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Water has amazing properties which help to control our climate and make life on Earth possible. Although we call our planet Earth, only 29% of its area is actually land; the rest is covered by water and almost all of this water is in the oceans. Ocean waters continuously move around the globe as if they were on a huge conveyor belt, moving from the surface waters to the deep and back again. Wind, the saltiness of the water and temperature all control this movement. This ocean circulation helps to spread the heat from the Sun throughout the Earth.

The oceans also take up huge amounts of carbon dioxide from the atmosphere. Around a quarter of the carbon dioxide we humans produce by burning fossil fuels ends up being stored in the oceans. In some ocean areas this carbon can be stored for centuries, helping to reduce the effects of global warming.
Part 1: Properties of water

The special properties of water

71% of the Earth is covered by water and 97% of this water is in the oceans. Water is made up of two atoms of hydrogen and one atom of oxygen. Because of water’s electronic structure, the oxygen atom has a slight negative charge on it and the hydrogen atoms are slightly positive. When water molecules are close together, their positive and negative regions are attracted. These attractive forces are known as hydrogen bonds. Hydrogen bonds are the reason for water’s very special properties which make life on Earth possible.

1. The structure of water showing the slight negative charge on the oxygen atom and the slight positive charges on the hydrogen atoms. The charged nature of the water molecule enables it to form hydrogen bonds with other water molecules. Author: Lucinda Spokes.

- Water is the only natural substance that is found as a gas (water vapour), a liquid and a solid (ice) on Earth.

- Density is a measure of how compact a substance is. It is defined as the mass of a substance divided by its volume. Solids are almost always the most dense form of a substance, then liquids and then gases. As temperature increases, the density generally decreases. Pure water is an exception to this and is the only substance which has its highest density as a liquid. Water is at its most dense at about 4 °C. This is because hydrogen bonds between water molecules give ice a very stable open ordered structure. At low temperatures, water has a higher density than ice and this means that ice floats.

2. How the density of pure water changes with temperature. This graph shows that pure water has its highest density at 4 °C when it is still a liquid. Author: Lucinda Spokes.

- Adding salt to water increases its density. It also prevents the formation of hydrogen bonds. This means seawater, unlike pure water, doesn't have its maximum density at 4 °C, but when it freezes into ice. It also means that seawater freezes below 0 °C (this is why we put salt onto roads on cold nights to lower the risk of ice being formed).

3. How seawater density changes with temperature. At a fixed salt concentration (in this case a salinity of 35), the density of seawater decreases with temperature. Author: Lucinda Spokes.
Water has a very high specific heat capacity. This means that a lot of energy is needed to increase its temperature (energy is needed to overcome the hydrogen bonds). As the Earth is 71% water, energy from the sun causes only small changes in the planet's temperature. This stops the Earth getting too hot or too cold and makes conditions possible for life. Heat is stored by the ocean in summer and released back to the atmosphere in winter. Oceans, therefore, moderate climate by reducing the temperature differences between seasons.

Water also has a high heat of vaporisation. This means a lot of energy from the sun is needed to turn liquid water into vapour. As water vapour moves from warm areas to cooler regions it changes back to a liquid and may form rain. This releases heat which warms the air. The enormous amount of energy involved powers the storms and winds on Earth.

Many substances dissolve in water and are stabilised by the hydrogen bonds. This allows the transport of oxygen, carbon dioxide, nutrients and waste materials in water and makes biological processes possible.

Because oil molecules are large and not electrically charged, they can't be broken down into smaller charged molecules and be stabilised by water. This means that they do not dissolve in water.

Part 2: Ocean Circulation

Energy from the Sun doesn't fall equally all over the Earth. Most of the Sun's energy enters the Earth at the equator. This leads to large temperature gradients between the equator and the Poles. Movement of both the air and the oceans is controlled by these temperature differences and the result is a transfer of heat from the equator to the poles. About half the heat transport around the planet is by the oceans so the oceans are an extremely important part of the Earth's climate control system. If ocean circulation is changed by global warming, major changes in climate are therefore likely. Ocean circulation also transports oxygen from the air into the ocean making marine life possible.
Seawater continuously moves around the globe as if it is on a huge conveyor belt, moving from the surface to the deep waters and back. Because the distance the water has to travel is so large, it takes about 1000 years for seawater to go all the way around the Earth.

The movement of water around the oceans has two parts which are strongly linked:

1. a density driven circulation which is driven by the differences in the density of seawater at different locations. The density of seawater depends on its temperature and how salty it is. As a result, this movement is known as the thermohaline circulation (thermo - heat, haline - salt).

2. a wind driven circulation which results in huge surface currents like the Gulf Stream.

Thermohaline circulation

In the Northern Hemisphere
Ocean circulation transports surface seawater to the polar region where it cools. This cooling releases heat which warms the air and makes the water cold and, therefore, dense enough to sink to the bottom of the ocean. This results in the formation of new deep water which displaces existing deep water pushing it towards the equator. The major regions for this deep water formation are the Labrador and Greenland Seas in the northern North Atlantic Ocean. This North Atlantic Deep Water then flows south along the ocean floor allowing more warm surface water to flow into the region to replace it. Strong cooling also occurs in the Bering Sea in the North Pacific, but the structure of the ocean floor here prevents the deep water that forms from entering the ocean circulation.

Antarctica
Deep water formation also occurs around Antarctica during the production of sea ice. This ice contains very little salt and so, as the ice forms, the surrounding water becomes saltier and more dense. This very dense water slides down the edge of the Antarctic continent to form Antarctic Bottom Water. This water then spreads out and moves around most of the ocean floor.
2. This NOAA map shows the different elevations of the Earth's surface. Pale colours on the ocean floor are the mountainous areas. Mixing of water over these areas forces the deep water to rise to the surface.

For some time we thought that the deep waters that formed at the poles moved towards the equator, slowly warming and rising to the surface over the whole ocean, and that this water then returned to the poles in warm surface currents to complete the cycle. However, recent studies have shown that this gradual upwelling process is too slow to explain the age of seawater.

We now think that as deep water circulates around the bottom of the ocean, it meets the mid ocean ridges which are mountainous areas on the sea floor. The roughness of these causes strong mixing which forces the deep water to rise to the surface. The wind also causes strong mixing in the Southern Ocean and this also brings the deep water back to the surface. Once at the surface, the water returns to the poles in wind driven surface currents to complete its cycle.

Wind driven circulation

The Gulf Stream

The Gulf Stream is one of the most important wind driven currents. It transports very warm tropical water from the Caribbean Sea and the Gulf of Mexico across the North Atlantic to northern Europe. The warmth of the water heats the air above and the movement of this warm air is a very important way by which heat is transported northwards. As a result of this heat transport, northern Europe is very much warmer than corresponding latitudes in North America and countries around the Pacific Ocean.

For example, the yearly average temperature at Iqaluit (64°N, 068°W) in the Northwest Territories of Canada is -9.1 °C. This compares with an average for Trondheim (63°N, 010°E) in Norway of +4.8 °C. Long term records suggest that, as a result of the Gulf Stream, average temperatures in Northern Europe are 9 °C higher than the average temperatures for the same latitude elsewhere.

The Gulf Stream is an example of a western boundary current, a current which flows along the western side of a major ocean basin. The corresponding current in the Pacific Ocean is the Kuroshio Current, and in the Indian Ocean, the Aghulas Current. They result from an interaction between the shape of the ocean basin, the general direction of the wind and the rotation of the earth. They all have a high velocity (the Gulf Stream has an average velocity of 1 m s⁻¹, that is 3.6 km h⁻¹) they are all quite narrow (between 100 and 200 km wide) and all have a very important influence on the climate of the region. Eastern boundary currents also occur; these transport cold surface waters from the poles to the equator. They tend to be weaker than their western counterparts.
Part 3: Uptake of carbon dioxide

How oceans take up carbon dioxide

The most important greenhouse gas, apart from water vapour, is carbon dioxide (CO$_2$). Levels have changed over time both naturally and because of humans. Much of the carbon dioxide produced by humans does not stay in the atmosphere but is stored in the oceans or on land in plants and soils. By far the largest carbon store on Earth is in sediments, both on land and in the oceans, and it is held mainly as calcium carbonate (CaCO$_3$). The second biggest store is the deep ocean where carbon occurs mostly as dissolved carbonate (CO$_3^{2-}$) and hydrogen carbonate ions (HCO$_3^-$). We think that about a third of the carbon dioxide from fossil fuel burning is stored in the oceans and it enters by both physical and biological processes.

Physical processes

Carbon dioxide dissolves more easily in cold water than in warm water. It also dissolves more easily in seawater compared to pure water because seawater naturally contains carbonate ions.

$$\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCO}_3^-$$

Reaction of the carbon dioxide with carbonate produces hydrogen carbonate. Because of this reaction, only 0.5% of the inorganic carbon in seawater occurs as carbon dioxide gas. Since levels of carbon dioxide are so low in seawater, more carbon dioxide can enter the oceans from the atmosphere (the chemists will recognise this as an example of Le Chatelier's Principle). If the water stays at the surface and warms up as it moves around the globe, the carbon dioxide will relatively quickly escape back to the atmosphere. However, if the water sinks to the deep ocean, the carbon can be stored for more than 1000 years before ocean circulation returns it to the surface. Cold waters sink to the deep ocean at high latitudes in the Southern Ocean and in the Nordic and Labrador Seas in the North Atlantic Ocean. These regions are therefore the major physical carbon dioxide removal areas of the ocean.
**Biological processes**

As well as physical removal, carbon dioxide is also taken up by phytoplankton in photosynthesis and converted into plant material. Land plants and marine phytoplankton take up about the same amounts of carbon dioxide as each other but marine phytoplankton grow much much faster than land plants. Most of the carbon dioxide taken up by phytoplankton is returned to the atmosphere when the phytoplankton die or are eaten but some is lost to the deep sea sediments in sinking particles. The sinking of this plant material is known as the biological pump because it acts to pump carbon dioxide from the atmosphere into the deep ocean. Most of this loss is at high latitudes because the phytoplankton which live there are large enough to sink out of the surface waters into the deep ocean when they die.

Computer models suggest that human activity may alter the types of phytoplankton in the ocean. Humans, therefore, could change how much carbon is stored in the deep ocean. For instance, some phytoplankton produce calcium carbonate skeletons, particularly the very abundant *Emiliania Huxleyi*. In making their skeletons, these phytoplankton actually cause the release of carbon dioxide and this reduces the overall uptake of atmospheric carbon dioxide by seawater.

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

At the moment, we don't know all the reasons why certain phytoplankton species grow in particular ocean regions. This means we can't predict whether future human activity will change the abundance of phytoplankton which produce calcium carbonate skeletons and, if so, what impact this will have on our climate.
On land it’s easy to see that different areas have very different amounts of plant growth. The tropical rain forests have the most biological growth and the deserts have the least. Although it’s not so easy to see, it’s similar in the oceans. Oceanographers call the desert areas of the oceans the OLIGOTROPHIC regions. Oligo is the Greek word for small and troph is derived from the Greek for "to feed" so the name oligotrophic simply means an area with little food. Low levels of the major plant nutrients, nitrogen and phosphorous, in these areas means that little grows. In this unit we will look at where these nutrients come from and how phytoplankton grow in the oceans.

Large inputs of nitrogen and phosphorous from land make coastal waters the most biologically active region of the ocean. Most of these nutrients come from human activities. Areas with excess nutrients are known as EUTROPHIC regions (based on the Greek for "to nourish"). Large amounts of phytoplankton growth in these areas can cause eutrophication problems and we will discuss these in this Unit.

We use chlorophyll (the photosynthetic pigment in plants) as a measure of how much biological growth there is in the oceans. The blue areas with little chlorophyll are the deserts of the oceans. The red areas, which are generally around the coasts, are the most biologically active. Image taken by the NASA SeaWiFS satellite.
Part 1: Phytoplankton and nutrients

Phytoplankton and nutrients in the oceans

Phytoplankton (phyto = plant, planktos = to wander) are single celled plants which live in the surface waters of the oceans. Most of them simply drift around the ocean in the surface currents but some can move a tiny bit on their own.

They use sunlight, carbon dioxide (CO$_2$) and water, in a process called photosynthesis, to produce organic compounds which they use for food and to make their cells. One waste product is oxygen and this makes it possible for animals to live on earth. Phytoplankton remove almost as much carbon dioxide from the air as land plants and, therefore, help regulate our climate.

Phytoplankton also need nutrients to grow. They need a wide variety of chemical elements but the two critical ones are nitrogen and phosphorous since they are needed in quite large amounts but are present in low concentrations in seawater. Nitrogen and phosphorous are like the fertilisers we add to land plants and are used to make proteins, nucleic acids and other cell parts the phytoplankton need to survive and reproduce. Phytoplankton need nutrients in well defined ratios. For every 106 atoms of carbon they make into organic matter, they need 16 atoms of nitrogen and 1 atom of phosphorous. Most can't use atmospheric nitrogen gas (N$_2$) directly but need chemically reactive forms of nitrogen such as nitrate (NO$_3^-$) or ammonium (NH$_4^+$). There is always plenty of carbon dioxide so phytoplankton keep growing until they have used up all of the useable nitrogen or all of the phosphorous, which ever runs out first. In most of the ocean, nitrogen runs out first and growth is said to be nitrogen limited. The Eastern Mediterranean Sea is phosphorous limited, here growth stops when phytoplankton have used up all the phosphorous even though there is still nitrogen in the water.
Nutrient sources

Nutrients come naturally from the weathering of rocks and from the conversion of atmospheric nitrogen gas (N₂) into biologically usable forms. Human activity has dramatically added to these inputs.

Phosphorous

The main human sources of phosphorous are detergents and sewage. Improved sewage treatment and use of phosphate free detergents has reduced phosphorous inputs to rivers and seas.

Nitrogen

Nitrogen compounds in rivers are mainly the result of intensive agricultural activity and come from the overuse of nitrate (NO₃⁻) based fertilisers and from ploughing up land. Both nitrate and ammonium are found in the atmosphere. Nitrate comes from the high temperature combustion of nitrogen in vehicle engines and during power generation. Ammonium (NH₄⁺) comes from the storage and spreading of animal manure. Both fall from the atmosphere and enter the rivers and oceans in rain and as gases and particles.

Silicon

Another important nutrient is silicon which comes from the weathering of rocks. Lack of silicon prevents the growth of a certain type of phytoplankton, the diatoms, who use it to make their shells.

If nitrogen or phosphorous runs out, phytoplankton stop growing. If silicon runs out, phytoplankton keep growing but the types which grow changes.

Trace metals

Phytoplankton also need very small amounts of metals such as iron, copper, zinc and cobalt. There are large areas of the oceans where there isn't enough iron for phytoplankton to grow. This has important implications for climate and we discuss this in the Oceanic nutrients Unit of the Read More Section.
Remineralisation

Phytoplankton grow very quickly, only living for a day or so. When they die, they are eaten by bacteria or zooplankton (tiny animals) which convert their organic matter back into carbon dioxide, release the nutrients they have used back into the water and use up oxygen. This process is known as remineralisation and it takes place mainly in surface waters. The carbon dioxide escapes back to the air or is reused, along with the re-released nutrients, in photosynthesis. If this happens, there is no change in atmospheric carbon dioxide levels. However, if the phytoplankton sink out of the surface and are remineralised in the deep ocean, the nutrients and carbon dioxide are stored in the deep ocean and the carbon dioxide can't return to the atmosphere. This lowers carbon dioxide levels in surface waters, allows more carbon dioxide to enter from the air and helps reduce atmospheric carbon dioxide concentrations.

The carbon dioxide only returns to the air when ocean circulation brings the deep water back to the surface, a process which takes around 1000 years. This is the biological pump and is explained more in the Water in the oceans Unit in the Basics Section.

About 15% of the carbon taken up by photosynthesis is stored in the deep ocean. A very small part of this settles out and becomes sediments. An even smaller amount eventually becomes oil and coal. By burning fossil fuels, we are releasing this stored carbon about a million times faster than natural biological cycles do. Forests and phytoplankton can't take up the carbon dioxide fast enough to keep up with the increases in emissions and atmospheric carbon dioxide levels have, therefore, risen dramatically over the past few decades.

Part 2: Phytoplankton growth

Seasonal cycle of phytoplankton growth

There is a well defined seasonal pattern of phytoplankton growth in the temperate and polar oceans. It is controlled by physical, biological and chemical processes.
1. Seasonal cycle of phytoplankton in Northern Hemisphere temperate oceans. Highest phytoplankton growth is seen in the spring when there is plenty of light and nutrients. A secondary peak in phytoplankton biomass occurs in the autumn. These large growths of phytoplankton are known as blooms. Author: Lucinda Spokes.

The density of seawater is controlled by its temperature and how salty it is. As the temperature of water increases due to heating from the sun, the water molecules become more energetic, there is more space between them and the density decreases. As temperature lowers, the water molecules have less energy, don't move around as much and are closer together. This allows more hydrogen bonding to occur and the density increases.

The salinity of water is a measure of how many salts are dissolved in it. The most common salt by far in seawater is sodium chloride (common table salt) but there are also lots of other chemicals dissolved in seawater which have some effect on the salinity of the water. Evaporation of water from the ocean increases its density. Inputs of rain and river water decreases the density of the water. The result of changes in temperature and salinity around the globe leads to an ocean which has a layered structure made up of water bodies of different densities. Less dense waters float on top of more dense waters.

As we are interested in processes which control the growth of phytoplankton, we will concentrate on how changes in heating affect the vertical structure of the first few hundred meters of the ocean.

### Spring

In the spring, the sun heats the surface waters of the ocean making them less dense. This warm water effectively floats on top of the colder, more dense, waters below and there is almost no mixing between them. This means that the growing phytoplankton are kept in the surface waters. Here they have plenty of light and nutrients which were mixed up from the deep waters during winter. These conditions are excellent for phytoplankton growth. Rapid increases in phytoplankton numbers are seen and this is called the spring bloom.

### Summer

As the phytoplankton grow, they use up the nutrients in the surface waters. Since there is little mixing with the waters below, the phytoplankton stop growing when all the available nutrients have been used up. Remineralisation of nutrients in the surface waters and inputs of nutrients from the atmosphere do allow some phytoplankton growth but the summer isn't a very biologically active time in temperate latitudes compared to the spring.
4. small phytoplankton bloom in autumn

**Autumn**

Less heating from the sun as the day length becomes shorter means that the surface waters cool down and their density increases. Because there is a smaller density difference between the surface waters and the waters below, a little mixing between them occurs. This allows some nutrient rich waters to mix into the surface and, as there is still enough light for photosynthesis, a small phytoplankton bloom sometimes occurs.

**Winter**

In the winter, even less heating from the sun means that the surface waters cool further, increasing their density. This allows the surface waters to mix with the waters below. This mixing brings deep water nutrients back to the surface. Although there are plenty of nutrients, there isn't enough light for phytoplankton to photosynthesise effectively so not much grows.

In the tropics this seasonal cycle isn’t as pronounced as the strength of the sun doesn’t vary much through out the year and phytoplankton can grow all the time.

**Part 3: Eutrophication**

**Nutrients and the problems of eutrophication in coastal waters**

More than 60% of the world’s population lives within 100 kilometers of the coast and future population growth in the coastal region is predicted to be greater than anywhere else on Earth. We not only use the coast as a place to live but also for commercial activities such as mineral extraction, disposal of waste products such as sewage and industrial waste, fishing and tourism. Large populations and high levels of industrial activity mean that in some coastal areas human activity has damaged natural ecosystems.

One of the main problems affecting coastal waters are the high levels of nitrogen and phosphorous based pollutants entering the water. These pollutants come mainly from human activities and include inputs from agriculture, industry and vehicles (see Page 1 of this Unit). Many of these pollutants can be used by phytoplankton as nutrients. Overloading coastal waters with nutrients results in excessive phytoplankton growth. Large growths of phytoplankton are known as blooms and these large blooms can have undesirable effects.
Eutrophication is defined simply as 'enhanced phytoplankton growth due excess supply of nutrients'.

So what are the problems associated with eutrophication?

1. High concentrations of nutrients may lead to large phytoplankton blooms. These blooms occur throughout the water and prevent light reaching the waters below. This stops the growth of plants deeper in the water and reduces biological diversity. Photograph from NOAA.

2. When phytoplankton die they are remineralised (eaten) by bacteria. This process uses up oxygen in the water. When the blooms are really large, this bacterial decomposition can use up so much oxygen in the deep waters that there isn't enough left for fish to breathe and they have to swim away or else they die. Animals living on the sea floor can't easily move away and they also die. The European Union is the third most important fishing power in the world so maintaining the health of European coastal waters is economically very important.

3. Excess nutrients can sometimes encourage the growth of phytoplankton species which produce harmful toxins. These toxins may cause the death of other species including fish in fish farms. Shellfish become accumulate the toxin when they eat the phytoplankton and these toxins can then be passed to humans when we eat the shellfish. Shellfish poisoning generally causes upset stomachs but in rare cases it causes respiratory arrest and can therefore be life threatening. The picture shows a notice on a beach warning people not to eat the shellfish because they are contaminated with paralytic shellfish toxin. Click on the NOAA image for a better view (195 kb).
4. Large phytoplankton blooms can cause huge ugly foams on beaches. These blooms are not toxic but temporarily ruin the beach, reducing its recreational value. The income from tourism in areas badly affected by these blooms is low. Picture courtesy of the European Union.

Eutrophication can, therefore, be economically very costly and steps are being taken to reduce nutrient inputs to coastal waters. Intergovernmental organisations have agreed that we should halve nutrient inputs to waters around the North Sea and the Baltic Sea based on 1985 input values. If we achieve this, computer models suggest we should have healthy coastal waters by 2010.

**What have we achieved in Europe so far?**

**Inputs to rivers**
European directives on the treatment of sewage and use of phosphate free detergents have led to reductions in the inputs of phosphorous into our rivers and seas. However phosphorous concentrations are still high in coastal waters and it appears that phosphorous stored in sediments from earlier inputs is now slowly being released back into the water. Nitrate based fertiliser use has declined in Europe since the 1980's but nitrogen inputs to rivers from agricultural sources are still high.

**Inputs to the atmosphere**
Although there has been a general decline in emissions of air pollutants, levels of nitrogen oxides in the atmosphere are still high. Catalytic converters on new cars have reduced nitrogen oxide emissions but there has also been an increase in road travel which has partially offset the reductions in emissions per car. There has also been a decrease in ammonia emissions due to better management of animal wastes but we still have a long way to go to reach the targets which have already been set. One of the major problems with air pollution is that many species travel a long way from the place they are emitted to the place they are deposited. This may be in a different country, so we need European wide or even global action to reduce atmospheric inputs to coastal waters and this is politically difficult to achieve.

So we still have a way to go to reach the targets set by Intergovernmental Organisations such as The OSPAR Commission. By the time you read this, the situation may have changed. See if you can find the OSPAR web site and that of the European Environment Agency and find out how close we are to achieving our targets now.
The Oceans
Basics

Unit 3
Gases from phytoplankton

It was originally thought that the oceans and the atmosphere acted independently but we now know that both have a huge influence on each other. In this Unit we look at how phytoplankton living in the oceans affect our climate. We think that these tiny single celled plants emit almost as much sulphur into the air as do all the power stations on Earth put together! We concentrate on the gas dimethyl sulphide (DMS) which is probably the most important gas produced biologically. We look at how and why this gas is produced and why it is so important to our climate. We also look at other climatically important gases which are formed in seawater and how these are involved in global warming and ozone depletion in the stratosphere.

Part 1: Sulphur gases

Dimethyl Sulphide DMS (CH$_3$-S-CH$_3$)

One of the most important trace gases emitted from the oceans to the atmosphere is dimethyl sulphide (DMS). This is the one of the chemical compounds which gives the sea its characteristic smell.

DMS is produced by the breakdown of a chemical called dimethyl sulphoniopropionate (DMSP for short!!) which is found in the cells of many species of phytoplankton. We thought that phytoplankton produced DMSP to help them to survive the salty conditions in the oceans but it now looks as though they may also use DMS to get rid of harmful waste products, to allow them to live in very cold waters and perhaps even to prevent other animals eating them. Not all phytoplankton produce DMSP and we are not sure at the moment why only certain species do. One type of phytoplankton, the coccolithophores, are important DMSP producers. They have calcium carbonate skeletons.

This image shows a very important coccolithophore, *Emiliania Huxleyi*. This single celled marine phytoplankton surrounds itself with over 30 plates (or coccoliths) made up of calcium carbonate. Each coccolith is just 0.003 mm in diameter.

1. The coccolithophore *Emiliania Huxleyi*. Image from NOAA.
When phytoplankton are infected, die or are eaten, DMSP is released into seawater where it breaks down to form DMS. Much of the DMS stays in seawater and is consumed by bacteria or converted to other chemical species. A proportion, however, escapes and enters the atmosphere.

As DMS is the breakdown product of a biologically produced chemical compound, DMS emissions occur in the spring, summer and autumn when phytoplankton are growing. Emissions come from both coastal waters and from the open ocean but are larger in regions where particular phytoplankton grow. Lots of DMS is emitted from the north east Atlantic Ocean and from the Bering Sea in the North Pacific Ocean as there are regular blooms of coccolithophores in these areas. Lots of DMS also enters the atmosphere from coastal waters around Europe.

About the same amount of sulphur is emitted from natural sources as is produced during the burning of fossil fuels by humans. So the tiny phytoplankton you can see in the image above is as important to our climate as the huge power stations that we use to generate our energy. In regions far away from human activity, most of the sulphur present in the atmosphere comes originally from DMS emitted from seawater. It is thought that between 20 and 50 million tonnes of sulphur enters the atmosphere from the oceans each year.

Part 2: Aerosols and climate

Once dimethyl sulphide (DMS) enters the atmosphere it reacts with other chemicals to form sulphate aerosols (aerosols are simply particles or liquid droplets floating in the air). These sulphate aerosols are really important to our climate. They scatter sunlight directly back into space and can also start the formation of clouds.

Both sulphur dioxide ($\text{SO}_2$) and methane sulphonic acid ($\text{MSA} - \text{CH}_3\text{SO}_3\text{H}$) are formed when DMS is converted into sulphate aerosols. Sulphur dioxide is formed both from DMS and also during the burning of fossil fuels like coal. MSA is only formed from DMS so MSA acts as a good tracer for marine sulphur emissions into the atmosphere. Sulphur dioxide is then converted into sulphuric acid ($\text{H}_2\text{SO}_4$) so DMS plays a part in controlling how acidic the atmosphere is.

This sulphuric acid can then react with ammonia (NH$_3$) gas, which is also produced naturally by phytoplankton, to form ammonium sulphate aerosols. Both sulphuric acid and ammonium sulphate act as cloud condensation nuclei (CCN). These are particles which attract water and provide a surface for the water to condense onto. They are needed to start the formation of clouds.
So how does DMS affect climate?

1. Cartoon showing the importance of marine sources of sulphur to our climate. DMS stands for dimethyl sulphide, the most important sulphur containing gas produced by some species of phytoplankton. CCN stands for cloud condensation nuclei, the aerosols needed to start cloud formation. SO₂ is the gas sulphur dioxide, an intermediate species in the conversion of DMS into sulphate aerosols. Author: Lucinda Spokes.

Direct cooling of the Earth

Sulphate aerosols can directly absorb or scatter sunlight preventing it reaching the surface of the Earth. By preventing the sun's energy reaching us, sulphate aerosols help keep our planet cool. This cooling effect goes someway to counteract the warming effect of carbon dioxide and other greenhouse gases.

Indirect impact of aerosols on climate

By acting as cloud condensation nuclei and starting the formation of clouds, sulphate aerosols also have an indirect impact on our climate. Increasing the amount and whiteness of clouds over the Earth increases the albedo of our planet. Albedo is very simply defined as a measure of how much sunlight is reflected back into space. White surfaces such as clouds and ice reflect lots of sunlight back to space, whereas dark surfaces such as the ocean absorb sunlight efficiently. Since clouds reflect a lot of sunlight back into space they can cause cooling of the Earth. Over the oceans, the amount of sulphate aerosol is one of the most important factors governing the extent and type of clouds.

Some cloud types can also take up infra-red radiation from the Earth (like greenhouse gases). This effect traps heat and these clouds, therefore, cause a warming of our climate. We don't know enough about the types of clouds which form over the oceans and so we are not sure yet whether this warming effect partially or completely counteracts the cooling effect through the increase in albedo.
Clouds, snow and ice have a high albedo, they reflect a large amount of sunlight back into space. Water surfaces and forests have a low albedo, they absorb a lot of the sun's energy and only reflect a small amount back to space. Over the whole Earth, about 30% of incoming sunlight is reflected back to space, 50% is absorbed by the Earth and about 20% is absorbed in the atmosphere by chemicals, aerosols and clouds.

Phytoplankton are, therefore, not only the main source of acidity in marine air but are also an important source of aerosols and cloud condensation nuclei. As a result they affect the radiation budget of the Earth. At the moment we can't say accurately quite how important DMS really is to the cooling of our planet.

Have a look in the Clouds and Particles Topic for more details on how aerosols and clouds influence our climate.

**Part 3: Gases from seawater – 1**

**Other climatically important gases from seawater - 1**

A whole variety of different gases enter the atmosphere from seawater and many affect our climate. Some, like dimethyl sulphide, are produced during phytoplankton growth. Others are produced when sunlight reacts with organic (carbon based) compounds found in the surface waters of the oceans. Many of these organic compounds come originally from phytoplankton. Here we look at some of the gases which affect the troposphere, the lower layer of our atmosphere.

**Halocarbons**

Halocarbons are a group of simple organic (carbon based) compounds which contain halogen atoms. Halogen is the special name for Group VII of the Periodic Table of the Elements which includes chlorine, bromine and iodine. Halogens are very important constituents of seawater. In fact the word haline, which is used to mean saltiness, comes from the word halogen. Chlorine as its charged anion, chloride (Cl\(^-\)), is the most abundant chemical species (other than water!!) in seawater.

One of the most important marine derived halocarbons is methyl iodide which has the chemical formula CH\(_3\)I.
Where do marine halocarbons come from?

Halocarbons are produced in seawater by biological processes and by sunlight. Methyl iodide is produced by some species of seaweeds and by a few species of phytoplankton but we’re not really sure why they produce the compound. There is also evidence that methyl iodide is produced by the action of sunlight on iodine-containing organic matter and, in the open ocean, this may be the most important source. Once produced, a small proportion of halocarbons escapes from seawater into the air.

Why are halocarbons important?

Many iodine and bromine containing halocarbons can be broken down by sunlight in the troposphere (the lower layer of the atmosphere) to form very reactive halogen radicals. In this way they differ from chlorofluorocarbons (CFC's) which are man-made halogen containing chemical compounds. CFC's can only be broken down to halogen radicals by ultra-violet radiation in the stratosphere (the upper atmosphere).

Halogen radicals are extremely reactive and one of their most important reactions is the destruction of ozone (O₃). In the troposphere, ozone is harmful to human health and also acts as a very strong greenhouse gas (responsible for about 15% of the enhanced greenhouse effect). So the emission of halocarbons from the sea may lower tropospheric ozone levels and reduce global warming. However lowering ozone amounts also reduces the concentration of hydroxyl (OH) radicals in the troposphere. Because these hydroxyl radicals clean the air of harmful chemicals, lower levels of them may reduce air quality.
Methane (CH4)

Methane (the major component of natural gas) is a major greenhouse gas which comes from both natural and man-made sources. Rice paddies and intensive cattle farming are the biggest methane sources to the atmosphere but the ocean is a small natural source of the gas.

What is the source of this marine methane?

When oxygen concentrations in the water or the sediments are zero, bacteria produce methane when they eat organic matter. Estuaries, saltmarshes and coastal waters are responsible for about 75% of the total oceanic methane emissions.

Methane can also be produced by the action of heat and pressure on buried organic matter and there is a huge store of methane in ocean sediments which we use as our natural gas supply. Most of the methane released naturally from these sediments is used up by bacteria in the water before it reaches the air.

Why is methane important?

In the troposphere, methane is a major greenhouse gas (62 time more powerful than carbon dioxide over a 20 year timescale) and therefore contributes to global warming. In fact, it is responsible for about 15-20% of the enhanced greenhouse effect. It is also important in controlling the abundance of hydroxyl radicals. These radicals are responsible for cleaning the atmosphere of harmful chemicals. If methane levels rise, the concentration of OH radicals is likely to decrease. This reduces the ability of the atmosphere to clean itself. One of the outcomes of eutrophication is lower levels of oxygen in the water. If eutrophication continues to be a problem in coastal waters, it is likely that the marine source of methane will rise. One possible outcome of global warming is an increase in methane emissions from ocean sediments. If this happens, we’re not sure at the moment whether bacteria will be able to cope with the rise in levels. So it’s possible that the marine methane source will grow further in the future.

Non Methane Hydrocarbons (NMHC)

Hydrocarbons are a group of organic chemicals which are made up just of carbon and hydrogen and are used extensively as fuels. The simplest hydrocarbon is methane and this is discussed above. However, other hydrocarbons are also climatically important. The ocean is a small source of NMHC's to the atmosphere compared to land based sources. These are both natural and man-made and include plants, soils and fossil fuels.
Where do NMHC’s come from?

In seawater, NMHC’s are produced biologically and by the action of sunlight on organic matter. One of the most important NMHC’s is isoprene (2, methyl buta-1, 3 diene H₂C=C(CH₃)CH=CH₂). This compound is produced by both land plants and by all of the marine phytoplankton species we have studied so far. At the moment we don’t know why plants produce isoprene, it may simply just be a by-product of photosynthesis.

Why are NMHC’s important?

Once NMHC’s escape to the air they are highly reactive with ozone. In polluted air they contribute to ozone production whereas in clean air, such as that over the oceans, they destroy ozone. Reactions of NMHC’s in the atmosphere are also important in controlling levels of hydroxyl radicals and so play a role in cleaning the air of harmful chemicals.

Part 4: Gases from seawater – 2

Other climatically important gases from seawater - 2

Some of the gases formed in seawater are not broken down in the troposphere, the lower layer of our atmosphere. This allows them to reach the upper layer of our atmosphere, which we call the stratosphere. The stratosphere is very important to our climate. It contains the ozone layer which protects us from harmful ultra-violet rays from the Sun. It also contains a layer of sulphate aerosols which prevent some of the energy from the Sun reaching the Earth. Even though the stratosphere starts over 11 km above the surface of the Earth, gases from seawater can affect it’s chemistry.

Nitrous Oxide (N₂O)

Another important biologically produced gas is nitrous oxide. Because it isn’t broken down in the troposphere, it has a very long lifetime in the atmosphere, lasting around 120 years.

Where does nitrous oxide come from?

The largest source of nitrous oxide is soils, particularly in the tropics and emissions have risen over time probably due to increased fertiliser use. The oceans are also a very important source, particularly estuaries and coastal waters. Here nitrous oxide is produced by bacteria converting nitrogen compounds into nutrients.
Why is nitrous oxide important?

In the troposphere, nitrous oxide is 275 times more powerful a greenhouse gas than carbon dioxide so it contributes greatly to global warming. Because it has such a long atmospheric lifetime, it can get all the way to the stratosphere and affect climate there as well. In the stratosphere, nitrous oxide is destroyed by ultra-violet radiation to produce nitrogen oxide (NO) radicals. These are involved in the destruction of stratospheric ozone. Although a problem in the troposphere, we need stratospheric ozone to protect us from ultra-violet radiation. Emissions of nitrous oxide from coastal waters are likely to increase as our climate gets warmer and sea levels rise. Further eutrophication may also lead to enhanced production of nitrous oxide. There is already evidence for increasing nitrous oxide emissions along the Indian coast as a result of human activity.

Carbonyl Sulphide (COS)

Carbonyl sulphide is the dominant sulphur gas in the atmosphere. It is formed mainly in the oceans but also has a small industrial source.

Where does marine carbonyl sulphide come from?

Marine derived carbonyl sulphide is formed by the action of sunlight on sulphur-containing organic matter in the upper layers of the ocean, particularly in coastal waters. Because it doesn’t dissolve easily in water, it enters the atmosphere easily.

Why is carbonyl sulphide important?

Carbonyl sulphide isn’t broken down in the troposphere so, like nitrous oxide, it can get all the way to the stratosphere. Here it is converted to sulphate aerosols. Sulphate aerosols reflect incoming sunlight back into space and so help cool our planet.

\[
\begin{align*}
N_2O + \text{ultra-violet light} &\rightarrow N_2 + O
\\
O + N_2O &\rightarrow 2NO
\\
NO + C_3 &\rightarrow NO_2 + O_2
\\
NO_2 + O &\rightarrow NO + O_2
\\
\text{overall: } C_3 + O &\rightarrow 2O_2
\end{align*}
\]
The Oceans

Read more

Unit 1
Oceans and climate

We know that the oceans are a really important part of the Earth's climate control system. We don't know, though, how ocean circulation is likely to change as a result of global warming. We don't know either whether natural weather patterns such as the North Atlantic Oscillation, which influence wither time climate in Europe, will be altered by global warming. In this unit we look at the predictions of up-to-date computer models of ocean circulation and see how global warming is likely to affect the oceans and therefore the climate of our Earth.

Part 1: Oceans and climate change

Consequences of global warming on ocean circulation

Global warming is likely to have a number of effects on the ocean. We know that carbon dioxide dissolves more easily in cold water than in warm water so warmer temperatures will reduce the ability of the oceans to take up carbon dioxide and this will further enhance the greenhouse effect. Higher temperatures are also predicted to increase the input of freshwater into the high latitude oceans. Computer models suggest that this additional freshwater comes from increased rain at mid and high latitudes and from the melting of ice sheets. Warmer temperatures also cause expansion of water and, along with the additional water from ice melt, will result in a rise in sea level and may cause flooding.

Ocean circulation is very sensitive to the amount of freshwater entering the system. Freshwater controls the density of seawater and therefore the ability of seawater to sink when it is cooled. If the water is too fresh, cooling won't make it dense enough to sink into the deep ocean. If water doesn't sink at high latitudes there is only wind driven forcing for the Gulf Stream and therefore reduced water circulation around the oceans.

We have some geological evidence that the thermohaline circulation has shut down in the past. Warming at the end of the last ice age ~15,000 years ago melted the ice sheets over North America and increased the freshwater input to the North Atlantic. This reduced the saltiness of seawater, preventing it sinking, and therefore decreased deep water formation. There is evidence that this caused the shutdown of the thermohaline circulation, caused the Gulf Stream to move south and reduced heat transport to Northern Europe. This interrupted the warming seen at the end of the last Ice Age. Ice core and deep sea sediment records show that temperatures in north west Europe fell by 5 °C in just a few decades returning the North Atlantic region to Ice Age conditions. This era of the Earth's history is known as the Younger Dryas Cold Period. We also have some evidence that ocean circulation is changing now as a result of global warming. Observations show that the North Atlantic has become steadily less salty over the past 40 years.

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1. Around 13,000 years ago the last Ice Age ended and the Earth became warmer. This warming increased the amounts of freshwater entering the North Atlantic Ocean as the ice sheets melted. Ocean circulation shut down and the North Atlantic region became colder again. Freshwater inputs stopped once all the ice had melted and ocean circulation was able to start up again. This caused a rapid (on geological timescales!) increase in temperature as warm water from the tropics was able to flow again into the North Atlantic. Figure courtesy of R. Alley and the CLIVAR project.

Trying to predict the impact of global warming requires use of complex computer models which all include assumptions about future conditions that cannot be tested properly. As a result, different models predict differing outcomes of global warming. Some models suggest that global warming will lead to a weakening of the thermohaline circulation during this century but that ocean circulation will not shut down completely, others show a complete breakdown of ocean circulation as a result of increased inputs of freshwater. It is difficult, therefore, to estimate how our climate would be if ocean circulation changed.

2. Nine different computer models all predict very different changes to ocean circulation as a result of global warming. Some models suggest little or no change in the amount of deep water formed in the North Atlantic and therefore little change to the thermohaline circulation. Others, however, suggest that global warming will reduce deep water formation by a huge amount. The unit used is the Sverdrup (Sv) which gives the volume of water moving over time. 1 Sv is a million cubic meters of water moving every second! The worst case scenario is that global warming will reduce the flow of water from the surface to the deep in the North Atlantic by 15 Sv by the year 2100, greatly reducing the thermohaline circulation. Figure courtesy of the CLIVAR Project.

Complex models suggest a cooling of around 2 °C over most of Europe as a result of the reduced transport of heat from the Caribbean as the Gulf Stream weakens.
3. This figure shows how air temperatures are predicted to change if the thermohaline circulation simply stopped. Most computer models suggest that temperatures in Europe would become colder as the Gulf Stream slowed down and less heat was brought from the Tropics to northern Europe. Courtesy of Michael Vellinga and Richard Wood and the CLIVAR Project. The impact of greenhouse gas induced warming has to be superimposed on this to give an overall prediction of climate. Over the world as a whole, temperatures are predicted to increase. Over Europe, however, most models suggest that temperatures would change little or that there would be a slight warming if the thermohaline circulation collapsed. Along with this slight warming, the climate is suggested to become wetter and more stormy. Predicting where and when these storms occur is really difficult. So we still need better observations and more realistic computer models to reduce our uncertainty about what will happen to our climate in the future.

Part 2: North Atlantic Oscillation

The North Atlantic Oscillation is one of the oldest recognised weather patterns. It governs whether winters in northern Europe will be wet and warm or cold and dry. We don't really know what controls the North Atlantic Oscillation and we don't know whether it is likely to be influenced by climate change.

Atmospheric Pressure

Air pressure at the Earth's surface is different in different places and this is partially due to the different amounts of heat they receive from the sun. When the Sun heats up the earth, the air above warms, becomes less dense, expands and rises. The air above is pushed upwards and then spreads out horizontally at height in the troposphere. Because of this horizontal air movement there is less air above the ground where the heating took place and this leads to an area of low pressure. As the air rises, it cools. As it cools, the air becomes more dense and sinks. This sinking means that there is more air above the ground in this area and a region of high pressure is formed. Air moves from high pressure areas to low pressure regions to even out the pressure differences, generating winds and atmospheric circulation as a result.
1. This figure shows the atmospheric circulation patterns which give rise to the major bands high and low pressure around the Earth. The pressure cells between the equator and 30°N and 30°S are known as Hadley Cells after George Hadley who suggested their existence way back in 1735. These cells transport heat from the equator to the colder temperate and polar regions.

The North Atlantic Oscillation

Pressure differences between the Azores at ~30°N and Iceland at ~60°N result in one of the oldest known natural weather patterns, the North Atlantic Oscillation (NAO). The NAO is most important in winter and has two phases. Each causes distinct weather conditions around the North Atlantic. Agricultural harvests, water management, energy supply and fisheries are all directly affected by the phase of the NAO. It even governs where new deep water is formed and therefore influences the thermohaline circulation.

2. This figure shows the North Atlantic Oscillation Index over the past 200 years. Up until around 1900, the NAO index seemed to change almost every year but since then it appears that the NAO index has been predominantly positive leading to warm wet winters in Northern Europe. We don’t know whether this change is simply natural climate variability or whether human influence through global warming has changed how this natural climate phenomenon operates. Thanks to Dr. Tim Osborn at the Climatic Research Unit, University of East Anglia, Norwich, U.K. for use of this figure.

Positive NAO conditions

Positive NAO winters occur when there is a very large pressure difference between the Azores and Iceland. This results in more and stronger winter storms crossing the Atlantic travelling

Negative NAO conditions

Negative NAO winters occur when there is only a small pressure difference between the Azores and Iceland. This leads to fewer and weaker winter storms. These storms
in a northeasterly direction. These bring heat from the ocean to northwestern Europe leading to warm and wet winters here but cold and dry winters in the Mediterranean region. Strong northwesterly winds travel over the Labrador Sea causing cooling, resulting in the formation of new deep water and cold dry winters in Canada and Greenland. These winds don't make it over the Greenland Sea so this region doesn't cool so much, reducing deep water formation here.

follow a more southerly track than those associated with positive NAO conditions and bring warm moist air to the Mediterranean. They also allow cold air from the north and the east to blow into northern Europe. This cold northerly wind travels from the North Pole over the Greenland Sea cooling the water enough for it to sink and form new deep water here.

3a. In positive NAO winters it's very stormy over the North Atlantic Ocean. These storms bring warm air containing lots of water vapour to Northern Europe making the winters wet and warm here. Further south, winds bring cold dry air from the land into the Mediterranean area making the winters sunny but cold here.

3b. In negative NAO winters, it's much less stormy over the North Atlantic. Any storms which do occur bring warm wet air from the ocean into the Mediterranean region. The small pressure difference allows northerly air to blow into Northern Europe making the winters dry and sunny but very cold here.

**What controls the NAO?**

We still really don't know what controls the phase of the NAO. Processes which are controlled just by the atmosphere occur over time periods of seconds to weeks. The phase of the NAO, however, changes over years to decades. This suggests that the ocean as well as the atmosphere is an important control. Computer models suggest that the NAO responds to slow changes in global temperatures with changes around the equator appearing to be most important. Winds high up in the stratosphere may also affect the climate of the North Atlantic.

**Climate change**

The NAO is an important topic in climate change. The phase of the NAO has been consistently more positive recently leading to mild winters in northern Europe and we really don't know why. It may be that this is simply natural climate variability or that global warming is changing how the NAO and other natural climate variations work.
Part 3: Sea level rise

Changes in sea level have occurred throughout the history of the Earth. During the most recent ice age, sea level was much lower than it is now because so much of the water was frozen and stored on land. At the moment our sea level is rising and the main culprit is global warming.

Sea levels vary either because the amount of water in the oceans changes or the land moves. Because it takes a long time for the Earth to adjust to changes in the weight of ice and water on it, land movements today are often the result of processes which occurred many thousands of years ago. Changes to the amount of water held in the oceans can happen faster.

What processes affect sea level and how much is the sea rising?

Geological data shows that, over the last 6000 years, sea level has risen on average between 0.5 and 1.0 mm every year. The extent of the sea level rise varies with the location because the land can be either rising or falling in response to ice loss at the end of the last ice age. Over the 3000 years, sea level has risen slower, averaging 0.1 to 0.2 mm per year. During the 20th Century, the rate of sea level rise has increased again and is now about 10 times faster than this, between 1.0 and 2.0 mm every year. For every centimetre the sea rises, around one metre of coastal land is lost to the sea. Although most people think sea level rise is just due to the melting of ice on land, the most important factor is simply that the density of water decreases as it gets warmer. This leads to an increase in the water volume, a process known as thermal expansion. As the oceans are like basins, a rise in sea level is the only way the oceans can cope with the increase in volume.

1. Rising temperatures decrease the density of seawater. This leads to an increase in its volume. As the oceans are like basins, a rise in sea level is the only way the oceans can adjust to this change in volume. The end result is flooding. Author: Lucinda Spokes.

Melting of ice on land is the second most important part of sea level rise (melting of floating icebergs doesn't affect sea level, an example of Archimedes' Principle). If all the ice sheets in Antarctica and Greenland melted, sea level would rise by 70 metres! This means that small changes in their volume can have big effects on sea level. Even the much smaller ice caps and glaciers on the rest of the Earth contain enough water to raise sea level by half a metre.

Archimedes' Principle says "An object totally or partially immersed in water is lifted up by a force which is equal to the weight of water it displaces".
Although the big ice sheets on Antarctica contain huge amounts of water, we don't think they have actually contributed much to sea level rise over the last century. Even with global warming, it's still not warm enough in summer for much of the ice to melt. Global warming seems rather to make it snow more, cause more ice to form and sea level to fall here. There have been lots of studies on the Western Antarctic Ice Sheet as this, on its own, contains enough water to raise sea level by six metres. Recently large bits of the floating Larsen Ice Sheet have broken off. Our worries are that this will make the big ice sheets actually on Antarctica less stable, allowing them to slip into the sea and cause huge rises in sea level. Summer temperatures in Greenland are warm enough to allow parts of the ice caps here to melt so this region is likely to contribute more than Antarctica to sea level rise.

Changing the amount of water we store on land in reservoirs and in groundwater is also likely to alter sea level but at the moment we're not sure how much.

Computer models predict that sea level will continue to rise in the next century. There are still huge uncertainties mostly because we don't have enough long term data from around the world to test our models. However, the best predictions are that sea level will rise between 11 and 77 centimetres by the end of the 21st Century. Although there are great variations in these estimates, all the studies show that the rise in sea level will not be the same all over the world.

What are the consequences of sea level rise?

For every centimetre the sea rises, about one metre of land is lost to the sea. The consequences of this are huge.

- Most of the human population lives close to the sea. In Bangladesh, for example, about 17 million people live less than one metre above sea level.
- Extensive flooding is a threat to human health. Many people will die and moving huge numbers of people away from flooded regions, particularly in the developing world, will increase the risk of diseases spreading. There is also likely to be a reduction in the quantity and quality of freshwater, further affecting human health.
- Important biological communities are likely to be lost because some species will not be able to adapt quickly enough to changes in salinity or loss of ice cover.
- Coastal regions are important for ports, fisheries, agriculture and tourism. Flood defences prevent natural variations in the coastline and protect these economically important activities. However, they can also lead to increases in water levels in coastal areas by isolating the sea from its natural coastal flood plain. This can lead to catastrophic flooding if the sea defences fail.
In large areas of the ocean there are plenty of the nutrients nitrogen and phosphorous but not many phytoplankton. One of the biggest discoveries in oceanography over the past few decades has been that concentrations of iron in some ocean waters are lower than the levels that phytoplankton need to grow. In this unit we look at the importance of iron in the oceans and why iron is important to our climate. We also look at the pros and cons of deliberate large scale open ocean iron fertilisation and whether this could solve our global warming problems.

Part 1: Iron in the oceans

Iron is the fourth most abundant chemical element in the Earth's crust, making up around 4% of the total mass. It is an essential micronutrient for all living species. The most important source of iron to the oceans is dust and this comes almost entirely from the desert areas of the Earth. There are large regions of the oceans where there are plenty of nitrogen and phosphorous containing nutrients but not many phytoplankton. These areas are far away from the deserts and it is assumed that lack of iron prevents phytoplankton growing here.

Where does the iron in the oceans come from?

The atmosphere is probably the largest source of iron to the oceans and this iron comes mainly from the wind erosion of soils to form dust. The dust mainly comes from arid and semi-arid desert regions, most of which are in the mid-latitudes of the Northern Hemisphere. The amount of dust produced by the deserts depends on how much it rains and on how strong the winds are. Highest dust concentrations are seen near the deserts and lowest amounts are seen in in the air above the Southern Ocean near Antarctica as this is as far away from the dusty deserts as is possible.
**Dust inputs to the oceans**

Large dust particles rapidly settle out of the atmosphere but particles with a diameter of less than 10 µm (that is 0.00001 m) can travel great distances. Winds rapidly carry the particles high into the air, up to 5 km over the Atlantic and 8 km over the Pacific. It takes about one week for African dust from the Sahara to cross the Atlantic Ocean and two weeks for dust to travel from the Chinese deserts to the Central Pacific Ocean. The dust particles then either fall out of the air as dry particles or are scavenged by water drops and enter the oceans in rain.

![Advanced Very High Resolution Radiometer (AVHRR) images of particle transport in the atmosphere between June and August. These images show the major dust transport routes across the Atlantic and Indian Oceans. As they measure all particles in the air, they also show particles coming off southwest Africa from biomass burning and pollutants coming off the eastern coast of North America. Copyright American Geophysical Union.](image)

Even though iron is very abundant in dust and lots of dust enters the oceans, iron concentrations are extremely low in seawater (generally less than 1 nmol L$^{-1}$, that is <0.000000001 mol L$^{-1}$). We now know that the iron in dust occurs mainly as oxidised iron(III) complexes which are not very soluble in water. As dust is transported through clouds it encounters very acidic conditions which increase the solubility of the iron a bit. However, we still think that less than 2% of the iron entering seawater from the atmosphere is soluble and can be taken up by phytoplankton and used as a nutrient.

**High Nitrate, Low Chlorophyll (HNLC) regions of the oceans**

The major nutrients which control phytoplankton growth in the oceans are nitrate and phosphate and, to a lesser extent, silicate. In most oceans, phytoplankton grow until they have used up all of the nitrate or all of the phosphate, whichever runs out first. The subarctic Pacific, the equatorial Pacific and the Southern Ocean, however, all have plenty of these nutrients all year round but have low phytoplankton growth and corresponding low levels of chlorophyll, the photosynthetic pigment in plants. These regions are known as the HNLC regions of the oceans and make up about 20% of the total area of the ocean.

![Map of annual average nitrate concentrations in the surface waters of the oceans. This image clearly shows the high levels of nitrate in the subarctic Pacific, the equatorial Pacific and the Southern Ocean. Data from the Levitus World Ocean Atlas 1994.](image)
The scientist John Martin first suggested that it was a lack of iron in these HNLC ocean areas which prevented phytoplankton growing and scientific experiments conducted at sea confirmed this. Oceanographically these HNLC regions are all sites where the ocean circulation brings large amounts of deep water to the surface in a process known as upwelling. These deep waters contain high concentrations of the major nutrients and the waters should, in theory, be very biologically active. However, these regions are all far from the large deserts so not much dust (and therefore iron) enters the surface waters. Similar upwelling is seen north of 40°N in the North Atlantic, but this ocean area isn’t a HNLC region as it has large inputs of iron from Saharan dust.

Part 2: Iron, dust and climate

The effect of iron and dust on climate

The presence of iron both in the atmosphere and in seawater affects our climate. In the atmosphere, iron containing particles scatter sunlight back into space and cause cooling. The iron in these particles helps to form sulphate aerosols. These sulphate aerosols scatter sunlight back into space and also start the formation of clouds. By influencing phytoplankton growth, iron in seawater affects the ability of the oceans to take up the very important greenhouse gas, carbon dioxide.

In the atmosphere

Before dust even enters seawater it influences climate. Dust particles in the atmosphere scatter sunlight back into space and cause a cooling at the Earth’s surface by preventing the Sun’s energy from reaching the ground. Chemical reaction of the iron in the dust with certain sulphur containing species in the air, forms sulphate aerosols (the word aerosol just means a particle or a liquid droplet in air). These aerosols cool the planet both by scattering solar radiation back into space and also by acting as cloud condensation nuclei (CCN). Cloud condensation nuclei are very small aerosols which are needed to start the formation of clouds. Clouds over the oceans also cool the planet, again by scattering sunlight back into space. This is discussed more in Unit 3 in the Basics Section and in the Topic on Clouds and Particles.

1. Cartoon of the importance of dust and sulphate aerosols in climate. CCN stands for Cloud Condensation Nuclei, the tiny aerosols which are needed to start the formation of clouds. DMS stands for dimethyl sulphide, a sulphur containing gas which is produced by some species of phytoplankton. This gas is converted to sulphate aerosols in the air and these aerosols affect climate. Author: Lucinda Spokes.
Once in seawater

As iron is an essential micronutrient, inputs of iron from the atmosphere are necessary for phytoplankton to grow. We know that phytoplankton take up carbon dioxide (CO₂) during photosynthesis and that carbon dioxide is an extremely important greenhouse gas which contributes to global warming. We also know that if the phytoplankton sink out of the surface waters into the deep ocean, they take their carbon with them and, to make up for this carbon removal, carbon dioxide enters the ocean from the atmosphere. This, along with physical carbon dioxide removal processes (see Unit 1 in the Basics Section), reduces atmospheric carbon dioxide levels and, as a consequence, reduces global warming. Some phytoplankton species also produce the gas dimethyl sulphide (DMS) as they grow. This gas is also climatically very important. When it enters the air, it is oxidised to sulphate aerosols which affect climate both by scattering sunlight back into space and also by acting as cloud condensation nuclei and starting the formation of clouds (see again Unit 3 in the Basics Section and the Topic on Clouds and Particles).

The High Nitrate, Low Chlorophyll (HNLC) regions of the oceans have much less phytoplankton growth than we would predict based on the levels of the major nutrients (nitrate and phosphate) which are present. So low phytoplankton growth in these large areas of the ocean means that, overall, the ocean is a smaller carbon dioxide sink than we initially thought. Lack of iron appears to limit the growth of a particular group of phytoplankton known as the diatoms which are large with a shell made of silicate material. Because of their size, these phytoplankton can sink out of the surface waters in to the deep ocean when they die.

So lack of iron limits the total amount of phytoplankton which grow in the oceans and therefore means that less than expected amounts of carbon dioxide are removed from the atmosphere. It also prevents the growth of diatoms, in particular, and therefore reduces biological removal and storage of carbon in the deep ocean.

Because a ready supply of iron is critical for phytoplankton growth and phytoplankton are so important to our climate, John Martin suggested that the deliberate addition of iron to the HNLC ocean areas would increase carbon storage in the deep sea and would reduce the impact of global warming. His most famous quote was "give me a tanker load of iron and I will give you the next ice age".

In the next section, we look at the pros and cons of deliberately adding iron to the oceans as a way to control our climate.
Part 3: Iron and climate change
Can large scale open ocean iron fertilisation help stop global warming?

Humans are responsible for the current rapid increases in levels of carbon dioxide (CO₂) and other greenhouse gases in the atmosphere and the build up of these gases is causing global warming. We have two possible ways of slowing the rising levels of greenhouse gases in the atmosphere. We can either reduce our emissions of greenhouse gases in line with the Kyoto Protocol or we can remove carbon dioxide from the atmosphere by increasing the ability of the Earth to store carbon over the long term.

Land plants are important carbon stores and many of the suggestions on how to increase carbon storage on land have concentrated on reducing the rate at which forests are being lost and by planting new trees. Storing more carbon in the oceans has also been considered. People have suggested that adding iron to large areas of the oceans would increase phytoplankton growth and the resulting increase in photosynthesis would cause a decrease in the levels of carbon dioxide in the atmosphere. We now have the technical capacity to do large scale open ocean iron fertilisation, but do we have the knowledge and wisdom to determine whether it is acceptable to use the oceans in this way?

**Reasons for large scale iron fertilisation**

Supporters of iron fertilisation suggest that:

1. increased photosynthesis from higher phytoplankton growth will reduce carbon dioxide levels in the atmosphere and decrease global warming.
2. once the phytoplankton die, they will sink out of the surface waters taking the carbon with them and this carbon will be stored in the deep ocean for centuries.
3. more phytoplankton means more food for other species, more fish and more food for the growing human population.

Supporters also state that deliberate ocean iron fertilisation is simply using the oceans in the same way as we used the land for agriculture and is a very cheap option for carbon removal compared to other current alternatives. They also believe that it will not harm the environment and is a long term solution to global warming. They suggest that the carbon stored in the deep ocean could be sold as credits in the global carbon marketplace.

**Reasons against large scale iron fertilisation**

Scientific iron fertilisation experiments show that adding iron to the High Nitrate Low Chlorophyll (HNLC) regions of the oceans does lead to and increase in phytoplankton growth. However these experiments have also show that:

1. adding iron completely changes the marine biological community.
2. decay of huge phytoplankton blooms reduces oxygen levels in the water.
3. microbial activity associated with low oxygen levels may produce potent greenhouse gases such as methane (62 times more powerful a greenhouse gas than carbon dioxide) and nitrous oxide (275 times more powerful than carbon dioxide).
4. to have any benefit as a way to store carbon, iron fertilisation needs to be done in the Southern Ocean as this is the only HNLC region where the water sinks to the deep ocean taking carbon with it.
1. Two possible outcomes of deliberate ocean iron fertilisation. Supporters claim that adding iron would increase carbon dioxide uptake by the ocean and would encourage a healthy marine biological community. Those against iron fertilisation suggest that it would not significantly change the ability of the ocean to take up carbon dioxide and would fundamentally damage the marine ecosystem. Thank you to Ken Buesseler at Woods Hole Oceanographic Institution for allowing us use this image.

**What should we do?**

People have already suggested that large scale ocean iron fertilisation could be used to reduce carbon dioxide levels in the atmosphere and it is currently possible for anyone to try to do this. However scientific studies show that adding iron would only reduce carbon dioxide levels by 16% at best. It would also change the ecology of the oceans and we don't know the long term consequences of this.

We all need to think about the implications of iron fertilisation as the ocean is so important to us and to our climate. Should individuals be able to add iron to the oceans or do we need international agreements between countries? Should scientists decide what to do or should the views of industry also be considered? Are there better ways to tackle the problems of global warming? What do you think we should do?
The impact of carbon dioxide on our climate depends on how much of the gas is in our atmosphere. About a third of the carbon dioxide we produce from fossil fuel burning is stored in the oceans, greatly reducing the impact of global warming. In this unit we look at how the carbon dioxide enters seawater. We also look at how climatically important gases such as dimethyl sulphide, which are formed in the oceans, leave seawater and enter the air. We also look at the suggestion made by Jim Lovelock in the 1960's that the Earth is a self regulating system that acts to keep our planet a fit place for life and show one example of how this may happen. He called this system GAIA after the Greek Goddess of the Earth.

Part 1: Air-sea gas exchange

Movement of gases occurs both from the atmosphere into the oceans and from the oceans into the atmosphere. The most important factors which influence gas exchange are the difference in the concentration of the gas between the air and the water and the speed of the wind. At the moment, we don't know all the factors which control the movement of gases across the sea surface. Once we know more, we will be better able to determine how important air-sea gas exchange is to our climate and the quality of the air we breathe.

The impact of carbon dioxide (CO$_2$) on our climate depends on how much carbon dioxide there is in the atmosphere. Around a third of the carbon dioxide produced when we burn fossil fuels is transferred across the sea surface into the oceans. By removing carbon dioxide from the atmosphere, this transfer greatly reduces the potential impact of global warming. Over most of the ocean the movement of man-made carbon dioxide is from the air to the sea. Why is the movement generally in this direction? Both physical and biological processes occur in seawater which allow the oceans to efficiently take up carbon dioxide. Have a look in the Basics Section at the Page on Carbon dioxide in the Unit on Water in the oceans for more details.

Very briefly, once carbon dioxide enters seawater it reacts with the carbonate ions (CO$_3^{2-}$) which are present to form hydrogen carbonate (HCO$_3^-$). This moves the reaction to the right and allows more carbon dioxide to enter from the atmosphere.

$$\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCO}_3^-$$

In addition to this physical removal, carbon dioxide is also taken up biologically through photosynthesis during phytoplankton growth and converted to plant material.
As well as the transfer of gases from the air to the sea, there is also a movement of gases from the oceans to the atmosphere. Climatically important gases such as dimethyl sulphide (DMS) and methyl iodide (CH$_3$I) are produced in the oceans but they only influence climate once they get into the atmosphere. Because their concentrations in air are almost always really low compared to their levels in seawater, they tend to move from the water to the air.

We know that gas exchange depends very strongly on the wind speed. Generally the faster the wind, the more gas exchange occurs. One of the reasons why high winds encourage gas exchange is that these high winds produce big waves, make the surface of the sea rough and mix up the waters below.

As the waves break they introduce billions of bubbles into the surface waters. These bubbles transfer gases from the atmosphere into the water. As well as moving gases from the air to the sea, the bubbles mix up the water. This extra mixing helps gases escape from the water and enter the air.

When the bubbles rise up through the water and reach the surface, they burst and a jet of seawater enters the air. As this jet rises, it breaks up into droplets. The water evaporates and leaves aerosol particles made up of seasalt. Billions of tonnes of salt enter the atmosphere this way. A lot falls straight back into the sea but a significant amount of salt is transported to land. Seasalt aerosol particles are very important in the atmosphere. Not only do they scatter sunlight back into space and so cause a direct cooling of our planet but they also act as very efficient cloud condensation nuclei and start the formation of clouds. In this way they cause indirect cooling of the Earth.

Wind speed isn't the only factor which influences gas exchange. We know that the temperature of the water is important, that rainfall can also increase the emission of gases from the ocean and that the presence of sea ice alters gas exchange rates.
Because gas exchange depends on such a variety of environmental factors, we are still not very good at working out what controls the transfer of gases across the sea surface. One piece of information we really lack is what happens when it's really windy. This is because it's very difficult and not very safe to do field measurements when the ship you are sampling from is rocking and rolling all over the place!

**Part 2: GAIA and CLAW**

**GAIA - The Greek Goddess of the Earth**

In the 1960's the scientist Jim Lovelock suggested that all living matter on Earth acts together to keep our planet a fit place for life. He, and his co-worker Lynn Margulis, proposed that the Earth has the ability to react to changes in conditions in such a way as to correct itself and keep conditions on Earth suitable for life. Lovelock named this control system, Gaia, after the Greek Goddess of the Earth.

**Is there evidence for this whole Earth control system?**

**The CLAW Hypothesis**


In 1987, Robert Charlson and his colleagues suggested that phytoplankton don’t just simply affect climate by producing the gas dimethyl sulphide (DMS) but actually play a role in regulating the climate of the Earth. The CLAW hypothesis (named after the authors of the paper) says that if a change in the temperature of the Earth occurs, for example due to global warming, phytoplankton respond to reduce this change. The authors idea was that if temperature increases, phytoplankton will grow more and produce more DMS. The increase in DMS concentrations would subsequently lead to an increase in the amounts of sulphate aerosol in the atmosphere and these aerosols would both directly and indirectly cool the planet, reducing the initial temperature rise.

The CLAW hypothesis is an example of a negative feedback loop where some mechanism acts to counteract the initial change in such a way to maintain the status quo. Positive feedback occurs when the initial change is amplified by subsequent processes.
1. A simplified representation of the CLAW Hypothesis, an example of a negative climate feedback loop. DMS stands for dimethyl sulphide and CCN for cloud condensation nuclei. Author: Lucinda Spokes.

**Do we have evidence to confirm the CLAW Hypothesis?**

All scientific studies conducted so far show that sulphate aerosols are important in climate control and models suggest that they do cause cooling. Ice cores, which give a record of the Earth's past, show that sulphate aerosol levels in the atmosphere have changed in phase with climate cycles over glacial and interglacial time scales. Recent studies have also shown that there is a link between DMS emissions and the number of cloud condensation nuclei (CCN) present in the atmosphere and that increases in the temperature of surface seawater do lead to increases in DMS concentrations in the air.

So we now have evidence that some of the steps within the CLAW hypothesis are correct but we still don't know whether the system really operates as a negative feedback loop. This makes it very difficult to represent the process in climate models and so we are still unsure quite how important DMS is to the cooling of our planet.