square feet home may consume about 1/2 gallon of preservative if the contractor takes care to fully reseal the exposed lumber. This preservative contains 0.33 lbs of copper.

## 3.3 Factory-Preserved Wood Shingles

Copper arsenate is mentioned in the literature as a preservative used in wood shingles made of pine. <sup>[7]</sup> Conversations with local roofing suppliers suggests that redwood and cedar shingles are more commonly used in the Bay Area. These two woods do not typically need a preservative, although fire retardant chemicals that sometimes include preservatives are required by code. It is recommended that samples of these shingles be tested for copper content.

# 4. Release of Copper To The Environment

This section of the report presents an order-of-magnitude estimate of the amounts of copper that rainfall will release from roofs, gutters, downspouts, and other architectural features in the Palo Alto RWQCP service area. The estimate is in five parts:

- 1. Local Rainfall Data
- 2. Background Copper (Wet & Dry Deposition)
- 3. Copper from Individual Building Features
- 4. Copper from Representative Buildings
- 5. Total Amount of Copper Released in the Service Area

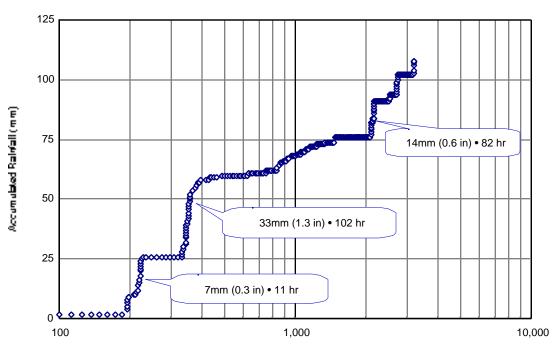
Monitoring data from various researchers contribute to the estimates of copper deposited from the atmosphere and also released by corrosion of individual features. However, the extent to which these building features are actually used in the RWQCP service area is not yet known. Therefore, the overall estimate of total copper released in the service area is only approximate.

#### 4.1 Local Rainfall Data

The State of California publishes real-time internet weather data for a number of observation points throughout the San Francisco area, including one located at the Palo Alto Airport. Rainfall amounts and intensities reported at this site for the 1999 - 2000 winter are summarized in Exhibit 4. [32]

About 110 mm (4 in) of rain fell in Palo Alto during January - May 2000. Half of this amount (54 mm) occurred in three major storms that ranged in duration from 11 to 102 hours. Intensities for these highlighted storms varied from 0.17 to 0.64 mm/hr. The latter value is used later in the report to conservatively estimate the flow capacity required of alternative copper removal treatment systems. [29]

Exhibit 4
Accumulated Rainfall (1/00 - 4/00) - Palo Alto Airport



Elapsed Time (Hours Since Midnight 1/6/00) .

	Rai	nfall	Runoff		
	Intensity	Duration	Rate	Volume	
	(mm/hr)	(hr)	(liters/sqm/hr)	(liters/sqm)	
Storm 1	0.64	11	0.64	7.1	
Storm 2	0.32	102	0.32	33	
Storm 3	0.17	82	0.17	14	
Other Rainfalls	0.36	817	0.36	296	
Full Year		1,012		350	

These data show that local rainfall occurs with an average intensity of about 0.35 mm/hr spread over 1,012 hours per year.  $^{[32]}$  This rainfall has a pH of about 5.1 [see Exhibit 5], and according to local monitoring data  $^{[16]}$  contains 0.0005 mg/l of copper. See Appendix A-2 for details.

Source of rainfall data: <a href="http://cdec.water.ca.gov">http://cdec.water.ca.gov</a>>. The station ID is "PAA".

Rain fell for a total of 312 hours during January - May 2000 (i.e., about 10% of the total time), with an average intensity of 0.35 mm/hr. On this basis it is estimated that the annual rainfall of 14 inches occurs in a total of 1,012 hours.

The National Atmospheric Deposition Program (NADP) maintains two field monitoring stations in California that are within about 100 km (62 mi) of Palo Alto. Exhibit 5, obtained from the indicated NADP website, shows that pH values at these stations were in the range of 5.1 to 5.8 for Calendar 1998.

#### Exhibit 5

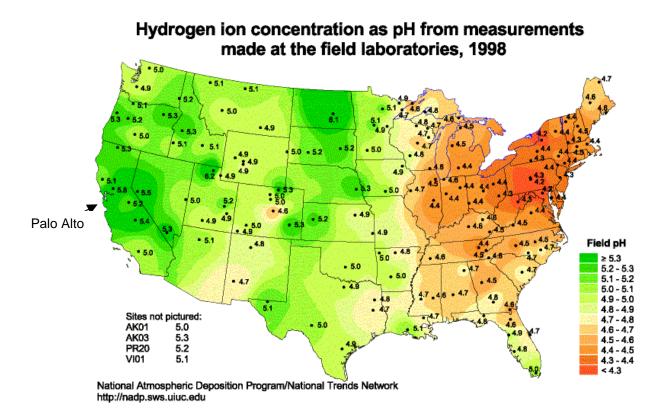


Exhibit 6, also adapted from the referenced NADP website, shows that the sodium content of local rainfall is in the range of  $400 \,\mu\text{g/l}$ . Exhibit 7 is a composite satellite image from the US Geological Survey which emphasizes that this salinity level results from the proximity of the Palo Alto RWQCP service area to the San Francisco Bay and the Pacific Ocean to. [38]

### Exhibit 6

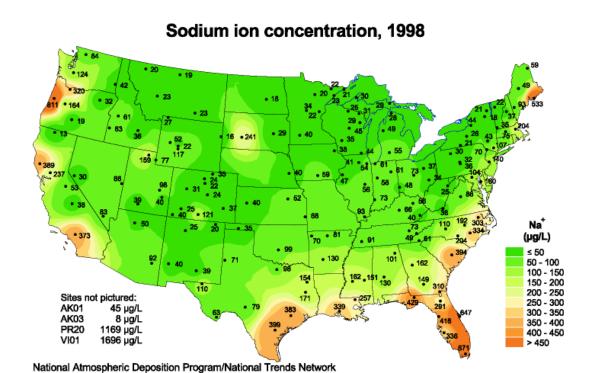


Exhibit 7
Palo Alto RWQCP Service Area

http://nadp.sws.uiuc.edu



## 4.2 Background Copper (Dry & Wet Atmospheric Deposition)

As shown by Exhibit 8, copper is present in rainfall and airborne dust. These background levels are excluded from subsequent estimates in this report of copper released by rainfall from building roofs.

The San Francisco Estuary Institute (SFEI) is monitoring atmospheric copper deposition at the NASA Ames Research Center, which is just south of the RWQCP service area. The following SFEI data for August - December 1999 are used to adjust the estimates that appear later in this report. [16]

- <u>Dry Deposition</u>: 2 μgrams per square meter per calendar day, which is equivalent to 728 μg/sqm/yr; and
- Wet Deposition: 3.1 μgrams for 24 hours of rainfall, which is equivalent to 130 μg/sqm/yr.

Exhibit 8
Background Copper Levels (Dry & Wet Atmospheric Deposition)

<u>Parameter</u>	<u>Deposition</u>	Deposition (µg/sqm)		Conc. Rainfall	Source of Data
	per day	per year	mg / I	рН	
Dry Deposition *					
(Airborne Dust)	2.0				South San Francisco Bay; Tsai [16]
	5.6				Switzerland; Zobrist [12]
(per <u>calendar</u> day)	8.7 - 18				Switzerland; Mason [14]
	9.3				Alameda County Woodward-Clyde [15]
	3.8	1,400			Sweden; Mohlander [34]
Used for this study	2	728	•••	•••	SFEI Observations [16]
Wet Deposition **					
(Rainfall)	3.1	130	0.0005	•••	South San Francisco Bay; Tsai [16]
	4		0.001	5.3 - 6.2	Switzerland; Zobrist [12]
(per <u>rainfall</u> day)	11		0.003	6±	Switzerland; Boller [13]
	6.0 - 6.7		0.002	6.9	Switzerland; Mason [14]
				6.4	Alameda County; Woodward-Clyde [15]
				5.4	Oregon; Bullard [18]
				• • •	Sweden; Mohlander [34]
		1,200		5.1	Nat'l. Atmospheric Deposition Proj. [38]
Used for this study	3.1	130	0.0005	5.1	SFEI [16]; NADP [38]

<sup>\*</sup> Dry deposition occurs every day of the year, so annual amounts are 364 times the number shown. The estimates made for this report use a dry deposition rate of 2 μg/sqm/day, or 728 μg/sqm/yr.

<sup>\*\*</sup> Wet deposition obviously occurs just during rainfall events. The numbers shown here are expressed as μg/sqm per each full 24 hours of rainfall. Rain actually falls in the South San Francisco Bay only about 1,000 hours (42 days) per year, or 11% of the time. Therefore, the wet deposition rate used in this report is 42 times the daily amount of 3.1 μg/sqm/rainfall day, or 130 μg/sqm/yr. The pH is from NADP measurements.

## 4.3 Estimated Copper Releases From Individual Features

Exhibit 9 lists the parameters that influence the amount of copper released from roofs, gutters, downspouts, and other architectural features.

# Exhibit 9 Factors Affecting Copper Releases

<u>Factor</u>	Pertains To	Anticipated Effects
Initial copper content	Algae resistant composition shingles	More granules> More Cu released Larger granules> Cu released longer
Age of feature	All Features	Copper release lower in new features
Weathered patina	Copper metal	Patina consists of copper sulfides, etc., that slow development of copper corrosion after 30+ years [24]
Physical orientation	Gutters & Downspouts; Ornamentals	North facing or somewhat sheltered features may not dry, thereby increasing corrosion rate [18, 19, 37]
Galvanic action	All	Adjacent use of incompatible metals or presence of electrically induced currents will increase corrosion rates
Nearness to ocean	All	Salt content of air will increase corrosion rate [18] [20]
Rainfall chemistry	All	Low pH rain removes more copper
Rainfall frequency	Roof	More frequent and intense rainfall: more Cu removed
Rainfall frequency	Gutters	More frequent rainfall: less Cu removed from gutters where organic matter would otherwise accumulate and increase corrosion
Maintenance	All	Re-exposed / re-soldered copper features corrode faster than untouched features
Runoff or groundwater	Foundation wood	Higher flows -> increased leaching of copper-containing wood preservative. However, this source releases much less copper than a roof made of that metal.

Exhibit 10 provides various estimates of the unit amounts of copper that may be released from individual architectural features. These data, which are from published literature sources and experiments performed at the Palo Alto RWQCP, were evaluated in the process of selecting approximate runoff release rates for use in this report. This selection was based upon:

- rainfall amounts, pH, and salinity;
- typical copper corrosion rates reported for each type of feature; and
- typical copper release rates for the corrosion products that do form.

Exhibit 10
Estimates of Unit Copper Releases - Individual Building Features

	Corrosion	Released In Runoff			
	Mass (g/sqm/yr)	Mass (g/sqm/yr)	Conc. (mg / l)	Rainfall (m / year)	Source of Data
Copper Roof	8.4 - 11.7	(9/04/11/91)	(mg / i)	2.03	Oregon • Unsheltered test coupons 1km - 50km from ocean [18]
(Per sqm of roof)		1.1	0.9	1.19	Connecticut • 10/98 Data for 6 yr old 1,100 sqm roof. [23]
		3.6	2.1	1.19	Connecticut • 2/2/99 Data for 6 yr old 1,100 sqm roof. [21, 22]
		5.2	2.0 - 8.7	1.19	Connecticut • 2/18/99 Data for 7 yr old 1,100 sqm roof. Conc. = 8.7 mg/l is 'first flush', while 2.0 mg/l after 120 minutes. [24, 29]
	12.0	1.8			Sweden • Fresh test coupons. [25]
		2.0		1.19	Connecticut • Data for 71 yr old copper roof with full patina. [24]
	6.3	1.4		0.53	Sweden • 2 Yr coupons. [25, 34, 35]
Used for this study>	5.0	1.0		0.35	
Copper Gutter & Downspout	7.8		0.22	1.29	Switzerland • New gutter. [12]
	7 - 15		0.22	1.29	Switzerland • New gutter [13]
(Per sqm of feature, <u>not</u> sqm of roof)	3.5		0.07	1.29	Switzerland • 15 yr old Gutter. [12]
		4.4	0.1 - 2.1	0.35	Palo Alto • Various ages [27]
Used for this study>	10	2.0		0.35	In terms of roof area this load is equivalent to 0.06 g/sqm/yr
Algae-Resist Shingles		0.17	0.1 - 1.0	0.35	Field tests at the Palo Alto RWQCP, 4/00 - 5/00 [see Appendix A-3].
Used for this study>	•••	0.17		0.35	
Regular Comp. Shingles -		0.009	0.01 - 0.04	0.35	Field tests at the Palo Alto RWQCP, 4/00 - 5/00. These tests produced inconclusive results, and so will be repeated.
Used for this study>	•••	tbd		0.35	tbd = to be determined

Exhibit 10, above, provides average annual copper releases measured for metal roofs, gutters, and downspouts. The amount of copper actually released from these features during a particular storm depends upon the daily corrosion rate, type and solubility of corrosion products that form, number of days since last rainfall, and both the intensity and amount of current rainfall. [24, 25]

This variability is illustrated by Exhibits 11 and 12. Exhibit 11 shows how the annual rate of copper corrosion decreases through time as a patina forms and begins to protect the surface. The amount of corrosion byproducts that rainfall washes from the roof is initially small, and then increases over a period of years to reach a steady state equal to the rate of corrosion. [35] Salt in the air and acidic rainfall tend to increase both the corrosion and copper release rates. [18]

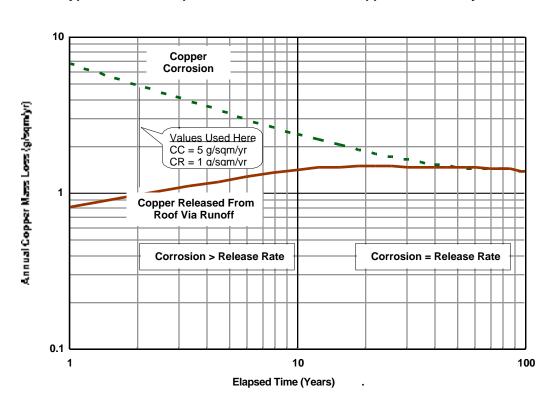


Exhibit 11

Typical Relationship Between Corrosion and Copper Removed By Runoff

Note: This chart is for illustration only. It does not portray data obtained from actual field measurements. CC = Copper Corrosion. CR = Copper Release.

Exhibit 12 shows accumulative corrosion and runoff releases predicted for a hypothetical building in Palo Alto with a newly-installed copper roof. These

estimates conservatively reflect the impacts of airborne salt from the Pacific Ocean, local rainfall chemistry, and atmospheric deposition. [33]

Exhibit 12 also shows the key conclusion that, overall, the copper mass released from corrosion is about 1,000 times the amount of copper added to the roof via wet and dry atmospheric deposition. In addition:

- The line of diamond symbols represents cumulative corrosion of copper from an example roof, which reaches an estimated total of about 1,800,000 μg/sqm in the first 3,000 hours of the Year 2000.
- This amount is equivalent to an estimated annual corrosion rate of 5 g/sqm/yr [see Exhibit 10].
- The upper solid line represents the intermittent release of copper mass in rainfall runoff from the example roof. This copper mass totals an estimated 300,000 µg/sqm in the first 3,000 hours of the year.
- Annually the copper mass runoff rate is estimated as 1 g/sqm/yr.
- The graph shows that for the first several hundred hours almost all of the corrosion products are removed during two storm events. Thereafter, copper releases continue, but at a rate that is less than the corrosion.
- The lower line in Exhibit 12 shows that atmospheric deposition of copper totals about 300 μg/sqm in 3,000 hours.
- Annually, combined wet and dry atmospheric deposition will together add 860 µg/sqm/yr to the roof surface. [see Exhibit 8]

This evaluation concludes that atmospheric deposition is significantly less per unit area than the amount of copper mass released by corrosion from a roof of that metal. Therefore, wet and dry deposition are neglected in the estimates that follow.

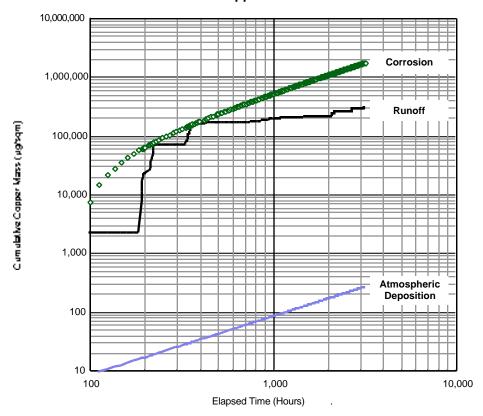


Exhibit 12
Predicted Unit Copper Mass Loss in Rainfall Runoff

Note: The runoff curve matches storm events during the first 3,000 hours of the Year 2000.

## 4.4 Estimated Annual Copper Release From One Building

Exhibit 13 provides estimates of how much copper could be released each year from new structures that have various architectural features. These estimates are based upon average rainfall and ocean air exposure conditions in the Palo Alto RWQCP service area.

- Copper releases from bare metal roofs in later years will be significantly less than the amounts shown here when a protective patina develops.
- Copper releases from gutters will also decrease over time, but may stay above that of the roof itself because of acidity from organic debris.
- Releases from algae resistant shingles will vary according to the amount of rainfall in each year.

Exhibit 13
Predictions of Annual Copper Releases from Various Example Buildings

	Building Type	Copper Release (grams/year)	Basis of Estimate
1 <u>2,500</u>	sqft Home with Copper Gutter & Downspot	<u>ıt</u> 0	Slate Roof
(232 s	sqm of total roof area)	14	New copper gutters & downspouts
	Total	g/yr 14	= 0.06 g/sqm/yr = 0.01 lbs/1,000 sqft/yr
	sqft Home with Copper Roof, Gutter &	232	New bare copper roof
(232 s	<del></del>	14	New copper gutters & downspouts
(232 8	Total	g/yr 246	= 1.06 g/sqm/yr = 0.22 lbs/1,000 sqft/yr
3 <u>2,500</u>	sqft Home with Algae-Resist Shingle Roof	39	New algae-resist shingles
(232 s	sqm)	0	Steel gutters & downspouts
	Total	g/yr 39	= 0.17 g/sqm/yr = 0.03 lbs/1,000 sqft/yr
	0 sqft Retail with Copper Roof, Gutter &	928	New bare copper roof
<u>5041135041</u> (020 34111)	<u></u> (0_0 04)	56	New copper gutters & downspouts
	Total	g/yr 984	= 1.06 g/sqm/yr = 0.22 lbs/1,000 sqft/yr

See Appendix A-3 for details of these estimates.

## 4.5 Estimated Total Service Area Copper Release

Exhibit 14 presents an order-of-magnitude estimate showing that about 136 kg/yr (298 lbs/yr) of copper are released from roofs, gutters, and downspouts in the Palo Alto RWQCP service area.

This copper release into the environment from corrosion of architectural products is about 20% of the 700 kg/yr (1,540 lbs/yr) copper load observed in local creeks flowing through the Palo Alto RWQCP service area. [39]

# Exhibit 14 Estimates of Copper Releases - All of Palo Alto RWQCP Service Area

Building Type	Annual Copper Load kg / year	Basis of Estimate
Architectural Copper		
Copper Roofs	124	Est. 70 homes + 11 other structures with bare metal copper roofs that all together have a total area of 124,000 sqm
Algae-Resist Shingles	2	Est. 42 homes with these roofs (total area of 9,600 sqm)
Regular Composition Shingles	to be determined	Est. 83,000 homes and 54 other buildings (total area of 20,000,000 sqm).
Gutters & Downspouts	10	Est. 650 structures with copper gutters, downspouts, etc. (equivalent roof area of 160,000 sqm)
Total Copper Release	136	(298 lbs/year)
Copper In Creeks	700	(1,540 lbs/year)
		Copper mass contained in annual flows from San Francisquito, Adobe, Barron, and Matadero Creeks. [Table 4-3 of Ref. 39]

#### Basis of Estimate (See Appendix, Page A-4)

Service area contains 37,800 acres (15,303 hectares), of which an estimated 70% are residential, 15% other developed land, and 15% open space.  $^{[28]}$ 

Roof coverage is 30% for residential land, and 50% for commercial, industrial and other developed land.  $^{[15]}$ 

Number of copper roofs are very roughly estimated to be 0.05% of residences, 0.3% of industrial/commercial buildings, and 1.5% of other structures.  $^{[2, 3, 5]}$  To improve this estimate, an inventory of copper roofs could be made from digital aerial photographs, as has been done in Stockholm.  $^{[40]}$ 

Algae-resistant composition shingles are estimated to be used on 0.03% of residences. [5]

Regular composition shingles are estimated to be 60% of residential and 10% of commercial & industrial roofs. [2]