

# Outputs of the EMPIR project SapHTies: Metrology for standardised seawater $pH_T$ measurements in support of international and European climate strategies

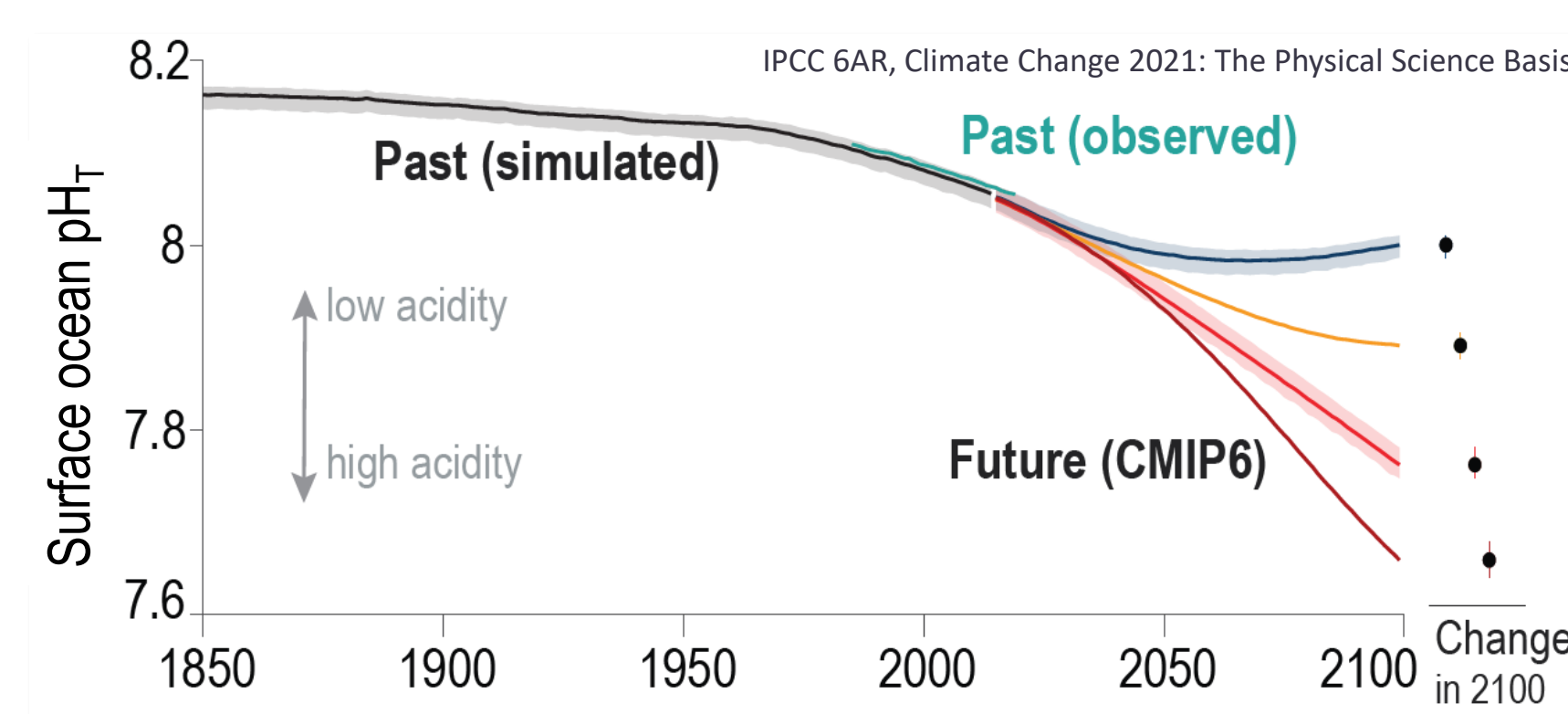
Alasonati E.<sup>a</sup>, Bastkowski F.<sup>b</sup>, **Capitaine G.**<sup>a</sup>, Fischer N.<sup>a</sup>, Fisicaro P.<sup>a</sup>, Jayachandran S.<sup>c</sup>, Lamande N.<sup>d</sup>, Martínez-Cabanas M.<sup>c</sup>, Naykki T.<sup>e</sup>, Pellegrino O.<sup>f</sup>, Quendera R.<sup>f</sup>, Salvetat F.<sup>d</sup>, Schäfer R.<sup>b</sup>, Seitz S.<sup>b</sup>, Snedden A.<sup>g</sup>, Zaouali J.<sup>a</sup>, Zukauskas A.<sup>g</sup>

<sup>a</sup>LNE (France), <sup>b</sup>PTB (Germany), <sup>c</sup>GEOMAR (Germany), <sup>d</sup>Ifremer (France), <sup>e</sup>SYKE (Finland), <sup>f</sup>IPO (Portugal), <sup>g</sup>DFM (Denmark)

Corresponding author: gaelle.capitaine@lne.fr

## Introduction & metrological needs

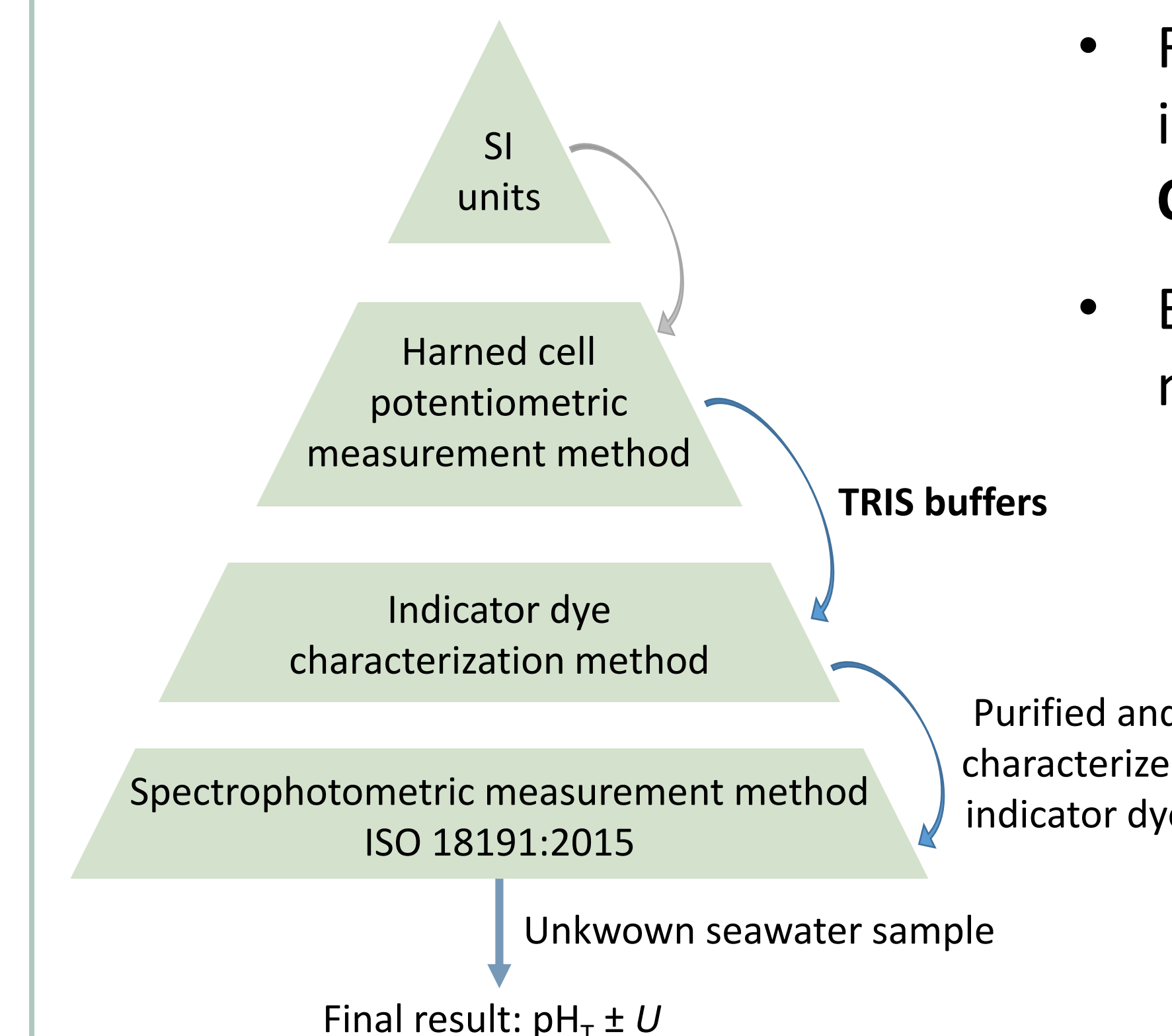
- Oceans absorb 26 % of anthropogenic  $CO_2$   
→ Acidification of marine waters  
→ Biodiversity loss and socio-economic impacts
- Total  $pH$ , noted  $pH_T$ : key variable for monitoring ocean acidification



- International recommendation and best practices guidelines set a  $pH_T$  expanded uncertainty target of 0.006 ( $k=2$ ) for climate assessments

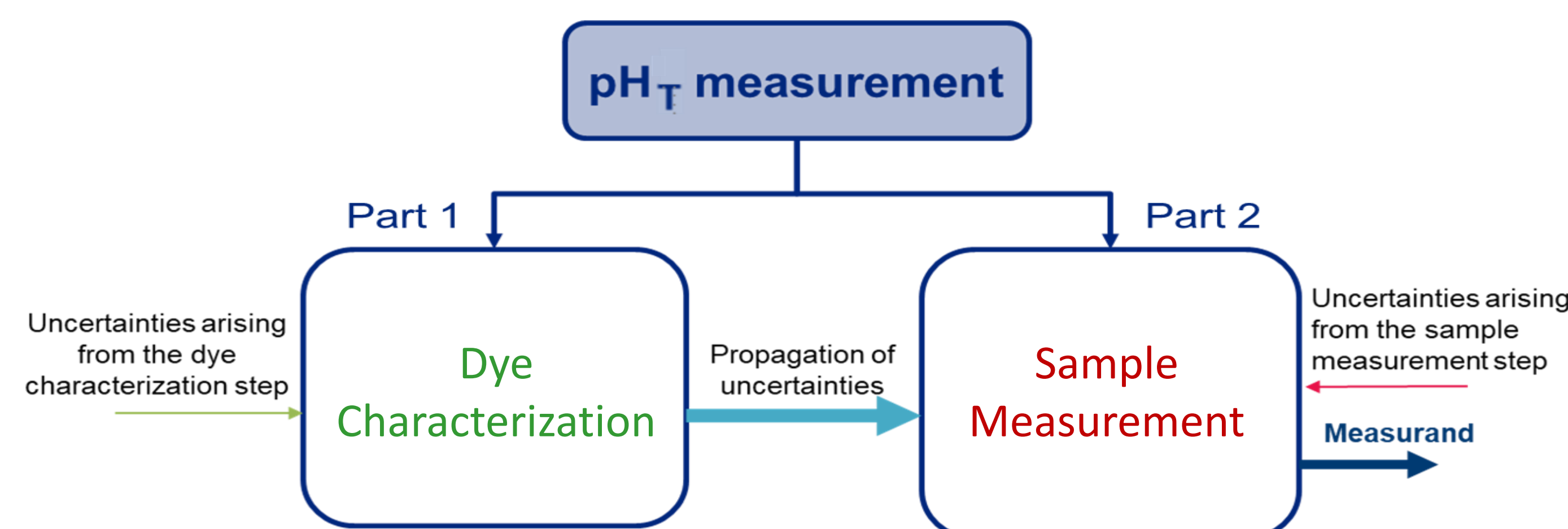
- ISO 18191:2015 defines routine spectrophotometric  $pH_T$  measurement but lacks full metrological compliance (traceability, uncertainty, validation). The EMPIR project SapHTies aimed to address these gaps by **developing robust metrological tools for seawater  $pH_T$  measurements.**

## Traceability



- Reference materials consisting in TRIS buffers prepared in an artificial seawater (ASW) matrix were produced. **Certified  $pH_T$  value expanded uncertainty,  $U_{RM} = 0.005$**
- Buffers characterized across various TRIS molalities ; nominal practical salinity 5-40 ; temperature 5-40 °C
- TRIS buffers extrapolated to zero TRIS molalities (i.e., pure ASW matrix) → allow representing a true  $pH_T$  scale → achieving **perspective for SI traceability in intervals most relevant for oceanographic measurements**
- Buffers were used for the characterization of the indicator dye

## Uncertainty budget



- Spectrophotometric  $pH_T$  uncertainty sources identified:** Some remain unquantified (dye characterization). Minimum expanded uncertainty,  $U_{min} = 0.02$  → exceeding international standards target
- Study highlights key uncertainty sources for improvement
- A **software tool** for uncertainty quantification was developed

## Inter-laboratory comparison

- Interlaboratory comparison (ILC) to assess spectrophotometric method performance, with **12 laboratories**
- Tested on TRIS buffer and standard seawater

	TRIS Sample	Natural Seawater Sample
Repeatability Standard Deviation, $S_r$	0.0039	0.0029
Reproducibility Standard Deviation, $S_R$	0.0053	0.0039

- Repeatability and reproducibility are promising but do not meet the uncertainty target
- QA/QC guide has been proposed based on ILC results

## Conclusion

**Metrological tools developed to support oceanographers in their  $pH_T$  spectrophotometric measurement:**

- development of Reference Materials
- enhancement of the traceability to the SI units
- uncertainty budget evaluation and development of a software tool for uncertainty quantification
- ILC exercise
- QA/QC guidelines

Strengthening of **comparability of measurement results**  
→ Support the establishment of **long-term trends in ocean acidification**

