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## Raw Water Quality

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# Water

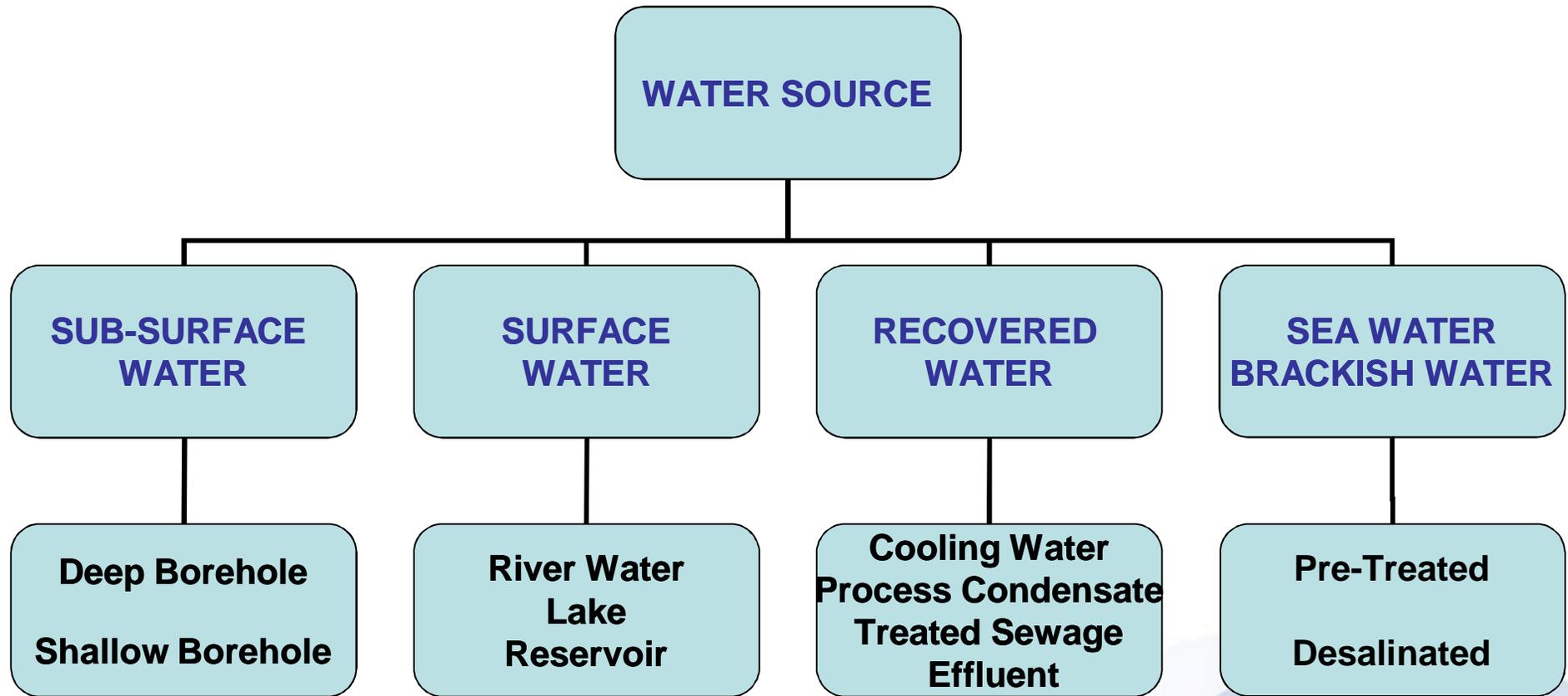


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# Raw Water – Where Does It Come From?



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# Sub-Surface Water Sources

- **Deep Borehole**
  - Composition is characteristic of rock strata from which it is drawn
  - May be “old” geologically
  - Relatively constant composition
    - Chemical constituents and temperature
  - May vary in minor ways dependent on depth of pumping from borehole.
- **Shallow Borehole**
  - Often in porous strata, e.g. gravels
  - Potential for greater variability
    - Intrusion from local rivers or “sink holes”
    - Dependent on rainfall pattern

## Surface Water - Rivers (1)

- **Wide variety of compositions**
- **Composition depends on geological strata with which water has been in contact**
  - Igneous rocks e.g. granite
    - Low dissolved solids content
    - High organics and colour if from peat moorland
    - River in spate may produce suspended and colloidal solids, including colloidal silica
  - Limestone / chalk strata
    - Higher dissolved solids content
    - High hardness and high bicarbonate alkalinity
    - Lower levels of organic matter
- **River water quality can be very variable depending on size of river, catchment area, rainfall, seasonal factors**

## Surface Water - Rivers (2)

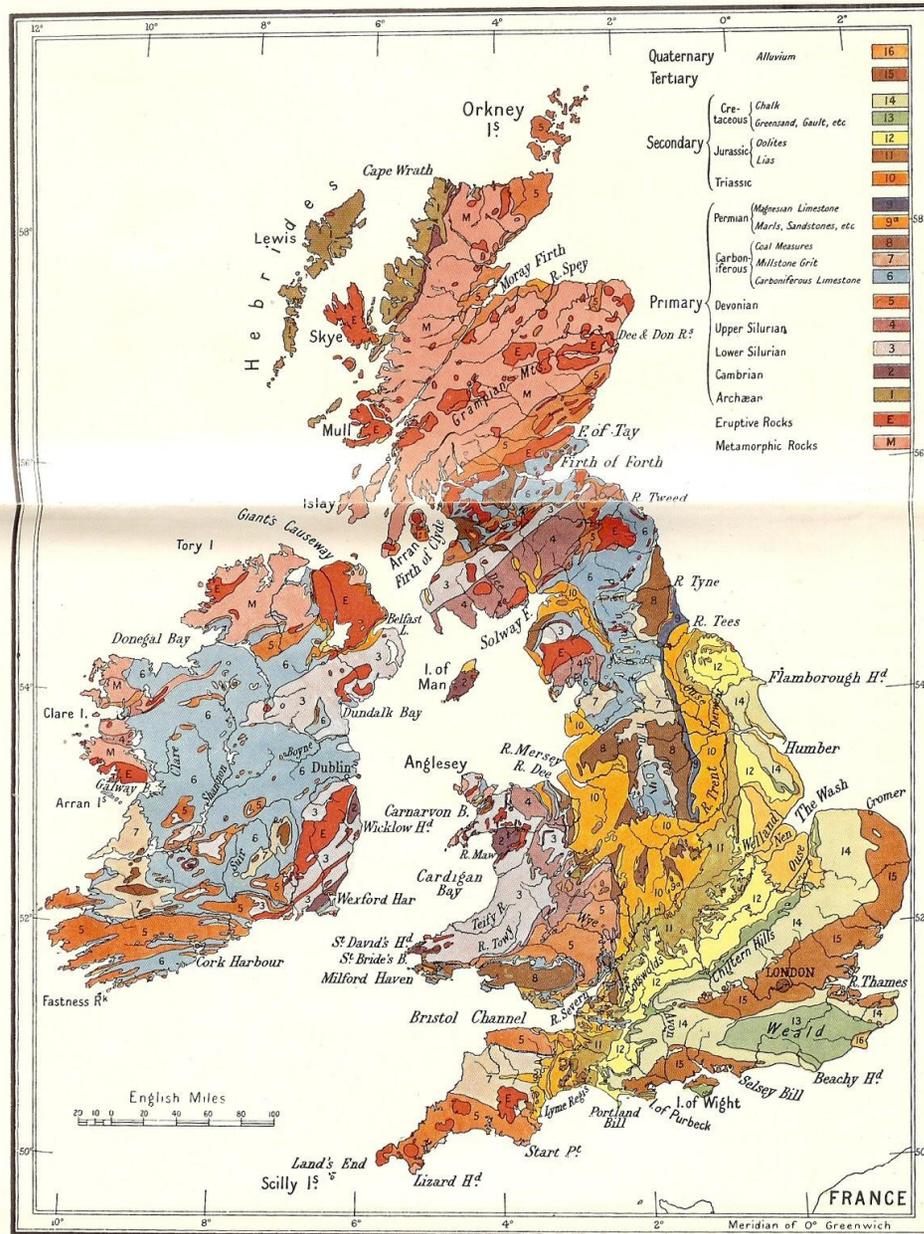
- **Composition also dependent on discharges into rivers**
  - Industrial Discharges
    - Process waste water
    - Power plant waste water (e.g. Flue Gas Desulphurization, high in Ca and Cl)
    - Mine drainage (acidic and high in metals)
    - Oils, greases and disturbance of sediments on navigable rivers
  - Municipal Discharges
    - Sewage effluent (treated or untreated)
    - Surface drainage
  - Agricultural Drainage
    - Slurries and animal wastes (ammonia and organic matter)
    - Fertilisers (ammonium, potassium, nitrate, phosphate, sulphate)
    - General surface drainage (suspended solids)
- **Stratification**
  - Can occur in deep and slow moving rivers

# Surface Water - Reservoirs and Lakes

- **Catchment (Retention) Reservoirs and Lakes**
  - Supplied by natural water courses
  - Similar characteristics to rivers which feed into source
  - Often drain upland areas
  - Can be low in dissolved solids, high in organics
- **Storage Reservoirs**
  - May be fed from multiple sources dependant on availability
  - Often abstracted from rivers
  - Consequent variability in composition
    - Depends on size of reservoir
    - Larger reservoirs even out variations

# Geology of the British Isles

## GEOLOGICAL MAP OF THE BRITISH ISLES.



An old, simplified, geological map of the British Isles, probably Victorian, and reproduced in Derryhouse (1910). The outcrop pattern has not changed significantly. However, the terminology is old, and out-of-date, but it will be readily understood by a geologist. For "Lower Silurian" read Ordovician. For "Archaean" read Precambrian. For "Primary" read Palaeozoic. For "Secondary" read Mesozoic. For "Oolites" read Middle and Upper Jurassic. For "Eruptive Rocks" read Igneous, - including granites, Borrowdale Volcanics etc. Ian West & Tonya West (c) 2008.

## Potable vs Non-Potable

- **Fundamentally no difference relative to treatment by ion exchange.**
- **Potable has been**
  - Pre-treated
  - Disinfected
  - Low in suspended solids
  - Composition may be variable due to blending
- **Non Potable**
  - Often requires pre-treatment
    - Removal of suspended solids and colloidal matter
    - Reduction in TOC
    - Not disinfected – potentially microbiologically active

## Recovered Water

- **Covers a variety of potential sources.**
- **Process Cooling Water**
  - Often surface water supply
  - Temperature above ambient – may be more concentrated due to evaporation
  - May have added chemicals for disinfection / corrosion control
- **Recovered Process Condensates**
  - Need to understand third party process(es)
  - Need to assess contamination risks
  - Temperature can be up to 100°C
- **Treated Sewage Effluent**
  - Composition should be similar to surface water
  - Risk of organic / microbiological contamination

# Desalinated Water

- **Thermal Desalination**

- Impurities in desalinated water are:
  - Representative of source water
  - Water may have had bicarbonate alkalinity removed
  - Dependent on droplet carry-over
  - Generally low in concentration of all species

- **Reverse Osmosis Desalination**

- Impurities in desalinated water are:
  - Dependant on membrane selectivity / rejection
  - Concentration depends on number of RO stages
  - Low in TOC
  - Carbon dioxide passes through RO membrane and requires degassing

## Analytical Data – General Requirements

- **Ionic species**
  - with potential for exchange that affect the basic process design.
  - in minor concentrations which may have adverse influence of the process.
- **Non ionic species**
  - particulate or colloidal suspensions which interfere with the process.
- **Soluble or colloidal organic matter**
  - which may interfere with the process or affect the product quality.
- **Oxidants** - which may attack the resins.
- **Microbiological activity** - which may foul resin beds

## Analytical Data – Trend Data

- **Conductivity**
  - Non specific
  - Simple and accurate measurement
  - Useful indicator for tracking changes in composition
- **pH**
  - Non specific
  - Less accurate than conductivity
  - Also highlights changes in composition or contamination
    - $\text{HCO}_3^- / \text{CO}_3^{2-}$  equilibrium linked to pH

## Analytical Data – Units

- **Historically a variety of units have been used to express the analysis of water.**
  - Ion exchange works on a chemical equivalent basis (i.e. ionic charge), but equivalents are no longer officially recognised!
- **Current units of concentration**
  - mg/l CaCO<sub>3</sub> (Conversion to a common base.)
  - mg/l of individual ion
  - meq/l of individual ion (also mval/l)
  - m mol/l of individual ion (Do not use to calculate ionic balance.)
- **It is not unusual to get analyses with mixed units!!**
  - **Be careful**

## Analytical Data - Definitions

- **Total Dissolved Solids (TDS)** is the total concentration of cations and anions. It may be reported in mg/l or ppm or milliequivalents/l or mg CaCO<sub>3</sub>/l
- **Total Hardness (TH)** is the sum of the concentration of soluble alkaline earth and transition metal cations (i.e. Ca, Mg, Fe, Mn etc). It is usually reported as mg CaCO<sub>3</sub>/l
- **Equivalent Mineral Acidity (EMA)** is the total concentration of the **strong mineral acids (SMA)** sulphate, chloride and nitrate anions. It is usually reported as mg CaCO<sub>3</sub>/l
- **Total Alkalinity (TAlk)** is the total concentration of hydroxide, carbonate and bicarbonate anions. It is usually reported as mg CaCO<sub>3</sub>/l
- **Total alkalinity** is sometimes referred to as **M-Alk** i.e. alkalinity measured by titration to methyl orange end point.. It is usually reported as mg CaCO<sub>3</sub>/l
- **Temporary Hardness (TH)** or bicarbonate hardness, is the concentration bicarbonate anions associated with Ca + Mg. Called “temporary” because it can be removed by boiling. It is usually reported as mg CaCO<sub>3</sub>/l

# Analytical Data - Analytes

- **Cations**

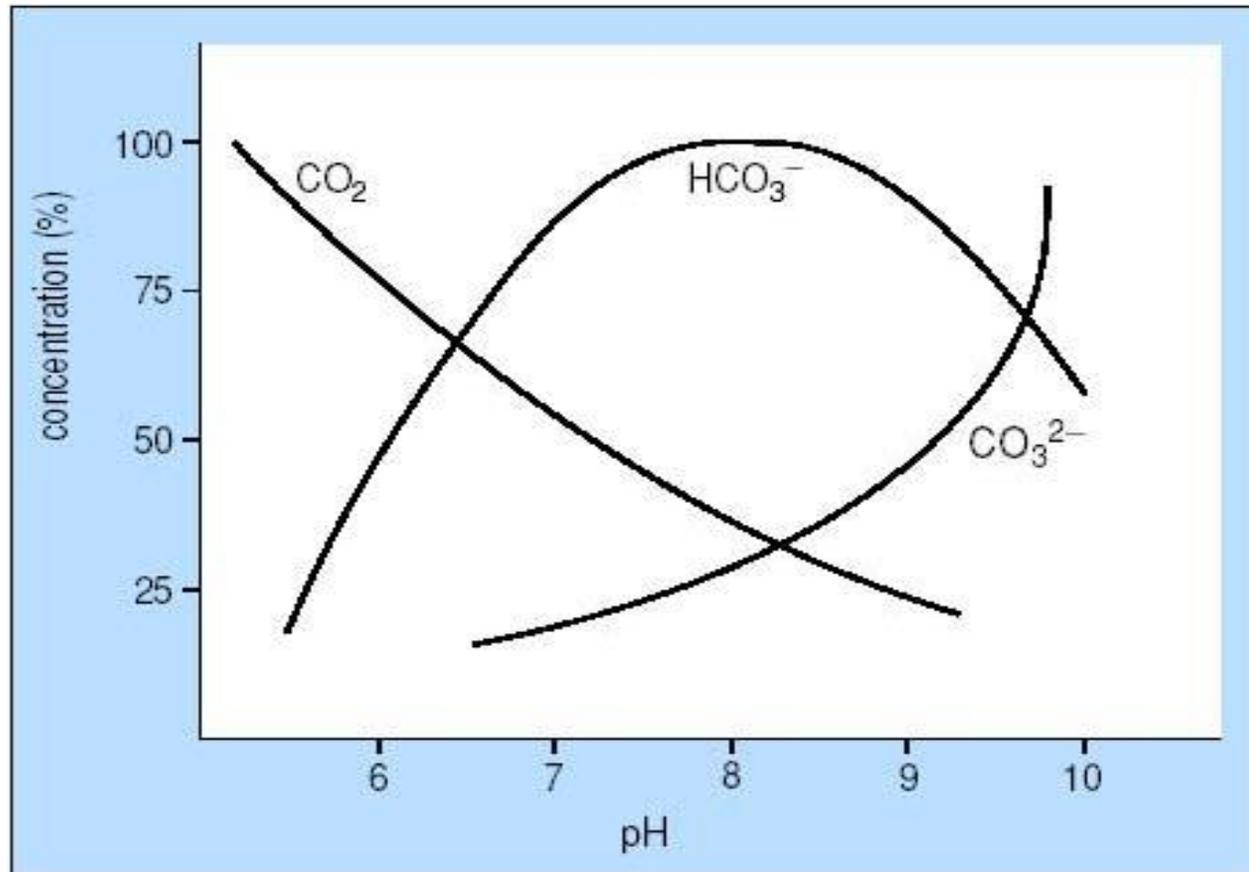
- Process Parameters
  - Sodium, Potassium,
  - Calcium, Magnesium
  - Ammonium ion, Amines (particularly for condensates)
- Interference Parameters
  - Iron, Aluminium (total and soluble)
  - Manganese
  - Barium, Strontium (H<sub>2</sub>SO<sub>4</sub> regeneration only)

- **Anions**

- Process Parameters
  - Chloride, Sulphate, Nitrate
  - Alkalinity = Bicarbonate / carbonate
  - Silica (reactive – i.e. soluble)
- Interference Parameters
  - Silica (Total - includes non reactive, colloidal silica)
  - Total Organic Carbon
  - Phosphate, Fluoride

**Note: The ratio of ionic species is important in ion exchange**

## Bicarbonate / Carbonate Equilibrium vs pH



## Analytical Data – Other Essentials

- **Suspended Solids**
  - Fouling potential
- **Residual Oxidants (residual chlorine)**
  - Chemical attack on resins
- **Microbiological Activity** (e.g. untreated sewage)
  - Fouling potential

## Sources of Data – Potable Supplies

- **Potable Water Suppliers have quality records which are available to public.**
  - Need to know supply area or if multiple supply sources likely (e.g. near a supply boundary).
- **Most of the parameters of interest for IX treatment are not analysed very frequently and some (e.g.  $\text{SiO}_2$ ) not at all.**
  - Often quoted as annual averages based on quarterly (or less frequent) figures – limited practical value
  - Suppliers often reluctant to part with data
- **Main purpose is public health – “potable quality”**
  - The industrial user has no leverage over potable water quality as long as it meets national and international standards (EU, WHO, etc)

## Sources of Data – Surface Waters (1)

- **Environment Agency (UK) publish public records on river quality,**
  - Good historical data and many sample points.
  - Can be difficult to access on-line, unless licensed.
- **The data of interest for IX design / operation is limited in frequency of analysis.**
  - Similar to potable supplies potable supplies,
- **Publish as quarterly or annual averages**
  - Useful to establish long term trends of variability.
  - No value to pick out short term variations.

## Sources of Data – Surface Waters (2)

- **Questions to ask**
  - Do other potential sources of contamination feed into your water supply source upstream?
    - Industrial process effluents
    - Sewage treatment plant discharges
    - Other rivers likely to change character suddenly
- **What is the likelihood of any of these impacting on your supply quality?**
- **You may have to ask a lot of people or do your own research.**

## Sources of Data –Surface Waters (3)

- **More questions**
- **Does the water originate from or via a reservoir?**
- **Collection or storage reservoir?**
  - Collection reservoir takes in natural waters from specified catchment area
  - Storage reservoir may be fed from multiple sources
- **What is the size of the reservoir and rate of turnover?**
  - If turnover > 1 year, seasonal variations, e.g. algal blooms and resulting organics, may be redistributed through the year.

## Analytical Data – All Sources

- **Third party data is likely to be averaged over a period of time: up to 1 year.**
- **Check if there is an ionic balance, based on equivalents (meq/l)**
  - If in balance > 95% likely to be good data
  - If balance < 90% query or reject data.
- **Never discard an outlier unless you are absolutely sure it is a sampling or analytical error!!!!**

## Analytical Data – Self Generated

- **Do not rely on your IX plant or main contractor to obtain any data on your behalf – even if the contract stipulates he should do so!!**
- **Are there other industries already treating the same water supply. They may have more useful analytical records.**
- **Set up your own sampling and analysis programme to cross check third party data.**
- **Local knowledge is invaluable!!!!**

## How Much Data?

- **ANSWER: – As much as possible!**
  - Absolute minimum is data over four seasons (1 year).
  - Preferable at least two years seasonal data.
  - Ideal at least five years data.
  - If there is more historical data check key parameters for variability.
- **Historical data requirement depends on variability of the water source.**
  - Deep boreholes less susceptible to seasonal variation
  - Large rivers can show significant seasonal and annual variation

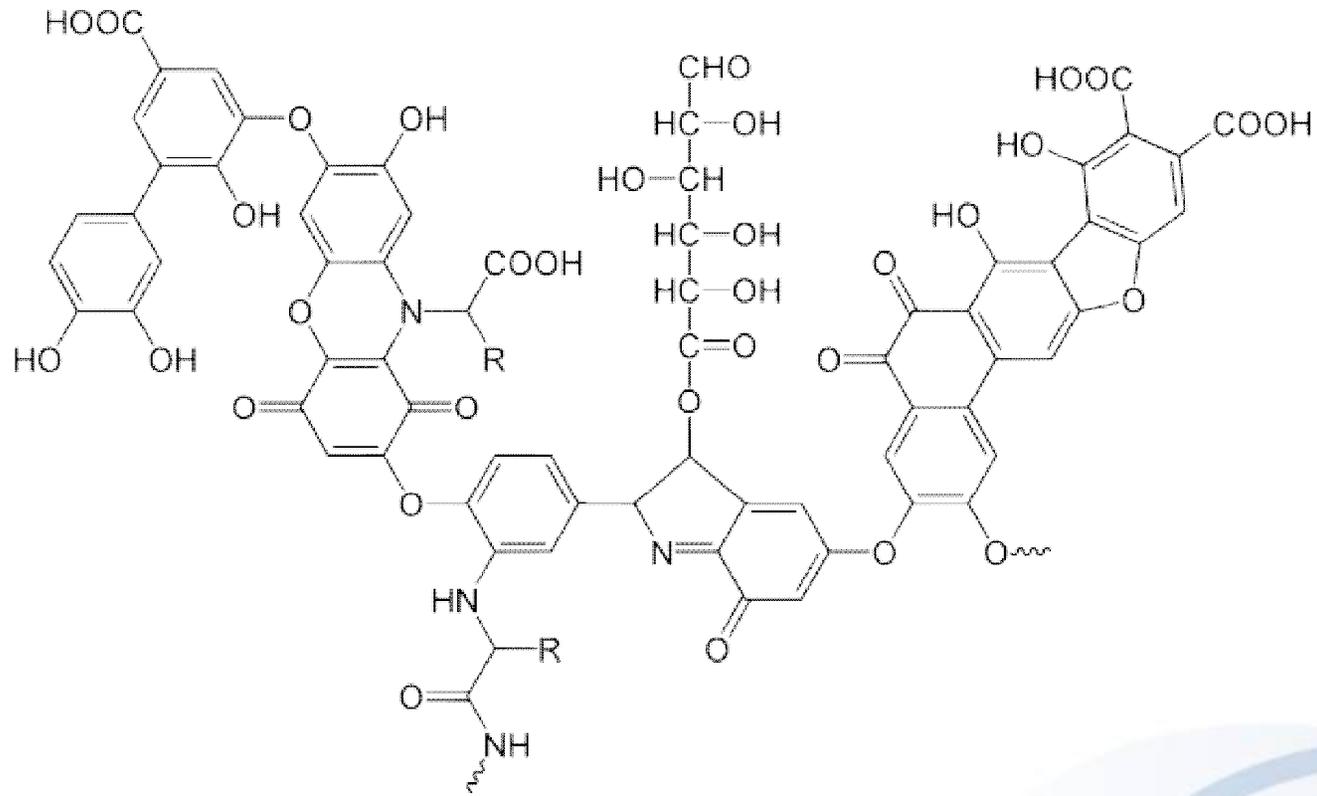
# Total Organic Carbon

- **A non specific measure of organic matter in water samples**
  - Chemical oxidation measurement (e.g. persulphate and UV enhanced)
    - Also measures total inorganic carbon (TIC) and total carbon (TC)
    - $TOC = Total\ C - Total\ Inorganic\ C$
    - Be aware of potential errors in the measurement
  - Thermal oxidation measurement
  - Sampling requires care: into clean glass bottles
  - Sample storage under refrigerated conditions to minimise microbiological growth
  - Calibration and oxidation conditions of TOC instrument appropriate to organics being measured

## Natural TOC - Humic / Fulvic Acids

- **Product of vegetative decay**
  - From peat moors and areas of high tree cover
  - Often seasonal in nature
  - Dependent on rainfall to wash organics into natural water sources
  - Not found in deep boreholes
  - May ingress to shallow borehole systems via sink holes
  - Molecular weights 5,000 – 500, 000
  - Difference between humic and fulvic acids
    - Both have carboxylate acidity
    - Fulvic acid soluble at pH 1; lower MW; higher ratio of oxygen to carbon
    - Humic acid insoluble at pH 1; higher MW; lower ratio of oxygen to carbon

# TOC – Schematic of Fulvic Acid Fragment (MW ~ 1000)



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## Natural TOC – Algal Blooms (Diatoms And Polysaccharides)

- **Algal blooms are generally summertime sources of TOC**
  - Require nutrients: nitrate , phosphate
  - Require energy source : sunlight
  - Generally occur in large open storage reservoirs
- **Sequential seasonal growth pattern**
  - Diatoms - early season
    - Microscopic silica based skeleton – non reactive silica
  - Green algae – mid season
  - Blue green algae – late season
    - By-products are poly-saccharides
    - Difficult to remove completely by IX
    - Cause foaming in degassers and during anion exchange regeneration

## Natural TOC – DOC Classification

- **DOC = Dissolved Organic Carbon**
  - Liquid chromatographic technique
  - Remains non specific – peaks given attributions
    - Hydrophobics
    - Bio-Polymers – includes Polysaccharides / proteins
    - Humic substances – humics / fulvics
    - Building blocks (Breakdown products of humics / fulvics)
    - Low molecular weight neutrals and amphiphilics
    - Low molecular weight organic acids.

## Other Sources of TOC / Organic Matter

- **Natural and Surface Waters**
  - Oil spillage into water source
  - Other organic spillages
- **Condensates and Recovered Water**
  - Lubricating oils
  - Process fats and oils
  - Other process organics
- **Organics may be emulsified or floating on the surface of a water supply**
  - Difficult to obtain representative sample

## TOC – Interpretation of Data

- **Concentration is no guide to the difficulty of treatment.**
- **Local knowledge is the most valuable factor**
  - Other sites treating the same water
  - Known sources of contamination
  - Frequency of events and variability of the water supply
- **Pilot scale tests may be required**
- **Review technology options for pre-treatment.**

## Interpretation of TOC Analyses – Historical Data

Method	Relative Concentration (Approximate)
TOC (Wet or thermal oxidation)	1 ppm as C
KMnO <sub>4</sub> – 10 min boil (Kubel)	3 ppm as O <sub>2</sub> 12 ppm as KMnO <sub>4</sub>
KMnO <sub>4</sub> – 30 min at 100 °C	2 to 2.5 ppm as O <sub>2</sub> 8 to 10 ppm as KMnO <sub>4</sub>
KMnO <sub>4</sub> – 4 hr at 27 °C	1 ppm as O <sub>2</sub> 4 ppm as KMnO <sub>4</sub>
Ultraviolet (UV Oxidation)	3 ppm as CO <sub>2</sub>

# Condensates – Conventional Power Plant

- **Area 1 – Condensate polishing**
  - Low concentrations of ionic impurities
  - Particulate metal oxides at system disturbances
  - High flow rate – exchange is kinetic dependent
  - Temperatures typically 30 – 50 °C
- **Area 2 – Recovered “clean water”**
  - Low concentrations of ionic impurities
  - Particulate metal oxides
  - Lubricating oils
  - Potentially large volumes of start-up dump water
  - Temperatures can be variable up to 100 °C

## Process Condensates - (e.g. Combined Heat & Power Plant)

- Heat recovery as important as water recovery
- Condensate may require cooling for treatment
  - Plate heat exchangers to recover heat
- Knowledge of processes essential to understand contamination risk
  - Customer often reluctant to release details
  - Materials in plant important: e.g. high Cu alloy content
  - Contamination risks (examples)
    - Cooling water
    - Organic chemicals and oils
    - Sludges: e.g. paper pulp

## Raw Water Classification - Major Species (Courtesy TV Arden)

	Water A "Thin"		Water B "Medium"		Water C "Thick"		Water D "Brackish"	
IONIC SPECIES	mg/l	<i>meq/l</i>	mg/l	<i>meq/l</i>	mg/l	<i>meq/l</i>	mg/l	<i>meq/l</i>
Sodium	2.3	<i>0.1</i>	18	<i>0.8</i>	23	<i>1.0</i>	200	<i>8.8</i>
Calcium	8	<i>0.4</i>	24	<i>1.2</i>	120	<i>6.0</i>	16	<i>0.8</i>
Magnesium	1.2	<i>0.1</i>	5	<i>0.4</i>	12	<i>1.0</i>	5	<i>0.4</i>
Chloride	7.1	<i>0.2</i>	14	<i>0.4</i>	64	<i>1.8</i>	250	<i>7.0</i>
Sulphate	9.6	<i>0.2</i>	19	<i>0.4</i>	58	<i>1.2</i>	48	<i>1.0</i>
Alkalinity (HCO <sub>3</sub> <sup>-</sup> )	12.2	<i>0.2</i>	98	<i>1.6</i>	305	<i>5.0</i>	122	<i>2.0</i>

## Raw Water Analyses - Alternate Potable Sources to Single Site

ION	SOURCE "A"		SOURCE "B"	
	mg/l	meq/l	mg/l	meq/l
Conductivity ( $\mu\text{S/cm}$ )	535		110	
pH	7.3		7.3	
Sodium	14	0.61	4	0.17
Calcium	79	3.95	14	0.70
Magnesium	24	2.0	2	0.17
Chloride	36	1.01	9	0.25
Sulphate	42	0.88	12	0.25
Alkalinity ( $\text{HCO}_3^-$ )	281	4.61	34	0.56
Silica ( $\text{SiO}_2$ )	9		1.5	
TOC	0.2		2	
Total cation: Total Anion		6.56 : 6.50		1.04 : 1.06

## Raw Water Analyses - Variation in River Composition (R Trent)

	Early November 2007		Late November 2007	
	mg/l	meq/l	mg/l	meq/l
<b>Sodium + Potassium (as Na)</b>	82	3.57	64	2.78
<b>Calcium</b>	92	4.60	60	3.00
<b>Magnesium</b>	21	1.75	13	1.08
<b>Chloride</b>	91	2.56	92	2.59
<b>Sulphate</b>	138	2.88	71	1.48
<b>Nitrate</b>	50	0.81	32	0.52
<b>Alkalinity (HCO<sub>3</sub><sup>-</sup>)</b>	212	3.48	129	2.12
<b>Silica (Reactive /Total)</b>	10.45 / 10.5		7.5 / 8.3	
<b>Phosphate (as PO<sub>4</sub>)</b>	4.5		1.2	
<b>TOC</b>	6.7		7.9	
<b>Total Suspended Solids</b>	10		48	
<b>Conductivity</b>	986	[T <sub>Cat</sub> 9.92]	720	[T <sub>Cat</sub> 6.86]
<b>pH</b>	7.6	[T <sub>An</sub> 9.73]	7.5	[T <sub>An</sub> 6.71]

## Raw Water - Indicative Typical Concentrations of Minor Species (UK Water Supplies)

SPECIES	UNITS	TYPICAL RANGE	PEAK VALUES
<b>Silica (Reactive)</b>	mg/l SiO <sub>2</sub>	1 - 10	15 - 20
<b>Silica (Non Reactive)</b>	mg/l SiO <sub>2</sub>	0.02 - 2	5
<b>TOC</b>	mg/l C	0.2 - 10	15 - 20
<b>Suspended Solids</b>	mg (dry wt)/l	0.05 - 10	100 - 200
<b>Phosphate</b>	mg/l PO <sub>4</sub>	0.1 - 5	5 - 10
<b>Barium</b>	mg/l Ba	0.02 – 0.5	1 - 2
<b>Iron (Soluble)</b>	mg/l Fe	0.02 – 0.05	
<b>Iron (Total)</b>	mg/l Fe	0.05 – 0.2	1 - 5
<b>Aluminium (Soluble)</b>	mg/l Al	0.02 – 0.1	0.2 – 0.5
<b>Aluminium (Total)</b>	mg/l Al	0.02 – 0.2	0.5 - 10
<b>Residual Chlorine</b>	mg/l Cl <sub>2</sub>	0.2 – 0.5	1 - 3

# Water



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## Design Basics (1)

- **Define basic plant parameters**
  - Throughput
  - Storage (How long can I operate with plant o/s?)
  - Plant availability (Can my process be shut down?)
- **Define raw water source(s)**
- **Define termination points for treatment plant: inlet and outlet**
- **Define raw water composition**
  - This will become the contractual basis for all further negotiation / argument
- **Define treated water quality**

## Design Basics (2)

- **Give the contractor as much information as possible.**
- **Statistical analysis on limited data has limited value.**
- **Assuming sufficient data available, tabulate the following:**
  - Average values (checking ionic balance)
  - Variability, i.e. max – min range, say at 90% or 95% percentile point
  - Note peak values, even if you are unsure of veracity.
    - Do not discard peak values just because you do not believe them. They are often true and can rebound on you!

## Conclusions – Raw Water Source

- **Understand as much as possible about your raw water supply.**
  - Where it comes from
  - What might influence its composition
  - Its potential for variability
  - The nature of change in composition
    - e.g. rainfall dependent, river in spate
  - The nature of any organic matter
  - The minor constituents that may affect/foul the process
  - Monitor the water regularly
    - Conductivity is non specific but is very sensitive to changes

## Conclusions – Design Basics

- **Obtain as much historical data as possible**
- **Do not discard apparently high results**
  - Note them in any specification
- **In specification of raw water composition**
  - Present average values and number of years data
  - Present a statistically defined band of maximum and minimum for each parameter
- **Give your contractor / supplier as much information as possible**



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