

tween rain seasons. Some very small effects on rainfall are associated with both the full moon and new moon which occur every 14.7 d (refs 4, 9). This particular lunar phase effect would give roughly equal rainfall contributions (14.7 d apart) to the drier and rainier halves of the Los Angeles 27-d rain cycle and is probably not related to it. The Sun and solar sector structure also produce atmospheric effects<sup>10</sup>. But our studies of the rainfall cycle's phase indicate that it is not simply driven by either solar or lunar processes. If the periodicity is of solar or lunar origin, then its phase must be determined by another mechanism.

Just off the northwest coast of the United States, confluence (narrow, strong jet stream) is associated with the Gulf of Alaska surface low surmounting the eastern cell of the Pacific high<sup>11</sup>. These unusual circumstances provide very good conditions for high zonal index so storm tracks can stay north of Southern California a long time. We now consider the possibility that the spectral peaks in Fig. 2 arise from resonances of the atmospheric subsystem regulating the weather, including the Gulf low and the Pacific high, in the Eastern Pacific region at northern hemispheric mid-latitudes. The spectra suggest the possibility that this resonance is excited by time dependent processes with energy at frequencies closer to higher harmonics than to the fundamental of the subsystem and closer to some harmonics than to others. Since atmospheric systems are "deformable", we might expect a somewhat different fundamental and a different set of harmonics in years when the atmospheric conditions were different. The differences in the spectra in curves 4 (1936-1971) and 5 (1900-1935) may be the result of a long term change in the state of the atmosphere. Thus, Conover<sup>12</sup>, citing work by Petterssen<sup>13</sup>, states that the global trend of rising temperatures diminished after about 1937-1940. He relates changes in temperature trends to changes in the mean atmospheric state of meridional flow relative to zonal circulation.

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## Concentrating solutes with membranes containing carriers

WE have developed membranes which can rapidly concentrate a specific solute against its concentration gradient. These membranes depend on mobile carriers and are examples of *in vitro* systems which exhibit characteristics of biological transport. When combined with the 'liquid surfactant membrane' geometry, they offer a method for wide classes of large scale separations. We show here how our specific results provide a blueprint for designing additional membrane systems.

The membranes operating in our laboratories at present are summarised in Table 1. These membranes depend on mobile carriers which react rapidly and selectively with the solutes being transported. Two mechanisms are involved. In the first (Fig. 1), the flux of the protons which supply the energy is in the opposite direction to the flux of the solute being moved against its gradient, resulting in counter-transport<sup>1,2</sup>. The second mechanism is analogous to that shown in Fig. 1, except that both the protons and the solute being separated combine with the carrier on the same side of the membrane. As a result, the two fluxes are in the same direction, resulting in co-transport. Moreover, because all of these membranes are chemically well defined, they can be understood on a molecular basis, and the diffusion and chemical reaction responsible for their operation can therefore be studied in detail<sup>3</sup>.

Additional membrane systems can be developed in a straightforward manner. An organic solution containing a complexing agent for the relevant solute must be chosen. This solution and the complexing agent will become the membrane material and the mobile carrier, respectively. The degree of complex formation must vary strongly with pH, and both carrier and complex must be soluble in the membrane solution but insoluble in aqueous acid and base. One then runs two extractions sequentially. For example, a solution of 500 parts per million (p.p.m.) mercuric ion in 2 M NaCl and 1 M HCl is mixed with a membrane solution of 10% trioctylamine in *o*-xylene. The mercuric ion and the protons complex with the amine and dissolve in the organic phase. When this organic phase is

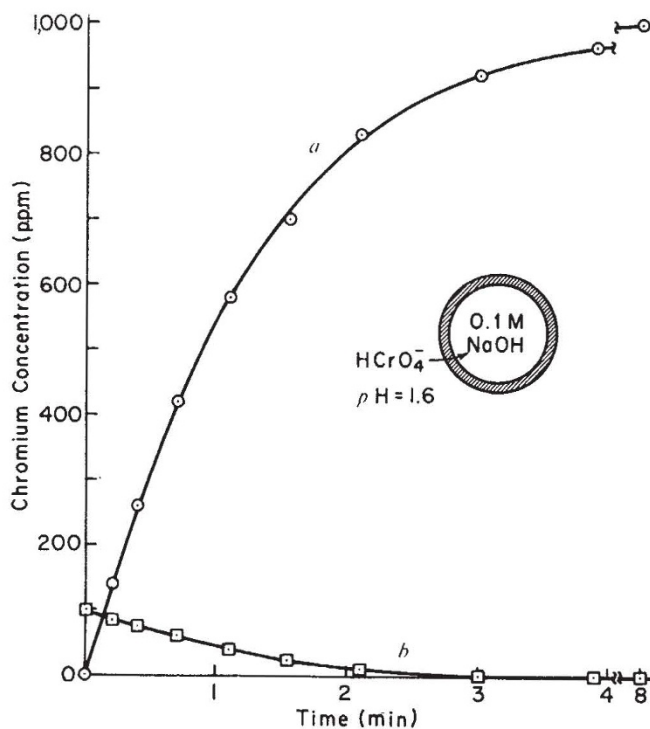


Fig. 1 Counter-transport mechanism involving a mobile carrier.



**Table 1** Existing membrane systems\*

Solute	Carrier	Transport mechanism	Energy	Remarks
Na <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> , Cs <sup>+</sup>	Monensin in octanol	counter-	HCl into NaOH	Selective for Na <sup>+</sup> ; strong biological parallel
Na <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> , Cs <sup>+</sup>	Cholanic acid in octanol	counter-	HCl into NaOH	Non-selective analogue of above
Cu <sup>2+</sup>	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \phi\text{CCH}_2\text{CCH}_3 \end{array}$ in chloroform or in carbon tetrachloride	counter-	HCl into NH <sub>4</sub> OH	Works best at 0.01 M Cu <sup>2+</sup> ; selective for Cu <sup>2+</sup> over Ni <sup>2+</sup> and Co <sup>2+</sup> ; carriers poisoned by Fe <sup>3+</sup>
	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \phi\text{CCH}_2\text{CCF}_3 \end{array}$ in xylene	counter-	HCl into NaOH	
Zn <sup>2+</sup>	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \phi\text{CCH}_2\text{C}\phi \end{array}$ in chloroform	counter-	0.5 N HCl into pH 8.5 citrate	Works best at high dilution Selectivity depends on pH difference
Pb <sup>2+</sup>	Dithizone in carbon tetrachloride	co-	HCl into NaOH	
Hg <sup>2+</sup>	Trioctylamine in xylene	co-	HCl into NaOH	Works best at 1,000 p.p.m. with 2 M Na <sup>+</sup> on both sides
Cl <sup>-</sup>	Trioctylamine in xylene	co-	HCl into NaOH	Selectivity depends on pH difference
SO <sub>4</sub> <sup>2-</sup>	Trioctylamine in xylene	co-	H <sub>2</sub> SO <sub>4</sub> into NaOH	
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	Tridodecylamine in hydrocarbon oils	co-	H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> into NaOH H <sub>2</sub> SO <sub>4</sub> into NaOH	

\* All these systems have been checked by double extraction and in a membrane geometry.

extracted with 500 p.p.m. mercuric ion in 2 M NaCl and 0.3 M NaOH, the mercury concentration of the basic solution is increased. The two extractions produce a net transfer of

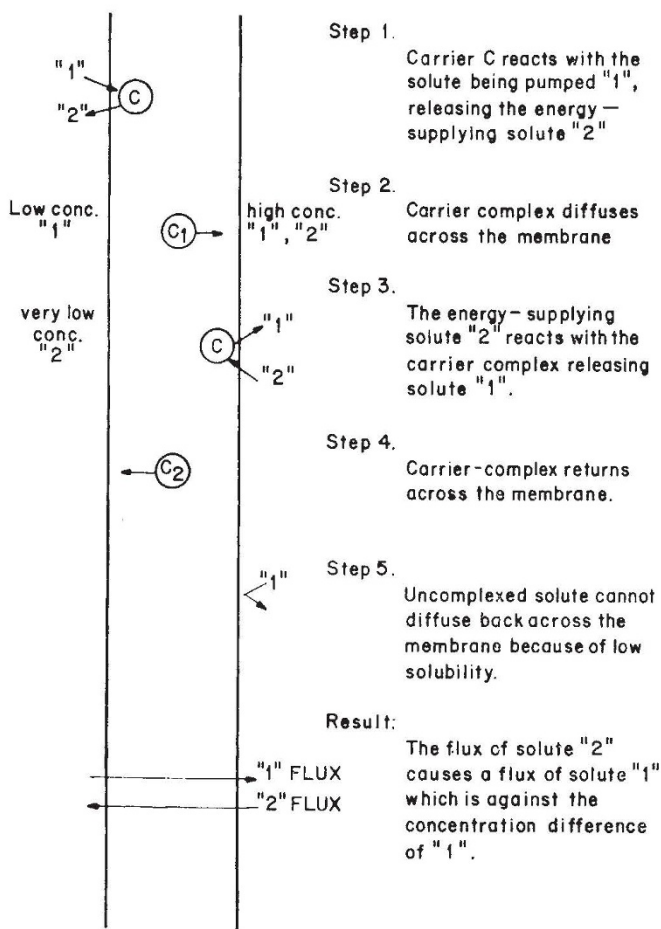
material, and therefore this chemical system provides a potential separation process. As a thin layer dividing two aqueous solutions, it will function as a membrane capable of concentrating a specific solute.

The real interest in these membranes, however, arises when they are converted into the geometry of synthetic vesicles or 'liquid surfactant membranes'<sup>4</sup>. This geometry consists of small drops of solution coated with the liquid membrane and suspended in a solution of different concentration. Because these bubbles have such a large area per volume, diffusion in and out of the bubbles is much faster than is possible with classical membrane geometries. Separation has been achieved on an industrial scale, but the selectivity of these separations was controlled by solubility differences alone.

Bubbles coated with membranes containing carriers, like those in Table 1, have three advantages over those based on solubility alone: they can concentrate as well as separate a given solute; they have inherently much greater selectivity; and they are applicable to a much wider variety of chemical systems. These advantages accrue from the specific chemical reactions between carrier and solute. Because these reactions include a much wider spectrum of effects than solubilities do, a much greater variety of phenomena are possible.

An example of the properties of the bubbles coated with membranes containing carriers is shown in Fig. 2. In this experiment, 10 ml of 0.1 M NaOH was prepared. The membranes were made of light mineral oil containing 4 weight % trioctylamine and 1 weight % sorbitol monooleate. These bubbles were added, whilst stirring, to 100 ml of solution containing 100 p.p.m. chromium at pH = 1.6. The concentration of chromium in the bubbles rose from an initial value of zero, past the concentration in the bulk solution, to a value of 900 p.p.m. after 4 min, and the chromium concentration in the bulk solution decreased correspondingly. The very rapid uptake with very little amine provides an intriguing alternative to conventional ion exchange.

We have shown here how the membrane mechanisms postulated in biology can be generalised to produce a variety of chemically well defined analogues to living membranes. Although we have reported only data for inorganic ions, these principles can be extended to other solutes, including antibiotics, detergents, and amino acids. When these transport systems are used in conjunction with the technology developed for liquid surfactant membranes, separations of considerable



**Fig. 2** Concentration of chromium against its concentration gradient using liquid surfactant membranes. *a*, In bubbles; *b*, in bulk solution.



practical potential are obtained.

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## Removal of ozone from the atmosphere by soil and vegetation

OZONE is the principal constituent of the photochemical smog that plagues many cities in the United States. Produced by the action of sunlight on the hydrocarbons and oxides of nitrogen emitted by vehicles and industry, concentrations of ozone greater than  $25 \times 10^{11}$  molecules  $\text{cm}^{-3}$  ( $1 \times 10^{11}$  molecules  $\text{cm}^{-3} = 0.4$  parts per hundred million =  $8 \mu\text{g m}^{-3}$ ), used as evidence of photochemical smog<sup>1</sup>, have been observed in Los Angeles for more than two decades<sup>2</sup>. Because of lower air temperatures, less sunshine and fewer vehicles, photochemical pollution was considered unlikely to occur in Western Europe but concentrations indicative of photochemical smog have now been reported from Germany<sup>3</sup>, the Netherlands<sup>4,5</sup> and southern England<sup>6,7</sup> on calm, sunny days. High concentrations of ozone cause respiratory difficulties in humans<sup>8</sup> and damage many plants<sup>9</sup> including crops<sup>10</sup>.

The Earth's surface acts as a sink for ozone produced in the upper atmosphere<sup>11</sup>. The rate of removal of ozone varies with the surface: water, snow, grass, and a juniper bush remove it increasingly quickly<sup>12,13</sup>. Since soil bare of vegetation also removes ozone from the atmosphere at rates similar to those previously observed over land<sup>14</sup>, the role of vegetation is not clear. Laboratory studies with individual plants have indicated that vegetation removes ozone from the air when the stomata are open<sup>15-17</sup>.

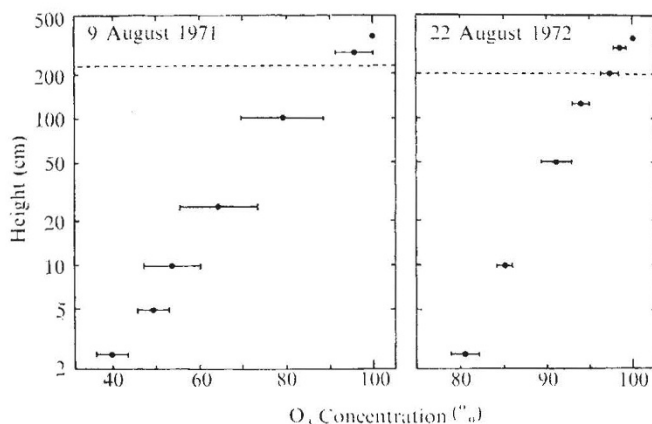
We have examined the role of vegetation and soil as sinks for atmospheric ozone in the field. For this we constructed a mathematical simulator of ozone removal by vegetation and soil. In the laboratory, the rate at which bean plants removed ozone from the air corresponded to a resistance to ozone removal about the same as that encountered by water leaving the leaves through the stomatal pores<sup>15</sup>. After taking into account the different rates of diffusion of water vapour and ozone, we obtained similar results for young maize plants. The resistances to ozone removal and evaporation were 271 and 270  $\text{s cm}^{-1}$  respectively in the dark and only 3 and 4  $\text{s cm}^{-1}$  respectively in the light. This similarity of resistance to ozone removal and transpiration of water implies that at the cell walls beneath the stomata, where the air is saturated with water, the concentration of ozone must be essentially zero. Thus ventilation and

stomata alone control ozone removal by a leaf. This inference has suggested that simulators of evaporation can be modified to calculate the ozone removal by vegetation<sup>18</sup>.

Our simulator of ozone removal is based on a simulator of evaporation<sup>19,20</sup>. The salient features of the simulator of evaporation are its conception of evaporation as an energy exchange process, the predominance of vertical exchange between the canopy and air above over horizontal exchange, the division of the canopy of leaves into strata, the use of stomatal and atmospheric resistances to evaporation, and the use of boundary conditions of temperature and humidity above and below the leaf canopy. The exchange of ozone can be compared with the flow of a direct electrical current through a series of resistances. This clarifies the concept of exchange and simplifies the algebra. The maize canopy may be depicted with eight strata of leaves and a basal stratum of stems.

The flux of ozone into each stratum of leaves or into the soil is opposed by vertical resistances to exchange from one stratum to the next, and within each stratum the exchange is opposed by the resistances of the boundary layer and stomata. The vertical transfer resistances and boundary layer resistances are the same as encountered by sensible heat or vapour transfer, and the stomatal resistance only needs to be modified for the different rates of diffusion of ozone and water vapour. Using the rules of electrical currents, as shown elsewhere<sup>18-21</sup>, we can relate the products of the fluxes of ozone into the leaves and soil, and the resistance to these fluxes to the differences in concentration of ozone at the canopy top and near the ground. Thus, the simulator enables us to calculate the ozone removal by soil and vegetation from the concentration of ozone at the top and bottom of the canopy if we know the vertical transfer resistances, the resistances to removal by the stomata and leaf boundary layer, and the leaf area distribution.

We first calculated the evaporation from measurements of temperature and humidity above a canopy of known leaf area per stratum, the temperature and humidity near the ground, the radiation absorbed by the canopy, the stomatal



**Fig. 1** Relation between ozone concentration and logarithm of height within and above a maize field. The concentration is presented as a percentage of that at 350 cm:  $11 \times 10^{11}$  mol  $\text{cm}^{-3}$  in 1971 and  $31 \times 10^{11}$  mol  $\text{cm}^{-3}$  in 1972. The dashed line indicates the height of the maize and the bars denote twice the standard error of the mean of four observations in 1971 and eight observations in 1972. Ozone concentrations were measured with a model 724-2 Mast (Mast Development Company, Davenport, Iowa) ozone meter fitted with a trap for sulphur dioxide. The meter was suspended from a vertical tower, so that it could be rapidly moved between pre-set heights from 2.5 to 350 cm above the soil. Each observation at a particular height was quickly compared with the concentration at 350 cm. Concentrations at seven heights were usually measured during a 20 to 30 min sampling period.