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Ecosystems as Sinks for Atmospheric Fluoride[1]

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In a study of two areas of mixed eucalypt open forest, fluoride inputs were estimated. The bulk fluoride input to a fluoride-polluted area is estimated to be 17.8 kg ha^{-1}yr^{-1}. The sink efficiency of the vegetation in the fluoride-polluted area is estimated to be 21.3 kg ha^{-1}yr^{-1} and in the unpolluted area 0.9 kg ha^{-1}yr^{-1}. These inputs are discussed in relation to fluoride transfer processes operating in these ecosystems, in which wildfires are an important agent for the release of fluoride from vegetation, and soil is the important sink.

1 Introduction

Fluoride as an air pollutant, possesses a number of characteristics which confer on it the potential to induce serious impacts on ecosystems (Groth, 1974). Extremely low concentrations of fluoride can cause injury to plants (Hill, 1969), fluoride accumulates in plant leaves, and it can be passed along food chains (Carlson and Dewey, 1971; Groth, 1975; Murray, 1981a). Due to these properties fluoride has the potential to undergo a number of complex biogeochemical cycles in ecosystems which may have an influence on numerous ecosystem components as a result of transfer processes.

In order to understand fluoride interactions in ecosystems it is fundamentally important to understand and quantify the inputs, outputs, sinks and transfer processes.

When airborne fluoride passes over a terrestrial ecosystem, its rate of input varies according to factors which

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control the various deposition processes, many of which are discussed by Smith (1981).

The primary sites of fluoride deposition are vegetation and soil surfaces. The vegetation canopy represents the first surface available to most air pollutants on their way from the atmosphere to the terrestrial ecosystem. Characteristics of the plant community such as height, structure and biomass, as well as the physical and chemical properties of the vegetation canopy, will determine the sink efficiency of each vegetation type.

Soils also receive fluoride directly from the atmosphere, although the relative proportions that soils receive by means of the input processes, may vary with the characteristics of the vegetation, as well as soil physical and chemical characteristics.

Fluoride input mechanisms are regarded as complex processes which may be categorised as wet deposition and dry deposition. Wet deposition comprises clearfall which is precipitation directly transferred to the earth's surface, and throughfall which is precipitation transferred to the surface through a canopy of vegetation. Dry deposition is a combination of several complex processes, including gaseous exchange, aerosol impaction and gravitational settling. It is clear that dry deposition flux to soil is greatly reduced by the presence of tall, structured plant communities with a high biomass. Under these conditions, vegetation often acts as the initial site of fluoride uptake, although soil remains the ultimate terrestrial sink as fluoride is lost from vegetation to the soil by processes to be described later in this paper.

Vegetation absorbs gaseous fluorides rapidly. Bennett and Hill (1973) showed that a hydrogen fluoride concentration of 40.1 $\mu g/m^3$ above a 40 cm tall alfalfa canopy was reduced to 8.03 $\mu g/m^3$ at 10 cm above ground level.

Gaseous fluorides are absorbed on the outer surfaces of leaves or may enter the leaf through the stomata. Wet vegetation surfaces favour the former process (Smith, 1981). Once fluoride enters the leaf, it may move in the transpiration stream to the tips and margins (Jacobson *et al.*, 1966). Particulate fluorides do not usually enter the leaf. They are usually loosely bound to the cuticle surface (NAS, 1971).

The present research involves the characterisation of fluoride inputs to fluoride-polluted and unpolluted ecosystems. The polluted ecosystem is around an aluminium smelter at Kurri Kurri, New South Wales. The smelter began operation in 1969 and has been emitting approximately 700 tonnes of fluoride per year in recent years (J.B. Croft and Associates, 1981), although emission rates fell during the course of the investigation due to the installation of dry scrubbing facilities as emission controls. Current emission rates may be half of the previous figure (SPCC, 1980).

2 Materials and Methods

A. The Study Areas

Two study areas were chosen for these investigations. One area is 600 metres west of the Alcan Australia Ltd. aluminium smelter at Kurri Kurri, New South Wales. The vegetation of the area consists of mixed eucalypt open forest which has been described previously (Murray, 1981b).

The soils of this area are podzols with a low nutrient availability and a pH of about 5. They show variable plasticity and have developed on Permian shales.

Another study site was chosen at Tomago, representing an area with a low fluoride input. At this site, ambient fluoride concentrations were always less than 0.1 $\mu g\ F\ m^{-3}$ and foliar fluoride concentrations were less than 10 $\mu g\ F\ g^{-1}$ dry weight. The vegetation of the area is mixed eucalypt open forest and the soils are sand podzols.

B. Rainfall Collectors

In order to estimate the deposition rates for fluoride at a polluted site and at a control site, a series of collectors were located close to the aluminium smelter at Kurri Kurri, and at the unpolluted site at Tomago. The clearfall collectors actually measured wet deposition plus dry sedimentation when placed in an open position, and the throughfall collectors measured the same parameters plus fluoride removed from external and internal plant surfaces, when placed under a canopy. Five collectors were placed in an open position and five were placed under a canopy at each site. Stemflow, the portion of throughfall which reaches the earth after interception by the canopy and flow down the bark of trees, was also determined using five collectors.

All rainfall samples were collected on an event basis in order to minimise subsequent chemical transformations, and data were collected over a 12 month period.

C. Fluoride Analysis

Fluoride analysis of vegetation and aqueous solutions followed methods described previously (Murray, 1981a).

3 Results and Discussions

The data relating to the deposition rates for fluoride at Kurri Kurri and Tomago are presented in table 1.

TABLE 1. *The Fluoride Flux and pH of Rainfall at Kurri Kurri and Tomago. Data Represent Means and Standard Errors of Five Samples Collected After Each Rainfall Period Over Twelve Months.*

	Kurri Kurri			Tomago		
	pH	Fluoride concentration mg L^{-1}	Fluoride Flux kg $ha^{-1}yr^{-1}$	pH	Fluoride concentration mg L^{-1}	Fluoride Flux kg $ha^{-1}yr^{-1}$
Clearfall	4.7 ± 0.1	3.1 ± 0.5	10.9	5.1 ± 0.2	0.1 ± 0.02	0.4
Throughfall	4.7 ± 0.1	8.2 ± 0.6	31.6	4.7 ± 0.1	0.4 ± 0.1	1.3
Stemflow	4.1 ± 0.1	11.5 ± 0.8	N.D.[a]	4.5 ± 0.1	0.6 ± 0.1	N.D.[a]

[a] Not Determined

It can be seen that the fluoride concentration and fluoride flux are greatest in the collectors placed beneath the tree canopies in the polluted zone and these concentrations and fluxes were approximately twenty five times greater than corresponding data for the unpolluted site at Tomago. No flux estimates were made for stemflow as this has been shown to represent less than 0.5% of nutrient input in other studies (Ovington, 1954; Guthrie *et al.*, 1978).

The fluoride input to the polluted area as clearfall, representing a bulk precipitation input, is substantial, equivalent to 10.9 kg $ha^{-1}yr^{-1}$. The bulk fluoride input, calculated as the sum of bulk precipitation and net throughfall, corrected for the percentage tree cover in the ecosystem, is estimated to be 17.8 kg $ha^{-1}yr^{-1}$ at Kurri Kurri and 0.75 kg $ha^{-1}yr^{-1}$ at Tomago.

If a steady-state situation is assumed, it is possible to estimate the rate of fluoride uptake by this vegetation canopy. The sum of fluoride deposition as net throughfall (the fluoride component of throughfall contributed by the canopy of vegetation), and fluoride deposited as plant litterfall, provides a general estimate of the fluoride uptake rate for the vegetation. This estimate is given in table 2. It can be seen that litterfall represents a very small fluoride flux, compared with net throughfall. The estimate includes gaseous and particulate fluorides which are adsorbed to external leaf surfaces, as well as gaseous fluorides which have penetrated the leaf. The estimate does not take into account any net internal fluoride transfer between above-ground and below-ground plant organs. Translocation of fluoride between plant organs is normally considered to be minimal (NAS, 1971).

These estimates are approximate and the actual fluoride uptake rates will vary widely with a large number of biological and environmental factors. These factors include fluoride emission rate and height, windspeed and direction, humidity, precipitation, incidence of inversions, plant canopy height and structure, biomass, and diurnal and seasonal factors. Despite these problems, the data represent the first estimates of the rate of fluoride uptake by vegetation in forested areas known to the author.

The results allow a comparison to be made with the data obtained by Ares (1978) who studied a semi-arid area around an aluminium smelter in Argentina. He estimated a fluoride flux from atmosphere to leaves of between 3 and 13 mg m^{-2} day^{-1} and a litterfall flux of between 0 and 7 mg m^{-2} day^{-1} at 1 km from the smelter. The total of these fluxes provides an estimate of between 2 and 7.3 g $m^{-2}yr^{-1}$.

TABLE 2. *An Estimate of Fluoride Uptake Rate by Vegetation.*

	Kurri Kurri		Tomago	
	Fluoride Concentration mg L^{-1}	Fluoride Flux kg ha^{-1} yr^{-1}	Fluoride Concentration mg L^{-1}	Fluoride Flux kg ha^{-1} yr^{-1}
Net throughfall	5.1	20.7	0.3	0.9
Litterfall	119[a]	0.6	6.6[a]	0
Sink efficiency		21.3		0.9

[a] measured in μgF/g^{-1} dry weight.

The ecosystem around the smelter in Argentina is shrub steppe characterised by plant communities with low biomass (150-400 g m^{-2}), low height (usually less than 1 m), and low precipitation (mean annual precipitation is 169 mm yr^{-1}). Consequently, a low fluoride flux from atmosphere to vegetation is expected. With larger biomass, taller vegetation and higher precipitation, greater fluoride fluxes may be anticipated. The consistency between the estimates presented in this study, and the estimates presented for an ecosystem with a much lower biomass by Ares, underlines our lack of understanding of these transfer processes.

A. *The Soil Sink*

Fluoride transfer from vegetation to soil takes place chiefly by means of the plant litterfall and by the removal of external and internal foliar fluorides by precipitation, as rainfall, snow, dews, fogs and mists. A number of laboratory experiments have shown that fluorides can be readily removed from foliar surfaces. Particulate fluorides adsorbed on the external surfaces of leaves may be removed by washing. Between 70 and 100% of the fluoride accumulated from particulates may be washed from the leaf by mild detergents (McCune *et al.*, 1965). Gaseous fluorides which have been adsorbed on the leaf surface may also be readily removed. A proportion of the fluoride which has penetrated the leaf may be removed by washing (Jacobson *et al.*, 1966). Precipitation is generally regarded as reducing foliar fluoride accumulation (Brewer *et al.*, 1969) by the leaching out internal fluorides, although an increase in foliar accumulation by the deposition of soluble fluorides from air to the leaf surface has been demonstrated (Less *et al.*,1975).

Fluoride which is bound internally or adsorbed externally on the leaf surface may be transported to the soil surface as a result of litterfall. Upon reaching the soil surface the process of mineralisation occurs. In general, soils are regarded as efficient sinks for fluoride as they have been shown to possess high retention capacities for fluoride (MacIntire and Associates, 1949; MacIntire *et al.*, 1955; Specht and MacIntire, 1961).

Soils from the Tomago site have been shown to possess fluoride retention capacities in excess of 95% in lysimeter experiments (Murray, unpublished).

It is anticipated that the soils of the Kurri Kurri area will also demonstrate a high fluoride retention capacity, due to the high relative abundance of iron, aluminium and clay, which have been shown to possess strong affinities for fluorides (MacIntire *et al.*, 1955; Hansen, 1958; Specht and

MacIntire, 1961; Omueti and Jones, 1977). Associated with this characteristic of fluoride retention in soils is the strongly heterogenous nature of fluoride binding in some developed soil profiles. It has been shown by leaching experiments in which fluoride has been added to sand podzols, that fluoride is heavily localised in the A_1 and B_2 horizons which also concentrate many of these retention agents (Murray, unpublished).

Soils have critical roles in ecosystem function and soil organisms play an important role in maintaining efficient nutrient cycling. This has been shown to be a process sensitive to some pollutants such as heavy metals (Ruhling and Tyler, 1973) and sulphur (Roberts *et al.*, 1980). It has been suggested that fluoride accumulation in some surface soil horizons may interfere with litter breakdown due to inhibition of the fauna and microflora of soil (Rao and Pal, 1978). As fluoride is an accumulative pollutant to which components of the fauna are known to be sensitive (NAS, 1971), this finding is not unexpected.

A recent study of fluoride distribution in a wetland ecosystem around a fluoride emission source demonstrated high fluoride concentrations in soil isopods and arthropods important in the detritus cycle (Murray, 1981a), although no data were collected on the effects of these accumulations.

B. *The Effect of Fire on Fluoride Cycling*

Another important feature of most Australian open forest ecosystems and similar ecosystems in other parts of the world, is the fundamental role in nutrient cycling played by fire. Fire is a common event to which most vegetative components of these ecosystems are well adapted.

Estimates have been made of the amount of fluoride in plant litter which is available for release by fire. In the polluted ecosystem at Kurri Kurri and the control area of Tomago, estimates have also been made of the relative proportions of this fluoride which are exported from the ecosystem as gaseous and particulate fluorides and the proportion which is retained on the soil surface as ash. These data are shown in table 3.

Table 3 demonstrates that large amounts of fluoride may be available for plant uptake or leaching into soils in fluoride-polluted ecosystems after fire.

Data collected immediately before and after a wildfire in the study area, indicate that when high fluoride concentrations accumulate in plant ash and soils in a polluted ecosystem as a result of a fire, a large proportion of the water-soluble fluoride may be removed from the soil

Table 3. Fluoride Retention in Open Woodland Ecosystems After Combustion of Plant Litter. Means of Four Determinations.[a]

	Kurri Kurri mg m^{-2}	Tomago (control) mg m^{-2}
Fluoride stock in plant litter	178	19
Fluoride exported during fire	121	12.9
Fluoride retained in ash:		
a) H_2O Soluble	34	3.6
b) H_2O Insoluble	23	2.5

[a]Adapted from Murray (1981c).

solution within a period of eight months. These data are presented in Table 4.

The process of fluoride cycling in ecosystems has a number of important features that are of scientific interest, and fluoride cycling also has implications for the monitoring of polluted ecosystems.

A generalised scheme of some aspects of fluoride cycling in the ecosystems under study is provided by figures 1 and 2. This model ignores a number of minor cycles, concentrating on some of the major components and processes in the two ecosystems. It should be pointed out that the estimates presented in figures 1 and 2 are estimates only, and that at each site precise figures will vary from year to year, according to emission rates, dispersion factors and seasonal factors. It should also be stressed that these estimates were taken from a study area extremely close to a very large emission source, and as a consequence, these estimates represent maximum inputs to the ecosystem around the smelter. Because of the inherent variability of climatic and biological factors, these estimates may not be representative of other areas with different characteristics.

Monitoring programmes around fluoride emission sources often place a heavy emphasis on measuring fluoride concentrations in air and vegetation. This is based on the premise that vegetation represents the most sensitive ecosystem receptor for fluoride. Vegetation accumulates fluoride and hence it provides an indication of recent

TABLE 4. The Variation in the Fluoride Content of Vegetation, Plant Ash and Soils With Distance From an Aluminium Smelter. Data Represent Means of Three Samples. All Units are µg F g^{-1} dry wt, except as Indicated.[a]

Distance from potline (m)	Fluoride content of vegetation	Total fluoride content of plant ash	Water-soluble fluoride content of soil		
			Before fire	Immediately after fire	8 months after fire
350	350	1,181	16.8	36.0	11.2
400	419	941	8.2	12.8	3.2
450	313	1,599	3.1	6.3	0.7
500	283	1,177	5.8	12.4	3.1
550	247	1,236	3.0	7.4	4.9
600	252	896	3.4	7.8	2.5

[a] adapted from Murray (1981c)

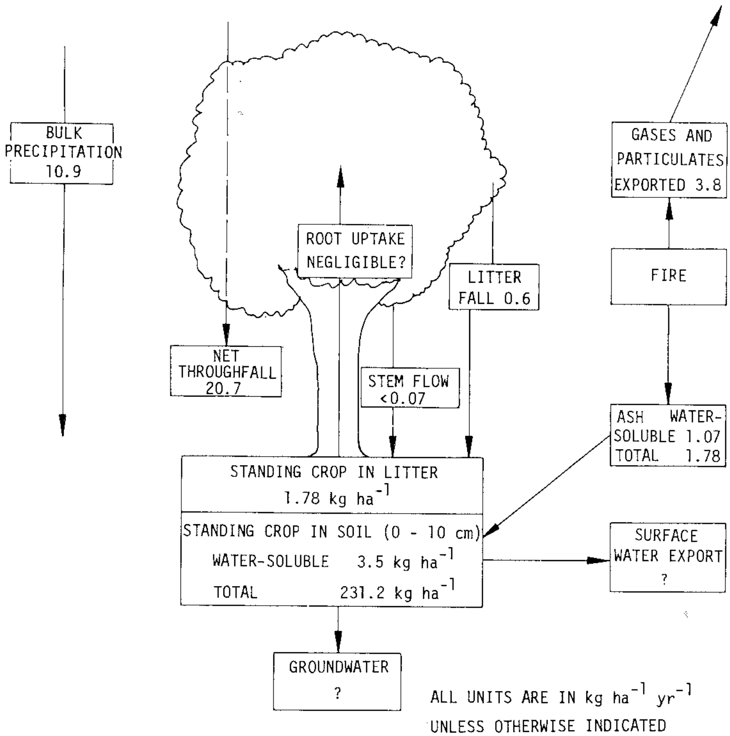

Fig. 1. A generalised scheme of fluoride cycles in a polluted ecosystem at Kurri Kurri. The model is based upon a model for sulphur in Hurditch et al.*(1980).*

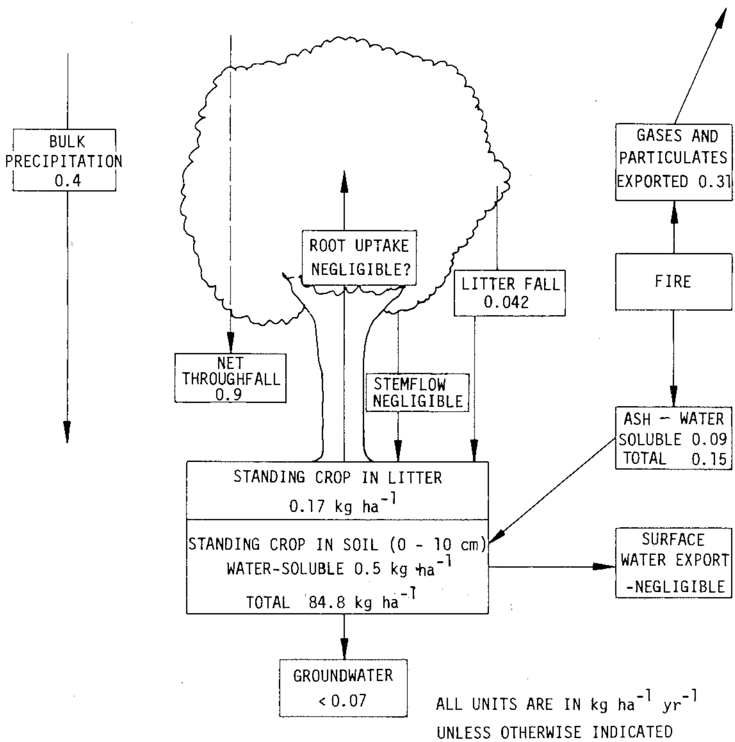

Fig. 2. A generalised scheme of fluoride cycles in a relatively unpolluted ecosystem at Tomago.

exposure history. It is at the bottom of food chains and vegetation is relatively easily sampled. Air represents the fluoride vector, and derives it's importance for monitoring from this.

Fluoride monitoring programmes in natural areas should take into consideration possible impacts of emissions on sensitive plant and animal species that while not obvious or direct receptors of fluoride could represent important species to which fluoride may be transferred. The fluoride fluxes quantified in figure 1 are significant and illustrate the potential for fluoride accumulation in ecosystem components. These components may include soil detrivores which have been found to accumulate fluoride in one polluted ecosystem (Murray, 1981a). The consequences of fluoride accumulation in detrivores could include increased litter accumulation, impaired nutrient cycling and increased nutrient export from the ecosystem. These processes could severely affect nutrient-poor ecosystems such as the ecosystem under study at Kurri Kurri. In the long term, this may result in changes in species composition, reduced biomass and ecosystem regression. These changes may become apparent as a result of ecosystem monitoring. Ecosystem monitoring would provide data on any changes of this nature that occurred and would allow appropriate remedial action to be taken. Whether the ecosystem monitoring takes the form of input/output analyses, or determinations of species composition and biomass changes, is a site-specific decision.

Studies of fluoride cycling in natural ecosystems which are subject to fluoride loads should elucidate fluoride accumulating organisms, and detailed ecological monitoring may lead to a better understanding of the effects of fluoride on ecosystems and hence a clearer picture of ecosystem function.

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