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POTENTIAL SULPHUR GAS EMISSIONS FROM A TROPICAL RAINFOREST AND A SOUTHERN APPALACHIAN DECIDUOUS FOREST

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ABSTRACT

Potential emission rates of reduced sulphur gases were estimated for a tropical rainforest and a southern Appalachian deciduous forest. Potential emissions were sampled by using cuvettes placed on the forest floor, by incubating samples of leaf litter and soil in closed containers, by incubating living plant material in closed containers, and by pumping air from around plant canopies enclosed in transparent Tedlar bags. A gas chromatograph fitted with a sulphur specific detector identified and quantified sulphur gases from cuvette sampling and incubations. Quantification of potential H_2S emissions from plant canopies was attempted by Zn+Na acetate trapping followed by colorimetry. Sulphur emissions were not detected with cuvette sampling. Potential sulphur emission rates ($\pm$ standard deviation) from the litter of the tropical rainforest at La Selva, Costa Rica estimated by incubations were 5.9 (29.1), 8.4 (16.7) and 5.1 (12.9) g $S.ha^{-1}.y^{-1}$ for mature, secondary, and flooded stands, respectively. Potential rates from soil were 0.6 (3.2), 42 (184) and 1.2 (6.1) g $S.ha^{-1}.y^{-1}$ for the same stands. Relative to the 11.7 kg $S.ha^{-1}.y^{-1}$ SO_4-S input-output discrepancy that volatile sulphur loss was hypothesized to explain, the observed potential emission rates are at least 200 times too small. Potential emission rates from the leaf litter of the southern Appalachian deciduous forest at Coweeta ranged from 0.4 to 2.1 g $S.ha^{-1}.y^{-1}$ and were less than 1 x 10^{-5} g $S.ha^{-1}.y^{-1}$ for soil. These rates are too low to account for the SO_4-S input-output discrepancy at Coweeta. Potential emissions may be underestimated due to surface adsorption in sampling devices.

Some rainforest legumes emitted sulphur gases from seeds, wood samples, roots, or leaves, or from all these organs. The sulphur gases are ethyl mercaptan and carbon disulphide. These emissions, which are new to plant physiology research, may have community implications as anti-microbial or anti-herbivore agents and, as point sources in a rainforest, may create a sampling problem for ecosystem level studies. Sampling for H_2S emissions from plant canopies in the rainforest and at Coweeta has yet to detect this sulphur gas.

Quantifying the contribution of natural sulphur emissions to the atmospheric sulphur burden and to acid rain on a global scale is hampered by the great diversity of habitats, the temporal and

spatial variability of sulphur emissions within habitats, and by analytical problems. Sulphur gases exist at low concentrations in nature, consist of numerous chemical species, are transformed from one species to another, and react with analytical surfaces. Quantification of the contribution of natural sulphur emissions to acid rain on a global basis is challenging.

INTRODUCTION

The proportional contributions of anthropogenic sulphur emissions and natural sulphur emissions to the global atmospheric sulphur burden (Ivanov 1983) and to the formation of acid rain are uncertain. Natural sulphur emissions come from geologic processes such as volcanoes and degassing of the earth's crust and from biological processes such as oxidation of organic sulphur compounds, and the reduction of sulphate by microbes, algae, and higher plants. Uncertainties in estimating the magnitudes of human-controlled and especially natural sulphur gas source strengths (Ivanov 1983; Moller 1984) and magnitudes of sulphur sink strengths make it difficult to balance the global sulphur budget. Estimation of global sulphur biogenesis is challenging both in biostatistical sampling and in analytical chemistry. The biostatistical challenge results from the broad scale diversity of terrestrial and aquatic habitats, and within habitats, from spatial and temporal variability in microbial and plant-mediated sulphur biogenic processes. The analytical challenge results from: 1) the low concentrations of sulphur gases in nature, 2) numerous sulphur gas species emitted by organisms, 3) variety of transformation rates among sulphur gas species, and 4) reactivity of sulphur gases with surfaces of sampling and analytical equipment.

Acidic precipitation is known for tropical rainforests in the Amazon (Anon 1972; Clark et al. 1980; Haines et al. 1983; Galloway et al. 1982) and in Costa Rica (Johnson et al. 1979; Hendry et al. 1984). These sites are relatively remote from industrial pollution sources. Acid precipitation has been reported from other remote sites including Amsterdam Island in the South Indian Ocean (Galloway et al. 1982). Acid precipitation at remote sites might result from: 1) long distance transport of acid-forming materials from industrial regions, 2) from local natural emissions, and 3) from some combination of the two sources (Haines 1983).

Excesses of SO_4^{-2} inputs over SO_4^{-2} outputs are known for some forested ecosystems (Haines 1983). Alternative hypotheses (Haines 1983) to explain these input-output discrepancies include 1) sulphur accumulation in growing biomass, 2) sulphur adsorption to soil, 3) conversion of SO_4^{-2} to organic sulphur compounds which leave the system undetected by the SO_4^{-2} analytical methods, 4) sulphur loss as gases, and 5) errors of estimation. If the SO_4^{-2} input-output discrepancies result from sulphur biogenesis, the magnitude of the contribution to the atmospheric sulphur burden would be sufficient to account for some of the rainfall acidity reported for Amazonian and Costa Rican rainforest (Haines 1983). An investigation of hypothesis 4 was begun

relatively close to Athens, Georgia, in order to develop methodology and later extended to include sampling in a tropical rainforest. Progress with estimation of emissions from a southern Appalachian forest and a tropical rainforest is summarized here. Details of the several component studies will be reported elsewhere.

SITES AND METHODS

Potential emissions were estimated for a successional Robinia stand and a successional Pinus-mixed hardwood stand on watershed 6 and for a mature Quercus-Carya deciduous forested watershed 14 at the U.S. Forest Service Coweeta Hydrologic Laboratory, Otto, North Carolina in the Southern Appalachians (35° 04' N. Lat, 83° 26' W. Long, Elev 700-1500m) and for the tropical rainforest at the La Selva Biological Station of the Organization for Tropical Studies, Puerto Viejo de Sarapiqui, Heredia Prov., Costa Rica, Central America (10° 26'N. Lat, 84° 00' W. Long, Elev 35-150m).

Sulphur Quantification

Gas Chromatography: Gas samples were analyzed with a Perkin-Elmer Sigma 4B chromatograph (Perkin-Elmer, Norwalk, CT) fitted with a sulphur specific flame photometric detector, a 2 mm internal dia. teflon column packed with either a 4.5 or a 16.5 cm section of acetone washed (de Souza et al. 1975) Porapak QS (Supelco, Bellefonte, PA) supplied with N_2 carrier gas at 20 mL.min^{-1} and heated to between 60 and 100°C depending on the particular analysis. Reference sulphur dioxide, hydrogen sulphide, carbonyl sulphide, dimethyl sulphide, dimethyl disulphide, methyl mercaptan and ethyl mercaptan were supplied from permeation tubes (VICI Metronics, Santa Clara, CA) inserted into a Tracor model 432 Tri-Perm Permeation Calibration system (Tracor, Inc. Austin, TX). Standards were transferred from the permeation system into the chromatograph through multiposition zero dead volume sampling valves and a teflon sample loop using a sampling pump. Sample loop, valves and connecting teflon gas lines were heated to 65°C to minimize condensation of sulphur gases on surfaces. Identification of ethyl mercaptan and dimethyl sulphide in incubations of leaf litter and of ethyl mercaptan and carbon disulphide in incubations of legume roots was confirmed with a Finnigan OWA 3B gas chromatograph-mass spectrograph (Finnigan Corp., Sunnyvale, CA).

Colorimetry: Potential hydrogen sulphide emissions from the forest floor and from living plant leaves were quantified colorimetrically by aspirating air samples through pairs of impingers connected in series and containing 25 mL of Zn-Na acetate buffer (Johnson and Nishita 1952), through bubble flow meters, and through a battery powered vacuum pump. At the end of the sampling period p-aminodimethylaniline and ferric ammonium sulphate were added for colour development. Optical density was determined at 670 nm using a 2 cm cuvette in a Bausch and Lomb Mini Spectronic 20 (Bausch and Lomb, Rochester, NY) in Costa Rica or in a 10 cm cuvette in a Bausch and Lomb 700 Spectrophotometer at Coweeta. A standard curve was developed by aspirating H_2S

from a permeation standard through aliquots of the Zn-Na acetate trapping solution followed by colour development.

Sulphur Gas Samplings

The Forest Floor: Potential sulphur gas emissions from forest soil and forest floor litter were sampled with cuvettes placed on the forest floor and by the incubation of soil and litter samples in linear polypropylene bottles followed by analysis of head space gases.

Cuvettes, 50 x 50 x 3.5 cm, were constructed of stainless steel and lined with teflon film and fitted teflon bulkhead ports for removal of gas samples. Three cuvettes were placed on the rain-forest floor in Costa Rica in two sampling episodes.

In Cuvette Sampling Episode 1, the gas in the head space was sampled to detect possible changes during a 30-day period. If the emission rates were of the magnitude of the 11.7 $kg.ha^{-1}.y^{-1}$ SO_4-S input-output discrepancy (Johnson et al. 1979), the emissions would change the concentration of sulphur in the head space by 2.7 x 10^{-6} $g.mL^{-1}.30$ $days^{-1}$, well above the 1.9 x $10^{-10}g$ dimethyl sulphide-S/mL detection limit of the gas chromatograph. Sulphur was not detected, thus the emissions are either less than the detection limit or emitted gases are rapidly converted to SO_4^{-2} in condensed moisture on the surfaces of the forest leaf litter and of the cuvettes.

In Cuvette Sampling Episode 2, cuvettes were modified to dynamic flux chambers similar to those described by Aneja (1984) where the air was stirred by two fans (Model 6000-16 LiCor, Inc., Lincoln, NB). Air was sampled from inside the cuvette (experimental stream) and from near the point of air entry port of the cuvette (control) by aspirating through two impingers in series, a bubble flow meter, to a 12 VDC vacuum pump.

Incubations: Litter and soil samples for incubations were taken from the deciduous forest of the Coweeta Hydrologic Lab., Otto, North Carolina and from a flooded forest, a secondary forest, and a mature forest stand in the rainforest at La Selva, Costa Rica. In each rainforest stand 12 sampling points were established at 10 m intervals on transects parallel to access trails. At each sampling point leaf litter was removed from a 0.0625 m^2 quadrat to a 250 mL Nalgene linear polypropylene wide mouth centrifuge jar (Nalge Co., Rochester, NY) fitted with a 5 x 9 mm rubber serum stopper. At the same point 2-4 soil cores 3 cm in dia. and 3 cm in depth were removed to other polypropylene jars. The time course of sulphur gas accumulation in the head space of the bottle was quantified by sampling with a gas syringe through the serum stopper followed by injection into the gas chromatograph.

Sulphur Emissions from Plants: During a study of the formation of nitrogen-fixing root nodules in legumes at La Selva, one of us (McHargue) found that some plants smelled of sulphur gases. Greenhouse- and field- grown plants of fourteen species were incubated in Nalgene polypropylene bottles and sampled to quantify sulphur gas emissions. Gas samples from incubation of

roots of Pithecellobium catenatum Donn. Smith grown in Miami, FL were analyzed with a gas chromatograph-mass spectrograph. Potential H_2S emissions from plant leaves were also investigated at La Selva (Haines and McHargue) and at Coweeta (Howell) by placing plant stems and leaves inside 30-liter capacity Tedlar gas sample bags (SKC, Eighty Four, PA). Air inside the bags was stirred with muffin fans at 980 $L.min^{-1}$ to minimize boundary layer resistance and leaf heating. Air was drawn from Tedlar bags through two impingers in series and through bubble flow meters at 0.5 to 1.5 $L.min^{-1}$. Control samples were obtained with an identical system of bags, fans, impingers, flow meters, and pumps but without an enclosed plant. Plants sampled at the Costa Rican site were seedlings of the early successional trees Heliocarpus appendiculatus Turcz. and Ochroma lagopus SW. grown in a 1:1 forest soil/river sand potting mix in plastic containers. Plants sampled at Coweeta were branches of stump sprouting trees exposed to full sunlight. Species sampled were Liriodendron tulipifera L., Carya glabra (Miller) Sweet, Quercus rubra L., Acer rubrum L., and Robinia pseudo-acacia L. The detection limits were less than 2 x $10^{-10}g$ $H_2S.m^{-2}.h^{-1}$ or 4 x $10^{-12}g.g^{-1}$ $dwt.h^{-1}$ for the two Costa Rican plants. Detection limits for Coweeta plants were less than 3 x 10^{-10} to 5 x $10^{-9}g.m^{-2}.h^{-1}$ depending on volume of air sampled.

RESULTS AND DISCUSSION

Estimated sulphur emission rates from the forest floors of the tropical rainforest and the southern Appalachian deciduous forest are shown in Table 1. Sampling with cuvettes in Costa Rica did not detect sulphur gas. Incubations of litter and soil in bottles showed that dimethyl sulphide + ethyl mercaptan were the predominant species emitted at all sites. Methylmercaptan was occasionally detected. The analytical strategy was to screen some of the samples for all of the sulphur gases listed in the footnote of Table 1, then to quantify the predominant sulphur species in all of the samples. Thus, if sulphur gas appeared at low concentration or in just a few samples it would not have been quantified in all of the samples. Emissions per forest floor area were greater from the decomposing leaf litter than from the underlying soils in each of the forested ecosystems. Emissions from the soil may have resulted from incomplete removal of leaf litter from the soil surface.

Emission rates from the floors of the successional and mature southern Appalachian deciduous forests at Coweeta Hydrologic Laboratory are lower. The greater emission rates from the tropical rainforest than from the temperate forests is consistent with the hypothesis that forest floor emission rates increase towards the equator (Adams et al. 1981).

Sulphur emissions were detected by the flame photometric detector from excised roots of 10 out of 14 legume species tested (Table 2). Emissions from seeds, leaves, wood samples, and intact seedlings will be reported elsewhere.

Table 1. Potential DMS and C_2H_5SH sulphur gas emission rates, g $S.ha^{-1}.y^{-1}$ ($\pm$ standard deviation) of leaf litter and soils of three tropical and three temperate forest stands. Numbers of incubations are indicated as "n" and numbers of incubations in which sulphur was detected are indicated as "d". Incubations were screened for compounds listed in footnote[a] but DMS and C_2H_5SH were predominant forms detected.

Forest compartment and stand	n	d	DMS + C_2H_5SH	s.d.
Rainforest, La Selva, Costa Rica				
Litter, flooded	48	15	5.13	12.95
Litter, secondary	48	21	8.36	16.72
Litter, mature	48	11	5.93	29.14
Soil, flooded	24	1	1.23	6.05
Soil, secondary	24	2	41.8	184.0
Soil, mature	24	1	0.66	3.24
Temperate forest, Coweeta, North Carolina, USA				
Litter, Robinia	48	27	2.07	3.6
Litter, Pinus-hardwood	48	17	1.08	2.0
Litter, mature hardwood	48	8	0.43	1.2
Soil, Robinia	48	0	--	
Soil, Pinus-hardwood	48	0	--	
Soil, mature hardwood	48	0	--	

[a]

Abbreviation	Formula	Name
SO_2	SO_2	Sulphur dioxide
H_2S	H_2S	Hydrogen sulphide
COS	COS	Carbonyl sulphide
CS_2	CS_2	Carbon disulphide
DMS	CH_3SCH_3	Dimethyl sulphide
DMDS	CH_3SSCH_3	Dimethyl disulphide
CH_3SH	CH_3SH	Methyl mercaptan (methanethiol)
C_2H_5SH	CH_3CH_2SH	Ethyl mercaptan (ethanethiol)

Table 2.—Emission rates of ethyl mercaptan + carbon disulphide sulphur (g $S.g^{-1}$ dwt tissue.h^{-1} ± standard deviation (S.D.)) for incubation times less than and greater than 24h for roots of 14 legume species. Numbers of samples with detectable sulphur/total numbers of samples analyzed are indicated in parentheses. Mean (x) rates calculated only for samples with detectable emissions. NT = not tested.

	< 24 h			> 24 h		
	$\bar{x}$ (x 10^{-7})	S.D. (x 10^{-7})	(d/n)	$\bar{x}$ (x 10^{-7})	S.D. (x 10^{-7})	(d/n)
Acacia mangium Willd.						
Gliricidia sepium (Jacq.) Stend.	3.5	NT	(2/3)	3.28	NT	(3/3)
Enterolobium cyclocarpum (Jacq.) Griseb.	3.9	1.9	(1/1)	0.41	1.17	(1/1)
Leucaena multicapitula Schery	0.9	0.5	(3/3)	0.46	0.15	(3/3)
Mimosa pigra L.	128	100	(2/3)	45.5	3.54	(3/3)
Mimosa pudica L.	1.9		(1/1)	2.2		(1/1)
Mimosa sp.	16.7	3.04	(2/2)	0.94	0.45	(2/2)
Pentaclethra macroloba (Willd.) Kuntze	0		(0/3)	0		(0/3)
Pithecellobium arboretum (L.) Urban	225	65	(2/2)	0.7	0.32	(2/2)
P. catenatum Donn. Smith	203	NT	(1/1)	8.76		(1/1)
P. gigantifolium (Schery) J. Leon	NT	NT		0		(0/1)
P. longifolium (H. & B.) Standl.	NT			0		(0/1)
P. pedicellare (DC.) Benth.	39.1	14.5	(3/3)	21.7	14.6	(3/3)
Stryphnodendron excelsum Harms	717	428	(3/3)	16.2	7.9	(3/3)

Since the retention times of ethyl mercaptan and carbon disulphide were identical the proportions of the two compounds are unknown, and therefore, the results are expressed as total sulphur. A gas chromatographic-mass spectrograph analysis found ethyl mercaptan and carbon disulphide in the proportions of 1:7 in gas samples from incubation of roots of _Pithecellobium catenatum_ grown in Miami, Fla. Ethyl mercaptan + carbon disulphide emissions are potentially significant at three ecological levels. First, ethyl mercaptan emissions are new to plant physiology and carbon disulphide emissions are known for only four plant species. In a review of the literature on natural plant products, sulphur chemistry, and plant pathology we have found no mention of the occurrence of ethyl mercaptan among the many sulphur compounds known for plants (Daly and Deverall 1983; Lewis and Papavizas 1971; Misaghi 1982; Nicholas 1973; Richmond 1973; Schönbeck and Schlösser 1976). Carbon disulphide emissions are known from the minced leaves of _Brassica oleracea capitata_ L. (Bailey _et al._ 1961) and from _Medicago sativa_ L., _Zea mays_ L. and _Quercus lobata_ Nee (Westberg and Lamb 1984). Second, the material may have community implications because it may confer anti-microbial, anti-nematode, or anti-insect properties upon the producing plant. Third, at the ecosystem level some plant species may constitute point sources of sulphur emissions to the atmosphere from within tropical forests.

Potential emission rates of H_2S from live leaves were less than 2 x 10^{-10}g and 5 x 10^{-9}g $H_2S.m^{-2}.h^{-1}$, the detection limits of the method for Costa Rica and Coweeta, respectively. Sampling was performed because H_2S emissions have been reported from the leaves of _Avena sativa_ L., _Beta vulgaris_ L., _Coleus blumei_ Benth., _Cucumis sativus_ L., _C. melo_ L., _Cucurbita pepo_ L., _Glycine max_ L. Merr., _Gossypium hirsutum_ L., _Hordeum vulgarae_ L., _Medicago sativa_ L., _Nicotiana tabacum_ L., _Phaseolus vulgaris_ L., _Pinus sylvestris_ L., _Picea abies_ (L). Karsten and _Zea mays_ L. (Kinraide and Staley 1985; Sekiya _et al._ 1982; Wilson _et al._ 1978; Winner _et al._ 1981; Hallgren and Fredriksson 1982; Filner _et al._ 1984; Rennenberg 1984; Spaleny 1977). Subsequent to our sampling efforts, the emissions of various combinations of the sulphur gases COS, DMS, CS_2, and DMDS (see footnote of Table 1 for definitions) have been reported from _Medicago sativa_ L., _Zea mays_ L., _Phaseolus vulgaris_ L., _Lycopericon_, _Pisum_, _Quercus lobata_ Nee and _Pinus ponderosa_ Dougl. by Westberg and Lamb (1984).

These studies were designed to quantify the contribution of sulphur emissions from forests to the atmospheric sulphur burden and to acid rain. If, following additional sampling, the CH_3SCH_3 and C_2H_5SH emission rates fall between the 1.0 x 10^{-5}g $S.ha^{-1}.y^{-1}$ detection limit and the highest reliable value of 8.0 g $S.ha^{-1}.y^{-1}$ (Table 1) and if the emissions of other sulphur compounds are not detected, two conclusions can be drawn. First, the rates of CH_3SCH_3 + C_2H_5SH emissions reported for the rain-forest at La Selva fall within the range of 1-70 g $S.ha^{-1}.y^{-1}$ and are close to the weighted average of 20 g $S.ha^{-1}.y^{-1}$ which can be calculated from summary statistics reported for forest and swamp

soils of the United States by Adams _et al._ (1979). Second, the magnitude of the sulphur emissions from the forest floors of the two forests are too small to account for either the SO_4-S input-output discrepancy or for the rainfall acidity reported earlier for the rainforest at La Selva (Johnson _et al._ 1979) or at Coweeta (Swank and Douglass 1977).

Possible alternative explanations of the SO_4-S input-output discrepancy which have yet to be excluded are sulphur accumulation in biomass (Hypothesis 1), sulphur accumulation in soils (Hypothesis 2), loss of organic sulphur compounds in streamwater (Hypothesis 3), or volatile emissions from live plant leaves (variation of Hypothesis 4).

FUTURE RESEARCH

Emission rates estimated here must be considered minimum esti-mates for the forest floor. The magnitude of underestimation due to adsorption of sulphur compounds to surfaces of sampling cuvet-tes, incubation bottles, and gas sampling bags is presently unknown. Problems of underestimating natural sulphur emissions have recently been explored by Westberg and Lamb (1984) and by Adams and Farwell (1984) and will not be discussed here. Balan-cing the global sulphur budget will be more challenging than balancing the global carbon budget. The exchange of sulphur gases between the atmosphere and the surfaces of the land and water involves numerous sulphur gas species each at relatively low concentrations. The exchange of carbon along the same pathways is dominated by CO_2 at relatively high concentrations, making quantification far easier. After decades of research, the global carbon budget still is not understood well enough to balance (Bolin _et al._ 1979) and is the subject of continuing active research (Woodwell 1984; Lemon 1983). We hope that a cooperative international effort can be organized in the 1990s as part of the International Geosphere-Biosphere Program (National Research Council 1983) to sample sulphur exchange processes bet-ween the atmosphere and biosphere at selected sites around the globe to refine our understanding of the global sulphur budget.

Future efforts of our group will focus on three general problems: improved trapping, lighter weight analytical systems, and more extensive sampling. Improved sampling efforts will involve: 1) continued development of sample pre-concentration by solid adsor-bent trapping (Black _et al._ 1978; Steudler and Kijowski 1984) for use in remote areas where cryogenic trapping is not possible; 2) learning cryogenic trapping methodology for use in regions where liquid N_2 is available; 3) quantification and subsequent correc-tion for surface adsorption of sulphur gases to incubation jars, teflon lined cuvettes, and transparent Tedlar gas sampling bags. A lighter weight analytical gas chromatograph having a flame photometric detector, which can be dismantled into pieces weighing no more than 32 kg each for transport as passenger baggage on international air carriers, needs to be developed.

More extensive sampling is envisaged to include collaboration with local investigators both in North America and in rainforests

around the globe. Comparisons are planned among sites of the US National Science Foundation supported Long Term Ecological Research (LTER) program (Callahan 1984). These include desert, prairie, coniferous forest, deciduous forest, salt marsh and freshwater swamp ecosystems. Rainforest sampling will be expanded to include Australian, Malaysian, Mexican, and West African sites. The goals are both to perform comparative ecological studies among systems as well as to quantify the contributions of these systems to the global sulphur balance. Collaboration with persons using aerodynamic approaches to estimate CO_2 fluxes between plant communities and the atmosphere would be useful. If we measured sulphur gas concentration profiles while they measure CO_2 profiles, we would calculate simultaneous CO_2 and sulphur exchange, thereby learning about the interactions of the two gas exchange processes while at the same time contributing toward the refining of both global carbon and sulphur budgets.
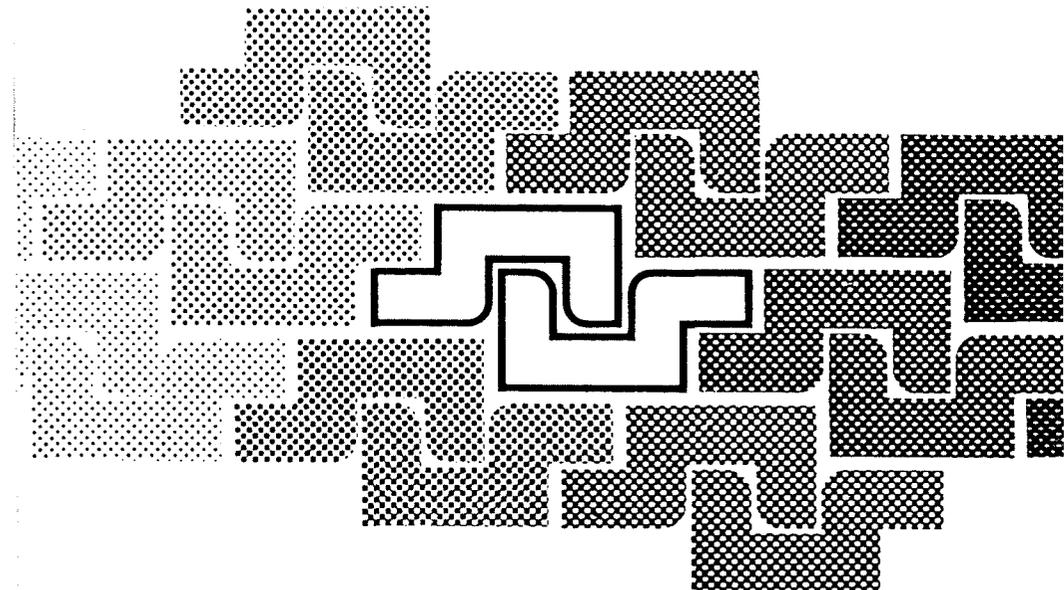
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