Primary and Secondary Pollutants:

When fuels are burnt in both car exhausts and power stations primary pollutants are released into the atmosphere. Secondary pollutants are formed when primary pollutants undergo further reactions.

For example Ozone is a secondary pollutant formed when sunlight shines on nitrogen oxides and hydrocarbons. Ozone is a major component of photochemical smog.

Primary Pollutants	Secondary Pollutants
Nitrogen oxides (NO_x) Carbon Monoxide (CO) Hydrocarbons (CxHy)	Ozone (O_3) Peroxyacetyl nitrate (PAN) HNO_3 NO_2 H_2O_2

There are 2 main types of primary pollutants responsible for photochemical smog.

1. Oxides of nitrogen formed when nitrogen in the air reacts with oxygen, under high temperatures and pressure.
2. Hydrocarbons emitted from car exhausts as unburnt fuel.

Photochemical smog is formed by the action of the suns rays on these primary pollutants.

How are Primary Pollutants formed ?

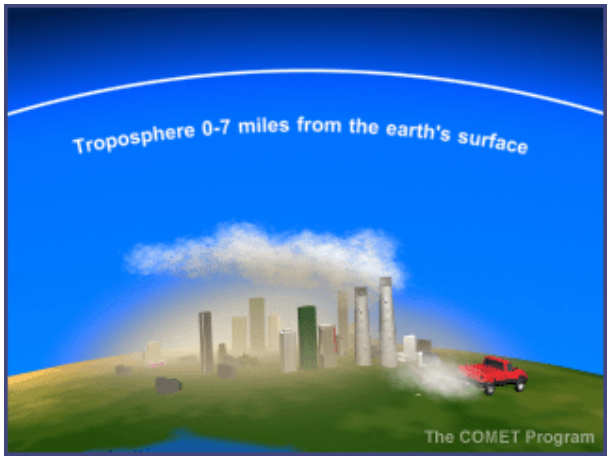
Primary pollutants are formed during the combustion of fuel in coal fired power stations. Carbon dioxide, sulphur oxides and nitrogen oxides are all primary pollutants produced when coal is burnt.

When the coal burns the sulphur compounds found in all living organisms are converted to oxides of sulphur, these oxides of sulphur can cause serious environmental damage if they get into the atmosphere. The amount of sulphur in coal depends on the types of organisms from which the coal was originally formed.

What are the best conditions for forming photochemical smog?

Nitrogen oxides are formed when nitrogen and oxygen in air react together and carbon dioxide is formed when oxygen and fuel react.

Photochemical smog forms during high pressure (anticyclonic) conditions in the troposphere. . Tropospheric ozone is formed when nitrogen oxides and hydrocarbons, emitted by car exhausts, fossil fuel power plants and refineries, react together in the presence of sunlight at high temperatures.



A hot, sunny, still day is the perfect environment for ozone production. The still air means tha t there is less mixing of lower atmosphere air and higher altitude air. The pollutants are trapped in the troposphere.

When Nitrogen dioxide concentration is high and there is plenty of sunlight, then the oxygen atom splits from the Nitrogen dioxide mol ecule.

$$NO_2 + h\nu \rightarrow NO + O$$

The Oxygen atom then reacts with radical (O_2) in air to form ozone.

$$O + O_2 \rightarrow O_3$$

Ozone reacts with NO to reform NO_2. The concentration of troposphere ozone remains constant when a steady state is reached between the breaking and reforming of NO_2. When there is more NO_2 being produced from car exhausts etc… more ozone is produced.

Higher concentrations of hydrocarbons also increases ozone levels because the breakdown of hydrocarbons regenerates NO_2 from NO, so as a result ozone concentrations in troposphere increase.

$$C_xH_yO_2 + NO \rightarrow C_xH_yO + NO_2$$

Ozone concentrations are increased during smog formation. One ozone molecule leads to the production of two OH radicals. Each OH radical can then lead to the production of one ozone molecule.

In sunnier conditions there is more light energy to react with the Nitrogen dioxide, this increased light intensity results in a quicker rate of reaction. On sunny days there is more light energy, so there will be more ozone produced.

Also in sunny conditions there is enough sunlight to react with all or most of the oxides of nitrogen produced by car exhausts, whereas in cloudy conditions there is less sunlight available so fewer reactions will occur, and so less oxygen atoms will be broken away from the Nitrogen dioxide.

Formation of ozone is one of the most important photochemical reactions in the lower atmosphere. So increasing amount of ozone will increase the amount of photochemical smog.

The most favourable conditions for photochemical smog are warm sunny conditions so that hν (light intensity) is increased, and therefore quicker reactions take place resulting in more photochemical smog is formed.

In still air the pollutants are trapped so there will be more pollutants present to react with sunlight and form photochemical smog.

Longannent power station

At Longannet power station sulphur dioxide emissions are minimised by dissolving the flue gases in sea water. Flue gases created during the combustion of coal are passed through sea water.
Sulphur dioxide dissolves in water to form sulphate ions SO_3^{2-} and H^+ ions.

$$SO_2 + H_2O \rightarrow SO_3^{2-} + 2H^+$$

Sea water is naturally alkaline with a pH of 7.5. The HCO_3^- ions present react with the H^+ ions to form carbon dioxide and water.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

Air is then passed through the solution to oxidise the sulphite ions to less harmful sulphate ions.

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$

The water containing dilute sulphate ions is discharged into the sea, and the carbon dioxide is dispersed into the atmosphere.

This process has probably been chosen at Longannent instead of the limestone process because the key raw material, sea water is readily available, as the power station is situated on the banks of a river. Whereas limestone is less available and would need to be transported to Longannet from a nearby site. This would be more costly and would cause environmental spoilage. Sea water scrubbing is the BPEO for flue gas desulphurisation.

To lower NOx emissions Longannet uses the gas reburn process. There are 2 burning zones in the boiler furnace. In the primary combustion zone powdered coal is oxidised in low air concentration, so the combustion rate is lowered and less NOx produced.

Natural gas is then injected into the boiler just above the reburning zone. The NOx reacts with these alkanes to produce N2, CO2 and H2O.

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O$$

This process chemically removes all NOx by reacting the NOx with natural gas to produce less harmful gases. This method is cheap and environmentally friendly because it does not put unwanted NOx's into the atmosphere.

Chemists research:

A lot of research is being conducted by chemists into the formation of photochemical smog.

1. Monitoring of tropospheric pollutants. Chemists have set up several monitoring stations to record pollutants present in the troposphere and their concentrations.
2. Studying individual reactions in a laboratory enables chemists to make predictions about pollution.
3. Modelling studies. Computer simulators are used to reproduce and predict behaviour of the pollutants during a smog episode.
4. Smog chamber simulations. Chemists create photochemical smog conditions so that concentrations of various species can be monitored as the smog builds up.

References

1. Chemical Storylines 2nd Edition, George Burton et al, Heinemann, 2000 Pg 292 and 32-33.
2. Article 2 Open Book Paper 2003 / adapted from “What is Photochemical Smog” by Gwen and Mike Pilling, Chemistry Review, Volume 5, Number 5, May 1996.
3. Article 1 Open Book Paper 2003 / adapted from “Environmental Pressure” by Donald Miller, Chemistry Review, Volume 9, Number 4, March 2000.
4. www.ucar.edu/learn/1_7_1.htm