Measurements of Salinity and Conductivity: Principles and Challenges

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- History and motivation
- Ocean salinity determinations, changing algorithms
- Accuracy and precision
- Future requirements, Climate change

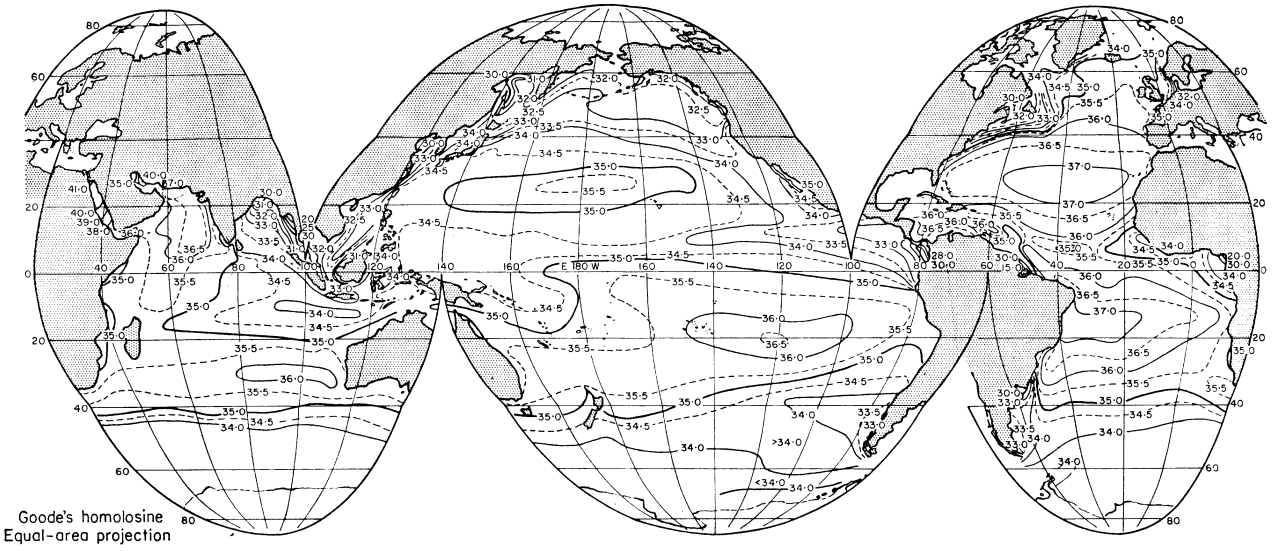


FIG. 2. Surface salinity of the oceans in the northern summer (Sverdrup, 1945). By permission of George Allen & Unwin Ltd.

Salinity in the World Ocean

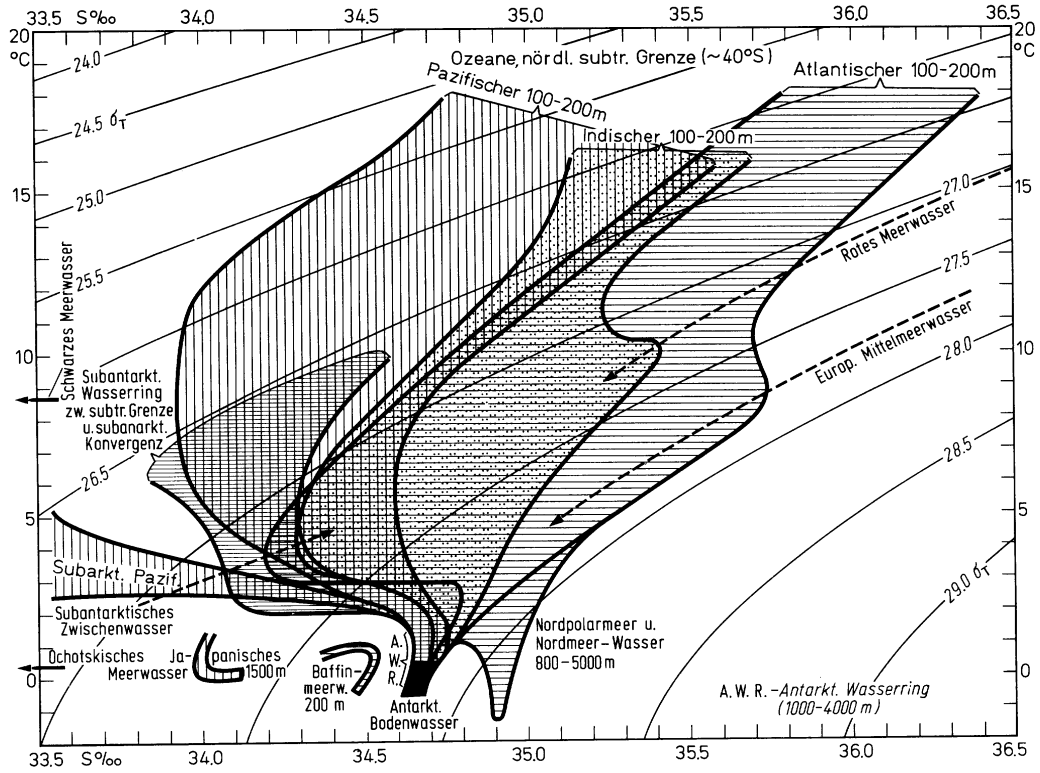
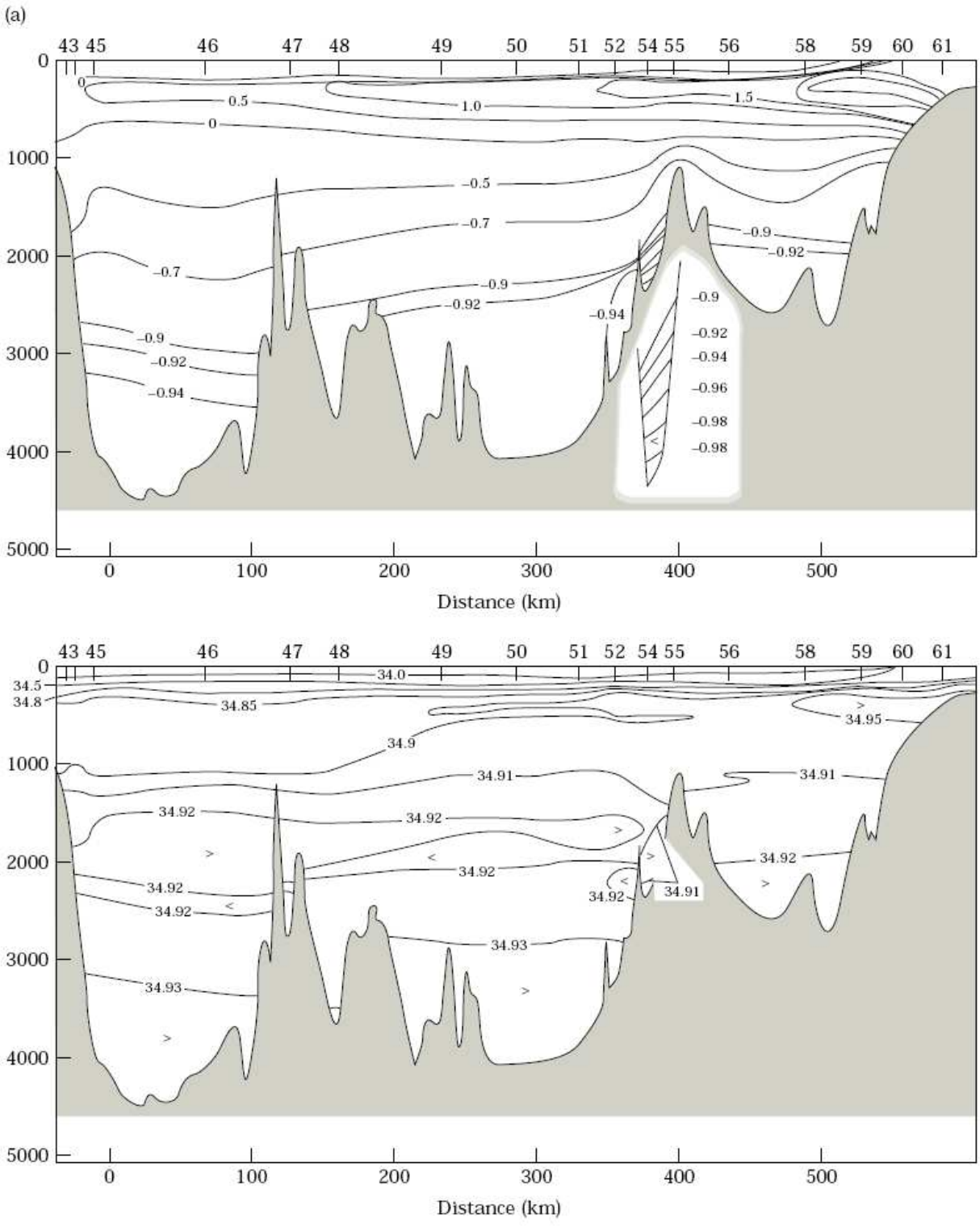


Abb. 5.20. Beziehung Temperatur–Salzgehalt im gesamten Weltmeer unterhalb der oberflächennahen Störungsschicht (nach DIETRICH, 1950a).

Sverdrup et al. (1946), Dietrich (1950)



Meincke et al., (1997)

Large reservoirs, slow changes:
E.g., Arctic Ocean Deep Water.

Salt mass in the world ocean

- Volume: 22 Mill. km^3
- Evaporated: 60 m height on ocean bottom
- Larger than Africa above sea level:

Where does the saltiness come from?

- Greek philosophers
  - Sun and Stars drink sweet water (Plinius)
  - Earth too small to feed the stars (Aristoteles)
  - Earth perspirates salt water (Empedokles, Demokrit)
  - Chaos at earth's origin (Seneca)
- Arabian scientists
- First scientific chemistry: 17th century

Composition of Seawater

- (1670) R. Boyle
  - Evaporating samples: unsatisfactorily
  - Specific gravity: Accurate measurement
  - River waters contain salt $\Rightarrow$ ocean salinity
- (1772) A. L. de Lavoisier:
  - Water is a compound of H and O
  - Chemical analysis by selective precipitation
- (1779) T. O. Bergman: Alcalinity
- (1813) A. Vogel: Improved quantification
- (1818) J. Murray: Gravimetric analysis
- (1819) A. Marcet
  - 14 samples from the Arctic and Atlantic Ocean
  - Constancy of ratio of components

Georg Forchhammer (1865)

- Geologist: Interest in Earth's history
- 20 years of work
- World ocean (e.g. Ross, Nordenskild)

- High precision:
  - Cl: $< 5 \times 10^{-4}$
  - SO_3: $< 5 \times 10^{-3}$
  - Mg, Ca: $< 10^{-2}$
- Ratio of salts/ions is almost constant
- $S = (1.811 \pm 0.005)$ Cl (present day: 1.815)
- Circulation: Less Cl in deep waters; conclusions on North Atlantic Current + Gulf Stream
- Seawater cannot derive from river runoff

Forchhammer (1865):

- *"Thus the quantity of the different elements in seawater is not proportional to the quantity of elements which river-water pours into the sea, but inversely proportional to the facility with which the elements in sea-water are made insoluble by general chemical or organo-chemical actions in the sea; and we may well infer that the chemical composition of the water of the ocean in a great part is owing to the influence which general and organo-chemical decomposition has upon it, whatever may have been the composition of the primitive ocean."*
- Ocean salinity is a consequence of life in the ocean

The Residence Times of Elements in Seawater

	Residence time (M years)	
Element	**River input**	**Sedimentation**
Na	210	260
Mg	22	45
Ca	1	8
K	10	11
Sr	10	19
Si	0.935	0.01
Li	12	19
Rb	6.1	0.27
Ba	0.05	0.084
Al	0.0031	0.0001
Mo	2.15	0.5
Cu	0.043	0.05
Ni	0.015	0.018
Ag	0.25	2.1
Pb	0.00056	0.002

Millero and Sohn (1992)

1873-76 H.M.S. Challenger

H.M.S. Challenger under Sail, 1874.

W. Dittmar (1884)

- Complete analysis of major ions, highest standard
- Accuracy better than $< 10^{-2}$
- Precision better than $< 10^{-3}$
- Ca^{2+}/Cl^{-} ratio increases in deep water

Salinity from Chlorinity

- $S_T = 1.811$ Cl (Forchhammer, 1865)
- $S_T = 1.8056$ Cl (Dittmar, 1884)
- 1899: International Councel for the Exploration of the Sea (ICES)
  - sophisticated evaporation method (Forch, Sörensen and Knudsen, 1902)
  - New definition of salinity: *"... the weight in grams of dissolved inorganic salts in one kilogram of seawater, when all bromides and iodides are replaced by an equivalent quantity of chlorides and all carbonates are replaced by an equivalent quantity of oxides"*
  - HCO_3^- and CO_3^{2-} not included
  - New $S \approx$ old $S_T/1.0049$
- $S = 1.8050$ Cl + 0.03 ("Knudsen's relation")

Salinity from Conductivity

- $S = 1.8050$ Cl + 0.03 ("Knudsen's relation") was used for 60 years
  - Based on chlorinity from titration
  - Accuracy: $\approx 5 \times 10^{-4}$
  - Some account for different river water salinities
- 1960s: Salinometer for routineous conductivity measurements
- 1964: JPOTS (Joint Panel of Oceanographic Tables and Standards)
  - $S = 1.80655$ Cl, from chlorinity
  - $S = -0.090 + f(R_{15})$, from conductivity ratio R_{15}
- Not satisfactorily (negative threshold, pressure dependence)

1978, JPOTS: Practical Salinity Scale

Standard seawater with S=35.000:

- has unity conductivity ratio $K_{15} = 1$ with a 32.4356 g/kg aqueous KCl solution at 15 ^{o}C
- matches $S = 1.80655$ Cl at Cl = 19.374
- $S = 0.008 + f(K_{15})$, slight zero-offset
- Precision ranking (for $S \approx 35$):
  - 0.001 (Conductivity)
  - 0.002 (Chlorinity, endpoint calibration)
  - 0.004 (Density)
  - 0.01 (Evaporation to dryness)
  - 0.01 (Summing up all ions)
  - 0.03 (Sound speed)
  - 0.05 (Refractive index)

All good ???

1983-2002 (WOCE)

World Ocean Circulation Experiment

- 0.001 in S was target accuracy
- not fulfilled (0.003 turned out to be realistic)
- Why?

Calculation of the Infinite Dilution Equivalent Conductance of Various Waters at 25°C

		$E_i \Lambda^0_i$ [a]		
Ion	Λ^0_i	**Seawater**	**World river water**	**St. Lawrence River**
Ca^{2+}	59.51	46.97	31.41	35.40
Mg^{2+}	53.50	9.32	12.71	13.15
Na^+	50.10	38.71	9.67	7.24
K^+	73.50	1.24	3.06	0.91
HCO_3^-	44.50	0.14	29.79	25.19
SO_4^{2-}	89.02	7.46	13.14	13.89
Cl^-	76.35	68.77	11.83	18.61
NO_3^-	71.46	0.20	0.81	—
	Λ^0 = 127.85[b]		112.2	114.41

[a] E_i is the equivalent function of species.

[b] $\Lambda^0 = \Sigma^E_i, \Lambda^0_i$.

Millero and Sohn (1992)

Mixing with river water

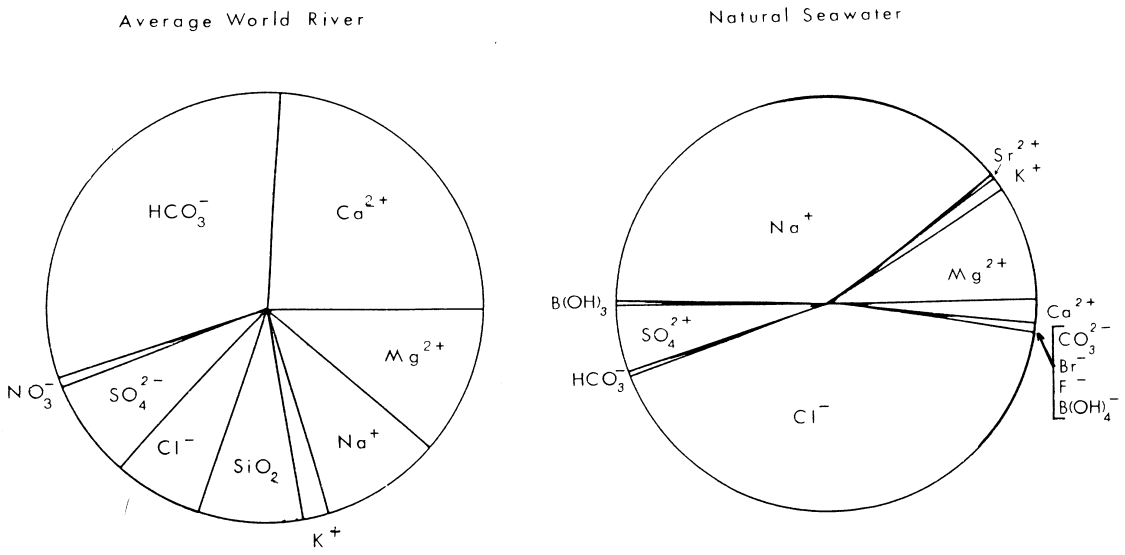


FIGURE 2.7. The equivalent fraction of the major constituents of the average world river and seawater.

$$\Delta S/dS \approx 0.0015$$

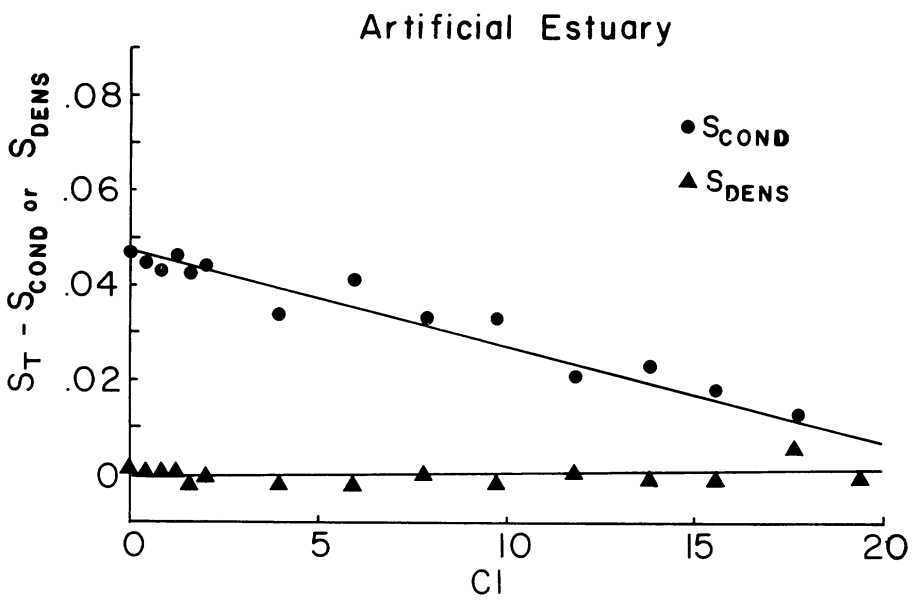


FIGURE 2.18. Comparison of the salinity determined from conductivity and density for estuarine waters.

Millero and Sohn (1992)

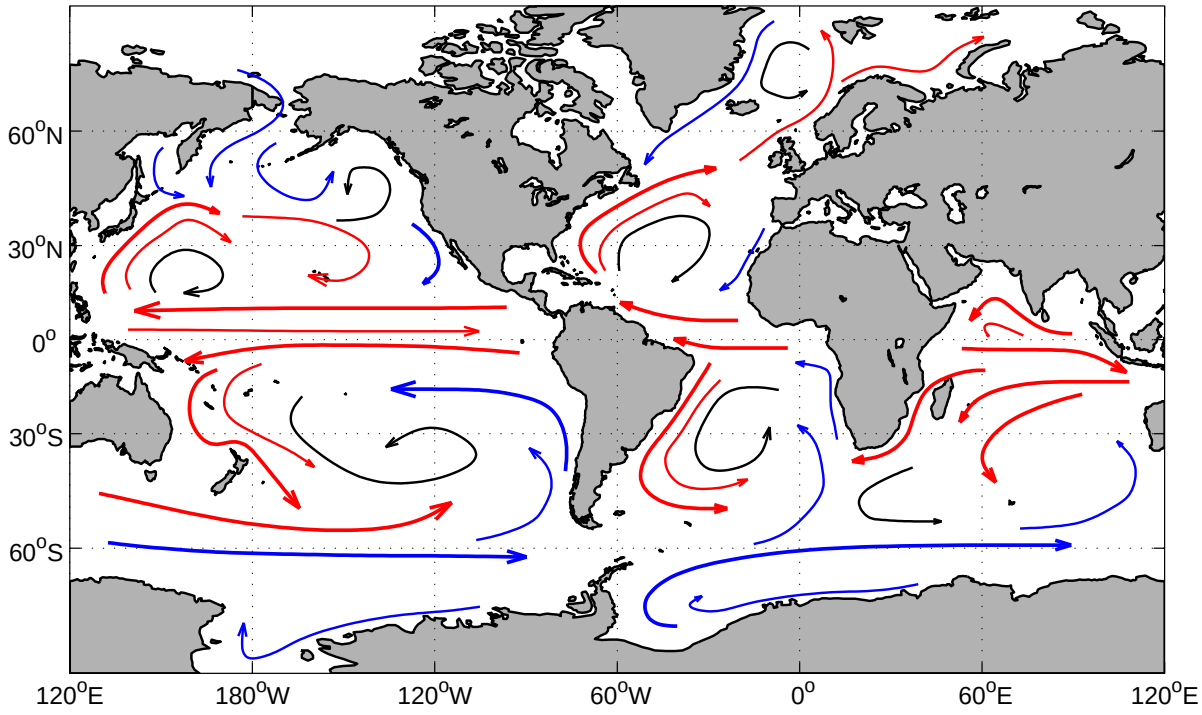
Other causes for compositional changes

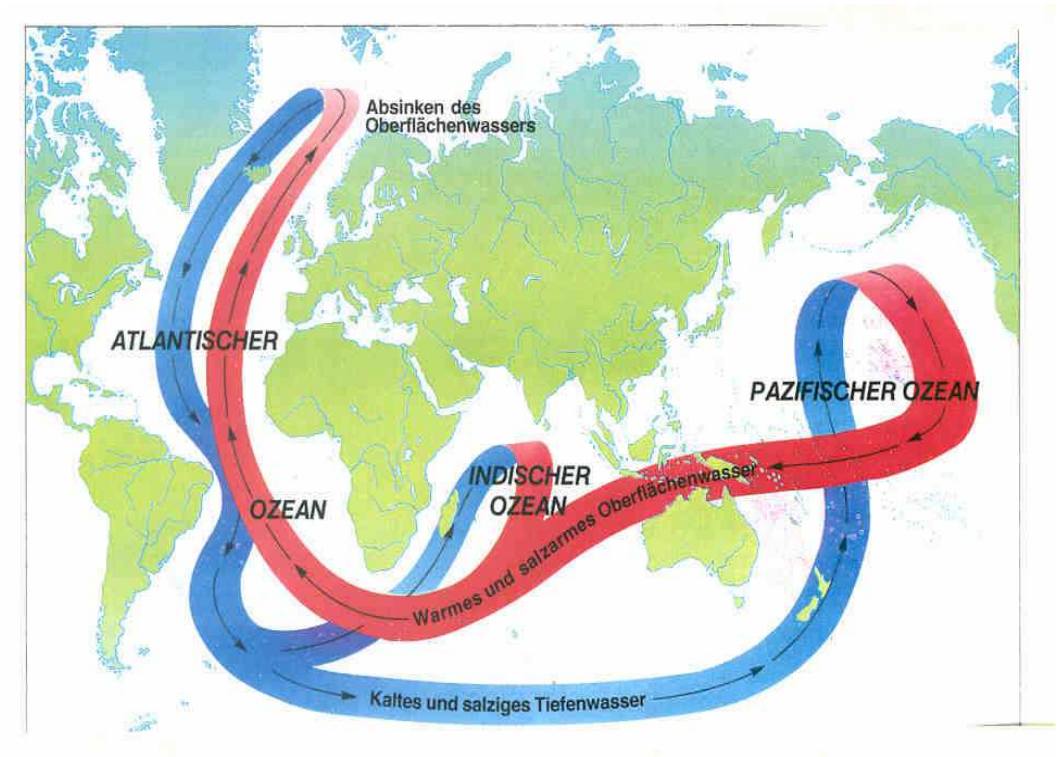
- Biological interactions
- Carbon System
- Sea ice

Examples

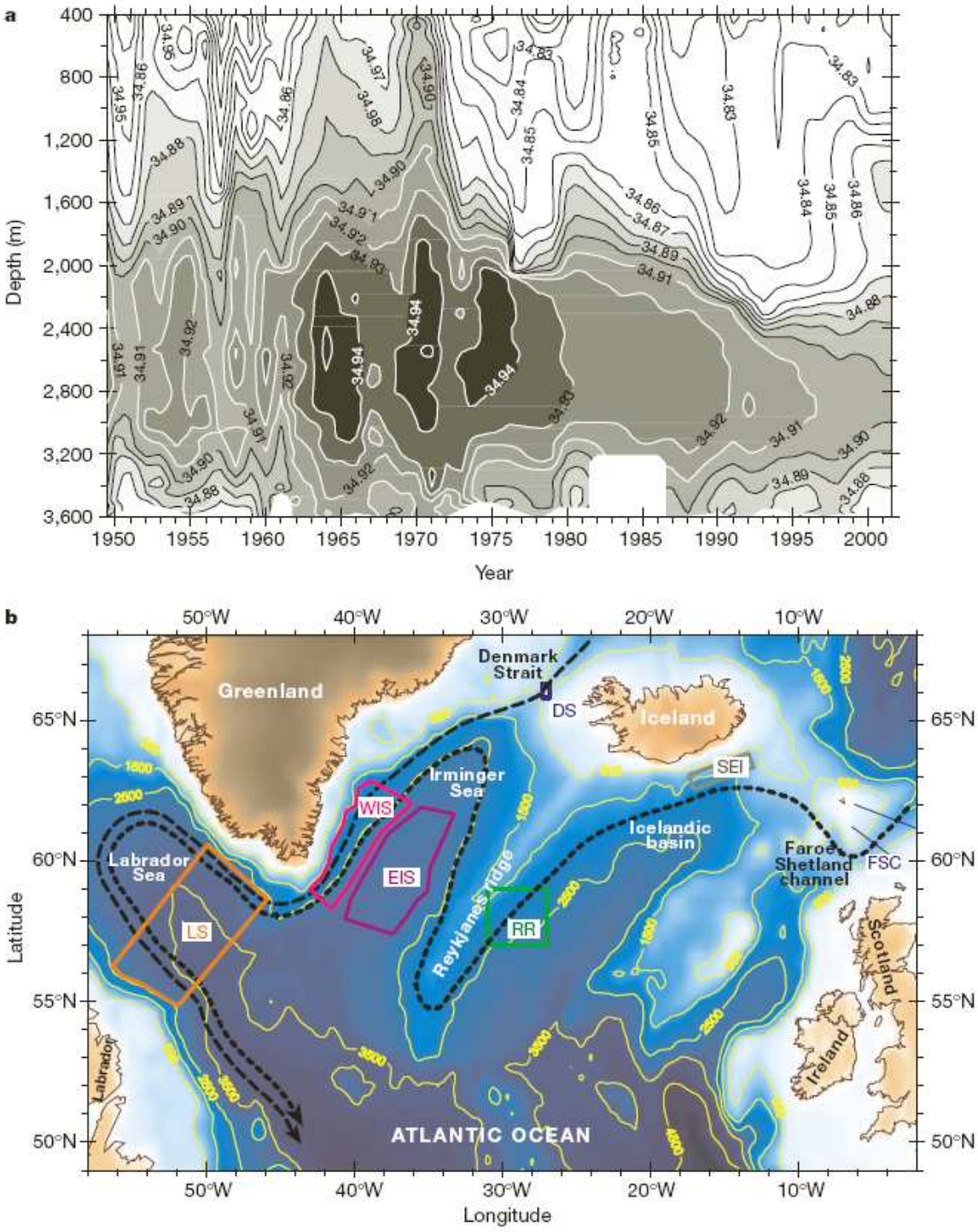
- 1 % increase in Ca/Cl ratio
  - Carbon system, sea ice
  - 0.001 underestimate in S by conductivity
- 1 % increase in SO_4^{2-}/Cl ratio
  - Ion fractionation, sea ice growth
  - 0.003 overestimate in S by conductivity

Challenge: Climate Change?





Example: Labrador Sea Deep Water: $\Delta S \approx 0.01$ / 50 years



Dickson et al. (2002)

Conclusions

Requirememements on seawater salinity determination

- 0.001 to 0.003 in S to understand bio-chemo-physical processes
- 0.002 in S: bias due to freshwater mixing
- 0.005 in S for climate change detection

An accuracy of 0.001 in S from conductivity sensors is urgently required.