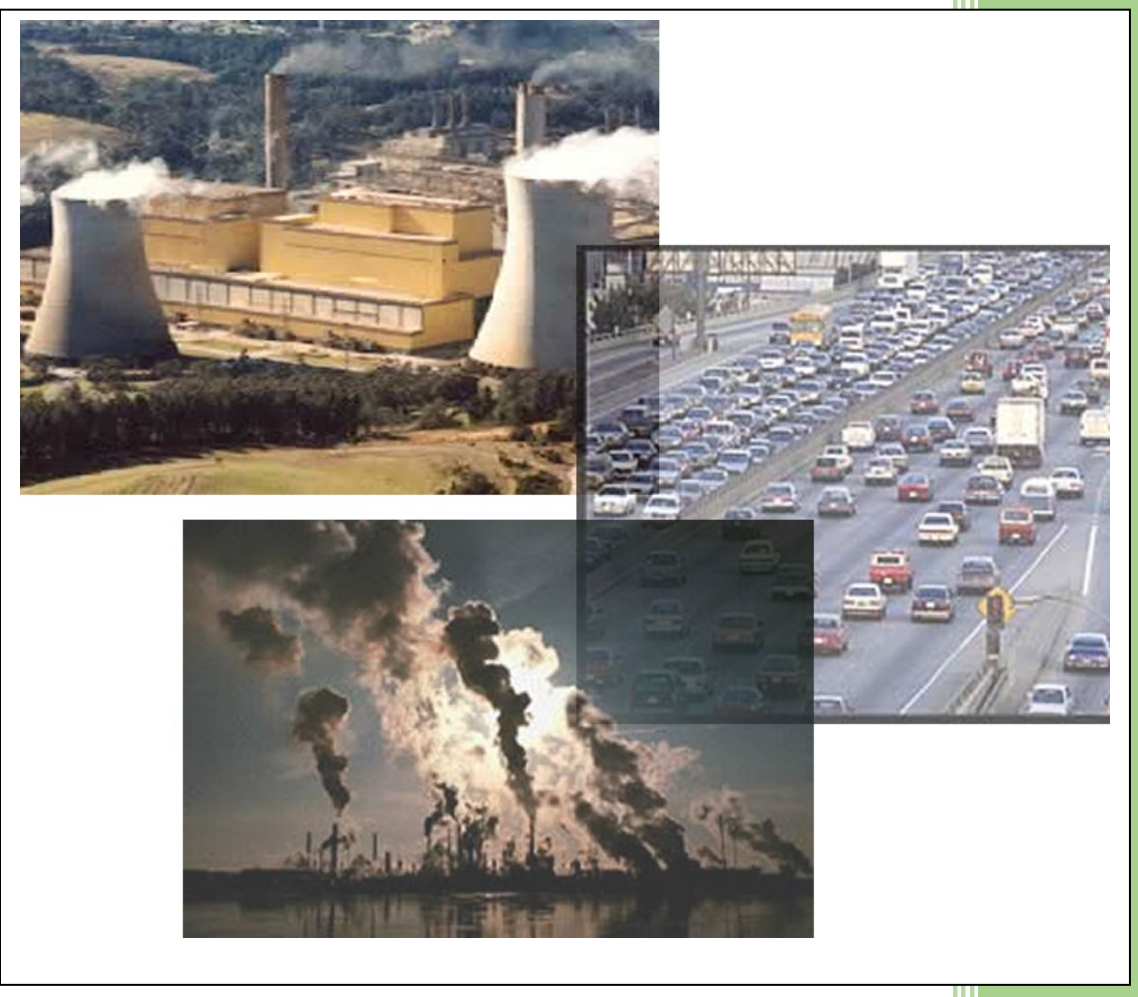
Acid Rain



Peter Razos

Natural Acidity of Rainwater

Rainwater is naturally slightly acidic, even in environments far from human pollution. This is because atmospheric carbon dioxide dissolves into water droplets in clouds to form carbonic acid, a weak acid:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

Carbonic acid then partially ionises, producing small amounts of hydronium ions:

$$H_2CO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HCO_3^-(aq)$$

Because of this natural process, unpolluted rainwater typically has a pH between 5 and 6. Students often assume rainwater should be neutral (pH 7), but pure water is only pH 7 in the complete absence of dissolved gases — a situation that does not occur in the atmosphere.

This mild natural acidity plays an important role in the chemical weathering of rocks. Over millions of years, solution weathering has shaped landscapes, helped form soils, and released essential nutrients such as K^+, Ca^{2+} and Mg^{2+}. The dramatic limestone formations of the Buchan Caves in Gippsland are a well-known example of landscapes shaped by this process.

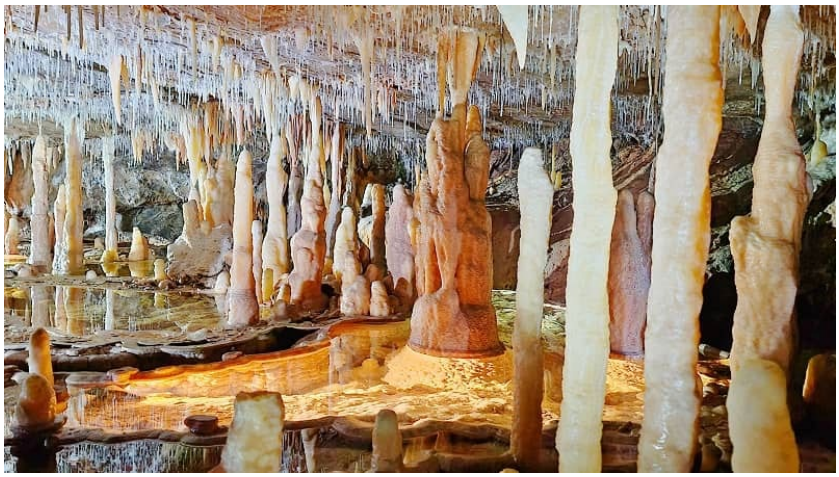


Figure 1 – Limestone cave (Buchan in Gippsland Australia)

The rate of solution weathering depends on temperature, CO_2 concentration and the movement of water through rock structures. CO_2 produced by decaying organic matter in soils can accumulate in enclosed spaces, increasing the acidity of groundwater and accelerating mineral dissolution.

Release of Heavy Metals by Natural Acids

Many heavy metals exist naturally in soils as insoluble carbonates, oxides, hydroxides or silicates. In neutral or alkaline soils these minerals are stable and do not enter groundwater. However, carbonic acid can dissolve these minerals, releasing toxic metal ions into waterways.

Examples of reactions

Lead carbonate (cerussite)

$$PbCO_3(s) + H_2CO_3(aq) \rightarrow Pb^{2+}(aq) + 2HCO_3^-(aq)$$

Figure 2 – Cerussite ($PbCO_3$)

Malachite ($Cu_2CO_3(OH)_2$)

$$Cu_2CO_3(OH)_2(s) + 2H_2CO_3(aq) \rightarrow 2Cu^{2+}(aq) + 4HCO_3^-(aq) + H_2O(l)$$

Figure 3 – Malachite ($CuCO_3(OH)$

Common heavy metal ions mobilised by soil acidification include:

- Pb^{2+} (lead)
- Cu^{2+} (copper)
- Zn^{2+} (zinc)
- Mn^{2+} (manganese)
- Al^{3+} (aluminium – highly toxic to plants)

Natural Rain vs Acid Rain

What causes acid rain?

Acid rain is produced when atmospheric pollutants dissolve in rainwater to form acids stronger than carbonic acid. The most important pollutants are:

- Sulfur dioxide (SO_2) → sulfurous and sulfuric acids
- Nitrogen dioxide (NO_2) → nitric acid
- Additional CO_2 from human activity

Sources of these pollutants include:

- Coal-fired power stations
- Motor vehicle exhausts
- Smelting of metal sulfide ores
- Industrial processes
- Diesel engines
- Biomass burning (including bushfires)
- Burning fossil fuels for heating

Key reactions

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$
$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$
$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

These acids are much stronger than carbonic acid, giving acid rain a typical pH around 4.

Environmental Consequences of Acid Rain

1. Soil acidification

Acid rain increases soil acidity, causing:

- Dissolving and leaching of important minerals → nutrient depletion
- Reduced plant growth
- Release of toxic aluminium ions from clays

Soils rich in organic matter contain negatively charged $–COO^-$ groups that bind essential metal cations such as Ca^{2+}, Mg^{2+} and K^+, preventing them from being washed away.

$$2R–COO^- + M^{2+} \rightarrow (R–COO)_2M$$

In acidic soils, excess H^+ ions displace these metal ions.

$$(R–COO)_2M + 2H^+ \rightarrow 2R–COOH + M^{2+}$$

The freed metal ions are then leached from the soil, reducing fertility. Aluminium ions released in this way can become toxic to plant roots.

A well-documented example is the forest dieback of the Black Forest (Germany) in the 1970s–80s, caused mainly by SO_2 emissions from high-sulphur coal combustion.

Figure 4 – Damage to the conifer trees of the Black Forest in Germany

Farmers treat soil acidification from acid rain by adding **agricultural lime** (calcium carbonate, $CaCO_3$). Calcium carbonate does not react strongly with water; instead, it dissolves only slightly, releasing a small amount of carbonate ions according the equation below.

Figure 5 – application of lime powder to the soil.

$CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$

The carbonate ion is a very weak base, so it undergoes slight hydrolysis in water to produce hydroxide ions according to the equation below.

$CO_3^{2-}(aq) + H_2O(l) \rightarrow HCO_3^{-}(aq) + OH^{-}(aq)$

These hydroxide ions can react with dissolved metal ions such as Al^{3+}, forming **insoluble metal hydroxide precipitates**. This removes toxic aluminium from solution and prevents root damage.

Because $CaCO_3$ is only sparingly soluble, it increases soil pH slowly. It also neutralises soil acidity through direct reaction with hydronium ions, according to the equation below.

$CaCO_3(s) + 2H_3O^{+}(aq) \rightarrow CO_2(g) + 3H_2O(l) + Ca^{2+}(aq)$

This neutralisation reaction further helps restore the soil to a healthier pH.

2. Acidification of Lakes and Oceans

Acidic water dissolves calcium carbonate, which forms the shells and exoskeletons of many aquatic organisms:

$$CaCO_3(s) + 2H^{+}(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

This impacts corals, molluscs, crustaceans, and many freshwater species. Ecosystems can collapse when pH drops below critical thresholds.

Figure 6 – aquatic animals with exoskeletons formed from $CaCO_3$.

3. Damage to Buildings and Monuments

Limestone and marble (both calcium carbonate) react with acidic rainwater:

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

This leads to:

- Surface deterioration, creating small holes
- Loss of carved detail
- Black crusts and discolouration
- Long term structural weakening

Historic buildings and statues across Europe and Asia have experienced significant acid-rain damage

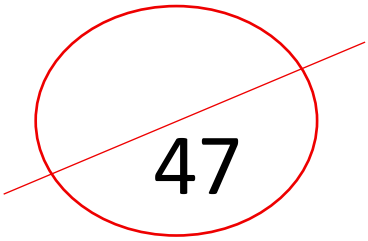
Figure 5 – Marble statue damaged by acid rain.

Before you attempt the question on the following page familiarise yourself with the acid and metal roasting reactions listed below as well as the solubility table, item 9, page 8 of the VCE Chemistry Data Booklet (2024-2027 study design).

Reaction Type	General Reaction	Example Reaction
Acid + Metal Carbonate	Metal carbonate + acid → salt + H_2O + CO_2(g)	$CaCO_3$(s) + 2HCl(aq) → $CaCl_2$(aq) + H_2O(l) + CO_2(g)
Acid + Metal Hydrogen Carbonate	Metal hydrogen carbonate + acid → salt + H_2O + CO_2	$NaHCO_3$(aq) + HNO_3(aq) → $NaNO_3$(aq) + H_2O(l) + CO_2(g)
Acid + Metal Hydroxide	Metal hydroxide + acid → salt + water	2NaOH(aq) + H_2SO_4(aq) → Na_2SO_4(aq) + 2H_2O(l)
Acid + Metal Oxide	Metal oxide + acid → salt + water	CuO(s) + 2HCl(aq) → $CuCl_2$(aq) + H_2O(l)
Acid + Metal Sulfide	Metal sulfide + acid → salt + H_2S(g)	FeS(s) + 2HCl(aq) → $FeCl_2$(aq) + H_2S(g)
Roasting (Metal Sulfide + O_2)	Metal sulfide + O_2 → metal oxide + SO_2(g)	2FeS(s) + 3O_2(g) → 2FeO(s) + 2SO_2(g)
Roasting (Metal sulfide + O_2)	Metal sulfide + O_2 → metal oxide + SO_2 (g)	2ZnS(s) + 3O_2(g) → 2ZnO(s) + 2SO_2(g)

Table 1 – Acid reactions and roasting of metals.

Short Answer Assessment Acid Rain.



1. Using balanced chemical equations, explain why the pH of unpolluted natural rainwater is not 7.

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_____ 3 marks

2. Using balanced equations, explain why minerals such as $PbCO_3$ and CuO are usually insoluble in neutral soils but soluble in acidic soils.

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_____ 3 marks

3. Describe how carbonic acid can release toxic heavy metal ions into groundwater.

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_____ 3 marks

4. Other than CO_2 what two anthropogenic pollutants are responsible for acid rain? Give two balanced chemical equations.

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_____ 2 marks

5. Explain why natural rainwater (from CO_2) is only mildly acidic while acid rain has a much lower pH. Include the sources and balanced chemical equations.

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_____ 4 marks

6. Write a balanced equation for the reaction between limestone ($CaCO_3$) and carbonic acid.

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_____ 2 marks

7. Write the balanced chemical equation for the reaction when malachite ($Cu_2CO_3(OH)_2$) reacts with nitric acid in water.

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_____ 2 marks

8. Explain how soil abundant with organic matter keeps metal ions in the soil.

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_____ 2 marks

9. Acid rain falls on a region with marble monuments. Using one chemical equation, predict a lasting effect and explain the chemistry using nitric acid as an example.

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_____ 2 marks

10. A forest near a 11.coal fired power station shows signs of dying back. Describe how soil acidification could be responsible and explain the mechanism by which soil acidification kills trees.

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_____ 2 marks

11. A lake's pH drops from 7.1 to 5. Predict what may happen to the organisms with calcium carbonate shells.

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_____ 2 marks

12. Explain why regions with high rainfall and high organic matter tend to have more rapid chemical weathering.

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_____ 2 marks

13. Devise an experiment to test the effect of pH on the rate of limestone dissolution (include variables and controls).
    Include the following .
    - Title (1 mark)
    - Aim (1 mark)
    - Hypothesis (2 marks)
    - Variable:
        -IV (1mark)
        - DV (1 mark)
        - controlled
            - list four controlled (2 marks)
            - select one controlled variable and explain why this variable needs to be controlled to get **valid** data. (2 marks)
    - Material (2 marks)
    - Procedure(include section on safety) (6 marks)

18 marks