

Report Card 10. STREAM water quality analytical results

Introduction

The physical and chemical properties of seawater are influenced by various factors, including freshwater inputs, nutrient loads, proximity to land, depth, and local geological influences. These properties greatly impact the success of all marine organisms, both plants and animals.

As part of the STREAM projects work to assess the sites where sensors were deployed saline water samples were collected at Wexford Harbour, Wellington Bridge, Bannow, Waterford Pontoon, Dunmore East, Dungarvan and Castletownbere (Figure 1). Previously SETU had sent a "Quote Request" to commercial laboratories for the analysis of saline water samples, as in Table 1 below.

A tender was awarded to a commercial analytical laboratory because of their high level of accredited analysis, the straightforward range of sample bottles that were required (which they supplied), and cost (see Table 1).

Table 1. Analytes, the limits of Quantification for Saline Water Matrix and accreditation where applicable.

Analyte	Please Provide: Your Limit of Quantification -LOQ	Matrix	Please Provide: Accreditation for analysis of specified parameter in saline water
Ammonia in Saline Waters as N	0.010mg/l N	Saline	INAB ISO17025 accredited
Nitrate in Saline Waters as N	0.003mg/l N	Saline	INAB ISO17025 accredited
Nitrite in Saline Waters as N	0.003mg/l N	Saline	INAB ISO17025 accredited
Phosphate in Saline Waters	0.003mg/l P	Saline	INAB ISO17025 accredited
Chlorophyll	1ug/l	Saline	Not ISO17025 accredited, but analysis is ISO9001:2015 approved.
Salinity (PSU)	1mg/l	Saline	Not ISO17025 accredited, but analysis is ISO9001:2015 approved.
pH	4.0 pH Units	Saline	INAB ISO17025 accredited: pH 4-10, lower can be read but won't be accredited.
Total suspended solids	2mg/l	Saline	INAB ISO17025 accredited
Dissolved Organic Carbon (DOC)	1mg/l	Saline	Not ISO17025 accredited, but analysis is ISO9001:2015 approved.
Total Organic Carbon (TOC)	1mg/l	Saline	INAB ISO17025 accredited



The parameters analysed in the laboratory were:

Salinity

To evaluate the characteristics of seawater, salinity and conductivity are utilised. Salinity is measured in practical salinity units (PSU) or parts per thousand (ppt). Meanwhile, specific conductance is reported in microsiemens per centimeter and gauges the seawater's capacity to conduct electricity, which is affected by the quantity and types of dissolved substances present. The specific conductance in estuaries can fluctuate significantly because of tidal effects and oceanic/freshwater inputs.

pH

Measuring the acidity or alkalinity of seawater is done through pH, which is rated on a scale of 0 to 14. A pH of 7 indicates neutrality, while values below signify acidity, and values above suggest alkalinity. Monitoring pH is crucial in determining water quality as it affects water treatment, chemical reactions, and the well-being of plants and animals.

Chlorophyll

Chlorophyll is a pigment/molecule found in plant cells essential for photosynthesis and is used as an indicator of algal biomass in seawater. Chlorophylls absorb light most strongly in the blue and red portions of the electromagnetic spectrum. Chlorophyll sensors rely on fluorescence, which is the emission of light by a substance that has absorbed light. Chlorophyll measurement units include relative fluorescence units (RFU) and micrograms per litre ($\mu\text{g/L}$).

Nutrients

Traditionally, measurements of nutrients in seawater involve taking discrete water samples using a dedicated water sampling device or bottle and subsequently analysing them in a laboratory. Seawater nutrients consist primarily of nitrogen (N) and phosphorous (P). These nutrients have a controlling role in primary productivity and carbon sequestration in seawater. Nitrogen exists in different forms within the marine environment, with nitrate being the primary form of fixed dissolved inorganic nitrogen that organisms assimilate.

Total suspended solids (TSS)

Turbidity is primarily attributed to total suspended solids (TSS), and the estimation of TSS levels using sensors has been calculated using linear regression modelling based on turbidity measurements.



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DOC and TOC

The Dissolved Organic Content (DOC) of seawater is the concentration of carbon remaining in a seawater sample after removing particulate and inorganic carbon. Total Organic Carbon (TOC) is the total of the particulate and DOC when existing inorganic carbon is removed in a laboratory analysis by acidification.

Figure 1. Exo2 Sonde, calibration solutions and sample bottles



Results

The dates on which samples were collected and dates of analysis are shown in Table 2 along with the parameter analysed for - Salinity ppt, Phosphates as P mg/L, Nitrate as N mg/L, Nitrite as N mg/L, Chlorophyll a µg/L, Suspended solids mg/L, pH units, Total Organic Carbon (TOC) mg/L, Dissolved Organic Carbon (DOC) mg/L and Ammonia as N mg/L. For further information on these parameters see other STREAM report cards such as:

<https://www.marinestream.eu/tool-kit-monitoring-for-coastal-and-marine-water-quality-physiochemical-parameters/>

Table 2 Dates and times of sample collection along with analytical results for Salinity ppt, Phosphates as P mg/L, Nitrate as N mg/L, Nitrite as N mg/L, Chlorophyll a mg/L, Suspended solids mg/L, pH units, Total Organic Carbon (TOC) mg/L, Dissolved Organic Carbon (DOC) mg/L and Ammonia as N mg/L.

Sample No.	Report No.	Receipt Date	Sample ID	Date sampled	Time (red estimates to confirm)	Salinity	Phosphate as P filtered (low level SW or saline)	Nitrate as N saline waters	Nitrite as N saline waters	Chlorophyll a	Suspended Solids	pH	TOC	DOC	Ammonia as N (saline water)
						ppt	mg/l	mg/l	mg/l	ug/l	mg/l	pH Units	mg/l	mg/l	mg/l
1514550	495290	12/08/22	Dungarvan	11/08/2022	13:00	33.6	0.010	<0.003	<0.003	10.3					
1514552	495292	12/08/22	Wexford	11/08/2022	08:30	30.2	0.024	0.118	0.005	5.78					
1514553	495293	12/08/22	Wellington Bridge	10/08/2022	09:30	5.9	0.003	2.39	0.028	250					
1537626	500961	07/10/22	Wexford	07/10/2022	18:30	25.7	0.023	0.661	0.023	2.40	14	8.0	2.89	2.07	0.128
1537627	500962	07/10/22	Wellington Bridge	07/10/2022	19:10	2.4	0.106	3.70	0.021	8.28	13	7.8	2.24	2.47	0.100
1537628	500962	07/10/22	Castletownbere	03/10/2022	13:00	34.5	0.009	0.036	0.006	<1	13	8.0	1.48	<1	0.027
1537629	500963	07/10/22	Castletownbere	03/10/2022	13:00	34.5	0.011	0.043	0.007	<1	12	8.1	1.62	<1	<0.010
1547444	503624	04/11/22	Wexford	03/11/2023	09:00	1.3	0.036	3.20	0.018	1.53	30	7.7	7.90	7.66	0.079



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1547445	503625	04/11/22	Wellington Bridge	03/11/2023	10:15	<1	0.063	2.00	0.015	1.19	8	7.1	8.06	7.72	0.043
1547446	503626	04/11/22	Bannow	03/11/2023	10:45	11.0	0.043	1.96	0.021	4.01	31	7.7	6.06	5.70	0.102
1547447	503627	04/11/22	Waterford Pontoon	03/11/2023	12:05	<1	0.065	1.71	0.016	3.20	35	8.0	9.63	9.21	0.154
1547448	503628	04/11/22	Dunmore East	03/11/2023	12:30	21.4	0.036	1.02	0.010	<1	12	8.0	5.09	4.87	0.046
1547449	503629	04/11/22	Castletownbere	03/11/2023	11:30	33.0	0.007	0.046	0.006	1.07		8.0	1.52	1.29	0.025
1553102	504990	18/11/22	Wexford	16/11/2022	07:30	18.4	0.021	1.90	0.019	<1	<2	7.8	3.63	3.01	0.117
1553103	504991	18/11/22	Wellington Bridge	16/11/2022	08:30	<1	0.043	3.13	0.021	<1	<2	7.2	6.16	5.53	0.029
1553104	504992	18/11/22	Bannow	16/11/2022	09:00	12.5	0.043	2.19	0.027	<1	11	7.6	4.73	4.34	0.087
1553105	504993	18/11/22	Waterford Pontoon	16/11/2022	10:45	1.7	0.036	2.17	0.019	<1	<2	7.9	6.63	6.01	0.079
1553106	504994	18/11/22	Dunmore East	16/11/2022	11:30	19.3	0.030	1.45	0.011	<1	10	7.9	4.79	4.35	0.034
1553107	504995	18/11/22	Castletownbere	17/11/2022	11:00	31.3	0.015	0.100	0.009	1.07	6	7.9	1.82	1.20	<0.010
1560991	506852	08/12/22	Wexford	07/12/2022	08:00	10.4	0.034	3.26	0.014	1.14	13	7.8	3.53	2.83	0.051
1560992	506853	08/12/22	Wellington Bridge	07/12/2022	08:35	<1	0.021	2.92	<0.003	1.87	4	7.5	3.49	3.03	0.038
1560993	506854	08/12/22	Dungarvan	07/12/2022	11:00	26.8	0.011	0.908	0.009	1.64	13	8.1	2.39	2.07	0.056
1560994	506855	08/12/22	Castletownbere	08/12/2022	11:00	33.5	0.021	0.131	0.005	<1	5	8.1	1.98	1.37	<0.010
1583660	512330	20/02/2023	Wexford	16/02/2022	07:30	12.9	0.02	0.675	0.013	1.07	5	8.1	2.12	2.07	0.038
1583661	512331	20/02/2023	Wellington Bridge	16/02/2022	08:15	<1	0.017	0.999	0.011	<1	<2	7.5	1.81	1.51	0.022
1583662	512332	20/02/2023	Dungarvan	12/02/2022	13:40	29.5	0.017	0.719	0.007	<1	13	8	1.5	1.39	0.028
1583663	512333	20/02/2023	Waterford Pontoon	16/02/2023	11:14	5.3	0.031	0.775	0.008	1.34	11	8.2	2.34	2.27	0.038
1583664	512334	20/02/2023	Dunmore East	16/02/2023	11:55	26.8	0.02	1.14	0.005	1.07	7	8	1.91	1.54	<0.010
1583665	512335	20/02/2023	Castletownbere	17/02/2023	10:52	34.5	0.021	0.119	0.003	<1	4	8	1.11	1	0.018
1593776	514882	16/03/2023	Wexford	14/03/2023	11:10	16.6	0.015	2.05	0.01	2.14	7	8.1	2.57	2.18	0.037
1593777	514883	16/03/2023	Wellington Bridge	14/03/2023	12:00	<1	0.053	2.7	0.013	2.4	5	7.3	6.95	6.69	0.05
1593779	514885	16/03/2023	Bannow	14/03/2023	12:41	9.3	0.035	2.09	0.015	2.14	17	7.8	5.83	5.44	0.086
1593781	514886	16/03/2023	Waterford Pontoon	14/03/2023	13:30	<1	0.036	2.74	0.01	11.3	108	8.1	4.34	3.95	0.038
1593782	514887	16/03/2023	Dunmore East	14/03/2023	14:30	32.7	0.014	0.07	0.004	1.33	18	8	1.33	1.05	0.013
1593784	514889	16/03/2023	Castletownbere	15/03/2023	11:00	34.3	0.019	0.02	0.004	2.14	9	8.1	1.25	<1	<0.010
1601464	517034	07/04/2023	Wexford	05/04/2023	07:45	20.2	0.023	1.455	0.01	<1	11	7.9	3.3	3.38	0.022



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1601465	517035	07/04/2023	Wellington Bridge	05/04/2023	08:40	<1	0.018	4.195	0.008	<1	7	7.7	2.41	2.43	0.018
1601466	517036	07/04/2023	Bannow	05/04/2023	08:59	25.4	0.022	1.16	0.009	2.14	15	8	1.96	1.86	0.047
1601467	517037	07/04/2023	Waterford Pontoon	05/04/2023	10:45	2.7	0.019	2.987	0.01	2.14	70	7.9	4.26	4.04	0.044
1601468	517038	07/04/2023	Dunmore East	05/04/2023	11:20	29.9	0.011	0.119	0.007	1.33	31	8	2.02	1.92	0.014
1601469	517039	07/04/2023	Castletownbere	06/04/2023	12:00	33.9	0.026	0.014	0.004	2.14	17	8	1.36	1.32	0.06
1613720	520517	12/05/2022	Wexford	10/05/2023	08:20	21.1	<0.003	1.18	0.018	18.2	61	7.9	3.52	3.07	0.296
1613725	520520	12/05/2022	Wellington Bridge	10/05/2023	09:20	<1	0.006	3.01	0.011	5.87	7	7.5	4.27	3.17	0.146
1613731	520522	12/05/2022	Bannow	10/05/2023	09:55	31.5	<0.003	0.189	0.003	17.1	24	8.2	2.12	1.82	0.054
1613734	520524	12/05/2022	Waterford Pontoon	10/05/2023	11:15	11.4	0.005	2.17	0.01	3.74	34	8	3.68	2.79	0.129
1613737	520525	12/05/2022	Dunmore East	10/05/2023	12:15	33.5	<0.003	0.041	<0.003	6.41	4	8.1	1.96	1.25	0.058
1613741	520526	12/05/2022	Castletownbere	11/05/2023	11:00	34.4	0.01	0.039	<0.003	<1	38	8	1.38	0.691	0.024



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The results of the samples analysed by the laboratory were divided by the author geographically (Table 3 – Bannow, Castletownbere, Dungarvan, Dunmore East, Waterford pontoon, Wellington Bridge and Wexford). The Substitution Method was used to replace values reported by the laboratory as less than their detection limit ($0.5 \times$ detection limit) before calculating the average and other values. This assumes that the actual value is likely around this midpoint, but it is only a crude estimate with no other basis than for calculating overall results.

Table 3 Average, SD, Max, Min and Bannow, and n for Salinity, Phosphate, Nitrite, Nitrate, Chl a, Suspended Solids, pH, TOC, DOC and ammonia at Bannow Bay, Castletownbere, Dungarvan, Dunmore East, Waterford pontoon, Wellington Bridge and Wexford.

Bannow

	Sal ppt	Phos mg/L	Nitrite mg/L	Nitrate mg/L	Chl a ug/L	Sus Solids mg/L	pH	TOC mg/L	DOC mg/L	Amm mg/L
Average	17.94	0.03	1.52	0.02	5.18	19.60	7.86	4.14	3.83	0.08
SD	9.90	0.02	0.85	0.01	6.78	7.92	0.24	1.98	1.89	0.02
Max	31.50	0.04	2.19	0.03	17.10	31.00	8.20	6.06	5.70	0.10
Min	9.30	0.00	0.19	0.00	0.50	11.00	7.60	1.96	1.82	0.05
n	5	5	5	5	5	5	5	5	5	5

Castletownbere

	Sal ppt	Phos mg/L	Nitrite mg/L	Nitrate mg/L	Chl a ug/L	Sus Solids mg/L	pH	TOC mg/L	DOC mg/L	Amm mg/L
Average	33.77	0.02	0.06	0.01	0.99	13.00	8.02	1.50	0.93	0.02
SD	1.06	0.01	0.04	0.00	0.69	11.03	0.07	0.27	0.38	0.02
Max	34.50	0.03	0.13	0.01	2.14	38.00	8.10	1.98	1.37	0.06
Min	31.30	0.01	0.01	0.00	0.50	4.00	7.90	1.11	0.50	0.01
n	9	9	9	9	9	8	9	9	9	9



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Dungarvan

	Sal ppt	Phos mg/L	Nitrite mg/L	Nitrate mg/L	Chl a ug/L	Sus Solids mg/L	pH	TOC mg/L	DOC mg/L	Amm mg/L
Average	29.97	0.01	0.54	0.01	4.15	13.00	8.05	1.95	1.73	0.04
SD	3.42	0.00	0.48	0.00	5.36	0.00	0.07	0.63	0.48	0.02
Max	33.60	0.02	0.91	0.01	10.30	13.00	8.10	2.39	2.07	0.06
Min	26.80	0.01	0.00	0.00	0.50	13.00	8.00	1.50	1.39	0.03
n	3	3	3	3	3	2	2	2	2	2

Dunmore East

	Sal ppt	Phos mg/L	Nitrite mg/L	Nitrate mg/L	Chl a ug/L	Sus Solids mg/L	pH	TOC mg/L	DOC mg/L	Amm mg/L
Average	27.27	0.02	0.64	0.01	1.86	13.67	8.00	2.85	2.50	0.03
SD	5.89	0.01	0.63	0.00	2.26	9.73	0.06	1.64	1.67	0.02
Max	33.50	0.04	1.45	0.01	6.41	31.00	8.10	5.09	4.87	0.06
Min	19.30	0.00	0.04	0.00	0.50	4.00	7.90	1.33	1.05	0.01
n	6	6	6	6	6	6	6	6	6	6

Waterford
Pontoon

	Sal ppt	Phos mg/L	Nitrite mg/L	Nitrate mg/L	Chl a ug/L	Sus Solids mg/L	pH	TOC mg/L	DOC mg/L	Amm mg/L
Average	3.68	0.03	2.09	0.01	3.70	43.17	8.02	5.15	4.71	0.08
SD	4.18	0.02	0.79	0.00	3.91	39.72	0.12	2.60	2.55	0.05
Max	11.40	0.07	2.99	0.02	11.30	108.00	8.20	9.63	9.21	0.15
Min	0.50	0.01	0.78	0.01	0.50	1.00	7.90	2.34	2.27	0.04
n	6	6	6	6	6	6	6	6	6	6



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Wellington
Bridge

	Sal ppt	Phos mg/L	Nitrite mg/L	Nitrate mg/L	Chl a ug/L	Sus Solids mg/L	pH	TOC mg/L	DOC mg/L	Amm mg/L
Average	1.31	0.04	2.78	0.02	30.12	5.75	7.45	4.42	4.07	0.06
SD	1.83	0.03	0.93	0.01	82.50	3.96	0.24	2.37	2.27	0.04
Max	5.90	0.11	4.20	0.03	250.00	13.00	7.80	8.06	7.72	0.15
Min	<1	0.00	1.00	0.01	0.50	1.00	7.10	1.81	1.51	0.02
n	9	9	9	8	9	8	8	8	8	8

Wexford

	Sal ppt	Phos mg/L	Nitrite mg/L	Nitrate mg/L	Chl a ug/L	Sus Solids mg/L	pH	TOC mg/L	DOC mg/L	Amm mg/L
Average	17.422	0.022	1.405	0.014	3.696	17.750	7.913	3.683	3.284	0.096
SD	8.547	0.010	1.027	0.006	5.672	19.499	0.146	1.785	1.838	0.090
Max	30.200	0.036	3.200	0.023	18.200	61.000	8.100	7.900	7.660	0.296
Min	1.300	0.002	0.118	0.005	0.500	1.000	7.700	2.120	2.070	0.022
n	9	9	8	9	9	8	8	8	8	8



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Correlations between parameters

We calculated the Pearson correlation coefficients between each pair of parameters to analyse the correlations between all the measured parameters. The correlation coefficient measures the strength and direction of the linear relationship between two variables, with values ranging from -1 to 1.

These correlations provide insights into how the measured parameters at all sites are related to each other in the dataset (draft calculations – Table 4).

Table 4 Parameters (Salinity, Phosphate, Nitrite, Nitrate, Chl a, Suspended Solids, pH, TOC, DOC) and their correlation values.

Parameter 1	Parameter 2	Correlation
Salinity	Phosphate as P	-0.552
Salinity	Nitrate as N	0.54
Salinity	Nitrite as N	0.198
Salinity	Chlorophyll a	0.36
Salinity	Suspended Solids	0.184
Salinity	pH	-0.59
Salinity	TOC	-0.437
Salinity	DOC	-0.415
Salinity	Ammonia as N	0.43
Phosphate as P	Nitrate as N	-0.227
Phosphate as P	Nitrite as N	0.324
Phosphate as P	Chlorophyll a	0.041
Phosphate as P	Suspended Solids	-0.323



Phosphate as P	pH	-0.012
Phosphate as P	TOC	0.224
Phosphate as P	DOC	0.139
Phosphate as P	Ammonia as N	-0.23
Nitrate as N	Nitrite as N	0.8
Nitrate as N	Chlorophyll a	0.314
Nitrate as N	Suspended Solids	-0.012
Nitrate as N	pH	0.066
Nitrate as N	TOC	0.354
Nitrate as N	DOC	0.365
Nitrate as N	Ammonia as N	0.623
Nitrite as N	Chlorophyll a	0.331
Nitrite as N	Suspended Solids	-0.134
Nitrite as N	pH	0.06
Nitrite as N	TOC	0.106
Nitrite as N	DOC	0.173
Nitrite as N	Ammonia as N	0.11
Chlorophyll a	Suspended Solids	-0.054
Chlorophyll a	pH	0.376
Chlorophyll a	TOC	0.424
Chlorophyll a	DOC	0.43
Chlorophyll a	Ammonia as N	0.396



Suspended Solids	pH	0.017
Suspended Solids	TOC	-0.072
Suspended Solids	DOC	-0.09
Suspended Solids	Ammonia as N	-0.09
pH	TOC	0.049
pH	DOC	0.013
pH	Ammonia as N	-0.15
TOC	DOC	0.927
TOC	Ammonia as N	0.265
DOC	Ammonia as N	0.344

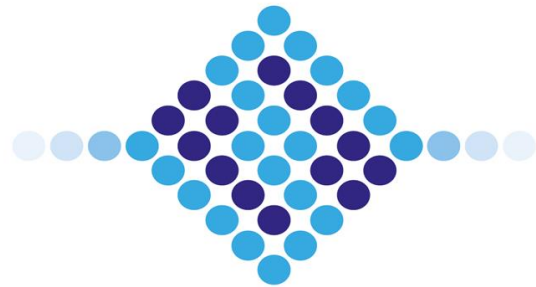
Conclusion

Some key correlations to note which are to be expected in Table 4, such as:

Nitrate as N and Nitrite as N have a positive correlation (0.2832).

Chlorophyll a and Suspended Solids have a strong positive correlation (0.7327).

TOC and DOC have a very strong positive correlation (0.8839).



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Sensor Technologies for Remote Environmental Aquatic Monitoring



The STREAM project is part-funded by the European Regional Development Fund (ERDF) through the Ireland-Wales Cooperation programme



Acknowledgements

Wexford County Council - Brendan Cooney

EPA – Dr Robert Wilkes

BIM - Brian O’Loan

BIM Shane Begley - Weather Station and Barge (Castletownbere), Dave Millard, Regional Development Officer

Marine Institute -Dave Clarke and Jonathan Kelly

Tramore Coast Guard

Dunmore East Harbour - Monitoring sites

Waterford City River Rescue - Monitoring sites

Southern Regional Assembly - Breda Curran

Report

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