AMMONIA, PARTICULATES, AND NITROGEN OXIDES: SOURCES, MONITORING AND TOXICOLOGY

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NITROGEN AND ITS COMPOUNDS ARE PARAMOUNT AND HAVE MASSIVE ENVIRONMENTAL IMPLICATIONS; REQUIRE MONITORING AND POLLUTION ABATEMENT

THEY CONTINUE TO MERIT RESEARCH ACTIVITY AND FUNDING

CYCLING THROUGH BIOGEOCHEMICAL CYCLES CONTINUES TO PRODUCE IMPORTANT DATA BUT MORE RESEARCH IS ESSENTIAL IN MANY SYSTEMS AND PROCESSES

RESEARCH IS REQUIRED ON ASPECTS INCLUDING TOXICOLOGIAL EFFECTS OF NITROGEN OXIDES, e.g., IN RELATION TO SYNERGISTIC CONSIDERATIONS

- **HUMANS, SINCE EARLY IN OUR HISTORY, HAVE DISCHARGED POLLUTANTS INTO THE ENVIRONMENT**

- **INITIALLY THIS WAS LIMITED DUE TO**
  - **LIMITED POPULATION SIZES and**

  LACK OF TECHNOLOGICAL EXPERTISE

- **WITH POPULATION INCREASES AND TECHNOLOGICAL ADVANCES, CHANGES OCCURRED INCLUDING:**

  a) Massive resource exploitation

  b) Pollution of the atmospheric, terrestrial and aquatic ecosystems.

- THE ATMOSPHERE IS/HAS BEEN EMPLOYED AS A SINK TO CHEAPLY VOID POLLUTANTS; IT CONTAINS A DIVERSITY OF POLLUTANTS RECEIVED FROM c.0.5m – SEVERAL HUNDRED METRES.

ATMOSPHERE – FACTORS OF IMPORTANCE

- **CONCENTRATION OF POLLUTANTS**
- **WIND VELOCITY AND DIRECTION**
- **PRECIPITATION**
- **REACTIVITY**
- **HEIGHT OF DISCHARGE**
- **TEMPERATURE AT DISCHARGE**
- **INCIDENCE OF INVERSION CONDITIONS**
- **BREAKDOWN OF POLLUTANTS**
- **TREATMENT**
- **EFFECTS ON ORGANISMS, POPULATIONS AND ECOSYSTEMS**

- **ATMOSPHERIC POLLUTION AFFECTS ANIMALS, PLANTS, ECOSYSTEMS AND MANY OF THE VISIBLE MANIFESTATIONS OF OUR CIVILISATION**
- **THE ATMOSPHERE PROVIDES A ROUTE FOR THE *TRANSPORT* , BOTH *LOCAL* AND *LONG DISTANCE* OF POLLUTANTS**
- **IT ALLOWS DILUTION OF THE POLLUTANTS: gaseous and particulates**

- **IT FACILITATES THE RAPID TRANSFER OF POLLUTANTS TO OTHER SYSTEMS – PEDOSPHERE AND HYDROSPHERE**

- **ATMOSPHERIC QUALITY IS AFFECTED BY BOTH *PRIMARY* AND *SECONDARY* POLLUTANTS WHICH EMANATE FROM ANTHROPOGENIC ACTIVITIES and NATURAL SOURCES**

MONITORING INCLUDES:

DETECTION, MEASUREMENT AND ASSESSMENT OF CHANGES IN THE BIOTIC AND ABIOTIC COMPONENTS OF ECOSYSTEMS.

ECOLOGICAL MONITORING REFLECTS *LONG TERM EFFECTS* AND EXAMINES EFFECTS ON *RECIPIENT* ORGANISMS, POPULATIONS AND ECOSYSTEMS

A GOOD BIOMONITOR WILL

Accumulate without being killed

Should be abundant throughout the study area

Should preferably be of reasonable size

Should be SEDENTARY to be representative of the area under investigation

Should be long-lived to allow the sampling of more than one age class (cf ammonia, etc.)

Genetic variability should be limited

Sampling should be relatively uncomplicated

Organism should ideally be able to survive in the laboratory/incubator environment

POLLUTION MONITORING MAY INVOLVE A VARIETY OF DISCIPLINES INCLUDING:

Ecology/environmental sciences

Chemistry (analytical) and physics

Geography and geology

Physiology

Archaeology and history

Media and the classics

Medicine and epidemiology

Statistics

Aerial photography and satellite imagery

TECHNIQUES TO MONITOR ATMOSPHERIC POLLUTION INCLUDE

Warren Spring Apparatus

Lead dioxide candle

Draeger, Casella, IRGA, AA, EDMA, ICP-MS

Particulate/rainfall gauges

Ecological indicators

Physiological- effects on individuals, communities and ecosystems

Literature surveys

Sediment and peat bog geochemistry, tephra, etc.

Meteorology

Others as this is essentially and INTERDISCIPLINARY field of study.

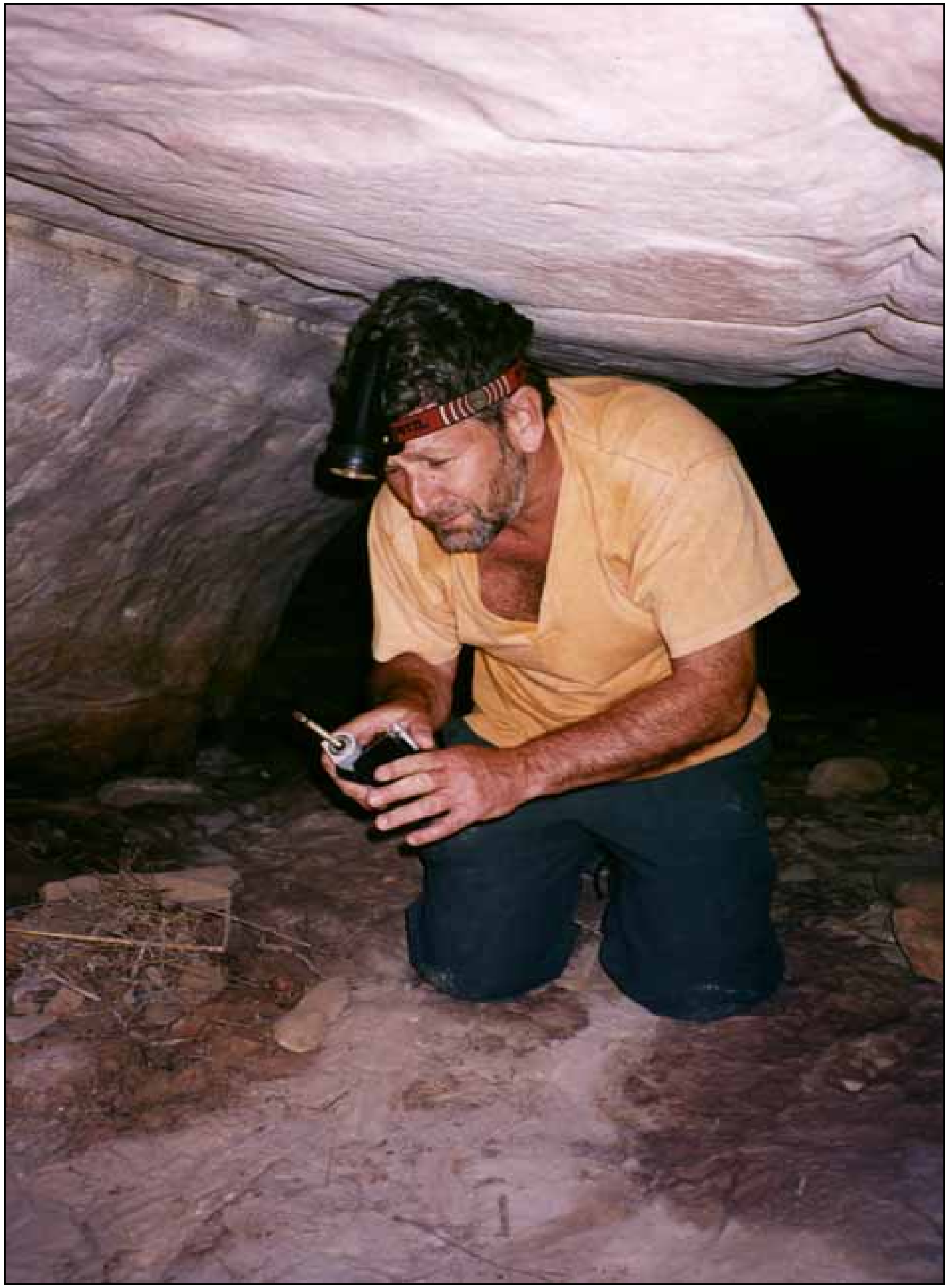
AMMONIA

A natural atmospheric constituent: often at c. 20µg/m3

Approximately 3.7 x 10^9 tonnes of NH_3 are annually released into the atmosphere. Produced by natural biological decay processes, e.g., decay of organic wastes, e.g., in stock yards and rearing chambers. Anthropogenic sources include fuel combustion, waste incineration and processes involved in production or use of ammonia (e.g., production of nitric acid, organic compound synthesis, fertiliser preparation).

High concentration in some caves e.g., Cueva del Tigre (McFarlane *et al.,* 1990) at 1338-1779ppm. TLV c. 25ppm.

Control e.g., wet scrubbers, bag filters, charcoal filters, etc.



NIAH GREAT CAVE

SARAWAK, BORNEO

LIES WITHIN LIMESTONE

HARRISSON’S TEAM IN THE 1950s LOCATED A HUMAN SKULL - THE ‘DEEP SKULL’ DATED AT 40,000 BP NEAR CAVE ENTRANCE.

FLOOR AREA OF CAVE = 10 ha

HEIGHT UP TO c. 75m

The west mouth is a single large entrance; there are four main entrances to the eastern and southern sides.

Variety of organisms present e.g., invertebrates. Vertebrates include BATS and SWIFTLETS – important economically and ecologically; provide income for those inhabiting the nearby long houses.

They collect from the vast accumulation of GUANO (fertiliser) and swiftlets nests (bird's nest soup).

People are hence exposed to NH_3 : both now and in ancient times.

Ammonia concentrations monitored 2000 – 2002 at various distances into the cave and at various heights above the guano surface. Values monitored at noon on each occasion using portable monitoring system previously calibrated against known ammonia concentrations

Ammonia volatilisation is an important biogeochemical pathway in dry caves inhabited by birds/bats and accounts for the removal of most of the urea-derived nitrogen.

NH_3 concentrations (2000)

Metres into cave	Conc. (ppm)
0	0.25
50	12
200	32-33
500	51-54

Period of air stagnation. Movement of organisms + normal diurnal heating/cooling processes. All measurements at 2.0m above guano surface.

NH_3 concentrations (2002)

Metres into cave	Conc. (ppm)
0	0
10	0.25
50	0.25
150	1.8
200	2.1

200 in freshly excavated pit 8.0

Air flowed gently into cave from north at 0.7m/s and diluted the NH_3

7 day pH shift: 5.85 – 7.4

Changes in NH_3 concentrations with increasing vertical height from guano surface in 2000

Vertical height (m)	Conc. (ppm)
0	39-41
1	37
2	33

Changes in NH_3 concentrations (ppm) with increasing vertical height from guano surface in 2002 (at various sites)

Distance into cave (m)	Height		
	0m	1m	2m
0	0	0	0
50	0.4	0.2	0.2
150	2.3	1.9	1.8
200	2.4	2.2	2.1

1 REDUCTION IN NH_3 CONCENTRATION WITH INCREASING HEIGHT FROM GUANO SURFACE

2 AIR FLOW HAS MASSIVE DILUTION EFFECT

3 NH_3 CONC. INCREASES AS CAVE IS PENETRATED

4 ATMOSPHERE IN NIAH IS NOT LONG-TERM RESIDENT (cf Cueva del Tigre).

5 CONCENTRATION IN CAVE EXCEEDS THE ODOUR THRESHOLD.

ARGUED THAT IN THE PAST (40,000 radio-carbon years BP) humans confined most of their activities to the less contaminated outer parts of the cave. The ‘Deep Skull’, other artefacts and burial sites are interestingly found here. Furthermore, if early humans were using fires, air quality would be unpleasant away from the cave mouth and synergistic effects e.g., with SO_2 & particulates likely.

NH_3 TOXICOLOGICAL IMPLICATIONS

Silverman (1949) noted that NH_3 at 350,000µg/m^3 (c. 493ppm) caused human nose and throat irritation and impaired respiration.

Jacobs (1964) – NH_3 inhalation affects mainly the upper respiratory tract.

Miner (1993) – NH_3 acts as an asphyxiant.

Friberg (1995) – inhibition of cilia activity reversible unless concentration exceeded 210,000µg/m^3.

Strongly alkaline in water (mucous?): exothermic reaction –

NH_3 + $H_2$0 --> NH_4OH…thermal injury

Pyatt (2003) – extent of thermal injury affected by NH_3 concentration, extent of inhalation, exposure duration, synergism/addition with other pollutants, general health of recipient and recovery potential, transfer to unpolluted air, etc.

NH_3 in Niah may adversely affect those with pre-existing respiratory problems. Effects may be enhanced as Pyatt (2003) noted: 'adverse effects of ammonia may occur where synergistic reactions with, for example, airborne particulates derived from atmospheric erosion or generated by disturbance resultant from extraction activities of the massive guano beds occurs.'

EFFECTS FROM SURVEY (Pyatt, 2003) include: HEADACHES, SORE THROATS, DRY THROATS, PRODUCTIVE COUGHS, DRY COUGHS, DIZZINESS, WATERING EYES.

SCHIFFMAN (1998) REVIEWED HEALTH EFFECTS OF LIVESTOCK ODOURS ON HUMANS AND REPORTED SIMILAR EFFECTS AND ALSO POTENTIAL CHANGES ON MOOD AND MEMORY

KIRKHORN AND GARRY (2000) INDICATED THAT FUNGAL SPORES AND BACTERIAL ENDOTOXINS MAY BE PRODUCED IN ANIMAL HOUSES AND MAY INFLAME THE UPPER AND LOWER AIRWAY. ORGANIC DUSTS AND ANIMAL CONFINEMENT GASES THEY NOTE CAN CAUSE HYPERSENSITIVITY PNEUMONITIS, CHRONIC BRONCHITIS AND AN ASTHMA-LIKE SYNDROME

DEWEY *et al.,* (2000) FOUND IN ANIMAL REARING BARNS THAT IN 52% OF THE CASES, NH_3 CONCENTRATIONS 'EXCEEDED 7.5ppm ; AMMONIA CONCENTRATIONS GREATER THAN 7.5ppm ARE ASSOCIATED WITH RESPIRATORY PROBLEMS IN HUMANS'

ATMOSPHERIC PARTICULATES

- **EXIST IN VARIOUS FORMS, e.g., SOOT, DUSH, ASH AND SMOKE.**
- **DERIVED FROM INDUSTRIAL/DOMESTIC/EROSION SOURCES.**
- **CAN CONSIDER CATEGORIES SUCH AS AEROSOLS, DUSTS, FUMES, MISTS AND SMOKE OR SIZE, e.g., $PM_{10.}$**
- **ALTERNATIVELY VIABLE (e.g., POLLEN GRAINS, MICRO-ORGANISMS), NON-VIABLE (e.g., EMANATING FROM SOILS AND VOLCANOES) AND RADIOACTIVE (PYATT, 2004).**
- **MONITORING: AVST, DEPOSIT GAUGES, HAM AEROSOL/PARTICULATE ANALYSER, WARREN SPRING, etc.**

VALUES IN BORNEO RAIN FOREST ADJACENT TO CAVE WERE LOW AT 4 – 7.2µg/m^3.

VALUES IN CAVE GENERALLY 7.4 – 40.8µg/m^3.

DISTURBANCE LEADS TO VALUES UP TO 1300µg/m^3 WITH A PM_{10} CONTRIBUTION OF1050µg/m^3 (MILLIPORE ISOPROVE™ MEMBRANE FILTER).

WILL ENHANCE NH_3 EFFECTS

DEEP LUNG PENETRATION (OLD, YOUNG, PRE-EXISTING RESPIRATORY IMPAIRMENTS)

BC MINISTRY (2001) – values of PM_{10} in excess of 25µg/m^3 'are likely to generate adverse health effects

A STUDY IN CANADA (1995) SUGGESTED – 'DAILY HUMAN MORTALITY INCREASES BY 1% FOR EACH 10μg/m^3 INCREASE IN PM_{10}'. AGGRAVATED BY NH_3.

CANADIAN HEALTH BUREAU (1995) NOTED THAT SHORT INCREASES IN AMBIENT INHALABLE PARTICLES (PM_{10}) ARE ASSOCIATED WITH:

Increase in total mortality

Increase in respiratory and probably cardiac diseases

Increase in asthma and other respiratory conditions

Small decreases in the level of pulmonary function in children and in adults with 'obstructive airway disease'.

CYSTS OF PROTOZOA

MICRO-ORGANISMS

INTEGRATION / SYNERGISM / ANCIENT HEALTH PROFILES

NITROGEN OXIDES – AN OVERVIEW

Nitric oxide (NO) and a little nitrogen dioxide (NO_2) formed under high temperatures- fuel combustion, furnaces, stacks.

NO oxidised in atmosphere to more toxic and irritant NO_2. The oxidation is accelerated by photochemical processes involving reactive hydrocarbons.

Nitrous oxide (N_2O) is largely derived from the decomposition of nitrogen compounds by soil bacteria & reactions between nitrogen and atomic oxygen/ozone in upper atmosphere.

N_2O_4, N_2O_3 and N_2O_5 are rarer but N_20_3 and N_20_5 may be involved in reactions leading to photochemical air pollution.

NITRIC OXIDE (NO)

$N_2 + O_2$ reversible 2NO

Natural sources yield c. 50 x 10^7 tonnes pa

Anthropogenic sources yield c. 5 x 10^7 tonnes **NOx** pa

NITROGEN DIOXIDE (NO_2)

$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$ or

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Reduces visibility and colours horizon.

Concentration of NOx in urban environment is c. 10-100 times greater than in non-urban environment.

NOx control: 2-stage combustion, catalysts, batches, air pre-heat temperature, etc.

NO and NO_2 concentrations display diurnal variations linked to intensity of solar ultraviolet light, pollution and atmospheric mixing. Stagnation = conc. enhancement.

SOME NOx EFFECTS

Fading/yellowing of textile dyes, deterioration of cotton fabrics, acceleration of metal corrosion. High-particulate-nitrate values can cause stress-corrosion fractures of nickel-brass wire springs on relays.

Vegetation: phytotoxicant. Involved in production of atmospheric oxidants e.g., peroxyacylnitrate (PAN). More research needed. Effects include acute injury (e.g, necrosis), chronic injury (e.g., chlorosis) and physiological effects (various, e.g., on photosynthesis). More research needed.

NOx – some toxicological effects

Include:

Asphyxiation

CNS paralysis and convulsions

Pneumonitis

In rats, can become more toxic with temperature increase.

Alteration of configuration of lung tissue structural proteins – collagen and elastin.

HUMANS – includes

IRRITANT: **irritation leading to pain, burning and choking in chest. Violent cough, yellow sputum**

REVERSIBLE: **vomiting, vertigo, feeling of intoxication, fainting**

SHOCK: **severe symptoms of asphyxiation, convulsions and respiratory arrest.**

COMBINED: **CNS type symptoms, vertigo, staggering gait.**

In a community exposure to NOx (Chattanooga) the ventilatory capacity of children was reduced and there was a 20% relative excess of respiratory illnesses in the elevated NOx area.