

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

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14 Abstract

15 In a wastewater treatment plant (WWTP), several sludge streams exist and the composition
16 of their liquid phase varies with time and place. For evaluating the potential for formation of
17 precipitates and equilibria for weak acids/bases the ionic strength and chemical composition
18 needs to be known. This information is often not available in literature, and neglected even
19 in chemical model-based research. Based on a literature review, we proposed 3 ranges of
20 concentration (low, typical and high) for the major constituents of the liquid phase of the
21 different streams in a WWTP. The study also discusses the reasons for the concentration
22 evolution, and the exceptional cases, to allow readers to consider the right range depending
23 on their situation. The ionic strength of the different streams and the contribution of its
24 constituent was calculated based on the ionic composition. The major contributors to the
25 ionic strength for the wastewater-based streams (influent, effluent and mixed sludge) were
26 Na^+ , Cl^- , Mg^{2+} and Ca^{2+} representing 50-70% of the ionic strength. For digestate, NH_4^+ and
27 HCO_3^- accounted for 65-75% of the ionic strength, due to their formation under anaerobic
28 conditions. Even though the ionic strength is recognised to impact several important
29 wastewater treatment processes, its utilization in literature is not always adequate, which is
30 discussed in this study.

1. 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 wastewater was treated in 2018 **(86)**.

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 **(87)**. Even higher salt loads can be found in specific places like Hong-Kong, where seawater is directly used to flush toilets **(17, 18, 19)**. 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 ending 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 acid (VFA) are progressively produced **(35, 36)**. 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 **(23)** associated with a slight increase in pH. 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) (29). Considering that the composition of wastewater and sludge soluble phase can vary a lot, evaluating their typical composition is complicated.

Ionic strength can be deducted from the composition of the soluble phase. Ionic strength is an important parameter in wastewater treatment since it impacts for example nitrogen removal (68, 69) or the stability of sludge flocs (64, 65). Especially all kind of precipitation reactions will strongly depend on the ionic strength of the solution since the activity coefficient are calculated from ionic strength (39). However, ionic strength is often misused in literature, by considering extremely wide ranges (64, 65), or unrealistic values (76, 83), 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 deducted from thorough analyses of the liquid phase composition, but this is not always possible. Therefore, such a study could provide a way to quickly estimate the ionic strength of a sludge stream without the need of a complete characterization. We reviewed the literature for data on the main compounds influencing the ionic strength of wastewater and sludge, and critically evaluated the data availability. Ionic strength ranges were eventually calculated and used to evaluate the current choices of ionic strength in literature.

2. 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 3 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 decomposed in 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 composition of the influent and effluent are different, the elements that contribute the most to their ionic strength (e.g. Na^+ , Cl^-) presents 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 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.

3. Results & discussion

3.1. 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. 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 (17, 18, 19). 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 (16).

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	1, 2, 3, 4, 5, 6, 7, 8, 9
Na^+ (mg/L)	40	100	400	2, 4, 6, 9, 10, 11, 12
Cl^- (mg/L)	30	300	600	2, 9, 13, 14, 15

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 (4, 5, 20, 21, 22, 23). The dissolved sulphur in the influent is mainly present as SO_4^{2-} (5, 20). Almost all sulphur is also present as SO_4^{2-} in secondary sludge and reduction of sulphate to sulfide gradually happens during gravity-thickening (20): for example, 60-80%

of the dissolved sulphur is sulphide after thickening of PS and WAS according to (5). Then, dissolved sulphide can be eliminated by precipitation as FeS, provided enough iron is present or dosed to prevent H₂S in the biogas.

3.2. Variable parameters in non-digested streams

The concentration of PO₄³⁻, Mg²⁺, Ca²⁺, K⁺, VFA, NH₄⁺ and HCO₃⁻ are usually lower in influent/effluent than in the mixed sludge, therefore they are presented separately. 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 (12), while nitrate (19, 26) or dissolved organic nitrogen (30) are the major nitrogen compounds in the effluent. Typical values for phosphorus in effluent in Europe are 1mg/L (91) 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 (28). The concentration of magnesium in the influent is greatly influenced by the presence of seawater (up to 350 mg/L according to (17, 18, 19) while potassium is mainly influenced by the presence of industrial wastewater (up to 3000 mg/L according to 10). Similarly to calcium (4, 23), magnesium and potassium usually go untreated from the influent to the effluent. A small decrease in their concentration can be sometimes observed (4, 23), possibly due to their accumulation by Phosphate Accumulating Organisms (PAO's) as counter ion for the negatively charged polyphosphates (29). We expect this decrease to be more important for WWTPs using EBPR, but no full-scale experimental data were found to confirm it.

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	3, 4, 9, 13, 24
PO ₄ -P (mg/L)	0.1	5	15	2, 4, 9, 12, 13, 24, 25
Mg ²⁺ (mg/L)	1	15	60	3, 4, 9, 12, 15, 23
Ca ²⁺ (mg/L)	10	60	150	3, 4, 9, 12, 15, 23
K ⁺ (mg/L)	10	20	35	2, 4, 9, 10, 12, 23
NH ₄ ⁺ -N (mg/L)	10	35	75	2, 12, 13, 24, 25, 26
Alkalinity (mg/L CaCO ₃)	50	200	550	2, 4, 9, 13, 24
HCO ₃ ⁻ (mg/L)	20	90	350	From Alkalinity and VFA
VFA (mg/L HAc)	10	30	120	13, 23, 24, 27

Under aerobic conditions, NH₄⁺ is gradually oxidized to NO₂⁻ and NO₃⁻, consuming 7.14g of alkalinity per gram of N oxidized. In the later anoxic conditions, NO₃⁻ is reduced to N₂O and then release as gaseous N₂, producing 3.57g of alkalinity per gram of N reduced (92). Alkalinity represents the internal pH buffer of a system and is mainly influenced by HCO₃⁻, NH₄⁺, PO₄³⁻ and VFA concentrations in a WWTP (24). During the oxidation of the biodegradable organic matter in activated sludge systems, 1.375kg of CO₂ is produced per kg of Biological Oxygen Demand (BOD) (93). The effect of this large CO₂ release on the alkalinity does not appear to be important: desorption predominates in weakly alkaline solution (like wastewater), meaning that CO₂ is emitted in the air and does not greatly influence the pH (94). As soon as

anaerobic conditions are present, fermentation can occur and significant release of some compounds can be observed, mainly due to biological activity. Volatile Fatty Acids (VFA) concentration can strongly increase, especially during prefermentation, due to the decomposition of organic matter **(23)** that mainly takes place during the first two days of fermentation **(31, 36)**. The VFA produced, composed of 50-80% of acetate **(35)**, explains why the pH of thickened sludge is usually lower than in influent/effluent **(7, 37)**.

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 deducted 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 PAO's. 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 **(4, 23)**. The extend of the release of PO_4^{3-} , K^+ , Ca^{2+} and Mg^{2+} is very dependent on the advancement of the fermentation **(4, 7, 24, 40)**. 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 PAO's in the first place in EBPR sludges **(23, 29, 37)**.

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	4, 7, 23, 31, 32, 33, 34, 35
PO₄-P (mg/L)	0.5	20	150	4, 6, 7, 23, 32, 33, 34, 36, 37
Mg²⁺ (mg/L)	5	20	90	4, 6, 7, 11, 23, 32, 34
Ca²⁺ (mg/L)	20	80	200	4, 6, 7, 11, 23, 32, 34
K⁺ (mg/L)	10	50	120	4, 6, 11, 23, 34
NH₄⁺-N (mg/L)	0	20/200*	50/500*	11, 23, 32, 33, 34, 36, 37, 38
Alkalinity (mg/L CaCO₃)	80	500	4000	31, 35, 37, 38
HCO₃⁻ (mg/L)	20	200	2400	From Alkalinity and VFA
VFA (mg/L HAc)	50	250	2500	23, 27, 34, 35, 36, 37, 38

*Secondary sludge/primary sludge

No clear differences were noticed in the concentration of PO₄³⁻, Mg²⁺, Ca²⁺ and K⁺ between primary sludge and Waste Activated Sludge (WAS). We believe that those concentrations (except Ca²⁺) will depend on the amount of phosphorus stored by PAO's, and therefore, on the design of the WWTP. On the other hand, the pH seems to be lower in primary sludge than in WAS (33), which is in line with the fact that primary sludge starts to ferment immediately into VFA, while VFA are produced slower in WAS and are then directly converted to CH₄. A clearer difference is observed for nitrogen since 5-15 times more soluble Nitrogen was measured in primary sludge than in WAS (23, 33). It seems logical considering that ammonia

is removed during secondary treatment, producing a sludge poorer in soluble nitrogen. This observation is backed up by the study of (11) where the NH_4^+ concentration in 7 WAS ranged from 0 to 50, while it reached up to 480 mg/L in thickened primary sludge in some cases (37). It can be assumed that most of the soluble nitrogen in the primary sludge is NH_4^+ as it is the form under which it arrives to the WWTP (12). On the contrary, most of the soluble nitrogen in WAS could nitrate (19, 26) or dissolved organic nitrogen (30), as in the effluent, but nitrogen will be released from WAS as NH_4^+ on sludge hydrolysis.

3.3. 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 according to (44)). VFA levels cannot be too high in digester since they can inhibit the digestion; from 800mg/L according to (59) or from 2000-4000mg/L according to (44). Concentration higher than the typical value of 100mg/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 (41, 45, 52, 53), and is commonly around 0.1 in practice (34, 49). 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 (85). During digestion, HCO_3^- is produced to balance the formation of NH_4^+ , so an equimolar ratio can be assumed for these two ions as suggested by (90). This hypothesis is in line with the few cases where both ammonia and bicarbonates concentration were measured (35, 43, 63, 89). Therefore, the bicarbonates ranges were calculated from NH_4^+ concentration, for which many sources exist.

218 Chloride and sodium concentrations should not change during digestion since they are not
219 converted during the process (4, 21, 22, 23) and not present in large amounts in the waste
220 sludge. Concentration of 3500-5000 mg/L for sodium and 6000 mg/L for chloride can inhibit
221 the digestion and should be avoided (44). High concentration of these two ions can be found
222 in case of industrial wastewater treatment, intrusion (or use) of seawater, or control of H₂S
223 production by iron chloride salts addition (47, 56). Since data on chloride concentration in
224 digesters are rarely reported in literature (45), information was derived from the composition
225 of dewatered sludge from Slibverwerking Noord-Brabant (SNB), which incinerates roughly
226 25% of all sewage sludge produced in the Netherlands.

227 *Table 4: Ranges for the compounds whose concentration is identical in CPR and EBPR digestates. The*
 228 *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	6, 23, 34, 40, 42, 43, 44, 53
Total S (mg/L)	5	10	30	4, 5, 6, 8, 45, 47
Na ⁺ (mg/L)	40	100	400	4, 6, 44, 45, 49
Cl ⁻ (mg/L)	70	300	800	45
NH ₄ ⁺ -N (mg/L)	200	700	1450	35, 43, 45, 48, 49, 50, 51, 63, 89
Alkalinity (mg/L CaCO ₃)	1500	2500	4400	23, 34, 35, 40, 43, 45, 48
HCO ₃ ⁻ (mg/L)	850	3000	6300	Calculated from NH ₄ ⁺
VFA (mg/L)	20	100	500	23, 34, 35, 43, 52

229

230 Sulphate is reduced to sulphide under anaerobic conditions, and can then precipitate as FeS_x.

231 Iron is sometimes added to digesters to control the H₂S in biogas, since H₂S concentrations of

232 50-200mg/L can inhibit digestion and methanogenesis activity (44, 55), and H₂S is detrimental

233 for the biogas use. The concentration of soluble sulphide essentially depends on the quantity

234 of Fe present in the digested sludge (4, 6) and can be very low (0.1mg/L) if enough Fe is

235 present. It has been observed in several cases that 20-50% of the dissolved sulphur can still

236 be sulphate in the digestate (4, 5, 54). This result is surprising since sulphate reduction rate is

237 short compared to the residence time in an anaerobic digester (95). Such observations could

238 be due to error in the analyses.

Most of the soluble nitrogen (>99%) in the digestate is present as NH_4^+ (58). Concentrations above 1500 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 (57).

3.4. Variable parameters in digested streams

In WWTPs using EBPR, phosphorus, magnesium and potassium are accumulated by the PAO's in the waterline and later released in the digester (34, 48, 60). In digested sludges, phosphorus precipitates preferentially with iron to form vivianite (4, 6), then with magnesium to form struvite, and finally with calcium to form calcium phosphate (88). 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. Concentration down to 50 mg/L were observed when Mg was dosed in a digester processing EBPR sludge to form struvite (62).

254

255 *Table 5: Ranges for the compounds whose concentration differs between CPR and EBPR digestates.*256 *The values are for the liquid fraction of sludge from CPR installations. The data were essentially*257 *collected from installations using iron as coagulant.*

	Low	Typical	High	Reference
PO₄-P (mg/L)	1	30	80	4, 6, 48, 49
Mg²⁺ (mg/L)	5	20	40	4, 6, 45, 48, 49
Ca²⁺ (mg/L)	20	60	200	4, 6, 45, 48, 49
K⁺ (mg/L)	60	100	320	4, 6, 45, 48, 49

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259

260 *Table 6: Ranges for the compounds whose concentration differs between CPR and EBPR digestates.*261 *The values are for the liquid fraction of sludge from EBPR installations.*

	Low	Typical	High	Reference
PO₄-P (mg/L)	40	200	500	4, 6, 23, 34, 40, 48, 49, 60, 61
Mg²⁺ (mg/L)	1	10	25	4, 6, 23, 34, 40, 49, 60, 61, 62
Ca²⁺ (mg/L)	5	35	70	4, 6, 34, 40, 49, 60
K⁺ (mg/L)	130	300	600	4, 6, 23, 34, 40, 48, 49, 60, 62

262

263 **3.5. Data availability**

264 To evaluate the relevance of the ranges proposed, it is important to evaluate the quality of
265 data. We believe that information from enough installations were collected in most of the
266 cases to propose representative ranges of concentration. An additional weight was given to
267 full ranges (opposed to single data point) since they have most likely been obtained by
268 gathering data from multiple sources.

269 Table 7 indicates that information from a minimum of 8 different installations (or less if ranges
270 were available) were collected to consider the data satisfying.

271 Table 7: Number of sources used to propose concentration ranges. On the left of the slash: number of
 272 installations from which data have been collected for the parameter. On the right of the slash: number
 273 of ranges found in literature for the parameter. Red highlights indicate that additionnal information
 274 should be gathered to improve the range proposed.

Case/Range	Before digestion		After digestion	
	Influent/Effluent	Mixed sludge	CPR	EBPR
SO ₄ ²⁻ /H ₂ S	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	

275

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

- 278
- Chloride concentration is generally not well-measured. While the data were satisfying
- 279 for influent (2 ranges) and effluent (7 installations), no data were found for mixed
- 280 sludge. Even though chloride should not be affected by the different treatments,

additional information could be interesting since chloride and sodium concentration 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 sludge 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 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 BOD, 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, that can contain very high VFA concentrations, on the contrary to VFA production from WAS seems to be limited and little data is available. Therefore, the range deducted from literature review (150/500/3500) was lowered to 50/250/2500 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 4 reference found for digestates), therefore, it was estimated from NH_4^+ concentration assuming an equimolar mix as discussed in 3.3. HCO_3^- concentration is even more rarely measured in non-digested streams, and therefore, had to be determined indirectly. It was deducted 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.

3.6. 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 (39):

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

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, as described in (39). For wastewater systems, in which the ionic strength should always be <0.5M, the approximation of Davies is always applicable and is expressed as:

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

Where:

- (γ_i) the activity coefficient of the ion considered

- $A = 1.82 \cdot 10^6 \cdot (\epsilon \cdot T)$ with ϵ being the dielectric constant and T the temperature. A is worth 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).

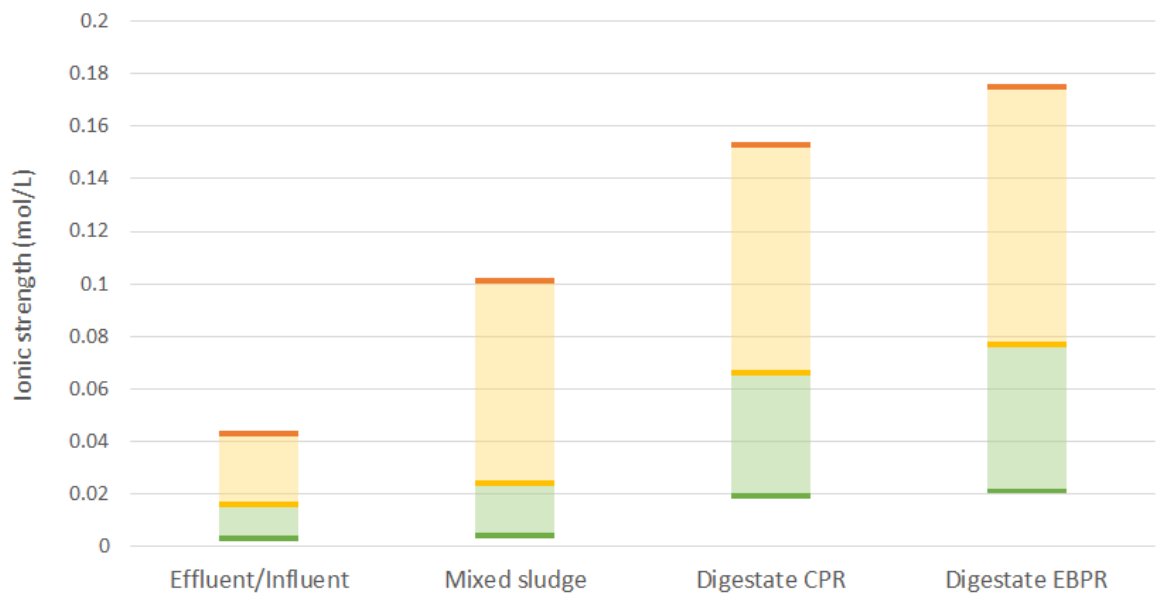


Figure 1: Calculated ionic strength for three ranges (low, typical and high) for the 4 different streams of sludge studied. The average value for NH_4^+ in primary sludge and waste activated sludge was considered for the mixed sludge.

Since ionic strength in sludge streams is rarely determined in literature, it is complicated to verify the ranges proposed in this study. In (63), the ionic strength of five digestates was

calculated and ranged from 0.018 to 0.094M with an average of 0.054M. Overall, their results are consistent with the range proposed in this study. An ionic strength of 0.1M, consistent with our range was given for a EBPR digestate in (29), but not calculation details were given.

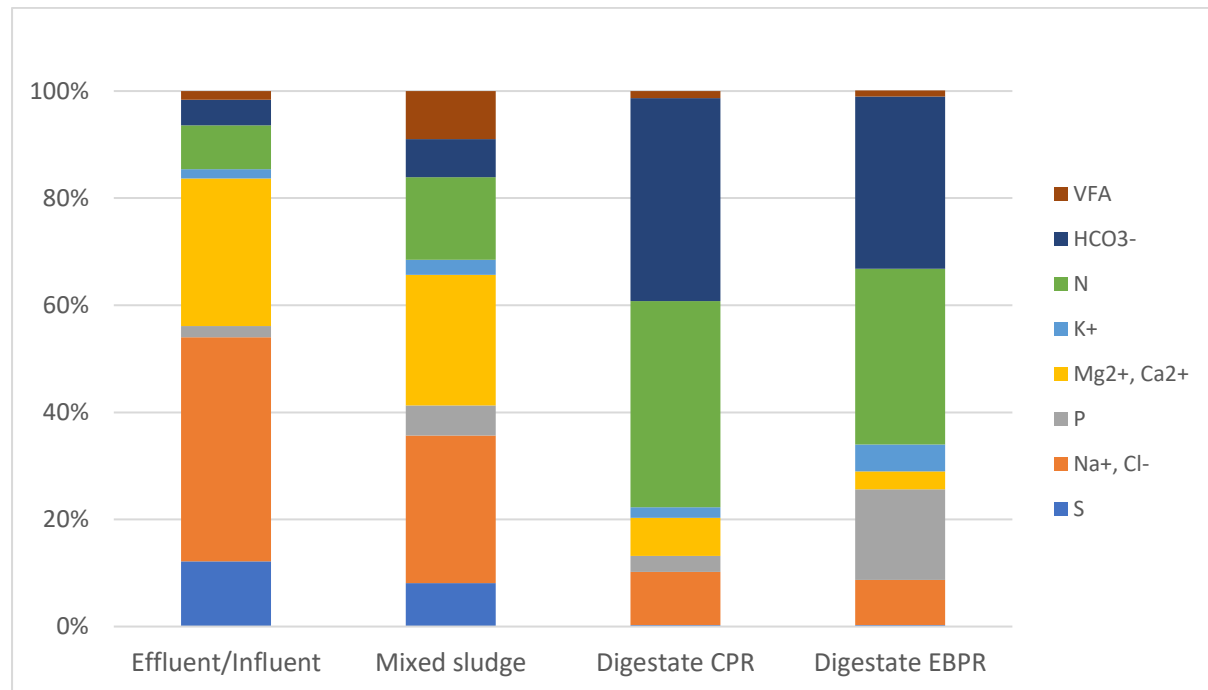


Figure 2: : Contribution of the major soluble compounds to the ionic strength of the 4 sludge streams evaluated. The values determined for the “typical” range were selected to do the calculation.

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.

3.7. Importance of ionic strength in wastewater treatment

The importance of ionic strength and its influence on several processes in wastewater treatment was already highlighted by various studies. Chemical precipitation processes are especially impacted by the ionic strength through its influence on the activity coefficients (96). The effect can be very important, even at typical ionic strength encountered in WWTP (70). It is the case for the crystallization of struvite (63, 71, 72, 73) and calcium phosphate (74, 75, 76). 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 (72). Its consideration is also relevant to predict and remediate to unwanted struvite precipitation in WWTP (77). Additionally, a study indicates that the purity of recovered struvite from animal manure was influenced by the ionic strength (72), 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 (64) before being destabilized at $IS > 0.1M$ (65). High ionic strengths have a negative effect on the dewatering behaviour of digested sludge (66, 67). Another key process of wastewater treatment, nitrification/denitrification, is influenced by the salinity via the modification of the microbial community of the waste activated sludge (68, 69). The effect is positive at first, and negative for $IS > 0.1M$ (68). 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 (0.001-0.1M) (78, 79). 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 MBR reactor (80). Lastly, ionic strength variation and absence of activity correction led to significant differences in predicted process performance evaluated with anaerobic digestion models (81, 96).

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 (66, 82). In other cases, the tested range is so wide ($0.00005 < IS < 0.05M$) that not enough information is gathered under conditions of actual sludge systems (64, 65). Moreover, the values chosen for ionic strength to study its influence are not always adequate. For example, ionic strength ranges from 0.01 to 0.4M in (76) and is fixed at 0.15M in (83), while real wastewater would typically have an ionic strength ten times lower (Figure 1). Similarly, values ranging from 0.09 to 0.3M for digester influent were used to model anaerobic digestion in (81), while the ionic strength for undigested sludge was evaluated to be 0.1M at the highest (Figure 1). Some of these problems could be solved if the studies would be based on measurements of actual sludge/wastewater sample, which is not always done (64, 66, 67, 76, 81). Alternatively, the ionic strength has been derived from the conductivity in some studies (65, 71, 84). However, the linear coefficient linking conductivity and ionic strength greatly depends on the type of stream studied as discussed in (63), so extreme care should be taken while using this approximation.

4. 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 the main constituents of influent/effluent, undigested sludge, CPR and EBPR digestate. 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 studied range is rarely motivated and not always adequate in literature, which can weaken the conclusion.

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