Water Supply

Water Supply Vol 23 No 2, 657 doi: 10.2166/ws.2023.020

Full-scale determination of pipe wall and bulk chlorine degradation coefficients for different pipe categories

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ABSTRACT

Having good information about parameters that impact water quality can improve the management of water distribution systems in the short-term (optimising disinfection) and the long-term (planning rehabilitation). Full-scale data on the degradation of the residual disinfectant for various pipe characteristics are difficult to obtain but necessary. As the most common disinfectant is chlorine, this paper aims to determine the most important pipe and/or hydraulic system characteristics in the chlorine degradation coefficients. Such characteristics were identified based on statistical analyses that relate them with range values of bulk and pipe wall degradation coefficients estimated in full-scale conditions in a real distribution system. The results showed that among pipe characteristics, the period of installation impacts significantly k_w and k_t. Results of k_w for three different materials confirmed that residual chlorine degradation at the pipe walls for grey-cast iron, which is older and metallic, is much higher than that for ductile cast iron and PVC pipes. In older pipes, up to 97% of residual chlorine can be degraded at the pipe walls, while the role of bulk reactions can reach about 35% in newer pipes. The obtained information can be integrated to identify pipes for rehabilitation/renewal and locations for booster rechlorination.

Key words: bulk coefficient, chlorine degradation, pipe material, wall coefficient, water distribution systems

HIGHLIGHTS

- Methodology can be used to estimate k_w and k_b in real water distribution systems.
- The use of categories allows to identify the impact of the period of installation on k_w.
- Regressions showed that the period of installation is the most important factor that impacts k_t and k_w.
- Statistical analyses showed that diameter does not impact the degradation coefficients significantly in this case study.
- The chlorine degradation at the pipe walls for GCI is much higher than DCI and PVC.

INTRODUCTION

Having safe, odourless, and colourless drinking water in municipal water distribution systems (WDS) promotes public health and social acceptance of public water while decreasing plastic use associated with bottled water that can be harmful to the environment. Among the solutions to control water quality throughout a WDS are manipulating pressure set points and valves to control water paths (Vrachimis *et al.* 2020) to reduce water residence times and improving the management of secondary disinfectants to minimize bacterial regrowth (Chen *et al.* 2020). To safely monitor and manage water quality, some microbial indicators are used like total coliform and *Escherichia coli* (Wen *et al.* 2020). Monitoring residual disinfectant throughout the distribution system is a complementary strategy to microbiological monitoring. Nowadays, the most common secondary disinfectant is chlorine which should be detectable all the time, everywhere to minimize acute risks associated with microorganisms in the water (Luo *et al.* 2011). Chlorine is 'detectable' when its concentration is above the limit of quantification of the equipment used to measure it. However, water quality changes spatially and temporally throughout a WDS (Betanzo *et al.* 2008) mostly due to physico-chemical reactions that consume the residual disinfectant (Saidan *et al.* 2017). Residual chlorine degradation due to the physico-chemical reactions takes place in the bulk volume and at the pipe walls throughout a WDS (McGrath *et al.* 2021). Bulk degradation is mainly a function of natural organic and inorganic matter, water temperature, and disinfectant concentration, while pipe wall degradation depends mainly on pipe age, the presence of corrosion and/or biofilm and pipe material (Monteiro *et al.* 2020). Biofilm and corrosion, specifically in metallic pipes, can accelerate chlorine degradation, so pipe physical characteristics and ageing need to be closely studied and understood (Pasha & Lansey 2009).

Although the reactions of residual chlorine in water depend on many factors, it has been shown that their coefficients are not very sensitive to input parameters like water age (Gibson *et al.* 2020). Free residual chlorine (FRC) deterioration (Powell *et al.* 2000) according to water residence time (WRT) can be estimated as follows:

$$C_i = C_0\, e^{-k_t\, \mathrm{WRT}_{0\to i}} \tag{1}$$

where C_i is the chlorine concentration at point i (mg/l); WRT is the water residence time (h); C_0 is the initial chlorine concentration (mg/l); k_t is the first-order chlorine decay constant (h^{-1}). Long WRT increases the risk of undetectable FRC spatially and/or temporally and, consequently, increases vulnerable zones like network extremities and loops with low water demands (Rochette *et al.* 2017). The total rate of chlorine deterioration (k_t) occurs in both bulk water (k_b) and pipe walls (k_w) (Vasconcelos *et al.* 1997; Hallam *et al.* 2002):

$$k_t = k_b + k_w \tag{2}$$

k_w depends on pipe physical characteristics (Pasha & Lansey 2009), while k_b depends mainly on initial concentration (C_0), water temperature, and organic matter content (Powell *et al.* 2000). Bulk degradation can be a complicated parameter to determine as models in the literature do not generally provide a good fit with observed data (Fisher *et al.* 2011). By making some assumptions like constant water temperature, uniform pipe characteristics, plug flow, and first-order reactions, detectable FRC degradation in a single pipe can be expressed as follows (Hallam *et al.* 2002):

$$C_b(t) = C_{b,0}\, \exp\left[-(k_b + k_w)\, t\right] \tag{3}$$

where $C_b(t)$ represents FRC at the outlet of the pipe at time t (mg/l); $C_{b,0}$ denotes FRC at the inlet of the pipe (mg/l); t denotes WRT (h); k_b represents bulk degradation kinetic coefficient (h^{-1}); and k_w denotes wall degradation kinetic coefficient (h^{-1}).

There are no direct methods to determine pipe wall degradation (Lee *et al.* 2010). Pipe wall degradation can be estimated as the difference between total free chlorine degradation and bulk degradation (McGrath *et al.* 2021). Some pilot-scale studies have been also conducted to estimate pipe wall degradation, like the one by Liu *et al.* (2015). There are only a few studies that have produced values and ranges of k_b and k_w. Table 1 presents those found in the literature.

Since most of the previous studies have been conducted in laboratory-scale or -controlled conditions, there is a lack of conducted studies in real full-scale conditions. A full-scale study also highlights all the challenges that managers are faced with in a real WDS: in many older WDS, information is lacking on pipe materials and the period of installation to determine wall coefficients in the WDS. This lack of accurate data is an important issue that makes working on a full-scale case study difficult. In addition, it is not clear in previous studies which, among all pipe and system characteristics, play a vital role in the chlorine degradation kinetics coefficients. To overcome these shortcomings, the purpose of this paper is to develop and apply a methodology for estimating chlorine degradation kinetics coefficients in a WDS at full-scale conditions and determine the most effective hydraulics and pipe characteristics that impact the chlorine degradation coefficients. Hence, the specific objectives in this study are to (i) obtain k_t, k_b, and k_w from full-scale sampling campaigns per pipe characteristics in a real WDS; (ii) analyse statistically the obtained k_t, k_w, and k_b results to determine the most important system/pipe characteristics which affect the degradation coefficients, (iii) evaluate the range of k_b and k_w on the chlorine degradation according to the most important characteristics, and (iv) quantify the proportion of chlorine degradation from k_b and k_w. Generating knowledge about bulk and wall chlorine degradation coefficients for different pipe categories and the most important pipe characteristics that affect them is key to good decision-making. The proposed methodology can help managers to make appropriate decisions and reduce potential costs associated with secondary disinfection management with chlorine (including rechlorination) and with rehabilitation/renewal of WDS pipes.

Table 1 | Kinetic constants k_b (first-order) and k_w in the literature

k_b (10^{-3} h^{-1})	T (°C)	$C_{b,0}$ (mg/L)	Reference
7.9–160.8	NR[a]	0.50–2.50	Powell *et al.* (2000)
22.9	25.0	NR	Biswas *et al.* (1993)
3.3–737.5	13.2–22.2	NR	Vasconcelos *et al.* (1997)
90–210	18.0	NR	Lu *et al.* (1999)
70–110	NR	NR	Zhang *et al.* (1992)
10–740	NR	NR	AWWARF (1996)
6	NR	NR	Hallam *et al.* (2002)
11.7	NR	NR	Al-Jasser (2007)
8–35	5–40	≈1	Saidan *et al.* (2017)
4.1–43.8	4–22	0.64–1.05	McGrath *et al.* (2021)
Average k_w (10^{-3} h^{-1})	T (°C)	Pipe material	Reference
130	NR	Cast iron	Hallam *et al.* (2002)
90	NR	PVC	Hallam *et al.* (2002)
50	NR	MDPE	Hallam *et al.* (2002)
8.5–27.6	11–14	PVC	McGrath *et al.* (2021)
24.9–114.9	11–14	Ductile cast iron	McGrath *et al.* (2021)
58.8–114.9	11–14	Grey-cast iron	McGrath *et al.* (2021)
12	11–14	Pre-stressed concrete	McGrath *et al.* (2021)

NR, not reported.

METHODOLOGY

This section presents the steps to reach the proposed objectives, the description of the case study, the determination of pipe categories based on their characteristics, the identification of long pipe sections to conduct residual chlorine sampling in the field, the sampling strategy, and the calculation and statistical analysis of degradation coefficients (k_t, k_b, and k_w), followed by the results, discussion, and concluding remarks. The research uses the WDS of Quebec City (Canada) as a case study for implementing and applying the proposed methodology. Figure 1 presents the flowchart that summarizes the proposed research.

Case study

Quebec City, which is located along the St. Lawrence River in Southern Quebec (Canada), was selected as a case study for this research project. Its climate is characterized by cold, windy, and snowy winters (average air temperature of -18 °C and snowfall of about 300 cm/year) and warm, humid, and rainy summers (average air temperature of $+25$ °C and rainfall of about 900 mm/year). Quebec City's main WDS (Figure 2), supplied by the St-Charles River, with Lake St-Charles as the main raw water reservoir, was chosen to characterize full-scale chlorine degradation per pipe category. The water treatment plant that supplies the selected WDS has a complete physico-chemical chain (including coagulation–flocculation, sedimentation, and filtration) (WPP; Figure 2) and uses ozone for primary disinfectant and chlorine for secondary disinfection.

Pipe categorization

Pipes of the WDS were categorized according to their main physical characteristics including length, diameter, material, and the period of installation; the two latter influenced their Hazen–Williams coefficient. Pipes having the same range of diameter, material, and the period of installation were classified into one category, then the series of pipes in the same category were georeferenced to produce the longest series of pipes possible. The considered pipe materials were grey-cast iron (GCI), ductile cast iron (DCI), and polyvinyl chloride (PVC), which are the most common in our case study. At first, pipe diameters were divided into three groups: (1) small (less or equal to 150 mm, which are the local pipes); (2) medium (more than 150 mm up to 350 mm, which are the secondary pipes); and (3) large (more than 350 mm, which are the main distribution pipes). As Quebec City's main WDS is not densely populated (229/km^2) and spreads over 486 km^2, unsurprisingly, 150 and 200 mm

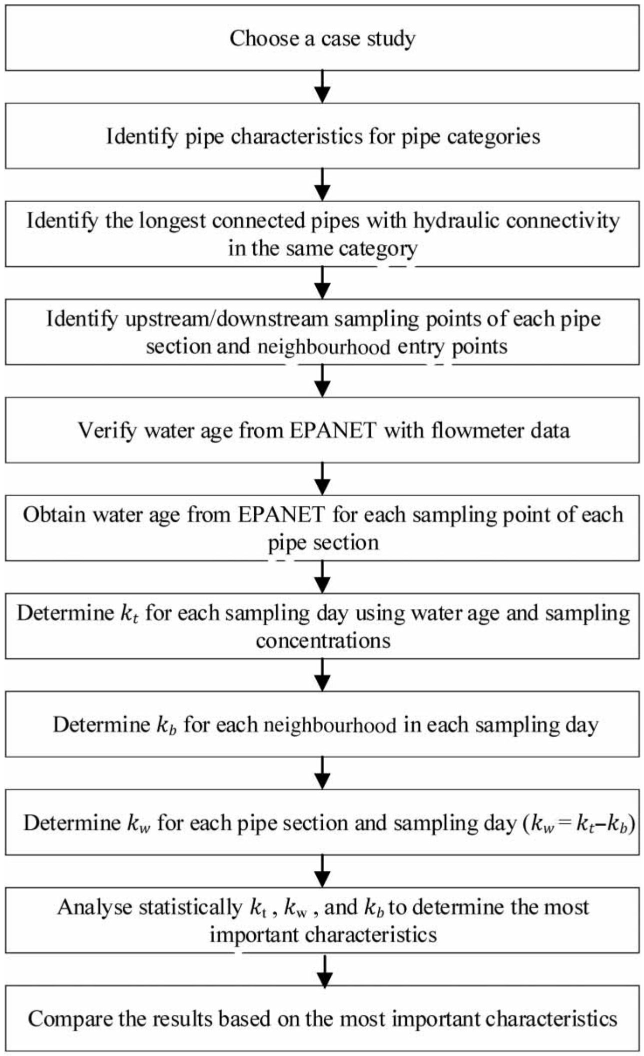

Figure 1 | Steps of the proposed methodology.

diameters dominated the neighbourhoods and, therefore, nominal diameters were kept individually instead of ranges. Years of installation were grouped into periods of installation based on the municipality's development phases: (1) before 1945; (2) 1945–1960; (3) 1960–1970; (4) 1970–1980; and (5) after 1980.

Longest pipe sections in the same category and their sampling points

After categorizing all the pipes using the three characteristics, the longest series of connected pipes in the same category were identified through ArcGIS with the goal of identifying upstream and downstream sampling points for each long series of pipes. A preliminary sampling campaign showed that chlorine degradation is generally detectable in sections of at least 300 m. By mapping the long series of connected pipes, it was possible to identify three neighbourhoods (sub-systems Lac-Saint-Charles (LSC), Quebec-Nord (QN), and Val-Belair (VB)) of the WDS with a high diversity of pipe categories and the least number of entry points to minimize the number of points for which the bulk coefficient (k_b) needed to be determined, as all the long pipe sections with the same entry point into a neighbourhood were assigned the same k_b. Hydraulic paths are the main flow paths from the entry point of a WDS (or sub-system) to each model node. Pipes' hydraulic connectivity (the same flow direction and similar flow without major inflow/outflow along the entire section) needed to be verified using the hydraulic paths in the EPANET model provided by the City. The upstream (C_1) and downstream (C_2) model nodes of the pipe sections are the potential sampling points. For water sampling purposes, a building with an exterior tap needed to

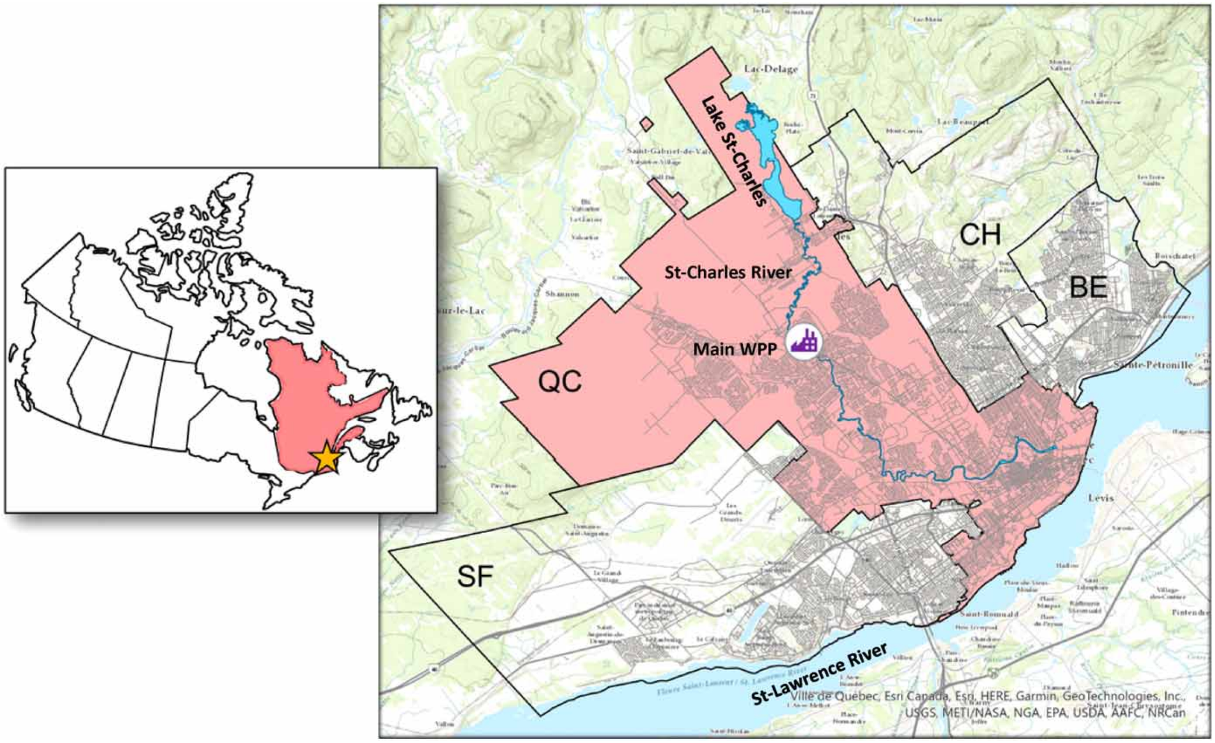

Figure 2 | Quebec City (QC) main WDS and the three other WDS (SF, CH, BE; each from a different surface water source) supplying the region.

be located near those model nodes. Since pipe length plays a vital role in the degradation of chlorine, if the distance between the two buildings identified for sampling is less than 300 m, that pipe section was not considered for the reasons mentioned above. To identify the longest series of connected pipes, a difference of one nominal pipe diameter was accepted to have a longer series. These criteria resulted in a total number of identified pipe sections was 95 in three sub-systems but, due to some barriers like the inability to access some sampling points, the final number was 65 sections. The characteristics of the selected pipe sections according to their material, diameter, and the period of installation are represented in Figure 3.

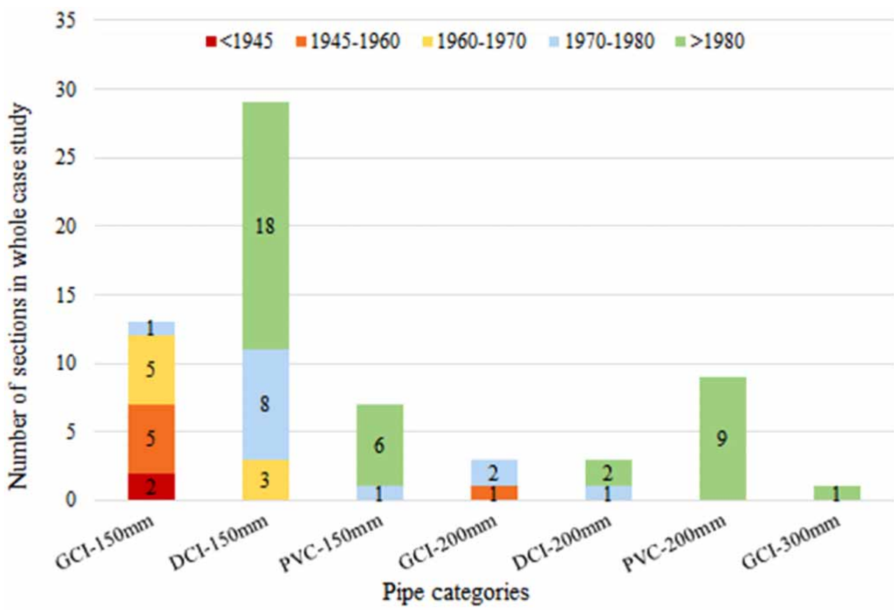

Figure 3 | Number of pipe sections (65) in each of the 15 pipe categories.

Water age and volume/flow verification

The EPANET model was run over 48 h to obtain water ages within the WDS based on the City's best estimate of average water demands subjected to their best estimate of hourly patterns. Model results showed that most of the pipes have a velocity of less than 0.18 m/s, which can be considered low. These low velocities would favour mass diffusion at the pipe walls in terms of chlorine demand. The water age outputted by EPANET is highly dependent on the water demands in the model. Although dynamic simulations were performed, these simulations did not influence the average water age significantly due to low variability in water demand patterns. Thus, water demands in EPANET were verified against flowmeter data in two ways. Firstly, the total consumed volumes within a neighbourhood in EPANET were compared with volumes obtained from the flowmeter data considering the water balance (inflow/outflow) in each neighbourhood for each sampling day. Secondly, flow passing through the main entry pipes of each neighbourhood for each sampling day was compared with the flowmeter data at the same location. Considering the difficulties associated with full-scale studies, a criterion $\pm 25\%$ between EPANET and field data was chosen in order to keep the sampling data for that sampling day for analysis. In the final step, WRT was calculated as the difference of water age at downstream/upstream points, which reduces uncertainties in the calculation of WRT, water losses, and their impact on WRT.

Sampling to determine k_t, k_b, and k_w

To determine k_t and k_b and consequently k_w, an extensive sampling campaign was essential. Water quality parameters such as detectable FRC, total chlorine concentrations, and temperature were measured *in situ* by using DPD colorimetric methods (Mercier Shanks *et al.* 2013) with a HACH colorimeter (DR900). The accuracy of the equipment used for chlorine measurement *in situ* was 0.02 mg/l. k_t was determined from the FRC measurements obtained from the sampling campaign and WRT for each pipe section by Equation (1). A series of 12 bottle tests per neighbourhood entrance was also collected to obtain k_b for each sampling day (García-Ávila *et al.* 2020). Chlorine concentrations were determined at different time intervals at the Université Laval laboratory for each entry point into a neighbourhood (C_0). k_b is assumed constant for each neighbourhood; this simplifying hypothesis is justified by the fact that there is little variation in temperature and water characteristics within a WDS for the same treated water during the same sampling day. k_w was then obtained for each pipe category by subtracting k_b from k_t (Equation (2)).

Sampling campaigns were conducted for 36 days from May to August 2021 on Tuesdays, Wednesdays, and Thursdays between 9 and 16 h, outside the morning and evening peak water demands shown by the flowmeter data, to be closest to the average water demand in the EPANET model. The total number of sampling points was 133 points: upstream and downstream points of 65 pipe sections and 3 entry points of neighbourhoods. After each sampling day, a verification was made that the FRC concentration at the entry point into each neighbourhood (C_0) was larger than the concentration at the upstream sampling point (C_1) and the latter was larger than the concentration at the downstream sampling point (C_2). The details about the sampling campaigns are presented in Table 2.

Pipe categories

The 65 sampled pipe sections were grouped into 15 distinct categories, whose proportions in length are shown in Figure 4: 9 categories in LSC (Figure 4(a)), 12 in QN (Figure 4(b)) and 9 in VB (Figure 4(c)). LSC has no pipe section in PVC with a 150-mm diameter (Figure 4(a)), while only QN has a 300-mm pipe category and no pipe section in GCI with a 200-mm diameter (Figure 4(b)). Pipe diameters of 150 mm represented 75.4% of the pipe sections, while 200-mm pipes represented 23.1% and 300-mm pipes, 1.5%, overall. Concerning pipe materials, 17 pipe sections were in GCI representing 26.2% of the total pipe sections, 32 in DCI (49.2%), and 16 in PVC (24.6%), overall. DCI is the most common pipe material in LSC and QN (Figures 4(a) and 4(b)), while GCI dominates in VB, which was not expected since it is a newer neighbourhood (Figure 4(c)). For the period of installation, a high proportion of pipe sections were installed after 1980 in all three neighbourhoods: 59.7% in LSC, 54.8% in QN, and 49.3% in VB. Only 7.3 and 3.3% of pipe sections were installed before 1945 in LSC and QN, respectively, while VB had none.

RESULTS AND DISCUSSION

Number of sampling points after validation

The 65 sampled pipe sections, each with an upstream and downstream sampling point, were visited multiple times (3–5) over the summer to consider possible variabilities in water quality and temperature, resulting in a total of 556 collected samples.

Table 2 | Details of sampling campaigns

Parameter	Number	Comment
Neighbourhood	3	Figure 2
Category	15	Colours in Figure 3
Selected diameter	2	Mostly 150 and 200 mm; three 300-mm pipe sections
Selected materials	3	GCI, DCI, and PVC
Selected period of installation	5	Based on the municipality's development phases
Identified pipe sections	95	Some of them are not accessible
Accessible pipe sections	65	Numbers in Figure 3
Total sampling points	133	Upstream and downstream points of 65 pipe sections and 3 neighbourhood entrances
Sampling days	36	May to August 2021
Sampling time	9–16 h	Tuesday, Wednesday, and Thursday
Water temperature range in the neighbourhoods (for valid data only)	8–23 °C	The coldest day: May 19th, the warmest day: August 25th
Water temperature range at neighbourhood entrances	11.5–22 °C	The coldest day: May 27th, the warmest August: 24th and 25th
Number of samplings at the same point	3–5	Decision based on previous results
Collected samples to obtain k_t	556	3–5 times at upstream/downstream points of 65 pipe sections
Collected samples to obtain k_b	108	3 neighbourhood entrances over 36 days
Collected hermetically sealed water bottles	12	At each sampling from neighbourhood entrances
Total collected samples	664	To obtain total and bulk coefficients
Pipe sections with valid k_t	178	Validation criteria $C_1 > C_2$
Pipe sections with valid k_b	174	Entry point
Pipe sections with valid k_w	152	Validation criteria $k_t > k_b$

However, following the hydraulic (volume and flow) and sampling (concentration) verifications, the total numbers of pipe sections with associated valid data for all the sampling days for the determination of k_t, k_b and k_w coefficients were 178, 174, and 152, respectively. About half of the valid results are related to QN (44.6%), which is the largest neighbourhood in our case study, and the rest are split almost equally between LSC (29.3%) and VB (26.1%).

Statistical analyses of k_t, k_w, and k_b

To determine the most important hydraulic and/or pipe characteristics for chlorine degradation, some statistical analyses between chlorine degradation coefficients and identified hydraulic and/or pipe characteristics were done in the RStudio platform (Version 1.1.456). As the characteristics were independent and their number was more than two, multiple linear regression was chosen for the analyses. Three regressions were done to consider the role of various characteristics affecting k_t, k_w, and k_b. To identify the most important characteristics, the obtained $\Pr(>|t|)$ from the regressions for each characteristic was considered. $\Pr(>|t|)$ is the probability of observing any value equal to or larger than t. If the $\Pr(>|t|)$ is less than a certain significance level, then the regressors (in this study, the characteristics) are said to have a statistically significant relationship with the regressands (k_t, k_w, and k_b). According to Ganesh & Cave (2018), $\Pr(>|t|) < 0.001$ indicates a very strong relationship, while $\Pr(>|t|) < 0.01$ indicates a strong relationship, $\Pr(>|t|) < 0.05$ a moderate relationship, $\Pr(>|t|) < 0.1$ a weak relationship or a trend, and $\Pr(>|t|) \geq 0.1$ indicates no significant relationship. In this study, the significance for all the tests was set at 5% ($\Pr(>|t|) < 0.05$), which is a moderate relationship, considering the high uncertainty associated with full-scale studies. As the characteristics that affect k_t and k_w were different from k_b, the tested regressors were different. The characteristics (regressors) for each regression were chosen based on previous studies and preliminary work.

The first regression was done between k_t (regressand) and the following variables: diameter, period of installation, chlorine concentration in the upstream sampling point (mg/l), and water temperature (°C) as regressors (Table 3). In the

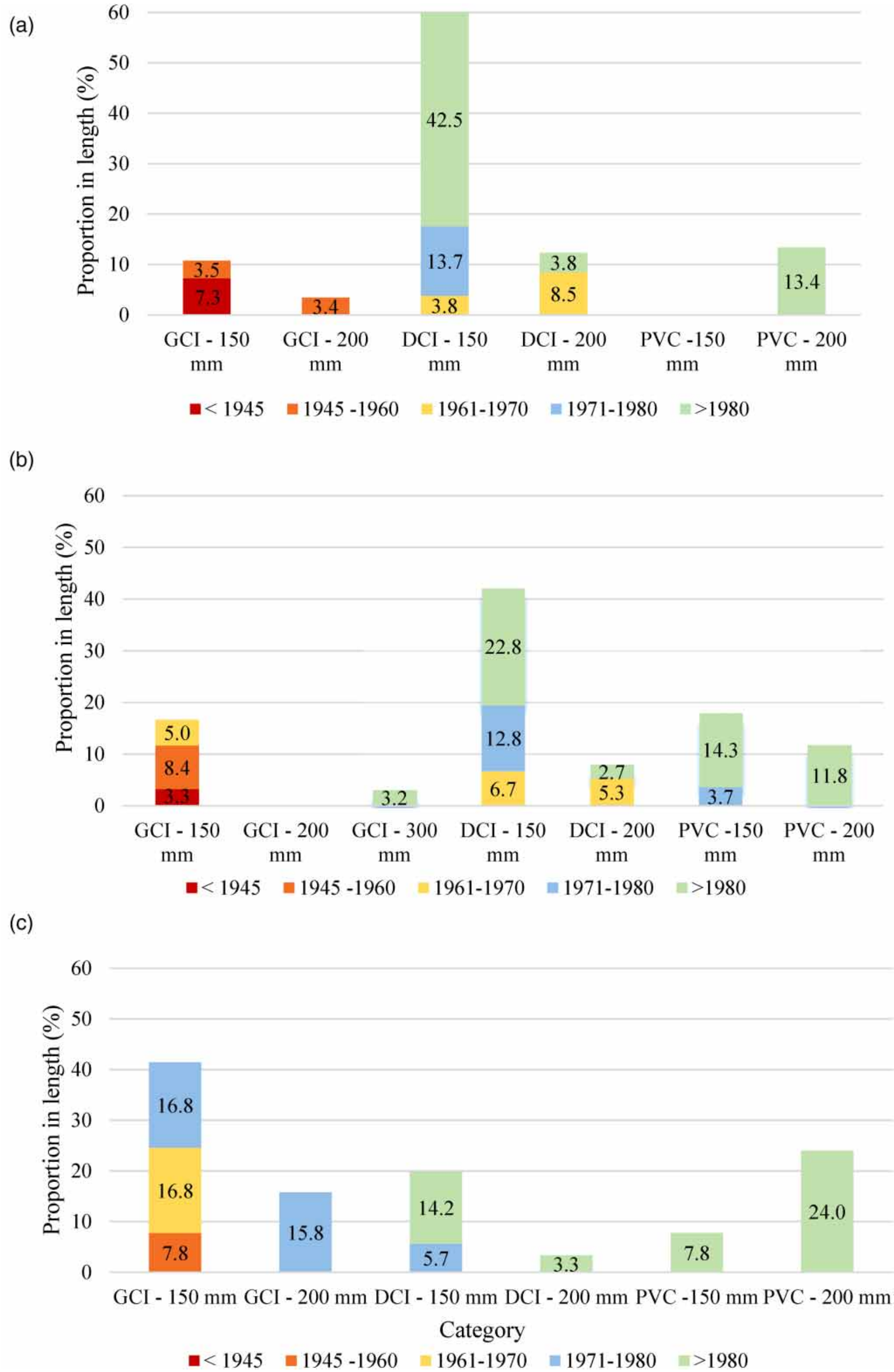

Figure 4 | Proportion in length (%) of the various pipe categories in each neighbourhood: (a) LSC; (b) QN; and (c) VB.

regression results, the period of installation with $\Pr(>|t|) = 8.2 \times 10^{-4}$ is the most important regressor, while pipe diameter with $\Pr(>|t|) = 9{,}730.6 \times 10^{-4}$ has the least impact on k_t in this case. In most residential WDS of this case study, the high representation of 150-mm and 200-mm pipes influences these results.

The second regression was done between k_w as the regressand and its regressors which are the same as in the previous one. Unsurprisingly, the obtained results for k_w are similar to the k_t regression with the period of installation with $\Pr(>|t|) = 8.4 \times 10^{-4}$ being the most important regressor and pipe diameter with $\Pr(>|t|) = 9{,}708.5 \times 10^{-4}$ having the least impact.

Table 3 | Regression results

Pipe/hydraulic characteristics (regressors)	Pr(>|*t*|) Regressands k_t (10^{-3} h^{-1})	k_w (10^{-3} h^{-1})	k_b (10^{-3} h^{-1})
Diameter (mm)	0.973062	0.970851	–
Period of installation (year)	0.000823	0.000838	–
Upstream chlorine concentration (mg/l)	0.035674	0.035653	–
Average water temperature (°C)	0.066298	0.061183	–
Chlorine concentration at the entrance of each neighbourhood (mg/l)	–	–	0.05036
Water temperature at the entrance of each neighbourhood (°C)	–	–	4.71×10^{-9}

The last regression is related to k_b. In this regression, k_b is the regressand and its regressors are water temperature (°C) and chlorine concentration at the entrance of each neighbourhood (mg/l); according to the results, the role of water temperature with Pr(>|*t*|) = 4.7×10^{-9} is significant in the model which previous papers have also confirmed (García-Ávila *et al.* 2020).

The main conclusion for the three neighbourhoods in this case study is that the period of installation affects k_w and k_t significantly. The upstream chlorine concentration also affects the kinetics coefficients to a certain extent, while the pipe diameter does not. For k_b, water temperature, unsurprisingly, has a strong impact and the role of initial chlorine concentration is moderate. Therefore, in the following sections, results were only analysed based on these important characteristics for different neighbourhoods, while the other characteristics (diameter and water temperature), which do not have any special impact on k_w and k_t, were not considered for analyses of them. Moreover, as the material strongly depends on the period of installation, different materials were also considered.

Values of k_b

Values for the k_b coefficients were determined in the laboratory using water samples taken at each main entry point of each neighbourhood on all the sampling days (36 days) and then associated with all pipe sections within the neighbourhood for the calculation of k_w. As was shown in the previous section, the most important characteristics for k_b were water temperature and then C_0. Results for k_b are thus based on these two characteristics. Figures 5(a)–5(c) show the water temperature, C_0 and k_b ranges, respectively, overall and in the three neighbourhoods for the valid data. The box plots in these figures present the minimal value, 1st quartile, median value, 3rd quartile, and maximal value, while the diamonds represent uncertain values. While the water originates from the same water production plant (WPP), water takes different routes to the entry points of the three neighbourhoods, along which the water temperature changes and FRC degrades at different rates. The approximate travel time from the WPP to the three entry points was 4.4 h for LSC, 2.3 h for QN, and 4.9 h for VB for average water demands. As shown in Figure 5(a), water temperature ranged from 13 to 20 °C for LSC and VB over the sampling period and QN had slightly warmer water (13.5–22 °C), although it has the shortest travel time between the WPP and the entry point. As presented in Figure 5(b), the C_0 values at the entry points varied significantly overall (from 0.5 to 1.3 mg/L, with a median value of 0.9 mg/L) and for each neighbourhood, with LSC having the largest value (median of 1.1 mg/L) that can be due to the presence of a chlorine booster station near the entrance of LSC; QN has the smallest median (0.7 mg/L) and the widest range, and VB the narrowest range (median of 0.9 mg/L). The full range of k_b, presented in Figure 5(c), extended from 3.1 to 29.0 (10^{-3} h^{-1}) with a median value between 7.9 and 17.1 (10^{-3} h^{-1}) depending on the neighbourhood. As mentioned above, LSC has the largest value of C_0 which seems to translate to the lowest values of k_b. QN, on the other end, has the lowest median of C_0 and the higher values of k_b. These values are in the same range as those in the lower range of the values reported in Table 1 for k_b reported by Biswas *et al.* (1993), Hallam *et al.* (2002), Al-Jasser (2007), Saidan *et al.* (2017), and McGrath *et al.* (2021). Such low values of k_b reflect a high-water treatment efficiency in removing organic matter. It should be noted that two values in LSC (22.3 and 23.1 10^{-3} h^{-1}), one in QN (87.3 10^{-3} h^{-1}), and one in VB (44.4 10^{-3} h^{-1}) were considered outliers could be caused by inaccuracy in collecting the sample or the laboratory test.

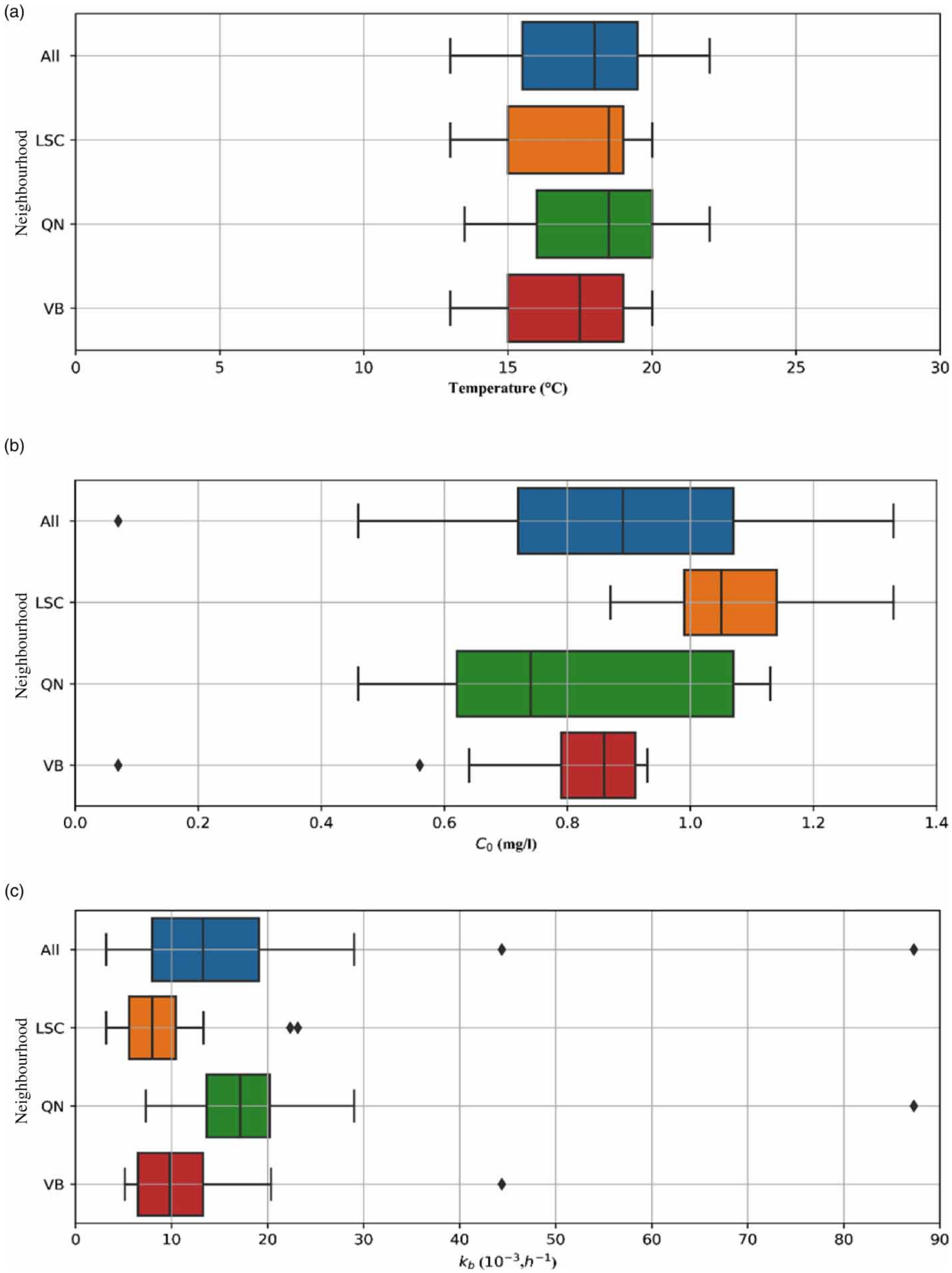

Figure 5 | Range of: (a) water temperature, (b) C_0; and (c) k_b coefficients, overall and by neighbourhood.

Values of k_w

The range of k_w for different categories was compared based on the period of installation which is the most important characteristic according to regressions. For this analysis, it is important to note that different materials were used at different installation periods making it impossible to study these two characteristics independently: GCI is the oldest pipe material (rarely used after 1970 except for replacements), followed by DCI (mostly used after 1970), and PVC is the newest (mostly used after 1980). Figure 6 demonstrates the role of different materials and the period of installation on k_w per neighbourhood and overall. As expected, GCI has the highest values of k_w overall and the widest range, from 2.4 to 3,333.6 10^{-3} h^{-1} (with a median value of 284.0 10^{-3} h^{-1}), followed by DCI (from 0.7 to 1,479.5 10^{-3} h^{-1} with a median value of 78.6 10^{-3} h^{-1}) then PVC (2.2–191.3 10^{-3} h^{-1}, with a median value of 40.4 10^{-3} h^{-1}). Unsurprisingly, the wall degradation of chlorine in metallic pipes like GCI and DCI is more than plastic pipes like PVC. Among metallic pipes in this case study, wall degradation in the older pipe is faster than for newer ones (GCI is more than DCI). Although most of the selected pipes in LSC and QN are DCI, the range of GCI in all the neighbourhoods is higher than other materials. Regarding DCI pipes, their k_w is mostly less than 400 (10^{-3} h^{-1}), although there are some sections with k_w of more than 500 (10^{-3} h^{-1}) in LSC and QN neighbourhoods in the 1970 and 1960 s, respectively, which could be due to inaccuracy in sampling and/or tests. About the PVC pipes, the obtained range of k_w in this case study (2.2–191 10^{-3} h^{-1}) is wider and comprised values obtained by McGrath *et al.* (2021) (8.5–27.5 10^{-3} h^{-1}) and to the value obtained by Hallam *et al.* (2002) (90 10^{-3} h^{-1}). The same holds true for the obtained range of k_w for GCI (2.4–3,333.6 10^{-3} h^{-1}) and DCI (0.7–1,479.5 10^{-3} h^{-1}) in this study, which are also within the range of reported values by McGrath *et al.* (2021) (58.8–114.9 10^{-3} h^{-1} for GCI and 24.9–114.9 10^{-3} h^{-1} for DCI) and close to the value of 130 (10^{-3} h^{-1}) for cast iron reported by Hallam *et al.* (2002). The differences between the obtained values in this study and the literature can be due to the limitation of the case study and the number of samplings in previous ones. Water temperatures in McGrath *et al.* (2021) were in the 11–14 °C range, while, in this study, they were between 10.2 and 22.2 °C, which can affect the range of k_w. Generally, in our case study, the wide range of k_w is observed when there were not many sections in some categories.

Proportion of chlorine degradation from k_w and k_b

In order to evaluate the role of bulk volume and pipe walls on FRC degradation, the relative proportion of k_w and k_b for each category was compared. As the sampling was done several times for each pipe section, firstly, the percentage of k_w and k_b for

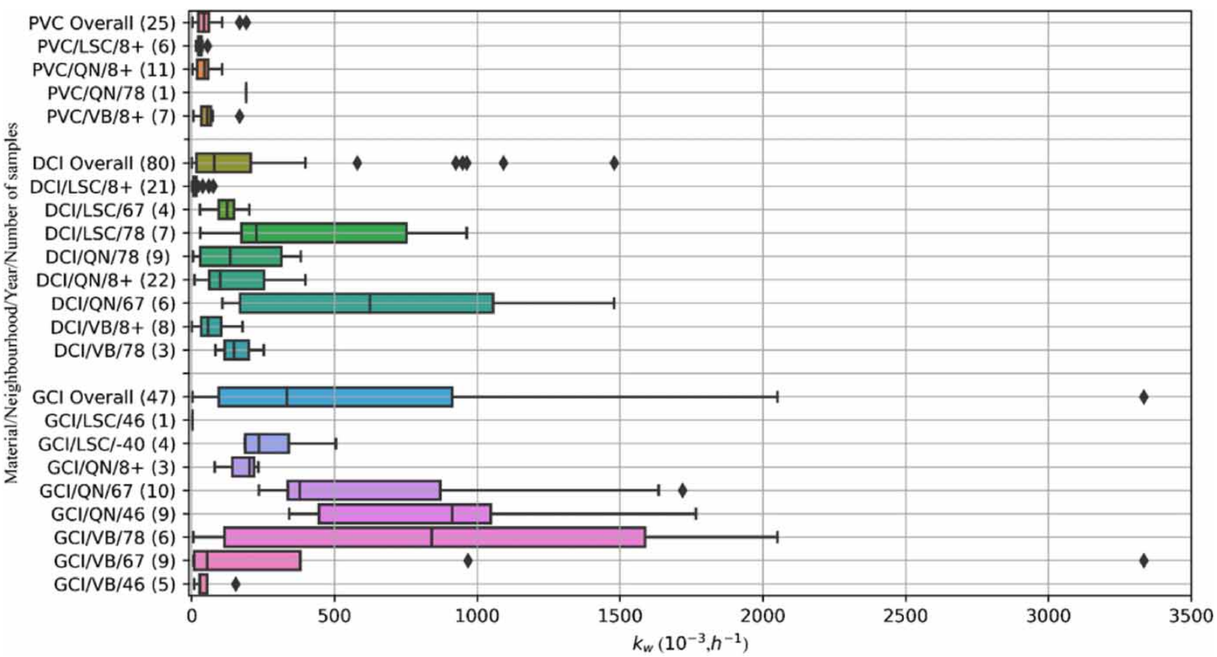

Figure 6 | k_w coefficient ranges for the different pipe categories overall and per neighbourhood with the number of pipe sections in parentheses.

each pipe section was calculated. Then, the average of k_w and k_b for different pipe sections for each category was calculated (Figure 7). As statistical analyses have shown, pipe ageing plays a vital role in pipe wall chlorine degradation: for pipes installed before 1945, the major proportion of chlorine degradation is due to k_w, while the wall chlorine degradation for newer pipes (after 1980) is much less than the older ones but still dominates the chlorine degradation kinetics. However, two pipe categories stand out in Figure 7: 'PVC-1970 to 80' showed higher pipe wall degradation than expected, but there is only one pipe section in this category and pipe sections in 'GCI-1945 to 60' showed less pipe degradation than expected, which could be due to rehabilitation works not logged in the database for some of these pipes. Furthermore, DCI pipes might not have had an interior coating before 1970, which could explain why the ones in category 'DCI-1960 to 70' have high pipe wall degradation.

CONCLUSION

This paper considered different pipe categories in a real case study (Quebec City's main WDS) to estimate the range of k_w, k_b, and their proportion in FRC degradation and identify which parameters have significant impacts on the degradation. Thirty-six 1-day sampling campaigns in the summer of 2021 (from May to August) in three neighbourhoods were performed. Results demonstrated that (i) the proposed methodology can be used to estimate k_w and k_b in real-scale WDS, (ii) the use of pipe categories allows to better identify the impact of the period of installation on k_w; (iii) the regressions showed that the period of installation is the most important factor that impacts k_t and k_w, (iv) the statistical analyses also showed that, considering the high proportion of 150-mm and 200-mm pipes in the sampling, diameter does not impact the degradation coefficients significantly, so 150 and 200 mm diameter pipes have similar k_w, (v) the ranges of k_b and k_w based on the most important characteristics (water temperature and chlorine concentration at the entrance of each neighbourhood for k_b; material and period of installation for k_w) were obtained, and (vi) the degradation at the pipe walls for GCI (median of 284 h^{-1}) is much higher than for DCI (median of 78.6 h^{-1}) and PVC (median of 40.4 h^{-1}). GCI pipes are both older and metallic, two factors that impact chlorine degradation. In older pipes (GCI installed before 1945), up to 97.7% of FRC can be degraded at the pipe walls, while the role of bulk reactions can reach 34.8% in newer pipes (plastic installed after 1980). Accepting up to a 25% difference in volumes and flows between the EPANET hydraulic model and flow meter data during validation might seem substantial, but it is often a drawback of working with full-scale case studies.

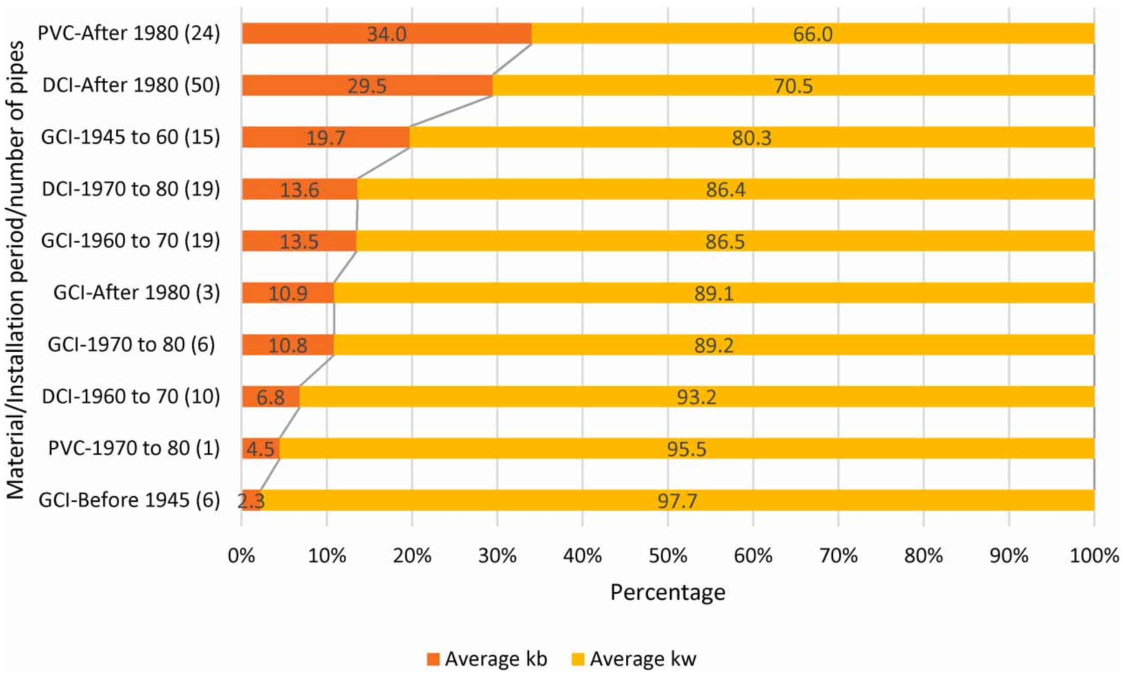

Figure 7 | Proportion of k_w and k_b in the degradation of FRC according to the pipe material and the period of installation.

Generating knowledge about bulk and wall chlorine degradation coefficients for different pipe categories and identifying the most important pipe characteristics that affect them are key to good decision-making such as identification of pipes for rehabilitation, renewal, and rechlorination. Future studies should focus on recognizing parts of WDS with low chlorine concentrations (vulnerable zones), finding the most cost-effective solutions to minimize chlorine degradation and vulnerable zones like improving water treatment at the plant to reduce organic matter content, optimise chlorine injection at the water treatment plant, and perform occasional or systematic rechlorination at key locations in the network.

DATA AVAILABILITY STATEMENT

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

CONFLICT OF INTEREST

The authors declare there is no conflict.

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First received 23 August 2022; accepted in revised form 19 January 2023. Available online 31 January 2023