.* (2014), Kumar *et al.* (2018), Wilfert *et al.* (2016), Kazadi Mbamba *et al.* (2016) and Genz *et al.* (2004)
Ca^{2+} (mg/L)	10	60	150	Roldán *et al.* (2020), Andersen *et al.* (2014), Kumar *et al.* (2018), Wilfert *et al.* (2016), Kazadi Mbamba *et al.* (2016) and Genz *et al.* (2004)
K^+ (mg/L)	10	20	35	Roldán *et al.* (2020), Andersen *et al.* (2014), Wastewater characteristics and effluent quality parameters, Wilfert *et al.* (2016), Arienzo *et al.* (2009) and Kazadi Mbamba *et al.* (2016)
NH_4^+-N (mg/L)	10	35	75	Wastewater characteristics and effluent quality parameters, Kazadi Mbamba *et al.* (2016), Henze *et al.* (2008), Sattayatewa *et al.* (2010), Barajas *et al.* (2002) and Hvitved-Jacobsen *et al.* (2013)
Alkalinity (mg/L $CaCO_3$)	50	200	550	Andersen *et al.* (2014), Wastewater characteristics and effluent quality parameters, Wilfert *et al.* (2016), Henze *et al.* (2008) and Barajas *et al.* (2002)
HCO_3^- (mg/L)[a]	20	90	350	Roldán *et al.* (2020), Andersen *et al.* (2014), Wastewater characteristics and effluent quality parameters, Wilfert *et al.* (2016), Henze *et al.* (2008) and Barajas *et al.* (2002)
VFA (mg/L HAc)	10	30	120	Roldán *et al.* (2020), Henze *et al.* (2008), Barajas *et al.* (2002) and Buchauer (1998)

[a]When data were not available in literature the range was calculated assuming that the total alkalinity is mainly represented by VFAs and HCO_3^-.

50–80% of acetate (Astals *et al.* 2012), explains why the pH of thickened sludge is usually lower than in influent/effluent (Bouzas *et al.* 2002; Pathak *et al.* 2018).

Total alkalinity increases together with sludge fermentation, and some experimental data are available for this parameter, which is not the case for bicarbonate alkalinity. Since VFA and bicarbonate should be the two main basic compounds contributing to the total alkalinity, bicarbonate concentration was deduced from VFA concentration and total alkalinity. While a lower pH can provoke a dissolution of some precipitates, the biological activity is the main mechanism for the release of PO_4^{3-}, K^+, and Mg^{2+}, following the hydrolysis of polyphosphates by the PAOs. The release of K^+ is usually more noticeable than the release of Ca^{2+} and Mg^{2+} since these latter can precipitate in sludge, for example with phosphate (Wilfert *et al.* 2016; Roldán *et al.* 2020). The extent of the release of PO_4^{3-}, K^+, Ca^{2+} and Mg^{2+} is very dependent on the advancement of the fermentation (Barajas *et al.* 2002; Martí *et al.* 2010; Wilfert *et al.* 2016; Pathak *et al.* 2018). This phenomenon should be even more important for EBPR sludge than for CPR sludge, since more PO_4^{3-}, Mg^{2+} and K^+ were accumulated by PAOs in the first place in EBPR sludges (Jardin & Pöpel 1994; Bouzas *et al.* 2002; Roldán *et al.* 2020).

No clear differences were noticed in the concentration of PO_4^{3-}, Mg^{2+}, Ca^{2+} and K^+ between PS and WAS. We believe that those concentrations (except Ca^{2+}) will depend on the amount of phosphorus stored by PAOs, and therefore, on the design of the WWTP. On the other hand, the pH seems to be lower in primary sludge than in WAS (Yuan *et al.* 2010), which is in line with the fact that primary sludge starts to ferment immediately into VFA, while VFA are produced more slowly in WAS and are then directly converted to CH_4. A clearer difference is observed for nitrogen, since 5–15 times more soluble nitrogen was measured in primary sludge than in WAS (Yuan *et al.* 2010; Roldán *et al.* 2020). It seems logical, considering that ammonia is removed during secondary treatment, producing a sludge poorer in soluble nitrogen. This observation is backed up by a study where the NH_4^+ concentration in seven WAS ranged from 0 to 50 mg/L (Novak & Park 2004), while it reached up to 480 mg/L in thickened primary sludge in some cases (Bouzas *et al.* 2002). It can be assumed that most of the soluble nitrogen in the primary sludge is NH_4^+, as this is the form under which it arrives to the WWTP (Kazadi Mbamba *et al.* 2016). On the contrary, most of the soluble nitrogen in WAS could be nitrate (Yu *et al.* 2002; Sattayatewa *et al.* 2010) or dissolved organic nitrogen (Pagilla *et al.* 2008), as in the effluent, but nitrogen will be released from WAS as NH_4^+ on sludge hydrolysis.

Table 3 | Ranges for the compounds whose concentration differs between influent/effluent and non-digested sludge. The ranges presented are for sludge before digestion (primary and secondary). We believe that these concentrations generally represent the highly-loaded streams that can be found before digestion.

	Low	Typical	High	Reference
pH	5.5	6.5	7.5	Astals et al. (2012), Roldán et al. (2020), Pathak et al. (2018), Wilfert et al. (2016), Yuan et al. (2011), Marti et al. (2008), Mitani et al. (2003) and Yuan et al. (2010)
PO_4-P (mg/L)	0.5	20	150	Soares et al. (2010), Roldán et al. (2020), Pathak et al. (2018), Wilfert et al. (2016), Wilfert et al. (2018), Bouzas et al. (2002), Marti et al. (2008), Mitani et al. (2003) and Yuan et al. (2010)
Mg^{2+} (mg/L)	5	20	90	Roldán et al. (2020), Pathak et al. (2018), Wilfert et al. (2016), Wilfert et al. (2018), Novak & Park (2004), Marti et al. (2008) and Mitani et al. (2003)
Ca^{2+} (mg/L)	20	80	200	Roldán et al. (2020), Pathak et al. (2018), Wilfert et al. (2016), Wilfert et al. (2018), Novak & Park (2004), Marti et al. (2008) and Mitani et al. (2003)
K^+ (mg/L)	10	50	120	Roldán et al. (2020), Wilfert et al. (2016), Wilfert et al. (2018), Novak & Park (2004) and Marti et al. (2008)
NH_4^+-N (mg/L)	0	20/200[a]	50/500[a]	Soares et al. (2010), Roldán et al. (2020), Novak & Park (2004), Bouzas et al. (2002), Marti et al. (2008), Mitani et al. (2003), Yuan et al. (2010) and Xu et al. (2018)
Alkalinity (mg/L $CaCO_3$)	80	500	4,000	Astals et al. (2012), Yuan et al. (2011), Bouzas et al. (2002) and Xu et al. (2018)
HCO_3^- (mg/L)[b]	20	200	2,400	Astals et al. (2012), Soares et al. (2010), Roldán et al. (2020), Buchauer (1998), Yuan et al. (2011), Bouzas et al. (2002), Marti et al. (2008) and Xu et al. (2018)
VFA (mg/L HAc)	50	250	2,500	Astals et al. (2012), Soares et al. (2010), Roldán et al. (2020), Buchauer (1998), Bouzas et al. (2002), Marti et al. (2008) and Xu et al. (2018)

[a]Secondary sludge/primary sludge.
[b]When data were not available in literature the range was calculated assuming that the total alkalinity is mainly represented by VFAs and HCO_3^-.

Constant parameters in digested streams

From all the references gathered, the operational pH for digesters treating sludge from EBPR or CPR processes is similar (6.5 to 8), which bears the favorable range for methanogens growth (6.5–7.2) (Appels et al. 2008). VFA levels cannot be too high in digesters since they can inhibit the digestion; from 800 mg/L (Hill & Bolte 1987) or from 2,000–4,000 mg/L (Appels et al. 2008). Concentrations higher than the typical value of 100 mg/L can be found for digesters working at short residence time or processing food wastes. The molar ratio VFA/Alkalinity should be <0.25 to maintain a good stability of the digestion (Water pollution control federation 1987; Wisconsin department of natural resources bureau of science services 1992; Palacios-Ruiz et al. 2008; Akhiar 2017), and is commonly around 0.1 in practice (Marti et al. 2008; STOWA 2016). No clear difference between alkalinity in EBPR or CPR digestates was observed, even though it could decrease in presence of metal salts due to precipitation with OH^-, for example (Maurer & Boller 1999). During digestion, HCO_3^- is produced to balance the formation of NH_4^+, so an equimolar ratio can be assumed for these two ions (Volcke et al. 2005). This hypothesis is in line with the few cases where both ammonia and bicarbonate concentrations were measured (Hellinga et al. 1998; Bhuiyan et al. 2009; Astals et al. 2012; Moretto et al. 2019). Therefore, the bicarbonate ranges were calculated in this study from NH_4^+ concentration, for which many references exist (Table 4).

Chloride and sodium concentrations should not change during digestion since they are not converted during the process (United States Environmental Protection Agency (EPA) 1975; Madison metropolitan sewer district. 2015; Wilfert et al. 2016; Roldán et al. 2020) and not present in large amounts in the waste sludge. Concentrations of 3,500–5,000 mg/L for sodium and 6,000 mg/L for chloride can inhibit the digestion and should be avoided (Appels et al. 2008). High concentrations of these two ions can be found in case of industrial wastewater treatment, intrusion (or use) of seawater, or control of H_2S production by iron chloride salts addition (Charles et al. 2006; Ge et al. 2013). Since data on chloride concentration in digesters are rarely reported in literature (Akhiar 2017), information was derived from the composition of dewatered sludge from Slibverwerking Noord-Brabant (SNB), which incinerates roughly 25% of all sewage sludge produced in the Netherlands.

Sulphate is reduced to sulphide under anaerobic conditions, and can then precipitate as FeS_x. Iron is sometimes added to digesters to control the H_2S in biogas, since H_2S concentrations of 50–200 mg/L can inhibit digestion and methanogenesis activity (Hulshoff Pol et al. 1998; Appels et al. 2008), and H_2S is detrimental for the biogas use. The concentration of soluble

Table 4 | Ranges for the compounds whose concentration is identical in CPR and EBPR digestates. The values are for the liquid fraction of the sludge for both CPR and EBPR digestates.

mg/L	Low	Typical	High	Reference
pH	6.5	7	8	Roldán et al. (2020), Wilfert et al. (2018), Martí et al. (2010), Marti et al. (2008), Appels et al. (2008), Water pollution control federation (1987), Moretto et al. (2019) and Zhang et al. (2014)
Total S (mg/L)	5	10	30	Du & Parker (2013), Fisher et al. (2017), Wilfert et al. (2016), Wilfert et al. (2018), Akhiar (2017) and Charles et al. (2006)
Na^+ (mg/L)	40	100	400	Wilfert et al. (2016), Wilfert et al. (2018), Appels et al. (2008), Akhiar (2017) and STOWA (2016)
Cl^- (mg/L)	70	300	800	Akhiar (2017)
NH_4^+-N (mg/L)	200	700	1,450	Astals et al. (2012), Akhiar (2017), STOWA (2016), Bhuiyan et al. (2009), Hellinga et al. (1998), Moretto et al. (2019), Johansson et al. (2018), Lackner et al. (2014) and Zuliani et al. (2016)
Alkalinity ($mg/L\ CaCO_{3-}$)	1500	2500	4400	Astals et al. (2012), Roldán et al. (2020), Martí et al. (2010), Marti et al. (2008), Akhiar (2017), Moretto et al. (2019) and Johansson et al. (2018)
HCO_3^- (mg/L)[a]	850	3,000	6,300	Astals et al. (2012), Akhiar (2017), STOWA (2016), Bhuiyan et al. (2009), Hellinga et al. (1998), Moretto et al. (2019), Johansson et al. (2018), Lackner et al. (2014) and Zuliani et al. (2016)
VFA (mg/L)	20	100	500	Astals et al. (2012), Roldán et al. (2020), Marti et al. (2008), Wisconsin department of natural resources bureau of science services (1992) and Moretto et al. (2019)

[a]Calculated assuming the same molar concentration for HCO_3^- and NH_4^+ (Volcke et al. (2005).

sulphide essentially depends on the quantity of Fe present in the digested sludge (Wilfert et al. 2016, 2018) and can be very low (0.1 mg/L) if enough Fe is present. It has been observed in several cases that 20–50% of the dissolved sulphur can still be sulphate in the digestate (Flores-Alsina et al. 2016; Wilfert et al. 2016; Fisher et al. 2017). This result is surprising since sulphate reduction rate is short compared to the residence time in an anaerobic digester (Rubio-Rincón et al. 2017). Such observations could be due to error in the analyses.

Most of the soluble nitrogen (>99%) in the digestate is present as NH_4^+ (Mantovani et al. 2020). Concentrations above 1,500 mg/L (reached with co-digestion) are usually avoided since they can inhibit the digestion process. One could expect that NH_4^+ concentration would be lower in digesters fed with sludge from EBPR plants due to the formation of struvite, but the pool of NH_4^+ is too big compared to PO_4^{3-} and Mg^{2+} to observe a significant difference (Bergmans et al. 2013).

Variable parameters in digested streams

In WWTPs using EBPR, phosphorus, magnesium and potassium are accumulated by the PAOs in the waterline and later released in the digester (Wild et al. 1997; Marti et al. 2008; Johansson et al. 2018). In digested sludges, phosphorus precipitates preferentially with iron to form vivianite (Wilfert et al. 2016, 2018), then with magnesium to form struvite, and finally with calcium to form calcium phosphate (van Rensburg et al. 2003). In digested sludge from CPR installations, a higher quantity of iron is generally available to bind the phosphate, explaining the higher concentration of soluble calcium and magnesium, and the lower concentration of phosphate (Table 5). Concentrations down to 50 mg/L were observed when Mg was dosed in a digester processing EBPR sludge to form struvite (Table 6) (DeBarbadillo 2016).

Table 5 | Ranges for the compounds whose concentration differs between CPR and EBPR digestates. The values are for the liquid fraction of sludge from CPR installations.

	Low	Typical	High	Reference
PO_4-P (mg/L)	1	30	80	Wilfert et al. (2016), Wilfert et al. (2018), STOWA (2016) and Johansson et al. (2018)
Mg^{2+} (mg/L)	5	20	40	Wilfert et al. (2016), Wilfert et al. (2018), Akhiar (2017), STOWA (2016) and Johansson et al. (2018)
Ca^{2+} (mg/L)	20	60	200	Wilfert et al. (2016), Wilfert et al. (2018), Akhiar (2017), STOWA (2016) and Johansson et al. (2018)
K^+ (mg/L)	60	100	320	Wilfert et al. (2016), Wilfert et al. (2018), Akhiar (2017), STOWA (2016) and Johansson et al. (2018)

The data were essentially collected from installations using iron as coagulant.

Table 6 | Ranges for the compounds whose concentration differs between CPR and EBPR digestates. The values are for the liquid fraction of sludge from EBPR installations.

	Low	Typical	High	Reference
PO_4-P (mg/L)	40	200	500	Roldán et al. (2020), Wilfert et al. (2016), Wilfert et al. (2018), Martí et al. (2010), Marti et al. (2008), STOWA (2016), Johansson et al. (2018), Wild et al. (1997) and Jeyanayagam et al. (2012)
Mg^{2+} (mg/L)	1	10	25	Roldán et al. (2020), Wilfert et al. (2016), Wilfert et al. (2018), Martí et al. (2010), Marti et al. (2008), STOWA (2016), Wild et al. (1997), DeBarbadillo (2016) and Jeyanayagam et al. (2012)
Ca^{2+} (mg/L)	5	35	70	Wilfert et al. (2016), Wilfert et al. (2018), Martí et al. (2010), Marti et al. (2008), STOWA (2016) and Wild et al. (1997)
K^+ (mg/L)	130	300	600	Roldán et al. (2020), Wilfert et al. (2016), Wilfert et al. (2018), Martí et al. (2010), Marti et al. (2008), STOWA (2016), Johansson et al. (2018), Wild et al. (1997) and DeBarbadillo (2016)

Data availability

To evaluate the relevance of the ranges proposed, it is important to evaluate the quality of data. We believe that information from enough installations was collected in most of the cases to propose representative ranges of concentration. An additional weight was given to full ranges (opposed to single data point) since they have most likely been obtained by gathering data from multiple sources. Table 7 indicates that information from a minimum of eight different installations (or fewer if ranges were available) was collected to consider the data satisfying.

While a satisfying amount of data could be found for most of the parameters, some were more challenging, and the quality of the data is assessed below:

- Chloride concentration is generally not well-measured. While the data were satisfying for influent (two ranges) and effluent (seven installations), no data were found for mixed sludge. Even though chloride should not be affected by the different treatments, additional information could be interesting, since chloride and sodium concentrations in streams before digestion represent 30–40% of the total ionic strength (Figure 2). Only one value was found in literature for chloride concentration in digestates, so an alternative method was used to propose a concentration range. The composition of 23 dewatered sludges before incineration was obtained from Slibverwerking Noord-Brabant (company incinerating roughly 25% of the sludge in the Netherlands). Assuming that the chloride present in digested sludge is essentially soluble, a

Table 7 | Number of sources used to propose concentration ranges

Case/Range	Before digestion		After digestion	
	Influent/Effluent	Mixed sludge	CPR	EBPR
SO_4^{2-}/H_2S	21/1		11/0	
Na^+	27/0		13/0	
Cl^-	7/2*		1/0*	
pH	8/1	9/0	10/4	
PO_4^{3-}	9/3	17/0	7/0	10/1
Mg^{2+}	9/0	17/0	8/0	10/1
Ca^{2+}	9/0	17/0	8/0	11/0
K^+	11/1	16/0	8/0	14/0
NH_4^+	6/3	19/0	26/0	
Alkalinity	7/2	4/0*	7/2	
HCO_3^-	0/0*	1/0 *	4/0*	
VFA	13/1*	20/0	4/2	

On the left of the slash: number of installations from which data have been collected for the parameter. On the right of the slash: number of ranges found in literature for the parameter.

* indicate that the range could benefit from additional data, which is discussed in the following section.

range for soluble chloride could be obtained. Chloride represents only ~5% of the ionic strength of digested streams (Figure 2), so the fact that the range proposed is only from installations in the Netherlands seems acceptable.

- While VFA data are available for influent wastewater, no information was found for effluents. Since VFAs are easily biodegradable organic compounds, they are oxidized in aerated sections and are poorly concentrated in the effluent. Most of the data collected for non-digested sludge were for thickened primary sludges, which can contain very high VFA concentrations; on the contrary, VFA production from WAS seems to be limited and little data is available. Therefore, the range deduced from literature review (150/500/,3500) was lowered to 50/250/2,500 to be more representative of both primary sludge and WAS.
- Alkalinity data are generally not widely available in literature. The range proposed for digestates seems reliable due to existing knowledge for digester stability, but the one given for mixed sludge should be taken with care due to scarce information. In general, the alkalinity should increase with sludge hydrolysis and ammonium release, so the range for mixed sludge should be an intermediate between influent/effluent and digestate.
- The concentration of HCO_3^-, or Partial Alkalinity, is important since it strongly contributes to the ionic strength, up to 38% for digested streams (Figure 2). It is rarely measured (only four references found for digestates); therefore, it was estimated from NH_4^+ concentration assuming an equimolar mix as discussed under the heading 'Constant parameters in digested streams'. HCO_3^- concentration is even more rarely measured in non-digested streams, and therefore, had to be determined indirectly. It was deduced from the alkalinity due to VFA and the total alkalinity, since VFA and bicarbonates should represent the major basic compounds in those streams. Even though the ranges proposed are in line with the few experimental data available, it should be taken with care since it was determined indirectly.

Since most of the available data were from installations in Europe and North America, the ranges proposed are regional. Considering that drinking water is the background of any wastewater, one could adjust the proposed ranges based on the drinking water composition of one's location, while taking into account possible seawater and industrial wastewater contribution.

Determination of the ionic strength for the different sludge streams

From the composition of the different sludge liquid fraction, the ionic strength could be calculated. The pH was always considered to be typical for the determination of the ionic strength. The interdependencies of the different concentrations were not considered, in order not to complicate the calculations. It means that to calculate the lowest limit of the ionic strength for a stream, all the concentrations from the 'low range' of this stream were considered.

The ionic strength of a solution is defined with the Debye-Hückel formula (Stumm & Morgan 1996):

$$IS = 0.5 * \sum_{i=1}^{n} C_i Z_i^2$$

where:

- IS is the ionic strength in mol/L
- C_i is the concentration of the ion in mol/L
- Z_i is the charge of the ion

Depending on the ionic strength of the ionic solution considered, the relation between activity coefficient and ionic strength will be different (Stumm & Morgan 1996). For wastewater systems, in which the ionic strength should always be <0.5 M, the approximation of Davies is always applicable and is expressed as:

$$Log\,(\gamma_i) = -A * Z_i^2 \left(\frac{\sqrt{IS}}{1 + \sqrt{IS}} - 0.2IS \right)$$

where:

– (γ_i) the activity coefficient of the ion considered
– $A = 1.82*10^6*(\varepsilon*T)$ with ε being the dielectric constant and T the temperature. A has the value of 0.5 in water at 25 °C.

Following the information found in literature and discussed above, NH_4^+ and NO_3^- were considered to be the only soluble nitrogen compounds in the influent/primary sludge and in the WAS, respectively. Similarly, SO_4^{2-} was taken as the only sulphur compound in the influent while H_2S alone was considered in the digester. Lastly, VFA were considered to be acetate and P to be HPO_4^{2-} (according to the pH).

Since ionic strength in sludge streams is rarely determined in literature, it is complicated to verify the ranges proposed in this study. In one study, the ionic strength of five digestates was calculated and ranged from 0.018 to 0.094 M with an average of 0.054 M (Bhuiyan et al. 2009). Overall, their results are consistent with the range proposed in this study. An ionic strength of 0.1 M, consistent with our range, was given for an EBPR digestate in another study (Jardin & Pöpel 1994), but no calculation details were given.

The major conclusion that can be drawn from Figure 2 is that the main contributors to the ionic strength vary depending on the sludge stream studied. Salts whose concentration won't be too influenced by the treatment process (Na^+, Cl^-, Mg^{2+}, Ca^{2+}) represent up to 50–70% of the ionic strength for the streams before digestion. Their contribution progressively decreases with the increase of the NH_4^+ and HCO_3^- concentrations, which will eventually account for around 60–80% of the ionic strength in digestate.
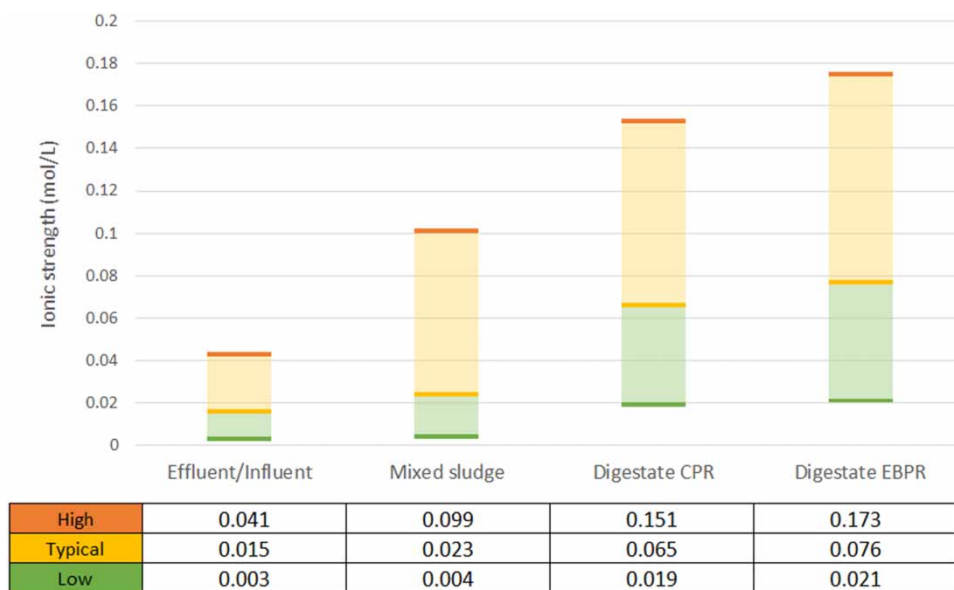
Importance of ionic strength in wastewater treatment

The importance of ionic strength and its influence on several processes in wastewater treatment have already been highlighted by various studies. Chemical precipitation processes are especially impacted by the ionic strength through its influence on the activity coefficients (Patón et al. 2018). The effect can be very important, even at typical ionic strength encountered in WWTP (Millero & Schreiber 1982). It is the case for the crystallization of struvite (Bhuiyan et al. 2007, 2009; Desmidt et al. 2013; Tao et al. 2016) and calcium phosphate (Song et al. 2002; Mañas et al. 2012; Kezia et al. 2017). A higher ionic strength decreases the activity of the ions, thus increasing the solubility of minerals. Not considering ionic strength while studying chemical precipitation has led to discrepancies in the solubility measurements of struvite (Bhuiyan et al. 2007). Its consideration is also relevant to predict and remediate unwanted struvite precipitation in WWTP (Ohlinger et al. 1998). Additionally, a study indicates that the purity of recovered struvite from animal manure was influenced by the ionic strength (Bhuiyan et al. 2007), which can have a big importance for its further use.

Additionally, small variations of ionic strength have a big effect on the structural properties, and therefore on the stability of sludge flocs. The flocs are first stabilized by an increasing ionic strength (Moghadam et al. 2005) before being destabilized at ionic strength > 0.1 M (Zita & Hermansson 1994). High ionic strengths have a negative effect on the dewatering behaviour of digested sludge (Rasmussen et al. 1994; Curvers et al. 2009). Another key process of wastewater treatment, nitrification/denitrification, is influenced by the salinity via the modification of the microbial community of the WAS (Zhu & Liu 2017; Li et al. 2018). The effect is positive at first, and negative for ionic strength > 0.1 M (Li et al. 2018). Such high ionic strength should only be encountered in WAS systems dealing with industrial, or very saline wastewater.

While chemical precipitation and enhanced biological removal are the two main routes for P removal, adsorption on iron oxides is a possible mechanism in some cases. It appears that ionic strength favourably influences this process in the range of 0.001–0.1 M (Antelo et al. 2005; Ajmal et al. 2018). The importance of ionic strength may even be higher for membrane-based treatments than for conventional treatment, since it was found to have an impact on the membrane fouling in the membrane bioreactor (MBR) (Wang et al. 2014). Lastly, ionic strength variation and absence of activity correction led to significant differences in predicted process performance evaluated with anaerobic digestion models (Solon et al. 2015; Patón et al. 2018).

From the information collected in literature, it is clear that ionic strength is an important parameter in wastewater treatment, since it is influencing several crucial processes. However, conclusions about the impact on ionic strength are sometimes drawn from only two values of ionic strength tested (Kaseamchochoung et al. 2006; Curvers et al. 2009). In other cases, the tested range is so wide (0.00005 < ionic strength < 0.05 M) that not enough information is gathered under conditions of actual sludge systems (Zita & Hermansson 1994; Moghadam et al. 2005). Moreover, the values chosen for ionic strength to study its influence are not always adequate. For example, ionic strength ranges from 0.01 to 0.4 M in Song et al. (2002) and is fixed at 0.15 M in Lei et al. (2017), while real wastewater would typically have an ionic strength ten times lower (Figure 1). Similarly, values ranging from 0.09 to 0.3 M for digester influent were used to model anaerobic digestion (Solon et al. 2015), while the ionic strength for undigested sludge was evaluated to be 0.1 M at the highest (Figure 1). Some of these problems could be solved if the studies were based on measurements of actual sludge/wastewater samples,

	Effluent/Influent	Mixed sludge	Digestate CPR	Digestate EBPR
High	0.041	0.099	0.151	0.173
Typical	0.015	0.023	0.065	0.076
Low	0.003	0.004	0.019	0.021

Figure 1 | Calculated ionic strength for three ranges (low, typical and high) for the four different streams of sludge studied. The average value for NH_4^+ in primary sludge and waste activated sludge was considered for the mixed sludge.

which is not always done (Rasmussen *et al.* 1994; Song *et al.* 2002; Moghadam *et al.* 2005; Curvers *et al.* 2009; Solon *et al.* 2015).

This study brings to light that the ionic strengths of the wastewater and sludge streams are generally not considered in literature and in databases. One of the reasons for this is likely that ionic strength determination is complex and of low interest for WWTP operators. Despite the fact that many processes are affected by the ionic strength, other parameters are easier to measure and give sufficient information to run a WWTP properly. Even in plants with seawater intrusion in sewer systems and in time variable salt loads, the ionic strength is generally not considered. As an example, ionic strength influences the stability of sludge flocs (Zita & Hermansson 1994; Moghadam *et al.* 2005) and thereby behaviour of sludge settling and suspended solids in effluent. Moreover, clarifiers are heavily influenced by density currents (Vanrolleghem *et al.* 2006) where the density is also a function of the salt content. For researchers working on chemical modelling the ionic strength is of greatest importance, since it controls the crystallization/precipitation processes (Patón *et al.* 2018). For those applications, an accurate determination of the ionic strength should not be neglected.

It seems unlikely that the entire composition of wastewater and sludge liquid streams will be measured in the future due to its complexity and the lack of commercial relevance. However, some indirect ways could be developed to get a close estimation of its value. For example, data on local drinking water composition are easily available and could be used to derive the concentration of the background ions (like Na^+, Cl^-, SO_4^{2-}) since drinking water is normally the matrix of wastewater. Intrusion of seawater and groundwater would modify the concentration of these ions and should also be considered. Alternatively, the ionic strength has been derived from the conductivity in some studies (Zita & Hermansson 1994; Fattah 2012; Tao *et al.* 2016). However, the linear coefficient linking conductivity and ionic strength greatly depends on the type of stream studied (Bhuiyan *et al.* 2009), so this strategy needs to be refined. The authors suggest that deriving the ionic strength from the conductivity could still be done but targeted research has to be undertaken for each type of streams to link the conductivity to ionic strength. The approach described in Bhuiyan *et al.* (2009) to study the crystallization of struvite in anaerobic digestor liquor is a good example of such work. The current study indicates the major contributors to the ionic strength depending on the stream considered (Figure 2). Focusing only on these ions to derive the ionic strength from the conductivity appears to be an interesting starting point.

CONCLUSION

The ionic composition of the liquid in the different sludge streams of a WWTP largely depends on the influent wastewater and on the process scheme of the WWTP. From an extensive literature review, three ranges of concentration were proposed for
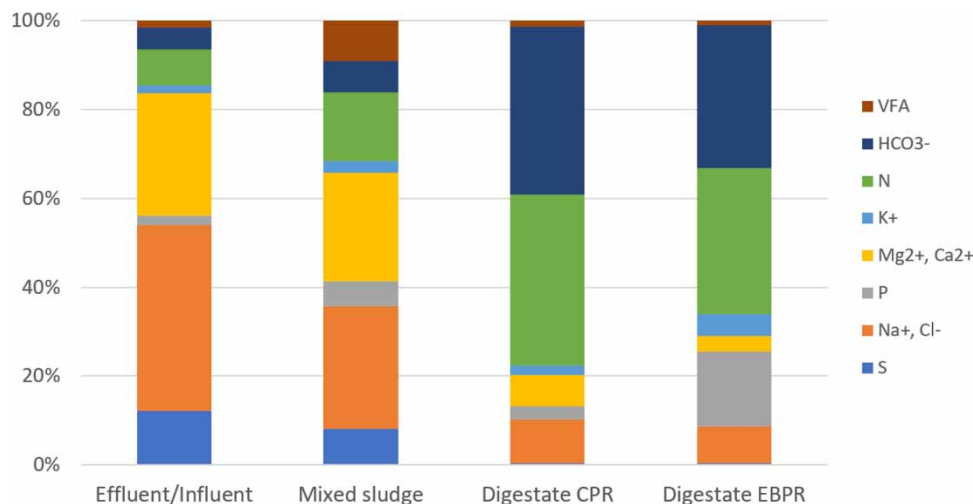
Figure 2 | Contribution of the major soluble compounds to the ionic strength of the four sludge streams evaluated. The values determined for the 'typical' range were selected to do the calculation.

the main constituents of influent/effluent, undigested sludge, and anaerobically digested chemical or biological phosphate removal sludge. From these data, the ionic strength of the different sludge streams was calculated. This study allows the reader to quickly estimate the ionic strength based on the concentration of the compounds influencing it the most. Reviewing numerous studies showed that ionic strength is a very important parameter, since it impacts important wastewater treatment processes. Nevertheless, the choice of the range of ionic strength used in literature studies is rarely motivated and not always adequate, which can weaken the conclusion.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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