

Faculté des bioingénieurs

Development of a field method for measuring river alkalinity

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Année académique 2025-2026

Mémoire de fin d'études présenté en vue de l'obtention du diplôme de Bioingénieur en chimie et bio-industries, à finalité spécialisée

Acknowledgements

First and foremost, I would like to thank my supervisor, Professor Pierre Delmelle. I still remember our first meeting last March, when you introduced me to this method and told me you were delighted that I was interested in it, apparently the only one. At the time, my main concern was that there would not be enough to investigate on the subject. I thought it would simply be a matter of adding excess acid and observing a pressure increase proportional to alkalinity, just as theory predicts. I was naïve.

I sincerely thank Matthieu Leclercq, who supported me throughout this work, both during laboratory preparations and in the field. Thank you for your good humour, your positivity, and your constant willingness to look for and propose solutions. It was a real pleasure working with you.

Many thanks to the MOCA platform, particularly Karine Henin, who took the time to show me how alkalinity measurements are performed and who was always available to answer my questions. I would also like to thank H  l  ne Dailly for sharing her workspace with me during these past months.

I would like to thank my readers for the time they will devote to this work. It is both a privilege and a genuine pleasure for me that Professor Christine Dupont, an emblematic and inspiring professor since my first year at university, will review my thesis. I would also like to thank Professor Patrick Gerin; I hope this work will meet your expectations, and I am equally grateful for the last-minute meeting you kindly organised.

My family, who have always supported me wholeheartedly in everything I undertake. Je ne doute pas que vous serez au premier rang à ma défense, même si comme vous aimez le dire vous-mêmes, vous n'y comprendrez rien. Merci d'être là pour moi.

A special thanks to my brother for proofreading my dissertation just before submission. It is always reassuring to have your approval before handing in such an important piece of work.

Célestin, I don't forget you. Even if those last few days you betrayed me to go to Switzerland to chill out, you have been so much support during this last year. Thank you for your kindness, your patience and the great breaks we spent together.

CRediT	Daphnis Lucie	Contributors	Artificial intelligence
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Validation	X	P.D.	
Redaction – first draft	X		X
Redaction – revision and edition	X	P.D.	X
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- Conceptualisation: developing the main research idea, formulating objectives and hypotheses;
- Methodology: designing the research protocol, selecting analytical methods;
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- Formal analysis: applying statistical, mathematical or other formal methods to analyse or synthesise the research data;
- Validation: verification and confirmation of results, replication of analyses;
- Redaction – first draft: drafting the first version of the manuscript;
- Redaction – revision and editing: revision and correction of both the intellectual content and the form;
- Visualisation: preparation, creation and/or presentation of the visual elements of the published work, in particular the representation of data;
- Supervision: responsibility for the direction and supervision of research activities, including planning and execution.

Use of artificial intelligence:

Chat GPT, M365 Copilot and Gemini were used for translation to English and to improve formulation.

Claude AI was used to generate multivariable graphs and Chat GPT was used to create images.

Table of contents

Acknowledgements	ii
CRedit	iii
Table of contents	iv
List of figures	vii
List of tables	x
List of appendix figures	xi
List of appendix tables	xii
Abbreviations	xv
1 Introduction.....	1
2 Literature review	3
2.1 Introduction to alkalinity and its importance in aquatic ecosystems.....	3
2.2 Alkalinity measurement methods	7
2.2.1 Standard analytical methods	7
2.2.2 Alternative analytical methods	10
Spectrophotometric methods	11
Total organic carbon analyser-based methods	11
Headspace method: a field method based on pressure measurements	11
3 Objectives.....	14
4 Methodological framework.....	15
4.1 Theoretical approach: estimation of CO ₂ headspace pressure following strong acid addition.....	15
4.2 Laboratory reference method: two end-points titration.....	16
4.3 Optimization of the headspace method's apparatus and protocol.....	17
4.4 Development and assessment of the analytical performance of the headspace method	17
5 Estimation of the CO₂(g) pressure in the headspace after strong acid addition	19
6 Materials and apparatus	22
6.1 Materials.....	22
Necessary materials.....	22
Backup materials.....	22
6.2 Apparatus	23

6.3	Seal integrity of the four apparatuses.....	24
6.4	Effect of pressure gauge connection and disconnection	24
6.5	Determination of the Schott bottle volume.....	25
7	Headspace method protocol	26
7.1	Direct calibration protocol	26
7.2	Standard addition protocol	28
7.3	Protocol optimization.....	29
7.3.1	Reduction of the injected volume.....	29
7.3.2	Injection of acid only instead of an acid-air combination	29
7.3.3	Temperature effects on thermodynamic equilibria in the headspace apparatus.....	30
7.3.4	Proper zero-pressure reference.....	32
7.3.5	Recording of p_{inj} for the standard addition method	33
7.3.6	Overview of protocol modifications and their stage of implementation	33
7.4	Determination of the required number of agitation cycles.....	33
7.5	Wang et al. protocol.....	35
8	Assessment of the headspace method on synthetic solutions	37
8.1	Calibrations and injection effects.....	37
8.2	Determination of the limit of detection and of the limit of quantification	39
9	Qualitative assessment of the headspace method on river and bottled water samples	42
9.1	Alkalinity determination on river water using direct calibration.....	42
9.2	Alkalinity determination on river water using standard addition	44
9.3	Alkalinity determination on bottled water brands using direct calibration and standard addition	47
10	Quantitative assessment of the headspace method on river and bottled water samples	49
10.1	Alkalinity determination results on river water using direct calibration and standard addition.....	49
10.2	Alkalinity determination results on bottled waters using direct calibration and standard addition	54
10.3	Discussion of the results obtained, considering the factors known to influence the headspace method	55
11	Conclusion	58
12	Perspectives.....	60

Appendices.....	63
Appendix 1 – Alkalinity conversion from $\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$ to conventional units	63
Appendix 2 – Verification of acid excess conditions for complete DIC conversion	64
Appendix 3 - Theoretical pressure estimation spreadsheet	65
Appendix 4 - Seal integrity of the four apparatuses.....	66
Appendix 5 - Agitation optimization: pressure data and statistical analysis	67
Appendix 6 - Evaluation of the Wang et al. (2014) protocol.....	69
Appendix 7 - Repeatability of TA measurements by two end-points titration	70
Appendix 8 - Raw pressure and alkalinity data from the first field measurements using the DC method	71
Appendix 9 - Standard addition data and regression plots for all replicates at the Orne and Houssière sampling sites	72
Appendix 10 - Raw data and summary tables for alkalinity measurements on bottled water brands using the DC and SA methods	76
Appendix 11 - Summary of alkalinity results and associated errors for the DC, ΔDC and SA methods across the five studied rivers.....	80
Appendix 12 - Summary of alkalinity results and associated errors for the DC, ΔDC and SA methods for the two bottled water brands	81
References.....	82

List of figures

Figure 1 - Relative distribution (%) of DIC species as a function of pH.....	4
Figure 2 - Carbon movement through a lake ecosystem (Franco-Cisterna et al., 2024).	5
Figure 3 - Carbon chemistry system (Ahmad et al., 2024).	5
Figure 4 - Titration curves obtained by standard alkalinity titration for two contrasting samples. (A) shows a curve with a clear, identifiable endpoint, whereas (B) corresponds to a sample with a total organic acid concentration of $\sim 100 \text{ mg}\cdot\text{L}^{-1}$, where the endpoint appears smeared and cannot be reliably identified (adapted from Kan et al., 2013).	8
Figure 5 - Calcium carbonate solubility ($\text{mg}\cdot\text{L}^{-1}$) as a function of bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$), calcium concentration ($\text{mg}\cdot\text{L}^{-1}$) and pH, produced with Claude Al.	9
Figure 6 - Schematic representation (left) and photograph (right) of the headspace method apparatus, adapted from Wang et al. (2014).	12
Figure 7 - Schematic representation of the equilibria governing DIC species and CO_2 transfer to the headspace after acid addition. Image generated with Chat GPT.	16
Figure 8 - Theoretical pressure in the headspace as a function of bicarbonate concentration at 21°C , for 1.5 mL injected (blue) and for 0.8 mL injected (orange).	21
Figure 9 - Photographs of the alkalinity measurement preparation materials. From left to right: graduated cylinder and Pasteur pipette used to collect 100 mL water samples; concentrated acid with syringe and needle used for acid injection.	23
Figure 10 - Photographs of the alkalinity measurement apparatus. From left to right: apparatus placed in a metal container filled with river water; apparatus in the river with bottle weights.	23
Figure 11 - Photographs of the cap showing the pressure gauge connector, the connector equipped with a valve and a polycarbonate tube for acid injection and the red plastic component used to screw the cap onto the bottle.	24
Figure 12 - Pressure (mbar) measured in an apparatus initially pressurized to ~ 30 mbar as a function of repeated connection and disconnection cycles of the pressure gauge (10 cycles).	24
Figure 13 - Acid remaining in the tube after injection.	29
Figure 14 - Zones where water/debris can get stuck.....	32
Figure 15 - Air injection using a 100 mL syringe to restore zero pressure by expelling residual water from the connectors.	32
Figure 16 - Pressure (mbar) as a function of cumulative agitation time (s) for four bicarbonate concentrations. Values obtained at 21°C with an injected volume of 0.5 mL acid and 0.3 mL air. $p_{30''}$ corresponds to the pressure measured after 30 s of agitation followed by 30 s of stabilization. The final pressure value ($P_{120'' + 240''}$) corresponds to a total of 120 s of mixing (four cycles of 30-30 s) followed by 240 s of stabilization.	34
Figure 17 - Pressure (mbar) as a function of cumulative agitation time (s) for a bicarbonate concentration of $200 \text{ mg}\cdot\text{L}^{-1}$ ($n = 4$). Values obtained at 21°C with an injected volume of 0.5 mL acid and 0.3 mL air.	34

Figure 18 - Pressure (mbar) as a function of measurement stage for a bicarbonate concentration of 200 mg·L ⁻¹ (n = 4). Values obtained at 21 °C with an injected volume of 0.5 mL acid and 0.3 mL air. p_0' corresponds to the pressure measured with the acid injection valve open. p_{ac} is the pressure recorded immediately after acid injection. $p_{15''}$ is the pressure measured after 15 seconds of continuous agitation, etc.	35
Figure 19 - Measured vs actual CA (mg·L ⁻¹) obtained using the Wang <i>et al.</i> protocol.	36
Figure 20 - Measured pressure (mbar) as a function of CA (mg·L ⁻¹) for a total injected volume of 1.5 mL; ~1.0 mL of acid and ~0.5 mL of air and for a total injected volume of 0.8 mL; ~0.5 mL of acid and ~0.3 mL of air, along with the corresponding theoretical lines.	38
Figure 21 - Measured pressure (mbar) as a function of CA (mg·L ⁻¹) for concentrations ranging from 0 to 50 mg·L ⁻¹ , used for LOD and LOQ determination (three independent sessions). ...	40
Figure 22 - Comparison of the alkalinity (mg·L ⁻¹) obtained using the DC method and the alkalinity (mg·L ⁻¹) obtained using the two end-points titration method for the five studied rivers. Colours indicate rivers, dots represent individual replicate measurements, black crosses indicate mean values and error bars correspond to SD. TA measurements obtained in the laboratory are represented by diamond symbols.	43
Figure 23 - First replicate of the alkalinity measurement at the Orne using the SA method: measured pressure (mbar) as a function of the amount of bicarbonate added to the sample (mg·L ⁻¹), along with the linear regression and the associated upper and lower CI extrapolated to y = 0.	45
Figure 24 - Alkalinity measurements (mg·L ⁻¹) using the SA method at the Orne and using the two end-points titration method in the laboratory.	46
Figure 25 - Alkalinity measurements (mg·L ⁻¹) using the SA method at the Houssière and using the two end-points titration method in the laboratory.	46
Figure 26 - Alkalinity measurements using the DC method, the SA method and the two end points titration method in the laboratory on bottled water brands along with the bicarbonate concentration on the bottle's label.	48
Figure 27 - Map of water hardness (hydrometric title, °f) by distribution area, adapted from Calceo.be (original data sourced from SPW), with the sampled sites indicated: (1) Orne, (2) Houssière, (3) Rau du Brou, (4) Lesse, and (5) Meuse.	50
Figure 28 - CA (mg·L ⁻¹) measured with the headspace method for five rivers. Each river is represented by a distinct colour. Dots show DC replicates (mean ± SD: black cross). Stars show ΔDC (same representation). Triangles denote SA (± SD) and diamonds TA measured in the laboratory.	51
Figure 29 - DC and ΔDC calibration curves and measurements for (A) Orne, (B) Houssière, (C) Rau du Brou, (D) Lesse and (E) Meuse.	53
Figure 30 - CA (mg·L ⁻¹) measured with the headspace method for two bottled waters. Each bottled water is represented by a distinct colour. Dots show DC replicates (mean ± SD: black cross). Stars show ΔDC (same representation). Triangles denote SA (± SD), diamonds TA measured in the laboratory and a square indicates the HCO ₃ ⁻ concentration on the label.	54
Figure 31 - Regression lines of the theoretical pressure (mbar) as a function of CA (mg·L ⁻¹) for a liquid volume (V _l) of 100 mL (blue) and 200 mL (orange).	60

Figure 32 - Conceptual illustration of the proposed floating support system for the headspace apparatus. Image generated with ChatGPT.	61
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List of tables

Table 1 - Overview of protocol modifications and their stage of implementation. –: not applicable; X: accounted for; 0: not accounted for. *: 0 = The metal container placed in the river was used.	33
Table 2 - Experimental pressure (mbar) vs. theoretical pressure (mbar; total pressure and CO ₂ partial pressure), for a total injected volume of 1.5 mL; ~1.0 mL of acid and ~0.5 mL of air and for a total injected volume of 0.8 mL; ~0.5 mL of acid and ~0.3 mL of air.	39
Table 3 - Characteristics of the five rivers studied for the first alkalinity measurements using the DC method: coordinates, conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$), temperature ($^{\circ}\text{C}$) and pH. The pH values are likely overestimated by approximately 0.5 pH unit.	42
Table 4 - Characteristics of the two rivers studied for the first alkalinity measurements using the SA method: coordinates, temperature ($^{\circ}\text{C}$) and pH.	44
Table 5 - Characteristics of the five rivers studied for the final alkalinity measurements using DC, ΔDC and SA methods: coordinates, conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$), temperature ($^{\circ}\text{C}$) and pH. ...	50
Table 6 - Overview of the advantages and limitations of the DC and SA methods.	58

List of appendix figures

Figure A1 - Spreadsheet used for the theoretical estimation of CO ₂ pressure in the headspace as a function of bicarbonate concentration.....	65
Figure A2 - Standard addition regression plots for all replicates at the Orne (A–D) and Houssière (E–F) sampling sites. (A) and (B): solid NaHCO ₃ addition (Eppendorf); (C) and (D): aqueous NaHCO ₃ addition; (E): solid NaHCO ₃ addition (Eppendorf); (F): aqueous NaHCO ₃ addition. The x-axis represents the added bicarbonate concentration (mg·L ⁻¹) and the y-axis represents the measured pressure (mbar).	73

List of appendix tables

Table A1 - Alkalinity ($\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$) conversion to conventional units	63
Table A2 - Pressure loss measured over 3 hours for each of the four apparatuses, initially pressurized to approximately 200 mbar. The observed pressure loss and relative deviation are reported for each apparatus.	66
Table A3 - Pressure (mbar) as a function of cumulative agitation time for four bicarbonate concentrations (30 s cycles)	67
Table A4 - Paired t-test results for successive 30 s agitation cycles: comparison of pressure values between consecutive measurement stages.	67
Table A5 - Pressure (mbar) as a function of cumulative agitation time for a bicarbonate concentration of $200 \text{ mg}\cdot\text{L}^{-1}$ in quadruplicate (15 s cycles)	67
Table A6 - Paired t-test results for successive 15 s agitation cycles: comparison of pressure values between consecutive measurement stages.	67
Table A7 - Pressure (mbar) as a function of measurement stage for a bicarbonate concentration of $200 \text{ mg}\cdot\text{L}^{-1}$ in quadruplicate (continuous agitation).....	68
Table A8 - Experimental data obtained using the Wang et al. (2014) protocol, including recorded pressures at each measurement step ($p^{\text{step } 2}$, $p^{\text{step } 3}$, $p^{\text{step } 4}$), measured alkalinity ($\text{mg}\cdot\text{L}^{-1}$), and associated CV.	69
Table A9 - Repeated TA measurements ($\text{mg}\cdot\text{L}^{-1}$) for five bicarbonate solutions of known concentration ($n = 5$), with associated standard deviation.	70
Table A10 - Repeated TA measurements ($\text{mg}\cdot\text{L}^{-1}$) for five commercial bottled waters ($n = 3$), with associated standard deviation.	70
Table A11 - Repeated TA measurements ($\text{mg}\cdot\text{L}^{-1}$) for five river water samples ($n = 2$), with associated standard deviation.	70
Table A12 - Raw pressure data (mbar) obtained during the first field measurements using the DC method. R indicates rejected values.	71
Table A13 - Raw alkalinity data ($\text{mg}\cdot\text{L}^{-1}$) obtained during the first field measurements using the DC method. R indicates rejected values.	71
Table A14 - Summary of pressure and alkalinity values ($\text{mg}\cdot\text{L}^{-1}$) obtained in the field using the DC method, alkalinity measured in the laboratory by two end-points titration, and associated relative error.	71
Table A15 - Standard addition data for replicate 1 at the Orne site (solid NaHCO_3 , Eppendorf).	73
Table A16 - Standard addition data for replicate 2 at the Orne site (solid NaHCO_3 , Eppendorf).	73
Table A17 - Standard addition data for replicate 3 at the Orne site (aqueous NaHCO_3 solution).	73
Table A18 - Standard addition data for replicate 4 at the Orne site (aqueous NaHCO_3 solution).	74

Table A19 - Summary of CA values ($\text{mg}\cdot\text{L}^{-1}$) determined by the SA method for all replicates at the Orne site, including individual and mean results, coefficient of variation, absolute and relative errors compared to TA.	74
Table A20 - Standard addition data for replicate 1 at the Houssière site (solid NaHCO_3 , Eppendorf).....	74
Table A21 - Standard addition data for replicate 2 at the Houssière site (aqueous NaHCO_3 solution).....	74
Table A22 - Summary of CA values ($\text{mg}\cdot\text{L}^{-1}$) determined by the SA method for all replicates at the Houssière site, including individual and mean results, coefficient of variation, absolute and relative errors compared to TA.	75
Table A23 - Standard addition data for Spa: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).....	76
Table A24 - DC measurements for Spa: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).	76
Table A25 - Standard addition data for Vittel: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).....	76
Table A26 - DC measurements for Vittel: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).	76
Table A27 - Standard addition data for Chaudfontaine: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).	77
Table A28 - DC measurements for Chaudfontaine: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).....	77
Table A29 - Standard addition data for Evian: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).....	77
Table A30 - DC measurements for Evian: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).	77
Table A31 - Standard addition data for Contrex: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).	77
Table A32 - DC measurements for Contrex: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).	78
Table A33 - Individual DC measurements ($\text{mg}\cdot\text{L}^{-1}$), mean DC value, standard deviation and coefficient of variation for the five bottled water brands.	78
Table A34 - SA measurements ($\text{mg}\cdot\text{L}^{-1}$), standard deviation and coefficient of variation for the five bottled water brands.....	78
Table A35 - Comparison of mean DC and SA values with TA: absolute and relative errors for the five bottled water brands.	79
Table A36 - Comparison of labelled HCO_3^- concentrations with TA values: absolute and relative errors for the five bottled water brands.	79

Table A37 - Mean DC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation and coefficient of variation, and absolute and relative errors compared to TA for the five studied rivers.	80
Table A38 - Mean ΔDC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation and coefficient of variation, and absolute and relative errors compared to TA for the five studied rivers.	80
Table A39 - SA values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation and coefficient of variation, and absolute and relative errors compared to TA for the five studied rivers.	80
Table A40 - Mean DC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation, coefficient of variation, and absolute and relative errors compared to TA for Spa and Chaudfontaine.....	81
Table A41 - Mean ΔDC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation, coefficient of variation, and absolute and relative errors compared to TA for Spa and Chaudfontaine.....	81
Table A42 - SA values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation, coefficient of variation, and absolute and relative errors compared to TA for Spa and Chaudfontaine.....	81

Abbreviations

ANC	Acid-neutralizing capacity
CA	Carbonate alkalinity
CI	Confidence interval
CV	Coefficient of variation
DC	Direct calibration
DIC	Dissolved inorganic carbon
LOD	Limit of detection
LOQ	Limit of quantification
SA	Standard addition
SD	Standard deviation
SI	Saturation index
SPW	Service public de Wallonie
TA	Total alkalinity

1 Introduction

Alkalinity is a key parameter in aquatic ecosystems, as it helps maintain pH within a biologically favourable range, typically between 4.5 and 9 (Stumm and Morgan, 2012). Acting as a buffer system, it limits pH fluctuations caused by external disturbances (e.g. acid rain), thereby ensuring stable conditions for aquatic life. This stability is essential for the proper functioning of biological activities and the maintenance of ecosystem structure. Furthermore, alkalinity is closely linked to geochemical processes, including the weathering, dissolution and precipitation of minerals (e.g. carbonates and silicates), which regulate water chemistry and contribute to the overall balance of the aquatic ecosystem (Dunnivant, 2005).

Alkalinity, which is defined as water's ability to neutralize acids, can be measured either in the laboratory or directly in the field, both approaches having their advantages and limitations (Ahmad et al., 2024). Laboratory methods are generally more precise and reliable. However, they require transporting samples, which can lead to significant changes in alkalinity. In particular, carbonate alkalinity (CA) defined as the alkalinity contributed by bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) species, is not stable: during transport from the sampling site to the laboratory, samples may undergo degassing (loss of CO_2 and H_2S), resulting in an increase in pH. This pH shift can trigger secondary chemical reactions, namely the precipitation of minerals like calcium carbonate (CaCO_3) or iron carbonate (FeCO_3) before analysis is performed (Rounds and Wilde, 2012). Therefore, the measured alkalinity may be artificially reduced. Field measurements, like colorimetric methods, are performed directly in the field after sample collection, thereby minimizing errors related to transport and storage. However, these methods are generally less precise, as they rely on the operator's visual interpretation. In addition, they can be relatively impractical under field conditions due to equipment requirements and long handling time (Somridhivej and Boyd, 2016).

Wang et al. (2014) developed another method for measuring alkalinity in oilfield produced waters, i.e. saline wastewaters generated during oil and gas extraction and production processes. This approach, called the headspace method, is based on measuring the pressure generated after the addition of an excess of strong acid to a water sample contained in a sealed container. The acid converts dissolved inorganic carbon (DIC; HCO_3^- and CO_3^{2-}) into carbon dioxide (CO_2) which spread into the headspace of the container and generates a measurable pressure increase. The method was designed to rapidly evaluate CA onsite, to predict carbonate scaling and corrosion risks affecting pipelines, wells and production equipment.

A subsequent study (Liu et al., 2023) further confirmed the accuracy and practical applicability of the method under field conditions. The authors demonstrated good agreement with conventional alkalinity measurements while emphasizing the advantages of rapid analysis, operational simplicity and eliminating degassing during sample transport and storage. However, the method has so far remained restricted to oilfield-produced waters and highly mineralized brines which typically exhibit relatively high alkalinity values, often several hundreds to several thousands of $\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$. In addition, Liu et al. (2023) reported analytical

limitations at low bicarbonate concentrations, below $\sim 100 \text{ mg}\cdot\text{L}^{-1} \text{ HCO}_3^-$, where pressure variations become difficult to resolve accurately.

While the headspace method has been validated for high-alkalinity, high-ionic-strength waters (Wang et al., 2014; Liu et al., 2023), its applicability to natural freshwater systems, which typically exhibit lower alkalinity (generally $10\text{--}350 \text{ mg}\cdot\text{L}^{-1} \text{ HCO}_3^-$; Nisbet and Verneaux, 1970) and lower ionic strength, has not yet been established. Especially since a significant proportion of surface freshwater's alkalinity falls within the low-concentration range ($<100 \text{ mg}\cdot\text{L}^{-1} \text{ HCO}_3^-$) identified by Liu et al. (2023) as analytically challenging. Given the essential role of alkalinity in assessing freshwater ecosystem health, there is a demand for rapid, reliable, and field-deployable methods to monitor this parameter (Wetzel, 2001). Current techniques, such as titration or laboratory-based analyses, are often time-consuming or may introduce errors due to transport and storage.

A validated headspace method could address these limitations by enabling rapid alkalinity measurements in situ. Consequently, the present work aims to evaluate the validity of the headspace method for surface freshwater, optimize the experimental protocol, assess the method under varying environmental and analytical conditions and investigate the possibility of lowering the current limit of quantification (LOQ).

2 Literature review

2.1 Introduction to alkalinity and its importance in aquatic ecosystems

The concept of alkalinity first appeared in the context of marine chemistry during the Challenger expedition of 1872–1876 (Dickson, 1992). Since then, the term has been refined into three distinct but related concepts. Total alkalinity (TA) encompasses all species with acid-base properties present in a filtered water sample, while CA refers specifically to the case where only bicarbonate and carbonate species are considered. A third concept, organic alkalinity, arises from biochemical processes in natural waters, as the composition of these waters is controlled by a combination of geochemical and biological processes (Muller and Bleie, 2008). Alkalinity is distinguished from acid-neutralizing capacity (ANC), which is determined on an unfiltered sample including particulates, whereas alkalinity is measured on a sample filtered through a 0.45- μm pore size membrane or smaller (Rounds and Wilde, 2012).

TA represents the equivalent sum of all dissolved species capable of accepting protons (H^+) relative to a defined zero proton condition (reference level), which corresponds to the dominant protonated forms of weak acids at the CO_2 equivalence point ($\text{pH} \sim 4.5$). This reference level, where species like H_2CO_3 , H_2O , H_2PO_4^- , and NH_4^+ are considered neutral, standardizes the calculation by quantifying only the excess bases that can buffer added protons, as expressed by the comprehensive equation (Stumm and Morgan, 2012):

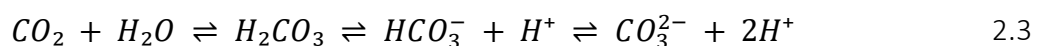
$$\begin{aligned} [\text{Alk}] = & [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{NH}_3] + [\text{HS}^-] + 2 [\text{S}^{2-}] + [\text{H}_3\text{SiO}_4^-] \\ & + 2 [\text{H}_2\text{SiO}_4^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{Org}^-] + [\text{HPO}_4^{2-}] + 2 [\text{PO}_4^{3-}] \\ & - [\text{H}_3\text{PO}_4] + [\text{OH}^-] - [\text{H}^+] \end{aligned} \quad 2.1$$

Despite this extensive list of potential contributors, alkalinity in most natural water systems is primarily governed by the carbonate system, with bicarbonate and carbonate ions being the main buffering agents (Wetzel and Likens, 2000; Wolf-Gladrow et al., 2007). Consequently, for many applications, alkalinity is simplified to the concentrations of bicarbonate, carbonate, and hydroxide and TA is often considered equivalent to CA in freshwater systems (Stumm and Morgan, 2012):

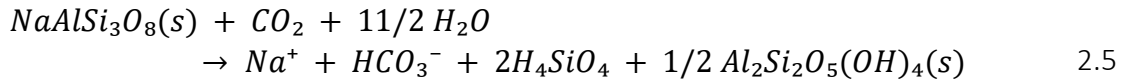
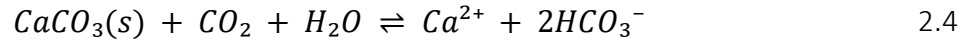
$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad 2.2$$

However, this equivalence does not hold in seawater, where additional contributors such as borate ions ($\text{B}(\text{OH})_4^-$) significantly contribute to TA (Anderson and Robinson, 1946).

Carbon dioxide from the atmosphere dissolves in rainwater droplets and forms carbonic acid (H_2CO_3), which is a weak acid ($\text{pK}_{a1} = 6.35$). It dissociates into bicarbonate and hydrogen ion; bicarbonate can further dissociate into carbonate and additional hydrogen ion. This equilibrium is expressed as follows (Michałowski and Asuero, 2012):



Thus, H_2CO_3 in rainwater acts as a source of H^+ for acid-base reactions responsible for chemical weathering of the Earth's crust rocks, according to the following general reactions (Stumm and Morgan, 2012):



Reactions 2.4 and 2.5 illustrate the dissolution of carbonates and silicate rocks, respectively.

The distribution of DIC species in aqueous systems is controlled by pH. Below pK_{a1} (≈ 6.35), dissolved CO_2 and carbonic acid (H_2CO_3^* ; Equation 2.6) predominate. Between pK_{a1} and pK_{a2} (≈ 6.35 – 10.33), bicarbonate becomes the dominant species, whereas above pK_{a2} (≈ 10.33), carbonate ions prevail. The carbonate speciation as a function of pH is shown in Figure 1. Since the pH of most freshwater systems typically ranges from 6.5 to 8.5, bicarbonate generally represents the principal contributor to alkalinity (Stumm and Morgan, 2012).

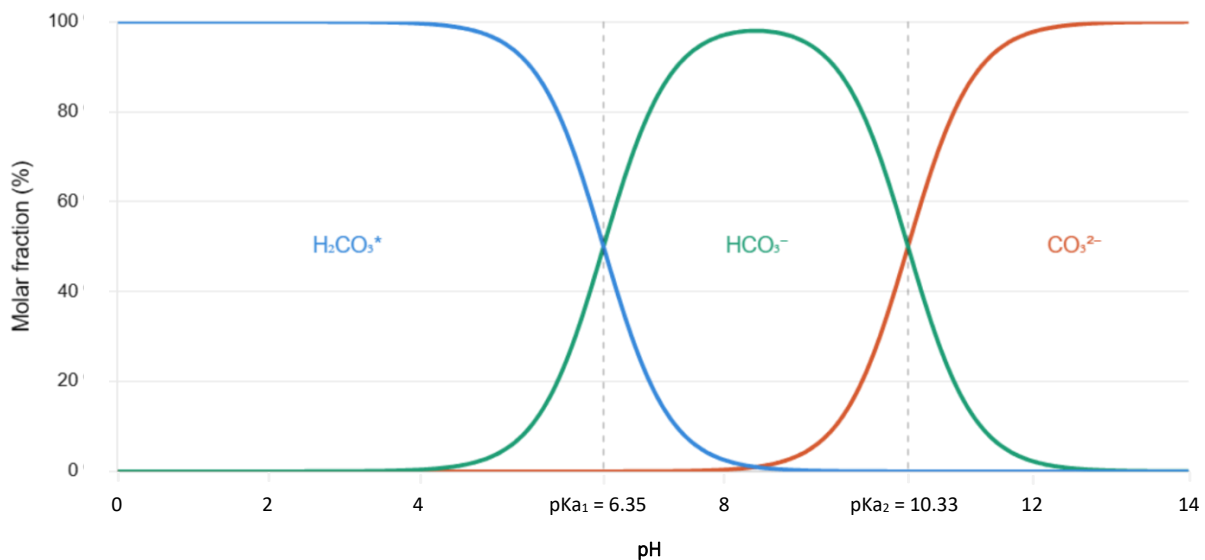
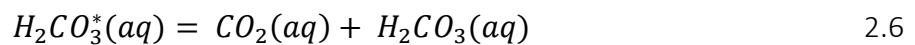


Figure 1 - Relative distribution (%) of DIC species as a function of pH.

H_2CO_3^* refers to an apparent species that encompasses both dissolved CO_2 and true carbonic acid (H_2CO_3 ; equation 2.6). Because the hydration equilibrium $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$ lies strongly to the left, most un-ionized inorganic carbon is present as $\text{CO}_2(\text{aq})$. Therefore, H_2CO_3^* represents the sum of these two forms, and its acid–base behaviour is described by a composite acidity constant, which accounts for both CO_2 hydration and the dissociation of true carbonic acid; in practice, this composite constant is the one commonly used and reported as K_{a1} (Stumm and Morgan, 2012).



Alkalinity plays a fundamental role in regulating pH and maintaining the stability of aquatic ecosystems by buffering against pH fluctuations caused by biological and chemical processes. For example, during photosynthesis, aquatic plants and phytoplankton consume dissolved CO_2

or bicarbonate as a carbon source (Beer and Beardall, 2025), which, without buffering, would cause pH to rise sharply. Conversely, respiration by aquatic organisms and decomposition of organic matter release CO_2 , leading to a decrease in pH (Huh, 2003). These processes are part of the short-term carbon cycle in aquatic systems, where CO_2 is continuously exchanged between the water, organisms, and atmosphere.

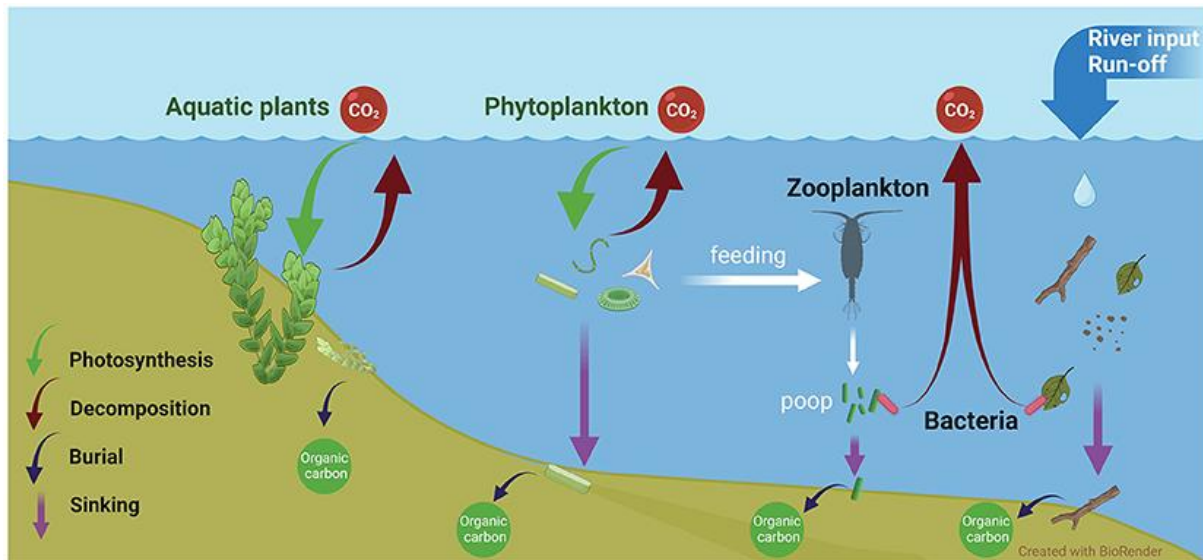


Figure 2 - Carbon movement through a lake ecosystem (Franco-Cisterna et al., 2024).

Over longer timescales, the global carbon cycle is also influenced by geochemical processes, such as the chemical weathering of rocks by carbonic acid (Equation 2.4 and 2.5). This process consumes atmospheric CO_2 and releases bicarbonate and carbonate ions into aquatic systems, contributing to alkalinity and regulating atmospheric CO_2 concentrations over geological timescales (Invernizzi and Terpin, 1997).

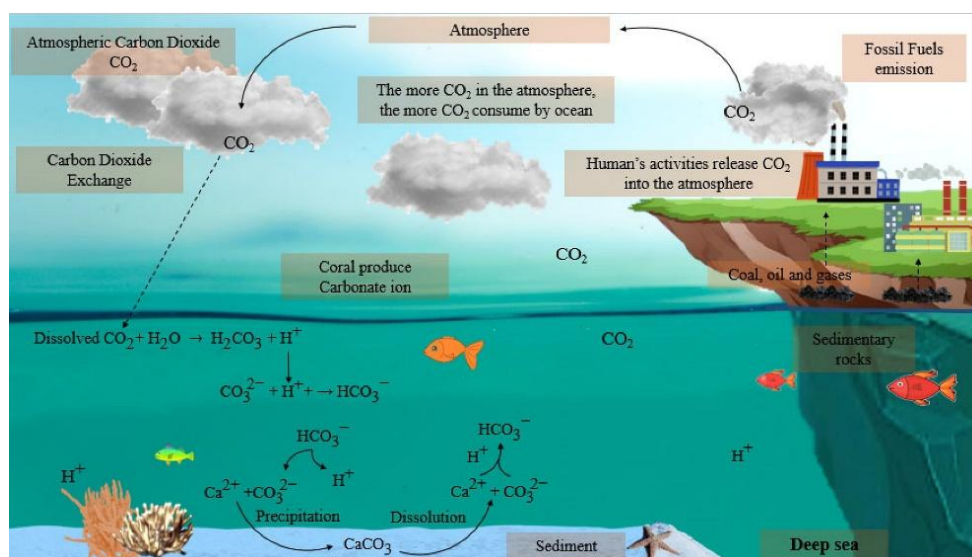


Figure 3 - Carbon chemistry system (Ahmad et al., 2024).

The stability provided by alkalinity is vital for aquatic life. Significant drops in alkalinity can lead to acidification, harming sensitive species, while minimum concentrations of calcium and

carbonate ions are essential for biological processes such as fish egg development (Boyd et al., 2016). Additionally, variations in DIC availability can influence the growth rates of phytoplankton species, thereby shaping community structure in marine ecosystems (Rigobello-Masini & Masini, 2001; Martz et al., 2006).

HCO_3^- and CO_3^{2-} ions contribute to the buffering capacity of water within the pH range defined by their acid–base equilibria (between $\text{pK}_{a1} \approx 6.35$ and $\text{pK}_{a2} \approx 10.33$). This buffering system influences the solubility of minerals, the bioavailability of nutrients, and the toxicity of various substances (Butler, 1991). Carbonate ions can react with metals like calcium to form calcite (CaCO_3) or magnesium to form magnesite (MgCO_3) and their precipitation shifts the chemical equilibrium, increasing the solubility of other ions present in solution (Brik, 2011; De Silva et al., 2009). In the presence of phosphate (PO_4^{3-}), calcium can also precipitate as calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), limiting phosphorus availability and potentially decreasing the growth of aquatic organisms (Yanamadala, 2005). Furthermore, bicarbonate and carbonate ions can complex with trace metals such as copper or lead, altering their speciation, transport, and reactivity, and generally reducing their toxicity compared to free ionic forms (Dunnivant, 2005; Yanamadala, 2005).

Given its importance, alkalinity measurements are routinely conducted as part of standard water quality assessment for ocean, marine, lake, and river waters and are used in diverse applications. These include environmental monitoring, to track changes in water quality and assess the impacts of pollution or land-use changes, understanding the efficiency of anaerobic digesters and wastewater treatment processes (Lahav and Morgan, 2004; Damasceno et al., 2007) and managing acidification threats. Aquatic environments currently face severe acidification from multiple sources, including acid rain, industrial discharges, and acid mine drainage (Short et al., 1990; Ahmad et al., 2024). Acidic, metal-laden drainage from mines causes significant environmental problems, and the alkalinity and acidity of the effluent and receiving water bodies are commonly measured to identify potential effects and plan appropriate treatment methods to remove metals and produce near-neutral pH effluents (Kirby and Cravotta, 2005b). On a global scale, the absorption of anthropogenic CO_2 emissions is driving ocean acidification, lowering seawater pH and reducing the saturation state of calcium carbonate minerals, directly impacting calcifying organisms like coral reefs and mollusks (Ahmad et al., 2024). Alkalinity is therefore an essential tool for studying the carbon cycle and enabling a better understanding of CO_2 exchanges between the atmosphere and aquatic systems (Bobicki et al., 2012; Blackford et al., 2015).

Measuring only TA masks specific information, as it cannot distinguish the portion of alkalinity due to geochemical processes (carbonates) from that due to biological processes (organic matter). This distinction is important in fields like anaerobic wastewater treatment or sediment studies, where TA and CA reflect, respectively, the effects of partial and total oxidation of organic matter as a proton source (Keller et al., 1987). High CA can also interfere with the effectiveness of coagulants in removing dissolved metals from water (Kurniawan et al., 2006; El Samrani et al., 2008).

Monitoring and understanding alkalinity are essential for facilitating the protection and management of water resources, providing information on the suitability of water for uses such

as irrigation, determining the presence of contamination, and maintaining ecosystem health (Anderson and Wedborg, 1983; Oesterheld et al., 1998; Sterner and Elser, 2003).

2.2 Alkalinity measurement methods

2.2.1 Standard analytical methods

The standard procedure for determining alkalinity relies on acidimetric titration of a known water sample volume with a standardized strong acid, such as hydrochloric acid (HCl) or sulfuric acid (H₂SO₄), until a specific endpoint or equivalence point is reached (Andrew 2005). These procedures are standardized by international methods like ISO 9963-1 (1994) and the APHA Method 2320 (APHA, AWWA, and WEF, 2017). The titration typically targets two equivalence points: pH 8.3 (phenolphthalein alkalinity), where carbonates are converted to bicarbonates, and pH 4.5 (total alkalinity), where all carbonate species are converted to dissolved CO₂ and water (Dunnivant, 2005; Stumm & Morgan, 2012).

Endpoint detection can be achieved through two primary techniques: visual colorimetry and potentiometry. Visual colorimetry utilizes pH-sensitive indicators such as phenolphthalein for the first stage and mixed indicators like bromocresol green-methyl red for the final endpoint (Cooper, 1941). Potentiometry relies on a pH electrode immersed in the sample to measure its acidity during the titration. As a strong acid is gradually added, the pH of the solution decreases, and the electrode records this change continuously. The titration curve plots pH versus acid volume, which is used to determine the sample's alkalinity. While potentiometry is more objective and precise than indicator-based methods, it requires frequent calibration to maintain accuracy and is sensitive to electrode stability during measurement (Ahmad et al., 2024).

Despite their status as reference methods, they present several limitations. First, these procedures are time-consuming, typically requiring around 20 to 30 minutes to process a single sample, making them unsuitable for high-throughput applications or real-time monitoring (Boyd et al., 2016). In addition, these methods are sensitive to interferences. For instance, dissolved organic matter can react with the added acid, resulting in a poorly defined endpoint that cannot be clearly identified, thereby compromising the accuracy of the alkalinity determination, as illustrated in Figure 4. Moreover, because the acid reacts indiscriminately with all basic species, the method can only determine TA. Furthermore, substances such as oils, soaps, or suspended solids may coat the electrodes, causing sluggish responses and delayed equilibrium (ISO 9963-1, 1994; Harris, 2010; Kan et al., 2013; Kerr et al., 2021).

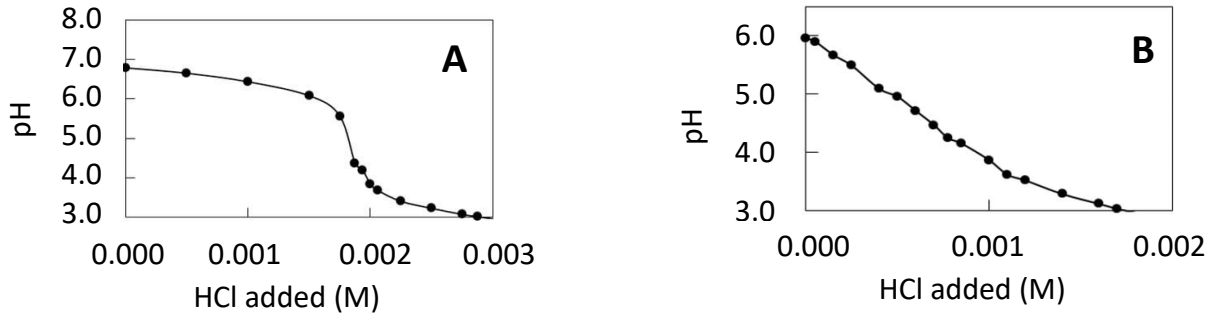
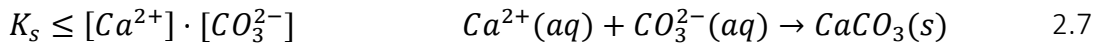


Figure 4 - Titration curves obtained by standard alkalinity titration for two contrasting samples. (A) shows a curve with a clear, identifiable endpoint, whereas (B) corresponds to a sample with a total organic acid concentration of $\sim 100 \text{ mg}\cdot\text{L}^{-1}$, where the endpoint appears smeared and cannot be reliably identified (adapted from Kan et al., 2013).

Another limitation lies in sample preservation, as CO_2 degassing during storage or transport induces an increase in pH and can therefore promote the precipitation of minerals such as calcite (CaCO_3), ultimately reducing the measured alkalinity (Dunnivant, 2005; Stumm and Morgan, 2012). Indeed, CaCO_3 starts to precipitate when:



where K_s is the thermodynamic solubility product of CaCO_3 , $[\text{Ca}^{2+}]$ is the concentration of calcium ($\text{mg}\cdot\text{L}^{-1}$) and $[\text{CO}_3^{2-}]$ is the concentration of carbonate ($\text{mg}\cdot\text{L}^{-1}$). On the other hand, the equilibrium constant K_2 is expressed as (Stumm and Morgan, 2012):

$$K_2 = \frac{[\text{H}^+] \cdot [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad [\text{HCO}_3^-] \leftrightarrow [\text{H}^+] + [\text{CO}_3^{2-}] \quad 2.8$$

$$\Rightarrow [\text{CO}_3^{2-}] = [\text{HCO}_3^-] \cdot 10^{pH-pK_2} \quad 2.9$$

The relation between bicarbonate concentration, sodium concentration and pH is established by injecting 2.9 into 2.7 and rearranging:

$$[\text{HCO}_3^-] = \frac{K_s}{[\text{Ca}^{2+}] \cdot 10^{pH-pK_2}} \quad 2.10$$

This relation is illustrated in

Figure 5. Typical Ca^{2+} and HCO_3^- concentrations range respectively from 1 to 200 $\text{mg}\cdot\text{L}^{-1}$ and from 10 to 350 $\text{mg}\cdot\text{L}^{-1}$ according to the nature of the terrain crossed (Nisbet and Verneaux, 1970; Bollens et al., 2021)

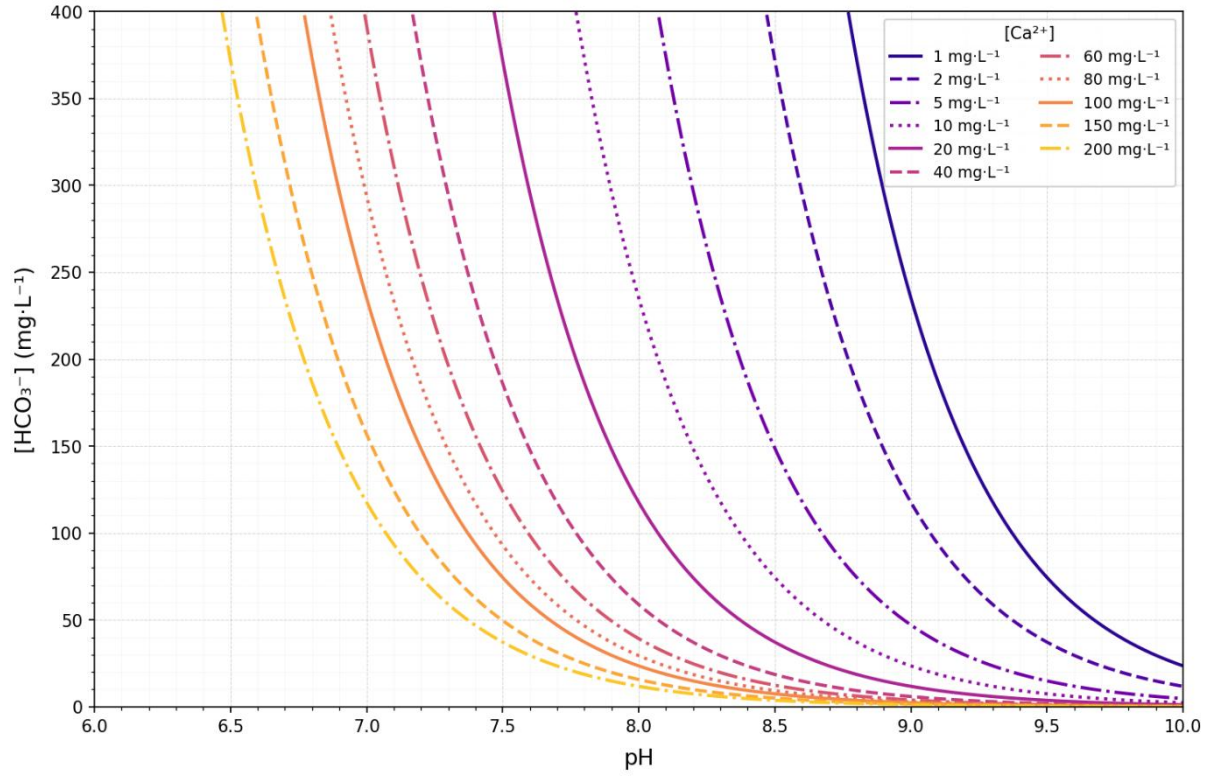


Figure 5 - Calcium carbonate solubility ($\text{mg}\cdot\text{L}^{-1}$) as a function of bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$), calcium concentration ($\text{mg}\cdot\text{L}^{-1}$) and pH, produced with Claude AI.

However, CaCO_3 precipitation induced by CO_2 degassing in natural waters is governed by a combination of thermodynamic and kinetic factors, making the process more complex than simple equilibrium considerations. Many natural waters are not in equilibrium with the atmosphere, partially because of unfavourable mixing conditions, but mainly because gas transfer kinetics are often slower than the biogeochemical reactions producing or consuming dissolved CO_2 in the aqueous phase, such as respiration, photosynthesis, mineral dissolution, and carbonate precipitation reactions (Stumm and Morgan, 2012). Consequently, when these waters undergo physical disturbance or pressure changes, dissolved CO_2 can degas to the atmosphere.

As seen previously (Equation 2.3), the removal of dissolved CO_2 shifts the carbonate equilibrium system and consumes protons, leading to an increase in pH. This increase modifies DIC speciation, favouring the formation of carbonate ions from predominant bicarbonate ions, as shown in Figure 1. When the ionic product of calcium and carbonate exceeds the solubility constant K_s , the water becomes supersaturated, and precipitation can occur (Equation 2.7; Choi et al., 1998).

The degree of supersaturation is commonly expressed using the saturation coefficient Ω (Hamdi and Tlili, 2024):

$$\Omega = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_s} \quad 2.11$$

where $a_{Ca^{2+}}$ and $a_{CO_3^{2-}}$ are the ionic activities of calcium and carbonate respectively. Waters with $\Omega > 1$ are thermodynamically supersaturated while $\Omega < 1$ indicates undersaturation (Hamdi and Tlili, 2024).

Supersaturation is also frequently expressed using the saturation index (SI), which corresponds to the logarithmic form of Ω (Cosmo et al., 2019):

$$SI = \log (\Omega) = \log \left(\frac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}}}{K_s} \right) \quad 2.12$$

Positive SI values indicate supersaturation, SI = 0 equilibrium conditions, and negative values indicate undersaturation. Saturation indices are used to evaluate carbonate scaling potential and mineral stability in natural and engineered water systems (Cosmo et al., 2019).

Nevertheless, supersaturation alone does not necessarily result in immediate precipitation. Natural waters frequently remain in a metastable state, sometimes at Ω values as high as 10 to 20, because crystal nucleation requires overcoming an energetic barrier associated with the formation of stable nuclei (Desoteux, 2025). The transition from dissolved ions to a solid mineral phase is therefore strongly controlled by kinetics. Once a critical nucleation threshold is exceeded, often associated with a critical pH (pH_c), rapid crystal growth may occur, leading to a measurable decrease in dissolved calcium concentration (Desoteux, 2025).

Several environmental parameters influence both the thermodynamic saturation state and the kinetics of precipitation. Temperature affects CaCO₃ and CO₂ solubility, CO₂ degassing rates, and reaction kinetics. Ionic strength modifies activity coefficients and therefore alters the effective saturation state of the solution. Hydrodynamic conditions, including turbulence and agitation, control gas transfer rates and can accelerate CO₂ degassing. In addition, dissolved ions such as magnesium may inhibit calcite precipitation by adsorbing onto crystal growth sites and increasing the energetic barrier for nucleation, thereby stabilizing supersaturated solutions and favouring metastable carbonate phases (Michel, 1973).

In summary, predicting CaCO₃ precipitation induced by CO₂ degassing in natural waters remains challenging because the process depends on both thermodynamic conditions and kinetic constraints. Consequently, when water samples are transported and analysed in the laboratory, there is no guarantee that their initial alkalinity has been fully preserved. Although certain approaches, such as field colorimetric methods, can be applied directly on site, they often remain impractical for continuous in situ measurements and field-based monitoring (Ahmad et al., 2024).

2.2.2 Alternative analytical methods

Several alternative approaches have been developed to determine alkalinity, each relying on different physicochemical principles and offering specific advantages and limitations. Some of them are discussed below.

Spectrophotometric methods

Spectrophotometric methods are based on the addition of a pH-sensitive indicator (e.g., bromocresol green or purple) to the sample solution and the measurement of absorbance at selected wavelengths corresponding to its acid and base forms (Fleger et al., 2025). The absorbance ratio allows accurate pH determination and, consequently, alkalinity calculation, sometimes from a single acid addition. These methods are generally precise and suitable for automation, but their performance depends on indicator purity and can be affected by sample turbidity or high particulate loads, which interfere with the optical signal (Fleger et al., 2025).

Total organic carbon analyser–based methods

Total organic carbon analyser–based methods rely on the conversion of all DIC species into CO_2 by acidification ($\text{pH} < 3$), followed by quantification using a nondispersive infrared detector (Rho et al., 2023). This approach is rapid and largely insensitive to dissolved organic matter or ionic strength, which often interfere with potentiometric titration. It is particularly advantageous for low-alkalinity or chemically complex samples. Its main disadvantage is the necessity of specialized and costly instrumentation, specifically a total organic carbon analyser equipped with an inorganic carbon reagent vessel and a non-dispersive infrared detector (Rho et al., 2023).

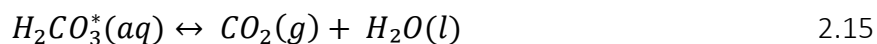
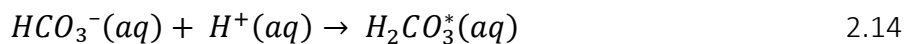
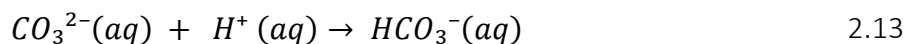
Headspace method: a field method based on pressure measurements

The headspace method was initially developed to determine CA in oilfield produced waters, i.e. highly saline wastewaters generated during oil and gas extraction processes (Wang et al., 2014). In these systems, accurate alkalinity measurements are critical because produced waters are frequently supersaturated with respect to carbonate minerals, with calcite SI commonly ranging from +1 to +3 (Cosmo et al., 2019). Such conditions result from elevated concentrations of dissolved calcium and bicarbonate combined with high dissolved CO_2 pressures. During production, pressure and temperature changes promote CO_2 degassing, leading to an increase in pH and a shift in carbonate equilibrium toward carbonate ion formation. This process induces calcium carbonate (CaCO_3) precipitation (Equation 2.7).

Calcium carbonate scaling represents one of the major operational challenges in the oil and gas industry. Mineral deposits can accumulate on well casings, tubing, pumps, valves, membranes, and pipelines, progressively reducing flow diameter and impairing fluid circulation. Even thin scale layers may significantly decrease heat transfer efficiency and increase hydraulic resistance. Consequently, rapid and reliable alkalinity determination under field conditions is essential for predicting scaling tendencies and implementing preventive strategies before CaCO_3 precipitation occurs (Cosmo et al., 2019).

The headspace method is based on the conversion of DIC species into CO_2 following the addition of an excess of strong acid to a water sample enclosed in a sealed container. Under

these conditions, bicarbonate and carbonate ions are quantitatively transformed into CO₂ gas according to the following reactions:



The generated CO₂ partitions between the liquid phase and the headspace, leading to an increase in gas pressure. This pressure change is then measured and related to the amount of DIC initially present, using mass balance equations combined with Henry's law and the ideal gas law (Wang et al., 2014).

In contrast to conventional titration methods, which rely on pH measurements and endpoint detection, the headspace method is based on pressure measurement. In classical titrations, the added acid reacts with all proton-accepting compounds, including organic bases. The presence of these species can obscure titration endpoints, making their identification difficult (Kan et al., 2013) and their contribution is therefore included in the measured TA. By contrast, they do not contribute to the measured signal in the headspace method, as only CO₂ produced from DIC is transferred to the gas phase and detected via pressure changes.

The method relies on a relatively simple experimental apparatus consisting of a sealed vial equipped with a pressure sensor and a system for acid injection, allowing for measurements in the field. A schematic representation of the apparatus is provided in Figure 6.

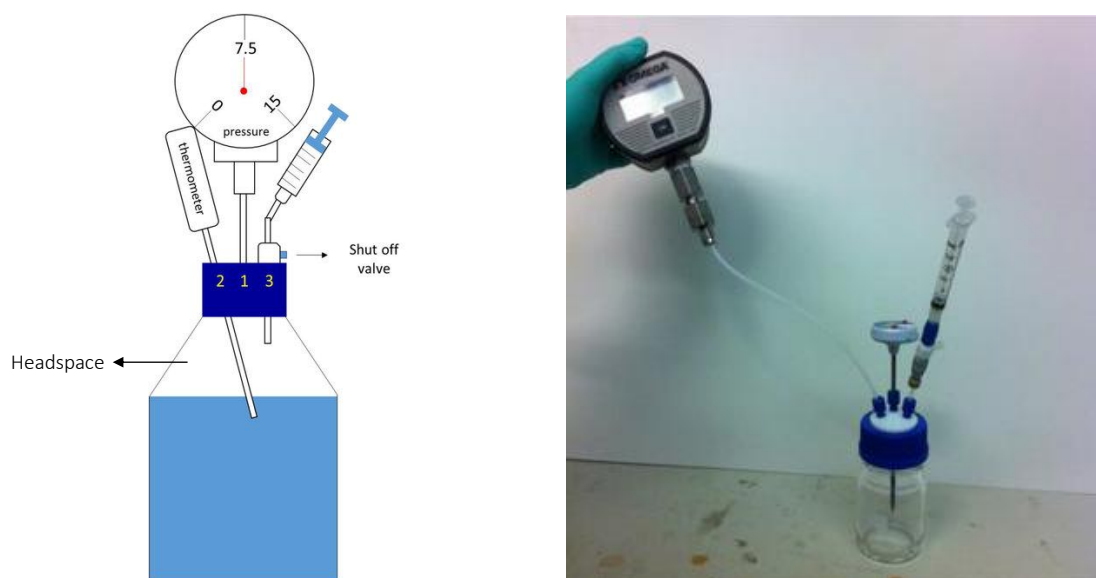


Figure 6 - Schematic representation (left) and photograph (right) of the headspace method apparatus, adapted from Wang et al. (2014).

Subsequent work by Liu et al. (2023) confirmed the applicability of the method to highly mineralized waters, including oilfield-produced waters and concentrated brines. Their results showed good agreement with conventional alkalinity measurements under these conditions, while highlighting practical advantages such as rapid measurements and reduced sensitivity to

CO₂ exchange during sample handling. This study identified analytical limitations: at low alkalinity (below approximately 100 mg·L⁻¹ HCO₃⁻), the pressure signal becomes weak and more difficult to quantify, resulting in decreased accuracy.

To date, the method has been applied to waters characterized by high alkalinity and high ionic strength. Its applicability to natural freshwater systems, which typically exhibit lower alkalinity and lower ionic strength, remains unexplored. Given the importance of alkalinity as an indicator of freshwater ecosystem functioning (Wetzel, 2001), there is a clear need for reliable and field-deployable measurement techniques. In this context, the headspace method represents a promising alternative, although its performance under such conditions still requires validation.

3 Objectives

The main objective of this research is to evaluate and further develop the headspace method introduced by Wang et al. (2014) for the rapid determination of CA directly in the field, with a particular focus on its applicability to natural water systems such as rivers.

The research seeks to optimize both the protocol and the apparatus of the headspace method. This includes evaluating the weaknesses of the initial experimental configuration, improving the apparatus and establishing a protocol that provides the best compromise between swiftness, simplicity and accuracy under field conditions.

The study aims to identify the physicochemical parameters influencing the measurements and to evaluate how they affect the method's analytical performance, including an assessment of its precision, accuracy, LOD (limit of detection) and LOQ. The headspace method will be assessed across laboratory-prepared solutions, commercial bottled waters and natural river waters, thereby evaluating its reproducibility under varying environmental and chemical conditions.

4 Methodological framework

In this study, alkalinity is expressed as the mass concentration of HCO_3^- in $\text{mg}\cdot\text{L}^{-1}$. Therefore, unless otherwise specified, all concentrations reported in $\text{mg}\cdot\text{L}^{-1}$ refer to $\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$. Although this choice deviates from commonly recommended conventions (ISO 9963), which favour reporting alkalinity in milliequivalents per litre ($\text{meq}\cdot\text{L}^{-1}$) or as $\text{mg}\cdot\text{L}^{-1} \text{CaCO}_3$, it is justified by both chemical and methodological considerations. In most natural freshwater systems, bicarbonate is the dominant contributor to alkalinity (see Section 2.1). Moreover, part of the methodology adopted in this work relies on aqueous solutions of sodium bicarbonate (NaHCO_3). This approach also ensures consistency with the methodological framework established by Wang et al. (2014) which reports alkalinity in $\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$. Conversion to conventional units is provided in Appendix 1 – Alkalinity conversion from $\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$ to conventional units

4.1 Theoretical approach: estimation of CO_2 headspace pressure following strong acid addition

A theoretical approach based on physicochemical principles was developed to predict the pressure increase under different experimental conditions. This approach combines the equilibria governing DIC species with the Ideal Gas Law and Henry's Law, to describe the partitioning of CO_2 between the headspace and the liquid phase after addition of an excess of strong acid, as illustrated in Figure 7 and in Equations 2.13, 2.14 and 2.15. The resulting pressure increase is directly related to the initial DIC concentration of the sample. The other parameters influencing the response include temperature, total, liquid and headspace volumes and injected acid volume. This theoretical framework is further developed in Section 5.

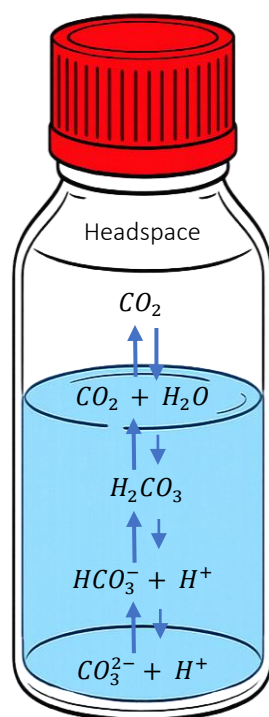


Figure 7 - Schematic representation of the equilibria governing DIC species and CO_2 transfer to the headspace after acid addition. Image generated with Chat GPT.

4.2 Laboratory reference method: two end-points titration

The two end-points titration method, a standardized laboratory procedure for alkalinity measurement (APHA, 1981; Rodier, 1981), was used as a reference for comparison with the headspace method. The principle of this method is based on the neutralization of alkaline species present in water, primarily bicarbonate and carbonate ions, through the addition of a strong acid. During titration, carbonates are first converted into bicarbonates, followed by the conversion of bicarbonates into carbonic acid. At the Mineral & Organic Chemical Analysis platform of the Earth and Life Institute (UCLouvain), the titration procedure is performed automatically using an autosampler coupled to a potentiometric pH electrode and an automated burette system, ensuring high repeatability and minimizing operator-related variability (Marchetto et al., 1999).

The sample is first titrated to a pH of 4.5, corresponding approximately to the bicarbonate equivalence region; the volume of acid added (V_1) is recorded. Acid addition is then continued until the pH decreases by exactly 0.3 pH unit and the new acid volume (V_2) is measured. Because a decrease of 0.3 pH unit corresponds to an exact doubling of the hydrogen ion concentration, the TA can be determined by extrapolation according to (APHA, 1981; Rodier, 1981):

$$TA = \frac{(2V_1 - V_2) \cdot N}{V} \quad 4.1$$

where **N** is the normality of the acid solution (eq·L⁻¹) and **V** is the sample volume (L). This approach can be considered a simplified Gran titration requiring only two pH and volume measurements while maintaining good analytical precision (Marchetto et al., 1999).

For the comparison between methods, two types of samples were considered. First, laboratory solutions prepared using only NaHCO₃ in demineralised water, thereby excluding the possibility of CaCO₃ precipitation. Under these conditions, any differences between the two methods can be attributed to the performance of the headspace method. In contrast, results obtained with river waters should be interpreted with caution, as the presence of calcium may lead to carbonate precipitation and affect alkalinity measurements.

4.3 Optimization of the headspace method's apparatus and protocol

The headspace method's apparatus and protocol were refined to improve measurement precision and accuracy by reducing potential sources of uncertainty, while keeping the procedure as time efficient as possible. At the beginning of the study, parameters expected to influence the measurements, namely injected acid volume and agitation conditions, were assessed and optimized. Temperature effects were also considered early on, since pressure is directly influenced by temperature according to the ideal gas law ($PV = nRT$). Temperature was therefore controlled throughout all experiments.

Repeated use of the method led to the identification of additional factors affecting measurement accuracy that had not been initially anticipated. These were addressed through adjustments to both the apparatus and the protocol. In addition, two analytical approaches were tested for the determination of alkalinity using the headspace method: direct calibration (DC) and the standard addition (SA) method. The optimization of the apparatus and protocol is further developed in Sections 6 and 7.

4.4 Development and assessment of the analytical performance of the headspace method

The development strategy adopted in this work aimed to assess whether the headspace method, initially designed for oilfield-produced waters, could be transferred to freshwater systems, characterized by lower ionic strength and alkalinity. A progressive approach was implemented, moving from synthetic solutions toward increasingly complex natural freshwater matrices.

The first stage consisted of laboratory experiments using synthetic bicarbonate solutions prepared by dissolving NaHCO₃ in demineralized water. These chemically simple matrices, with well-defined alkalinity, were used to establish calibration curves relating alkalinity (up to 1000

mg·L⁻¹) to the pressure measured inside the apparatus, enabling the assessment of method linearity. Under these controlled conditions, the precision of the method was evaluated without interference from natural organic matter or other alkalinity-contributing species. Repeatability was assessed through triplicate or quadruplicate measurements, depending on the number of available apparatuses. In addition, the LOD and the LOQ were estimated using repeated measurements at low alkalinity (0–50 mg·L⁻¹). This first stage is further developed in Section 8.

In a second stage, preliminary tests were carried out on both bottled waters and river waters¹. Bottled waters were used because they provide more realistic, yet still controlled, matrices. River waters, in contrast, introduced more complex and variable natural conditions. Together, these experiments represented the first application of the method to non-synthetic matrices and provided a qualitative evaluation of its feasibility under more realistic conditions, with the aim of identifying the factors influencing the measurements and the potential improvements required for its application to freshwater systems. Comparisons with the reference titration method were performed to obtain an initial assessment of the method behaviour and overall performance. This second stage is further developed in Section 9.

Finally, a third stage consisted of new experiments performed on bottled waters and river waters while considering the different sources of variability and methodological limitations identified during the previous stage. These experiments constituted the final evaluation phase of the method and were used for the quantitative assessment of its analytical performances. Repeatability was assessed through replicate measurements, reproducibility was evaluated across different matrices and sampling sites and accuracy was systematically assessed by comparison with the reference titration method. This third stage is further developed in Section 10.

¹ Strictly speaking, because the samples were not filtered prior to analysis, these measurements reflect the ANC rather than true alkalinity. Nevertheless, the term alkalinity is retained throughout this work.

5 Estimation of the CO₂(g) pressure in the headspace after strong acid addition

A theoretical estimation of the CO₂(g) pressure generated in the headspace following the addition of strong acid (6 M HCl) to a bicarbonate solution was carried out as a function of the solution's initial concentration. This estimation aims to determine the order of magnitude of the expected pressures and to provide a basis for comparison with the experimental results. The calculation is based on a CO₂ mass balance. The calculation steps are as follows:

1) Total CO₂ (aqueous and gaseous) present in the bottle

This corresponds to the CO₂(g) initially present in the air volume of the bottle, the CO₂(aq) initially present in the liquid volume of the bottle, and the CO₂ (aq and g) formed during the reaction. The CO₂(g) potentially introduced into the headspace during the acid injection due to air aspiration is considered negligible.

$$CO_{2,tot} = CO_{2,i(g)} + CO_{2,i(aq)} + CO_{2,formed} \quad 5.1$$

where:

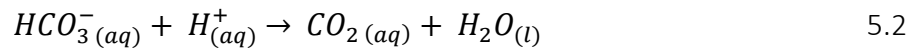
$CO_{2,tot}$ is the total amount of CO₂ present in the bottle, in both aqueous and gaseous forms (mol),

$CO_{2,i(g)}$ is the amount of CO₂ initially present in the air volume of the bottle (mol),

$CO_{2,i(aq)}$ is the amount of CO₂ initially present in the liquid volume of the bottle (mol),

$CO_{2,formed}$ is the amount of CO₂ formed during the reaction, both aqueous and gaseous (mol).

The CO₂ formed during the reaction results from the reaction between bicarbonate ions and the added strong acid. Due to the stoichiometry of the reaction (1:1 molar ratio) and the large excess of acid introduced (Appendix 2 – Verification of acid excess conditions for complete DIC conversion) the amount of CO₂ produced can be considered equal to the initial amount of HCO₃⁻ introduced into the system.



The total number of moles of CO₂ ($CO_{2,tot}$) in the system is therefore known.

2) Pressure at equilibrium between the gas and aqueous phases in the headspace

The total number of moles of CO₂ in the system ($CO_{2,tot}$) is given by:

$$CO_{2,tot} = CO_{2(g)} + CO_{2(aq)} \quad 5.3$$

where:

$CO_{2(g)}$ is the total amount of gaseous CO₂ present in the bottle at equilibrium (mol),

$CO_{2(aq)}$ is the total amount of aqueous CO_2 present in the bottle at equilibrium (mol).

Based on Henry's law:

$$[CO_{2(aq)}] = K_H \cdot p_{CO_2} \quad 5.4$$

where:

$[CO_{2(aq)}]$ is the equilibrium concentration of dissolved CO_2 ($\text{mol} \cdot \text{L}^{-1}$),

K_H is Henry's constant ($\text{mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$),

p_{CO_2} is the partial pressure of $CO_2(g)$ in the air volume of the bottle at equilibrium (atm).

Thus:

$$CO_{2(aq)} = K_H \cdot p_{CO_2} \cdot V_l \quad 5.5$$

where V_l is the liquid volume in the bottle (L).

Using the ideal gas law and equation 5.5, equation 5.3 can be written as:

$$CO_{2,tot} = p_{CO_2} \cdot \left(\frac{V_g}{RT} + K_H \cdot V_l \right) \quad 5.6$$

$$\Leftrightarrow p_{CO_2} = \frac{CO_{2,tot}}{\left(\frac{V_g}{RT} + K_H \cdot V_l \right)} \cdot 1013,25 \text{ (mbar)} \quad 5.7$$

where:

V_g is the gas volume in the bottle (L),

R is the ideal gas constant ($\text{L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$),

T is the temperature (K).

3) Pressure increase due to acid (and air) addition:

The pressure increase resulting from the addition of acid and air, p_{inj} , must be considered:

$$p_{inj} = \left(\frac{nRT}{V_{g,f}} - p_{atm} \right) \cdot 1013,25 \text{ (mbar)} \quad 5.8$$

where:

n is the total amount of gas in the bottle (mol):

$$n = n_i + n_{inj} \quad 5.9$$

where:

n_i is the initial amount of gas present in the gas volume of the bottle (mol),

n_{inj} is the amount of gas injected into the bottle (mol).

$V_{g,f}$ is the final gas volume after injection (L). Since the total bottle volume is constant and the liquid is assumed incompressible, the acid injection causes a decrease in the gas phase volume equivalent to the volume of acid introduced:

$$V_{g,f} = V_{g,i} - V_{l, inj} \quad 5.10$$

where:

$V_{g,i}$ is the initial gas volume before injection (L),

$V_{l, inj}$ is the volume of acid injected (L).

p_{atm} is the initial pressure inside the bottle, i.e., atmospheric pressure (atm).

For a constant total injected volume, whether the injection contains only acid ($n_{inj} = 0$) or an acid-air mixture, the resulting p_{inj} remains the same. The resulting variation in the final gas volume ($V_{g,f}$) almost exactly compensates for the presence or absence of n_{inj} . The difference between the cases with and without entrained air is therefore negligible (0.05 mbar).

For an injected volume of 1 mL of acid and 0.5 mL of air, $p_{inj} \approx 7.2$ mbar. For an injected volume of 0.5 mL of acid and 0.3 mL of air, $p_{inj} \approx 3.8$ mbar.

Figure 8 presents the theoretical pressure in the headspace as a function of bicarbonate concentration, defined as the sum of the partial pressure of $\text{CO}_2(\text{g})$ and the contribution related to injection ($p = p_{\text{CO}_2(\text{g})} + p_{inj}$).

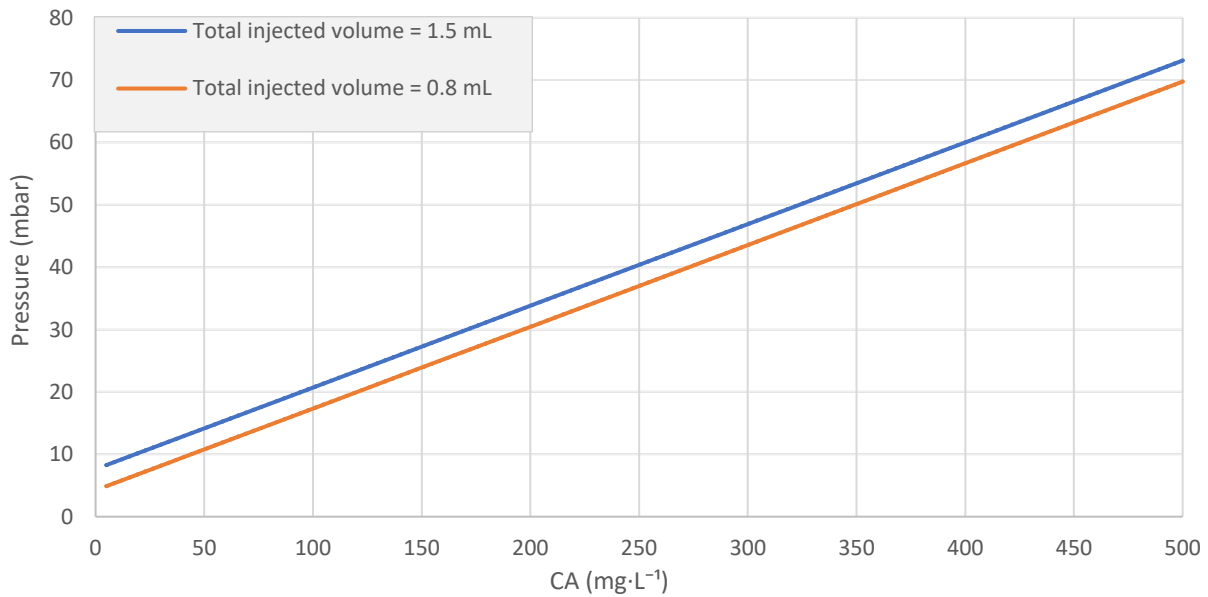


Figure 8 - Theoretical pressure in the headspace as a function of bicarbonate concentration at 21°C, for 1.5 mL injected (blue) and for 0.8 mL injected (orange).

The full set of calculations, including all physicochemical parameters and their interdependencies, is provided as a spreadsheet in Appendix 3 - Theoretical pressure estimation spreadsheet, which can be used to estimate the theoretical pressure for any combination of experimental conditions.

6 Materials and apparatus

6.1 Materials

Necessary materials

- Digital pressure gauge (Druck DPI 705E-IS model, resolution: 0.1 mbar);
- Four 250 mL Schott glass bottles (labelled 1, 2, 3 and 4; Figure 10);
- Four caps, each consisting of (Figure 11 in Section 6.2):
 - o a metal part with two independent connectors: one for connecting a pressure gauge, and the second fitted with a valve for acid injection;
 - o a plastic part for screwing onto the bottle;
 - o a thin rubber gasket ensuring airtightness (caps labelled 1, 2, 3 and 4);
- Four bottle weights (Figure 10);
- Strong acid solution (6 M HCl; Figure 9);
- 3 mL syringe with Luer lock needle (Figure 9);
- 100 mL graduated cylinder (Figure 9);
- Pasteur pipette (Figure 9);
- Metal container, used as water bath (Figure 10);
- 100 mL syringe;
- Additional connector for pressure gauge;
- Demineralised water (for DC);
- Pre-prepared calibration solutions (for DC);
- Pre-prepared concentrated solutions (for SA);
- 1 mL micropipette (for SA);
- Micropipette tips (for SA).

Backup materials

- Strong acid solution (6 M HCl);
- Needle;
- Syringe;
- Rubber gaskets;
- Batteries;
- Spanner.



Figure 9 - Photographs of the alkalinity measurement preparation materials. From left to right: graduated cylinder and Pasteur pipette used to collect 100 mL water samples; concentrated acid with syringe and needle used for acid injection.



Figure 10 - Photographs of the alkalinity measurement apparatus. From left to right: apparatus placed in a metal container filled with river water; apparatus in the river with bottle weights.

6.2 Apparatus

The apparatus was reproduced in quadruplicate to optimize experimental time, enabling four samples to be analysed simultaneously. To this end, four 250 mL Schott bottles were used, each sealed with an airtight cap into which two independent connectors were inserted. The first connector allows a pressure gauge to be connected while the second is fitted with a valve and allows a concentrated strong acid to be introduced using a syringe. A polycarbonate tube (1/8 inch) was inserted into the acid injection connector in an airtight manner to prevent corrosion of the stainless-steel plate and tube. During handling, the bottle is held by the plastic part of the cap (i.e., the red part used to screw the cap onto the bottle; Figure 11).

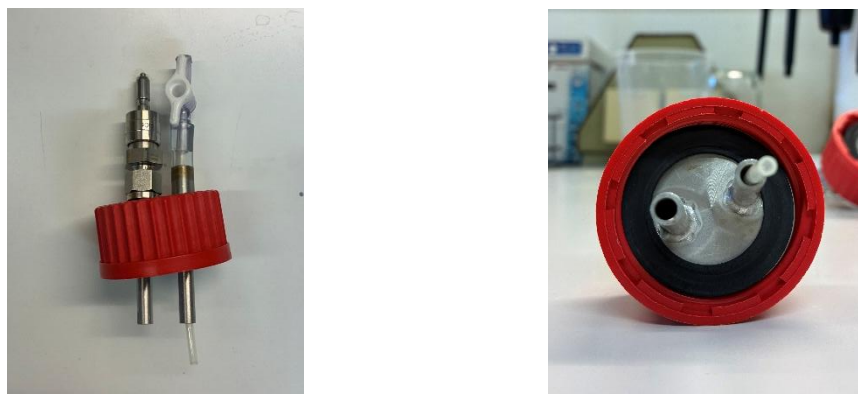


Figure 11 - Photographs of the cap showing the pressure gauge connector, the connector equipped with a valve and a polycarbonate tube for acid injection and the red plastic component used to screw the cap onto the bottle.

6.3 Seal integrity of the four apparatuses

The tightness of the apparatuses was verified over a period longer than the duration of a single measurement (≈ 2 minutes). To this end, each apparatus was pressurized to approximately 200 mbar and the pressure of each was measured after 3 hours.

The observed pressure loss was on the order of 7 to 9 mbar ($>5\%$) over 3 hours, representing a negligible variation over the timescale of a measurement (Appendix 4 - Seal integrity of the four apparatuses) The apparatuses can therefore be considered airtight under the experimental conditions.

6.4 Effect of pressure gauge connection and disconnection

The impact of connecting and disconnecting the pressure gauge from the apparatus was evaluated using an apparatus pressurized to approximately 30 mbar. The pressure gauge was connected and disconnected ten times; the results are shown in Figure 12.

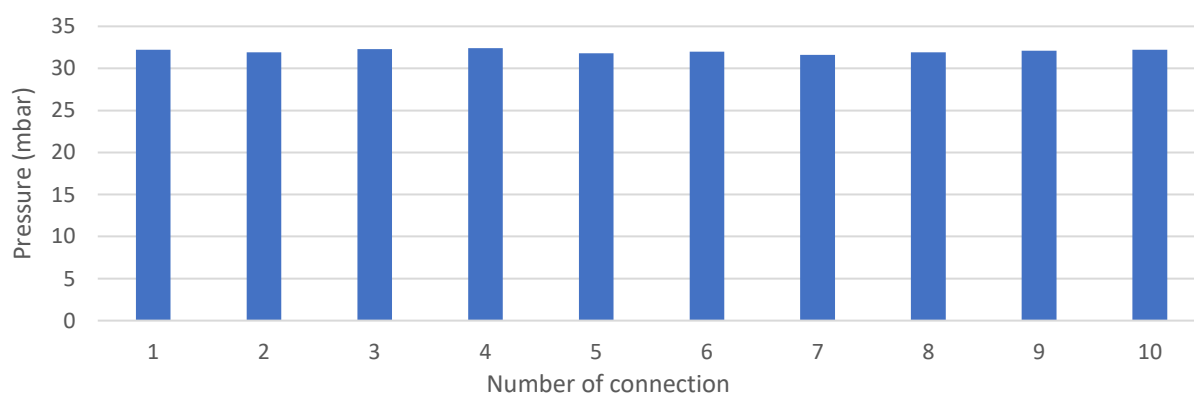


Figure 12 - Pressure (mbar) measured in an apparatus initially pressurized to ~ 30 mbar as a function of repeated connection and disconnection cycles of the pressure gauge (10 cycles).

The results show that the pressure remains overall stable. The slight variations observed can be attributed to handling effects, as the heat from the hand may warm the system and pressure is temperature dependent. It can therefore be concluded that connecting and disconnecting the pressure gauge does not lead to any significant change in pressure.

6.5 Determination of the Schott bottle volume

The volume of the Schott bottle was estimated based on the difference between the mass of the bottle (with its cap) filled with water and that of the bottle filled with air:

$$V = \frac{m_{\text{water}}}{d_{\text{water}}(20^{\circ}\text{C})} \quad 6.1$$

where:

V is the volume of the Schott bottle (mL),

m_{water} is the mass of water contained in the bottle and the cap (g),

$d_{\text{water}}(20^{\circ}\text{C})$ is the density of water at 20°C ($\text{g}\cdot\text{mL}^{-1}$).

$$V = \frac{m_{\text{full bottle}} - m_{\text{empty bottle}}}{d_{\text{water}}(20^{\circ}\text{C})} \quad 6.2$$

where:

$m_{\text{full bottle}}$ is the mass of the bottle with its cap filled with water (g),

$m_{\text{empty bottle}}$ is the mass of the bottle with its cap empty (g).

$$V = \frac{653 - 342}{0.998} = 312 \text{ mL} \quad 6.3$$

7 Headspace method protocol

7.1 Direct calibration protocol

1. Preparation of calibration solutions

Prepare in advance bicarbonate calibration solutions (adjust volumes and concentrations depending on the number of measurements and the expected concentrations, two concentrations and 200 mL of each will be needed per measurement).

2. Calibration measurements

0. Rinse the apparatuses with demineralized water 3 times.
1. Measure 100 mL of the calibration solution using a graduated cylinder and a Pasteur pipette; fill two bottles with the first solution and two bottles with the second one. Screw the caps tightly, close the acid injection valves (to prevent leakage/filling in case the bottle falls off).
2. Depending on site conditions and sheltered from direct sunlight:
 - If the sampling location is shallow and stable, place the apparatuses directly in the river, ensuring they remain upright using bottle weights.
 - If this is not feasible, fill a metal container with river water to create a water bath, place the apparatuses inside and (if possible) position the container within the river flow to maintain natural temperature conditions.
3. Verify pressure equilibration for each apparatus: open the acid injection valve and connect the pressure gauge. The reading should be 0 mbar. If not, inject air using a 100 mL syringe into both the acid connector and the pressure connector to remove any trapped water, then remove the syringe and recheck until the pressure returns to 0 mbar.
4. Draw the strong acid using a syringe, target 0.8 mL of acid when possible. If air bubbles enter, do not discard the sample; just ensure the syringe contains at least 0.5 mL of acid and a total volume (acid-air) of 0.8 mL.
5. Screw the syringe onto the acid connector, open the valve, inject the acid rapidly, and immediately close the valve; repeat for each apparatus.

Option A – Intermittent agitation

- 4a. Agitate vigorously two apparatuses for 30 s while holding the apparatus by the plastic (red) part to minimize heat transfer from the hands, then place them in the water bath, allowing intermediate thermal stabilization. Agitate the other two apparatuses for 30 s.

5a. Repeat one additional cycle of 30 s mixing followed by 30 s stabilization for each pair of apparatuses, maintaining handling by the plastic part.

6a. Before the first measurement, set the pressure gauge to zero using the additional connector open to the atmosphere. Be careful to handle the pressure gauge by its metallic part for the shortest time possible.

7a. While the second pair is stabilizing, measure the pressure of the first pair. Then, measure the second pair.

Option B – Continuous agitation

4b. Agitate vigorously the four apparatuses simultaneously for 1 min while holding the apparatuses by the plastic (red) part, to minimize heat transfer from the hands. Then, place them in the water bath for 1 min to ensure thermal equilibration.

5b. Before the first measurement, set the pressure gauge to zero using the additional connector open to the atmosphere. Be careful to handle the pressure gauge by its metallic part for the shortest time possible.

6b. Connect the pressure gauge and measure the pressure of all four apparatuses.

Once measurements are complete (both options): disconnect the pressure gauge. Be careful not to open the valve to avoid acid backflow. Unscrew the cap, discard the water downstream into the river flow and rinse each bottle three times. Once the cap has been removed, the valve may also be opened and rinsed using a 100 mL syringe previously filled with river water. It is recommended to remove the rubber gasket when rinsing the cap, as it can be easily lost.

3. River water measurements

1. Fill the four bottles with 100 mL of river water using a graduated cylinder and a Pasteur pipette; screw the caps tightly, close the valves.
2. Repeat the procedure described above starting from step 2.

A complete measurement set required approximately 30 minutes, including sample preparation, agitation, pressure measurement and cleaning for both calibration and sample measurements.

When implemented in the laboratory, the procedure remained essentially identical, with a few adaptations. Calibration solutions were prepared from a stock solution obtained by dissolving a known mass of NaHCO_3 in 1 L of water, followed by appropriate dilutions using 100 mL volumetric flasks and volumetric pipettes. Temperature control was ensured using a water bath set to laboratory temperature. The cleaning step was also simplified, as all equipment could be rinsed directly at the sink with demineralized water.

7.2 Standard addition protocol

Add 1 mL of concentrated bicarbonate solutions to three apparatuses to obtain concentration increases of 100, 200, and 300 mg·L⁻¹ respectively; leave the fourth apparatus without addition.

1. Preparation of standard solutions

Prepare in advance three bicarbonate solutions (adjust volumes depending on the number of measurements, 1 mL of each will be needed per measurement):

- 10 mL at 10 g·L⁻¹
- 10 mL at 20 g·L⁻¹
- 10 mL at 30 g·L⁻¹

2. River water measurements

1. Fill the four bottles with 100 mL of river water using a graduated cylinder and a Pasteur pipette; add 1 mL of each of the three bicarbonate solutions to the first three bottles, respectively, and leave the fourth bottle without addition. Carefully follow the bottle numbering to avoid confusion.
2. Screw the caps tightly, close the valves and depending on site conditions and sheltered from direct sunlight:
 - If the sampling location is shallow and stable, place the apparatuses directly in the river, ensuring they remain upright using bottle weights.
 - If this is not feasible, fill a metal container with river water to create a water bath, place the apparatuses inside and (if possible) position the container within the river flow to maintain natural temperature conditions.
3. Verify pressure equilibration for each apparatus: open the acid injection valve and connect the pressure gauge. The reading should be 0 mbar. If not, inject air using a 100 mL syringe into both the acid connector and the pressure connector to remove any trapped water, then remove the syringe and recheck until the pressure returns to 0 mbar. Leave the pressure gauge connected.
4. Draw the strong acid using a syringe, target 0.8 mL of acid when possible. If air bubbles enter, do not discard the sample; just ensure the syringe contains at least 0.5 mL of acid and a total volume (acid + air) of 0.8 mL.
5. Screw the syringe onto the acid connector, open the valve, inject the acid rapidly, and immediately close the valve. Record p_{inj} once pressure is stabilised. Repeat for each apparatus.
6. Proceed as described for the DC protocol from step 4.

A complete measurement set performed on four apparatuses required approximately 20 minutes, including sample preparation, agitation, pressure measurement and cleaning.

7.3 Protocol optimization

The protocol for CA determination using the headspace method was progressively refined throughout this thesis, ultimately leading to the protocol presented in Sections 7.1 and 7.2. However, due to time constraints, it was not possible to repeat all experiments using this final procedure. Consequently, only the experiments presented in Section 10 follow exactly the final protocol. The main modifications, as well as the stage at which they were introduced, are explained below and summarized in Table 1 (Section 7.3.6).

7.3.1 Reduction of the injected volume

The influence of the injected volume, and the importance of minimizing it, were identified relatively early during the study; unless explicitly stated, all experiments were performed using a total injected volume of 0.8 mL.

7.3.2 Injection of acid only instead of an acid-air combination

Initially, the protocol consisted of injecting 0.5 mL of acid together with 0.3 mL of air. The purpose of the additional air volume was to push the acid contained in the tube into the bottle. However, it was observed that 0.3 mL of air was insufficient to displace the acid remaining in the tube, as shown in Figure 13. Since the total internal volume of the tube was approximately 0.2 mL, injecting 0.8 mL of acid ensured that approximately 0.6 mL effectively reached the bottle while maintaining a sufficient excess of acid (Appendix 2 – Verification of acid excess conditions for complete DIC conversion



Figure 13 - Acid remaining in the tube after injection.

From a theoretical perspective, replacing 0.3 mL of air with 0.3 mL of acid should not affect the pressure measurement, since both contribute equally to the induced overpressure (Section 5). This modification was therefore introduced for practical and reproducibility reasons, as injecting only acid proved operationally simpler. In practice, however, the syringe occasionally aspirated small amounts of air together with the acid, meaning that some injections still consisted of a mixed acid-air volume. This effect was assumed to be negligible, as long as there were at least 0.5 mL of acid to ensure excess. Now, this step is simplified as “acid injection,” although the injected volume may still contain a small amount of air.

7.3.3 Temperature effects on thermodynamic equilibria in the headspace apparatus

Temperature is a critical parameter in headspace-based alkalinity measurements because it governs the thermodynamic state of the closed system. The measured pressure reflects not only the CO₂ released during acidification, but also contributions from several temperature-dependent physical and chemical processes. These include changes in water vapour pressure, thermal expansion of gases, modifications in dissolved gas solubility according to Henry's law and shifts in carbonate equilibria. To illustrate these effects concretely, the following discussion considers the case where river water is collected at 10 °C while ambient temperature is 20 °C, a common situation during temperate field measurements.

Water vapour pressure

One factor that cannot be neglected is the partial pressure of water vapour. In a closed bottle containing liquid water, the headspace rapidly becomes saturated with water vapour, and its partial pressure depends solely on temperature. The total pressure inside the bottle therefore results from the combination of the air initially enclosed in the headspace and the water vapour that evaporates from the liquid phase until saturation is reached. At 10 °C, the saturation vapour pressure of water is approximately 12.3 mbar, whereas at 20 °C it rises to approximately 23.4 mbar (Wagner and Kretzschmar, 2008). A temperature increase of 10 °C therefore produces an increase of roughly 11 mbar in the water vapour contribution to total pressure, entirely independently of any change in carbonate chemistry.

Other temperature-dependent effects

Beyond water vapour, temperature simultaneously affects several other physical and chemical processes. According to the ideal gas law ($PV = nRT$), an increase in temperature causes the gases enclosed in the headspace to expand, raising the total pressure in a closed, fixed-volume vessel. Temperature also governs the solubility of dissolved gases through Henry's law: as temperature increases, the solubility of CO₂ decreases, promoting its transfer from the aqueous phase to the gas phase and increasing its partial pressure in the headspace. Similar, though smaller, effects apply to dissolved atmospheric gases such as O₂ and N₂. Finally, the equilibrium constants of the carbonate system ($pK_{a1} = 6.35$ at 25 °C, $pK_{a2} = 10.33$ at 25 °C) are themselves temperature dependent, leading to slight redistribution between dissolved CO₂, bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) species. Any temperature change after sample collection therefore triggers several coupled processes acting simultaneously on the measured pressure, making it difficult to attribute observed pressure changes to a single cause. Three typical situations may arise during field sampling, each carrying different analytical implications.

Scenario 1: warming, sealed system. River water collected at 10 °C is sealed inside the bottle and subsequently allowed to equilibrate passively with ambient temperature (20 °C) without reopening the system. The gases in the headspace expand according to $PV = nRT$; additional water evaporates until the saturation vapour pressure corresponding to 20 °C is reached; dissolved CO₂ and other atmospheric gases become less soluble and partially degas into the headspace; and the carbonate equilibrium shifts slightly. Because the system remains closed

throughout, all these processes combine to produce an increase in total pressure before any acid is added.

An alternative to this configuration would be to allow the sample to warm fully to ambient temperature and then open the valve briefly to restore atmospheric pressure before measurement. However, warming the bulk liquid from 10 to 20 °C is considerably slower than cooling the enclosed air back to river temperature, making this approach less practical under typical field conditions.

Scenario 2: cooling, sealed system. The bottle is sealed and immediately immersed back into the river, while the headspace initially contains air at approximately 20 °C. As the gaseous phase cools to river temperature, gas contraction occurs, the saturation vapour pressure decreases and part of the water vapour previously evaporated condenses back into the liquid phase. Simultaneously, CO₂ and other dissolved gases become more soluble at the lower temperature and partially dissolve back into the water. Because the bottle remains closed, no exchange with the atmosphere is possible, and the combined effect of these processes results in a progressive decrease in total pressure before acid addition. This scenario thus introduces a negative pressure artefact into the measurement.

Scenario 3: cooling, valve briefly opened before measurement. The bottle is immersed back into the river immediately after sealing and allowed to reach thermal equilibrium at 10 °C, then briefly connected to the atmosphere to restore atmospheric pressure immediately before acid injection. Opening the valve restores atmospheric pressure while maintaining the equilibrium water vapour pressure corresponding to the river temperature. CO₂ remains in equilibrium with the aqueous phase according to Henry's law and the amount of dry air adjusts to satisfy the total pressure balance. Once the valve is closed, the bottle is at constant temperature, with stable gas–liquid equilibria and at atmospheric initial pressure.

Among these three configurations, Scenario 3 provides the most stable and reproducible initial conditions for pressure measurement. The system is fully characterised by a constant temperature equal to that of the river, a total pressure equal to atmospheric pressure, a water vapour pressure equal to the saturation vapour pressure at river temperature and stable CO₂(g)–CO₂(aq) and carbonate equilibria. Under these conditions, the subsequent pressure increase following acid addition can be attributed primarily to CO₂ generated from dissolved inorganic carbon, rather than to a combination of unrelated thermal and physical artefacts. Maintaining thermal equilibrium with the sample water and restoring atmospheric pressure immediately before the measurement should therefore minimise systematic errors.

Consequently, except for the first field experiments (Section 9.1) measurements were performed using the apparatus directly immersed in the river water and stabilised with weights wherever possible. During the first field measurements and in situations where immersion was impractical, the bottles were placed in a metal container filled with river water, itself positioned within the river. However, because the container was not always perfectly horizontal, water depth and therefore thermal conditions could vary slightly between bottles. Particular attention was also paid throughout all field experiments to avoiding direct sunlight exposure during analysis, including the use of the operator's shadow when necessary, to minimise

temperature fluctuations between the moment of sealing and the moment of measurement. In all cases, the valve was opened briefly to restore atmospheric pressure immediately before acid injection.

7.3.4 Proper zero-pressure reference

When the valve is opened to restore atmospheric pressure before measurement, the pressure inside the apparatus does not always return exactly to zero. Although the zero of the pressure gauges itself had previously been verified systematically, the zero-offset associated with the apparatus had not initially been considered. Rinsing the bottle caps can leave residual water trapped within the connectors (Figure 14), thereby affecting the pressure measurements by several mbar (up to approximately ± 7 mbar was observed). Such deviations correspond to errors of several tens of $\text{mg}\cdot\text{L}^{-1}$. Similarly, mud or other particulate matter can enter the connectors and affect the measurements.



Figure 14 - Zones where water/debris can get stuck

The significance of this issue was only recognized near the end of this study, and therefore only the latest field experiments (Section 10) fully account for this factor. To minimize these effects, an additional step was introduced, consisting of the injection of air through the acid connector while pressing the pressure-gauge connector to expel residual water from the connections as illustrated in Figure 15. The pressure reading was then checked to confirm a proper zero reading before analysis.



Figure 15 - Air injection using a 100 mL syringe to restore zero pressure by expelling residual water from the connectors.

7.3.5 Recording of p_{inj} for the standard addition method

Further thoughts about the SA mechanism revealed the necessity of measuring the pressure immediately after acid injection (p_{inj}) and subtracting this value from the pressure measured after agitation. Otherwise, the pressure increase induced solely by acid addition is incorrectly included in the alkalinity calculation. In practice, the pressure increases immediately after acid injection and may then fluctuate slightly while the system re-equilibrates thermally. As long as no agitation occurs, no further pressure increase is observed. The pressure can therefore be recorded once a stable value is reached prior to agitation.

7.3.6 Overview of protocol modifications and their stage of implementation

Table 1 - Overview of protocol modifications and their stage of implementation. —: not applicable; X: accounted for; 0: not accounted for. *: 0 = The metal container placed in the river was used.

Section	Reduction of injection volume	Temperature homogeneity*	Zero pressure offset	Record of p_{inj}
8.1	X	X	0	0 (-)
8.2	-	X	0	0 (-)
9.1	X	0	0	0 (-)
9.2	X	X	0	0
9.3	X	X	0	0
10.1	X	X	X	X
10.2	X	X	X	X

7.4 Determination of the required number of agitation cycles

Preliminary tests were conducted to evaluate the influence of agitation duration and mode on the measured pressure, with the aim of defining a protocol that ensures precise measurements while minimizing analysis time. Different approaches were tested, including successive agitation cycles (30 s and 15 s) and continuous agitation.

In the first approach, agitation was performed in successive cycles of 30 seconds, each followed by 30 seconds of stabilization. This procedure was partly dictated by practical constraints: when a single operator handles multiple apparatuses, simultaneous manual agitation is not always feasible. In practice, the agitation of one pair of apparatuses coincides with the stabilization period of the other. The 30 s stabilization time also ensures that the systems return to thermal equilibrium in the water bath, maintaining a homogeneous temperature. This is important because handling the apparatus may slightly increase its temperature, leading to an increase in headspace pressure. After approximately 30 seconds, this effect disappears.

The results (Figure 16, Table A3 - Pressure (mbar) as a function of cumulative agitation time for four bicarbonate concentrations (30 s cycles)) show that most of the pressure increase occurs between the first and second mixing cycles, while subsequent variations remain limited. Statistical analysis (two-tailed paired Student's t-test, $\alpha = 0.05$) confirms that the increase between the first and second cycles is significant ($p < 0.05$), whereas differences between cycles 2 to 4 and the final stabilization phase are not significant ($p > 0.05$, Table A4 - Paired t-test results for successive 30 s agitation cycles: comparison of pressure values between consecutive measurement stages.). Although a slight increasing trend can still be observed after the second cycle, its magnitude remains small (about 0.2 mbar is equivalent to $\sim 1.5 \text{ mg}\cdot\text{L}^{-1} \text{ HCO}_3^-$). Thus, a compromise between measurement duration and precision led to limiting the protocol to two mixing cycles.

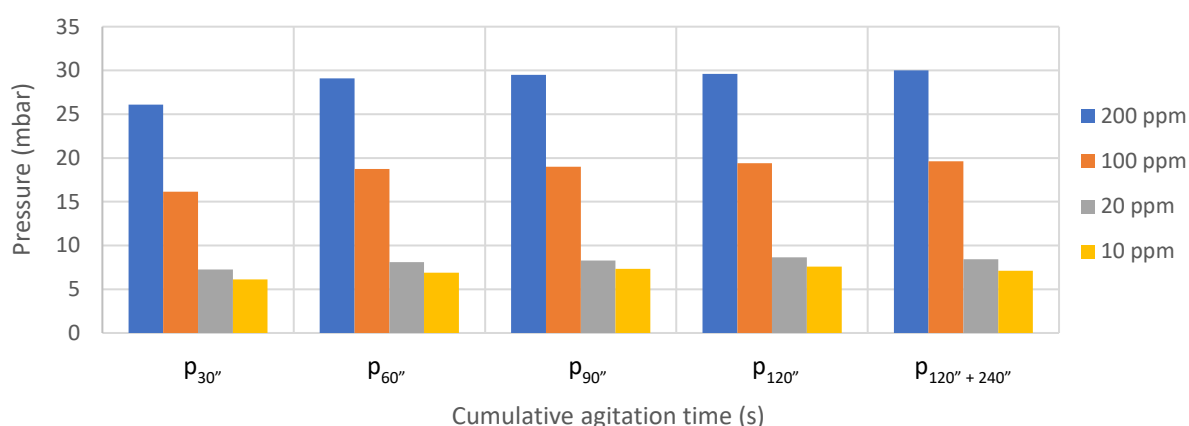


Figure 16 - Pressure (mbar) as a function of cumulative agitation time (s) for four bicarbonate concentrations. Values obtained at 21 °C with an injected volume of 0.5 mL acid and 0.3 mL air. $p_{30''}$ corresponds to the pressure measured after 30 s of agitation followed by 30 s of stabilization. The final pressure value ($p_{120''} + 240''$) corresponds to a total of 120 s of mixing (four cycles of 30-30 s) followed by 240 s of stabilization.

Additional tests were performed to evaluate whether the agitation duration could be further reduced. A solution containing $200 \text{ mg}\cdot\text{L}^{-1} \text{ HCO}_3^-$ was analysed in quadruplicate using six agitation cycles of 15 s each. The results (Figure 17 - Figure 17; Table A5 - Pressure (mbar) as a function of cumulative agitation time for a bicarbonate concentration of $200 \text{ mg}\cdot\text{L}^{-1}$ in quadruplicate (15 s cycles)) indicate that stopping agitation after 45 s could be considered instead of 60 s (Table A6 - Paired t-test results for successive 15 s agitation cycles: comparison of pressure values between consecutive measurement stages.. However, this 15 s time gain remains marginal and does not compensate for the increased practical constraints, such as handling the apparatus three times instead of two, which complicates the experimental procedure. Moreover, maintaining a slightly longer mixing time provides a safer margin to ensure complete equilibration. Consequently, shortening the agitation duration was not retained.

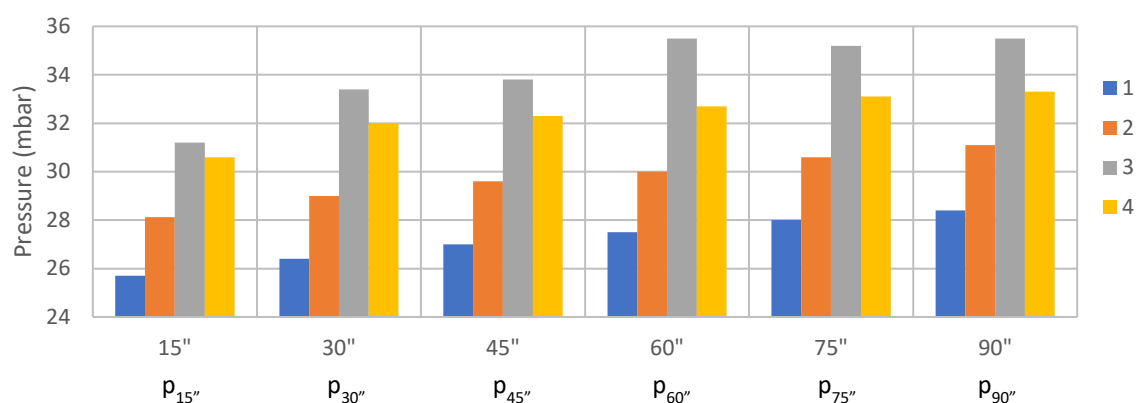


Figure 17 - Pressure (mbar) as a function of cumulative agitation time (s) for a bicarbonate concentration of 200 mg·L⁻¹ (n = 4). Values obtained at 21 °C with an injected volume of 0.5 mL acid and 0.3 mL air.

In parallel, continuous agitation over 1 min was also evaluated. To assess this configuration, four continuous measurements were performed on 200 mg·L⁻¹ HCO₃⁻ solutions with intermediate pressure readings (Figure 18, Table A7 - Pressure (mbar) as a function of measurement stage for a bicarbonate concentration of 200 mg·L⁻¹ in quadruplicate (continuous agitation)). At the end of the agitation period, pressure values showed slight fluctuations, both positive and negative, suggesting that equilibrium was being approached. After agitation, the apparatuses were placed in the water bath for 1 min to ensure thermal equilibration, as they are exposed to ambient conditions during agitation. The stabilized pressure was consistently lower than the end-of-agitation values, suggesting that agitation was sufficient (although the observed pressure decrease may be attributed to thermal equilibration in the water bath, which is at a lower temperature than the apparatus during agitation).

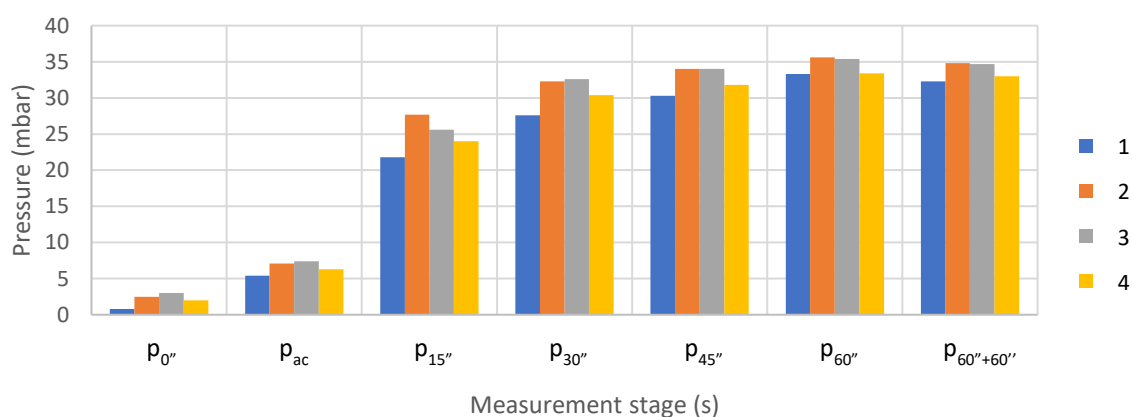


Figure 18 - Pressure (mbar) as a function of measurement stage for a bicarbonate concentration of 200 mg·L⁻¹ (n = 4). Values obtained at 21 °C with an injected volume of 0.5 mL acid and 0.3 mL air. p₀'' corresponds to the pressure measured with the acid injection valve open. p_{ac} is the pressure recorded immediately after acid injection. p₁₅'' is the pressure measured after 15 seconds of continuous agitation, etc.

Overall, these results indicate that two protocols, two successive 30 s agitation cycles or 1 min of continuous agitation, provide comparable performance. Continuous agitation is preferable when operationally feasible, as it simplifies the procedure and allows time optimization, even if a 1 min stabilization period is still required. During this stabilization step, the operator can prepare subsequent measurements, thereby improving overall efficiency.

7.5 Wang et al. protocol

The protocol proposed by Wang *et al.* (2014) was implemented in the laboratory with a modification: temperature was not monitored using a thermometer, but all experiments were conducted in a water bath to minimize thermal fluctuations.

An excerpt from the article by Wang *et al.* describing the protocol is given below:

“Procedures for headspace method

1. A 100 ml produced water sample was added into the vessel and the vessel was sealed with the cap. The reading on the pressure gauge was set to 0.
2. The apparatus was manually shaken for 30 seconds. After the vessel was shaken, the reading of pressure gauge was recorded as $P^{\text{step } 2}$ to allow dissolved CO_2 from the produced water sample to evolve and establish equilibrium in the reaction vessel.
3. A syringe containing 10 N HCl from which 1 mL of acid was injected into the vessel. Then the apparatus was manually shaken for 30 seconds and the reading of pressure gauge was recorded as $P^{\text{step } 3}$.
4. A second syringe containing 0.5 M NaHCO_3 solution from which 1 mL of solution was injected into the vessel. The apparatus was manually shaken for 30 seconds and the reading of pressure gauge was recorded as $P^{\text{step } 4}$.”

The results (Figure 19) show a good correlation between the measured values ($R^2 > 0.95$). However, large relative errors were observed (50–340%, Table A8 - Experimental data obtained using the Wang et al. (2014) protocol, including recorded pressures at each measurement step ($P^{\text{step } 2}$, $P^{\text{step } 3}$, $P^{\text{step } 4}$), measured alkalinity ($\text{mg}\cdot\text{L}^{-1}$), and associated CV.) indicating limited accuracy.

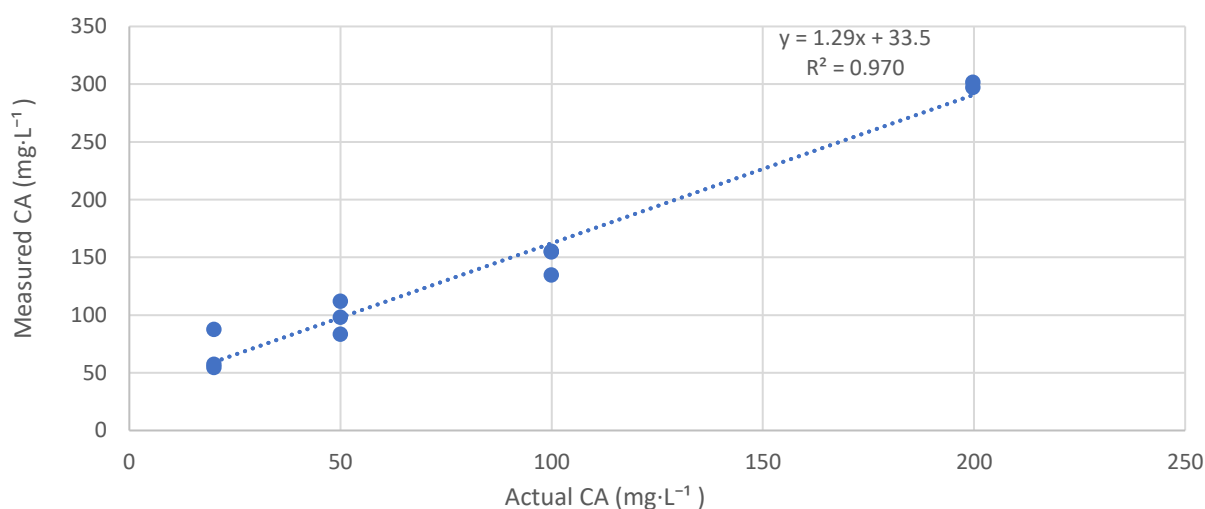


Figure 19 - Measured vs actual CA ($\text{mg}\cdot\text{L}^{-1}$) obtained using the Wang *et al.* protocol.

Although the calibration curve could be used, the protocol developed in this thesis was preferred, as it provides higher correlation ($R^2 > 0.99$), lower variability, and a simplified implementation. Indeed, injection steps represent sources of uncertainty due to uncontrolled

pressure perturbations. The Wang *et al.* protocol involves two injections and three pressure measurements, increasing both experimental complexity and potential error propagation.

8 Assessment of the headspace method on synthetic solutions

Regarding significant figures: by definition, the significant figures of a number include all certain digits together with the first uncertain digit (Skoog *et al.*, 2015). In this work, the method is still at the development stage. Consequently, the results were not all obtained under identical conditions, as different factors were considered depending on the experiment and the number of data points remains insufficient to allow for meaningful statistical analysis. Therefore, to present all obtained results consistently throughout this work, all values are reported to the nearest $\text{mg}\cdot\text{L}^{-1}$. This choice is not intended to give a false impression of precision, but rather to ensure that no information is lost.

8.1 Calibrations and injection effects

Calibrations of the headspace method were performed to establish the relationship between the measured pressure (p) and CA. Initially, a calibration curve covering concentrations from 5 to $500 \text{ mg}\cdot\text{L}^{-1}$ was established. This concentration range was selected because it encompasses the typical alkalinity values observed in surface waters (Nisbet and Verneaux, 1970; Batalla *et al.*, 2026). This first calibration curve was performed using a total injected volume of $\sim 1.5 \text{ mL}$; $\sim 1.0 \text{ mL}$ of acid and $\sim 0.5 \text{ mL}$ of air. A second calibration curve was established to evaluate the influence of injection volume on the pressure. A smaller injection volume was used: a total injected volume of $\sim 0.8 \text{ mL}$; $\sim 0.5 \text{ mL}$ of acid and $\sim 0.3 \text{ mL}$ of air. The acid remained introduced in large excess relative to the DIC present, ensuring its complete conversion (Appendix 2 – Verification of acid excess conditions for complete DIC conversion. For this second calibration, concentrations from 10 to $1000 \text{ mg}\cdot\text{L}^{-1}$ were measured to ensure linearity of the pressure–concentration relationship, for later SA measurements.

The calibration solutions were prepared by dissolving sodium bicarbonate (NaHCO_3) in demineralized water. Sodium bicarbonate was used due to its high solubility in water ($80 \text{ g}\cdot\text{L}^{-1}$ at 20°C ; Dean, 1999). Stock solutions were prepared and then diluted to obtain the various concentrations of interest. Figure 20 shows the measured pressure as a function of CA for both experimental conditions along with the corresponding theoretical relationships (see section 5).

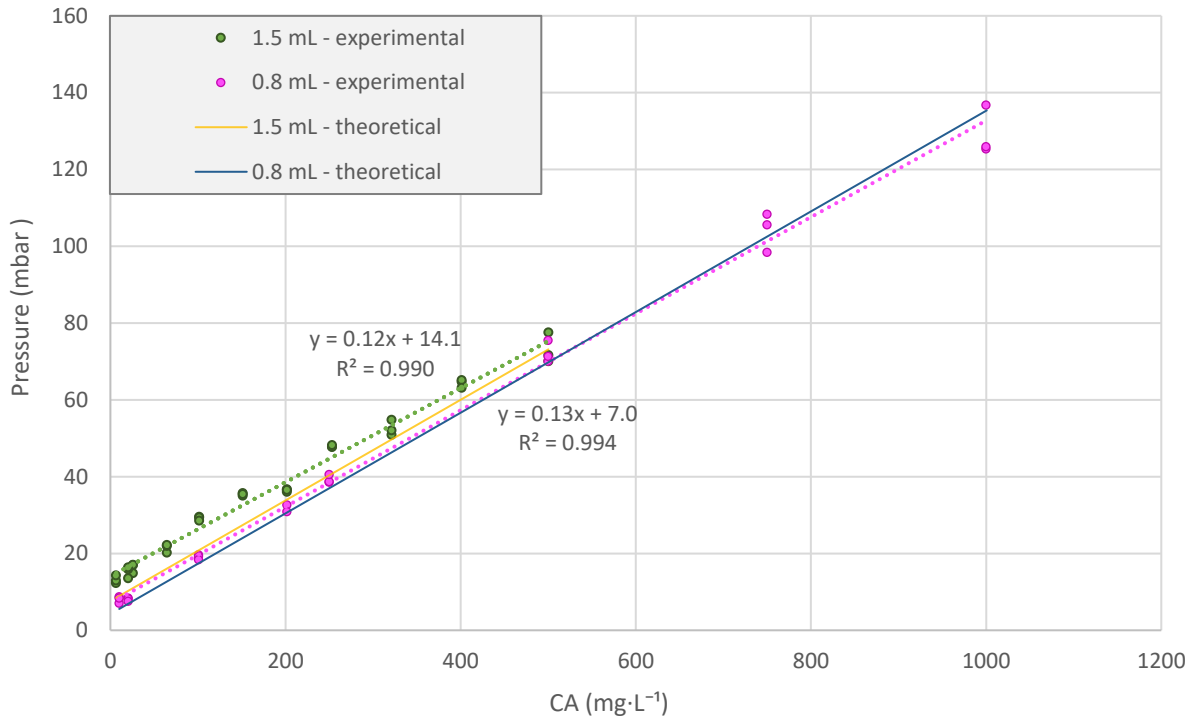


Figure 20 - Measured pressure (mbar) as a function of CA (mg·L⁻¹) for a total injected volume of 1.5 mL; ~1.0 mL of acid and ~0.5 mL of air and for a total injected volume of 0.8 mL; ~0.5 mL of acid and ~0.3 mL of air, along with the corresponding theoretical lines.

Both experimental regression lines showed coefficients of determination (R^2) greater than 0.99, indicating an excellent correlation between the experimental pressure and the CA. At the lowest concentrations (<50 mg·L⁻¹) the experimental pressure values were of the same order of magnitude and exhibited overlapping distributions, suggesting that the experimental variability was of the same order of magnitude as the measured signal.

Up to approximately 500 mg·L⁻¹, the experimental pressure remained higher than the theoretical prediction for both injection conditions. The deviation between the theoretical pressure and the experimental linear regression was particularly pronounced at low concentrations, especially for the 1.5 mL injection condition, suggesting the presence of uncertainty sources specific to this range. This deviation decreased from about 6 mbar to 3 mbar on the y-axis, when reducing injected volumes.

Table 2 shows, for a concentration of 20 mg·L⁻¹, the comparison between the pressures measured experimentally and the theoretical predictions, which include the expected pressure ($p_{\text{CO}_2} + p_{\text{inj}}$) and the contribution of the CO₂ partial pressure (p_{CO_2}), expressed in mbar and as a percentage, for both injection conditions.

Table 2 - Experimental pressure (mbar) vs. theoretical pressure (mbar; total pressure and CO₂ partial pressure), for a total injected volume of 1.5 mL; ~1.0 mL of acid and ~0.5 mL of air and for a total injected volume of 0.8 mL; ~0.5 mL of acid and ~0.3 mL of air.

	Experimental pressure	Theoretical pressure		
		At equilibrium	CO ₂ -related pressure	CO ₂ -related pressure
	p_{exp} (mbar)	$p_{CO_2} + p_{inj}$ (mbar)	p_{CO_2} (mbar)	p_{CO_2} (%)
1.5 mL injected	13.5	10.3	3.0	29.7
	15.9			
	16.4			
0.8 mL injected	8.4	6.9	3.0	44.3
	8.2			
	7.6			

The mean experimental pressure exceeds the theoretical prediction by approximately 50% (5 mbar) and 20% (1.4 mbar) for injected volumes of 1.5 mL and 0.8 mL, respectively. Theoretical estimates indicate that, for a 1.5 mL injection, only about 30% of the total pressure increase originates from CO₂ production, whereas the remaining 70% is attributable to the overpressure induced by the injection. When the injected volume is reduced to 0.8 mL, the relative contribution of CO₂ to the total pressure increases by nearly 15%

In theory, uncertainties associated with volume reading and injection may affect the pressure signal, since an error of 0.2 mL in the injected acid-air volume corresponds to approximately 1 mbar, equivalent to about 3 mg·L⁻¹ for a sample concentration of 20 mg·L⁻¹. Overall, these results demonstrate that variability associated with gas injection constitutes a source of uncertainty and can partially explain the discrepancy between experimental measurements and theoretical predictions.

8.2 Determination of the limit of detection and of the limit of quantification

As previously explained in Section 7.3, the initial zero-pressure of the experimental apparatus prior to acid injection was not verified (only the pressure gauge zero was adjusted). It may have significantly affected the measured pressure values, especially for this low concentration range, where the pressure varies up to ~18 mbar, a few mbar has a non-negligible impact. Nevertheless, the data still provided an acceptable order of magnitude.

The LOD and the LOQ were assessed by measuring six concentrations ranging from 0 to 50 mg·L⁻¹ (laboratory-prepared solutions) on three different days. Measurements were performed in quadruplicate during the first session and in duplicate during the two subsequent sessions, as showed in Figure 21.

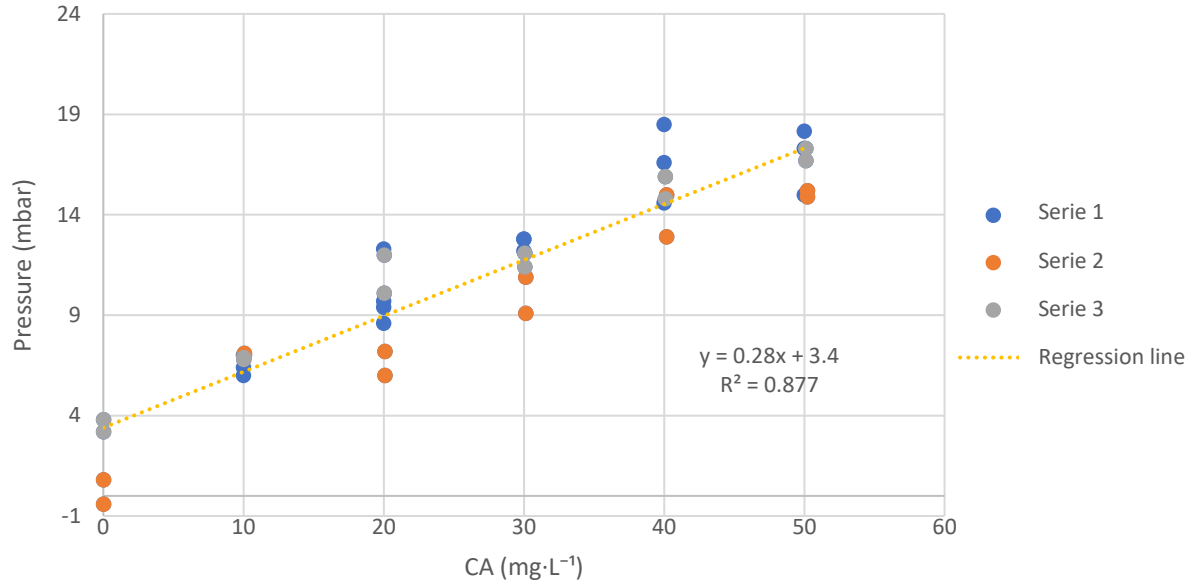


Figure 21 - Measured pressure (mbar) as a function of CA (mg·L⁻¹) for concentrations ranging from 0 to 50 mg·L⁻¹, used for LOD and LOQ determination (three independent sessions).

There were likely issues with the pressure measurements, as the CA = 0 mg·L⁻¹ values in series two are equal to or slightly below zero mbar, whereas it is known that the injection alone should generate a pressure of approximately 4 mbar. In addition, the coefficient of determination (R^2) is lower than typically observed, falling below 0.9, which indicates an increased variability of the measurements.

Based on the SD of y-intercepts of regression line and the slope of the calibration curve (Abraham, 2010):

$$LOD = \frac{3.3 \cdot \sigma}{S} = \frac{3.3 \cdot 0.53}{0.28} = 6 \text{ mg} \cdot \text{L}^{-1} \quad 8.1$$

$$LOQ = \frac{10 \cdot \sigma}{S} = \frac{10 \cdot 0.53}{0.28} = 19 \text{ mg} \cdot \text{L}^{-1} \quad 8.2$$

where σ is the SD of the y-intercepts of the regression line (mbar) and S is the slope of the calibration curve (mbar · (mg·L⁻¹)⁻¹).

Based on the residual SD of the regression line and the slope of the calibration curve (Abraham, 2010):

$$LOD = \frac{3.3 \cdot \sigma}{S} = \frac{3.3 \cdot 1.72}{0.28} = 20 \text{ mg} \cdot \text{L}^{-1} \quad 8.3$$

$$LOQ = \frac{10 \cdot \sigma}{S} = \frac{10 \cdot 1.72}{0.28} = 62 \text{ mg} \cdot \text{L}^{-1} \quad 8.4$$

where σ is the residual SD of the regression line (mbar).

Since this calibration curve was established without accounting for all the known factors affecting pressure measurements, these limits could be considered as upper estimates of the method's LOD and LOQ. However, these limits were determined under controlled laboratory conditions, which are more favourable than field conditions (more homogeneous temperature and easier handling of the apparatus). Therefore, the reported LOD and LOQ values should not be interpreted as definitive thresholds, but rather as preliminary estimates of the method's performance.

9 Qualitative assessment of the headspace method on river and bottled water samples

9.1 Alkalinity determination on river water using direct calibration

No calibration was performed during the first field alkalinity measurements with the headspace method using DC, hereafter referred to as the DC method, presented in this section. Therefore, the recorded pressure data were converted into alkalinity values using a calibration curve previously established under laboratory conditions. As the calibration and the measurements were not conducted under identical conditions, these values should be considered approximate and interpreted as orders of magnitude.

The DC method was performed on five rivers, their characteristics (coordinates, conductivity², temperature, and pH) measured in situ are summarized in Table 3. An issue occurred during the calibration of the pH meter: upon returning to the laboratory a standard solution of pH 7 was measured at 7.5, consequently the reported pH values are likely overestimated by approximately 0.5 pH unit.

Table 3 - Characteristics of the five rivers studied for the first alkalinity measurements using the DC method: coordinates, conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$), temperature ($^{\circ}\text{C}$) and pH. The pH values are likely overestimated by approximately 0.5 pH unit.

	Coordinates	Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	Temperature ($^{\circ}\text{C}$)	pH
Orne	50°37'56.1"N 4°37'32.6"E	796	10.8	8.50
Houssière	50°37'22.6"N 4°36'51.7"E	676	10.7	8.47
Malaise	50°39'38.9"N 4°35'31.9"E	803	9.6	8.56
Hubiessau	50°13'44.0"N 4°33'40.4"E	555	12.6	8.27
Forges	50°14'47.2"N 4°34'41.0"E	612	12.1	8.6

The DC method was applied on the five rivers to determine their CA; the results are presented in Figure 22. Water samples were transported to the laboratory for analysis using the two end-

² Conductivity is proportional to the concentration of dissolved ionizable salts and therefore constitutes an indicator of water mineralization (Nisbet and Verneaux, 1970). Although this parameter is not further used in the subsequent analyses, it is provided for informational purposes, as an additional factor for comparison among the studied rivers.

points titration method, these results are denoted as TA (as the method measures TA). To minimize degassing, samples were collected in glass bottles filled completely with river water and sealed without headspace. However, during analysis the samples were exposed to ambient air. Each measurement required approximately one hour per sample, and analyses were conducted in two times (2 and 3 rivers each time), resulting in exposure times of up to ~4 hours, including blank measurements. Nevertheless, it is assumed that $CA \approx TA$. No SD is reported for TA measurements, as repeated analyses showed a maximum variation of maximum $3 \text{ mg}\cdot\text{L}^{-1}$ (Appendix 7 - Repeatability of TA measurements by two end-points titration, which was considered negligible).

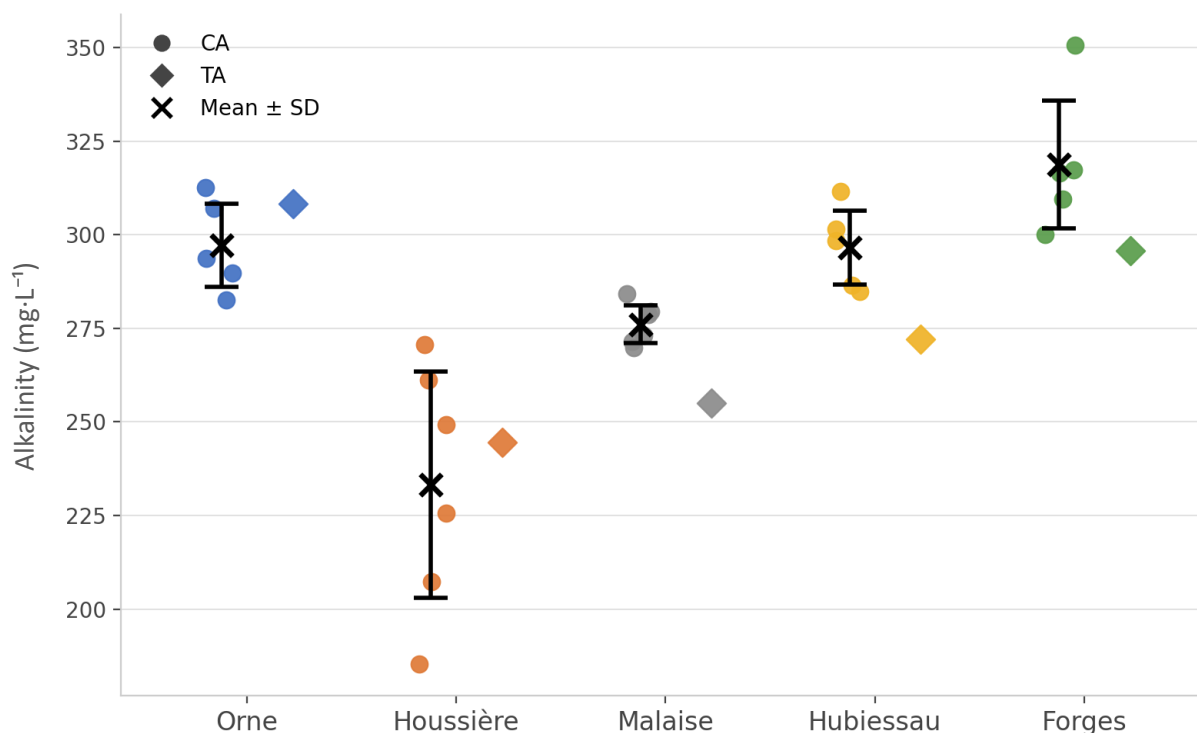


Figure 22 - Comparison of the alkalinity ($\text{mg}\cdot\text{L}^{-1}$) obtained using the DC method and the alkalinity ($\text{mg}\cdot\text{L}^{-1}$) obtained using the two end-points titration method for the five studied rivers. Colours indicate rivers, dots represent individual replicate measurements, black crosses indicate mean values and error bars correspond to SD. TA measurements obtained in the laboratory are represented by diamond symbols.

Although the results presented below should not be interpreted quantitatively due to the uncontrolled factors affecting the measurements, they nevertheless provide a useful qualitative assessment of the feasibility of the method under field conditions. The SD of the measured pressures ranged from 0.7 to 4.2 mbar (1.7–11.5% of the mean), which corresponds to a SD in alkalinity of 5 to $33 \text{ mg}\cdot\text{L}^{-1}$ (2–14% of the mean). For the first two rivers, the Orne and the Houssière, the TA values fell within the range defined by the mean $\pm$ SD of the headspace method measurements, with a relative error between CA_{mean} and TA below 5%. In contrast, for the three remaining rivers, TA values are lower by approximately 10, 20, and less than $5 \text{ mg}\cdot\text{L}^{-1}$, respectively for the Malaise, the Hubiessau and the Forges, corresponding to relative errors between 8 and 9% (Appendix 8 - Raw pressure and alkalinity data from the first field measurements using the DC method).

For the first two rivers, six replicates were performed (two series of three bottles, corresponding to the three apparatuses available at that time). For the remaining three rivers, an additional series of measurements was required due to the presence of outliers in the initial datasets, which were subsequently rejected (Appendix 8 - Raw pressure and alkalinity data from the first field measurements using the DC method)

As mentioned earlier, there is uncertainty regarding the initial pressure of the measurements, as it is not guaranteed that the system started at a true zero. Furthermore, the results rely on a calibration curve obtained under different analytical conditions, and finally temperature fluctuations are suspected to contribute to measurement inaccuracies. Indeed, environmental conditions differed between sampling sites: the first two rivers were analysed in stable conditions (in the shade, on a relatively flat dike), whereas for the remaining rivers, conditions fluctuated (intermittent cloud cover and variable positioning of the metal container). As a result, the apparatuses were inconsistently exposed to the sun and immersed in water, leading to variable thermal conditions.

The dependence on temperature stability became evident during a measurement exposed to the sunlight where pressure values continuously fluctuated. A test was then conducted: a sample bottle was immersed in the river (Hubiessau, 12.6 °C) and allowed to stabilize, yielding a pressure of 37.7 mbar (corresponding to 245 mg·L⁻¹). The bottle was then removed from the river and kept in the shade (ambient temperature of 20 °C), resulting in a pressure of 44.5 mbar (298 mg·L⁻¹), representing an increase of ~60 mg·L⁻¹, or an apparent 25% rise in alkalinity. This experiment highlights the strong influence of temperature on pressure measurements and, consequently, on alkalinity values.

These results are difficult to interpret given the number of uncontrolled factors. However, they can be considered generally encouraging: for two rivers, the range of CA values is consistent with the TA, and the relative error between the mean CA and TA remains below 10% in all cases, although these findings should still be interpreted with caution.

9.2 Alkalinity determination on river water using standard addition

The first field alkalinity measurements with the headspace method using SA, hereafter referred to as the SA method, were performed on two rivers, their characteristics (coordinates, temperature, and pH) measured in situ (measured using a different pH meter than that used in Section 9.1) are summarized in Table 4.

Table 4 - Characteristics of the two rivers studied for the first alkalinity measurements using the SA method: coordinates, temperature (°C) and pH.

	Coordinates	Temperature (°C)	pH
Orne	50°37'56.1"N 4°37'32.6"E	11.2	7.94

Houssière	50°37'22.6"N 4°36'51.7"E	10.8	7.45
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Two standard addition approaches were tested: (i) addition of 1 mL of a concentrated NaHCO_3 aqueous solution and (ii) addition of solid NaHCO_3 , previously weighed to correspond to 10, 20, and 30 mg of HCO_3^- and stored in 1.5 mL Eppendorf tubes. The latter followed the protocol described in Section 7.2, with the modification that the pre-weighed Eppendorf tube was opened and introduced upside down into the bottle instead of adding 1 mL of solution.

The SA method was applied four times at the Orne site: twice using solid NaHCO_3 (replicates 1 and 2) and twice using aqueous NaHCO_3 (replicates 3 and 4). At the Houssière site, two measurements were performed: one using solid NaHCO_3 (replicate 1) and one using aqueous NaHCO_3 (replicate 2). Water samples were transported to the laboratory for analysis using the two end-points titration method, following the same considerations described in Section 9.1.

CA was determined by extrapolating the linear regression to $y = 0$, the regression was fitted to the measured pressures as a function of the increasing amount of bicarbonate added to the solution (Skoog et al., 2015). The upper and lower confidence intervals (CI) of the regression line were calculated from the SD of the residuals. The SD associated with the CA value was estimated using extrapolation of the CI to $y = 0$. Figure 23 shows the results obtained for the first replicate at the Orne and serves as a representative example (all other graphs are provided in Appendix 9 - Standard addition data and regression plots for all replicates at the Orne and Houssière sampling sites) of the outputs from the SA method.

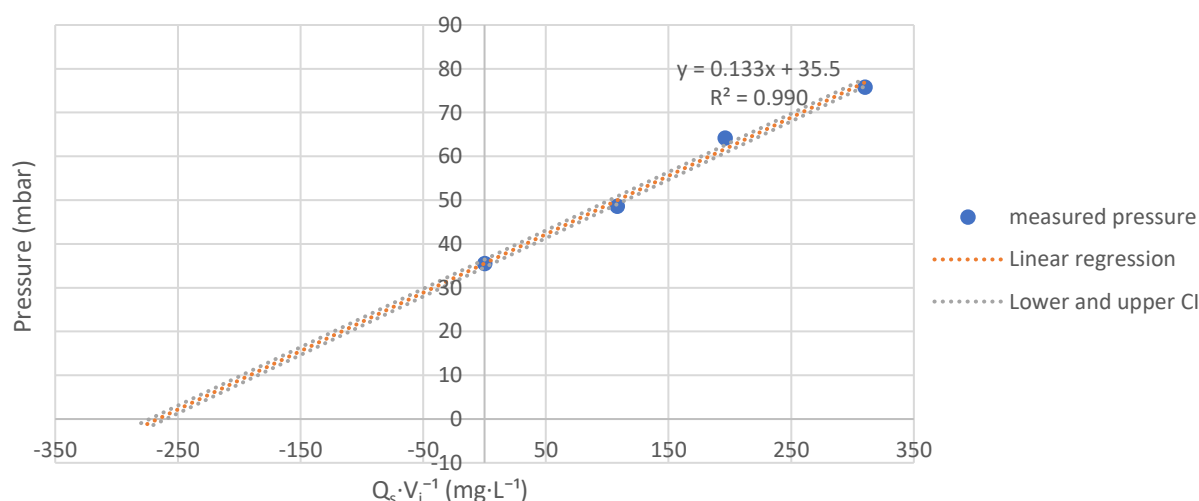


Figure 23 - First replicate of the alkalinity measurement at the Orne using the SA method: measured pressure (mbar) as a function of the amount of bicarbonate added to the sample ($\text{mg} \cdot \text{L}^{-1}$), along with the linear regression and the associated upper and lower CI extrapolated to $y = 0$.

Figure 24 and Figure 25 show the CA values extrapolated from their respective regression lines, along with the TA values obtained at the laboratory. Averages of the CA values obtained for each river with the SA method were calculated across the two addition methods. Although they are not strict replicates, it was assumed that the mode of NaHCO_3 addition does not significantly influence the outcome.

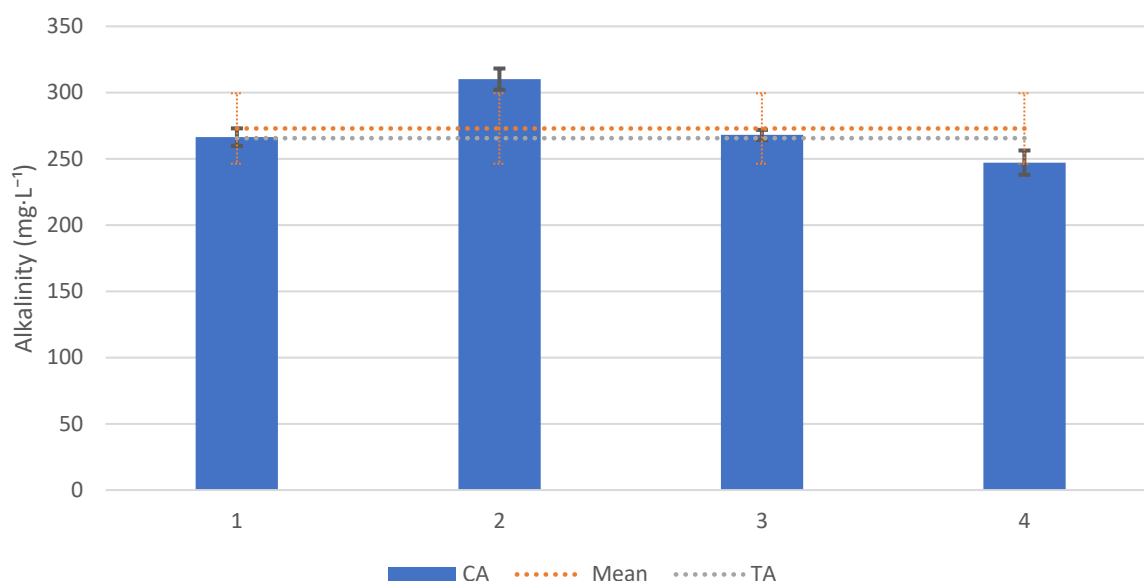


Figure 24 - Alkalinity measurements ($\text{mg}\cdot\text{L}^{-1}$) using the SA method at the Orne and using the two end-points titration method in the laboratory.

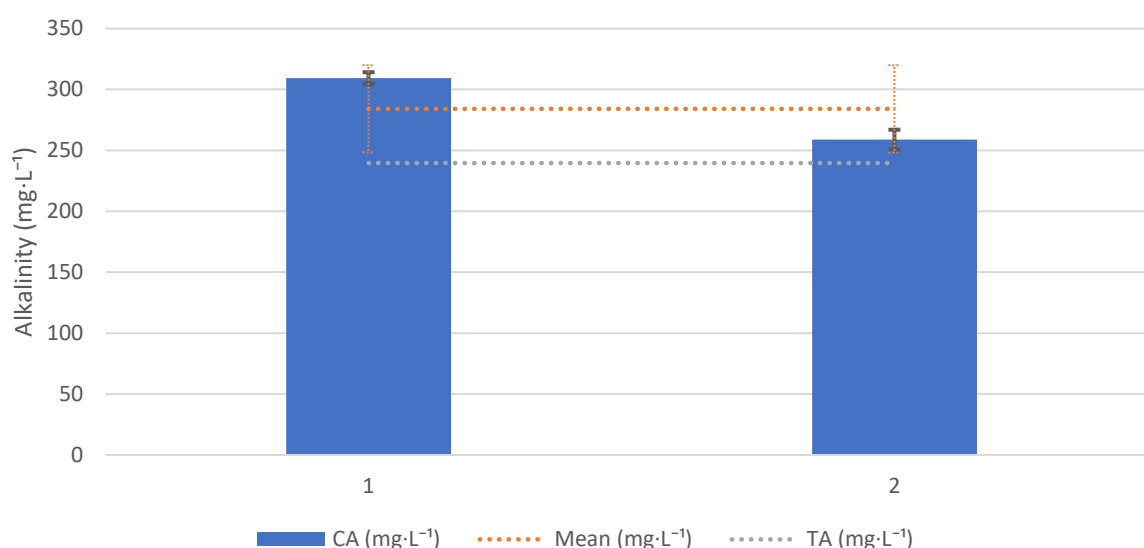


Figure 25 - Alkalinity measurements ($\text{mg}\cdot\text{L}^{-1}$) using the SA method at the Houssière and using the two end-points titration method in the laboratory.

Although the results presented below should not be interpreted quantitatively due to the uncontrolled factors affecting the measurements, they nevertheless provide a useful qualitative assessment of the feasibility of the method under field conditions. The SDs of the CA values for all individual measurements ranged from 4 to 9 $\text{mg}\cdot\text{L}^{-1}$, corresponding to approximately 1–4% of the estimated CA. The SDs of the mean values for each river were 27 mg/L (9% of the mean value) for the Orne and 36 $\text{mg}\cdot\text{L}^{-1}$ (13% of the mean value) for the Houssière.

For all individual measurements, the absolute error between TA and CA ranged from 1 to 70 $\text{mg}\cdot\text{L}^{-1}$, corresponding to a relative error of ~0–29%. When averaged by river, the absolute error

ranged from 7 to 44 mg·L⁻¹, corresponding to a relative error of 3% and 19% for the Orne and the Houssière respectively (Appendix 9 - Standard addition data and regression plots for all replicates at the Orne and Houssière sampling sites). Overall, the results are mixed, though relatively encouraging for the Orne, the discrepancies observed at the Houssière site are non-negligible.

Two important factors must be considered when interpreting these results:

- The issue of initial pressure offset in the apparatus, which although not systematic, can occasionally lead to negative pressure values on the order of a few mbar.
- Further thoughts about the SA mechanism revealed the necessity of measuring the pressure immediately after acid injection (p_{inj}) and subtracting this value from the pressure measured after agitation. Otherwise, the pressure increase induced solely by acid addition is incorrectly included in the alkalinity calculation. In practice, the pressure increases immediately after acid injection and may then fluctuate slightly while the system re-equilibrates thermally. As long as no agitation occurs, no further pressure increase is observed. The pressure can therefore be recorded once a stable value is reached prior to agitation.

It is therefore possible that errors may have compounded, cancelled out, or partially compensated for each other; however, this cannot be determined with certainty. Consequently, the results should be interpreted with caution. From a practical standpoint, the use of aqueous NaHCO₃ is simpler, requires less preparation, and generates less waste. This method was therefore selected for subsequent experiments.

9.3 Alkalinity determination on bottled water brands using direct calibration and standard addition

Five bottled water brands were analysed in the laboratory using both the DC method and the SA method. For the DC method, the calibration curve used to convert pressure into concentration was the one established in the laboratory, as measurements were conducted under identical conditions. For the SA measurements, the pressure immediately after acid injection (p_{inj}) was not recorded. All water samples were analysed using the two end-points titration method in the laboratory. Figure 26 summarizes all obtained results, together with the HCO₃⁻ concentrations reported on the bottle labels.

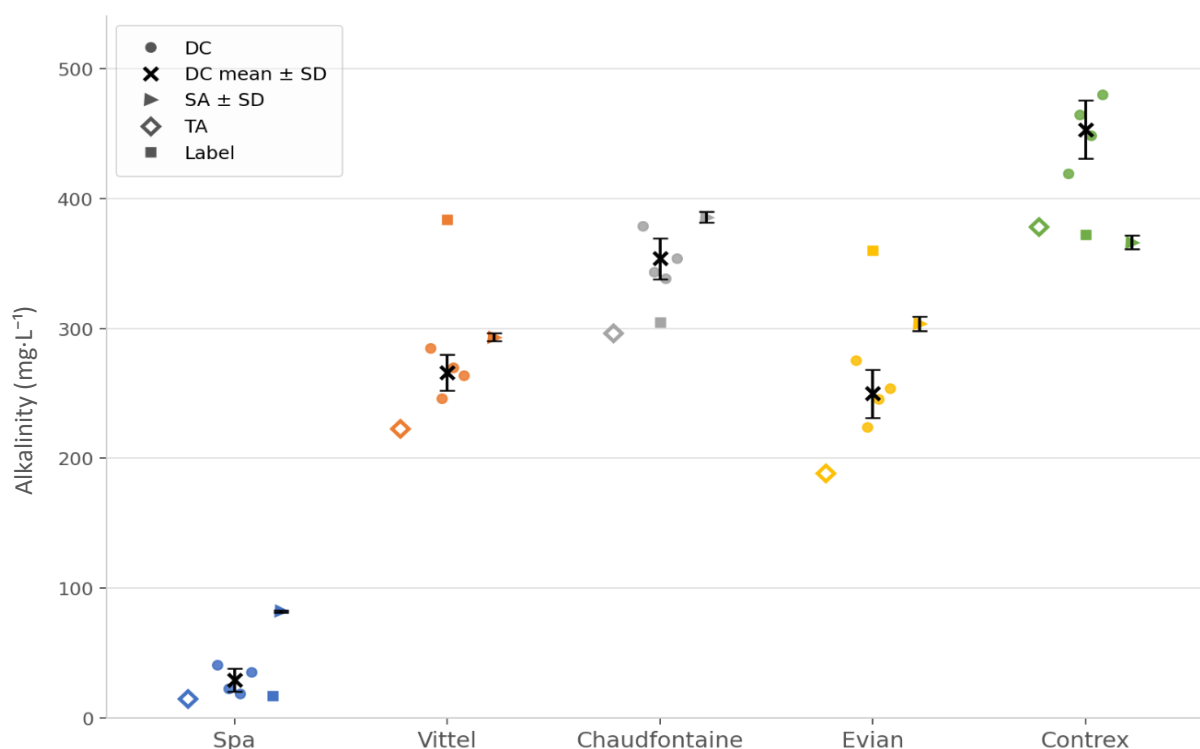


Figure 26 - Alkalinity measurements using the DC method, the SA method and the two end points titration method in the laboratory on bottled water brands along with the bicarbonate concentration on the bottle's label.

While the SA method showed lower SDs ($1\text{--}6\text{ mg}\cdot\text{L}^{-1}$) than the DC method ($10\text{--}26\text{ mg}\cdot\text{L}^{-1}$), both approaches displayed substantial deviations from the reference TA values. Absolute errors ranged from 14 to $75\text{ mg}\cdot\text{L}^{-1}$ for the DC method and from 12 to $115\text{ mg}\cdot\text{L}^{-1}$ for the SA method. TA values systematically fell outside the uncertainty ranges of the measurements. All DC values were systematically higher than the TA values, while four out of five SA values also overestimated TA. Discrepancies were observed between TA values and the HCO_3^- concentrations reported on bottle labels, despite bicarbonate being the only significant contributor to alkalinity in bottled waters. These differences may reflect either inaccuracies in the labelled values or potential biases in the TA measurements themselves.

Overall, the results should be interpreted cautiously, as several methodological limitations remain unresolved, notably uncertainties related to the initial pressure offset of the apparatus and for the SA method, the need to accurately account for the injection pressure (p_{inj}), which may partly explain the overestimation observed for SA measurements.

10 Quantitative assessment of the headspace method on river and bottled water samples

The results presented in this section were obtained using the final protocol, in which all previously identified factors influencing the measurements were controlled as best as possible (Table 1). These results therefore constitute the reference dataset used for the quantitative assessment and discussion of the method (Section 10.3).

For all measurements, the pressure immediately after acid injection (p_{inj}) was systematically recorded. Its importance has already been highlighted for the SA method. Its inclusion here allows for assessing its impact on DC measurements: whether abnormally high alkalinity values are associated with large p_{inj} values, whether this effect cancels out in the calibration curve and whether recording p_{inj} is necessary for DC measurements.

In the DC framework, pressure values corrected by subtracting the previously measured p_{inj} are denoted ΔDC and this approach is referred to as the ΔDC method. In contrast, no distinction is made between SA and ΔSA , all SA values correspond to extrapolations of regression lines constructed from Δp values.

For the DC method, calibration was systematically performed under the same experimental conditions as the measurements. In both laboratory and field experiments, a two-point calibration curve was constructed using calibration solutions of 150 and 250 $\text{mg}\cdot\text{L}^{-1}$, prepared in advance.

10.1 Alkalinity determination results on river water using direct calibration and standard addition

The objective of these measurements was to evaluate the influence of different water types on the headspace method, encompassing a range of alkalinities and matrix compositions, notably water hardness, given its role in carbonate precipitation processes driven by calcium (Ca^{2+}) and magnesium (Mg^{2+}). However, obtaining up-to-date compositional data for Belgian rivers proved challenging, as the relevant section of the Service Public de Wallonie (SPW) database was inaccessible at the time of the study. Consequently, the selection relied on a secondary source: a map published in 2013 (Figure 27) available on a commercial website (Calcéo) specializing in water softening systems, which cites the SPW as the original data source.

Based on this map, five rivers were selected to represent the range of water hardness observed across Wallonia. Water hardness is primarily determined by the concentration of dissolved calcium and magnesium ions. It is commonly expressed in French degrees ($^{\circ}\text{f}$), where 1 $^{\circ}\text{f}$ corresponds to 10 mg of calcium carbonate (CaCO_3) per litre of water (ISO, 2021). The characteristics (coordinates, conductivity, temperature, and pH) of the five rivers analysed were measured in situ and are summarized in Table 5.

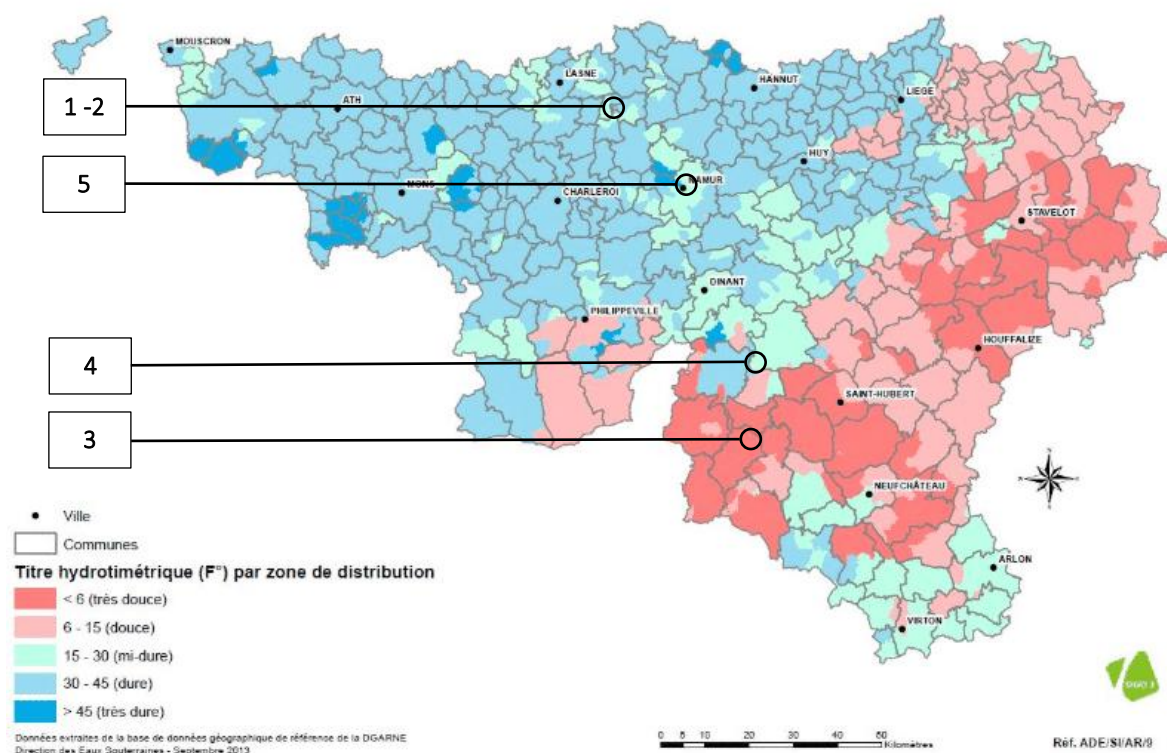


Figure 27 - Map of water hardness (hydrometric title, °f) by distribution area, adapted from Calceo.be (original data sourced from SPW), with the sampled sites indicated: (1) Orne, (2) Houssière, (3) Rau du Brou, (4) Lesse, and (5) Meuse.

Table 5 - Characteristics of the five rivers studied for the final alkalinity measurements using DC, Δ DC and SA methods: coordinates, conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$), temperature ($^{\circ}\text{C}$) and pH.

	Coordinates	Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	Temperature ($^{\circ}\text{C}$)	pH
Orne	50°37'56.1"N 4°37'32.6"E	800	15.3	8.12
Houssière	50°37'22.6"N 4°36'51.7"E	680	14.1	7.93
Rau du Brou	49°55'46.5" N 5°07'53.0 E	111	11.9	7.35
Lesse	50° 02'06.4" N 5°07'33.3" E	115	13.3	7.75
Meuse	50°27'54.0" N 4°54'35.6" E	423	16.2	8.25

The DC, Δ DC and SA methods were applied to the five rivers to determine their CA. Water samples were transported to the laboratory for alkalinity determination using the two end-

points titration method, following the same considerations described in Section 9.1. All results are shown in Figure 28. Rau du Brou was re-analysed in the laboratory using the collected sample, as p_{inj} was not recorded in the field. For the Meuse, field conditions prevented placing the apparatus directly in the river, and measurements were performed under direct sunlight due to the absence of shade, with the operator's shadow used when possible.

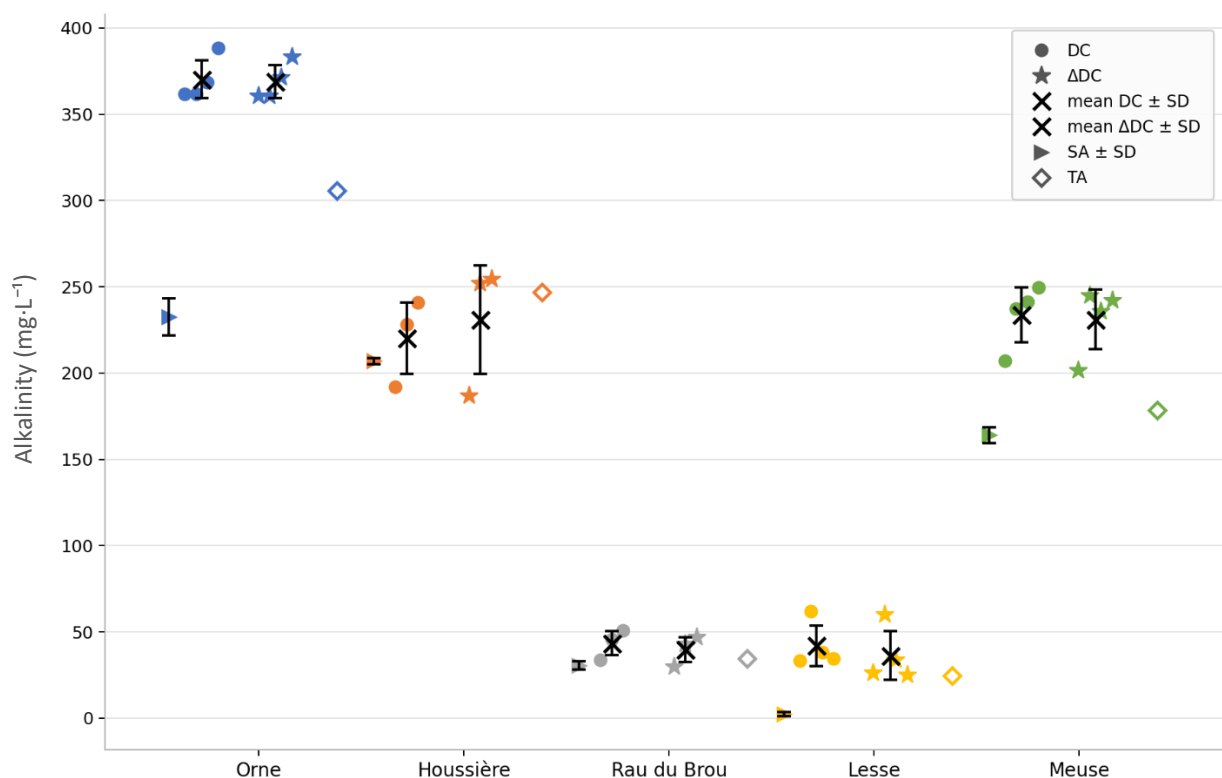


Figure 28 - CA ($\text{mg}\cdot\text{L}^{-1}$) measured with the headspace method for five rivers. Each river is represented by a distinct colour. Dots show DC replicates (mean $\pm$ SD: black cross). Stars show ΔDC (same representation). Triangles denote SA ($\pm$ SD) and diamonds TA measured in the laboratory.

For clarity, rivers were classified into two groups based on their alkalinity: low alkalinity ($<50 \text{ mg}\cdot\text{L}^{-1}$; Lesse and Rau du Brou) and high alkalinity ($>100 \text{ mg}\cdot\text{L}^{-1}$; Orne, Houssière, and Meuse).

DC method

SD values remained relatively consistent, ranging between 9 and $20 \text{ mg}\cdot\text{L}^{-1}$, except for the Houssière, which exhibited a higher SD of $25 \text{ mg}\cdot\text{L}^{-1}$.

In terms of accuracy, TA fell within the range defined by the mean $\pm$ SD for Rau du Brou and differed by only 2 and $4 \text{ mg}\cdot\text{L}^{-1}$ for the Houssière and the Lesse, respectively. However, for the Orne and the Meuse, deviations reached 51 and $37 \text{ mg}\cdot\text{L}^{-1}$ above TA, respectively. DC values were almost systematically higher than TA, with the Houssière being the only exception, where the mean DC value was lower than TA.

ΔDC method

SD values remained relatively consistent, ranging from 9 to $20 \text{ mg}\cdot\text{L}^{-1}$ (comparable to or up to $2 \text{ mg}\cdot\text{L}^{-1}$ higher than in DC), except for the Houssière, which exhibited a SD of $38 \text{ mg}\cdot\text{L}^{-1}$. In

terms of accuracy, TA fell within the range defined by the mean $\pm$ SD for the Houssière, the Rau du Brou, and the Lesse. However, for the Orne and the Meuse, this range reached 52 and 32 mg·L⁻¹ above TA, respectively. As with the DC method, values were almost systematically higher than TA, except for the Houssière, where the mean Δ DC value remained lower than TA.

Overall assessment of DC-based methods

Overall, SD values ranged between 9 and 20 mg·L⁻¹, except for the Houssière, which exhibited a higher SD. Differences between the mean value and TA exceeding 20 mg·L⁻¹ were observed for three rivers using the DC method and for two rivers using the Δ DC method.

Removing the acid injection parameter (p_{inj}) resulted in SD values that remained similar or slightly higher, while the error between the mean Δ DC values and TA remained similar or decreased. This suggested that errors induced by acid injection were partially removed. Differences between DC_{mean} and ΔDC_{mean} values ranged from 1 to 11 mg·L⁻¹, leading to a corresponding reduction in absolute error relative to TA.

Comments on DC and Δ DC graphs

Figure 29 shows the graphs obtained using the DC and Δ DC methods. Subtracting p_{inj} should theoretically lead to a zero intercept for Δ DC regression. For the calibration lines obtained at the Orne and in the laboratory (Rau du Brou), the intercepts are close to zero (+0.9 and -0.3 mbar, respectively). In contrast, higher intercepts are observed for the Houssière and the Meuse (3.7 and 3.8 mbar), while a lower value is obtained for the Lesse (-1.5 mbar). Notably, for the Meuse, the Δ DC intercept is approximately 1 mbar higher than that of DC, which is unexpected. These results suggest that sources of error other than the injection process affect the measurements.

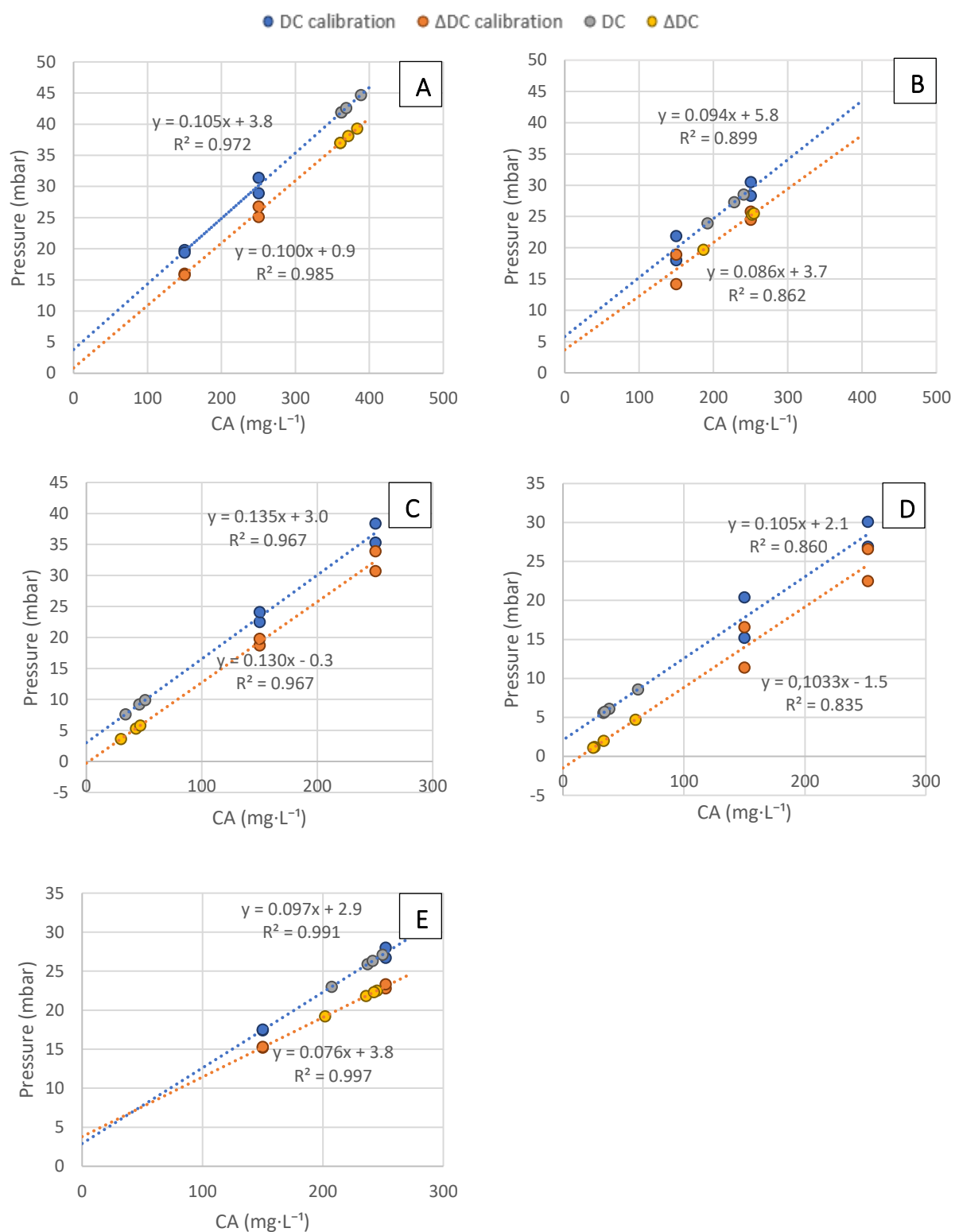


Figure 29 - DC and ΔDC calibration curves and measurements for (A) Orne, (B) Houssière, (C) Rau du Brou, (D) Lesse and (E) Meuse.

SA method

SD values were low, ranging between 0 and 4 mg·L⁻¹ for four rivers and reaching 11 mg·L⁻¹ for the Orne.

In terms of accuracy, TA did not fall within the range defined by the mean $\pm$ SD for any of the rivers, but the TA of Rau du Brou was 2 mg·L⁻¹ lower than this range. For the Meuse and the Lesse, TA was lower by 11 and 22 mg·L⁻¹ respectively. Larger discrepancies were observed for the Houssière and the Orne, reaching 38 and 62 mg·L⁻¹ respectively. SA values were systematically lower than TA across all rivers. Results and comparison of the methods will be discussed in Section 10.3.

10.2 Alkalinity determination results on bottled waters using direct calibration and standard addition

The CA of two bottled water brands (Spa and Chaudfontaine) was measured in the laboratory using the DC and Δ DC methods, the SA method and the two end-point titration method. Figure 30 shows all obtained results, together with the HCO₃⁻ concentrations reported on the bottle labels.

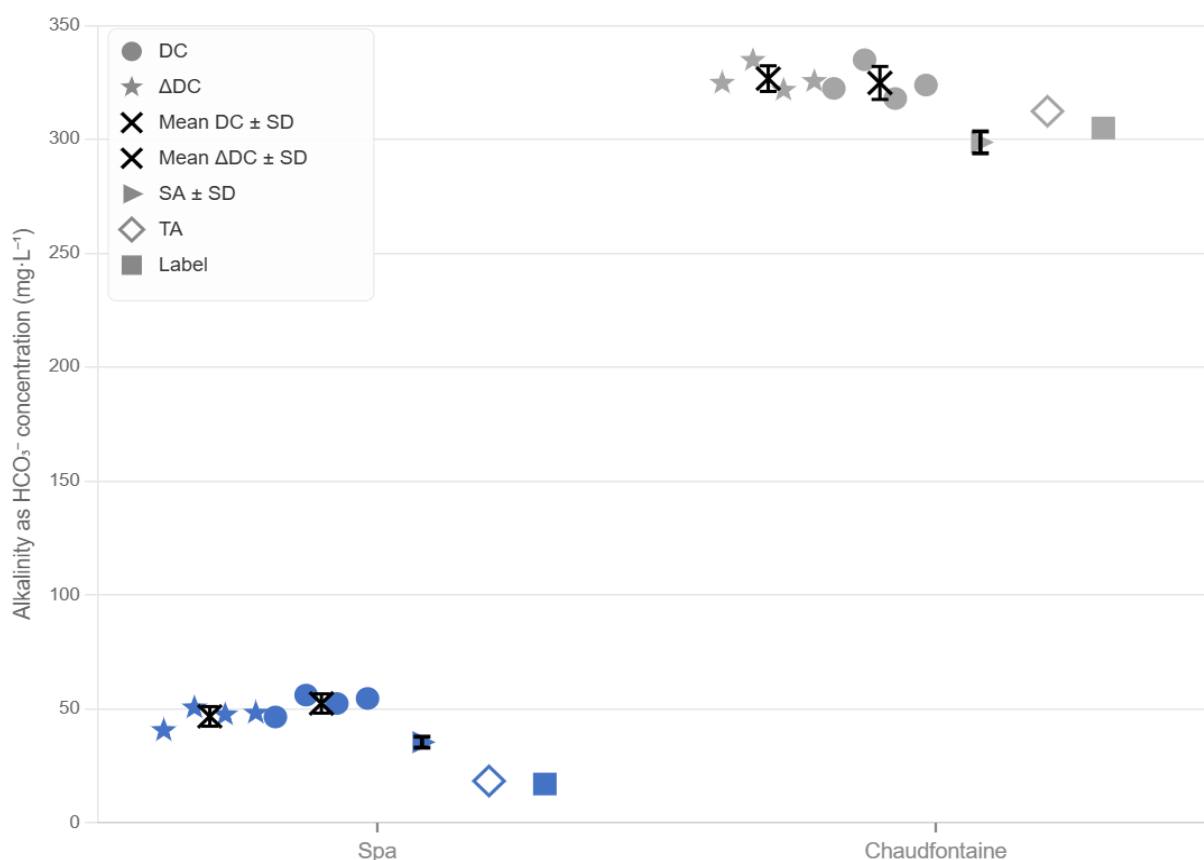


Figure 30 - CA (mg·L⁻¹) measured with the headspace method for two bottled waters. Each bottled water is represented by a distinct colour. Dots show DC replicates (mean $\pm$ SD: black cross). Stars show Δ DC (same representation). Triangles denote SA ($\pm$ SD), diamonds TA measured in the laboratory and a square indicates the HCO₃⁻ concentration on the label.

DC method

SD values remained low: 4 and 7 mg·L⁻¹ for Spa and Chaudfontaine, respectively. In terms of accuracy, TA fell outside the range defined by the mean ± SD, although it differed by only 5 mg·L⁻¹ for Chaudfontaine, TA was 30 mg·L⁻¹ below this range for Spa. DC values were systematically higher than TA.

ΔDC method

SD values remained low: 4 and 6 mg·L⁻¹ for Spa and Chaudfontaine, respectively. TA did not fall within the mean ± SD range, but the difference was limited to 8 mg·L⁻¹ for Chaudfontaine, while reaching 24 mg·L⁻¹ above TA for Spa. ΔDC values were systematically higher than TA.

Overall assessment of DC-based methods

SDs were nearly identical. The absolute error decreased by 6 mg·L⁻¹ for Spa and increased by 2 mg·L⁻¹ for Chaudfontaine. The same laboratory calibration curve as for the Rau du Brou was used, which had an intercept close to zero.

SA method

SD values remained low, at 2 and 5 mg·L⁻¹ for Spa and Chaudfontaine, respectively. TA did not fall within the mean ± SD range, with a difference of 8 mg·L⁻¹ for Chaudfontaine and 15 mg·L⁻¹ above TA for Spa. SA values were higher than TA in one case and lower in the other.

Label

The absolute difference between measured TA and the HCO₃⁻ concentration on the label was 1 mg·L⁻¹ for Spa and 7 mg·L⁻¹ for Chaudfontaine.

10.3 Discussion of the results obtained, considering the factors known to influence the headspace method

The number of water samples on which the headspace method has been applied is limited: two bottled water samples analysed in the laboratory and five river samples analysed in the field. Therefore, the observations cannot lead to definitive conclusions, they provide a preliminary assessment of the performance of the methods.

Recording p_{inj} (in ΔDC) generally resulted in a reduction of the absolute error between DC_{mean} and TA. However, this reduction remained below ~10 mg·L⁻¹, which is smaller than the overall SD of the method. Considering both the limited magnitude of this improvement and the additional time (+10 minutes in total) and procedural complexity associated with recording p_{inj} , this approach does not appear justified and no distinction between DC and ΔDC will be made in the following analysis.

Under laboratory conditions, both methods exhibited relatively good precision for the two bottled waters, with SD below 7 mg·L⁻¹. The absolute error relative to TA remained below 20

mg·L⁻¹ for both methods, except for one bottled water sample analysed with the DC method, which showed a higher deviation.

Under field conditions, the DC method showed a SD below 20 mg·L⁻¹ for four out of five rivers. For the SA method, the SD was below 11 mg·L⁻¹ for all rivers. Regarding absolute error, all three methods yielded values around a maximum of 20 mg·L⁻¹ for three rivers, whereas substantially higher errors were observed for two rivers; the reasons for these discrepancies remain unknown.

A systematic trend can be observed: DC results tend to be higher than TA, while SA results are generally lower than TA, suggesting the presence of a potential unknown bias. TA consistently lies between DC and SA values. This may indicate that no carbonate precipitation has occurred, as such precipitation would result in systematically lower TA values.

In terms of method comparison, the SA method appeared to provide better precision overall, although in some cases the SDs were comparable between methods. The calculation of SD differs between DC and SA. In DC, it is derived directly from replicate pressure measurements, whereas in SA it is linked to the fit of the linear regression (Section 9.2, based on residuals). Despite this methodological difference, SA calibration curves consistently showed R² values above 0.99, while DC values range between 0.85 and 0.99. As the SA method is known to reduce matrix effects, this may indicate that such effects are present and partially mitigated by SA. Overall, a reasonable upper bound for precision can be estimated at ±20 mg·L⁻¹ for the DC method and ±10 mg·L⁻¹ for the SA method.

In terms of accuracy, both methods can be assigned an approximate uncertainty of ±20 mg·L⁻¹. However, the occurrence of unexplained cases with significantly higher errors should be acknowledged. Based on the current dataset, it is not possible to definitively determine which method is more accurate.

The DC method could potentially be improved, by preparing a wider range of calibration solutions and first performing the measurement on the unknown sample. The calibration concentrations could then be selected based on the expected alkalinity range of the sample. This would ensure more appropriate bracketing of the measured value and potentially improve accuracy. However, this approach would require the preparation and transport of a larger number of calibration solutions, further increasing logistical constraints and reducing its practicality for field applications.

The coefficients of variation (CV; $SD \cdot mean^{-1} \cdot 100$) and relative errors were not discussed because the SD and absolute error appeared to be independent of sample alkalinity. Consequently, for low-alkalinity samples (up to 18 mg·L⁻¹ for Spa water), a SD or an absolute error of 20 mg·L⁻¹ corresponded to a CV or relative error close to 100%. The largest relative error was observed for the Spa sample, for which an absolute error of 34 mg·L⁻¹ between DC_{mean} and TA resulted in a relative error of 186%. This behaviour is characteristic of a constant systematic error, i.e., an error whose magnitude does not depend on the magnitude of the measured quantity (Skoog et al., 2015). Nevertheless, all coefficients of variation and relative errors are reported in the tables associated with the results in the appendices. Therefore, while

the methods may be suitable for estimating the general range of alkalinity, they may significantly overestimate or underestimate low-alkalinity samples.

Finally, the method appears to lack sufficient sensitivity: an error of a few millibars in pressure measurement translates into an error of several tens of $\text{mg}\cdot\text{L}^{-1}$ in CA. Given that pressure readings do not seem to be reliable at the millibar level, this represents a limitation of the method.

11 Conclusion

Throughout this work, the headspace-based CA measurement protocol was progressively refined. Several previously unrecognized factors affecting the measurements were identified, leading to methodological improvements. The dataset obtained using the final protocol, integrating all identified influencing factors, remained too limited to support definitive conclusions. The results presented below should therefore be considered as a preliminary assessment of the method. Further improvements of the headspace method are required (see Section 12), followed by validation on a larger sample set.

Two approaches were evaluated for CA determination using the headspace method: DC method and SA method. Their respective advantages and limitations are summarized in Table 6. While both methods exhibited a comparable accuracy of approximately $\pm 20 \text{ mg}\cdot\text{L}^{-1}$, the SA approach appears preferable. It offers practical advantages (shorter analysis time and reduced weight to carry), improved precision and a stronger theoretical basis, as the SA method helps mitigate matrix effects. Nevertheless, the DC method could be improved by using a broader set of calibration solutions and measuring the unknown sample first, allowing calibration concentrations to be adjusted to the expected alkalinity range. Although this could improve accuracy through better bracketing, it would also increase the number of solutions to prepare and transport, limiting practicality for field applications.

Table 6 - Overview of the advantages and limitations of the DC and SA methods.

Advantages		Disadvantages
DC method	- No need to measure p_{inj}, which simplifies and shortens the procedure	- Overall longer procedure due to the need to perform the experiment twice (total time ≈ 30 minutes). - Moderate precision ($SD \approx 20 \text{ mg}\cdot\text{L}^{-1}$) - Heavier to transport (400 mL per analysed water)
SA method	- Faster than DC (~ 20 minutes) - Higher precision ($SD_{max} \approx 10 \text{ mg}\cdot\text{L}^{-1}$) - Lighter to transport (3 mL standard solution per analysed water)	- Requires the measurement of p_{inj}, which is not always convenient

In terms of analytical performance, the SA method showed a precision of approximately $\pm 10 \text{ mg}\cdot\text{L}^{-1}$ compared to $\pm 20 \text{ mg}\cdot\text{L}^{-1}$ for the DC method, with an overall accuracy on the order of $\pm 20 \text{ mg}\cdot\text{L}^{-1}$ for both methods. However, occasional anomalous values were still observed, even with the final protocol, their origin remains unknown. Several potential sources of error were identified:

- Limited precision in the acid injection process, including air intake in the syringe and imprecise volume reading;
- Uncertainty in the accuracy of pressure measurements using the pressure gauge, possibly influenced by temperature effects and air–water temperature gradients within the apparatus;
- Temperature dependence of the system, including water vapour pressure, gas solubility and expansion, emphasizing the need to maintain the apparatus at river temperature throughout the measurement, which may not always be fully achieved under field conditions;
- Limited sensitivity of the method, where small pressure variations on the order of a few mbar can translate into significant alkalinity differences of several tens of $\text{mg}\cdot\text{L}^{-1}$.

Several measurements demonstrated the ability to resolve concentrations on the order of $10 \text{ mg}\cdot\text{L}^{-1}$. However, given the overall precision of approximately $\pm 20 \text{ mg}\cdot\text{L}^{-1}$, such a low LOQ is not meaningful in practice. Overall, these results nevertheless suggest that the LOQ could be reduced compared with the $100 \text{ mg}\cdot\text{L}^{-1}$ previously reported for saline production waters (Liu et al., 2023).

Despite its current limitations, the method presents practical advantages: it allows in situ CA measurements and does not require access to a full laboratory apparatus. The headspace equipment is relatively low-cost, with the pressure gauge representing the main expense ($\sim\text{€}1000$), and a total apparatus cost estimated between $\text{€}1400$ and $\text{€}1700$.

12 Perspectives

The waters analysed in this study were assumed not to have undergone carbonate precipitation. For such systems, conventional methods, such as the classical two end-points titration, remain the most appropriate approach for alkalinity determination. Consequently, if further development of the headspace method is pursued, its evaluation should be extended to more complex waters, where matrix effects or carbonate precipitation may compromise standard techniques. In such contexts, the added value of the method could be more clearly demonstrated.

Overall, the headspace approach appears promising, as it is based on a relevant physicochemical principle. However, its current implementation suffers from limited sensitivity of the method. Indeed, a pressure variation of only a few millibars corresponds to changes of several tens of $\text{mg}\cdot\text{L}^{-1}$ in alkalinity. In practice, pressure measurements are currently influenced by multiple factors and instrumental errors, making it unlikely that measurements can reliably achieve millibar-level precision. This limitation directly impacts the method's precision and accuracy.

Several improvements of the materials used could therefore be explored to enhance the method's performance. First, the accuracy of the pressure gauge should be verified, or an alternative model could be evaluated. Second, better control of the injection step could reduce variability: the use of a 1 mL syringe with a mechanical stop and equipped with a needle designed to prevent air aspiration would ensure reproducible acid volumes, thereby improving consistency between measurements.

A promising approach to increase sensitivity would be to modify the sample volume. Increasing the water volume from 100 mL to 200 mL would reduce the headspace volume and simultaneously double the amount of DIC introduced into the system. As shown in Figure 31, this results in a doubling of the slope of the regression line relating pressure to CA, thereby significantly enhancing the sensitivity of the method.

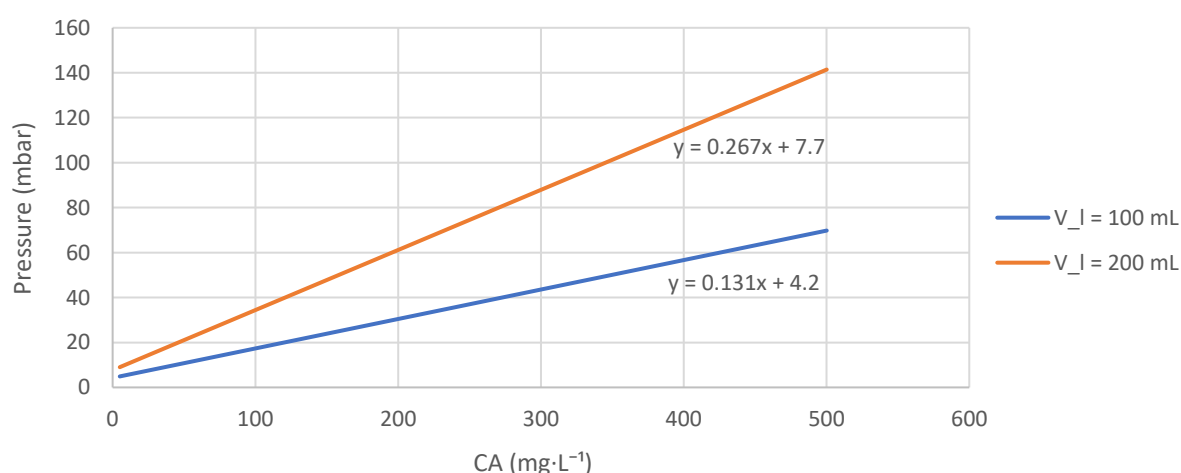


Figure 31 - Regression lines of the theoretical pressure (mbar) as a function of CA ($\text{mg}\cdot\text{L}^{-1}$) for a liquid volume (V_L) of 100 mL (blue) and 200 mL (orange).

On the other hand, it would also be interesting to use a broader set of calibration solutions for the DC method and first perform the measurement on the unknown sample. The calibration concentrations could then be selected based on the expected alkalinity range of the sample thus improving the bracketing. Further investigations will be necessary to evaluate these potential improvements and to determine whether they can provide precision and accuracy enhancement of the method under field conditions.

Another limitation of the headspace method lies in its lack of practicality under field conditions. The current apparatus, including the use of weights and a metal container, is cumbersome and difficult to transport. Ideally, the apparatus should be directly immersed in the river to ensure a homogeneous and stable temperature. However, this configuration is not always feasible, as it requires a water depth corresponding to bottle height (approximately 15 cm) and a relatively flat riverbed to allow stable placement of the apparatus. Such conditions are not consistently encountered across all sampling sites.

In addition, handling the equipment in the field proved challenging. Riverbanks are often uneven, making it difficult to safely place and manipulate materials such as acid bottles. The repeated opening and closing of the acid container during injections is time-consuming and impractical, particularly as the operator must simultaneously handle the syringe and other components. Furthermore, placing equipment such as syringes, caps, and bottles on the ground during rinsing or handling exposes them to dirt, mud, and debris, which may clog connectors and compromise the reliability of the system.

To address these limitations, one potential approach would be to use a floating support, such as a board with holes sized to fit the neck of the bottles. This would allow the bottles to be fixed in place by their caps. The system could be attached either to the operator or to a fixed element (e.g., a tree or a rock) to prevent it from drifting with the current. Figure 32 presents a conceptual illustration of this proposed system.

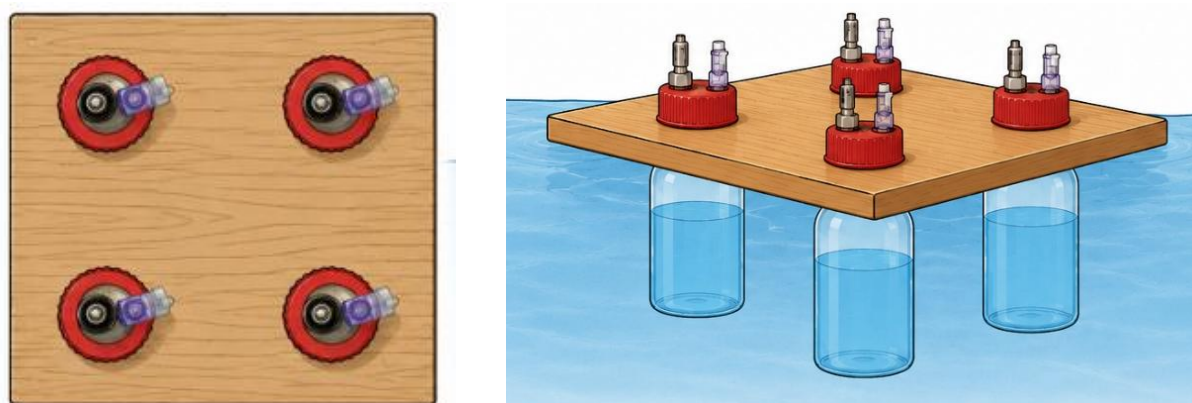


Figure 32 - Conceptual illustration of the proposed floating support system for the headspace apparatus. Image generated with ChatGPT.

Such a design would offer several advantages. First, the entire liquid phase within the bottles could remain immersed, enabling use in deeper sections of the river and improving temperature homogeneity. Second, the surface of the board could serve as a working area for handling equipment, thereby reducing contamination risks and improving ease of use (although

the stability of certain elements, such as acid containers, would need to be assessed under flowing conditions). During the agitation step, the operator could hold the edges of the board and agitate the system, ensuring consistent mixing across all samples. The feasibility of such a system remains to be evaluated, particularly with respect to its ease of transport (weight and bulkiness) and its ability to provide sufficient and reproducible agitation.

Appendices

Appendix 1 – Alkalinity conversion from $\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$ to conventional units

Table A1 - Alkalinity ($\text{mg}\cdot\text{L}^{-1} \text{HCO}_3^-$) conversion to conventional units

Alkalinity unit	Conversion factor
$\text{meq}\cdot\text{L}^{-1}$	$\frac{1}{61}$
$\text{mg}\cdot\text{L}^{-1} \text{CaCO}_3$	$\frac{50}{61}$
$^\circ\text{f}$	$\frac{5}{61}$

Appendix 2 – Verification of acid excess conditions for complete DIC conversion

1. Acid connector tube's volume

$$V_{cylinder} = \pi \cdot r^2 \cdot h \quad A.1$$

with r the radius of the connector (cm) and h the height of the connector (cm).

$$V_{cylinder} = \pi \cdot r^2 \cdot h = \pi \cdot 0.15^2 \cdot 3 \approx 0.2 \text{ mL} \quad A.2$$

2. Determination of the acid concentration

HCl 37%, $d=1.19 \text{ g/L}$, $MW = 36.46 \text{ g/mol}$

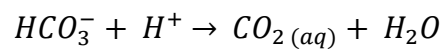
Mass of 1 mL of solution: 1.19 g

Mass of HCl in 1 mL of solution: $1.19 \cdot 0.37 = 0.4403 \text{ g}$

Number of moles per mL: $\frac{0.4403}{36.46} = 0.012 \text{ mol} \rightarrow C = 12.1 \text{ mol/L}$

Since it is diluted 2-fold (addition of 50 mL of 37% HCl to 50 mL of water), $C = 6.05 \text{ mol} \cdot \text{L}^{-1}$

3. Volume required to react with 100 mL of 1000 mg/L bicarbonate



$$C_{\text{HCO}_3^-} = 1 \text{ g} \cdot \text{L}^{-1} = \frac{1}{61} = 0.016 \text{ mol} \cdot \text{L}^{-1}$$

$$n_{\text{HCO}_3^-} = 0.016 \cdot 0.1 = 0.0016 \text{ mol} = n_{\text{H}^+}$$

$$V_{\text{H}^+} = \frac{n}{C} = \frac{0.0016}{6.05} \cdot 1000 = 0.28 \text{ mL}$$

To ensure complete conversion of DIC species into CO_2 , the amount of acid injected must be sufficient to neutralize all bicarbonate and carbonate ions present in solution. This condition was verified for the most extreme case considered in this study, namely a bicarbonate concentration of $1000 \text{ mg} \cdot \text{L}^{-1}$, which largely exceeds the alkalinity range expected in natural freshwater systems. At this concentration, taking into account the dead volume of the acid connector (up to 0.2 mL), the effective acid excess reaching the solution is estimated at between 0 and 0.3 mL in the worst case. This condition was further confirmed empirically: calibration curves established up to $1000 \text{ mg} \cdot \text{L}^{-1} \text{HCO}_3^-$ yielded pressure responses consistent with theoretical predictions, showing no deviation attributable to insufficient acid supply. The only situation in which acid insufficiency could become a concern would be if other acid-consuming species were present in significant amounts, such as dissolved organic matter or other alkalinity-contributing ions.

Appendix 3 - Theoretical pressure estimation spreadsheet

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1														
2	Total volume (L)	0.312		Initial volumes			Injection volumes			Initial volumes with injection volumes				
3	Temperature (K)	294.15												
4	R (L·atm·mol ⁻¹ ·K ⁻¹)	0.08206												
5	MW HCO ₃ ⁻ (g·mol ⁻¹)	61.02		V _i (L)	0.1		V _{inj,i} (L)	0.001		V _i (L)	0.101			
6	p _{CO2, air} (atm)	0.0004		V _g (L)	0.212		V _{inj,g} (L)	0.0005		V _g (L)	0.211			
7	K _H (20°C) (mol·(L·atm) ⁻¹)	0.0389												
8	From (Stumm and Morgan, 2012)			Initial air mol	pV=nRT		Injected air moles			Initial gas moles with injection			Pressure after injection	
9														
10				n _{air,i} (mol)	8.78E-03		n _{inj} (mol)	2.07E-05		n _{air,tot} (mol)	8.80E-03		p (atm)	1.007
11				n _{CO2,i} (mol)	3.51E-06		n _{CO2,inj} (mol)	8.29E-09		n _{CO2} (mol)	3.52E-06		Δp (atm)	0.007
12													Δp (mbar)	7.203
13														
14				CO ₂ balance										
15														
16														
17														
18				n CO _{2,i(g)} (mol)	3.52E-06									
19				n CO _{2,i(l)} (mol)	1.56E-06									
20				n CO _{2,i(aq)} (mol)	5.08E-06									
21														
22														
23														
24														
25														
26														
27				CHCO ₃ ⁻ (mg/L)	CHCO ₃ ⁻ (mol/L)	n CO _{2,pre} (mol)	n CO _{2,tot} (mol)	p _i (atm)	p _i (mbar)	p _i + Δp _{inj} (mbar)	if all CO _{2,g} (mbar)	p _i + Δp _{inj} if all (g) (mbar)		
28				5	8.2E-05	8.2E-06	1.3E-05	1.0E-03	1.1	8.3	1.5	8.7		
29				6	1.1E-04	1.1E-05	1.6E-05	1.2E-03	1.3	8.5	1.8	9.0		
30				20	3.3E-04	3.3E-05	3.8E-05	3.0E-03	3.0	10.3	4.4	11.6		
31				26	4.2E-04	4.2E-05	4.7E-05	3.7E-03	3.8	11.0	5.5	12.7		
32				65	1.1E-03	1.1E-04	1.1E-04	8.8E-03	8.9	16.1	12.9	20.1		
				101	1.7E-03	1.7E-04	1.7E-04	1.3E-02	13.7	20.9	19.8	27.0		

Figure A1 - Spreadsheet used for the theoretical estimation of CO₂ pressure in the headspace as a function of bicarbonate concentration

Spreadsheet used for the theoretical estimation of CO₂ pressure in the headspace as a function of bicarbonate concentration. The upper section contains the fixed physicochemical parameters (temperature, liquid and gas volumes, Henry's constant, injection volumes), which can be adjusted to simulate different experimental conditions. The lower table gives the theoretical pressure for any user-defined bicarbonate concentration, computed from the CO₂ mass balance, Henry's law and the ideal gas law as described in Section 5.

Appendix 4 - Seal integrity of the four apparatuses

Table A2 - Pressure loss measured over 3 hours for each of the four apparatuses, initially pressurized to approximately 200 mbar. The observed pressure loss and relative deviation are reported for each apparatus.

	Apparatus 1	Apparatus 2	Apparatus 3	Apparatus 4
p_0 (mbar)	194.4	196.3	195.2	195.4
p_3 (mbar)	186.4	189.1	186.6	187.8
Δp (mbar)	8.0	7.2	8.6	7.6
Δp (%)	4.1	3.7	4.4	3.9

Appendix 5 - Agitation optimization: pressure data and statistical analysis

Table A3 - Pressure (mbar) as a function of cumulative agitation time for four bicarbonate concentrations (30 s cycles)

	200 mg·L ⁻¹	100 mg·L ⁻¹	20 mg·L ⁻¹	10 mg·L ⁻¹
p ₁ (mbar)	26,1	16,2	7,3	6,1
p ₂ (mbar)	29,1	18,7	8,1	6,9
p ₃ (mbar)	29,5	19,0	8,3	7,3
p _{3,5} (mbar)	29,6	19,4	8,6	7,6
p _{8 (stab)} (mbar)	30,0	19,6	8,4	7,1

Table A4 - Paired t-test results for successive 30 s agitation cycles: comparison of pressure values between consecutive measurement stages.

Comparison	Mean difference (mbar)	p-value (-)
P _{30''} → p _{60''}	2.6 ± 0.4	0.002
P _{60''} → p _{90''}	0.4 ± 0.2	0.1
P _{90''} → p _{120''}	0.3 ± 0.2	0.3
P _{120''} → p _{120''+240''}	0.1 ± 0.3	0.8

Table A5 - Pressure (mbar) as a function of cumulative agitation time for a bicarbonate concentration of 200 mg·L⁻¹ in quadruplicate (15 s cycles)

	15" (mbar)	30" (mbar)	45" (mbar)	60" (mbar)	75" (mbar)	90" (mbar)
1	25.7	26.4	27	27.5	28	28.4
2	28.12	29	29.6	30	30.6	31.1
3	31.2	33.4	33.8	35.5	35.2	35.5
4	30.6	32	32.3	32.7	33.1	33.3

Table A6 - Paired t-test results for successive 15 s agitation cycles: comparison of pressure values between consecutive measurement stages.

Comparison	Mean difference (mbar)	p-value (-)
P _{15''} → p _{30''}	1.3 ± 0.7	0.03
P _{30''} → p _{45''}	0.5 ± 0.2	0.008
P _{45''} → p _{60''}	0.8 ± 0.6	0.06
P _{60''} → p _{75''}	0.3 ± 0.4	0.2
P _{75''} → p _{90''}	0.4 ± 0.1	0.01

Table A7 - Pressure (mbar) as a function of measurement stage for a bicarbonate concentration of 200 mg·L⁻¹ in quadruplicate (continuous agitation)

	P ₀ (mbar)	P _{ac} (mbar)	P _{15"} (mbar)	P _{30"} (mbar)	P _{45"} (mbar)	P _{1'} (mbar)	P _{1'+1'} (mbar)
1	0.8	5.4	21.8	27.6	30.3	33.3	32.3
2	2.5	7.1	27.7	32.3	34	35.6	34.8
3	3	7.4	25.6	32.6	34	35.4	34.7
4	2	6.3	24	30.4	31.8	33.4	33

Appendix 6 - Evaluation of the Wang et al. (2014) protocol

Table A8 - Experimental data obtained using the Wang et al. (2014) protocol, including recorded pressures at each measurement step ($p_{\text{step } 2}$, $p_{\text{step } 3}$, $p_{\text{step } 4}$), measured alkalinity ($\text{mg}\cdot\text{L}^{-1}$), and associated CV.

Actual value ($\text{mg}\cdot\text{L}^{-1}$)	p_2 (mbar)	p_3 (mbar)	p_4 (mbar)	Measured value ($\text{mg}\cdot\text{L}^{-1}$)	CV (%)
200	1.8	29.9	58.2	300	50
200	1.4	32.3	64.0	300	50
100	1.0	15.2	43.2	150	60
100	0.7	18.3	53.0	150	60
100	1.0	19.4	61.1	130	30
50	1.6	10.9	36.2	110	130
50	1.1	12.7	48.8	100	100
50	0.9	12.3	54.0	80	70
20	0.0	8.0	35.8	90	340
20	2.1	9.0	45.6	60	200
20	2.0	9.4	50.7	50	170

Appendix 7 - Repeatability of TA measurements by two end-points titration

Table A9 - Repeated TA measurements ($\text{mg}\cdot\text{L}^{-1}$) for five bicarbonate solutions of known concentration ($n = 5$), with associated standard deviation.

	$\sim 10 \text{ mg}\cdot\text{L}^{-1}$	$\sim 24 \text{ (mg}\cdot\text{L}^{-1})$	$\sim 49 \text{ (mg}\cdot\text{L}^{-1})$	$\sim 97 \text{ (mg}\cdot\text{L}^{-1})$	$\sim 242 \text{ (mg}\cdot\text{L}^{-1})$
	9.6	24.4	47.2	94,9	237,9
	9.6	24.6	47.1	95,1	238,7
	9.5	24.6	47.4	95,0	237,7
	9.6	24.6	47.2	95,1	240,3
	9.6	24.4	47.5	95,1	240,5
SD	0.0	0.1	0.2	0,1	1,3

Table A10 - Repeated TA measurements ($\text{mg}\cdot\text{L}^{-1}$) for five commercial bottled waters ($n = 3$), with associated standard deviation.

	Spa	Chaudfontaine	Cristalline	Contrex	Evian
	15,0	264,8	250,4	378,2	359,0
	18,7	262,6	245,7	378,1	359,0
	18,2	263,5	250,5	378,2	358,1
SD	2,0	1,1	2,8	0,1	0,5

Table A11 - Repeated TA measurements ($\text{mg}\cdot\text{L}^{-1}$) for five river water samples ($n = 2$), with associated standard deviation.

	Orne	Houssière	Malaise	Hubiessau	Forges
	306,9	244,8	254,1	271,9	295,2
	309,6	244,3	255,8	272,2	296,2
SD	1,9	0,3	1,2	0,2	0,7

Repeated TA measurements show low variability across all sample types, with standard deviations not exceeding $2.8 \text{ mg}\cdot\text{L}^{-1}$, confirming the high repeatability of the two end-points titration method under the conditions of this study.

Appendix 8 - Raw pressure and alkalinity data from the first field measurements using the DC method

Table A12 - Raw pressure data (mbar) obtained during the first field measurements using the DC method. R indicates rejected values.

Repetition	Orne (mbar)	Houssière (mbar)	Malaise (mbar)	Hubiessau (mbar)	Forges (mbar)
1	42.5	33.0	41.1	44.5	46.9
2	45.6	35.3	40.9	46.2	46.8
3	43.9	30.2	42.1	42.8	51.1
4	46.3	38.3	42.7	43.0	44.7
5	43.4	41.0	41.3	44.9	45.9
6	-	39.8	42.0	-	-
R1	-	-	28.2	13.2	37.2
R2	-	-	30.0	36.22	34.9
R3	-	-	36.4	34.5	44.5
R4	-	-	-	31.0	-

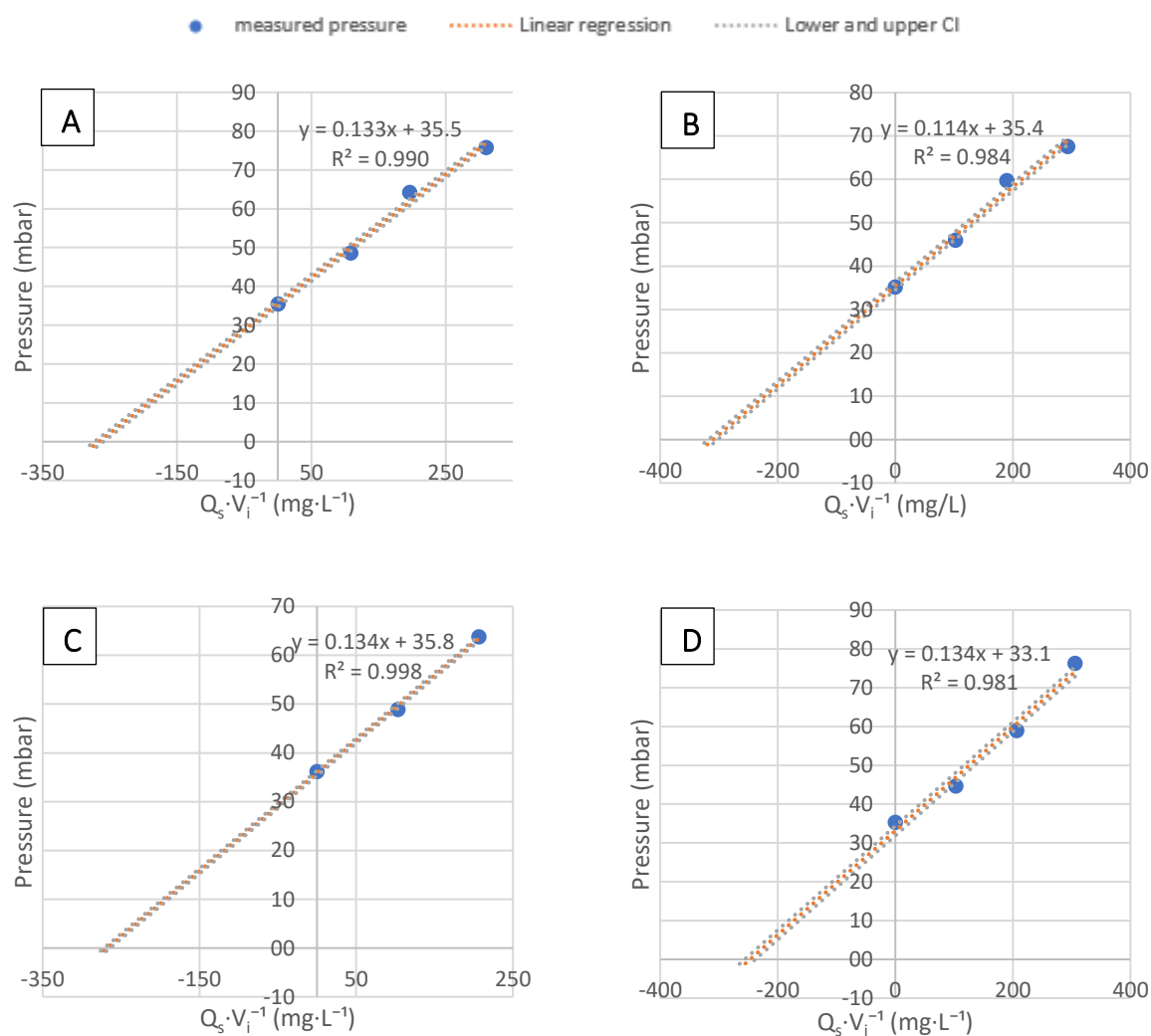
Table A13 - Raw alkalinity data (mg·L⁻¹) obtained during the first field measurements using the DC method. R indicates rejected values.

Repetition	Orne (mg·L ⁻¹)	Houssière (mg·L ⁻¹)	Malaise (mg·L ⁻¹)	Hubiessau (mg·L ⁻¹)	Forges (mg·L ⁻¹)
1	283	207	271	298	317
2	307	226	270	311	317
3	294	185	279	285	351
4	313	249	284	286	300
5	290	271	273	302	309
6	-	261	279	-	-
R1	-	-	169	51	241
R2	-	-	184	233	222
R3	-	-	234	219	298
R4	-	-	-	192	-

Table A14 - Summary of pressure and alkalinity values (mg·L⁻¹) obtained in the field using the DC method, alkalinity measured in the laboratory by two end-points titration, and associated relative error.

	$p_{\text{mean}} \pm \text{SD}$ (mbar)	p CV (%)	$\text{CA}_{\text{mean}} \pm \text{SD}$ (mg·L ⁻¹)	CA CV (%)	TA (mg·L ⁻¹)	Absolute error (mg·L ⁻¹)	CV (%)
Orne	44.3 ± 1.6	3.5	297 ± 12	4	308	11	4
Houssière	36.3 ± 4.2	11.5	233 ± 33	14	245	11	5
Malaise	41.7 ± 0.7	1.7	276 ± 5	2	255	21	8
Hubiessau	44.3 ± 1.4	3.2	297 ± 11	4	272	25	9
Forges	47.1 ± 2.4	5.1	319 ± 19	6	296	23	8

Appendix 9 - Standard addition data and regression plots for all replicates at the Orne and Houssière sampling sites



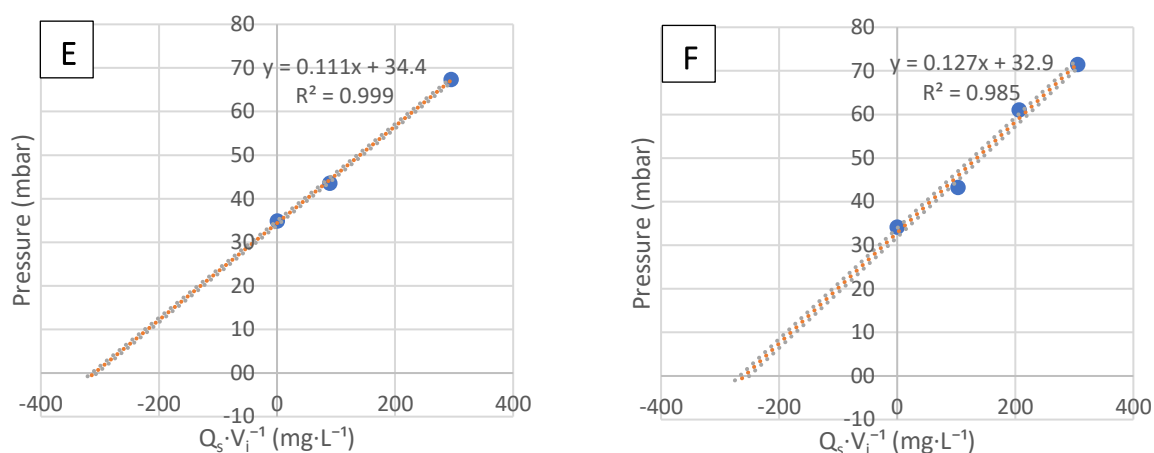


Figure A2 - Standard addition regression plots for all replicates at the Orne (A–D) and Houssière (E–F) sampling sites. (A) and (B): solid NaHCO_3 addition (Eppendorf); (C) and (D): aqueous NaHCO_3 addition; (E): solid NaHCO_3 addition (Eppendorf); (F): aqueous NaHCO_3 addition. The x-axis represents the added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$) and the y-axis represents the measured pressure (mbar).

Table A15 - Standard addition data for replicate 1 at the Orne site (solid NaHCO_3 , Eppendorf).

Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	35.5	35.5	36.4	34.6
108	48.6	50.0	50.9	49.1
196	64.2	61.7	62.6	60.8
310	75.8	76.9	77.8	76.0

Table A16 - Standard addition data for replicate 2 at the Orne site (solid NaHCO_3 , Eppendorf).

Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	35.2	35.4	36.3	34.5
102	46.0	47.1	48.0	46.2
190	59.7	57.1	58.0	56.1
293	67.6	68.9	69.8	68.0

Table A17 - Standard addition data for replicate 3 at the Orne site (aqueous NaHCO_3 solution).

Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
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0	36.2	35.8	36.4	35.3
103	48.9	49.6	50.2	49.1
206	63.8	63.4	64.0	62.9
306	65.3	76.7	77.3	76.2

Table A18 - Standard addition data for replicate 4 at the Orne site (aqueous NaHCO₃ solution).

Concentration (mg·L ⁻¹)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	35.3	33.1	34.4	31.9
103	44.6	47.0	48.2	45.7
206	58.9	60.8	62.0	59.6
306	76.2	74.1	75.4	72.9

Table A19 - Summary of CA values (mg·L⁻¹) determined by the SA method for all replicates at the Orne site, including individual and mean results, coefficient of variation, absolute and relative errors compared to TA.

CA ± SD (mg·L ⁻¹)	CV (%)	TA	Absolute error (mg·L ⁻¹)	Relative error (%)	CA _{Mean} ± SD (mg·L ⁻¹)	Absolute error CA _{Mean} -TA (mg·L ⁻¹)	Relative error CA _{Mean} -TA (%)
266 ± 7	2	266	1	0.3	273 ± 27	7	2.8
310 ± 8	3		45	16.8			
268 ± 4	1		2	0.9			
247 ± 9	4		-18	-6.9			

Table A20 - Standard addition data for replicate 1 at the Houssière site (solid NaHCO₃, Eppendorf).

Concentration (mg·L ⁻¹)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	34.9	34.4	34.9	33.9
89	43.6	44.3	44.9	43.8
295	67.4	67.2	67.7	66.7

Table A21 - Standard addition data for replicate 2 at the Houssière site (aqueous NaHCO₃ solution).

Concentration (mg·L ⁻¹)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	34.1	32.9	33.9	31.8
103	43.2	46.0	47.0	44.9
206	61.0	59.1	60.1	58.1
306	71.4	71.7	72.8	70.7

Table A22 - Summary of CA values (mg·L⁻¹) determined by the SA method for all replicates at the Houssière site, including individual and mean results, coefficient of variation, absolute and relative errors compared to TA.

CA ± SD (mg·L ⁻¹)	CV (%)	TA	Absolute error (mg·L ⁻¹)	Relative error (%)	CA _{Mean} ± SD (mg·L ⁻¹)	Absolute error CA _{Mean} - TA (mg·L ⁻¹)	Relative error CA _{Mean} - TA (%)
309 ± 5	2	240	70	29.1	284 ± 36	44	18.6
259 ± 8	3		19	8.0			

Appendix 10 - Raw data and summary tables for alkalinity measurements on bottled water brands using the DC and SA methods

Table A23 - Standard addition data for Spa: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).

Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	11.9	11.7	11.8	11.6
103	26.2	26.4	26.5	26.3
206	41.0	41.1	41.2	41.0
306	55.5	55.3	55.4	55.2

Table A24 - DC measurements for Spa: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).

Pressure (mbar)	CA ($\text{mg}\cdot\text{L}^{-1}$)
11.9	40
9.6	22
9.1	18
11.2	35

Table A25 - Standard addition data for Vittel: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).

Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	11.9	11.7	11.8	11.6
103	26.2	26.4	26.5	26.3
206	41.0	41.1	41.2	41.0
306	55.5	55.3	55.4	55.2

Table A26 - DC measurements for Vittel: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).

Pressure (mbar)	CA ($\text{mg}\cdot\text{L}^{-1}$)
42.8	285
37.9	246
40.9	270
40.1	264

Table A27 - Standard addition data for Chaudfontaine: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).

Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	54.7	53.8	54.4	53.2
103	67.5	68.2	68.8	67.6
206	81.3	82.6	83.2	82.0
306	97.6	96.5	97.1	95.9

Table A28 - DC measurements for Chaudfontaine: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).

Pressure (mbar)	CA ($\text{mg}\cdot\text{L}^{-1}$)
54.7	379
50.2	343
49.6	339
51.5	354

Table A29 - Standard addition data for Evian: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).

Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	41.6	40.7	41.5	40.0
103	54.2	54.6	55.3	53.8
206	66.5	68.4	69.2	67.7
306	83.2	81.8	82.5	81.0

Table A30 - DC measurements for Evian: measured pressure (mbar) and corresponding CA ($\text{mg}\cdot\text{L}^{-1}$).

Pressure (mbar)	CA ($\text{mg}\cdot\text{L}^{-1}$)
41.6	275
35.1	224
37.8	245
38.9	254

Table A31 - Standard addition data for Contrex: measured pressure (mbar), predicted regression line, and upper and lower confidence intervals (mbar) as a function of added bicarbonate concentration ($\text{mg}\cdot\text{L}^{-1}$).

Concentration (mg·L ⁻¹)	Measured pressure (mbar)	Predict line (mbar)	Upper CI (mbar)	Lower CI (mbar)
0	59.8	60.2	61.1	59.4
103	78.9	77.2	78.0	76.4
206	92.0	94.2	95.0	93.3
306	111.4	110.5	111.4	109.7

Table A32 - DC measurements for Contrex: measured pressure (mbar) and corresponding CA (mg·L⁻¹).

Pressure (mbar)	CA (mg·L ⁻¹)
59.8	419
65.5	464
63.5	449
67.5	480

Table A33 - Individual DC measurements (mg·L⁻¹), mean DC value, standard deviation and coefficient of variation for the five bottled water brands.

	DC (mg·L ⁻¹)	DC (mg·L ⁻¹)	DC (mg·L ⁻¹)	DC (mg·L ⁻¹)	DC _{mean} (mg·L ⁻¹)	SD_DC (mg·L ⁻¹)	CV_DC (%)
Spa	40	22	18	35	29	10	36
Vittel	285	246	270	264	266	16	6
Chaudfontaine	379	343	339	354	354	18	5
Evian	275	224	245	254	250	21	9
Contrex	419	464	449	480	453	26	6

Table A34 - SA measurements (mg·L⁻¹), standard deviation and coefficient of variation for the five bottled water brands.

	SA (mg·L ⁻¹)	SD_SA (mg·L ⁻¹)	CV_SA (%)
Spa	82	1	1
Vittel	293	3	1
Chaudfontaine	386	4	1
Evian	304	6	2
Contrex	366	5	1

Table A35 - Comparison of mean DC and SA values with TA: absolute and relative errors for the five bottled water brands.

	TA (mg·L ⁻¹)	Absolute error DC _{mean} - TA (mg·L ⁻¹)	Relative error DC _{mean} - TA (%)	Absolute error SA - TA (mg·L ⁻¹)	Relative error SA - TA (%)
Spa	15	14	96	67	454
Vittel	223	43	19	70	32
Chaudfontaine	296	57	19	89	30
Evian	188	61	33	115	61
Contrex	378	75	20	-12	-3

Table A36 - Comparison of labelled HCO₃⁻ concentrations with TA values: absolute and relative errors for the five bottled water brands.

	Label (mg·L ⁻¹)	Absolute error label - TA (mg·L ⁻¹)	Relative error label - TA (mg·L ⁻¹)
Spa	17	2	15
Vittel	384	161	72
Chaudfontaine	305	9	3
Evian	360	172	91
Contrex	372	-6	-2

Appendix 11 - Summary of alkalinity results and associated errors for the DC, Δ DC and SA methods across the five studied rivers

Table A37 - Mean DC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation and coefficient of variation, and absolute and relative errors compared to TA for the five studied rivers.

	DC_{mean} ($\text{mg}\cdot\text{L}^{-1}$)	SD_DC ($\text{mg}\cdot\text{L}^{-1}$)	SD_DC (%)	TA ($\text{mg}\cdot\text{L}^{-1}$)	Absolute error $\text{DC}_{\text{mean}} - \text{TA}$ ($\text{mg}\cdot\text{L}^{-1}$)	Relative error $\text{DC}_{\text{mean}} - \text{TA}$ (%)
Orne	370	13	3	306	64	21
Houssière	220	25	11	247	-27	-11
Rau du Brou	43	9	20	35	9	26
Lesse	42	14	32	25	18	71
Meuse	234	18	8	179	55	31

Table A38 - Mean Δ DC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation and coefficient of variation, and absolute and relative errors compared to TA for the five studied rivers.

	$\Delta\text{DC}_{\text{mean}}$ ($\text{mg}\cdot\text{L}^{-1}$)	$\text{SD_}\Delta\text{DC}$ ($\text{mg}\cdot\text{L}^{-1}$)	$\text{SD_}\Delta\text{DC}$ (%)	TA ($\text{mg}\cdot\text{L}^{-1}$)	Absolute error $\Delta\text{DC}_{\text{mean}} - \text{TA}$ ($\text{mg}\cdot\text{L}^{-1}$)	Relative error $\Delta\text{DC}_{\text{mean}} - \text{TA}$ (%)
Orne	369	11	3	306	63	21
Houssière	231	38	17	247	-16	-6
Rau du Brou	40	9	22	35	5	15
Lesse	36	16	45	25	12	47
Meuse	231	20	9	179	52	29

Table A39 - SA values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation and coefficient of variation, and absolute and relative errors compared to TA for the five studied rivers.

	SA ($\text{mg}\cdot\text{L}^{-1}$)	SD_SA ($\text{mg}\cdot\text{L}^{-1}$)	SD_SA (%)	TA ($\text{mg}\cdot\text{L}^{-1}$)	Absolute error SA - TA ($\text{mg}\cdot\text{L}^{-1}$)	Relative error SA - TA (%)
Orne	232	11	5	306	-73	-24
Houssière	207	2	1	247	-40	-16
Rau du Brou	31	2	8	35	-4	-12
Lesse	2	0	0	25	-22	-91
Meuse	164	4	2	179	-15	-8

Appendix 12 - Summary of alkalinity results and associated errors for the DC, ΔDC and SA methods for the two bottled water brands

Table A40 - Mean DC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation, coefficient of variation, and absolute and relative errors compared to TA for Spa and Chaudfontaine.

	DC_{mean} ($\text{mg}\cdot\text{L}^{-1}$)	SD_DC ($\text{mg}\cdot\text{L}^{-1}$)	SD_DC (%)	TA ($\text{mg}\cdot\text{L}^{-1}$)	Absolute error DC_{mean} - TA ($\text{mg}\cdot\text{L}^{-1}$)	Relative error DC_{mean} - TA (%)
Spa	52	4	8	18	34	186
Chaudfontaine	325	7	2	312	12	4

Table A41 - Mean ΔDC values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation, coefficient of variation, and absolute and relative errors compared to TA for Spa and Chaudfontaine.

	$\Delta\text{DC}_{\text{mean}}$ ($\text{mg}\cdot\text{L}^{-1}$)	$\text{SD_}\Delta\text{DC}$ ($\text{mg}\cdot\text{L}^{-1}$)	$\text{SD_}\Delta\text{DC}$ (%)	TA ($\text{mg}\cdot\text{L}^{-1}$)	Absolute error $\Delta\text{DC}_{\text{mean}}$ - TA ($\text{mg}\cdot\text{L}^{-1}$)	Relative error $\Delta\text{DC}_{\text{mean}}$ - TA (%)
Spa	47	4	9	18	28	155
Chaudfontaine	327	6	2	312	14	5

Table A42 - SA values ($\text{mg}\cdot\text{L}^{-1}$), standard deviation, coefficient of variation, and absolute and relative errors compared to TA for Spa and Chaudfontaine.

	SA ($\text{mg}\cdot\text{L}^{-1}$)	SD_SA ($\text{mg}\cdot\text{L}^{-1}$)	SD_SA (%)	TA ($\text{mg}\cdot\text{L}^{-1}$)	Absolute error SA - TA ($\text{mg}\cdot\text{L}^{-1}$)	Relative error SA - TA (%)
Spa	35	2	7	18	17	93
Chaudfontaine	299	5	2	312	-14	-4

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Development of a rapid method for measuring river alkalinity

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Alkalinity plays a fundamental role in aquatic ecosystems by buffering pH fluctuations, thereby maintaining the stable conditions required for aquatic life. While laboratory titration methods remain the reference standard, they require sample transport, which can induce CO₂ degassing and subsequent carbonate precipitation, potentially altering alkalinity values before analysis. Field-deployable methods are therefore needed to enable rapid, in situ measurements.

This work presents a preliminary methodological investigation into the applicability of the headspace method, originally developed for high-alkalinity oilfield produced waters by Wang et al. (2014), to natural freshwater systems characterised by lower alkalinity. The method is based on measuring the pressure increase generated in a sealed vessel following the addition of a strong acid, which quantitatively converts dissolved inorganic carbon into CO₂, thereby allowing carbonate alkalinity to be determined.

The protocol and apparatus were progressively refined throughout this study, and several previously unrecognized factors influencing the pressure measurements were identified and addressed. Two analytical approaches, direct calibration and the standard addition method, were tested on synthetic solutions, bottled waters, and natural river waters. The dataset obtained remained too limited to draw definitive conclusions. The standard addition method proved more precise, while both approaches showed limited accuracy. A systematic opposing bias was observed between the two methods relative to reference titration values.

Despite its practical advantages, including low cost, field portability, and avoidance of sample transport, the method currently suffers from limited sensitivity. Several improvements are proposed, including increasing the sample volume and developing a floating support system to improve thermal stability and ease of handling in the field. Further development and validation on a larger sample set are required before the method can be applied to freshwater alkalinity monitoring.